

Silver(I) Complexes as Antimicrobial and Anticancer Drugs

Robert J. Curran, B.Sc.

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Head of Department: Professor John Lowry

Supervisor: Dr. Malachy McCann

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To my parents

*You cannot teach a man anything; you can only help him find it
within himself.*

Galileo Galilei (1564-1642)

Declaration

I hereby certify that this thesis has not been submitted before, in whole or in part, to this or any other university for any degree and is, except where otherwise stated, the original work of the author.

Signed: _____

Date: _____

Robert Curran

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Abstract

This thesis describes the potential use of silver(I) complexes of 9-anthracenecarboxylic (9-acaH) and imidazoles as new antimicrobial and anticancer drugs. The detailed synthesis of silver(I)-containing carboxylates, such as polymeric $[\text{Ag}_2(9\text{-aca})_2]_n$ and $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$, and the ammonia-containing complex, $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$, are provided along with imidazole derivatives, such as $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ and $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$. Silver(I) carboxylates containing substituted imidazole ligands were also prepared and include the complex salts, $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ and $[\text{Ag}(1\text{-Bu-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$, along with $[\text{Ag}_2(1\text{-Me-imid})_2(9\text{-aca})_2]$, $[\text{Ag}(2\text{-Me-imidH})_2(9\text{-aca})]$, $[\text{Ag}_2(1\text{-Bu-imid})_2(9\text{-aca})_2]$, $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$, $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$ and $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$. Polymeric silver(I) imidazolate complexes were made from 2-phenylimidazole, 4,5-dicyanoimidazole, benzimidazole and 2-methylbenzimidazole. All complexes were characterised by IR and NMR spectroscopy, microanalysis and, in many instances, by X-ray crystallography. The fluorescence properties of a selection of the complexes were also recorded.

Complexes were screened, *in vitro*, for their antifungal (*Candida albicans*) and antibacterial activity (*Escherichia coli* and methicillin-resistant *Staphylococcus aureus* (MRSA)). Many of the new silver(I) complexes were more active than the prescription drugs currently used to treat microbial infections and cancerous tumours. For example, $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ was *ca.* 32 times more active than the prescription antifungal drug, Ketoconazole. This complex also exhibited high cytotoxicity towards bacterial cells, being *ca.* 9 times more active against both *E. coli* and MRSA than the known antibacterial agent, silver sulfadiazine. The hexanuclear imidazole complex, $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$, was the most active at inhibiting bacterial growth, being *ca.* 39 times better than silver sulfadiazine against *E. coli*.

The *in vivo* cytotoxicity and antifungal characteristics of the silver(I) complexes was also examined using the insect model, *Galleria mellonella*. Healthy *G.*

mellonella larvae appeared to be unaffected when treated with the silver(I) complexes at concentrations up to 100 $\mu\text{g cm}^{-3}$. The silver(I) complexes also increased the survival rate of larvae administered with a lethal dose of *C. albicans*. Again, the ammonia-containing complex, $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$, was the most effective at increasing the survival rate, greatly surpassing the efficacy of Ketoconazole.

The silver(I) complexes were screened, *in vitro*, against a number of mammalian tumour cell lines (MCF-7, HT-29, Hep-G₂ and A-498) and they all decreased cell proliferation. While most of the complexes were more active towards MCF-7 cells (breast cancer cells), $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$ was equally cytotoxic against HT-29 cells (colon cancer cells). $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$, $[\text{Ag}(1\text{-Bu-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$, $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ and $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ were all *ca.* 7 times more active against breast cancer cells than the anthracene-containing anticancer drug, Mitoxantrone.

Abbreviations

| | |
|-----------------------------|---|
| 1-Bu-imid | 1-butylimidazole |
| 1-Me-imid | 1-methylimidazole |
| 2-Me-imidH | 2-methylimidazole |
| 2-Me-imid ⁻ | 2-methylimidazolate anion |
| 2-Ph-imidH | 2-phenylimidazole |
| 2-Ph-imid ⁻ | 2-phenylimidazolate anion |
| 2-Mebenz-imidH | 2-methylbenzimidazole |
| 2-Mebenz-imid ⁻ | 2-methylbenzimidazolate anion |
| 2-Mebenz-imidH ₂ | protonated 2-methylbenzimidazole |
| 4-Ph-imidH | 4-phenylimidazole |
| 4-Ph-imid ⁻ | 4-phenylimidazolate anion |
| 9-acaH | 9-anthracenecarboxylic acid |
| 9-aca ⁻ | 9-anthracenecarboxylate anion |
| ac-9-caH | acridine-9-carboxylic acid |
| ac-9-ca ⁻ | acridine-9-carboxylate anion |
| amB | amphotericin B |
| apim | 1-(3-aminopropyl)-imidazole |
| Benz-imidH | Benzimidazole |
| Benz-imid ⁻ | Benzimidazolate anion |
| BINAP | 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl |
| cisplatin | <i>cis</i> -diaminedichloroplatinum(II) |
| DMSO | dimethylsulfoxide |
| DNA | deoxyribonucleic acid |
| EtOH | ethanol |
| fbCH | 4-fluorobenzoic acid |
| fbC ⁻ | 4-fluorobenzoate anion |
| H-bond | hydrogen bond |
| imidH | imidazole |
| imid ⁻ | imidazolate anion |
| imidHH | protonated imidazole |
| IR | Infra-red |

| | |
|-------------------|---|
| KP1019 | (indazolium- <i>trans</i> -[tetrachloro-bis(1H-indazole)ruthenate(III)]) |
| LFSE | ligand field stabilisation energy |
| MalH ₂ | malonic acid |
| MalH ⁻ | malonate anion |
| MeCN | acetonitrile |
| MeOH | methanol |
| NAMI-A | imadozolium- <i>trans</i> - [tetrachloro(dimethylsulfoxide(imidazole)ruthenate(III))] |
| NMR | nuclear magnetic resonance |
| NMR multiplicity | s = singlet d = doublet t = triplet q = quartet quin = quintet sex = sextet m = multiplet dd = doublet of doublets |
| phen | 1,10-phenanthroline |
| phendio | 1,10-phenanthroline-5,6-dione |
| RNA | ribonucleic acid |
| RT | room temperature |

Introduction

1.1 Structure of Introduction

The Introduction is structured to give the reader an understanding of the scope of this research and the terms used throughout this thesis. An introduction to fungal and bacterial infections concentrating on *Candida albicans*, *Escherichia coli* and methicillin resistant *Staphylococcus aureus* is provided, along with a brief review of current antimicrobial drugs. An insight into the history and methodology of *in vivo* antifungal screening is also given. An introduction to cancer is included along with a review of metal-based anticancer agents. Finally, the chemistry and biological activity of silver is discussed along with details of the ligands used in the synthetic processes.

1.2 Fungal Infections

Fungi are eukaryotic organisms, distinct from both plants and animals. Most are multicellular and differ from other eukaryotes in nutritional mode, structural organisation, growth and reproduction. Many fungi are parasites on plants and animals, causing conditions that can range from mild to life-threatening while others can form symbiotic relationships with their hosts. Fungi are also used as major sources of pharmacologically active drug compounds (e.g. penicillins) and are widely used in the food and brewing industry.

1.2.1 Candida albicans

The genus *Candida* is comprised of approximately 200 yeast species and, of these, about 12 are associated with human commensalism or disease¹. *Candida albicans* is an opportunistic fungal pathogen that usually resides harmlessly as commensals in human and animal hosts. It is the species that is most frequently associated with human infection² and is carried innocuously by a large proportion of people on the epithelial surfaces of the mouth, gastro-intestinal tract, vagina and skin, where it is generally kept in check by host defences and the normal microbial flora of the body³.

C. albicans exhibits structural dimorphism and, as such, can exist in two different morphologies. It can exist as ovoid blastospores (simple yeast cells) and as true hyphae, known as germ tubes (Figure 1). Both morphologies have been shown to cause disease in human and animal hosts.

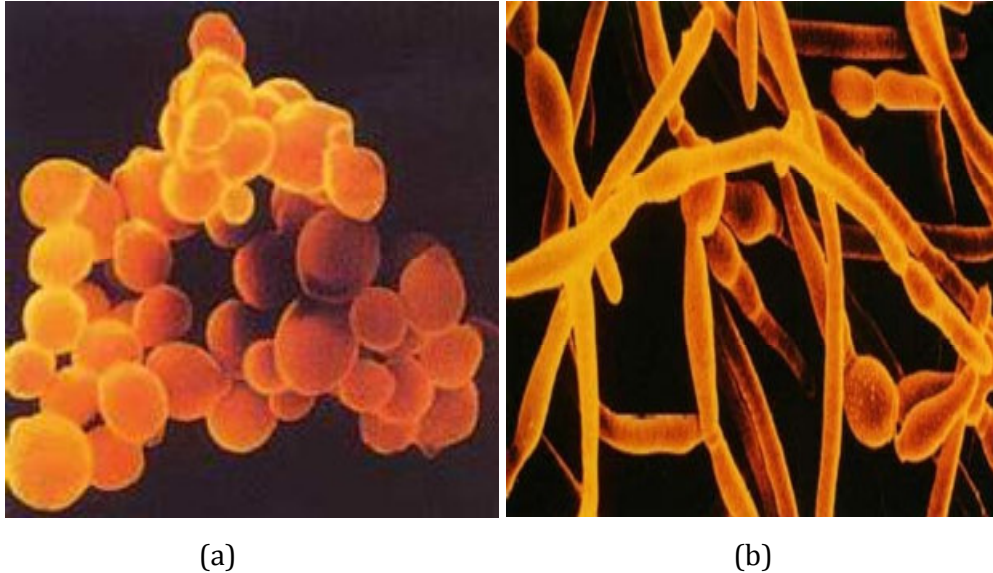


Figure 1. *C. albicans* cells: (a) ovoid blastospores and (b) germ tubes.

Candida infections of virtually every tissue of the human body have been reported, with the most common manifestations being superficial lesions of the mouth or vagina (Figure 2). It is capable of causing a wide range of infections and can be particularly problematic for immuno-compromised individuals such as AIDS patients, transplant recipients, cancer patients, burn patients and premature infants. The improper use of broad spectrum antibiotics can also lead to a *Candida* infection due to the lack of friendly bacteria to keep it under control. It can also cause more serious and potentially life-threatening systemic infections of organs, including the kidney, liver and brain. It is the fourth most common cause of nosocomially acquired bloodstream infections and candidal pathogenesis occurs in the following steps¹:

- *Candida* cells adhere to the epithelial surface via specific interactions between candidal adhesions and host ligands.

- Once they have bound to the tissue the fungal cells begin to proliferate and produce hyphae.
- Growth continues by budding and production of hyphae (often associated with the formation of a biofilm).
- Fungal hyphae and cells eventually penetrate through the epithelial layer to the tissues below, reaching the bloodstream and spreading through the body causing disseminated candidosis.



(a)

(b)

Figure 2. *C. albicans* infection of (a) the mouth and (b) the toes.

1.2.2 Current Antifungal Drugs

The development of drugs specific to fungal cells is a challenging task due to the close similarities of fungal and mammalian cells. The number of agents available to treat fungal infections has increased by 30% since the year 2000, yet still only 15 agents are approved for clinical use⁴. At present, fungal infections are generally treated by the use of echinocandins, polyene and azole drugs, but none of the existing systemic antifungals satisfies the medical need completely. There are weaknesses in the spectrum, potency, safety and pharmacokinetic properties of these drugs and new alternatives are urgently being sought.

1.2.2.1 Polyene Antifungal Drugs

Polyenes are a family of antifungal compounds isolated from *Streptomyces* species that contain alternating double bonds as part of their macrolide ring structure. Although many polyenes have been isolated from *Streptomyces*, only

amphotericin B and nystatin are in current widespread use (Figure 3). These two polyenes have the broadest activity spectrum of any antifungal agent in

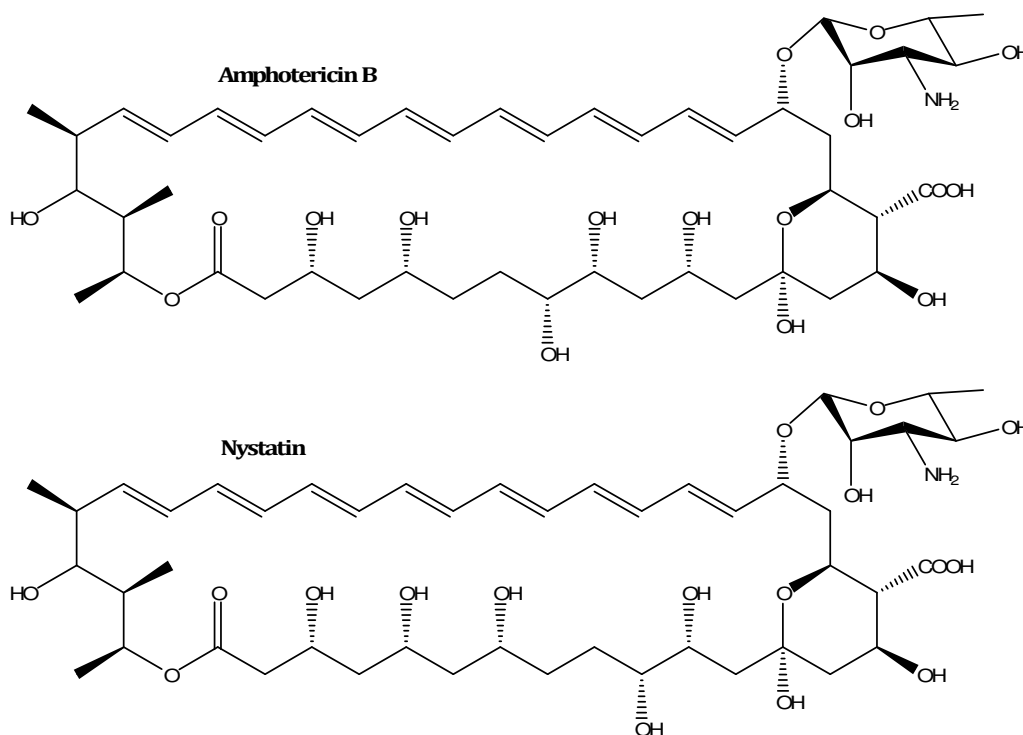
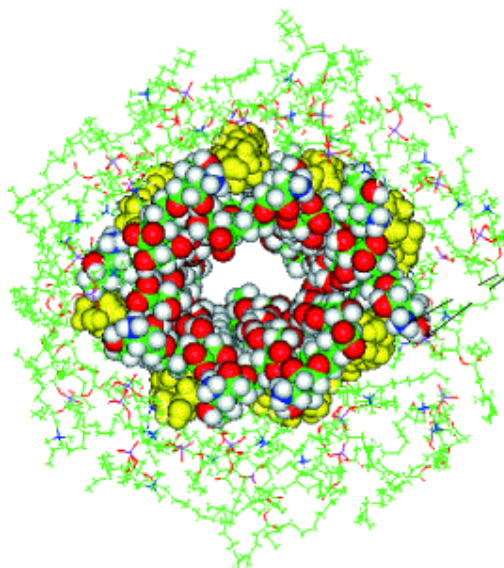


Figure 3. Structures of amphotericin B and nystatin.

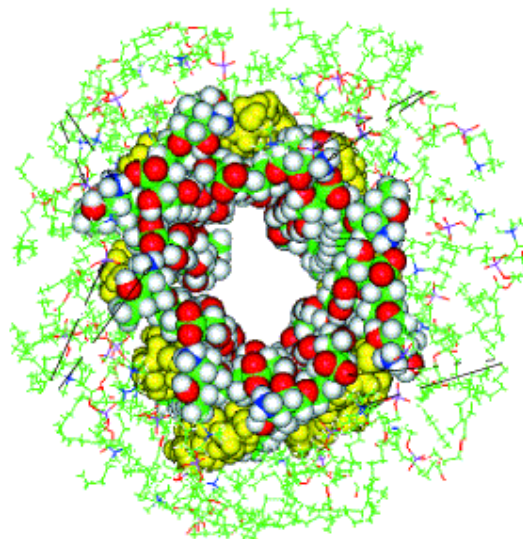
clinical use and they inhibit fungal growth by interacting with ergosterol in the fungal cell membrane and compromising its barrier function⁵. The biological activity of polyenes is attributed to their polar hydroxyl groups, which are located opposite to the double bonds on the macrocyclic ring, giving the compounds an amphipathic nature⁶. The polyenes bind to ergosterol in the fungal cell membrane forming pores through which vital cytoplasmic components, such as potassium ions, ammonium ions, small neutral sugars, phosphate esters and nucleotides, can leak from the cell, leading to cell death.

Due to the similarity between sterols in fungal and mammalian cell membranes (cholesterol in mammals and ergosterol in fungi), polyenes can affect both the pathogen and the host. Amphotericin B and nystatin have a higher affinity for ergosterol than cholesterol (Figure 4) but both have very poor solubility

properties⁷. They are not absorbed readily from the gastrointestinal tract and so must be administered intravenously.



AmB-cholesterol channel



AmB-ergosterol channel

Figure 4. Interaction of amphotericin B (AmB) with cholesterol and ergosterol forming different sized pores in the membranes through which vital cytoplasmic components leak (sterol molecules in yellow)⁸.

A major problem with polyenes is their side effects and toxicity, particularly nephrotoxicity. Side effects, such as depression, headaches, cramps, anorexia,

nausea and muscle pain are not uncommon. Approximately 30% of individuals who undergo treatment with amphotericin B suffer from acute renal failure⁶. To overcome this toxicity, they can be incorporated into liposomes which are less toxic. This combination maintains the beneficial therapeutic properties and can be administered in larger doses.

1.2.2.2 Azole Derivatives

The azole drugs are totally synthetic and are the most rapidly expanding group of antifungal agents. They can be classified as imidazoles (2 nitrogens in a 5-membered ring) or triazoles (3 nitrogens in a 5-membered ring)⁹. They inhibit the action of the cytochrome P450-dependent enzyme lanosterol demethylase, which is a major component of the fungal plasma membrane and a key ingredient in the biosynthesis of ergosterol. This enzyme is also present in mammalian cells but, at the required therapeutic concentrations, the azoles have a greater affinity for the fungal demethylase. In this way, the azoles cause a depletion of ergosterol and an accumulation of 14 α -methylated sterol. This disrupts both the structure of the membrane and its functions in nutrient transport and chitin synthesis⁶.

Imidazole-based compounds, including ketoconazole, miconazole and clotrimazole (Figure 5) were discovered in the 1960s but only ketoconazole was available for treatment of systemic infections due to its superior aqueous solubility. The nitrogen of the azole binds to the iron of the lanosterol demethylase enzyme and this prevents the activation of oxygen which is necessary for the demethylation of lanosterol¹⁰. A second nitrogen also interacts with the apoprotein of lanosterol demethylase and this may be the determining factor of the specificity of different azoles for the enzyme¹¹. The toxicity of azoles is relatively low but they can induce side effects such as a decrease in testosterone and glucocorticoids due to their interaction with mammalian cytochrome P-450⁵.

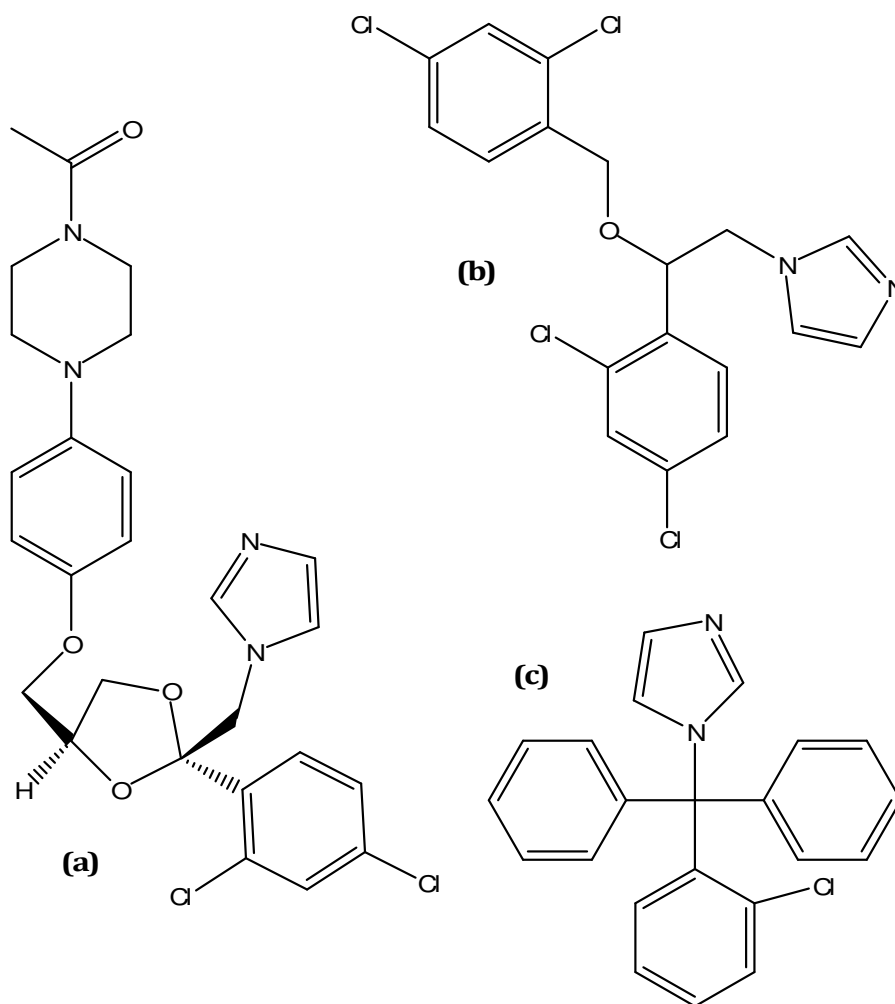


Figure 5. Azole structures: (a) ketoconazole, (b) miconazole and (c) clotrimazole.

Triazoles, such as fluconazole, itraconazole, voriconazole, posaconazole and ravuconazole (Figure 6), were developed at a later stage and these tend to be more specific in their mode of action. They can be used to treat both superficial and systemic infections.

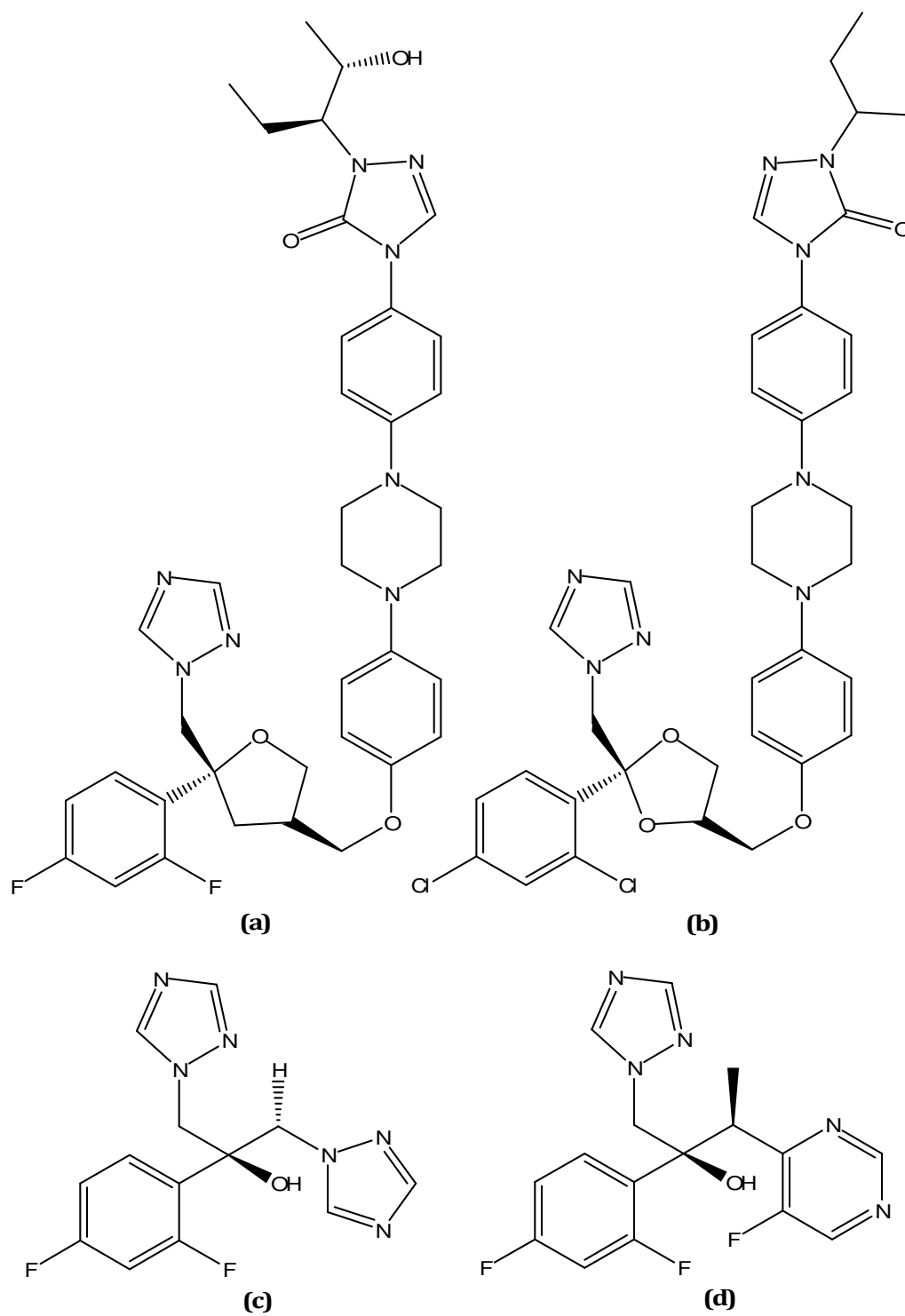


Figure 6. Triazole structures: (a) posaconazole, (b) itraconazole, (c) fluconazole and (d) voriconazole.

1.2.2.3 Echinocandins

The echinocandins are the first new class of antifungal drug to be introduced on the market in more than 15 years. They are synthetically modified lipopeptides originally derived from fermentation broths of various fungi¹². Echinocandins are large cyclic peptides linked to a long-chain fatty acid. Naturally occurring echinocandins have also been isolated and examples include aculeacin A (from *Aspergillus aculeatus*), echinocandin B (from *Aspergillus rugulovalvus*) (Figure 7), pneumocandin B (from *Zalerion arboricola*) and papulacandins (from *Papularia sphaerosperma*). While the toxicity of these natural echinocandins can be quite high, semi-synthetic analogues with reduced toxicity have been synthesised and licensed for clinical use. Examples include caspofungin (Merck), micafungin (Fujisawa) and anidulafungin (Versicor).

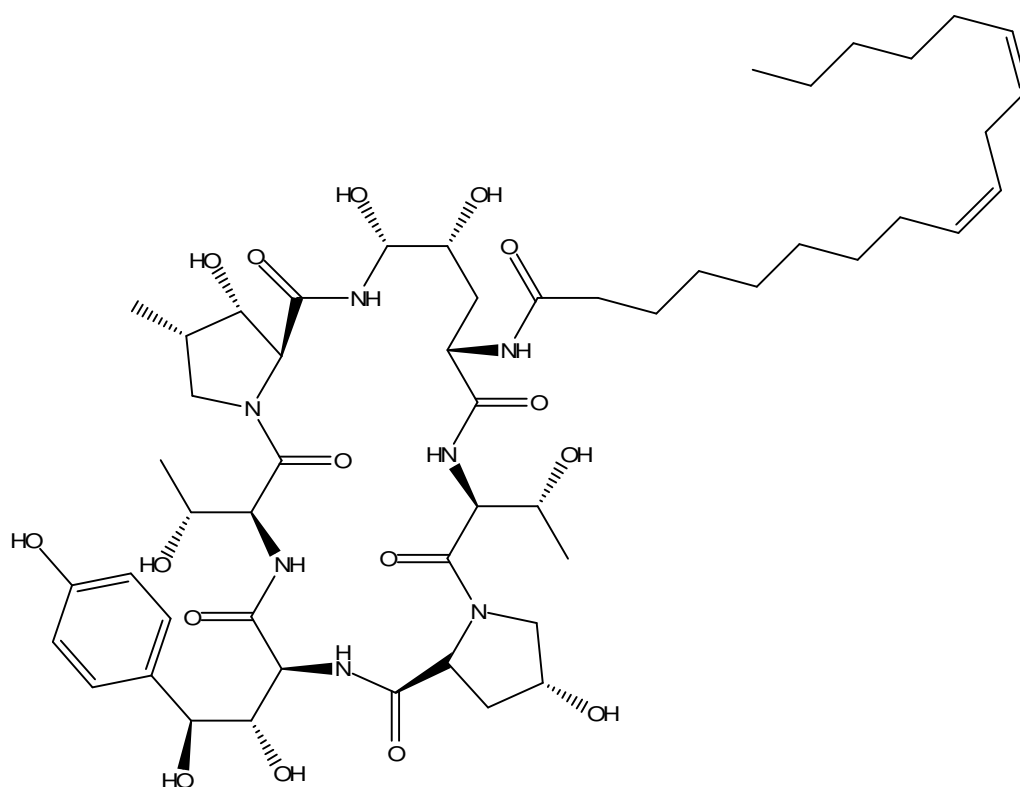


Figure 7. Structure of echinocandin B.

Echinocandins have a distinct target which is different from azoles and polyenes. These compounds inhibit the synthesis of β -D-glucan in fungal cell walls and their strengths include low toxicity, rapid fungicidal activity and

favourable kinetics which allows once a day dosing. However, echinocandins have poor oral absorption (*ca.* 3%) and therefore are administered intravenously. The drugs are concentrated in the liver, spleen and gut with equal concentrations distributed in the blood plasma and in the lungs, along with lower concentrations in other tissues.

1.2.2.4 Other Antifungal Agents

There are many other antifungal agents which do not fall into the three classes already discussed. These include the allylamines, terbinafine and butenafine, and flucytosine (Figure 8). The allylamines are synthetic, reversible, noncompetitive inhibitors of squalene epoxidase. This enzyme, together with squalene cyclase, converts squalene to lanosterol, which ultimately forms ergosterol in the fungal cells¹³. Terbinafine is an oral systemic agent whereas butenafine is used for the treatment of topical infections.

The fluoropyrimidine, flucytosine (5-fluorocytosine), is the only antimetabolite type antifungal drug available. It is converted into 5-fluorouracil within the fungal cells, which gets incorporated into the RNA and causes premature chain termination and inhibition of DNA synthesis. It is selectively toxic to fungal cells as mammalian cells lack cytosine permease which converts the flucytosine into the active 5-fluorouracil⁶. Due to its very limited activity spectrum it is mainly used in combination with amphotericin B⁵.

1.2.3 Fungal Resistance

Over many years, some strains of fungi have developed resistance to commercial antifungal agents¹⁴. Resistance usually arises either after long periods of exposure to the drug or in conditions that may support the gradual stepwise development of the fungus¹¹. It is very unlikely that any single mutation will transform a susceptible strain into a highly resistant one, but a combination of mutations and alterations can lead to the occurrence of resistant strains. The fungal cells have developed a number of mechanisms which give rise to this resistance, including alterations in sterol synthesis, targets sites,

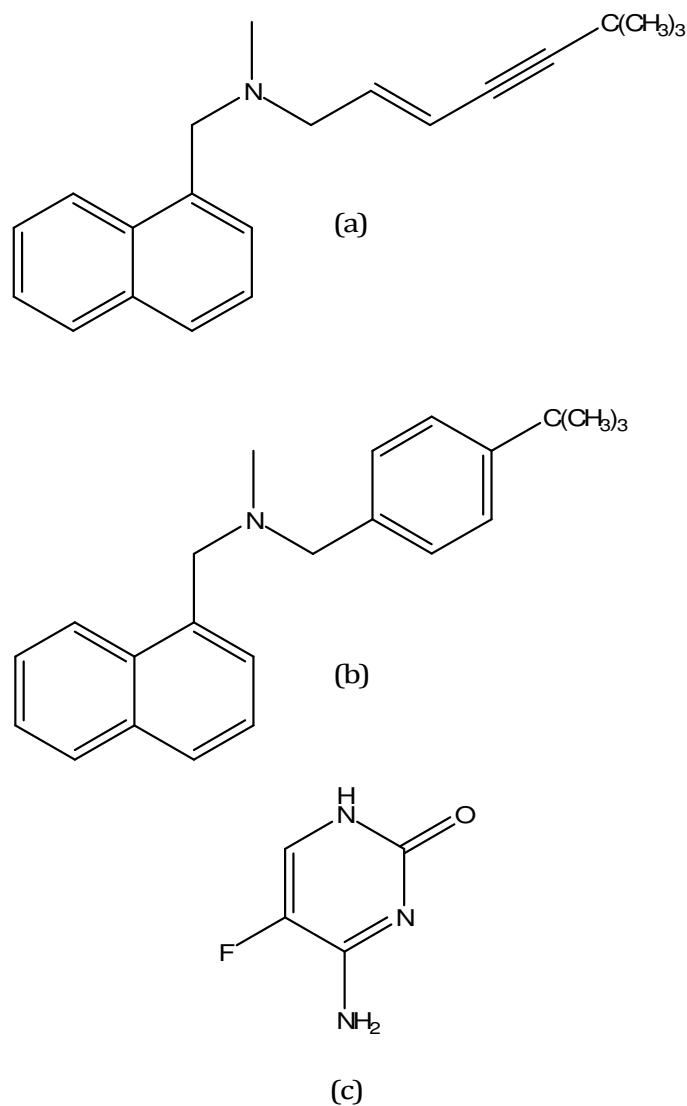


Figure 8. Structures of (a) terbinafine, (b) butenafine and (c) flucytosine.

along with the uptake and efflux of drugs¹⁰. To date, polyene resistance has not been a major clinical problem with very few polyene-resistant isolates being reported and characterised¹¹. However, resistance to azoles is much more common and widespread, being a major concern for immuno-compromised AIDS patients who regularly suffer from oropharyngeal *Candida* infections¹⁵. Resistance to allylamines has not been reported for medically important fungi, whereas resistance to flucytosine is a common occurrence¹¹.

1.2.4 In vivo Antifungal Screening Using *Galleria mellonella*

In vivo screening of compounds allows scientists to see how they may react when contained within a living organism. This is imperative in the development of candidate drug compounds for clinical use as it allows observations of any detrimental effects which could limit or even disqualify them for use. By using animal and insect models, the cytotoxic and antimicrobial properties of potential new drugs can be determined.

1.2.4.1 Immunity

The immune system of vertebrates comprises the innate immune system and the adaptive immune system. These two systems interact with each other via dendritic cells, macrophages and some T cells to yield an excellent defence mechanism against the invasion of harmful pathogens¹⁶ (Figure 9).

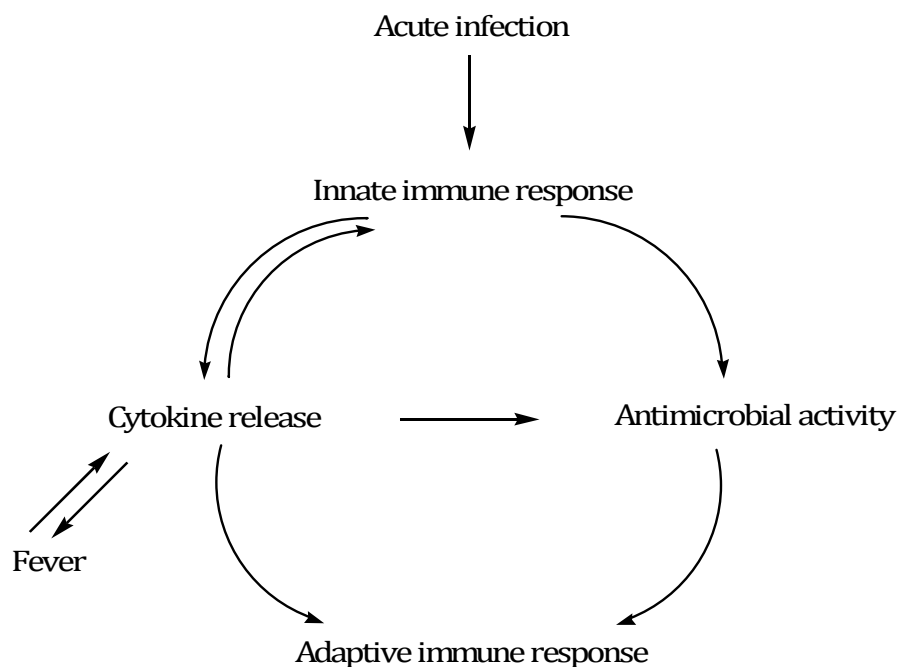


Figure 9. Interaction of the innate and adaptive immune systems.

The innate, or non-specific, immune system is the first line of defence against infection and constitutes a set of disease-resistant mechanisms that are not pathogen specific. Recent studies have shown that the initial cell responses of the innate immune system are critical in the initiation and maintenance of an

immune response to *C. albicans*¹⁷. The innate immune system has both cellular and molecular components that recognise classes of molecules common to frequently encountered pathogens. Whereas the innate immune system has defences that are already present at the time of infection, the adaptive or specific immune system requires days or even weeks to develop maximum efficiency against invading organisms. This latter system is antigen specific and reacts only with the organism that induced the response. Specificity such as this comes with the major advantage of immunological memory. Exposure to the same antigen in the future will result in a memory response which occurs faster and stronger than the initial response. The innate response does not demonstrate any immunological memory but it reacts equally well to a variety of organisms.

While the existence of an invertebrate adaptive immune system similar to that of vertebrates is still a matter of fierce debate^{18,19}, the innate immune system of insects and mammals has been shown to exhibit a high degree of structural and functional homology^{19,20}. This homology has led to further research into the response of insects to infection as this could provide valuable information into the functioning of the mammalian innate system²¹⁻²⁴. Many insects have been involved in the pathogenic study of microorganisms, including *Drosophila melanogaster*^{25,26}, *Galleria mellonella*^{23,27-29} and, more recently, *Locusta migratoria*³⁰. Insects are renowned for being the most successful groups of animals on Earth, accounting for nearly one million species and 10¹⁸ individuals³¹. They can be found in a vast array of differing habitats, with the oceans being one of the few places they have failed to colonise.

The key to insect survival is the methods they have developed methods to combat the large variety of pathogens which they encounter. The ability to detect an invading pathogen and activate an instantaneous defence is crucial for the survival of any species. The innate immune system provides this response and it has both cellular and humoral elements which consist of four parts:

- (i) anatomic barriers (the skin and mucous membranes);
- (ii) physiologic barriers (temperature, pH and chemical mediators);
- (iii) phagocytic/endocytic barriers (phagocytes/haemocytes);
- (iv) inflammatory barriers.

The cuticle and haemolymph of insects are analogous to the skin and blood of mammals. The haemolymph transports nutrients, waste products and signal molecules throughout the haemocoel or body cavity but, unlike blood, it plays no role in respiration. It is the main site of the immune response of insects to microorganisms. The haemolymph contains cells called haemocytes which are similar to phagocytes in mammals. Haemocytes can be subdivided into prohaemocytes, plasmatocytes, granulocytes, coagulocytes, spherulocytes and oenocytoids³².

The phagocytic/endocytic barriers of insects and mammals show many similarities²⁸. Plasmatocytes and granulocytes are the predominant phagocytic cells in insects, participating also in nodule formation and encapsulation³³. In mammals, the two main phagocytic cells are the neutrophils/polymorphonuclear cells and the monocytes/macrophages³⁴ (Figure 10). Phagocytic cells respond to signals generated at the site of an infection, which are usually peptides released by the invading microorganism or by tissues that have come into contact with the foreign pathogen. This leads to an increase in the glucose and oxygen consumption and is referred to as the respiratory burst³⁵. The burst produces a number of oxygen-containing compounds (reactive oxygen intermediates) which have been shown to kill invading microorganisms within the confines of the phagocytic vacuole in both mammals and insects^{36,37}.

The humoral immune response is mediated by antibodies, proteins and the processes that accompany the production of them. In mammals and other vertebrates this is usually more concerned with the adaptive immune system and the production of antibodies which bind to specific antigens on the surface of microorganisms identifying them as foreign bodies for destruction.

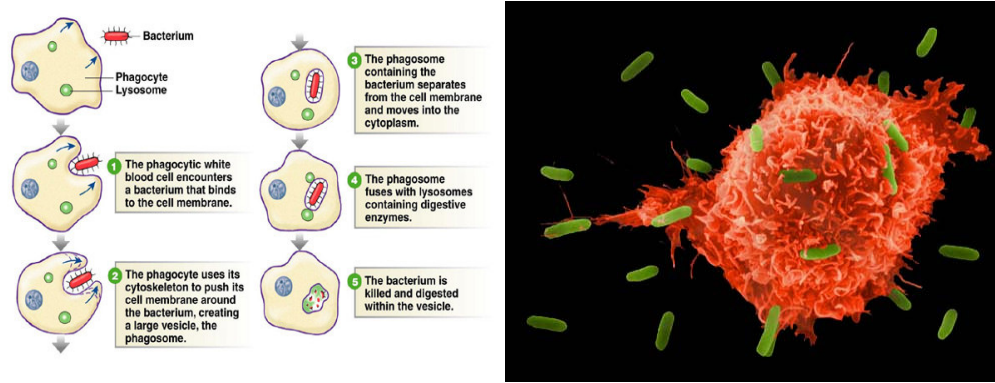


Figure 10. Steps in phagocytosis and an SEM image of macrophage attacking *E. coli* during phagocytosis.

Insects have a non-specific humoral immune response that involves the production of a range of antimicrobial peptides and proteins²⁰. This is the last line of defence in the case of a large infection by microorganisms and the antimicrobial peptides and proteins are released into the haemolymph where they attack the cell walls of the pathogens³⁸. The humoral immune response parallels the mammalian acute phase response and covers the processes of melanisation, haemolymph clotting and wound healing in response to injury³¹.

1.2.4.2 *Galleria mellonella* as an *In vivo* Model

The greater wax moth, *Galleria mellonella*, is approximately 12-18 mm long and has a wing span of 20-25 mm. The larvae can grow up to 25 mm in length and are pale yellow in colour (Figure 11). The life cycle usually takes from 3-6 months but under favourable conditions it can occur in as few as 6 weeks. The natural habitat of *G. mellonella* is in beehives containing older, dark honeycombs. The eggs are deposited in the cracks and crevices of the hives and the larvae which emerge feed on the wax within the hive. They bore holes and leave silk-lined tunnels (known as galleries) in the wax.

At present, most research into human pathogens involves the use of mammalian models, including rodent, simian and feline hosts. There are many concerns with the utilisation of these models, both from an ethical and a practical viewpoint. These studies are often very time consuming, incur considerable costs

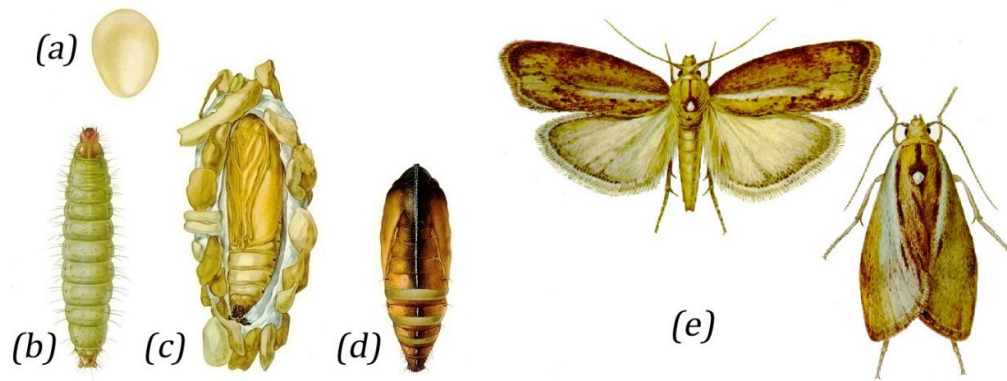


Figure 11. The different developmental stages of *Galleria mellonella*: (a) egg, (b) young larvae, (c) fully grown larvae wrapped in silken webbing, (d) cocoon and (e) adult moth.

and undoubtedly cause some amount of animal suffering. *In vivo* studies involving *G. mellonella* date back as far as 1982²⁷ and so far it has been used to study the pathogenicity of many different bacteria and fungi. Larvae of *G. mellonella* are inexpensive to purchase, easily cultured and inoculated, allowing a large number of test subjects to be screened in a relatively short period of time.

G. mellonella have been utilised to examine the properties of the bacteria *Pseudomonas aeruginosa*³⁹ and it is suggested that the underlying mechanisms of infection are similar to that in the mouse model⁴⁰. It has also been effective in the study of *Proteus mirabilis*⁴¹, *Aspergillus fumigatus*⁴², *Escherichia coli*, *Bacillus cereus*²⁷ and the pathogenic insect bacteria, *Xenorhabdus nematophilus*²⁹.

The use of *G. mellonella* larvae in the study of pathogenic fungi is also well documented. They have been proven to have the ability to distinguish between pathogenic and non-pathogenic yeast isolates, as well as heat-killed and viable cells²¹. *Cryptococcus neoformans*, a non-specific fungal pathogen, contains genes shown to be involved in mammalian virulence and which also play a role in the killing of *G. mellonella*²³. In the study of *C. albicans*, a correlation has been demonstrated in the fungal virulence and reduction of the fungal hyphal

formation in both *G. mellonella* and the mouse model⁴³. Studies into the response mechanism of *G. mellonella* have shown that, upon infection with *C. albicans*, the number of haemocytes in the body cavity of the larvae increases, along with the level of expression of the genes coding for antimicrobial peptides⁴⁴. It has also been shown that insect haemocytes phagocytose and kill microorganisms by a mechanism similar to that used by human neutrophils via the production of superoxide⁴⁵. The production of haemocytes in *G. mellonella* is also related to the physical surroundings and stresses experienced by the larvae. Exposure of the larvae to either mild thermal shock conditions (4 °C or 37 °C) or to non-lethal physical stress prior to infection induces the protective immune response of increased haemocyte production and elevated expression of antimicrobial peptides as previously mentioned^{46,47}.

Due to the high level of immunological homology shown by insects and mammals, insects are now being used to evaluate the therapeutic effects and *in vivo* activity of known and novel antimicrobial drugs. Previously, the assessment of these drugs relied heavily on immunocompetent and immunosuppressed animal models, but they are now also being screened using the fruit fly *Drosophila melanogaster*⁴⁸, the silkworm *Bombyx mori*⁴⁹ and, more recently, the larvae of the greater wax moth *G. mellonella*⁵⁰.

Amphotericin B, flucytosine and fluconazole all prolonged the survival of *C. neoformans* infected *G. mellonella*, with the combinational therapy of amphotericin B plus flucytosine being the most effective²³. These results were in agreement with the findings of other model systems, including mammalian models²³. The antifungal efficacy of the silver(I) compounds, AgNO₃ and [Ag₂(mal)(phen)₃] (malH₂ = malonic acid, phen = 1,10-phenanthroline) in *C. albicans*-infected *G. mellonella* has been determined⁵⁰. It was shown that administration of the silver(I) compounds 1 h prior to, or 1 h and 4 h subsequent to infection by a lethal dose of *C. albicans* can significantly increase the survival time of the larvae. It was suggested that the increase in concentration of haemocytes and the expression of genes for antimicrobial

peptides function in conjunction with the antifungal properties of the compounds⁵⁰.

1.3 Bacterial Infections

Bacteria are prokaryotic cells that are essential for life on Earth. They inhabit nearly all niches on the planet, from soil to hot springs and even deep within the Earth's crust⁵¹. Bacteria have a diverse roll in both the environment and in our bodies. They decompose matter from dead organism and return vital nutrients to the earth. Bacteria can live symbiotically with hosts, keeping other pathogenic organisms in check. Most bacteria are very beneficial to our environment but there are some which cause disease in animals and plants.

1.3.1 *Escherichia coli*

Escherichia coli is a Gram-negative bacterium (Figure 12) that is commonly found in the lower intestine of humans and warm-blooded animals⁵². They are part of the normal flora of the gastrointestinal tract and are the dominant species in the aerobic faecal flora of humans. They are actively mobile due to the presence of flagella. These bacteria benefit the host through the production of vitamin K and by preventing the unwanted growth of other bacteria.

Although most *E. coli* strains are harmless there are some which can cause serious illnesses (e.g. *E. coli* O157:H7) and distinguishing between commensal and pathogenic strains can be difficult⁵³. Transmission of *E. coli* is by faecal-oral contact (usually by ingestion of food and water) and the presence of *E. coli* in water or soil is an indicator of faecal contamination. The bacterium produces toxins, known as Shiga toxins, which damage the lining of the intestines and other target organs such as the kidneys. They can cause diarrhoea, urinary tract infections, meningitis, wound infections and pneumonia. *E. coli* O157:H7 is responsible for 73,500 cases of infection, 2,150 hospitalisations and 61 deaths in the USA every year⁵⁴. Strains of *E. coli* resistant to many broad spectrum

antibiotics (including cephalosporins) have emerged over the last number of years, mainly in hospital environments⁵².

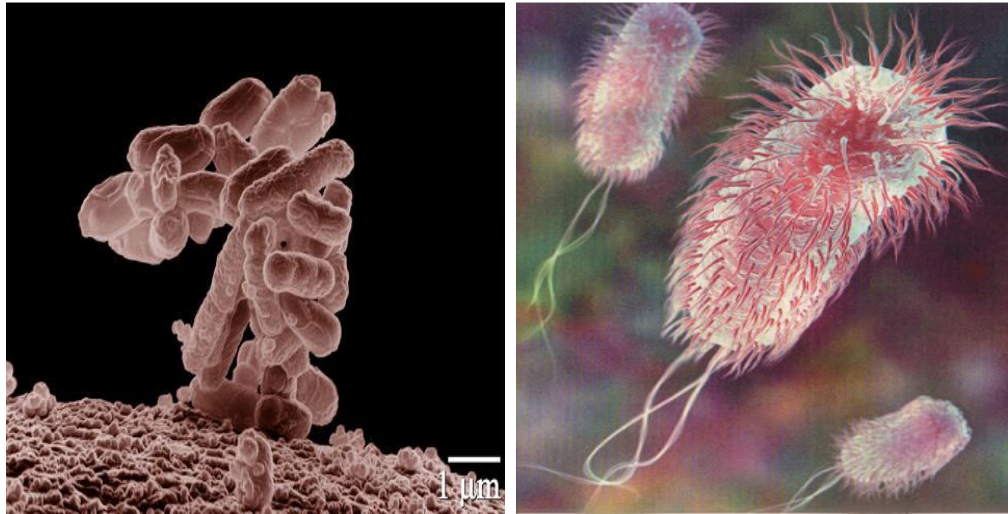


Figure 12. SEM of *E. coli* rods.

1.3.2 Methicillin-resistant *Staphylococcus aureus* (MRSA)

Staphylococcus aureus is a Gram-positive spherical bacterium that is commonly found in the nasopharynx or on our skin⁵² (Figure 13). It can cause infections ranging from minor skin abscesses to serious diseases such as meningitis, endocarditis and septicaemia. MRSA is a strain of *S. aureus* that is resistant to the β -lactam class of antibiotics, including the penicillins and cephalosporins. It is one of the most commonly acquired nosocomial infections and is known as the hospital superbug⁵³. It can be transmitted by touch alone, and due to this, hospitals and nursing homes, containing patients which are more susceptible to infection, are ideal breeding grounds for it. MRSA becomes particularly problematic if it enters the body and treatment is generally by administration of glycopeptide antibiotics like vancomycin and teicoplanin. These antibiotics inhibit the growth of bacterial cells by binding to the amino acids in the cell walls and preventing peptidoglycan synthesis.

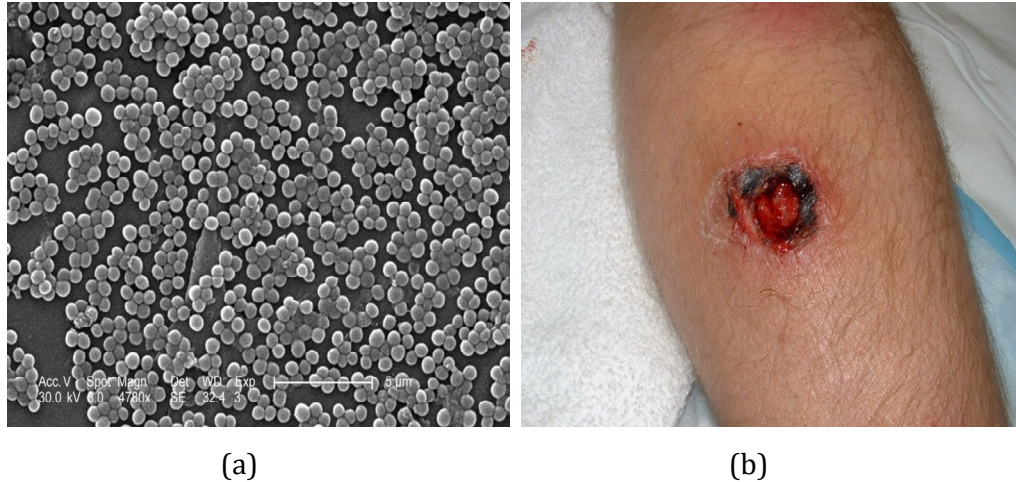


Figure 13. (a) SEM of *S. aureus* cells and (b) *S. aureus* infection of the leg.

1.3.3 Antibiotics and Antibacterial Agents

An antibiotic is any substance that kills or inhibits the growth of bacteria. There are many classes of antibiotics, with the classical ones being sulfonamides, penicillins, cephalosporins and aminoglycosides (Figure 14)^{55,56}. Many antibiotics are produced naturally by microorganisms (e.g. penicillin), while some of these natural compounds provide a building block for the manufacture of synthetic derivatives. Most antibiotics from microorganisms have fewer side-effects than synthetic chemical compounds and this can be largely accredited to their increased target specificity.

Sulfonamides are synthetic antibiotics that target bacterial enzymes by binding to them and inhibiting the production of essential compounds within the cell (e.g. co-factor tetrahydrofolate)⁵⁵. Penicillins and cephalosporins are β -lactam antibiotics which act on the cell wall of bacteria⁵⁶. They share the structural feature of a β -lactam ring and inhibit the formation of peptidoglycan cross-links within the cell wall, which weakens the wall osmotically and causes cell death. Aminoglycosides consist of a linked ring system composed of aminosugars and an aminosubstituted cyclic polyalcohol. They bind to proteins in the ribosome of the bacterial cell and prevent DNA replication. Aminoglycosides are poorly absorbed when given orally and so are administered intravenously. They also exhibit high toxicity, affecting the ear and kidney⁵⁶.

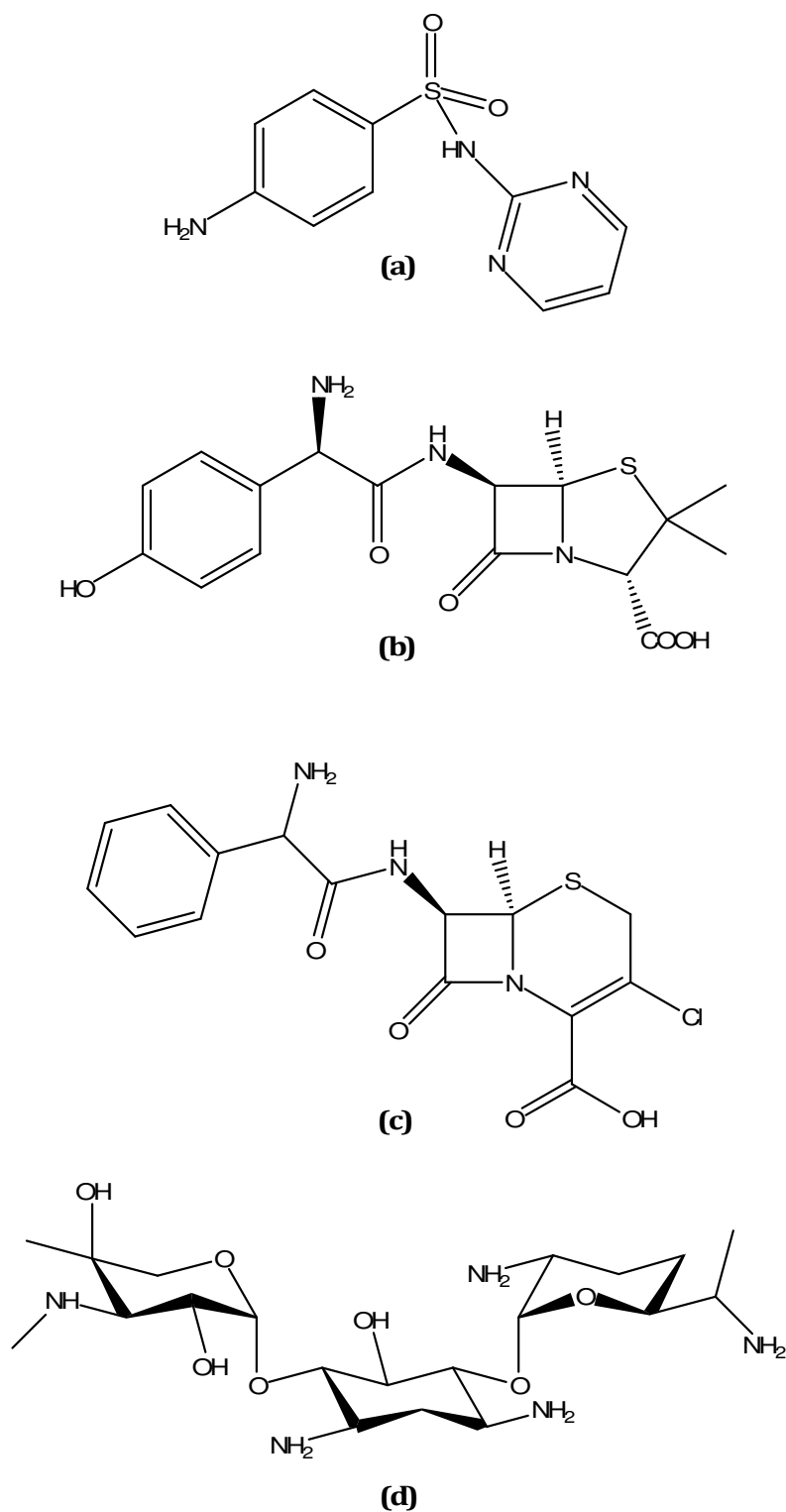


Figure 14. Current antibiotics: (a) sulfadiazine, (b) amoxicillin, (c) cefaclor and (d) gentamicin.

1.3.4 Bacterial Resistance

Bacterial resistance to antibiotics and antibacterial agents has emerged in much the same manner as fungal resistance. This is not a new phenomenon, with resistance to penicillin documented in the 1940s. Resistance can arise through either a modification of the target site or enzyme, prevention of access for the antibiotics or production of enzymes that destroy or inactivate the antibiotic⁵⁵. Resistance to bacteria usually begins in hospital environments, where patients suffering from severe illnesses are treated with the most recent and sophisticated antibiotics. Bacterial resistance in communities is a growing cause for concern and the indiscriminate use of broad spectrum antibiotics is thought to be one of the primary causes for the recent rise in its occurrence.

β -Lactam antibiotics all contain the β -lactam ring structure and it is this characteristic that has led to their downfall. All bacteria contain enzymes (β -lactamases) capable of hydrolysing the β -lactam ring and forming an inactive product⁵⁶. In general, these enzymes are only produced in small amounts, but in certain strains of bacteria an overproduction of the enzymes has been associated with treatment failure (e.g. MRSA, *Pseudomonas aureginosa*). Resistance to aminoglycosides results largely from interference with the drug transport mechanism following modification of the antibiotic by one or more of a series of enzymes produced by the bacteria.

1.4 Cancer

Cancer is a set of diseases characterised by unregulated cell growth leading to invasion of surrounding tissues and spread (metastasis) to other parts of the body⁵⁷. It is represented by a population of cells within the body which escapes from normal control and continues to increase until, unless treated, leads to the death of the host. It can affect almost any tissue of the body, with the skin, digestive organs, lungs and breasts being the most prone to infection. Cancer has been known for thousands of years, as far back as the early Egyptians⁵⁷. It is

one of the leading causes of death worldwide, accounting for 7.4 million deaths (~13% of total deaths) in 2004⁵⁸. Deaths from cancer are projected to continue rising, with an estimated 12 million deaths in 2030. The most frequent types of cancer differ between men and women, but tobacco smoking is the single most important risk factor. More than 30% of cancer could be prevented by modifying or avoiding key risk factors, including:

- tobacco use
- obesity
- low fruit and vegetable intake
- physical activity
- alcohol use
- pollution from fossil fuels.

1.4.1 Tumour Growth

Cancer can arise from a change in one single cell. This change may be initiated by external agents (carcinogens) or by inherited genetic factors. When cancerous cells begin to grow uncontrollably they form a swelling known as a tumour⁵⁹. This growth can invade and destroy surrounding normal tissues as well as travel through the lymphatic vessels or circulatory system to other sites forming secondary growths called metastases (process known as metastasis). Metastasis is the major cause of death from cancer⁵⁸.

Mitosis is the processes of cell division used by nearly all cells in the body (the exception being reproductive cells)⁵⁹. It is regulated by certain growth factors and environmental stimuli (e.g. contact with other cells) to limit the number of cells being produced. In general, normal, non-malignant cells divide to replace a cell which has been lost, thus maintaining a constant cell population. Cancer cells do not respond to these factors and so their proliferation goes unregulated⁵⁷. There can also be a decrease in the number of cells undergoing apoptosis (programmed cell death) and this, when combined with unrestricted proliferation, leads to a massive increase in cell populations.

1.4.2 Cancer Treatment

The treatment of cancer is very complicated due to the biological similarity of normal and malignant cells. Treatments include surgery, chemotherapy, radiotherapy, immunotherapy, hormonal therapy, angiogenesis or a combination of these. There is significant research into anticancer agents in the hope to find a cure, but it is very likely that a single cure will never be found. This is due to the vast number of ways in which cancer can affect different parts of the body.

1.4.2.1 Chemotherapy

Chemotherapy is the main form of drug treatment at all stages of cancer illnesses. The chemicals involved are aimed at interrupting the cell cycle, in particular by inhibiting cell division⁵⁹. Chemotherapy drugs can have very high toxicity levels and are generally not very specific. This can lead to many side effects, particularly in bodily systems that have a rapid turnover of cells similar to a malignant growth, such as the skin, hair, gastrointestinal and bone marrow. To increase their efficacy, combinational chemotherapy is often used. Chemotherapy agents can be divided into three main categories by their mechanism of action⁶⁰:

- stopping the synthesis of pre-DNA molecule building blocks (e.g. methotrexate, fluorouracil)
- directly damaging the DNA in the nucleus of the cell (e.g. cisplatin, doxorubicin)
- effect the synthesis or breakdown of the mitotic spindles (e.g. vinblastine, paclitaxel)

1.4.2.2 Metal-based Chemotherapy

The field of metal-based anticancer drugs was initiated by cisplatin (*cis*-diaminedichloroplatinum(II)) in the 1960s (Figure 15). It was approved for clinical use in 1978 and it revolutionised the treatment of many cancer forms, including testicular cancer for which, if tumours are discovered early, a highly impressive cure rate of nearly 100% is now achieved⁶¹. Since its discovery,

three other structurally related platinum drugs have also been approved for clinical use. These are, carboplatin, nedaplatin and oxaliplatin (Figure 15). Together, these drugs have sales in excess of US\$2 billion per year⁶². Their efficacy and importance is shown by the fact that there are very few cancer treatment regimens today that do not contain a platinum drug.

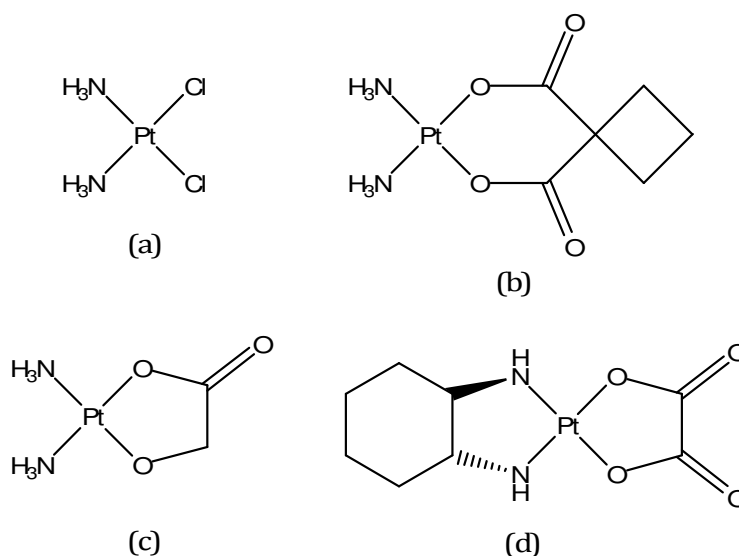


Figure 15. Structures of (a) cisplatin, (b) carboplatin, (c) nedaplatin and (d) oxaliplatin.

Cisplatin contains a square planar platinum(II) centre with two ammonia and two chloride ligands coordinated in a *cis* conformation. The complex inhibits cell growth through interaction with DNA. It is administered by injection and remains intact until it crosses the cell membrane, at which point one or both of the chloride ligands gets replaced by water. The cationic platinum complex then interacts with bases on DNA (most commonly guanine), disrupting it and inhibiting replication. The cell then gets flagged as damaged and apoptosis occurs⁶². Unfortunately, cisplatin is highly toxic and can only be administered in small doses. Side effects include nephrotoxicity, nausea, vomiting and loss of sensation in the extremities. These arise from the non-specificity of the drug and the resulting damage in tissues other than the targeted tumour.

The success of cisplatin led to a huge increase in the synthesis and screening of platinum compounds for their anticancer potential. Cisplatin was used as a benchmark, with the targeted structure being a square planar platinum(II) centre with two *cis*-amines and two leaving groups. The analogues of cisplatin were shown to have similar efficacy but with no real benefits over cisplatin⁶³. Carboplatin was shown to be less toxic than cisplatin but it also has reduced activity against testicular, head and neck cancers. In 2004, Sanofi-Aventis released oxaliplatin, a new platinum(II) drug with a different activity spectrum than cisplatin. It was effective against colorectal cancer, a disease not treatable by either cisplatin or carboplatin, and was also effective against some cisplatin-resistant cancers⁶².

Although the *cis*-isomer has been proven to provide anticancer activity, the *trans*-isomer has not been completely ignored. Transplatin has been shown to be biologically inactive⁶⁴, but *trans* compounds containing pyridine, alkylamine, isopropylamine and iminoether ligands have similar potency to cisplatin and, more importantly, are active against cisplatin-resistant strains⁶⁵⁻⁶⁸. There are many more platinum drugs currently in clinical trials but, for now, cisplatin remains the platinum-based drug of choice for many cancers.

Metal-based chemotherapy does not solely involve platinum, and complexes containing ruthenium, iron, titanium, gallium, arsenic, gold and silver are under investigation^{62,69-72}. The ligand exchange kinetics of ruthenium(II) are similar to that of platinum(II) and many research groups have based their work around this fact⁶². Ruthenium drugs have a similar mode of action to platinum drugs by interacting with DNA to inhibit replication. The first ruthenium drug to enter clinical trials was NAMI-A (imidazolium *trans*-[tetrachloro(dimethylsulfoxide(imidazole)ruthenate(III))] (Figure 16). Unusually, it was inactive against primary tumours but very potent against metastasis tumours. This particular quality could be very beneficial in combinational chemotherapy. The structurally similar complex, KP1019 (indazolium *trans*-[tetrachloro-bis(1H-indazole)ruthenate(III)]) (Figure 16), is active against primary tumours and is currently being investigated for use in

the treatment of colorectal cancers. A family of ruthenium(II)-arene complexes have also been designed which exhibit high *in vitro* and *in vivo* anticancer activity⁷³.

A number of iron-containing anticancer drugs based on substituted ferrocenes have shown good potential as anticancer agents⁶⁹. These include ferricenium picrate and ferrocifen, the ferrocene derivative of tamoxifen (Figure 16). These compounds do not interact with DNA directly but form reactive oxygen species which leads to oxidative DNA damage.

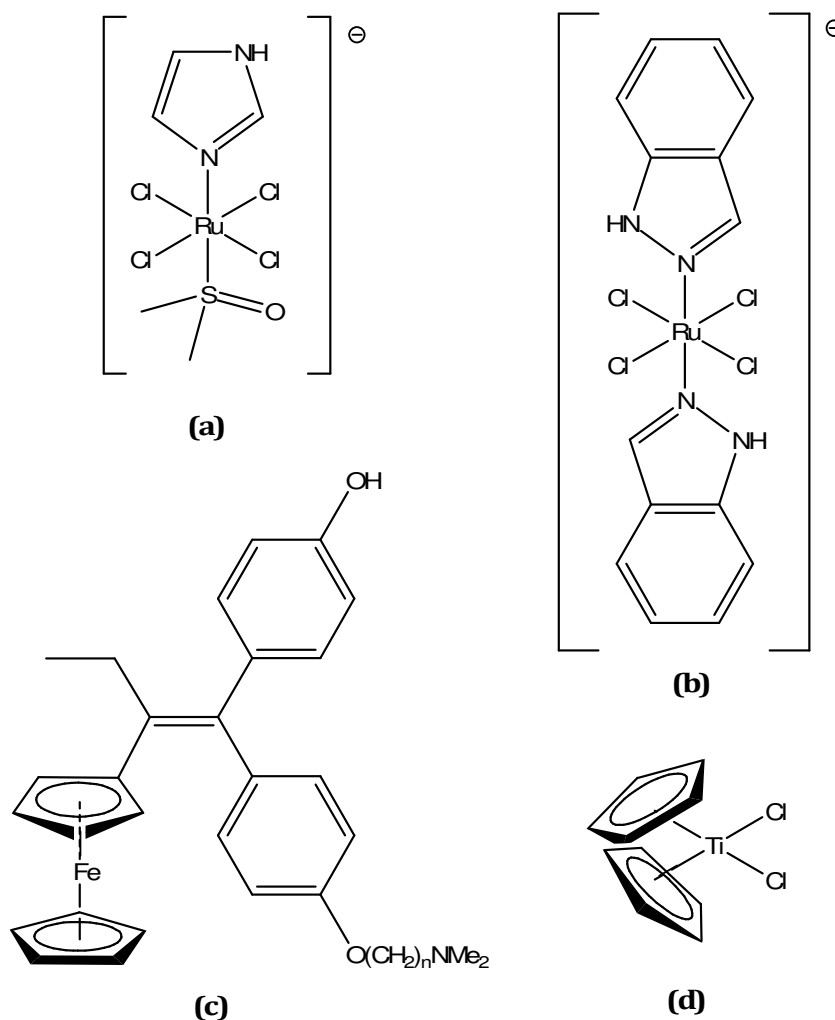


Figure 16. Structures of some anticancer agents: (a) NAMI-A, (b) KP1019, (c) ferrocifen and (d) titanocene dichloride.

Some titanium(IV) complexes have shown promising results and titanocene dichloride (Figure 16) was the first of these compounds to enter clinical trials. The downfall to these compounds is their poor aqueous solubility and substituted titanocenes are currently being developed to combat this (e.g. Titanocene Y)⁷⁴. The mechanism of action of titanocenes is not fully understood but they are thought to covalently bind to DNA and induce apoptosis⁷⁵.

Although arsenic can cause severe health problems in high concentrations, arsenic compounds (e.g. arsenic trioxide) have been shown to have many anticancer properties^{70,76}. Arsenic trioxide and its methylated species are known carcinogens,⁷⁷ yet As₂O₃ has been proven to be very effective against certain haematological malignancies, such as acute promyelocytic leukemia⁷⁸. Arsenic compounds target the mitochondrial proteins involved in regulating the production of reactive oxygen species. The inhibition of these proteins leads to an increase in reactive oxygen species and induces apoptotic signalling pathways⁷⁰.

The use of silver(I) in anticancer therapies has been very limited to date. There are now many research groups investigating the anticancer activity of silver(I) and the results appear promising. The silver(I) complex [Ag₂(phen)₃(mal)]·H₂O (phen = 1,10-phenanthroline, malH₂ = malonic acid) has been shown to be 3.5 times more active than cisplatin at inhibiting human renal and hepatocellular cancer cells *in vitro*⁷⁹, while silver(I)-coumarin complexes were found to be between 2.5 and 5.5 times more cytotoxic than cisplatin^{72,80}. There was also a tendency for the coumarin complexes to be selectively cytotoxic to the carcinoma-derived cell lines relative to normal renal and hepatic cells. Activity towards breast and ovarian cancer has also been reported, with preliminary *in vivo* studies in mice showing no serious side effects^{81,82}.

1.5 Introduction to Silver

1.5.1 A Brief History of Silver

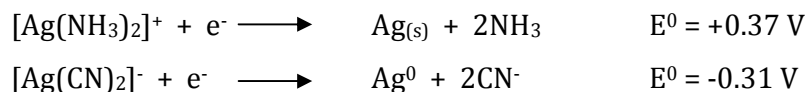
The chemical symbol for silver, Ag, is derived from the Latin *argentum*, meaning shiny or glistening. It is commonly found throughout nature as the metal and as sulfide ores, usually accompanied by sulfides of Fe, Cu and Ni⁸³. Its abundance in the Earth's crust is 0.07 ppm and it is isolated as a by-product in the processing of certain metal ores, such as galena (PbS) and copper pyrite (CuFeS₂), as well as cyanide leaching from silver ores⁸⁴. The final purification of silver is generally carried out by electrolysis. It has been widely used throughout history, in jewellery, ornaments and coinage material, and also has medicinal, photographic and catalytic applications.

1.5.2 The Chemistry of Silver

Silver exists in two isotopic forms, ¹⁰⁷Ag and ¹⁰⁹Ag, found in similar proportions. The metal has the highest known electrical and thermal conductivities of all metals and its outer electronic configuration is 5s¹ 4d¹⁰. Due to this configuration, silver metal is borderline between main group metals and transition metals. While Ag⁰ is relatively inert, the oxidised species, Ag⁺ and Ag²⁺, can undergo many reactions. The interconversion of Ag⁰ and Ag⁺ can be understood by studying the reduction potential of this couple in water⁸³:

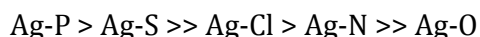


The reduction potential of +0.799 V indicates a relatively strong thermodynamic driving force for the reduction of free, uncomplexed Ag⁺ ions to the Ag⁰ state. However, the presence of complexing ligands can greatly affect this potential⁸³. For example, when the Ag⁺ ion is ligated with two ammonia ligands reduction to Ag⁰ becomes more difficult, while with cyanide ligands reduction becomes even less likely:



Phototropic glass utilises this reversible property of silver. It contains an Ag^+ halide salt, which darkens on exposure to sunlight. Under these conditions, the electrons in the halide ions acquire enough energy to move and reduce the Ag^+ ions to metallic Ag^0 . The resulting silver atoms then aggregate into tiny particles, scattering light and turning the glass dark. The reaction reverses upon the removal of the light source.

The Ag^+ ion, with its d^{10} electron configuration, has zero ligand field stabilisation energy (LFSE) and will form labile complexes in which there will be rapid exchange of the original ligand set for new ligands available from the surrounding system. The low charge density on Ag^+ allows it to act as a 'soft' Lewis acid and, as such, will tend to have a relatively small affinity for 'hard' O-donors, a large affinity for 'soft' S-, Se- and P-donors, and a moderate affinity towards N-donor atoms. Studies on ligand-exchange reactions have suggested the relative order of Ag^+ bond strengths to be⁸⁵:



Transition metals have been used widely in organic synthesis for many decades⁸⁶⁻⁸⁸. Silver is used in heterogeneous oxidation processes and homogeneous silver-mediated and catalysed reactions. Silver(I) is considered a mild oxidising agent and, as such, is suitable for the efficient oxidation of primary and secondary alcohols to aldehydes and ketones⁸⁹. Silver(I) oxide (Ag_2O) in aqueous ammonia is known as Tollens' reagent and is used to oxidise aldehydes to carboxylic acids, producing metallic silver in the process⁹⁰. In many cases, the application of silver in organic synthesis is driven by its Lewis acidity and the solubility of its salts, in particular its halogen salt formations⁹¹. The silver salts activate the reactions towards nucleophilic substitutions and eliminations by interacting with the halogen atom forming insoluble silver halides.

Research into the catalytic properties of silver(I) was inspired by the use of gold(I) as a catalyst in organic synthesis⁹²⁻⁹⁴ and these have been utilised extensively since then⁸⁹. The advantages of using a silver catalyst include shorter reaction times, increased stability towards exposure to air and moisture, and ease of preparation and storage. Some examples of silver(I) catalysts include the BINAP-Ag(I) catalyst (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) for enantioselective allylation of aldehydes with allylic stannanes,⁹⁵ and an amino acid derived phosphine-Ag(I) catalyst that efficiently promotes enantioselective Mannich reactions of silyl ethers and aryl imines regardless of the quality of the solvent or exposure of the reaction mixture to air⁹⁶.

1.5.3 Coordination Chemistry of Silver

Silver has four oxidation states, with Ag(I) being the most common. The spherically symmetric configuration of the Ag(I) ion allows the coordination number to vary from 2-6. The d_{z^2} and s orbitals of silver are close in energy allowing for extensive hybridisation to occur^{97,98}. Electrons within these hybrid orbitals (Ψ_1 and Ψ_2) form a high electron density circular region repelling ligands, and also a relatively low electron density region above and below this ring in which ligands are attracted. The further mixing of the Ψ_2 and p_z orbitals leads to two hybrid orbitals suitable for forming linear covalent bonds (Figure 17).

Silver(I) is stable in aqueous solution as $[\text{Ag}(\text{H}_2\text{O})_2]^+$ but the Ag^+ ion has a low affinity for the hard aqua ligand giving a tendency for its crystalline inorganic salts to be anhydrous. Silver halides (AgX) can easily be prepared by direct addition of X^- to Ag^+ solutions and their solubility in water increases in the order $\text{Cl} > \text{Br} > \text{I}$. The solubility of silver(I) halides is increased in an alkaline solution of ammonia due to the formation of $[\text{Ag}(\text{NH}_3)_2]^+[\text{X}]^-$ salts. Silver(I) halides can react with further halide ions to yield anionic complexes which can occur in polymeric form⁸⁴, while cationic species, such as $[\text{Ag}_2\text{X}]^+$ and $[\text{Ag}_3\text{X}_2]^+$, can be formed when silver halides are reacted with either AgNO_3 or AgClO_4 .

Silver halides are highly light-sensitive and it is this property that makes them useful in photography.

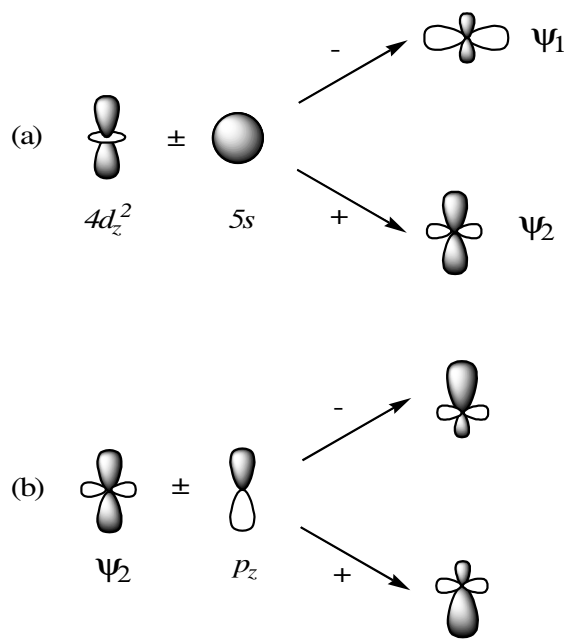


Figure 17. Hybrid orbitals from (a) a d_z^2 and s orbital (Ψ_1 and Ψ_2) and (b) the hybrids that can be formed from Ψ_2 and the p_z orbital.

Silver complexes containing N-donor ligands readily form in aqueous solutions with large formation constants observed for complexes of the type $[\text{AgL}]^+$ and $[\text{AgL}_2]^+$ due to their preference for linear coordination⁹⁹. Tetrahedral silver(I) complexes can be formed when nonaqueous conditions are employed⁸³ and complexes with a square planar geometry are also known¹⁰⁰. There has been extensive research into silver(I) complexes with N-donor ligands, including those of aromatic ligands such as azoles¹⁰¹⁻¹⁰³. The most important classes of O-donor ligands for complexation with silver(I) include carboxylates, crown ethers and calixarenes. Silver(I) carboxylates are light-sensitive and generally very insoluble, which leads to difficulty in their characterisation. Silver(I) also forms numerous complexes with the donor atoms S, Se, P and As, and also binds to peptides and proteins, with a preference for the thioether sulfur atoms and imidazole nitrogen atoms⁸³.

Argentophilicity is the tendency of Ag(I) ions to aggregate at distances below the van der Waals diameter of 3.44 Å¹⁰⁴. This tendency is also observed with the *d*¹⁰ gold(I) ion (called aurophilicity)¹⁰⁵. The covalent radius of a 2-coordinate Ag(I) ion (1.33 Å) is larger than that of both Cu(I) (1.13 Å) and Au(I) (1.25 Å)¹⁰⁶. The ionic radius of Ag⁺ is 1.29 Å⁸³. Whilst the interaction between the gold(I) ions is comparable in strength to hydrogen bonds, the Ag(I)⋯Ag(I) interactions appear to be much weaker. The strength of these interactions can be responsible for the structural arrangement of crystals. Whilst aurophilicity in gold(I) complexes can be a determining factor in the complex structure, the argentophilicity of silver(I) complexes is weaker and the structure may be governed by the strength of the hydrogen bonds.

The other oxidation states of silver include Ag(II), Ag(III) and Ag(IV). The Ag²⁺ ion is an orange, transient species ([Ag(H₂O)₆]²⁺) produced by the oxidation of Ag(I) salts with ozone in strongly acidic solution⁸⁴. Silver is known to have a catalytic effect on the reactions of many gases with fluorine. This is due to the formation of the dark brown Ag(II) species, AgF₂, as an intermediate. Fluoride ions and AgF₂ can interact to form the complexes [AgF₃]⁻, [AgF₄]²⁻ and [AgF₆]⁴⁻. Ag(II) also forms stable complexes with a variety of nitrogen donor ligands, such as pyridine, substituted bipyridines, phenanthroline and porphyrins. They are usually formed by reaction of a silver(I) salt with peroxodisulfate in the presence of the ligand. Ag(III) and Ag(IV) are not as commonly found. The commercially available oxide, AgO, has been shown not to contain Ag(II) but to be a mixed-valence compound containing Ag(I) and Ag(III)⁸³. The Ag(III) ion has square coordination while the Ag(I) ion has linear coordination. Trisilver tetroxide, Ag₃O₄, contains both divalent and trivalent silver and can be written as Ag^IAg^{III}₂O₄. Fluorination of a mixture of CsCl and AgCl under pressure yields the complex salt of tetravalent silver Cs₂[AgF₆], which contains Ag(IV)⁸⁴.

1.5.4 Biological Activity of Silver

Silver is present in the human body at very low concentrations (<2.3 µg l⁻¹) and is absorbed through the lungs, gastrointestinal tract, mucus membranes and the

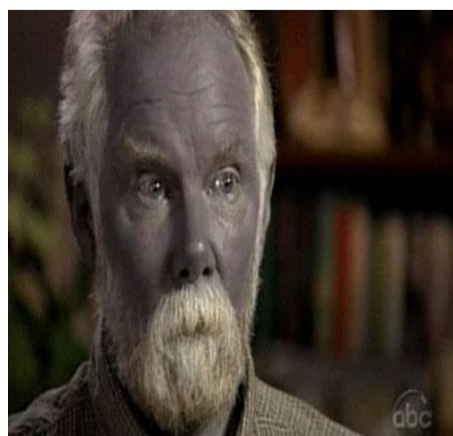
skin¹⁰⁷. It is absorbed mainly in the form of silver protein complexes but has no physiological or biochemical role within the body¹⁰⁸. It can be tolerated at high concentrations within the body, does not appear to be a cumulative poison and is eliminated from the body through the urine and faeces¹⁰⁷.

1.5.4.1 Argyria

Argyria is a condition associated with the accumulation of silver in the blood and soft tissues, particularly the skin. It occurs in individuals who are exposed to high levels of silver occupationally or through the consumption or inhalation of silver hygiene products for long periods. The condition presents itself by the darkening of the skin (from blue-grey to black depending on the severity) due to the deposition of silver sulfide, silver selenide or colloidal silver, particularly in the regions of the sweat glands and hair follicles (Figure 18). Argyria cases are quite rare and, although cosmetically undesirable, it is not thought to be life-threatening¹⁰⁹.



(a)



(b)

Figure 18. (a) Rosemary Jacobs, presented with argyria after using nasal drops containing colloidal silver for four years and (b) Paul Karason, an argyria sufferer.

1.5.4.2 Silver in Health Care

The antimicrobial properties of silver have been known for centuries. It was used in ancient Greece and Rome as a disinfectant, while the Macedonians used it to encourage the healing of wounds¹¹⁰. With the advent of modern antibiotics

in the 20th century, silver became less favoured. However, in more recent times silver has been incorporated into many medicinal and commercial products due to its high antimicrobial potency. Such products include plasters, dressings, clothing, mobile phones, washing machines, paints and even antiperspirant sprays (Figure 19).

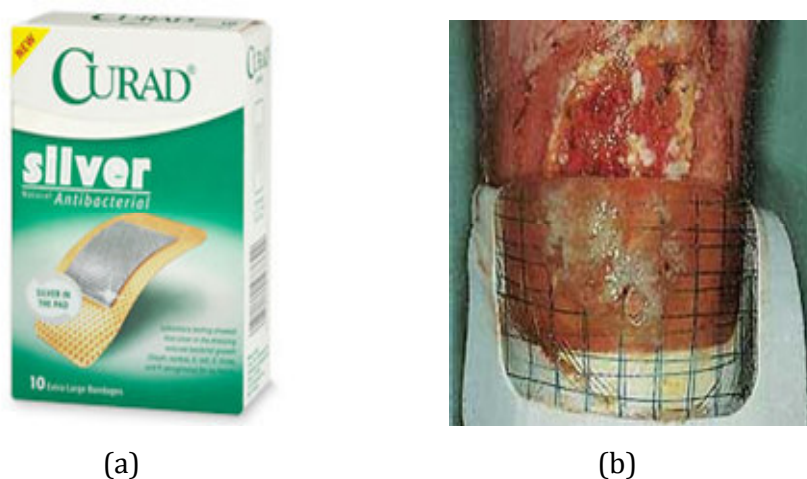


Figure 19. (a) Curad plasters which contain a fine mesh of silver(0) and (b) Aquacel Ag Hydrofibre dressing on a leg wound.

It is thought that the antimicrobial properties of silver complexes is dependent on the release of biologically active silver(I) ions^{108,111}. The exact mode of action of the Ag^+ ions is still a matter for debate, but silver-related degenerative changes in bacterial RNA and DNA, mitochondrial respiration and cytosolic protein have been shown to lead to cell death¹¹². In *C. albicans*, silver(I) inhibits the enzyme phosphomannose isomerase by binding to thiol groups on cytosine residues^{113,114}. This enzyme is essential in the synthesis of the cell wall and defects lead to the release of vital nutrients, such as phosphates and glutamine.

Silver is being incorporated into many materials to give increased antimicrobial protection¹¹⁵. Clinical catheters for central vascular insertion or for urethral drainage are notoriously prone to infection with nosocomial organisms, leading to biofilm formation, infection and blockages¹¹⁶. New technologies have incorporated silver as a component of catheter polymers or as a hydrophilic

coating to inhibit the growth of bacteria and fungi^{117,118}. Occasionally, other antibiotics (e.g. gentamycin) are included to compliment the activity of the silver. Infection associated with the insertion of surgical pins, screws and prostheses is also a common problem. Research is ongoing into the use of silver within these devices, or in the form of coatings, to prevent infection. Polymethacrylate bone cements containing silver have been proven to inhibit the growth of *P. aeruginosa*, *S. aureus* and *E. coli in vitro* but have yet to be proven in clinical trials¹¹⁶. Although infection associated with prosthetic valves in cardiovascular surgery leads to an 80% fatality rate, silver devices have had very limited success in lowering this figure¹¹⁶.

In the past number of years, a new generation of silver-containing wound dressings have become available for use, such as Arglaes (Medline), Aquacel Ag (Conva Tec) and Calgitrol (Magnus Bio-Medical Technologies). They have proven to be very effective at inhibiting the growth of *S. aureus*, *E. coli* and *C. albicans* with the form, location and release rate of the silver being a major influence on their efficacy¹¹⁹⁻¹²¹. In clinical use, these dressings have promoted wound cleansing, controlled inflammation and bacterial load, and improved the healing time of chronic wounds¹²². In each case, wound fluids and exudates trigger the release of free silver ions for antimicrobial action and absorption into tissues of the wound bed.

Silver sulfadiazine is the most important and widely used medicinal silver-containing product. It is marketed under the names of Silvadene and Flamazine and contains silver(I) sulfadiazine in a 1% concentration. It is used in the treatment of burns (Figure 20) where it releases silver ions into the wound site. It has been shown that approximately 10% of the silver released is absorbed into the wounds, with a higher percentage uptake in more vascularised wounds¹⁰⁹.

Research into the antimicrobial properties of silver has continued growing over the last number of years and there are now many different silver complexes exhibiting a broad spectrum of antimicrobial action. The present research work

aims to provide alternatives to some of the products on the market, to widen the spectrum of microbial pathogens susceptible to silver and also to target organisms which are resistant to current silver complexes.

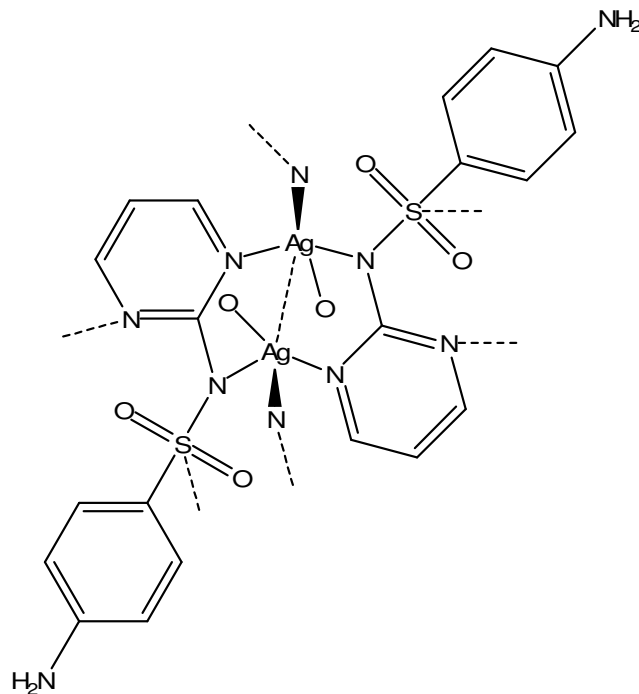
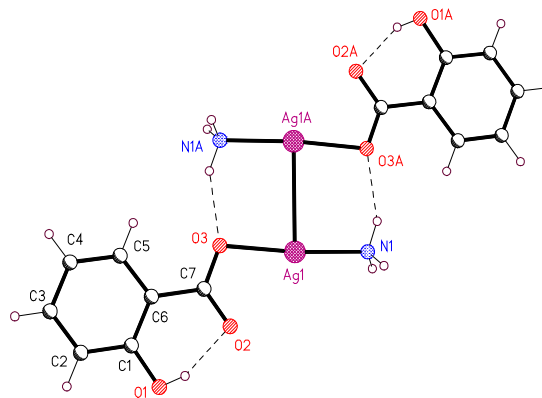
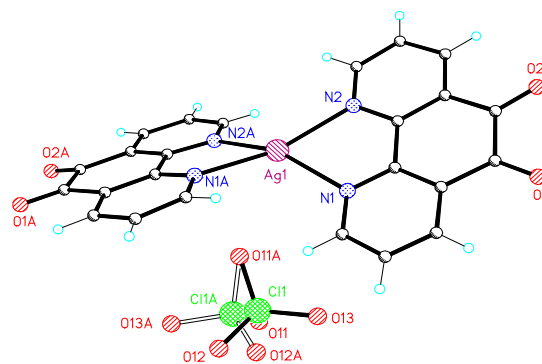


Figure 20. Silver sulfadiazine, the active ingredient in the antimicrobial burn cream Flamazine.

Previous research within our group in NUI Maynooth has shown the antimicrobial effect of various silver(I) complexes incorporating ligands such as, 1,10-phenanthroline, 1,10-phenanthroline-5,6-dione, imidazoles and salicylates^{79,123-127} (Figure 21).



(a)



(b)

Figure 21. X-ray crystal structures of the antimicrobial silver(I) complexes (a) [Ag₂(salH)₂(NH₃)₂] (salH₂ = salicylic acid) and (b) [Ag(phendione)₂]ClO₄ (phendione = 1,10-phenanthroline-5,6-dione).

A number of antimicrobially active silver(I)-coumarin complexes have also been prepared^{128,129}. These complexes possess an ability to disrupt microbial respiration and also block the synthesis of cytochromes¹³⁰. Some silver(I) carboxylate complexes have been shown to be highly cytotoxic to cancer cells but, unfortunately, they also damaged normal cells^{131,132}.

1.5.4.3 Resistance to Silver

Microbial resistance to heavy metals is well known¹³³. Unfortunately, silver is not exempt from this trend, although presently, silver-resistant microorganisms

are not a serious clinical problem¹²¹. Definitive evidence that an organism is resistant to silver or another metallic agent is provided by molecular biology and gene sequencing, which identifies the presence of a mutagenic change within its genome. True resistance must be stable within a population and not a once-off mutation. The basis of most resistance systems is either the energy-dependent efflux of toxic ions or the plasmid-mediated binding of toxins¹³⁴. Both mechanisms stop the accumulation of unwanted molecules/ions within the cell.

Resistance to silver has been known for many years and is most likely to be found in environments where there are high levels of silver present or a high usage of silver-containing products. In 1984, *Pseudomonas stutzeri* AG259 was isolated from a silver mine in Utah, USA¹³⁵. It was found that it carried a plasmid encoding for silver resistance, but the actual mechanism of action was not determined until recently¹³⁶. Resistance mechanisms specific to silver ions were discovered by analysis of a silver-resistant strain of *Salmonella typhimurium* isolated from a burn patient in Massachusetts General Hospital. This strain was transmitted between patients in adjacent rooms and caused severe septicaemia fatalities and the closure of the burns unit. The bacterium contained a plasmid determinant that encodes a periplasmic silver-specific binding protein (SilE) which binds silver at the cell surface, thus protecting the cell. Further genes were found (SilA, SilB, SilC, SilP, SilR, and SilS) that encode for two parallel efflux pumps which remove any silver ions that had slipped past the binding protein^{136,137} (Figure 22).

At present, there are a number of other bacterial species which have exhibited resistance to silver. These include strains of *E. coli*, *Enterobacter cloacae*, *Klebsiella pneumonia* and *Acinetobacter baumannii*^{134,138,139}. These strains have only emerged in rare, isolated instances, so it is thought that the risk of transfer of the silver resistance genes is low.

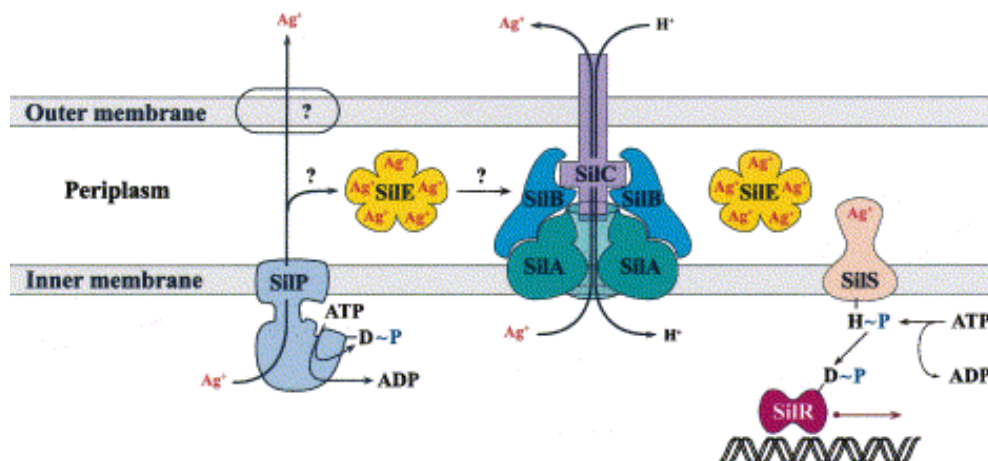


Figure 22. The proposed function of genes encoding for silver resistance¹⁴⁰.

1.6 Metal Carboxylate Chemistry

Carboxylates are a very important class of ligand in bioinorganic chemistry. This can be accredited to the versatility of the RCOO^- ligand and the wide range of coordination modes that it can adopt. A large number of carboxylate complexes have been characterised and the coordination chemistry of carboxylic acids is well documented¹⁴¹. In metal carboxylate complexes the cationic metal centres (M^{n+}) combine with the anionic carboxylate groups (RCOO^-). The bonding can range from ionic to polar covalent with the physical and chemical properties being dependant on the nature of the R group¹⁴¹.

1.6.1 Coordination Modes of Carboxylates

The carboxylate functional group has four lone pairs of electrons on the two oxygen atoms which are available for metal binding (Figure 23). These lone pairs can be divided into syn- and anti-lone pairs and are separated by *ca.* 120° . It has been suggested that the syn-lone pairs are more basic than those in the anti position¹⁴².

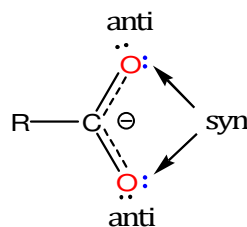


Figure 23. The carboxylate functional group showing syn- and anti-lone pairs of electrons on the oxygen atoms.

There are five different coordination modes for carboxylate groups¹⁴¹:

- (i) *Ionic.* The carboxylate salts of Na⁺, K⁺, Rb⁺ and Cs⁺ have been shown to be ionic and there are only coulombic interactions between the metal and the carboxylic anions (Figure 24(a)).
- (ii) *Monodentate.* The metal is coordinated to only one of the carboxylate oxygens (Figure 24(b)).
- (iii) *Bidentate chelating.* Carboxylates may coordinate to the metal through both oxygen atoms forming a chelate ring. They can do this in a symmetrical mode (Figure 24(c)) with the metal-oxygen bonds of the same length or in an asymmetrical mode (Figure 24(d)) with metal-oxygen bonds of different lengths. The 'bite angle' (O-M-O angle) for a chelating carboxylate is *ca.* 60°.
- (iv) *Bidentate bridging.* Carboxylates can form complexes which bridge two metal atoms (Figure 24(e)-(g)). Depending on the lone pair of electrons used in coordination, the complexes can be syn-syn, syn-anti or anti-anti. The syn-syn coordination mode allows for the possibility of short metal-metal bonds occurring in the complexes.
- (v) *Monodentate terminal bridging.* This is the rarest of the coordination modes and is thought to act as an intermediate between other carboxylate bridging modes¹⁴² (Figure 24(h)).

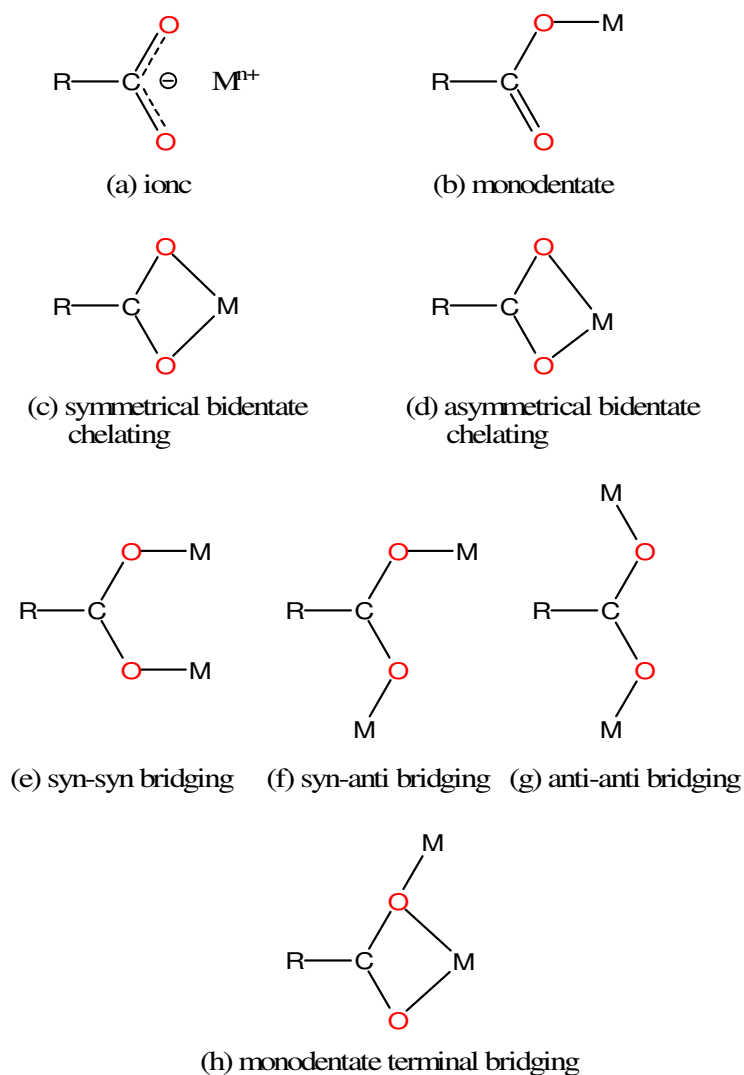
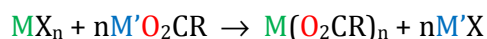


Figure 24. Coordination modes of carboxylate groups.

1.6.2 Synthesis of Metal Carboxylates

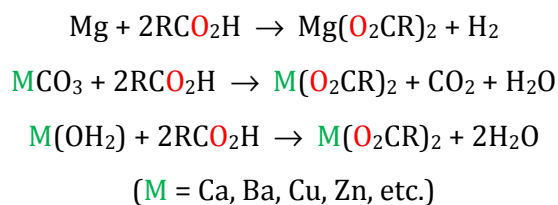
The main synthetic routes to metal carboxylates are:¹⁴¹

(i) *Precipitation reactions.* The metal salt is reacted with a stoichiometric amount of the carboxylic acid in aqueous or alcoholic media. Reactions are generally planned so that one of the products will remain in solution and the other will precipitate out.

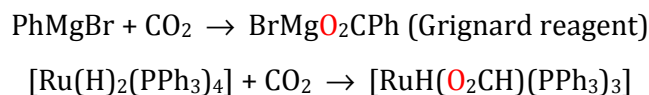


(M = Cr, Fe, Rh, Zn, Cu, Ag, etc.; M' = Na, K, NH₄, etc.; X = Cl, NO₃, SO₄, etc.)

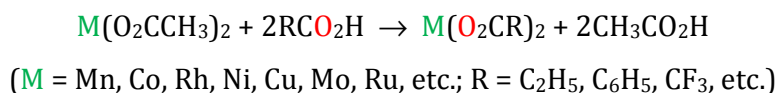
(ii) *Acid/base reactions.* Carboxylic acids can be reacted directly with electropositive metals or with basic metal salts.



(iii) *Carbon dioxide insertion reactions.* Carbon dioxide is inserted into the metal-alkyl/aryl or metal-hydride carbon bonds to form the alkyl/aryl carboxylate or formate.



(iv) *Metathesis reactions.* These are carboxylate ligand exchange reactions in which a metal carboxylate complex is treated with a large excess of new carboxylic acid or carboxylate salt and ligand exchange occurs to generate the new metal carboxylate. The reactions proceed by stepwise substitution with acetates being the most common starting material.



1.6.3 Infra-red Spectra of Carboxylate Complexes¹⁴³

The position of the strong C=O absorption band in the carboxylic acid group of the free carboxylic acid occurs at *ca.* 1760-1680 cm⁻¹. Upon complexation to a metal centre, this $\nu_{\text{C=O}}$ band disappears and two new bands relating to the asymmetric ($\nu_{(\text{OCO})\text{asym}}$) and symmetric ($\nu_{(\text{OCO})\text{sym}}$) stretches appear in the regions 1650-1550 and 1440-1335 cm⁻¹, respectively¹⁴⁴. The magnitude of the separation between these two bands ($\Delta_{(\text{OCO})}$ cm⁻¹) has been used, tentatively, as

a diagnostic aid in the determination of the nature of the carboxylate coordination¹⁴³.

$$\Delta_{(\text{OCO})} = (v_{(\text{OCO})\text{asym}} - v_{(\text{OCO})\text{sym}}) \text{ cm}^{-1}$$

Guidelines for diagnosing the type of carboxylate coordination based on the IR spectrum of the metal complex were compiled by Deacon and Philips¹⁴³, based on eighty four complexed acetates and halogenoacetates¹⁴³. Their findings were:

- (i) Ionic acetates (e.g. those of alkali metals) have $\Delta_{(\text{OCO})}$ values of *ca.* 165 cm^{-1} . For ionic trifluoroacetates the $\Delta_{(\text{OCO})}$ value was *ca.* 235 cm^{-1} .
- (ii) $\Delta_{(\text{OCO})}$ values $<105 \text{ cm}^{-1}$ indicated symmetric chelating carboxylate coordination. Complexes in which the carboxylates bridge short metal-metal bonds may also exhibit values in this region.
- (iii) $\Delta_{(\text{OCO})}$ values substantially less than the ionic values ($<150 \text{ cm}^{-1}$) indicate the presence of chelating or bridging carboxylates. Monodentate carboxylates containing hydrogen bonds (pseudo-bridging) may also fall into this category.
- (iv) $\Delta_{(\text{OCO})}$ values of transition metal complexes similar to that of ionic acetates (*ca.* 165 cm^{-1}) were found to be untrustworthy as many examples of each type of coordination mode were found in this category.
- (v) $\Delta_{(\text{OCO})}$ values of $>200 \text{ cm}^{-1}$ indicates monodentate coordination. This large difference in energy is thought to arise from the bonding of one oxygen atom to the metal with the other oxygen free, increasing the energy of the asymmetric stretching mode.

There have been many contradictions to the $\Delta_{(\text{OCO})}$ assignments¹⁴³, primarily concerned with locating the exact position of the $\Delta_{(\text{OCO})\text{sym}}$ absorption band, and

as such, great care is required when using these guidelines. Tentative assignments for the coordination modes of carboxylate ligands, based on $\Delta_{(\text{OCO})}$ values, are listed in Table 1.

Table 1. Infra-red spectra data ($\Delta_{(\text{OCO})}$) for coordinated carboxylate ligands.

| $\Delta_{(\text{OCO})}$ (cm^{-1}) | Coordination Mode |
|---|---------------------------------------|
| <105 | Symmetric chelating or short bridging |
| <150 | Chelating or bridging |
| ca. 165 | Untrustworthy assignments |
| >200 | Monodentate |

1.6.4 Silver Carboxylates

There are many known silver carboxylate complexes with varying modes of coordination. The silver-oxygen bonds have a strong influence on the morphology of the complexes but there are also π - π and argentophilic interactions to take into consideration.

Zhu *et al.* have shown coordination polymers containing Ag-Ag bonds with mono and bidentate chelation of the carboxylate groups (Figure 25)¹³¹. The Ag-Ag bonds in these complexes are shorter than that of metallic silver yet the Ag-O bonds are slightly longer than those of common Ag-O bonds in aromatic carboxylic acids. Yu *et al.* synthesised a silver(I) complex containing an anion of acridine-9-carboxylic acid and in which there is coordination to silver by the carboxylate oxygen atoms and the nitrogen of the acridine, forming a 1D polymeric chain (Figure 26)¹⁴⁵. Other silver(I) carboxylate complexes include adducts of AgCF_3COO and CH_3COO with 2,2'-bipyridyl¹⁴⁶, silver-1,2-benzenedicarboxylate monomethyl ester and silver-acetyl-benzoate (Figure 27)¹⁴⁷.

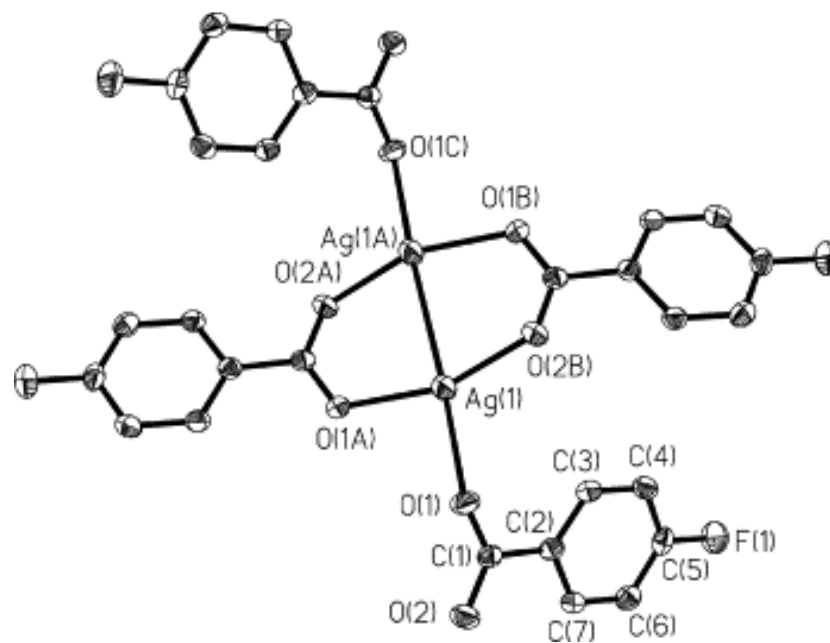


Figure 25. Coordination environment of $[\text{Ag}(\text{fbc})]_n$ (fbcH = 4-fluorobenzoic acid)¹³¹.

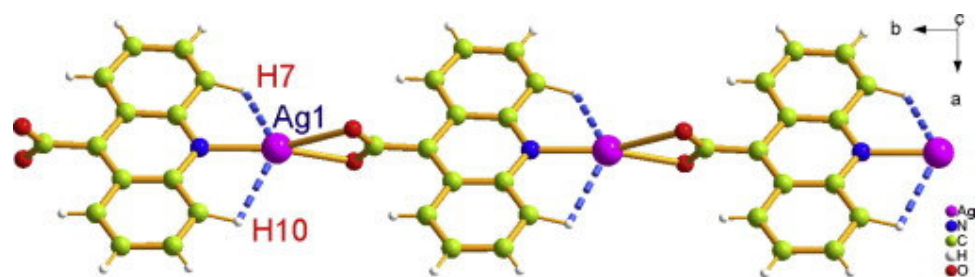


Figure 26. Polymeric structure of $[\text{Ag}(\text{ac-9-ca})]_n$ (ac-9-caH = acridine-9-carboxylic acid)¹⁴⁵.

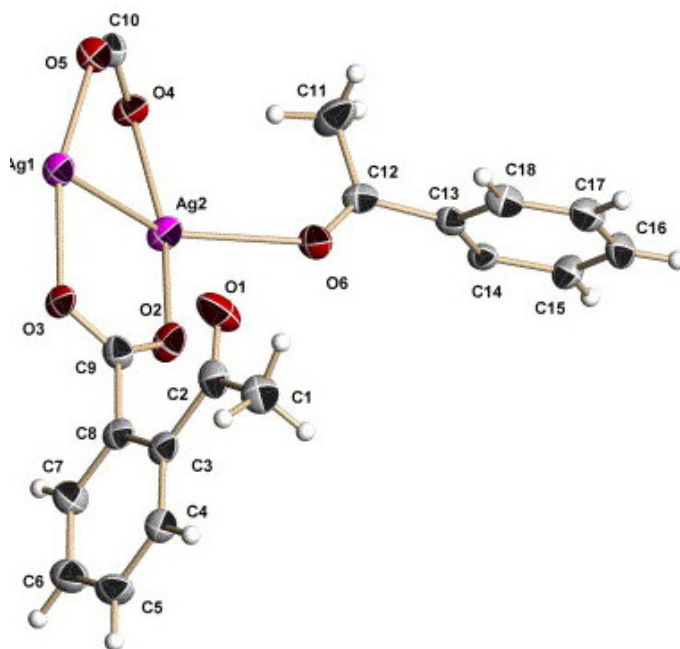


Figure 27. X-ray crystal structure of silver-acetyl-benzoate¹⁴⁷.

1.6.5 9-Anthracenecarboxylic Acid (9-acaH)

9-Anthracenecarboxylic acid (also known as 9-anthroic acid) is a polycyclic aromatic complex consisting of three fused benzene rings with a $-\text{COOH}$ group substituted at the 9-position (Figure 28). The large conjugated π -system of the anthracene ring is currently of interest in the development of fluorescent materials. The acid is used as a model compound for electroluminescence¹⁴⁸, chemosensors¹⁴⁹ and photoinduced electron-transfer sensors¹⁵⁰⁻¹⁵².

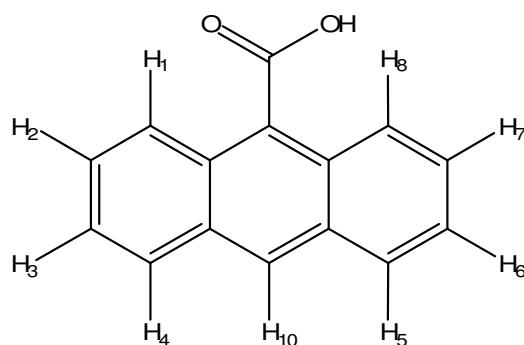


Figure 28. 9-Anthracenecarboxylic acid showing the proton numbering.

It has been shown that the photophysics of 9-acaH is quite different to that of its parent molecule, anthracene¹⁵³. In alcoholic solvents, 9-acaH forms a hydrogen-bonded dimer in its ground state¹⁵⁴ (Figure 29). This then associates with another dimer to form an excited tetramer which exhibits a distinctive broad fluorescence band at 470 nm¹⁵⁵. The dimer is thought to have a linear-type configuration in which the two anthracene rings lie on the same plane with the carboxylate bridge almost perpendicular to it. More recently, 9-acaH has been shown to photodegrade forming a dimer similar to that of anthracene (Figure 30)^{153,156}.

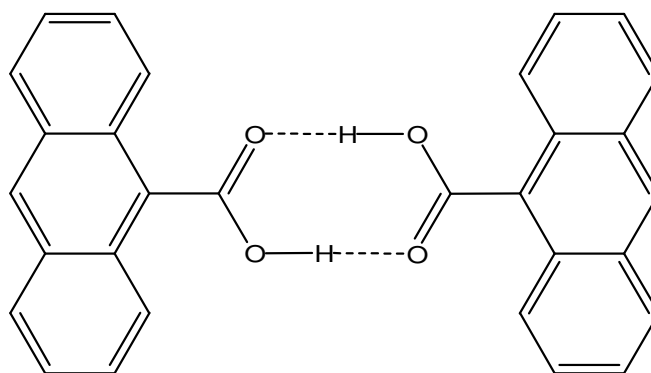


Figure 29. Hydrogen bonded dimer of 9-anthracenecarboxylic acid.

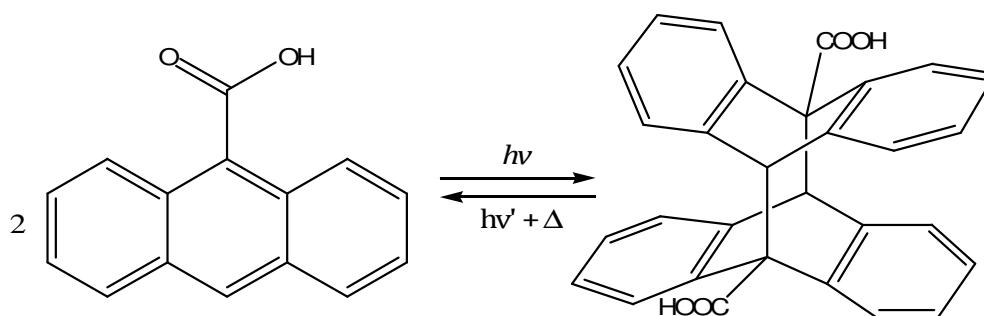


Figure 30. Photodimerisation of 9-anthracenecarboxylic acid.

1.6.6 Metal Complexes of 9-Anthracenecarboxylic Acid

Many metal complexes contain the 9-anthracenecarboxylate anion (9-aca⁻) as an O-donor ligand and it exhibits a number of different coordination modes. Recently, Amini *et al.* have made di- and triorganotin(IV) complexes with 9-acaH¹⁵⁷. The 9-acaH ligand can coordinate in a monodentate mode via a single

carboxylate oxygen atom (Figure 31 and 32) or via the bidentate chelating mode. Liu *et al.* have synthesised Cu(II), Co(II) and Ni(II) complexes containing 9-acaH¹⁵⁸. The dinuclear Cu(II) complex exhibits syn-syn bidentate chelating coordination and is linked into chains via intermolecular hydrogen bonds (Figure 33). Zinc(II) complexes involving 9-acaH have also been synthesised in which the 9-aca⁻ can have either mono- or bidentate coordination modes¹⁵⁹.

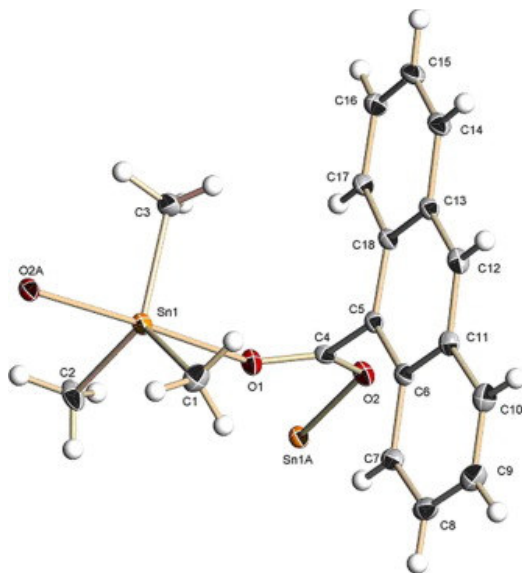


Figure 31. X-ray crystal structures of $[\text{Me}_3\text{Sn}(9\text{-aca})]^{157}$.

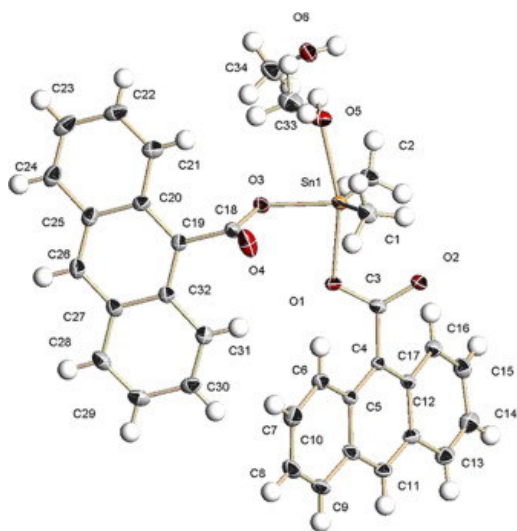


Figure 32. X-ray crystal structures of $[\text{Me}_2\text{Sn}(9\text{-aca})_2 \cdot \text{MeOH}]^{157}$.

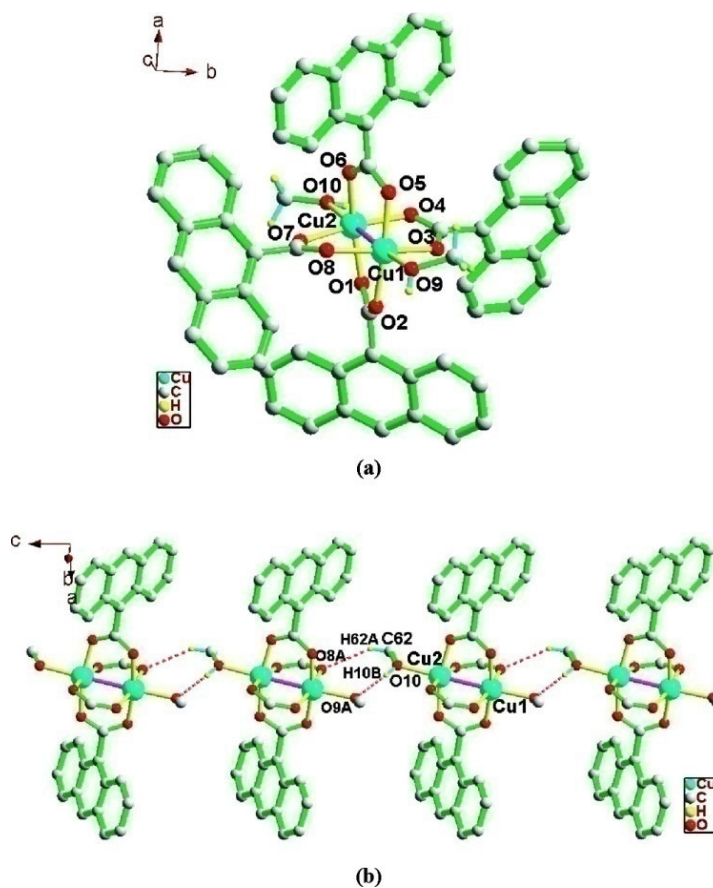


Figure 33. X-ray crystal structure of (a) $[\text{Cu}_2(9\text{-aca})_4(\text{MeOH})_2](\text{MeOH})$ and (b) the intermolecular H-bonding linking the dinuclear units¹⁵⁸.

1.7 Imidazoles

Imidazoles contain a 5-membered aromatic heterocyclic ring with nitrogen atoms at the 1- and 3- positions (Figure 34). The carbons are sp^2 hybridised and each donates one electron into the π -system. The imine nitrogen (3-position) donates one electron and the amine nitrogen (1-position) donates its lone pair of electrons into the π -system. The lone pair of electrons on the imine nitrogen gives imidazole both basic and nucleophilic properties, and it is through this lone pair of electrons that imidazole can bond to transition metals, such as silver(I). Free energy data obtained from potentiometric studies indicate that imidazole forms some of the most stable complexes of all the heterocyclic-N ligands¹⁰².

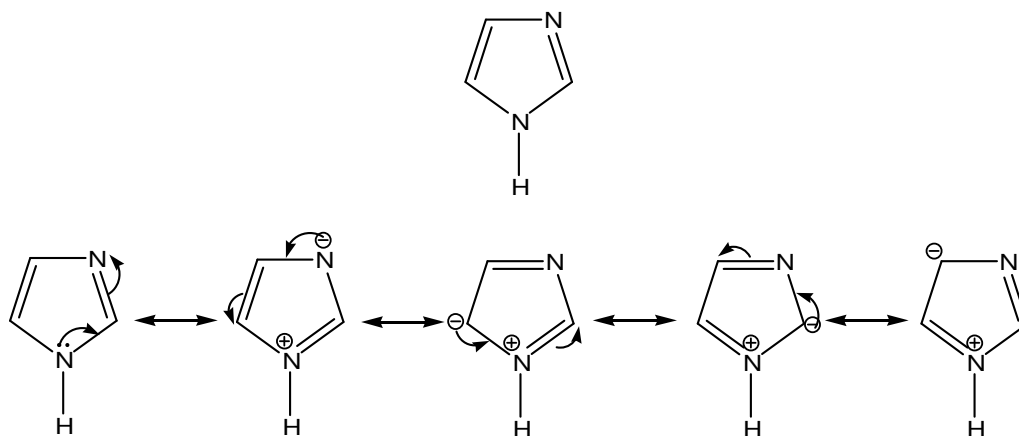


Figure 34. Imidazole and its resonance structures.

The imidazole ring is incorporated into many important biological molecules, such as the amino acid histidine. Imidazole has become an important constituent group in many active drug compounds, as already seen with theazole antifungal agents. Substitution may occur at each of the five atoms in imidazole, yielding a vast array of different ligand molecules for complexation to silver(I). Substituted imidazoles used in the current work are shown in Figure 35.

1.8 Aims of Research

The purpose of this research was to synthesise new silver(I)-containing complexes that would have novel structural features and would be effective antimicrobial and anticancer agents. The complexes would contain 9-anthracenecarboxylate and imidazole ligands and be screened, *in vitro*, against fungal and bacterial pathogens, as well as against selected human cancer cell lines. *In vivo* cytotoxicity and antifungal studies would also be conducted using the insect model, *Galleria mellonella*.

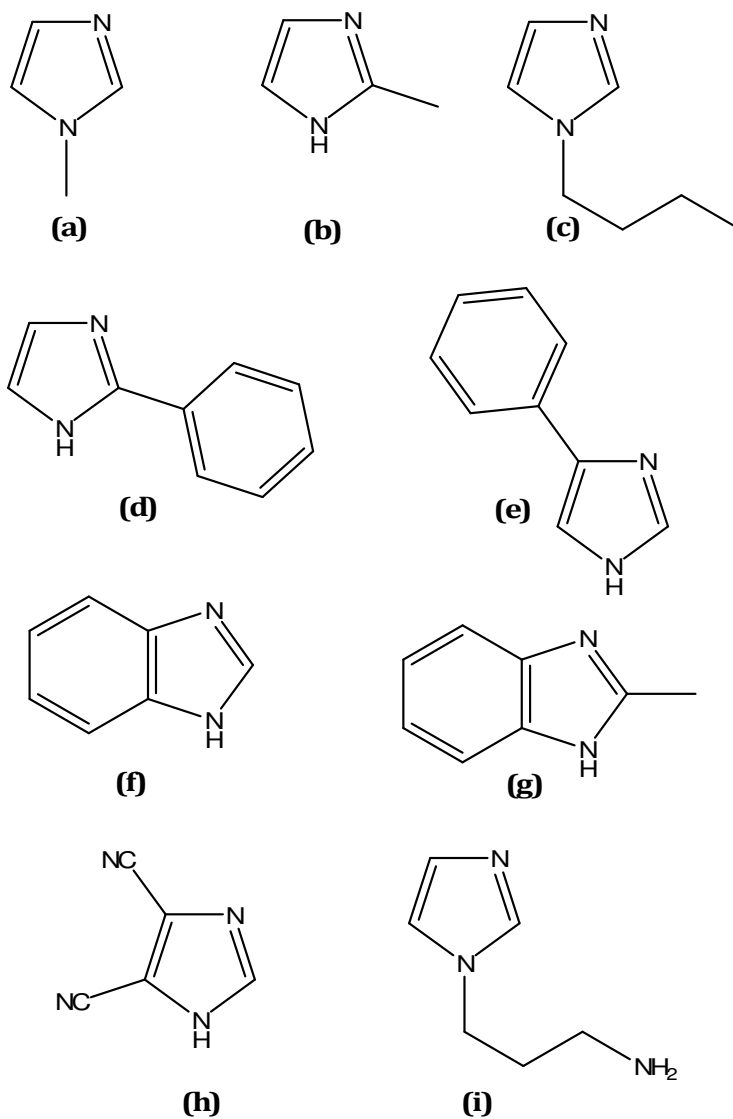


Figure 35. Imidazole derivatives used as ligands in the current work. (a) 1-Methylimidazole, (b) 2-methylimidazole, (c) 1-butylimidazole, (d) 2-phenylimidazole, (e) 4-phenylimidazole, (f) benzimidazole, (g) 2-methylbenzimidazole, (h) 4,5-dicyanoimidazole and (i) 1-(3-aminopropyl)imidazole.

Experimental

2.1 Instrumentation

Infrared (IR) spectra were recorded in the region 4,000–370 cm^{-1} on a Perkin Elmer System 2000 FT spectrometer. Solid samples were ground with an excess of anhydrous potassium bromide (KBr) and compacted into a disc. Oil samples were placed between two sodium chloride windows.

NMR spectra were recorded on a Bruker Avance spectrometer at a probe temperature of 25 °C, unless otherwise stated, operating at 300 MHz for the ^1H nucleus and 75.5 MHz for the ^{13}C nucleus. Spectra were recorded in deuterated dimethylsulfoxide ($(\text{CD}_3)_2\text{SO}$) unless otherwise stated. Chemical shifts are given in ppm downfield from the internal standard and coupling constants are given in Hz. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, m = multiplet, and dd = doublet of doublets), integration.

Microanalytical data were provided by the Microanalytical Laboratory, National University of Ireland Cork, Cork, Ireland and the Microanalytical Laboratory, University College Dublin, Belfield, Dublin 4, Ireland. Samples were analysed on an Exeter Analytical CE-440 elemental analyser in oxygen with a helium carrier gas at 975 °C in a combustion tube.

X-ray crystallography work was carried out by Prof. Vickie McKee, Chemistry Department, Loughborough University, Loughborough, Leics., LE11 3TU, UK. The data were collected at 150(2)K on a Bruker APEX II diffractometer. The structures were solved by direct methods and refined on F^2 using all the reflections. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms were inserted at calculated positions using a riding model. Parameters for data collection and refinement are summarised in the Appendix with a full list available in the Electronic Appendix.

Fluorescence studies were performed by Dr. Patrick Lynch and Dr. Mary McNamara, School of Chemical and Pharmaceutical Sciences, Dublin Institute of

Technology, Kevin Street, Dublin 2, Ireland. UV-Vis spectra were recorded using a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer using the preprogrammed “Sphere” instrumental method. This spectrometer has a double-beam, double monochromator ratio recording system with tungsten-halogen and deuterium lamps as sources. The spectrometer has a range of 175 to 3300 nm with an accuracy of 0.08 nm in the UV-Vis region. It has a photometric range of ± 6 in absorbance. Fluorescence spectra were measured using a Perkin Elmer LS55B Luminescence spectrometer and were recorded using an attenuated scan method which has a 1% attenuation setting. The sample was excited at the λ_{\max} of absorption determined using the UV-Vis absorption spectra. Excitation was provided by a pulsed xenon discharge lamp, of pulse width at half peak height of <10 micro seconds and pulse power of 20 kW. The source was monochromated using a Monk-Gillieson type monochromator with a range of 200-800 nm. The excitation and emission slits were set to allow maximum intensity in a complex ligand set. These settings were maintained for all measurements within the same complex ligand set to allow for comparison of emission intensity between complexes and ligands.

Atomic absorption spectroscopy was performed using a Perkin Elmer AAnalyst 200 atomic absorption spectrometer and calibration plots were made using AgNO_3 . Samples were ashed in a ceramic crucible over a Bunsen burner and dissolved in 50% (v/v) nitric acid.

Sterilisation of microbiological equipment and media was carried out in a Dixons ST2228 autoclave at 121 °C and 124 kPa for 20 min. Solutions that were susceptible to decomposition during autoclaving were sterilised by membrane filtration using 0.45 μm Millipore membrane filters. All worktops and benches were sterilised by washing with 70% (v/v) ethanol/water prior to use.

Round-bottomed microtitre plates were read using a Labsystems iEMS Reader MF at 540 nm (*Candida* strains). Flat-bottomed microtitre plates were read using a Bio-Tek Synergy HT plate reader at 600 nm (*E. coli* and MRSA strains).

Fungal cell density was measured using a Neubauer hemocytometer under a light microscope at a magnification of x400. Bacterial cell density was recorded at an optical density of 600 nm using an Eppendorf Biophotometer.

Significance of the survival rates of *G. mellonella* larvae was analysed at 24, 48 and 72 h intervals using the log rank (Mantel-Cox) method utilising GraphPad Prism software (version 5). Three categories of significance were used (* = $p < 0.05$, ** = $p < 0.01$ and *** = $p < 0.001$).

Anticancer studies were carried out by Dr. Denise Egan, Centre for Pharmaceutical Research & Development (CPRD), Institute of Technology, Tallaght, Dublin 24, Ireland (Hep-G₂ and A-498 cell lines) and Dr. Siobhan McClean, Centre of Microbial Host Interactions, Institute of Technology Tallaght, Dublin 24, Ireland (MCF7 and HT29 cell lines).

2.2 Chemicals, Materials and Biological Species

Chemicals were purchased from commercial sources and, unless specified, were used without further purification. Solvents were dried and purified in accordance with established procedures.

Candida albicans ATCC 10231 was obtained from the American Type Culture Collection, Manassas, VA, USA. *Escherichia coli* was obtained as a clinical isolate from the Clinical Microbiology Laboratory, St. James's Hospital, Dublin, Ireland, and was originally isolated from a wound infection. Methicillin Resistant *Staphylococcus aureus* (MRSA) was obtained as a clinical isolate from Microbiologics, North St. Cloud Mn, USA, and was originally isolated from a wound infection.

Cancer cell lines Hep-G₂, A-498, MCF7 and HT29 were purchased from the American Tissue Culture Collection (ATCC).

Galleria mellonella larvae in the sixth developmental stage were obtained from Livefoods Direct Ltd., Sheffield, S25 4JJ, UK. They were stored at 15 °C in wood shavings and used within 3 weeks of delivery.

2.3 Synthesis of Silver(I) Complexes

The syntheses of all silver complexes were conducted in the absence of light and the products were also stored in the dark at all times.

2.3.1 [Ag₂(9-aca)₂]_n

Method 1:

Silver(I) oxide (0.695 g, 3.00 mmol) was suspended in ethanol (20 cm³) and added to a refluxing solution of 9-anthracenecarboxylic acid (9-acaH) (1.332 g, 6.00 mmol) in ethanol (170 cm³). The resulting green suspension was refluxed for 1 h. The solid was filtered off and placed in refluxing ethanol (350 cm³) for 1 h. A brown precipitate was filtered off and the filtrate reduced to low volume to yield a yellow solid. The yellow solid was filtered, washed with cold ethanol and allowed to air-dry. Crystals suitable for X-ray structural analysis were obtained by recrystallisation from hot ethanol.

Yield: 0.41 g (21%).

Molecular formula (weight): C₃₀H₁₈O₄Ag₂ (658.18 g mol⁻¹).

Solubility: soluble in hot EtOH, hot MeOH, DMSO, CHCl₃ and MeCN.

Anal. Calc.: C, 54.74; H, 2.76%.

Anal. Found: C, 54.36; H, 2.66%.

IR (cm⁻¹, KBr): 3384, 3047, 1566, 1537, 1429, 1391, 1319, 1275, 1012.

¹H NMR (δ, DMSO): 8.44 (s, 2H); 8.18 (m, 4H); 8.03 (m, 4H); 7.47 (m, 8H).

Method 2:

Silver(I) oxide (0.695 g, 3.00 mmol) was suspended in ethanol (15 cm³) and added to a solution of 9-anthracenecarboxylic acid (9-acaH) (1.332 g, 6.00

mmoles) in ethanol (120 cm³). The mixture was stirred at room temperature for 24 h. The resulting green precipitate which was filtered, washed with cold ethanol and allowed to air dry. This green solid was then taken up in hot acetonitrile (160 cm³) and the solution filtered to remove any undissolved material. The filtrate was reduced to a low volume on a rotary evaporator to yield a yellow solid. This yellow solid was filtered off, washed with cold ethanol and allowed to air-dry.

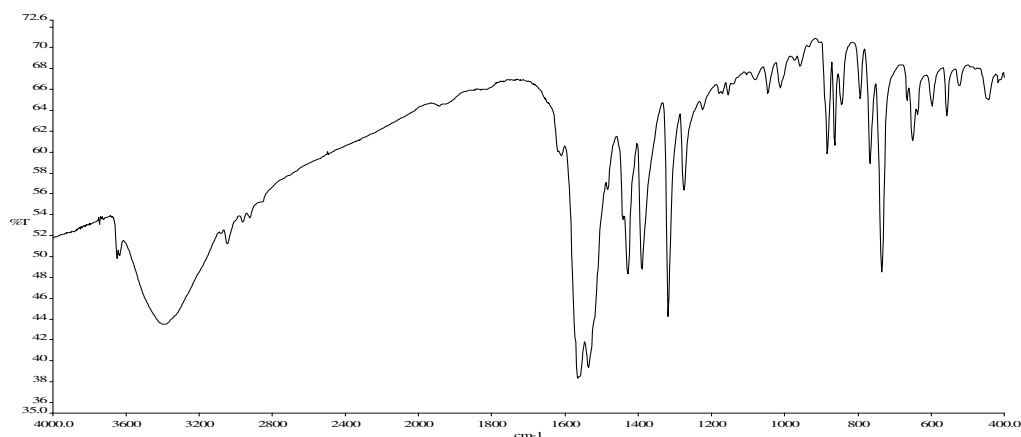
Yield: 1.373 g (70%).

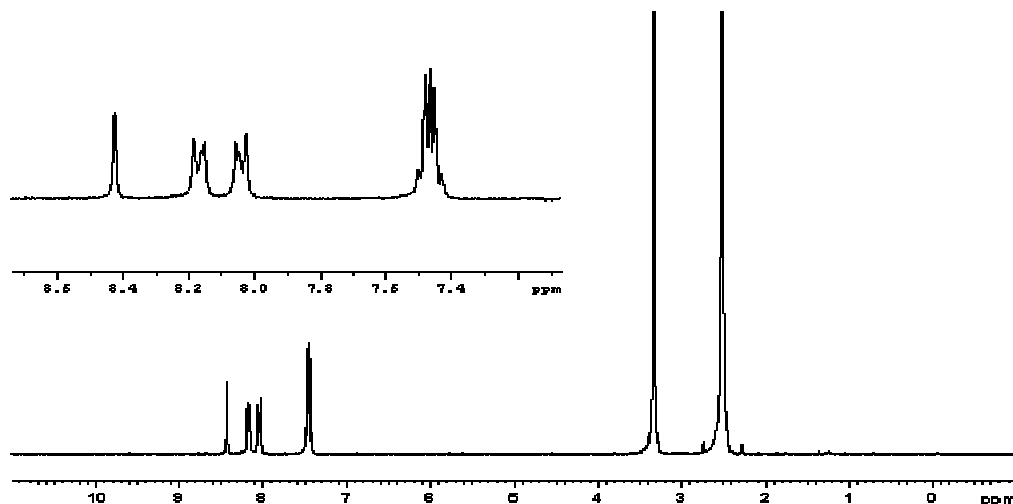
Method 3:

9-anthracenecarboxylic acid (9-acaH) (1.117 g, 5.03 mmoles) was added slowly to a solution of potassium hydroxide (0.282 g, 5.03 mmoles) in water (30 cm³). The pH was checked to ensure the solution was neutral and then it was filtered to remove any undissolved material. Silver nitrate (0.849 g, 5.03 mmoles) was dissolved in water (10 cm³) and added dropwise to the K⁺(9-aca)⁻ solution. A yellow precipitate immediately formed. The mixture was stirred for 0.5 h, filtered and the solid washed with ethanol. The solid was recrystallised from hot ethanol to yield crystals suitable for X-ray structural analysis.

Yield: 1.202 g (73%).

IR: [Ag₂(9-aca)₂]_n



$^1\text{H NMR (DMSO): [Ag}_2(9\text{-aca)}_2\text{]}_n$ **2.3.2 [Ag₂(9-aca)₂(DMSO)₂]_n**

[Ag₂(9-aca)₂]_n (0.100g, 0.15 mmol) was dissolved in dimethylsulfoxide (4 cm³). The mixture was heated to 80 °C for 20 min. Ethanol (15 cm³) was added and the solution was brought to reflux and then filtered. The filtrate was left to stand and after 3 days yellow needle-like crystals were collected by filtration, washed with ethanol and allowed to air-dry.

Yield: 0.062 g (50%).

Molecular formula (weight): C₃₄H₃₀O₆S₂Ag₂ (814.44 g mol⁻¹).

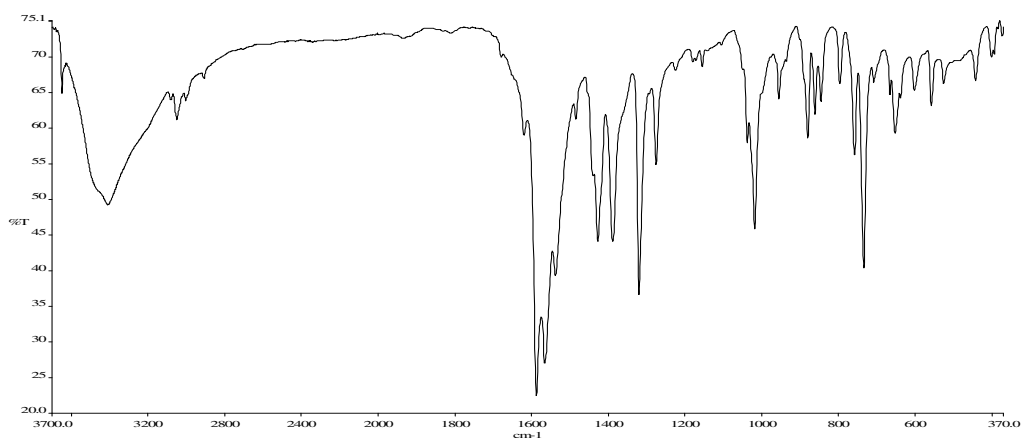
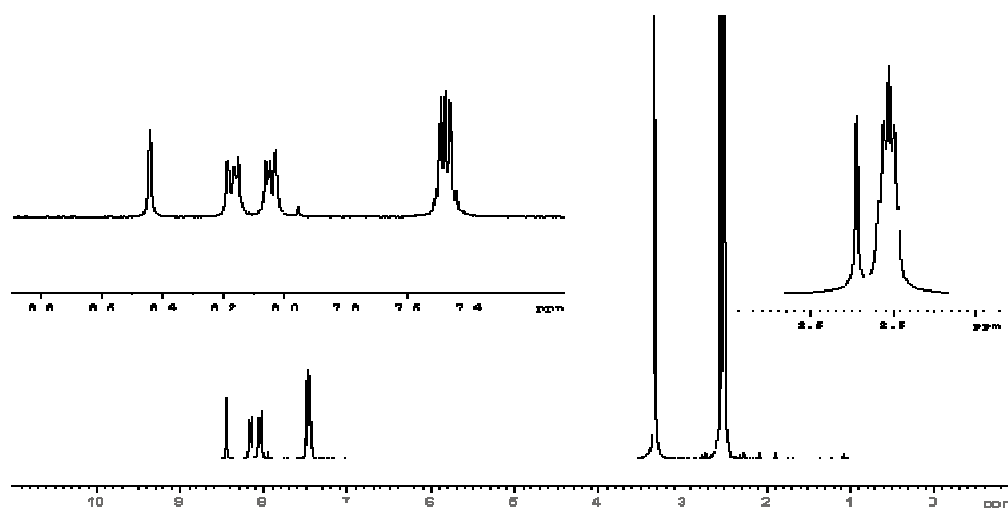
Solubility: soluble in MeCN and DMSO.

Anal. Calc.: C, 50.14; H, 3.71%.

Anal. Found: C, 50.22; H, 3.70%.

IR (cm⁻¹, KBr): 3411, 3050, 1620, 1587, 1565, 1538, 1427, 1389, 1320, 1276, 1018.

$^1\text{H NMR } (\delta, \text{DMSO}):$ 8.45 (s, 1H); 8.18 (m, 2H); 8.05 (m, 2H); 7.48 (m, 4H); 2.56 (s, 6H).

IR: [Ag₂(9-aca)₂(DMSO)₂]**¹H NMR (DMSO): [Ag₂(9-aca)₂(DMSO)₂]****2.3.3 [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca)**

[Ag₂(9-aca)₂]_n (0.329 g, 0.5 mmoles) was dissolved in hot acetonitrile (70 cm³) and the solution was filtered to remove any undissolved material. Imidazole (imidH) (0.207 g, 3 mmoles) was dissolved in acetonitrile (10 cm³) and added slowly to the [Ag₂(9-aca)₂]_n solution with constant stirring. A white cloudy precipitate formed which was removed by filtration. The clear filtrate was allowed to stand overnight and white crystals formed. The crystals were washed with acetonitrile and air-dried.

Yield: 0.09 g (18%).

Molecular formula (weight): C_{23.30}H_{20.30}N_{5.30}O₂Ag (514.42 g mol⁻¹).

Solubility: soluble in MeOH, hot EtOH and DMSO.

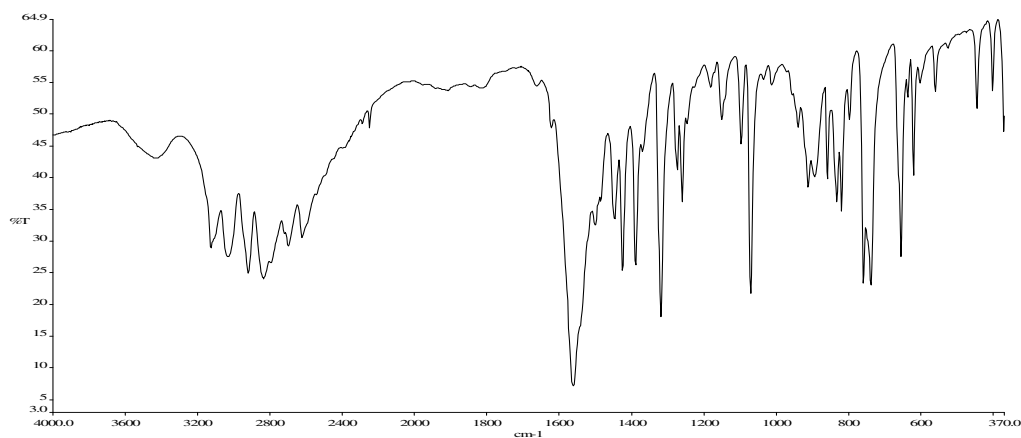
Anal. Calc.: C, 54.40; H, 3.98; N, 14.43%.

Anal. Found: C, 54.15; H, 3.91; N, 14.61%.

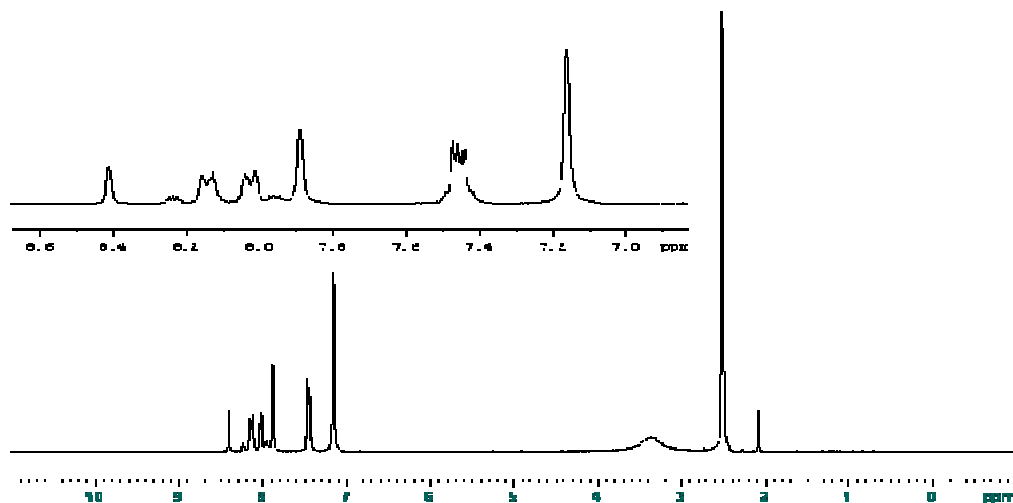
IR (cm⁻¹, KBr): 3436, 3128, 3030, 2923, 2837, 2700, 2624, 2250, 1625, 1562, 1448, 1426, 1390, 1320, 1275, 1261, 1072.

¹H NMR (δ, DMSO): 8.41 (s, 1H); 8.15 (m, 2H); 8.03 (m, 2H); 7.90 (s, 2.5H); 7.46 (m, 4H); 7.16 (s, 5H); 2.08 (s, 0.5H).

IR: [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca)



¹H NMR (DMSO): [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca)



2.3.4 $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$

$[\text{Ag}_2(9\text{-aca})_2]_n$ (0.109 g, 0.16 mmoles) was suspended in methanol (10 cm³) and to this was added a methanolic solution of imidazole (1 cm³, 0.16 M, 0.16 mmoles). The mixture was stirred for 1 h and then filtered. Diethyl ether was added to the filtrate to precipitate the pale yellow product. The solid was filtered off, washed with diethyl ether and air-dried.

Yield: 0.04g (44%).

Molecular formula (weight): C₁₀₄H₇₈N₈O₁₄Ag₆ (2310.96 g mol⁻¹).

Solubility: soluble in MeOH and DMSO.

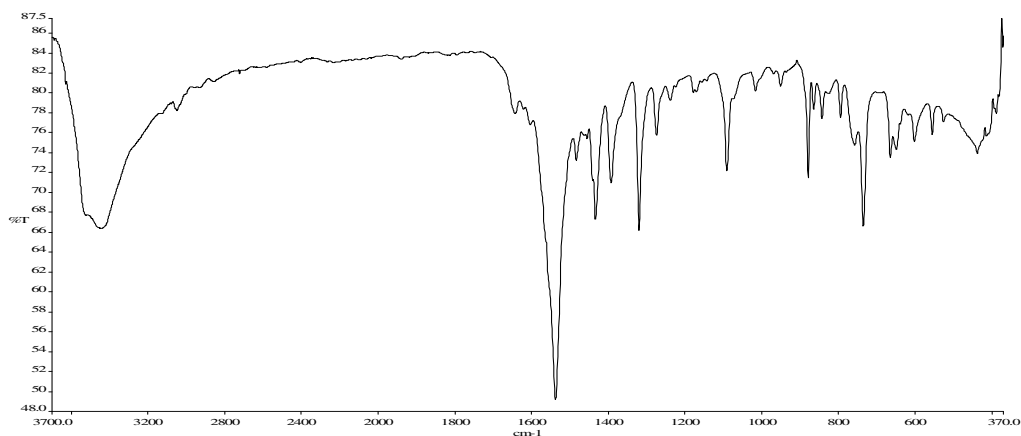
Anal. Calc.: C, 54.05; H, 3.40; N, 4.85%.

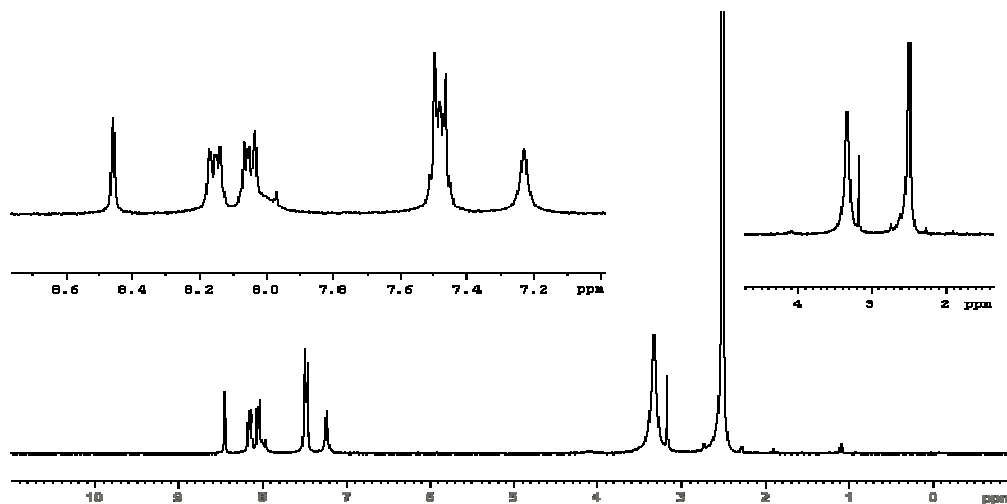
Anal. Found: C, 53.75; H, 3.39; N, 4.73%.

IR (cm⁻¹, KBr): 3448, 3045, 1625, 1538, 1484, 1433, 1393, 1320, 1273, 1238, 1178, 1090.

¹H NMR (δ, DMSO): 8.46 (s, 6H); 8.16 (m, 12H); 8.06 (m, 12H); 7.49 (m, 24H); 7.23 (s, 12H); 3.17 (s, 6H).

IR: $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$



^1H NMR (DMSO): $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$ **2.3.5 $[\text{Ag}(\text{1-Me-imidH})_2]_2[\text{Ag}_4(9\text{-aca})_6]$**

$[\text{Ag}_2(9\text{-aca})_2]_n$ (0.165 g, 0.25 mmoles) was suspended in ethanol (30 cm³) and heated gently. 1-Methylimidazole (0.82 g, 1 mmole) was added directly to the hot suspension of $[\text{Ag}_2(9\text{-aca})_2]_n$ and the mixture immediately turned clear. It was filtered to remove any insoluble particles and the filtrate was reduced to a low volume on a rotary evaporator. Diethyl ether was added to precipitate the beige solid, which was filtered off, washed with diethyl ether and allowed to air-dry. The solid was dissolved in DMSO and the solution reduced on a rotary evaporator to yield the beige product.

Yield: 0.075 g (37%).

Molecular formula (weight): C₁₀₆H₇₈N₈O₁₂Ag₆ (2303.01 g mol⁻¹).

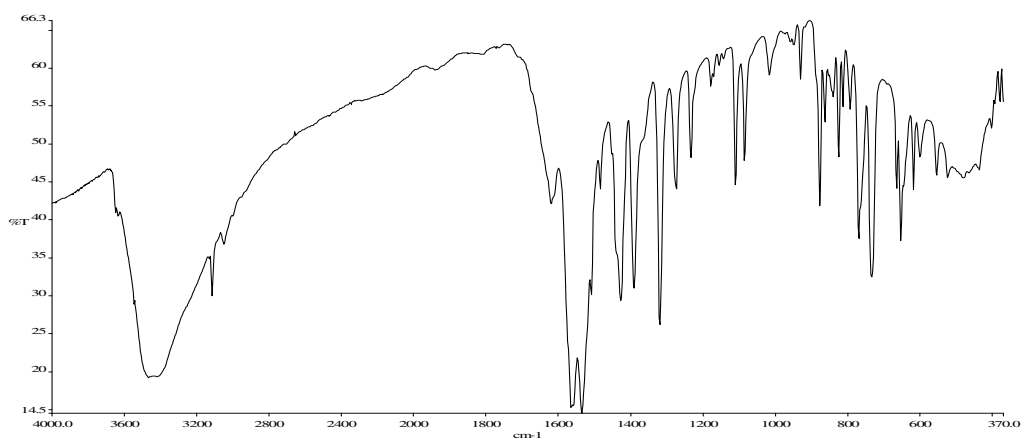
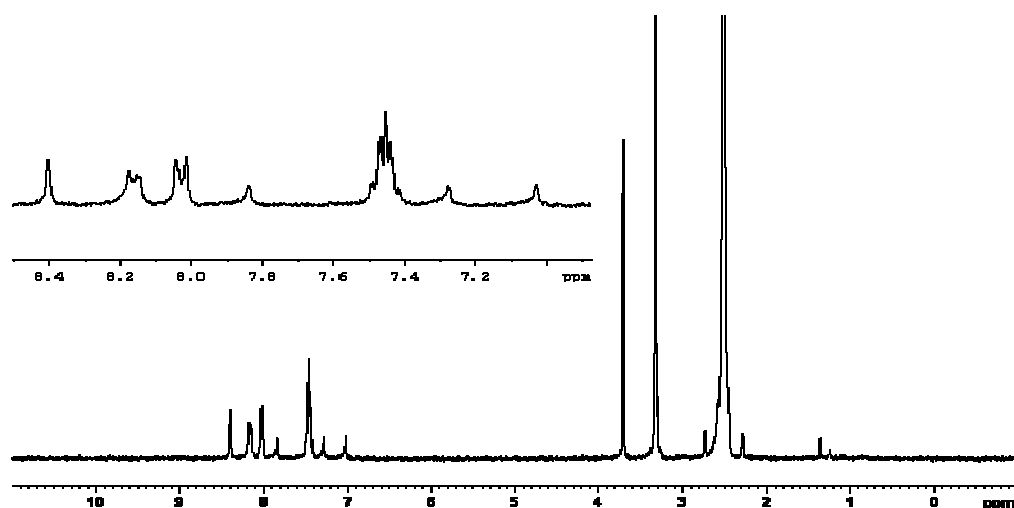
Solubility: soluble in hot MeOH, EtOH and DMSO.

Anal. Calc.: C, 55.27; H, 3.42; N, 4.87%.

Anal. Found: C, 54.98; H, 3.42; N, 4.63%.

IR (cm⁻¹, KBr): 3468, 3116, 1621, 1565, 1536, 1428, 1392, 1321, 1275, 1235, 1180, 1112, 1087, 1017.

^1H NMR (δ , DMSO): 8.40 (s, 6H); 8.16 (m, 12H); 8.05 (m, 12H); 7.84 (s, 4H); 7.46 (m, 24H); 7.28 (s, 4H); 7.03 (s, 4H); 3.72 (s, 12H).

IR: [Ag(1-Me-imidH)₂]₂[Ag₄(9-aca)₆]**¹H NMR (DMSO): [Ag(1-Me-imidH)₂]₂[Ag₄(9-aca)₆]****2.3.6 [Ag₂(1-Me-imid)₂(9-aca)₂]**

[Ag₂(9-aca)₂]_n (0.165 g, 0.25 mmole) was suspended in ethanol (30 cm³) and heated gently. 1-Methylimidazole (0.82 g, 1 mmole) was added directly to the hot suspension of [Ag₂(9-aca)₂]_n and the mixture immediately turned clear. It was filtered to remove any insoluble particles and the filtrate was reduced to a low volume on a rotary evaporator. Diethyl ether was added to precipitate the beige product, which was filtered off, washed with diethyl ether and allowed to air-dry.

Yield: 0.093 g (45%).

Molecular formula (weight): $C_{38}H_{30}N_4O_4Ag_2$ (822.46 g mol⁻¹).

Solubility: soluble in hot MeOH, EtOH and DMSO.

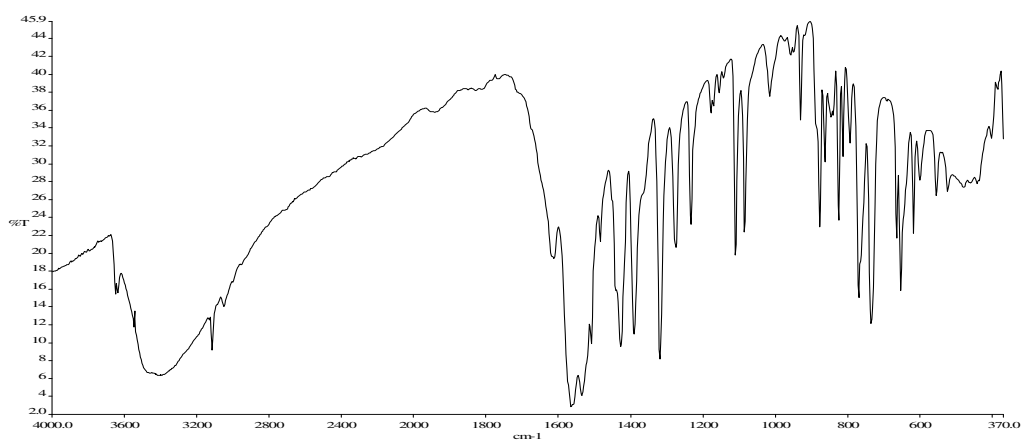
Anal. Calc.: C, 55.49; H, 3.68; N, 6.81%.

Anal. Found: C, 55.31; H, 3.72; N, 6.70%.

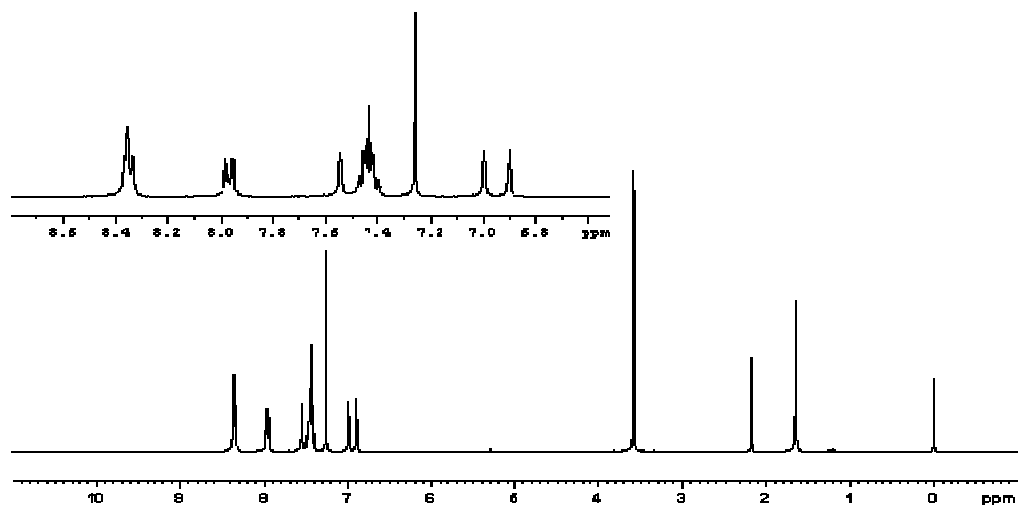
IR (cm⁻¹, KBr): 3411, 3116, 1612, 1566, 1536, 1428, 1391, 1320, 1275, 1235, 1180, 1111, 1086, 1017.

¹H NMR (δ, CDCl₃): 8.36 (m, 3H); 7.95 (m, 2H); 7.55 (s, 1H); 7.45 (m, 4H); 7.00 (s, 1H); 6.90 (s, 1H); 3.59 (s, 3H).

IR: [Ag₂(1-Me-imidH)₂](9-aca)₂



¹H NMR (CDCl₃): [Ag₂(1-Me-imidH)₂](9-aca)₂



2.3.7 [Ag(2-Me-imidH)₂(9-aca)]

[Ag₂(9-aca)₂]_n (0.068 g, 0.10 mmoles) was dissolved in acetonitrile (10 cm³) and a solution of 2-Methylimidazole (0.035 g, 0.40 mmoles) in acetonitrile (2 cm³) was added dropwise with stirring. A white precipitate immediately formed which quickly redissolved. The solution was stirred for 1 h at room temperature and a yellow precipitate formed. The yellow solid was collected by filtration, washed with a small portion of ethanol and diethyl ether. The yellow solid was recrystallised from acetonitrile to yield light yellow crystals suitable for X-ray crystal analysis.

Yield: 0.050 g (51%).

Molecular formula (weight): C₂₃H₂₁N₄O₂Ag (493.31 g mol⁻¹).

Solubility: soluble in MeOH, EtOH, MeCN and DMSO.

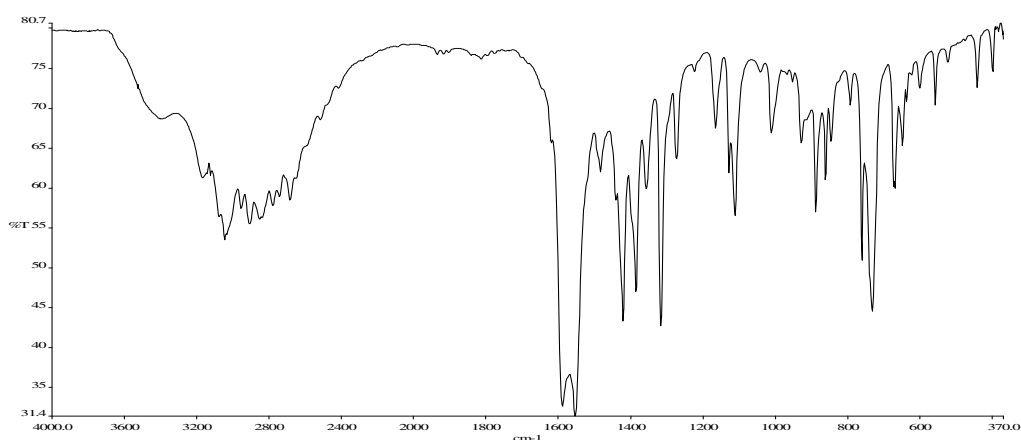
Anal. Calc.: C, 56.00; H, 4.29; N, 11.36%.

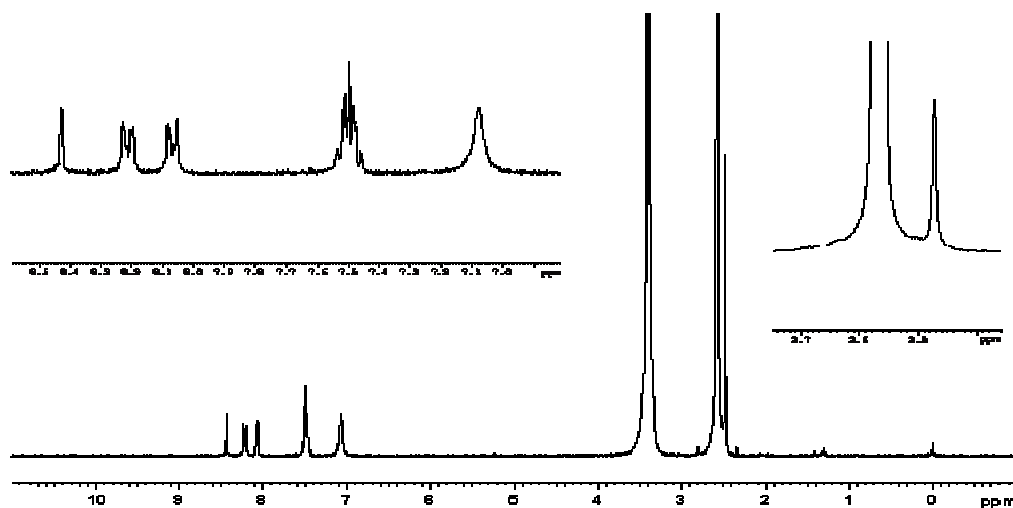
Anal. Found: C, 55.70; H, 4.29; N, 11.08%.

IR (cm⁻¹, KBr): 3047, 2909, 2855, 2685, 1590, 1554, 1484, 1422, 1386, 1358, 1318, 1275, 1166, 1130, 1113, 1013.

¹H NMR (δ, DMSO): 8.43 (s, 1H); 8.20 (m, 2H); 8.08 (m, 2H); 7.50 (m, 4H); 7.08 (s, 4H); 2.47 (s, 6H).

IR: [Ag(2-Me-imidH)₂(9-aca)]



^1H NMR (DMSO): $[\text{Ag}(\text{2-Me-imidH})_2(\text{9-aca})]$ **2.3.8 $[\text{Ag}(\text{1-Bu-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$**

$[\text{Ag}_2(\text{9-aca})_2]_n$ (0.750 g, 1.14 mmoles) was dissolved in hot acetonitrile (80 cm³) and the solution filtered and cooled to room temperature. 1-Butylimidazole (0.567 g, 4.56 mmoles) was added and the resulting solution was stirred at room temperature for 20 h. After gravity filtration the filtrate was reduced to a low volume on a rotary evaporator and diethyl ether added to yield a beige precipitate. The solid was filtered off, washed with diethyl ether and allowed to air-dry. The solid was recrystallised from hot to yield yellow crystals, which were filtered, washed with cold ethanol (1 cm³) and allowed to air-dry.

Yield: 0.301 g (51%).

Molecular formula (weight): C₁₁₈H₁₀₂N₈O₁₂Ag₆ (2471.30 g mol⁻¹).

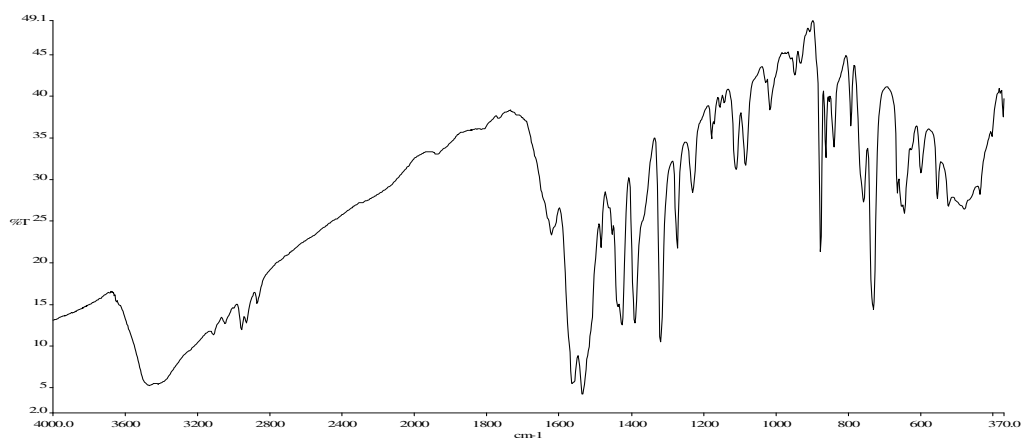
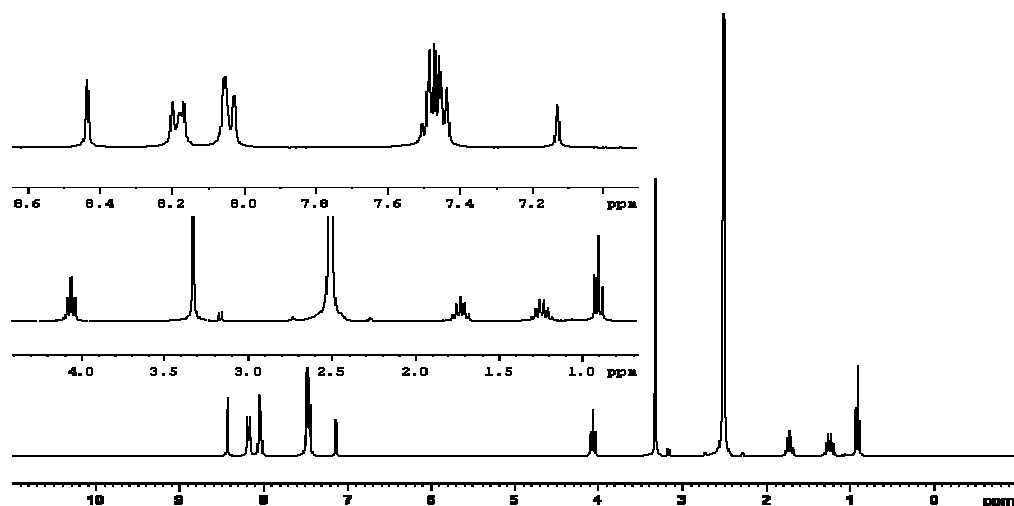
Solubility: soluble in MeOH, hot EtOH, CHCl₃ and DMSO.

Anal. Calc.: C, 57.35; H, 4.16; N, 4.53%.

Anal. Found: C, 57.23; H, 4.23; N, 4.47%.

IR (cm⁻¹, KBr): 3468, 2958, 1622, 1565, 1536, 1427, 1391, 1321, 1274, 1232, 1179, 1112, 1085, 1018.

^1H NMR (δ , DMSO): 8.44 (s, 6H); 8.20 (m, 12H); 8.06 (m, 16H); 7.47 (m, 28H); 7.13 (s, 4H); 4.06 (t, 8H); 1.73 (quin, 8H); 1.23 (sex, 8H); 0.90 (t, 12H).

IR: [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆]**¹H NMR (DMSO): [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆]****2.3.9 [Ag₂(1-Bu-imid)₂(9-aca)₂]**

[Ag₂(9-aca)₂]_n (0.750 g, 1.14 mmoles) was dissolved in hot acetonitrile (80 cm³) and the resulting solution was filtered and cooled to room temperature. 1-Butylimidazole (0.567 g, 4.56 mmoles) was added to the [Ag₂(9-aca)₂]_n solution and the mixture stirred at room temperature for 20 h. The solution was gravity filtered and the filtrate reduced on a rotary evaporator to a low volume and diethyl ether was added to yield a beige precipitate. The product was filtered, washed with cold ethanol and allowed to air-dry.

Yield: 0.734g (71%).

Molecular formula (weight): $C_{44}H_{42}N_4O_4Ag_2$ (906.56 g mol⁻¹).

Solubility: soluble in MeOH, hot EtOH, $CHCl_3$ and DMSO.

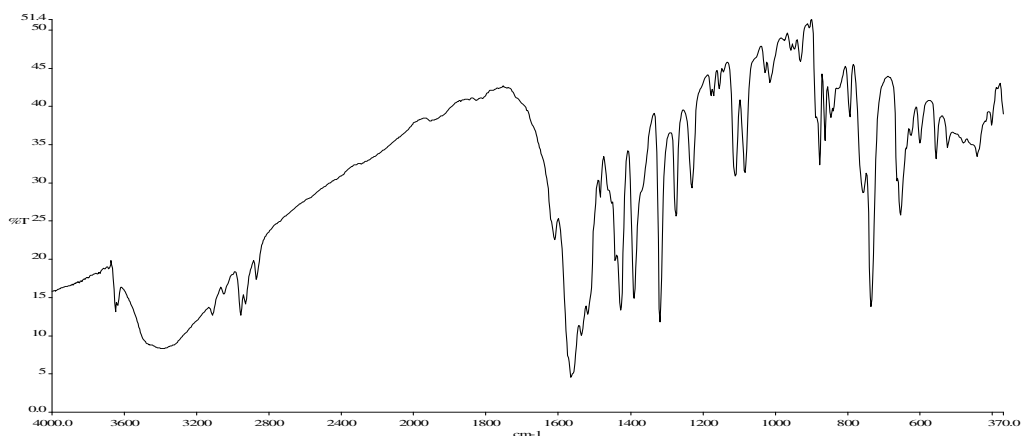
Anal. Calc.: C, 58.29; H, 4.67; N, 6.18; Ag, 23.80%.

Anal. Found: C, 58.33; H, 4.67; N, 6.16; Ag, 23.42%.

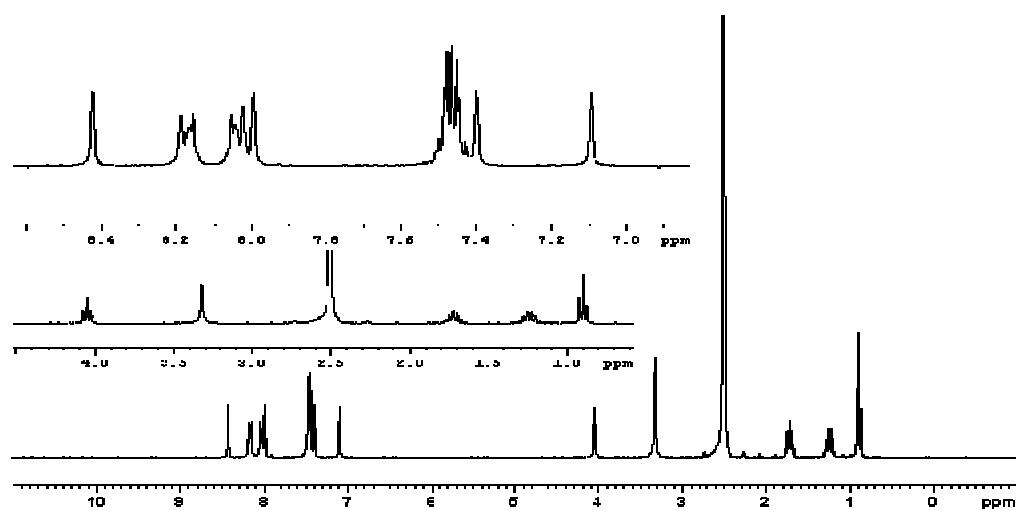
IR (cm⁻¹, KBr): 3652, 3393, 2958, 2872, 1611, 1567, 1429, 1392, 1320, 1275, 1232, 1172, 1156, 1112, 1086, 1016.

¹H NMR (δ , DMSO): 8.43 (s, 2H); 8.17 (m, 4H); 8.04 (m, 4H); 8.00 (s, 2H); 7.47 (m, 8H); 7.40 (s, 2H); 7.10 (s, 2H); 4.05 (t, 4H); 1.72 (quin, 4H); 1.25 (sex, 4H); 0.90 (t, 6H).

IR: [Ag₂(1-Bu-imid)₂(9-aca)₂]



¹H NMR (DMSO): [Ag₂(1-Bu-imid)₂(9-aca)₂]



2.3.10 [Ag(apim)](9-aca)·H₂O

[Ag₂(9-aca)₂]_n (0.500 g, 0.76 mmoles) was dissolved in hot acetonitrile (70 cm³) and the solution filtered to remove any undissolved particles. 1-(3-Aminopropyl)imidazole (0.190 g, 1.52 mmoles) was dissolved in acetonitrile (5 cm³) and added to the [Ag₂(9-aca)₂]_n solution with stirring. The suspension was stirred for 0.5 h at room temperature and the beige solid was filtered off, washed with acetonitrile and air-dried. The product was recrystallised from a 9:1 mixture of ethanol:methanol to yield colourless crystals suitable for X-ray analysis.

Yield: 0.589g (82%).

Molecular formula (weight): C₂₁H₂₂N₃O₃Ag (472.29 g mol⁻¹).

Solubility: soluble in MeOH, hot EtOH and DMSO.

Anal. Calc.: C, 53.40; H, 4.70%; N, 8.90%.

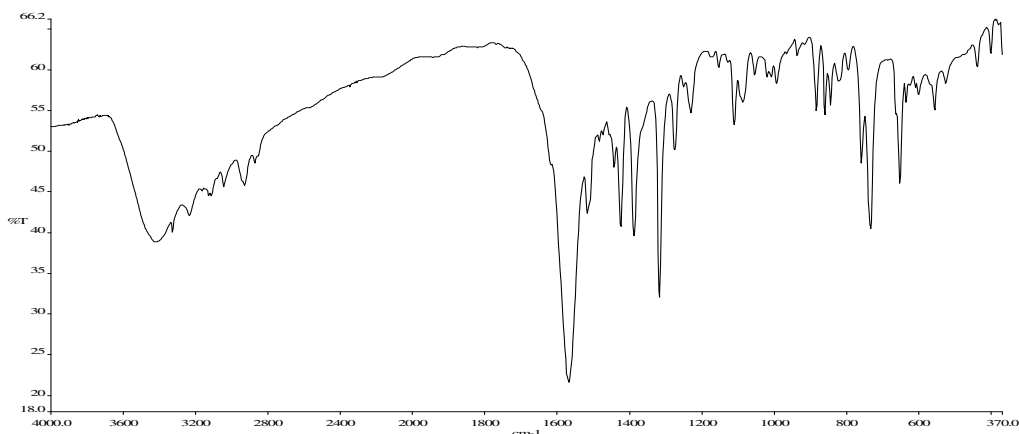
Anal. Found: C, 53.31; H, 4.58%; N, 8.89%.

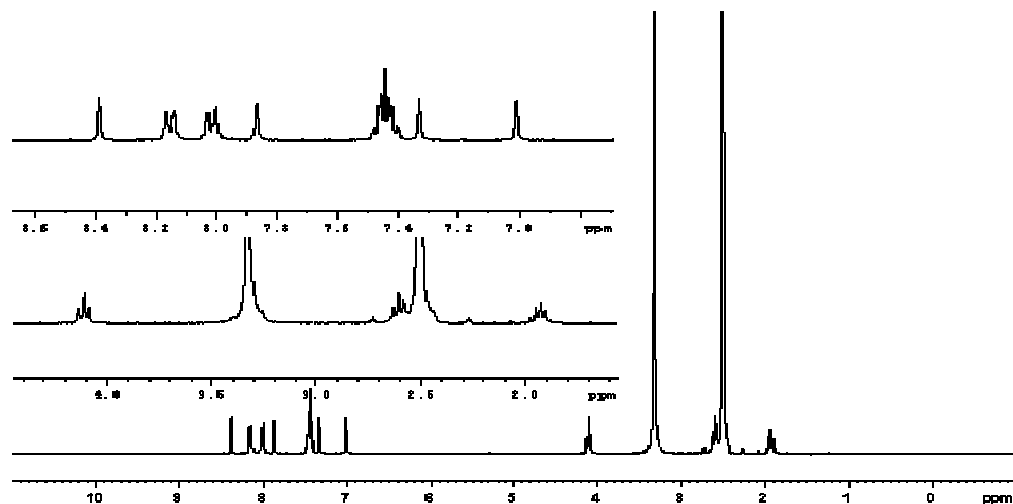
IR (cm⁻¹, KBr): 3427, 3236, 3129, 3046, 2932, 1568, 1518, 1425, 1389, 1319, 1277, 1231, 1112, 1089, 1055.

¹H NMR (δ, DMSO): 8.39 (s, 1H); 8.15 (m, 2H); 8.01 (m, 2H); 7.87 (s, 1H); 7.44 (m, 4H); 7.33 (s, 1H); 7.01 (s, 1H); 4.11 (t, 2H); 2.61 (t, 2H); 1.93 (quin, 2H).

COSY NMR (DMSO): shows coupling between protons on the imidazole ring that do not appear in the ¹H NMR spectrum.

IR: [Ag(apim)](9-aca)·H₂O



^1H NMR (DMSO): $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$ **2.3.11 [Ag(2-Ph-imid)]**

$[\text{Ag}_2(9\text{-aca})_2]_n$ (0.500 g, 0.76 mmoles) was dissolved in hot acetonitrile (40 cm^3) and the solution was filtered to remove any undissolved material. 2-Phenylimidazole (0.219 g, 1.52 mmoles) was dissolved in hot acetonitrile (20 cm^3) and this was added to the hot $[\text{Ag}_2(9\text{-aca})_2]_n$ solution. The resulting suspension was stirred at room temperature for 0.25 h. The beige precipitate was filtered, washed with ethanol and air-dried.

Yield: 0.246 g (64%).

Molecular formula (weight): $\text{C}_9\text{H}_7\text{N}_2\text{Ag}$ (251.05 g mol^{-1}).

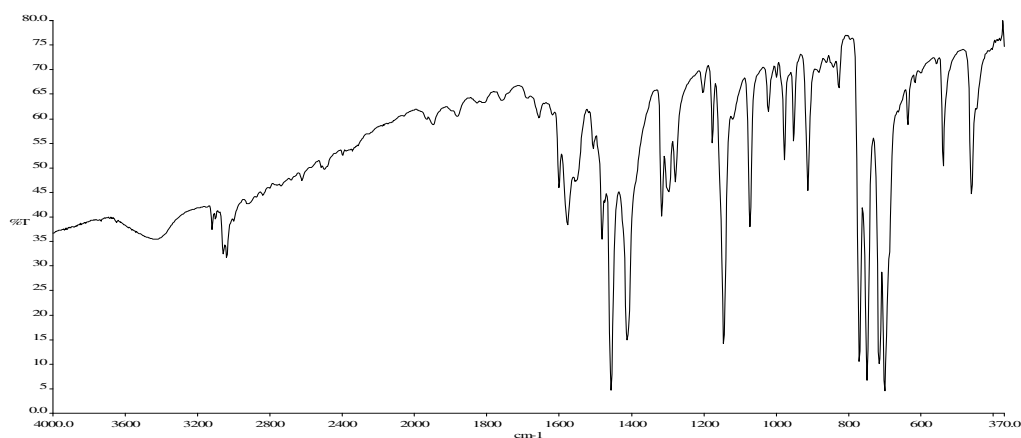
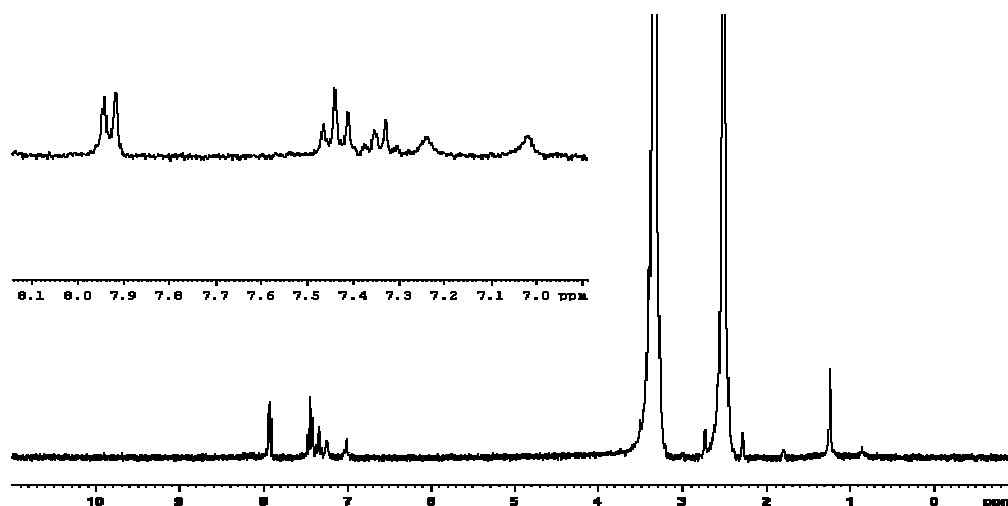
Solubility: The complex was only slightly soluble in DMSO.

Anal. Calc.: C, 43.06; H, 2.82; N, 11.16%.

Anal. Found: C, 43.62; H, 2.81; N, 10.58%.

IR (cm^{-1} , KBr): 3445, 3040, 1601, 1578, 1482, 1458, 1413, 1318, 1298, 1280, 1147, 1074, 1023.

^1H NMR (δ , DMSO): 7.92 (d, 2H); 7.41 (t, 2H); 7.33 (m, 1H); 7.24 (s, 1H); 7.02 (s, 1H).

IR: [Ag(2-Ph-imid)]**¹H NMR (DMSO): [Ag(2-Ph-imid)]****2.3.12 [Ag(4-Ph-imidH)₂(9-aca)]**

[Ag₂(9-aca)₂]_n (0.658 g, 1.00 mmoles) was dissolved in hot acetonitrile (100 cm³) and the solution was filtered to remove any undissolved material. 4-Phenylimidazole (0.438 g, 3.04 mmoles) was dissolved in hot acetonitrile and added to the hot solution of [Ag₂(9-aca)₂]_n. The mixture was stirred at room temperature for 0.5 h. The suspension was filtered and the beige precipitate was washed with a small portion of cold ethanol and air-dried.

Yield: 0.887 g (81%).

Molecular formula (weight): C₃₃H₂₅N₄O₂Ag (617.44 g mol⁻¹).

Solubility: soluble in DMSO.

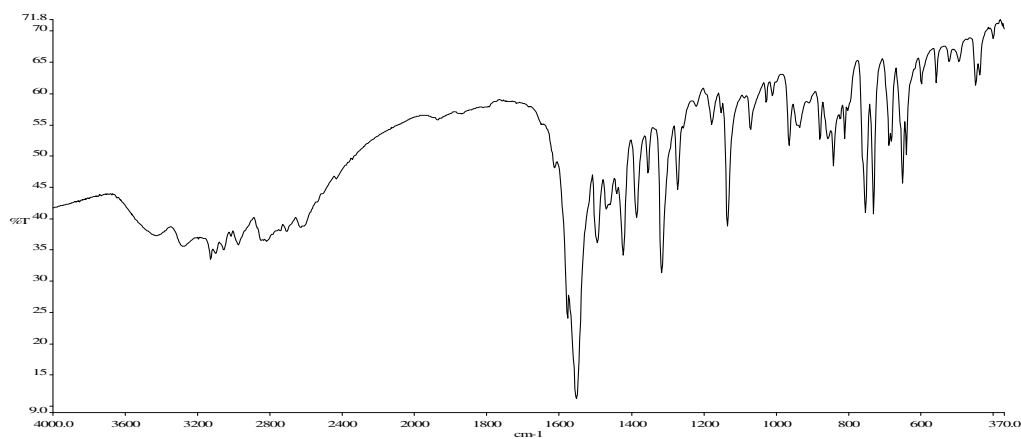
Anal. Calc.: C, 64.19; H, 4.08; N, 9.07; Ag, 17.47%.

Anal. Found: C, 63.74; H, 4.14; N, 8.88; Ag, 17.78%.

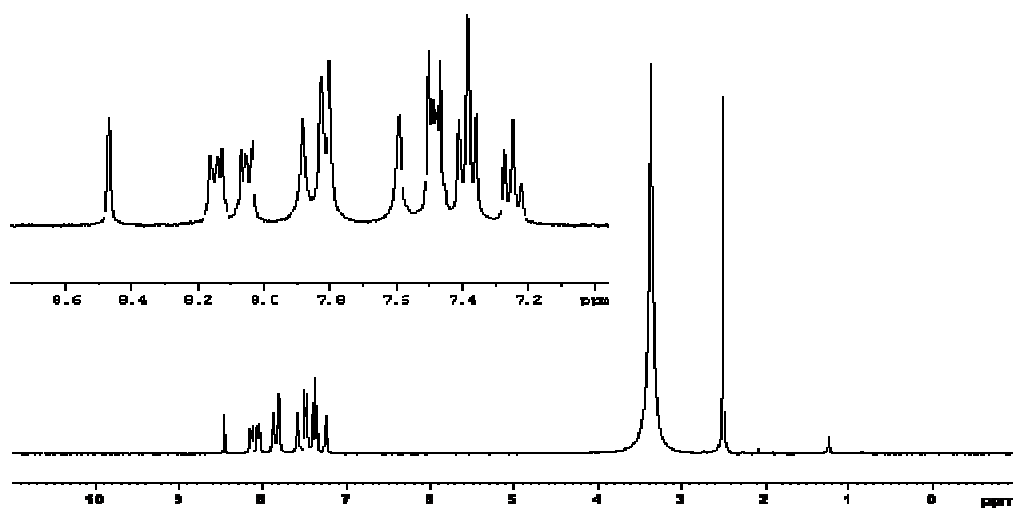
IR (cm⁻¹, KBr): 3430, 3280, 3129, 3057, 2977, 2821, 2709, 2633, 1614, 1579, 1553, 1495, 1442, 1424, 1387, 1355, 1318, 1273, 1180, 1136, 1073, 1029, 1012.

¹H NMR (δ, DMSO): 8.47 (s, 1H); 8.14 (m, 2H); 8.06 (m, 2H); 7.88 (s, 2H); 7.83 (s, 4H); 7.59 (s, 2H); 7.48 (m, 4H); 7.39 (t, 4H); 7.25 (t, 2H).

IR: [Ag(4-Ph-imid)₂(9-aca)]



¹H NMR (DMSO): [Ag(4-Ph-imid)₂(9-aca)]



2.3.13 [Ag(4,5-dicyanoimid)]

[Ag₂(9-aca)₂]_n (0.500 g, 0.76 mmoles) was dissolved in hot acetonitrile (50 cm³) and the solution filtered to remove any undissolved material. 4,5-Dicyanoimidazole (0.359 g, 3.04 mmoles) was dissolved in acetonitrile (5 cm³) and added to the hot [Ag₂(9-aca)₂]_n solution. A beige precipitate immediately formed and the suspension was stirred at room temperature for 1 h. The beige solid was filtered, washed with a small portion of cold ethanol and air-dried.

Yield: 0.240 g (70%).

Molecular formula (weight): C₅HN₄Ag (224.97 g mol⁻¹).

Solubility: insoluble in water and all common solvents.

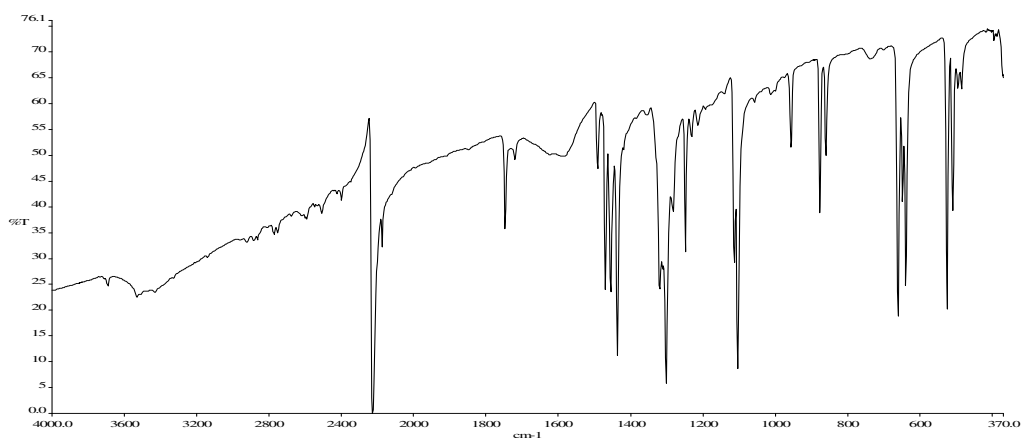
Anal. Calc.: C, 26.69; H, 0.49; N, 24.91%.

Anal. Found: C, 26.62; H, 0.41; N, 24.59%.

IR (cm⁻¹, KBr): 3534, 2227, 2176, 1748, 1720, 1583, 1492, 1471, 1457, 1438, 1321, 1303, 1283, 1250, 1115, 1105, 958, 878, 861.

¹H NMR: unable to obtain an NMR spectrum due to insolubility.

IR: [Ag(4,5-dicyanoimid)]



2.3.14 [Ag(Benz-imid)]

[Ag₂(9-aca)₂]_n (0.200 g, 0.30 mmoles) was suspended in methanol (40 cm³) at room temperature and a solution of benzimidazole (0.072 g, 0.60 mmoles) in methanol (5 cm³) was added to the suspension. A beige precipitate formed and

the suspension was stirred at room temperature for 0.5 h. The beige solid was filtered, washed with cold methanol and air-dried.

Yield: 0.093 g (68%).

Molecular formula (weight): $C_7H_5N_2Ag$ (225.01 g mol⁻¹).

Solubility: insoluble in water and all common solvents.

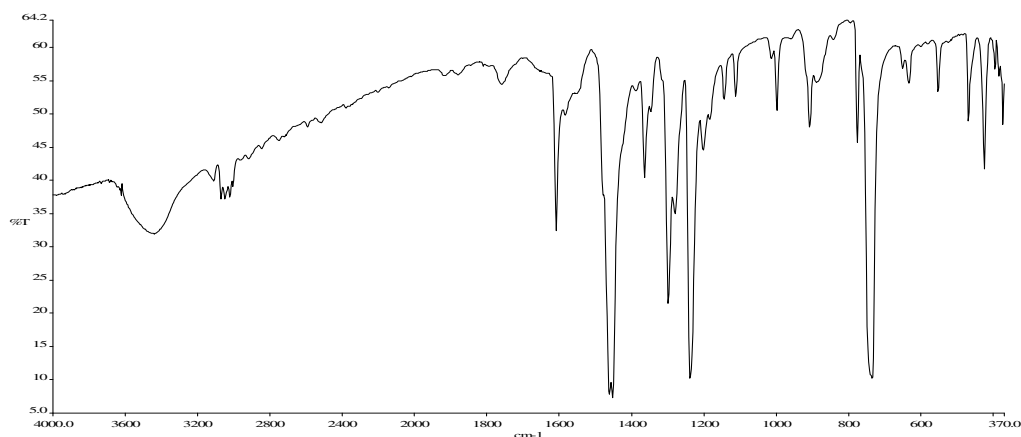
Anal. Calc.: C, 37.36; H, 2.24; N, 12.45%.

Anal. Found: C, 37.65; H, 2.29; N, 11.97%.

IR (cm⁻¹, KBr): 3443, 3073, 1759, 1609, 1584, 1463, 1453, 1365, 1300, 1281, 1239, 1185, 1145, 1113, 1015, 999.

¹H NMR: unable to obtain an NMR spectrum due to insolubility.

IR: [Ag(Benz-imid)]



2.3.15[Ag₂(2-Mebenz-imidH)₄](9-aca)₂

[Ag₂(9-aca)₂]_n (1.000 g, 1.52 mmol) was dissolved in hot acetonitrile (100 cm³) and the solution was filtered to remove any undissolved material. The filtrate was brought to reflux and a solution of 2-methylbenzimidazole (0.804 g, 6.08 mmol) in hot acetonitrile (30 cm³) was added. A white precipitate immediately formed. The suspension was removed from the heat source and was stirred at room temperature for 1 h. The beige solid was filtered off, washed with a small portion of cold ethanol and air-dried.

Yield: 1.562 g (87%).

Molecular formula (weight): $C_{62}H_{50}N_8O_4Ag_2$ (1186.88 g mol⁻¹).

Solubility: soluble in hot MeOH and DMSO.

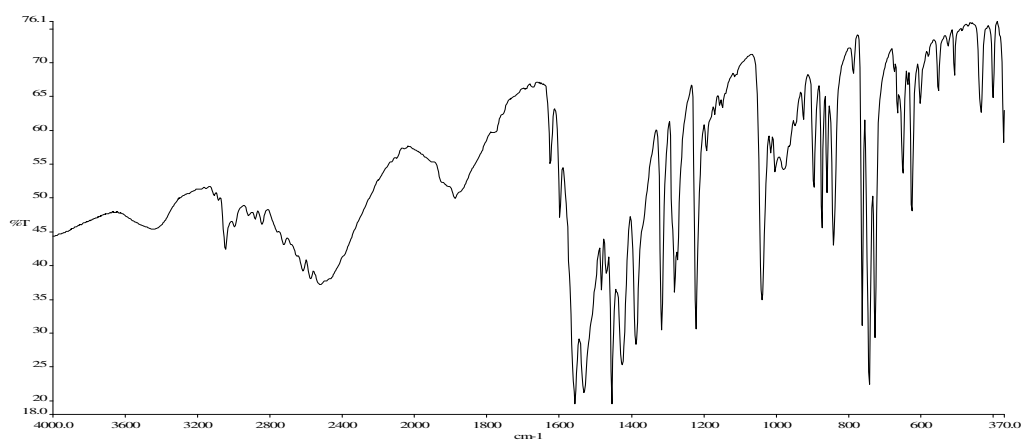
Anal. Calc.: C, 62.74; H, 4.25; N, 9.44%.

Anal. Found: C, 62.40; H, 4.17; N, 9.44%.

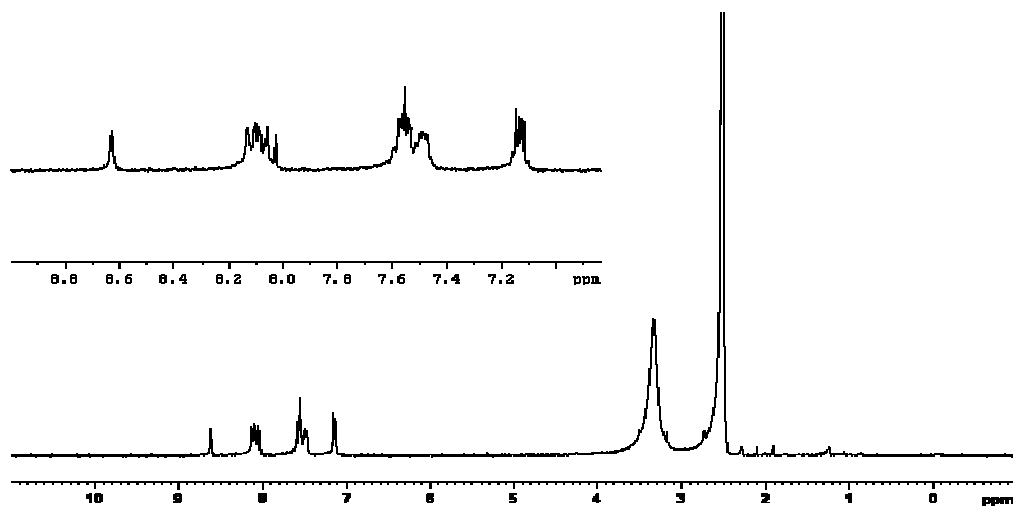
IR (cm⁻¹, KBr): 3446, 3047, 2524, 1888, 1625, 1599, 1558, 1532, 1456, 1427, 1388, 1318, 1282, 1223, 1041, 1005.

¹H NMR (δ, DMSO): 8.63 (s, 1H); 8.09 (m, 4H); 8.03 (s, 2H); 7.56 (m, 4H); 7.49 (m, 4H); 7.15 (m, 4H).

IR: [Ag₂(2-Mebenz-imidH)₄](9-aca)₂



¹H NMR (DMSO): [Ag₂(2-Mebenz-imidH)₄](9-aca)₂



2.3.16 [Ag(2-Mebenz-imid)]

[Ag₂(9-aca)₂]_n (0.500 g, 0.76 mmoles) was suspended in methanol (50 cm³) at room temperature. 2-Methylbenzimidazole (0.201 g, 1.52 mmoles) was dissolved in methanol (10 cm³) and added to the stirring suspension of [Ag₂(9-aca)₂]_n. The mixture was heated and a beige precipitate formed. The solid was filtered while hot, washed with methanol and allowed to air-dry.

Yield: 0.288 g (79%).

Molecular formula (weight): C₈H₇N₂Ag (239.04 g mol⁻¹).

Solubility: insoluble in water and all common solvents.

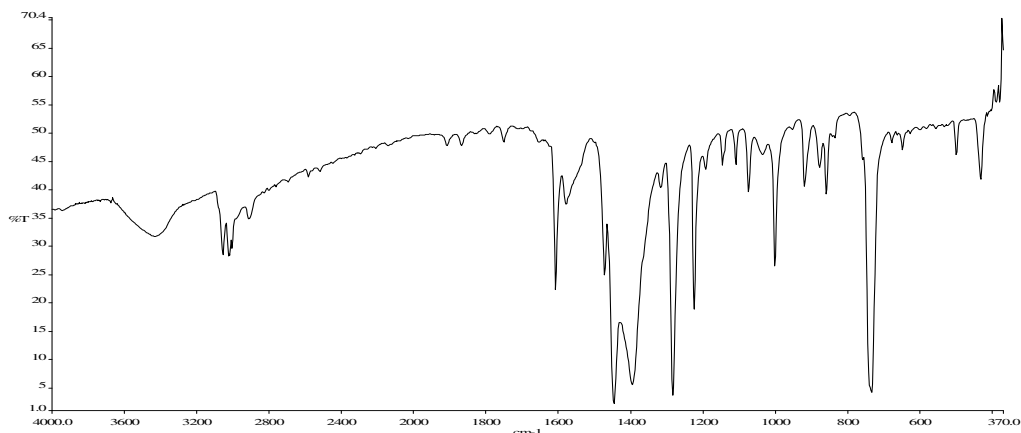
Anal. Calc.: C, 40.19; H, 2.96; N, 11.72%.

Anal. Found: C, 40.27; H, 2.97; N, 11.24%.

IR (cm⁻¹, KBr): 3434, 3056, 3025, 2915, 1868, 1751, 1608, 1579, 1473, 1448, 1397, 1285, 1226, 1148, 1110, 1076, 1002.

¹H NMR: unable to obtain an NMR spectrum due to insolubility.

IR: [Ag(2-Mebenz-imid)]



2.3.17 [Ag₄(9-aca)₄(NH₃)₂]

Silver nitrate (0.510 g, 3.00 mmoles) was dissolved in water (5 cm³) and conc. Ammonia (density = 0.88 g cm⁻³) (ca. 1 cm³) was added until all of the precipitate redissolved. This solution was added to a solution of 9-anthracenecarboxylic acid (9-acaH) (0.666 g, 3.00 mmoles) in 4:1 ethanol:water (100 cm³). Conc. ammonia (10 cm³) was added slowly with constant stirring

and after the addition was complete the solution was stirred for 0.5 h. The solution was reduced to near dryness using a rotary evaporator yielding a light yellow precipitate, which was washed with cold ethanol and allowed to air-dry. To obtain crystals suitable for X-ray structural analysis the original filtrate was allowed to slowly evaporate to a low volume over a period of days.

Yield: 0.457 g (45%).

Molecular formula (weight): $C_{60}H_{42}N_2O_8Ag_4$ (1350.44 g mol⁻¹).

Solubility: soluble in hot EtOH, MeCN and DMSO.

Anal. Calc.: C, 53.36; H, 3.14; N, 2.07%.

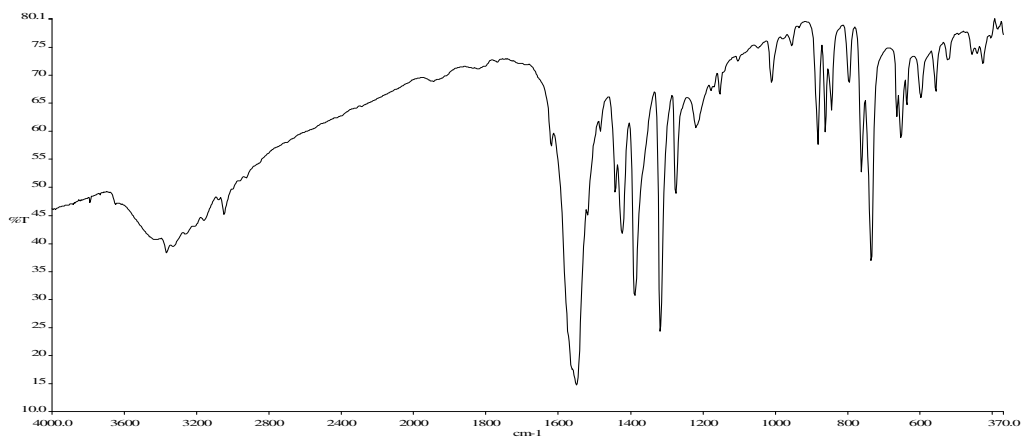
Anal. Found: C, 53.20; H, 3.03; N, 2.12%.

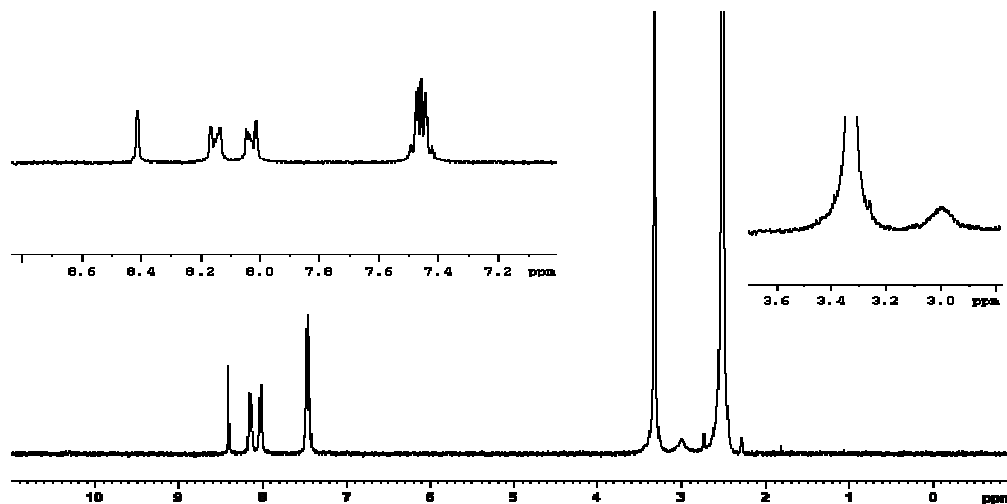
IR (cm⁻¹, KBr): 3370, 3050, 1620, 1551, 1443, 1424, 1390, 1319, 1277, 1220, 1155, 1011.

¹H NMR (δ, DMSO): 8.41 (s, 4H); 8.15 (m, 8H); 8.03 (m, 8H); 7.47 (m, 16H); 3.01 (s, 6H).

¹³C NMR (δ, DMSO): 172.84, 138.79, 130.96, 128.00, 127.15, 126.22, 125.21, 124.98, 124.44.

IR: [Ag₄(9-aca)₄(NH₃)₂]



^1H NMR (DMSO): $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ 

2.4 Fluorescence Studies

Spectra of the silver(I) complexes were recorded as 1×10^{-4} M solutions prepared in DMSO. Spectra of the metal-free ligands were recorded at the same concentration as the ligands that were present in the silver complex solutions.

2.5 *In vitro* Antimicrobial Screening

2.5.1 Microbial Growth Media

Deionised (Millipore) water was used to make all media.

Minimal Growth Media (MM) was composed of 2% (w/v) glucose, 0.5% (w/v) ammonium sulphate and 0.17% (w/v) yeast nitrogen base (without amino acids or ammonium sulphate). To solidify the media 2% (w/v) bacteriological agar was added when required.

Yeast Extract Peptone Dextrose (YEPD) media was composed of 2% (w/v) glucose, 2% (w/v) bacteriological peptone, and 1% (w/v) yeast extract. To solidify the media 2% (w/v) bacteriological agar was added when required.

Nutrient Broth was obtained from Scharlau Microbiology and made up according to the manufacturer's instructions (13 g in 1 litre deionised water).

Phosphate Buffered Saline (PBS) was obtained from Aldrich and made up according to the manufacturer's instructions (1 tablet in 200 cm³ deionised water).

2.5.2 In vitro Fungal Susceptibility Testing

Candida albicans (ATCC 10231) was grown on Yeast Extract Peptone Dextrose (YEPD) agar plates at 37 °C and maintained at 4 °C for short-term storage. Cultures were routinely sub-cultured every 4-6 weeks. All assays were run in triplicate and on 3 independent occasions.

Fresh solutions of complexes were prepared immediately prior to testing. Complexes (0.020 g) were dissolved in DMSO (1 cm³) and added to water (9 cm³) to give a stock solution (concentration 2000 µg cm⁻³). Complexes with low solubility were tested as fine suspensions. This stock solution (0.5 cm³) was added to water (9.5 cm³) to give a solution with a concentration of 100 µg cm⁻³.

Minimal Media (100 µl) was added to each well of a 96-well, round-bottomed microtitre plate. Water (100 µl) was added to column 1 of the plate (negative control, media with no fungal cells). Column 2 was the positive control (media and fungal cells only). 100 µl of the above complex solution (100 µg cm⁻³) was added to every well in column 3. Serial dilutions (1:1) were made from columns 3-12 to produce a test concentration range of 50–0.1 µg cm⁻³.

C. albicans was grown to the stationary phase overnight at 37 °C on YEPD media. The cells were washed with PBS solution and resuspended in minimal

media at a density of 5×10^5 cells cm^{-3} . The cell suspension (100 μl) was added to every well in columns 2–12. The completed plate was then covered with acetate foil (Sarstedt) to prevent dehydration. The plate was incubated at 37 °C with continuous shaking for 24 h. The optical density (at 540 nm) of each well was recorded at 1 h intervals. Minimum Inhibitory Concentration (MIC_{100}) values (minimum concentration required to inhibit 100% of cell growth) were then determined.

2.5.3 In vitro Bacterial Susceptibility Testing

Escherichia coli and Methicillin Resistant *Staphylococcus aureus* (MRSA) were grown on nutrient broth agar plates at 37 °C and maintained at 4 °C for short-term storage. Cultures were routinely sub-cultured every 4-6 weeks. All assays were run in triplicate and on 3 independent occasions.

Fresh solutions of complexes were prepared immediately prior to testing. Complexes (0.020 g) were dissolved in DMSO (1 cm^3) and added to water (9 cm^3) to give a stock solution (concentration 2000 $\mu\text{g cm}^{-3}$). Complexes with low solubility were tested as fine suspensions. This stock solution (1 cm^3) was added to water (9 cm^3) to yield a solution with a concentration of 200 $\mu\text{g cm}^{-3}$.

Nutrient broth (100 μl) was added to each well of a 96-well flat-bottomed microtitre plate. Water (100 μl) was added to column 1 of the plate (negative control). Column 2 was the positive control. 100 μl of the above complex solution (200 $\mu\text{g cm}^{-3}$) was added to every well in column 3. Serial dilutions (1:1) were made from column 3-12 to produce a test concentration range of 100–0.2 $\mu\text{g cm}^{-3}$.

E. coli and MRSA were grown overnight to the stationary phase in nutrient broth at 37 °C and 200 rpm. The cells were diluted to give an $\text{OD}_{600} = 0.1$. The cell suspension (100 μl) was added to every well in columns 2–12. The completed plates were incubated at 37 °C in a static incubator and the final optical density (600 nm) recorded. Minimum Inhibitory Concentration (MIC_{50})

values (minimum concentration required to inhibit 50% of cell growth) were then determined.

2.6 In vivo *Galleria mellonella* Studies

2.6.1 Cytotoxicity Studies

Galleria mellonella larvae in the 6th developmental stage were used to determine the *in vivo* cytotoxicity of the silver(I) complexes. Ten healthy larvae between 0.200-0.400 g in weight with no cuticle discolouration were used for each experiment. Fresh solutions of the test complexes were prepared immediately prior to testing. Complexes (0.020 g) were dissolved in DMSO (1 cm³) and added to water (9 cm³) to give a stock solution (concentration 2000 µg cm⁻³). Test solutions were made from this stock solution. Each compound was tested at three concentrations; twice their MIC₁₀₀ value, 10 µg cm⁻³ and 100 µg cm⁻³. The test solution (20 µl) was administered to the larvae by injection directly into the haemocoel through the last pro-leg. The base of the pro-leg can be opened by applying gentle pressure to the sides of the larvae and this aperture will re-seal after removal of the syringe without leaving a scar. Larvae were placed in sterile petri dishes and incubated at 30 °C for 72 h. The survival of the larvae was monitored every 24 h. Death was assessed by the lack of movement in response to stimulus together with discolouration of the cuticle.

Three controls were employed in all assays. The first consisted of untouched larvae maintained at the same temperature as the test larvae. The second was larvae with the pro-leg pierced with an inoculation needle but no substance injected into them. The third control was larvae that were inoculated with 20 µl of the same sterile water used to make the test solutions.

2.6.2 Antifungal Screening

G. mellonella larvae in the 6th developmental stage were used to determine the *in vivo* antimicrobial activity of the silver(I) complexes. Ten healthy larvae between 0.200-0.400 g in weight with no cuticle discolouration were used for each experiment. Fresh solutions of complexes were prepared immediately prior to testing. Complexes (0.020 g) were dissolved in DMSO (1 cm³) and added to water (9 cm³) to give a stock solution (concentration 2000 µg cm⁻³). Test solutions were made from this stock solution. Each compound was tested at three concentrations; twice their MIC₁₀₀ value (µg cm⁻³), 10 µg cm⁻³ and 100 µg cm⁻³.

C. albicans was grown to the stationary phase in YEPD media at 37 °C for 24 h. The cell concentration was assessed using a haemocytometer following a dilution of the culture in PBS. The cells were washed three times with PBS and resuspended in sterile PBS following harvesting by centrifugation at 4000 rpm for 10 min to yield a concentration of 1×10⁸ cell cm⁻³.

Two treatments were employed in the screening of the test solutions. In each case, four controls were employed in all assays along with a reference. The first control consisted of untouched larvae maintained at the same temperature as the test larvae (negative control). The second was larvae with the pro-leg pierced with an inoculation needle but no substance injected into them. The third control was larvae that were inoculated with 20 µl of the same sterile water used to make the test solutions, and the fourth is larvae inoculated with the same sterile PBS solution that was used to wash and make the *C. albicans* suspension. The positive control was larvae inoculated with *C. albicans* but no test solution was administered to them.

2.6.2.1 Prophylactic Treatment

The test solution (20 µl) was administered to the larvae by injection directly into the haemocoel through the last pro-leg. Larvae were then placed in sterile petri dishes and incubated at 30 °C for 1 h, after which time they were

inoculated with 20 μl of the *C. albicans* suspension (2×10^6 cells). The larvae were incubated at 30 °C for 72 h and larvae survival was monitored every 24 h.

2.6.2.2 Treatment of Infection

Larvae were inoculated with 20 μl of the *C. albicans* suspension (2×10^6 cells) by injection directly into the haemocoel through the last pro-leg. Larvae were then placed in sterile petri dishes and incubated at 30 °C for 1 h, after which time the test solution (20 μl) was administered by injection. The larvae were incubated at 30 °C for 72 h and larvae survival was monitored every 24 h.

2.7 *In vitro* Anticancer Screening

2.7.1 Hep-G₂ and A-498 cell lines:

Human hepatocellular liver carcinoma (Hep-G₂) and human renal carcinoma (A-498) cells were grown as a monolayer in Eagle's minimum essential medium, supplemented with 2.00 mM L-glutamine and Earle's balanced salt solution, containing 1.500 g dm⁻³ sodium bicarbonate, 0.10 mM non-essential amino acids, 1.00 mM sodium pyruvate, 100 $\mu\text{g cm}^{-3}$ penicillin and 100 $\mu\text{g cm}^{-3}$ streptomycin supplemented to contain 10% (v/v) foetal bovine serum. Cells were grown at 37 °C in a humidified atmosphere in the presence of 5% CO₂ and were in the exponential phase of growth at the time of assay. A 100 μl aliquot of Hep-G₂ and A-498 cells were seeded at a density of 5×10^4 and 2.5×10^4 cells cm⁻³, respectively, into sterile 96-well, flat-bottomed plates and grown in 5% CO₂ at 37 °C. Test complexes were dissolved in DMSO and diluted with culture media. The maximum percentage of DMSO present in all wells was 0.2 % (v/v). Each drug solution (100 μl) was added to replicate wells (5 replicates) in the concentration range of 0.1-500 μM and incubated for 96 h. A miniaturised viability assay, using 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT), was carried out. This method is based on the reduction of the tetrazolium salt, methylthiazolyldiphenyl-tetrazolium bromide (MTT) into a crystalline blue formazan product by the cellular oxidoreductases of viable cells.

The resultant formazan crystal formation is proportional to the number of viable cells.

Following drug incubation, cells were assayed by the addition of 20 μl of 5 mg cm^{-3} MTT in 0.1 M PBS (pH 7.2) and incubated for 4 h at 37 °C. The overlying medium was aspirated with a syringe and DMSO (100 μl) was then added to dissolve the formazan crystals. Plates were agitated at high speed in order to ensure complete dissolution of the crystals. The optical density was measured at 550 nm, and cell viability was expressed as a percentage of solvent-treated control cells. The complete assay was repeated 3 times giving a total of 15 readings for each concentration. The IC_{50} value was calculated and is defined as the concentration of test compound required to reduce the absorbance of the MTT-formazan crystals by 50%, indicating 50% cell deactivation. The significance of any reduction in cellular viability was determined using one-way ANOVA (analysis of variance). A probability of 0.05 or less was deemed statistically significant.

2.6.2 MCF7 and HT29 cell lines:

Human colon cancer cells, HT29 (passage 15 to 30, ATCC, USA), were grown in McCoys's 5a Medium supplemented with 2mM L-glutamine, 10% fetal bovine serum (FBS), penicillin-streptomycin solution with 100 $\mu\text{g cm}^{-3}$ penicillin and 100 $\mu\text{g cm}^{-3}$ streptomycin at 37 °C in a humidified atmosphere with 5% CO_2 . Human breast cancer cells, MCF-7 (passage 6 to 21, ATCC, USA), were grown in Eagle's Minimum Essential Medium containing 2.00 mM L-glutamine, penicillin-streptomycin solution with 100 $\mu\text{g cm}^{-3}$ penicillin and 100 $\mu\text{g cm}^{-3}$ streptomycin, FBS (10%), 100 mM sodium pyruvate solution (1%) and 1% (v/v) MEM non-essential amino acid solution at 37 °C in a humidified atmosphere with 5% CO_2 .

The cytotoxic potential of each test compound was determined following incubation of exponentially growing cells using the MTT assay. Cells were seeded at 4×10^5 cells cm^{-3} in 96-well plates and incubated at 37 °C in 5% CO_2

for 24 h. Cells were treated (in triplicate) with a four log range of concentrations of the test compounds (0.10-100 μM) or with a solvent control (0.5% DMSO) in complete medium.

Following 24 h incubation, cells were treated with 20 μl of MTT (5 mg cm^{-3}) in 0.10 M PBS, pH 7.4 at 37 °C in a humid atmosphere with 5% CO_2 for 4 h. Media was then gently aspirated from the test cultures and 100 μl of DMSO was added to all wells. The plates were shaken for 2 min in a microtiter plate reader and the absorbance was read at 550 nm. The IC_{50} value was calculated.

Discussion 1:
Drug Structures
and Properties

3.1 Synthesis and Structures of Ag(I) Complexes

In discussing the ^1H NMR spectra of all compounds in this section the numbering system for the hydrogen atoms on 9-anthracenecarboxylic acid is illustrated in Figure 35.

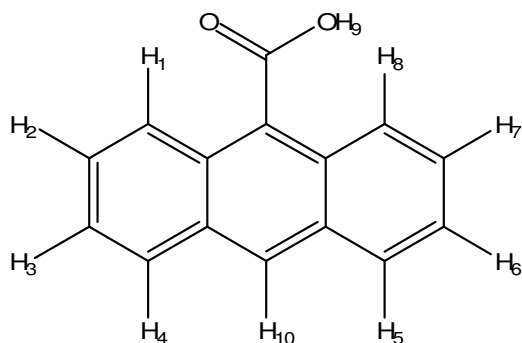


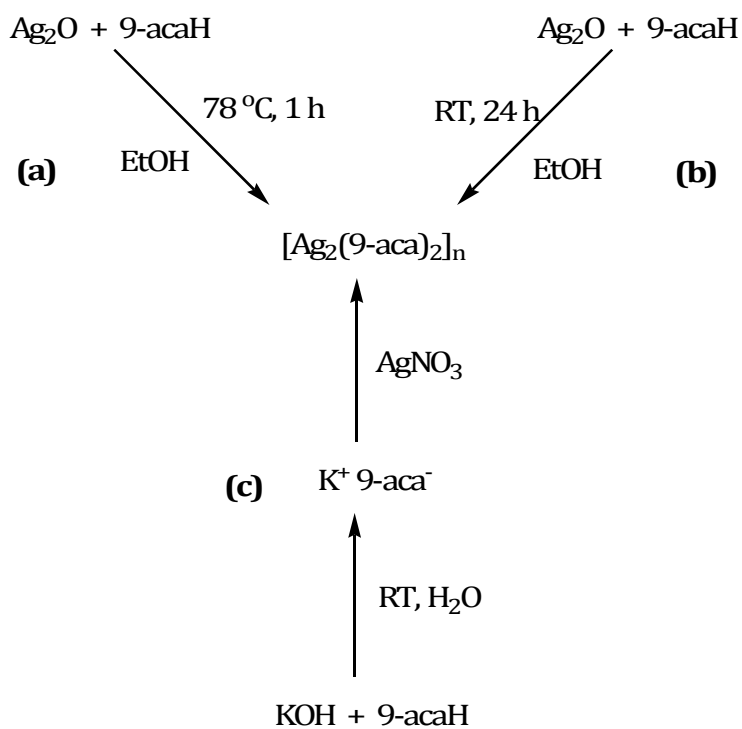
Figure 35. Proton numbering on hydrogen atoms of 9-anthracenecarboxylic acid.

3.1.1 $[\text{Ag}_2(9\text{-aca})_2]_n$

$[\text{Ag}_2(9\text{-aca})_2]_n$ was first synthesised from Ag_2O and 9-acaH in ethanol at $80\text{ }^\circ\text{C}$ for 1 h (Scheme 1(a)). A low product yield (21%) was accredited to the deposition of elemental silver on the reaction flask when the reaction mixture was refluxed for extended periods of time. This metal deposition problem was solved by either maintaining the reaction mixture at room temperature for an extended time period (Scheme 1(b), (70%)) or by synthesising the potassium-anthracene salt and using it as a precursor to $[\text{Ag}_2(9\text{-aca})_2]_n$ (Scheme 1(c), (73%)). In this way the product yield was increased from 21% to 73%.

The X-ray crystal structure of $[\text{Ag}_2(9\text{-aca})_2]_n$ is shown in Figures 36-38 and selected bond lengths and angles are given in Table 2. The structure consists of polymeric ribbons of linked disilver(I) dicarboxylate units. There are two independent $[\text{Ag}_2(9\text{-aca})_2]$ units in the asymmetric unit (Figure 36), generating two independent ribbons which differ principally in the angle of the anthracene

unit to the ribbon (Figure 37). Both types of ribbon run parallel to the b axis (Figure 38).



Scheme 1. Synthesis of $[\text{Ag}_2(9\text{-aca})_2]_n$.

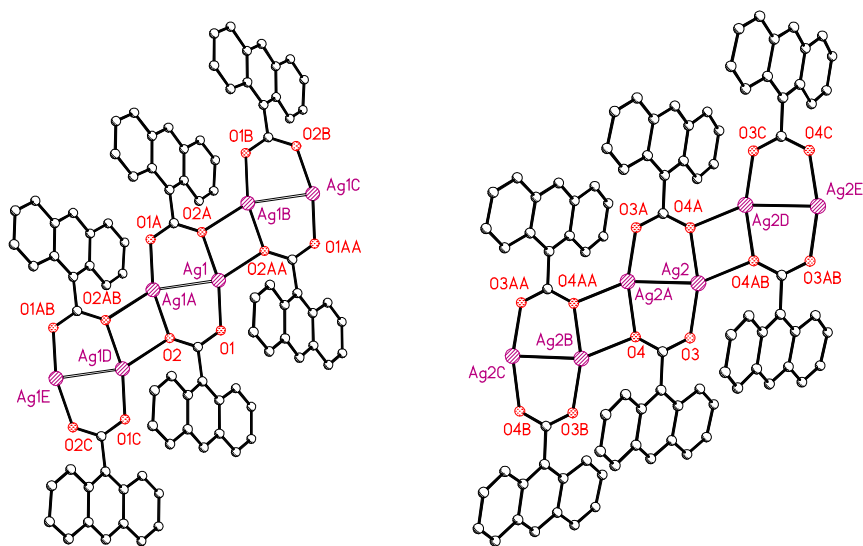


Figure 36. Structures of the two polymeric strands in $[\text{Ag}_2(9\text{-aca})_2]_n$.

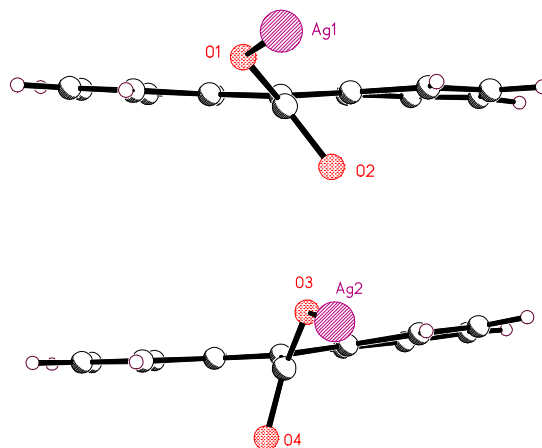


Figure 37. Overview showing the different angles within the ribbons of $[\text{Ag}_2(9\text{-aca})_2]_n$.

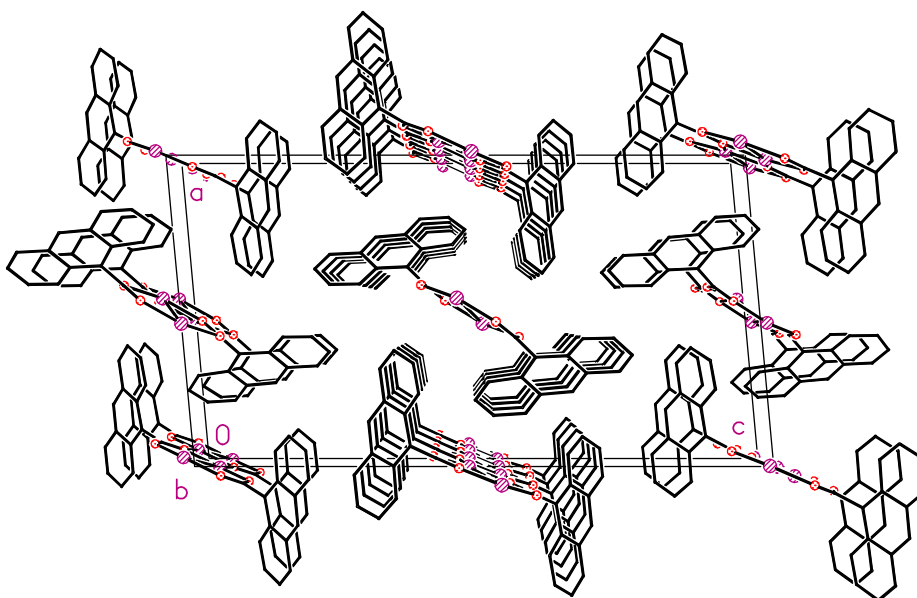


Figure 38. Packing diagram for $[\text{Ag}_2(9\text{-aca})_2]_n$.

Table 2. Selected bond lengths and bond angles for $[\text{Ag}_2(9\text{-aca})_2]_n$.

| Bond | Bond Length (Å) | Bond | Bond Angle (°) |
|--------------|-----------------|---------------------|----------------|
| Ag(1)-O(1) | 2.170 | O(1)-Ag(1)-O(2A) | 162.20 |
| Ag(1)-O(2A) | 2.190 | O(1)-Ag(1)-O(2AA) | 116.66 |
| Ag(1)-O(2AA) | 2.473 | O(2A)-Ag(1)-O(2AA) | 76.88 |
| Ag(1)-Ag(1A) | 2.851 | C(1)-O(1)-Ag(1) | 120.30 |
| Ag(1)-Ag(1B) | 3.657 | O(2A)-Ag(1)-Ag(1A) | 79.04 |
| Ag(2)-Ag(2D) | 3.615 | O(2AA)-Ag(1)-Ag(1A) | 150.71 |

The carboxylate ligands are syn-syn bridging to the bimetallic core (Ag-O average bond length of 2.183 Å) and this unit is further linked to neighbouring cores by weaker, equatorial Ag-O interactions (Ag-O average bond length of 2.393 Å). A similar coordination mode for the carboxylates was observed in the structure of the binuclear copper(II) complex, $[\text{Cu}_2(9\text{-aca})_4(\text{MeOH})_2](\text{MeOH})^{158}$. In this copper(II) complex the metals have square pyramidal geometry and the bimetallic units are linked into chains by hydrogen bonds (H-bonds).

Each silver is 4-coordinate and the Ag(1)-Ag(1A) distance in $[\text{Ag}_2(9\text{-aca})_2]_n$ is 2.851 Å, similar to that in $[\text{Ag}(\text{fbc})]_n$ (fbc = 4-fluorobenzoic acid), where the metal is also bonded to three different carboxylate groups (Figure 25)¹³¹. The Ag-Ag bond distance in $[\text{Ag}_2(9\text{-aca})_2]_n$ is also shorter than that in metallic silver (2.89 Å)¹⁰⁶. Besides the short Ag(1)-Ag(1A) bond there are also weaker Ag-Ag interactions (e.g. Ag(1)-Ag(1B) or Ag(2)-Ag(2D)), with Ag-Ag distances of 3.657 and 3.615 Å for the Ag(1) and Ag(2) chains, respectively.

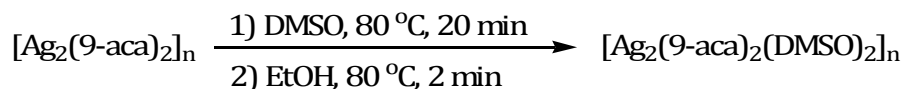
The IR spectrum of $[\text{Ag}_2(9\text{-aca})_2]_n$ shows a small, characteristic band at 1621 cm^{-1} for the ring system of the anthracene group¹⁴⁴ and a strong band at 1535 cm^{-1} for the C=C stretching vibrations of the aromatic rings. Two more bands for the anthracene ring vibrations are present at 736 and 768 cm^{-1} ^{144,160}. The $\nu(\text{OCO})_{\text{asym}}$ and $\nu(\text{OCO})_{\text{sym}}$ vibrations for the carboxylate function occur at 1566 and

1429 cm^{-1} , respectively, giving a $\Delta_{(\text{OCO})}$ value of 137 cm^{-1} . This value indicates a chelating or bridging coordination mode for the carboxylate ligand¹⁴³.

The ^1H NMR spectrum of $[\text{Ag}_2(9\text{-aca})_2]_n$ exhibits peaks for the aromatic protons at 8.44 (H_{10}), 8.18 ($\text{H}_{1,8}$), 8.03 ($\text{H}_{4,5}$) and 7.47 ppm ($\text{H}_{2,3,6,7}$). The attachment of the silver has caused a shielding of the anthracene protons and a shift upfield relative to uncoordinated 9-anthracenecarboxylic acid. This can be accredited to the changes in electron density and in π -electron circulation about the anthracene ring system caused by the coordination to the silver(I) ion¹⁰³.

3.1.2 $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$

The DMSO adduct of $[\text{Ag}_2(9\text{-aca})_2]_n$ was readily prepared in 50% yield from $[\text{Ag}_2(9\text{-aca})_2]_n$ by heating in DMSO and ethanol (Scheme 2).

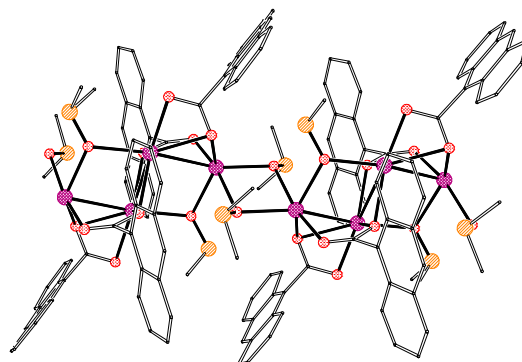


Scheme 2. Synthesis of $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$.

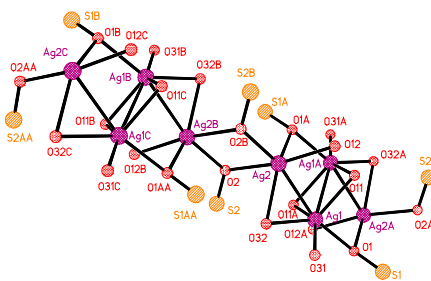
The X-ray crystal structure of $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ was determined (Figures 39-42) and selected bond lengths and angles are given in Table 3. The complex is polymeric with the chains lying parallel to the a-axis. The complex may also be viewed as being tetranuclear (Figures 39 and 41) with units being linked by DMSO.

The Ag(1)-Ag(2) bond length in $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ (2.914 Å) is longer than that in $[\text{Ag}_2(9\text{-aca})_2]_n$ (2.851 Å) and the distance between Ag(1) and Ag(1A) is 3.147 Å. This latter bond length is shorter than the corresponding silver-silver distances observed in $[\text{Ag}_2(9\text{-aca})_2]_n$ (3.657 Å). The Ag-O bonds of the carboxylate and bridging DMSO ligands in $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ are of similar length (average bond length of 2.440 and 2.465 Å, respectively), but are longer than those in $[\text{Ag}_2(9\text{-aca})_2]_n$ (2.183 Å). The longer metal-oxygen bond lengths in

$[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ may be a consequence of the increased number of donor atoms (increased electron density) surrounding the metal centres.



(a)



(b)

Figure 39. Structure of two tetrameric units of $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ (anthracene rings omitted for clarity in (b)).

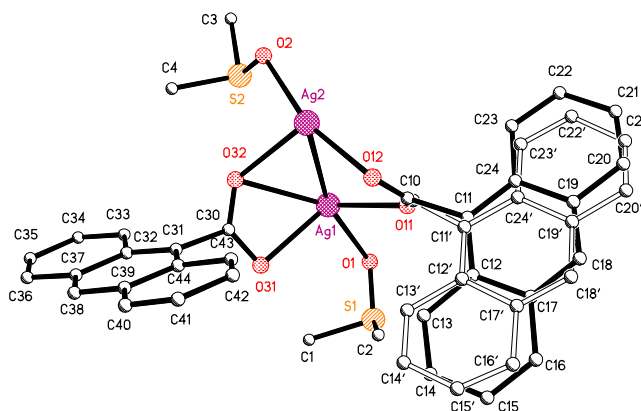


Figure 40. X-ray crystal structure of one asymmetric unit of $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ showing some disorder in the anthracene rings (60:40).

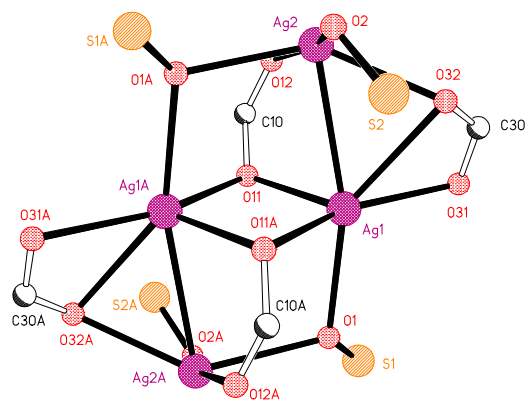


Figure 41. Structure of the tetrameric core of $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ with anthracene rings omitted for clarity.

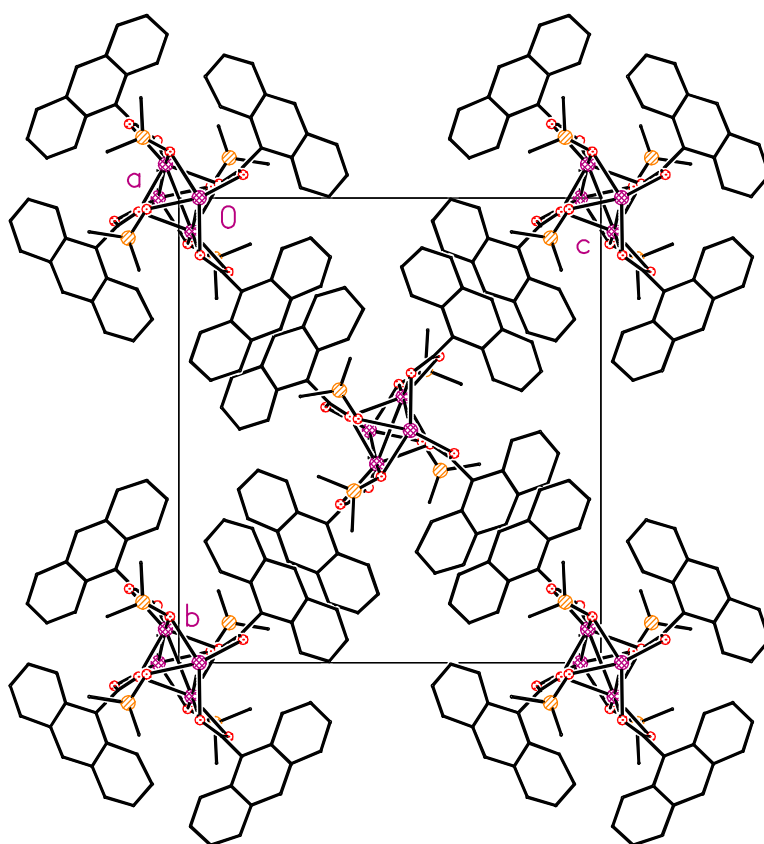


Figure 42. Packing diagram for $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$.

Table 3. Selected bond lengths and bond angles for $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$.

| Bond | Bond Length (Å) | Bond | Bond Angle (°) |
|--------------|-----------------|--------------------|----------------|
| Ag(1)-Ag(2) | 2.914 | O(11)-Ag(1)-O(11A) | 97.65 |
| Ag(1)-Ag(1A) | 3.147 | O(11)-Ag(1)-O(31) | 110.86 |
| Ag(1)-O(11) | 2.358 | O(11)-Ag(1)-O(1) | 90.51 |
| Ag(1)-O(11A) | 2.421 | O(31)-Ag(1)-O(1) | 99.46 |
| Ag(1)-O(1) | 2.428 | O(31)-Ag(1)-O(11A) | 151.23 |
| Ag(1)-O(32) | 2.598 | O(31)-Ag(1)-O(32) | 52.25 |

In $\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2$, the two carboxylate oxygen atoms (O(31), O(32)) bridge Ag(1) and Ag(2) in a similar syn-syn fashion as seen in $[\text{Ag}_2(9\text{-aca})_2]_n$ (Figure 40). The same oxygen atoms (O(31), O(32)) can also be viewed as chelating to Ag(1). This unusual bonding arrangement has not, to our knowledge, been previously reported for silver(I) carboxylates. This additional Ag-O bond (Ag(1)-O(32)) is longer than the syn-syn Ag-O bonds (2.598, 2.384 and 2.421 Å, respectively).

The IR spectrum of $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ is very similar to that of $[\text{Ag}_2(9\text{-aca})_2]_n$ apart from the inclusion of the bands associated with the DMSO ligands. A band is observed at 708 cm^{-1} for the symmetric stretching vibration of the S=O moiety along with a strong band at 955 cm^{-1} corresponding to the S-CH₃ rocking vibration of the methyl groups¹⁴⁴. The $\nu_{(\text{OCO})\text{asym}}$ and $\nu_{(\text{OCO})\text{sym}}$ stretching vibrations occur at 1587 and 1427 cm^{-1} , respectively, giving a $\Delta_{(\text{OCO})}$ value of 160 cm^{-1} . Using this value it is not possible to identify the carboxylate coordination mode as predictions with $\Delta_{(\text{OCO})}$ values of *ca.* 165 cm^{-1} have been shown to be untrustworthy¹⁴³.

The ¹H NMR spectrum of $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ is very similar to that of $[\text{Ag}_2(9\text{-aca})_2]_n$, the only difference being the presence of a singlet at 2.56 ppm for the methyl groups of the DMSO ligands. It is believed that the DMSO ligands dissociate in solution as the position of this singlet is unchanged when

compared to uncoordinated DMSO¹⁶¹. Coordination to the silver ion is expected to cause a shielding of the methyl protons but this is not evident from the spectrum.

3.1.3 [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca)

The imidazole complex, [Ag₂(9-aca)₂(DMSO)₂]_n, was synthesised in 18% yield from [Ag₂(9-aca)₂]_n and imidazole in the presence of acetonitrile (Scheme 3). In this process, polymeric [Ag₂(9-aca)₂]_n disintegrates and re-assembles as a mononuclear complex where the silver(I) is ligated by imidazole and acetonitrile. The 9-aca⁻ ligand has now become an uncoordinated counterion.



Scheme 3. Synthesis of [Ag(imid)_{2.3}(CH₃CN)_{0.7}](9-aca).

The X-ray crystal structure of [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca) was determined (Figures 43-47) and selected bond lengths and angles are given in Table 4.

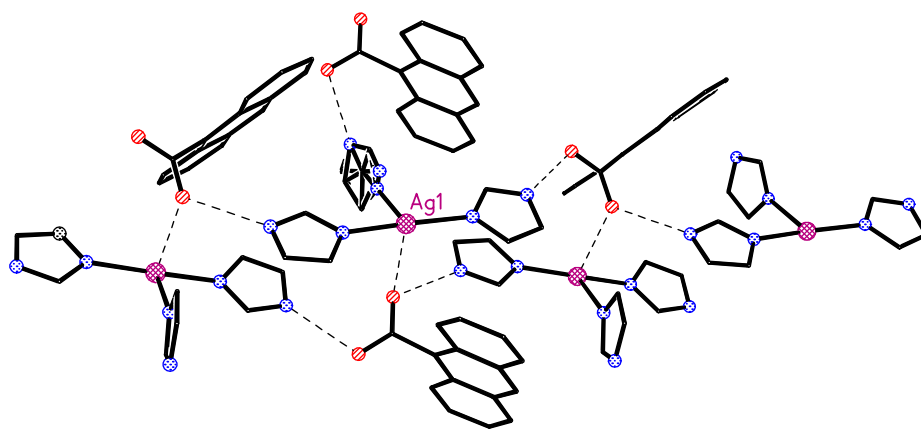


Figure 43. X-ray crystal structure of [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca).

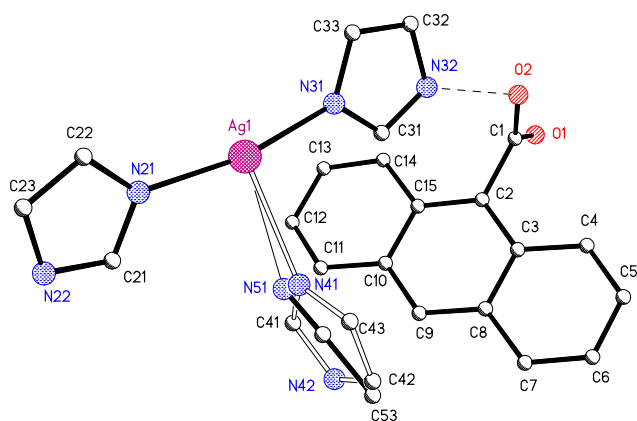


Figure 44. One of the asymmetric units of $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$ showing the disorder associated with the imidH and the CH_3CN .

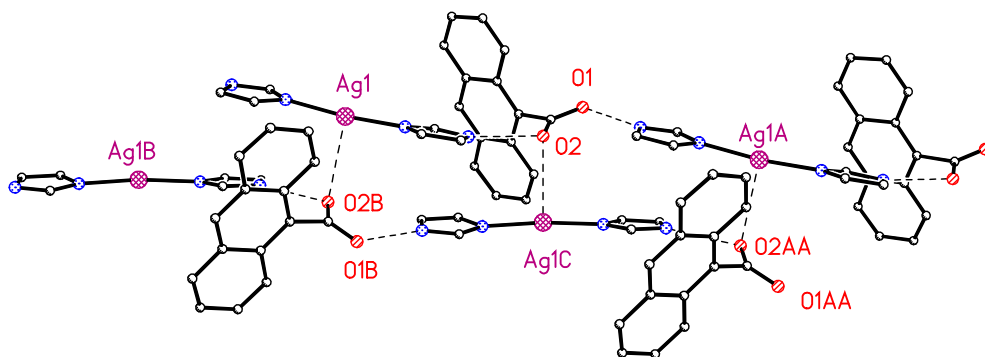


Figure 45. Weak interactions of the silver(I) centre with the carboxylate oxygen atoms and the H-bonding between the imidazole N-H and carboxylate oxygens in $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$.

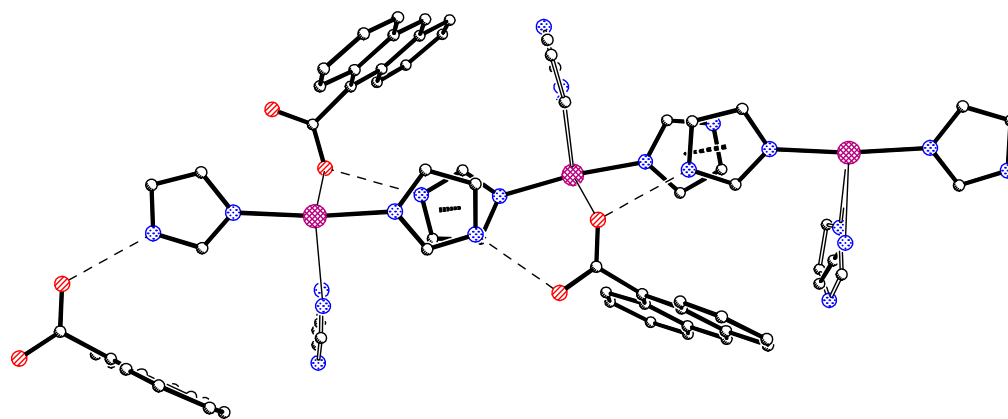


Figure 46. Chains of $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$ units showing the H-bonding and the π - π stacking of the imidazole groups.

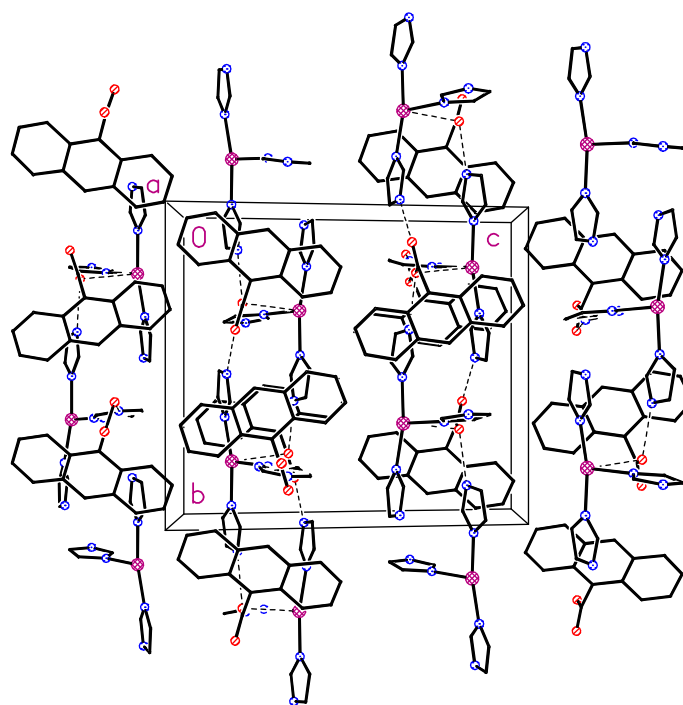


Figure 47. Packing diagram for $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$.

Table 4. Selected bond lengths and bond angles for [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca).

| Bond | Bond Length (Å) | Bond | Bond Angle (°) |
|-------------|-----------------|-------------------|----------------|
| Ag(1)-N(21) | 2.126 | N(21)-Ag(1)-N(31) | 168.51 |
| Ag(1)-N(31) | 2.126 | N(21)-Ag(1)-N(41) | 96.10 |
| Ag(1)-N(41) | 2.588 | N(31)-Ag(1)-N(41) | 94.70 |
| Ag(1)-N(51) | 2.713 | N(21)-Ag(1)-N(51) | 93.70 |
| Ag(1)-O(2B) | 3.009 | N(31)-Ag(1)-N(51) | 96.00 |

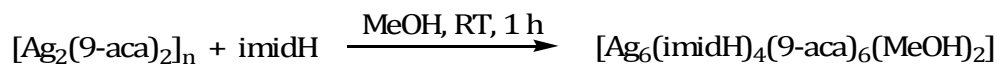
The Ag⁺ forms short bonds to the imine nitrogen of each of the two imidazole groups (2.126 Å) with a third ligand coordinated to the silver disordered 70:30 between acetonitrile and imidazole, respectively. These Ag-N bonds are similar in length to those found in the trisilver(I) complex, [Ag₃(imid)₆](ClO₄)₃ (2.075 Å)¹⁶². There is also a longer interaction (3.009 Å) with the carboxylate oxygen atom of a neighbouring 9-aca unit (Figure 45). In [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca) the silver is coordinated approximately linearly with the first two imidazole groups, with a N(21)-Ag(1)-N(31) bond angle of 169°. The third ligand is approximately perpendicular to this linear arrangement, with a N(21)-Ag(1)-N(51) angle of 94°. The structure is linked into chains by H-bonding between the carboxylate and imidazole groups. This assembly is further supported by π-π stacking of the imidazole groups, with a centroid-centroid distance of 3.638 Å (Figure 46).

The IR spectrum of [Ag(imid)_{2.3}(CH₃CN)_{0.7}](9-aca) exhibits a weak band at 2250 cm⁻¹ for the C≡N bond stretching vibration. Bands are also observed at 3436 and 1072 cm⁻¹ corresponding to the N-H and C-N stretching vibrations of imidazole, respectively. Bands for the anthracene ring system occur at 1625, 760 and 739 cm⁻¹ ^{144,160}. The ν_(OCO)asym and ν_(OCO)sym vibrations occur at 1562 and 1426 cm⁻¹, respectively, giving a Δ_(OCO) value of 136 cm⁻¹. This value indicates a bridging carboxylate which, in this case, corresponds to the “pseudo-bridging” of the H-bonds¹⁴³.

In the ^1H NMR spectrum of $[\text{Ag}(\text{imid})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$, peaks corresponding to the aromatic protons of the anthracene ring appear at 8.41 (H_{10}), 8.15 ($\text{H}_{1,8}$), 8.03 ($\text{H}_{4,5}$) and 7.46 ppm ($\text{H}_{2,3,6,7}$). The aromatic protons of the imidazole ligand occur at 7.90 (H in the 4- and 5-positions) and 7.16 (H in the 2-position) ppm. The aromatic protons on the imidazole rings are slightly deshielded in comparison to the free ligand (7.64 and 7.02 ppm) and the peak for the hydrogen on the amine nitrogen is absent. Such shifts in peak positions and the absence of the amine proton has previously been reported for Cu^{2+} and Ag^+ azole complexes^{103,163}. A peak is also present at 2.08 ppm for the methyl protons of the acetonitrile ligand.

3.1.4 $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$

$[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$ was synthesised from $[\text{Ag}_2(9\text{-aca})_2]_n$ and imidazole in MeOH, with a yield of 44% (Scheme 4). Thus, a minor change in the reaction conditions (methanol as solvent as opposed to acetonitrile) causes a dramatic change in the product formulation.



Scheme 4. Synthesis of $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$.

$[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$ was recrystallised from methanol and the X-ray crystal structure of the complex was obtained (Figures 48-51). A list of selected bond lengths and angles is presented in Table 5. The hexanuclear complex has a two-fold axis through the molecule and contains both three- and five-coordinate silver(I) ions (Figure 49).

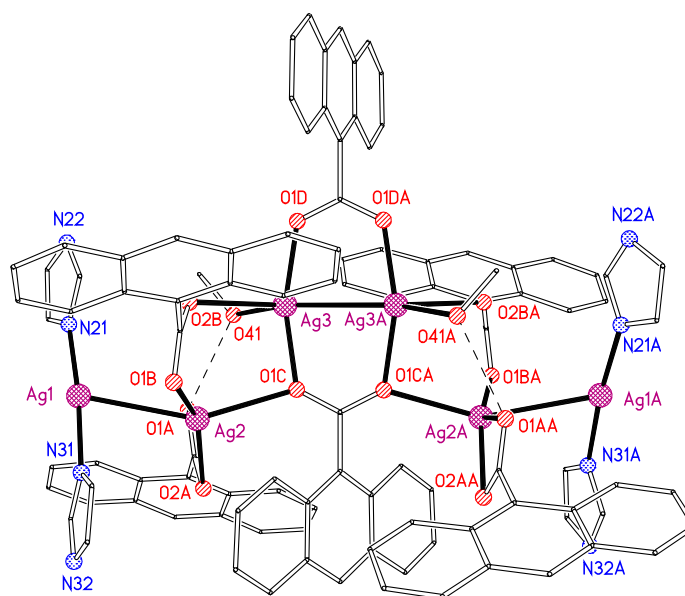


Figure 48. X-ray crystal structure of $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$.

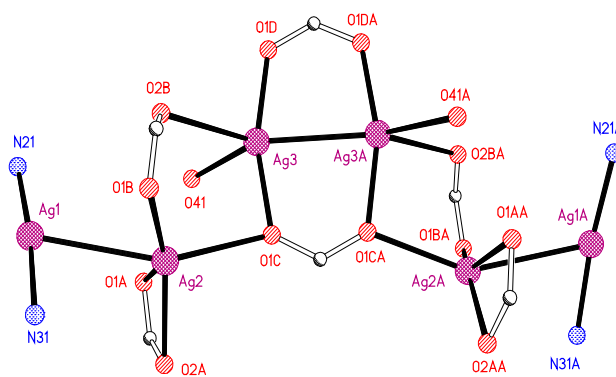


Figure 49. Simplified structure of $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$ with the imidazole and anthracene rings omitted for clarity.

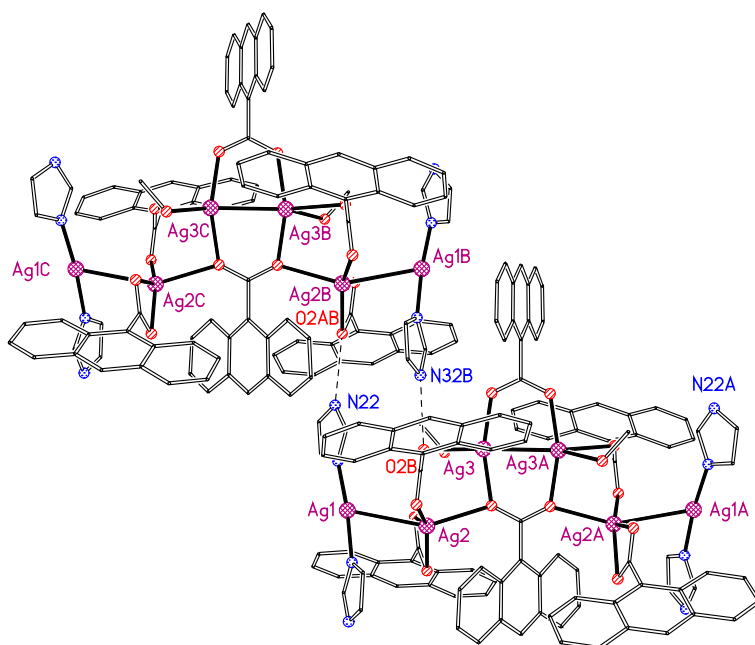


Figure 50. Intermolecular H-bonding in $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$.

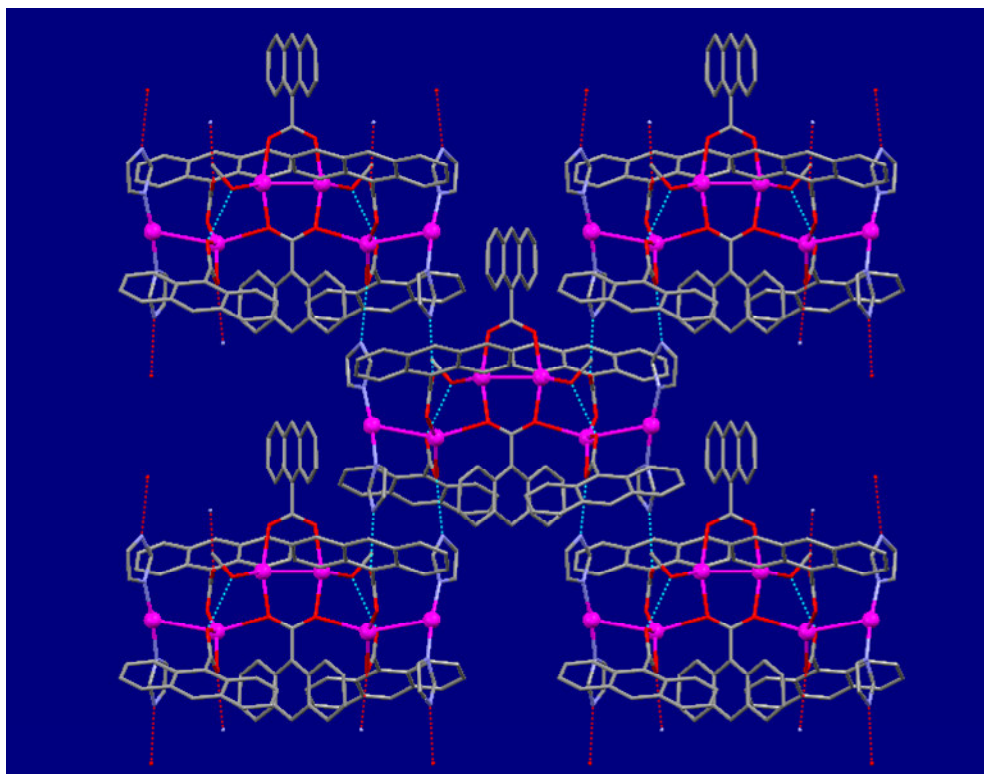


Figure 51. Packing diagram for $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$.

Table 5. Selected bond lengths and bond angles for $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$.

| Bond | Bond Length (Å) | Bond | Bond Angle (°) |
|--------------|-----------------|--------------------|----------------|
| Ag(1)-Ag(2) | 3.065 | N(21)-Ag(1)-N(31) | 174.33 |
| Ag(3)-Ag(3A) | 2.882 | N(21)-Ag(1)-Ag(2) | 111.93 |
| Ag(1)-N(21) | 2.088 | N(31)-Ag(1)-Ag(2) | 73.35 |
| Ag(3)-O(41) | 2.467 | O(1A)-Ag(2)-O(2A) | 54.34 |
| Ag(3)-O(1C) | 2.168 | O(1D)-Ag(3)-Ag(3A) | 81.52 |
| Ag(2)-O(1B) | 2.218 | O(1D)-Ag(3)-O(1C) | 162.45 |

The Ag(1)-Ag(2) bond length is 3.065 Å while the Ag(3)-Ag(3A) bond is significantly shorter at 2.882 Å. Ag(1) is coordinated approximately linearly by two imidazole groups (N(21)-Ag(1)-N(31) bond angle of 174°) with an Ag-N bond length of 2.088 Å. This latter bond is slightly shorter than the corresponding Ag-N bond of the ordered imidazole in $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$ (2.126 Å).

In $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$, Ag(2) is coordinated to three different carboxylate groups as well as being bonded to Ag(1). Ag(3) is also coordinated to three different carboxylate groups, plus the oxygen of a methanol and another silver ion (Ag(3A)). Two of the carboxylate ligands are in the syn-syn configuration (O1C and O1Ca, O1D and O1DA), two are syn-anti (O1B and O2B, O1BA and O2BA) and two are coordinated in a symmetrical, bidentate, chelation mode (O1A and O2A, O1AA and O2AA).

$[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$ also displays intramolecular H-bonding between the OH of the alcohol group and a neighbouring carboxylate oxygen atom (Figure 48), as well as intermolecular H-bonding between the amine hydrogen of the imidazole and a carboxylate oxygen of a neighbouring 9-aca molecule (Figures 50 and 51). A very weak π -interaction between Ag(1) and the anthracene ring of a neighbouring molecule is also observed.

The IR spectrum of $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$ exhibits peaks at 3448 and 1091 cm^{-1} for the N-H and C-N stretching vibrations of imidazole, respectively. Distinctive bands for the vibrations of the ring system of anthracene occur at 1625, 760 and 736 cm^{-1} ^{144,160}. The $\nu_{(\text{OCO})\text{asym}}$ and $\nu_{(\text{OCO})\text{sym}}$ vibrations occur at 1538 and 1433 cm^{-1} , respectively, giving a $\Delta_{(\text{OCO})}$ value of 105 cm^{-1} . This value indicates the presence of bridging carboxylates¹⁴³.

The ^1H NMR spectrum of $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$ contains peaks for the aromatic protons of the anthracene ring at 8.46 (H_{10}), 8.16 ($\text{H}_{1,8}$), 8.06 ($\text{H}_{4,5}$) and 7.49 ppm ($\text{H}_{2,3,6,7}$). As expected, this spectral region is very similar to that seen for $[\text{Ag}_2(9\text{-aca})_2]_n$. The aromatic C-H protons of the four imidazole ligands appear to be equivalent as there is only one singlet at 7.33 ppm integrating for 12 hydrogens. This equivalence was reported for $[\text{AgCl}(\text{imidH})(\text{PPh}_3)_2]$ ¹⁰³ and was accredited to the fluxional behaviour of the complex in solution. A peak is also observed at 3.17 ppm corresponding to the methyl protons of the methanol ligands in $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$.

3.1.5 $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$

$[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ was made from $[\text{Ag}_2(9\text{-aca})_2]_n$ and 1-methylimidazole (1-Me-imidH) in ethanol with a yield of 37% (Scheme 5).



Scheme 5. Synthesis of $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$.

$[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ was recrystallised from DMSO and the X-ray crystal structure was determined (Figures 52-56). Selected bond lengths and angles are listed in Table 6. The complex consists of two independent centrosymmetric molecules which differ in the angle between the planes of the anthracene ligands (Figure 53).

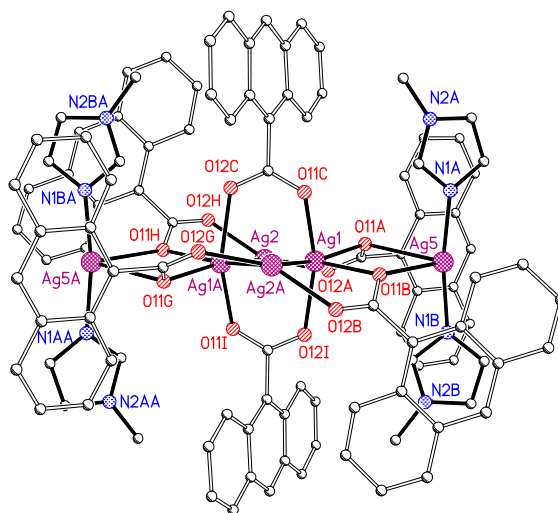


Figure 52. X-ray crystal structure of $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$.

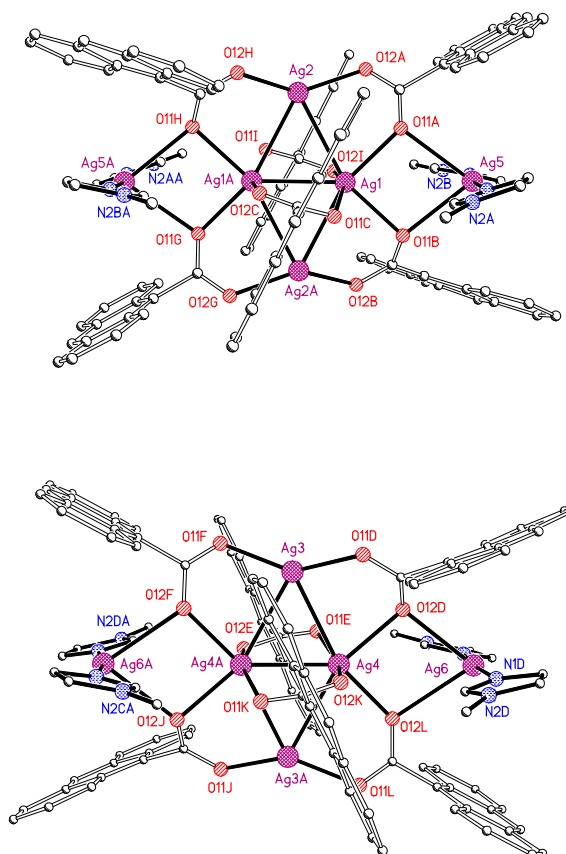
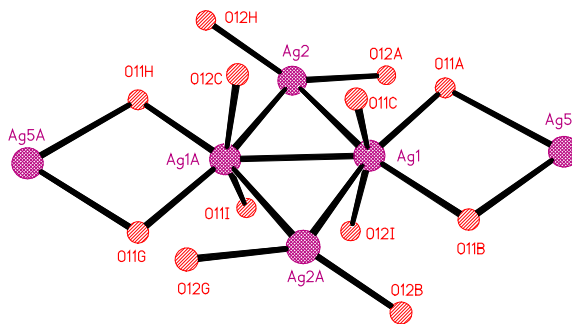
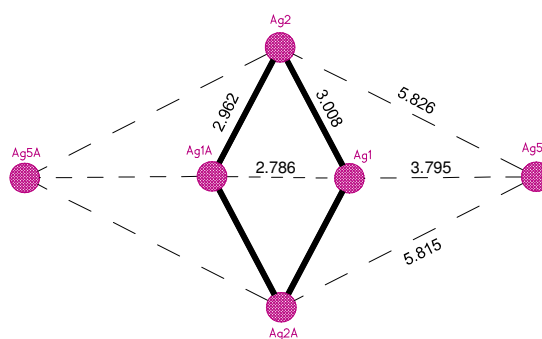


Figure 53. The two independent molecules of $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ illustrating the difference in arrangement of the anthracene ligands.



(a)



(b)

Figure 54. Simplified structures of $[Ag(1-Me-imid)_2]_2[Ag_4(9-aca)_6]$ showing (a) Ag-Ag and Ag-O bonding and (b) Ag-Ag bond lengths and distances.

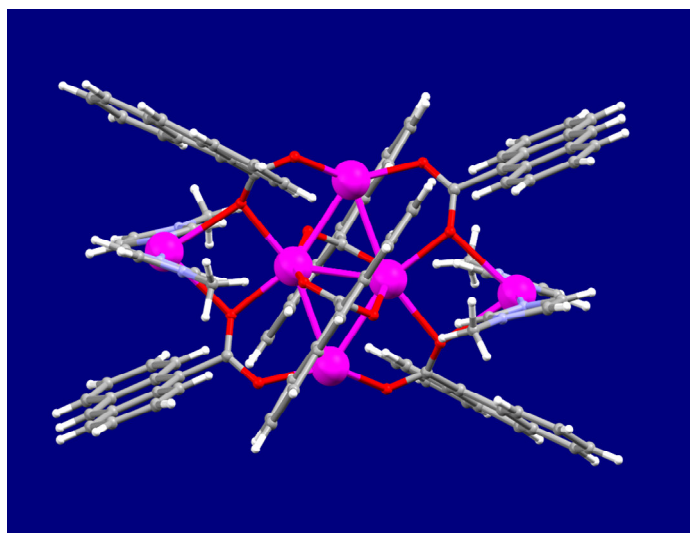


Figure 55. Ball and stick representation of $[Ag(1-Me-imid)_2]_2[Ag_4(9-aca)_6]$.

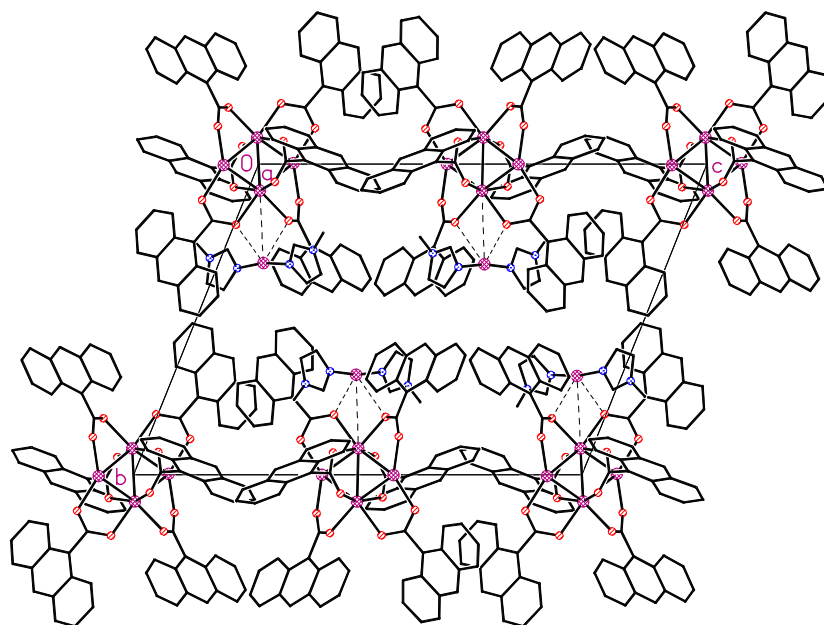


Figure 56. Packing diagram for $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$.

Both of the $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ molecules contain a dianionic complex central core, $[\text{Ag}_4(9\text{-aca})_6]^{2-}$, with the two complex cations, $[\text{Ag}(1\text{-Me-imidH})_2]^+$, on the periphery of the molecule. The central tetrasilver cluster contains Ag-Ag bond lengths ranging from 2.786-3.009 Å. The average distance from a core Ag^+ to a peripheral Ag^+ is 5.821 Å (Figure 54). Two 9-aca⁻ ligands (O(11C), O(12C) and O(11I), O(12I)) are coordinated in a sys-syn fashion to central silver(I) ions (Ag(1), Ag(1A)). The four remaining 9-aca⁻ ligands are coordinated to two central silver(I) ions and one peripheral silver(I) ion. The average core Ag-O bond length is 2.304 Å (eg. Ag(1)-O(11)) and the average peripheral Ag-O bond length is 2.671 Å (eg. (Ag(5)-O(11A)).

The 1-Me-imid ligands are coordinated to the metals through the imine nitrogen and lie in an approximately linear arrangement (N(1A)-Ag(5)-N(1B) bond angle of 171.10°). The methyl groups on each of the two imidazole ligands are *cis* to each other and are orientated towards the centre of the molecule.

Table 6. Selected bond lengths and bond angles for [Ag(1-Me-imid)₂]₂[Ag₄(9-aca)₆].

| Bond | Bond Length (Å) | Bond | Bond Angle (°) |
|---------------|-----------------|---------------------|----------------|
| Ag(1)-Ag(1A) | 2.786 | Ag(2)-Ag(1)-Ag(2A) | 124.37 |
| Ag(1)-Ag(2) | 3.009 | Ag(2)-Ag(1)-O(11C) | 107.63 |
| Ag(1)-Ag(2A) | 2.962 | O(11A)-Ag(1)-Ag(2) | 74.06 |
| Ag(1)-O(11C) | 2.270 | Ag(2)-Ag(1)-O(11B) | 158.49 |
| Ag(1A)-O(12C) | 2.248 | O(11A)-Ag(1)-O(11B) | 88.22 |
| Ag(1)-O(11A) | 2.314 | O(11A)-Ag(1)-Ag(1A) | 134.03 |
| Ag(1)-O(11B) | 2.383 | Ag(1)-Ag(2)-Ag(1A) | 55.62 |
| Ag(5)-O(11A) | 2.713 | Ag(2)-Ag(1)-Ag(1A) | 61.34 |
| Ag(5)-O(11B) | 2.629 | Ag(1)-O(11A)-Ag(5) | 97.72 |
| Ag(5)-N(1A) | 2.141 | O(11A)-Ag(5)-O(11B) | 75.46 |
| Ag(5)-N(1B) | 2.125 | N(1A)-Ag(5)-N(1B) | 171.10 |

The IR spectrum of [Ag(1-Me-imid)₂]₂[Ag₄(9-aca)₆] contains bands at 1621, 772 and 736 cm⁻¹ for the ring system of anthracene^{144,160}. There are also bands at 3468 and 1087 cm⁻¹ for the N-H and C-N stretching vibrations of imidazole, respectively. The $\nu_{(\text{OCO})\text{asym}}$ and $\nu_{(\text{OCO})\text{sym}}$ vibrations occur at 1565 and 1428 cm⁻¹, respectively, giving a $\Delta_{(\text{OCO})}$ value of 137 cm⁻¹. This value indicates the presence of carboxylates with a chelating and/or bridging mode of coordination¹⁴³.

The ¹H NMR spectrum of [Ag(1-Me-imid)₂]₂[Ag₄(9-aca)₆] shows peaks for the aromatic anthracene hydrogen atoms at 8.40 (H₁₀), 8.16 (H_{1,8}), 8.05 (H_{4,5}) and 7.46 (H_{2,3,6,7}) ppm. Peaks for the aromatic hydrogen atoms of the 1-methylimidazole ligand occur at 7.84 (H in the 2-position), 7.28 (H in the 4-position) and 7.03 ppm (H in the 5-position). The protons of the methyl group

on the imidazole are present as a singlet at 3.72 ppm. Peak integration confirmed the ratio of 9-aca:1-Me-imidH to be 3:2.

3.1.6 [Ag₂(1-Me-imid)₂(9-aca)₂]

[Ag₂(1-Me-imid)₂(9-aca)₂] was synthesised from [Ag₂(9-aca)₂]_n and 1-methylimidazole (1-Me-imidH) with a yield of 45% (Scheme 6). Unlike [Ag(1-Me-imid)₂]₂[Ag₄(9-aca)₆], [Ag₂(1-Me-imid)₂(9-aca)₂] was not recrystallised from DMSO and this would appear to cause the formation of a different product.



Scheme 6. Synthesis of [Ag₂(1-Me-imid)₂(9-aca)₂].

Unfortunately, repeated attempts to obtain crystals suitable for X-ray analysis by recrystallisation from alternative solvents proved unsuccessful. The IR spectrum of [Ag₂(1-Me-imid)₂(9-aca)₂] displays bands for the vibration of the anthracene ring system at 1612, 772 and 737 cm⁻¹ ^{144,160}. A broad band is present at 3411 cm⁻¹ for the N-H stretching vibration and a band at 1086 cm⁻¹ represents the C-N stretching vibration of imidazole. The ν_(OCO)asym and ν_(OCO)sym vibrations occur at 1566 and 1428 cm⁻¹, respectively, giving a Δ_(OCO) value of 138 cm⁻¹. This value indicates that the carboxylate ligands are coordinated in either a chelating or a bridging mode¹⁴³.

The ¹H NMR spectrum of [Ag₂(1-Me-imid)₂(9-aca)₂] shows peaks for the aromatic anthracene protons at 8.36 (H_{4,5,10}), 7.95 (H_{1,8}) and 7.45 ppm (H_{2,3,6,7}). The aromatic protons of the imidazoles occur at 7.55 (H_{2a}), 7.00 (H_{4a}) and 6.90 (H_{5a}) ppm and the methyl protons appear at 3.59 ppm (H_{6a}) (Figure 3.1.6a). Peak integration indicates that the ratio of 9-aca:1-Me-imid is 1:1 and the microanalytical data confirms the ratio of Ag:9-aca:1-Me-imid as 1:1:1.

A tentative structure for [Ag₂(1-Me-imid)₂(9-aca)₂] is given in Figure 57. The Δ_(OCO) value (138 cm⁻¹) was similar to that found for [Ag(1-Me-imid)₂]₂[Ag₄(9-aca)₆] (137 cm⁻¹) and corresponds to a bridging mode of coordination for the

carboxylate ligand. The proton peaks in the ^1H NMR spectra of $[\text{Ag}_2(1\text{-Me-imid})_2(9\text{-aca})_2]$ and $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ are slightly shifted relative to each other due to the use of different deuterated solvents (d^6 DMSO for $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ and d^4 MeOD for $[\text{Ag}_2(1\text{-Me-imid})_2(9\text{-aca})_2]$). It is proposed that $[\text{Ag}_2(1\text{-Me-imid})_2(9\text{-aca})_2]$ exists as a dimer, with the carboxylate ligands coordinating in a syn-syn bridging mode to the silver ions. The imidazole ligands are coordinated through the imine nitrogen making each silver(I) ion essentially four-coordinate.

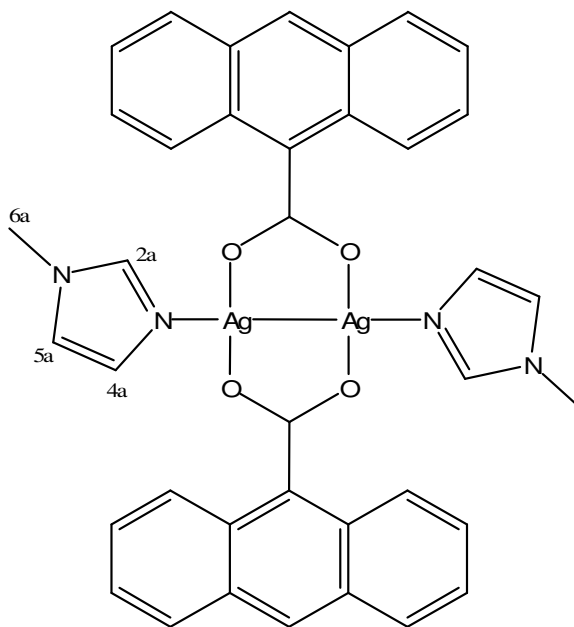


Figure 57. Tentative structure for $[\text{Ag}_2(1\text{-Me-imid})_2(9\text{-aca})_2]$.

It is evident from the formulations of $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$, $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$, $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ and $[\text{Ag}_2(1\text{-Me-imid})_2(9\text{-aca})_2]$ that a slight change in either the reaction solvent or the imidazole employed (1-methylimidazole as opposed to imidazole) causes quite a large change in the structure of the isolated product.

3.1.7 [Ag(2-Me-imidH)₂(9-aca)]

[Ag(2-Me-imidH)₂(9-aca)] was synthesised from [Ag₂(9-aca)₂] and 2-methylimidazole (2-Me-imidH) in 51% yield using acetonitrile as the reaction solvent (Scheme 7).



Scheme 7. Synthesis of [Ag(2-Me-imidH)₂(9-aca)].

[Ag(2-Me-imidH)₂(9-aca)] was recrystallised from acetonitrile and the X-ray crystal structure solved (Figures 58-62). Selected bond lengths and angles are listed in Table 7.

In [Ag(2-Me-imid)₂(9-aca)], the silver(I) ion is coordinated to the imine nitrogen atoms of the two imidazole rings and also to one carboxylate oxygen atom of the anthracene ligand. This monodentate Ag-O bond length (2.494 Å) is significantly longer than that in [Ag₂(9-aca)₂]_n where the carboxylates are bridging bidentate (Ag-O bond length of 2.183 Å). The average Ag-N bond length in [Ag(2-Me-imid)₂(9-aca)] (2.113 Å) is similar to that found for the ordered imidazole in [Ag(imid)_{2.3}(CH₃CN)_{0.7}](9-aca) (2.126 Å) and also to the Ag-N bonds in [Ag₆(imidH)₄(9-aca)₆(MeOH)₂] (2.088 Å). The imidazole ligands in [Ag(2-Me-imid)₂(9-aca)] are coordinated approximately linearly to each other (N(21)-Ag(1)-N(31) bond angle of 162°) with the 9-aca ligand almost perpendicular (N(31)-Ag(1)-O(1) bond angle of 97°). The methyl groups at the 2-position on the imidazole ring are in a *cis*-conformation to each other and lie approximately perpendicular to the plane of the anthracene ring (Figure 59).

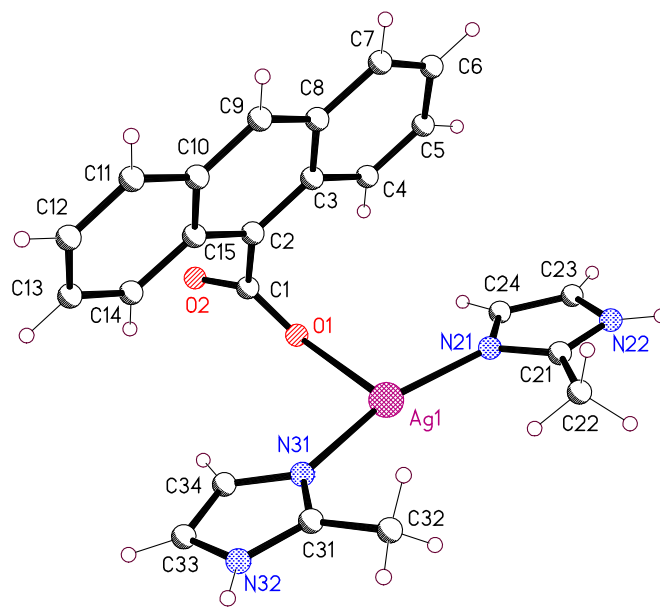


Figure 58. X-ray crystal structure of [Ag(2-Me-imidH)₂(9-aca)].

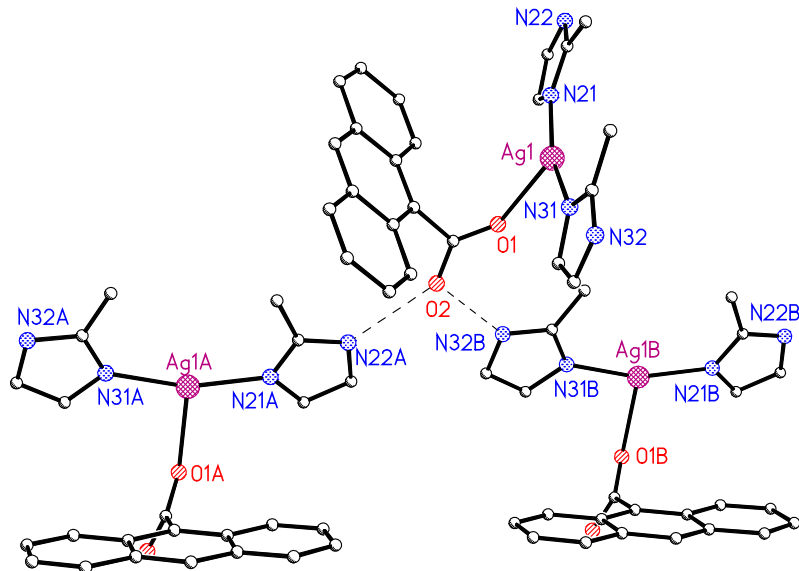


Figure 59. Intermolecular H-bonding in [Ag(2-Me-imidH)₂(9-aca)].

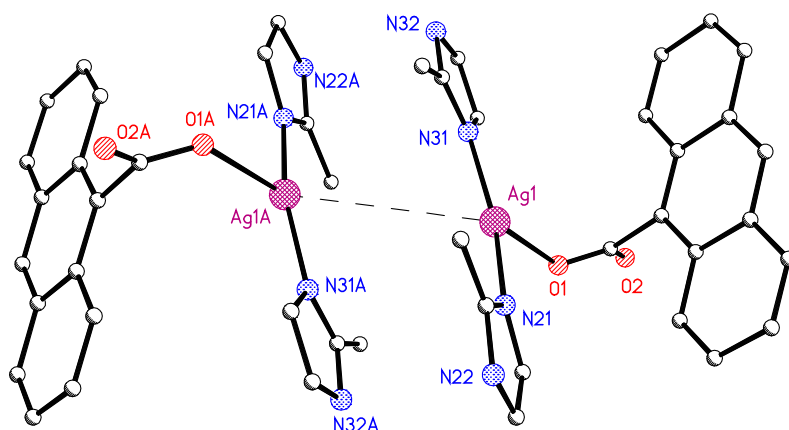


Figure 60. Stacking of the imidazole rings and long Ag-Ag interactions in $[\text{Ag}(2\text{-Me-imidH})_2(9\text{-aca})]$.

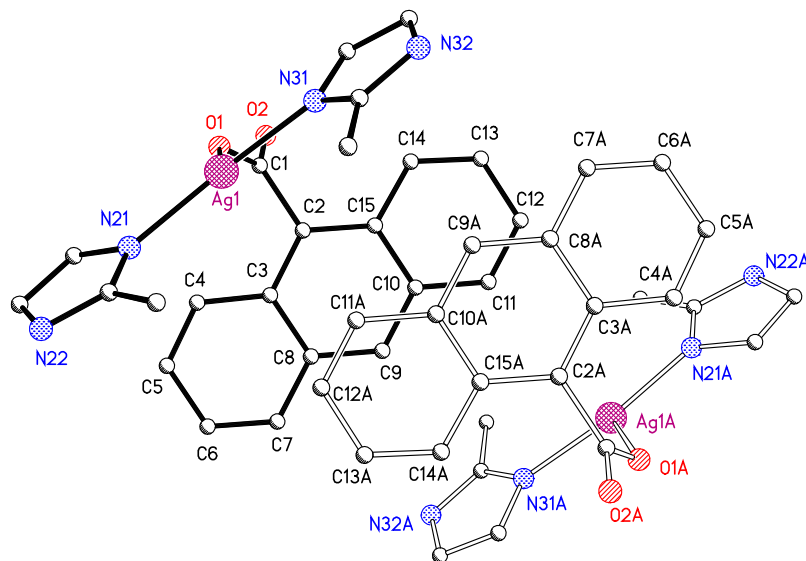


Figure 61. Stacking of the anthracene rings in $[\text{Ag}(2\text{-Me-imidH})_2(9\text{-aca})]$.

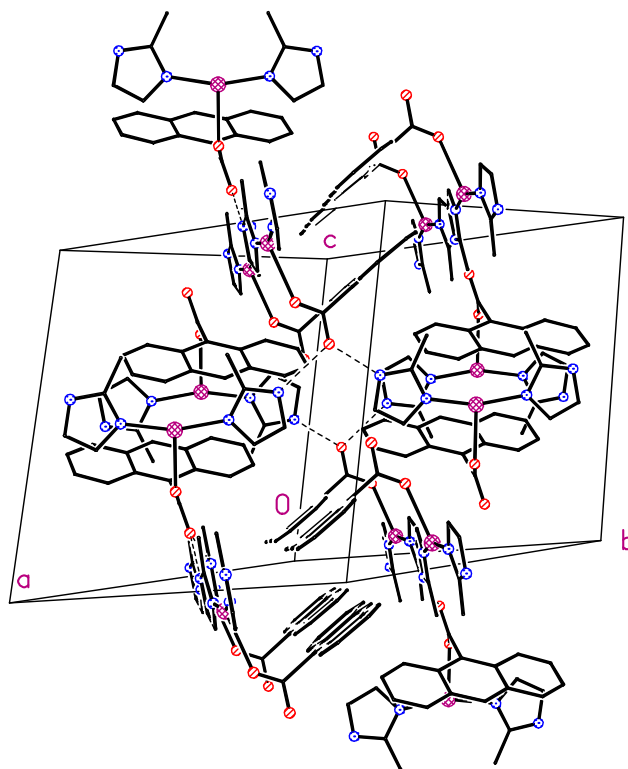


Figure 62. Packing diagram for $[\text{Ag}(2\text{-Me-imidH})_2(9\text{-aca})]$.

Table 7. Selected bond lengths and bond angles for $[\text{Ag}(2\text{-Me-imid})_2(9\text{-aca})]$.

| Bond | Bond Length (Å) | Bond | Bond Angle (°) |
|--------------|-----------------|--------------------|----------------|
| Ag(1)-N(21) | 2.115 | N(21)-Ag(1)-N(31) | 162.07 |
| Ag(1)-N(31) | 2.111 | N(21)-Ag(1)-O(1) | 101.00 |
| Ag(1)-O(1) | 2.494 | N(31)-Ag(1)-O(1) | 96.93 |
| Ag(1)-Ag(1A) | 4.193 | N(21)-Ag(1)-Ag(1A) | 95.26 |

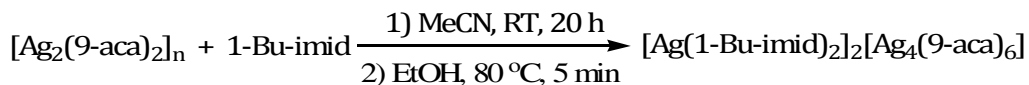
Three distinct intermolecular forces link the molecules of $[\text{Ag}(2\text{-Me-imid})_2(9\text{-aca})]$ together. There is H-bonding between the amine and the carboxylate group (Figure 59), π - π stacking interactions of the imidazole groups (Figure 60) and π - π stacking interactions of the anthracene groups (Figure 61). The Ag-Ag distance (4.193 Å) is considered to be too long to allow significant interaction between the metal centres.

The IR spectrum of $[\text{Ag}(\text{2-Me-imidH})_2(\text{9-aca})]$ has bands at 3047 and 1113 cm^{-1} representing the N-H and C-N stretching vibrations of the imidazole ligand, respectively. Bands are also evident at 1622, 762 and 734 cm^{-1} for the vibrations of the anthracene ring system^{144,160}. The $\nu_{(\text{OCO})\text{asym}}$ and $\nu_{(\text{OCO})\text{sym}}$ vibrations occur at 1590 and 1421 cm^{-1} , respectively, giving a $\Delta_{(\text{OCO})}$ value of 169 cm^{-1} . Unfortunately, this value does not allow an accurate assignment of the coordination mode of the carboxylate ligand¹⁴³.

The ^1H NMR spectrum of $[\text{Ag}(\text{2-Me-imidH})_2(\text{9-aca})]$ exhibits peaks for the aromatic anthracene protons at 8.43 (H_{10}), 8.20 ($\text{H}_{1,8}$), 8.08 ($\text{H}_{4,5}$) and 7.50 ppm ($\text{H}_{2,3,6,7}$), and these peaks are in similar positions to those of complexes previously discussed. The aromatic protons on the imidazole ring occur as a singlet at 7.08 ppm, with the protons of the methyl group appearing at 2.47 ppm.

3.1.8 $[\text{Ag}(\text{1-Bu-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$

$[\text{Ag}(\text{1-Bu-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$ was synthesised from $[\text{Ag}_2(\text{9-aca})_2]$ and 1-butylimidazole (1-bu-imid) in acetonitrile and ethanol and formed in a yield of 51% (Scheme 8).



Scheme 8. Synthesis of $[\text{Ag}(\text{1-Bu-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$.

The X-ray crystal structure of $[\text{Ag}(\text{1-Bu-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$ is shown in Figures 63-65 and selected bond lengths and angles are listed in Table 8. There are two very similar independent assemblies within one asymmetric unit of $[\text{Ag}(\text{1-Bu-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$, which are orientated at 90° to each other (Figure 63). There is also some disorder within the butyl chains of the imidazole ligands.

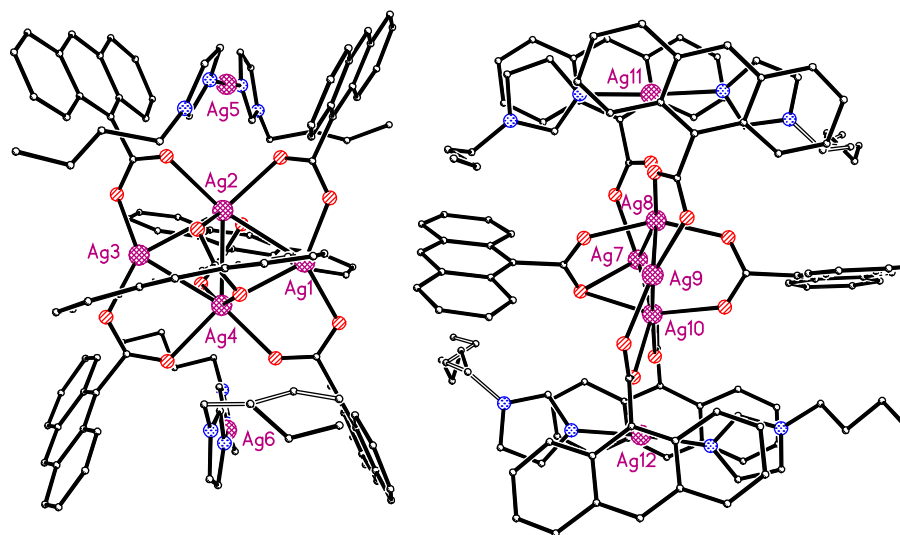


Figure 63. X-ray crystal structure of $[\text{Ag}(\text{1-Bu-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$ showing the two independent assemblies.

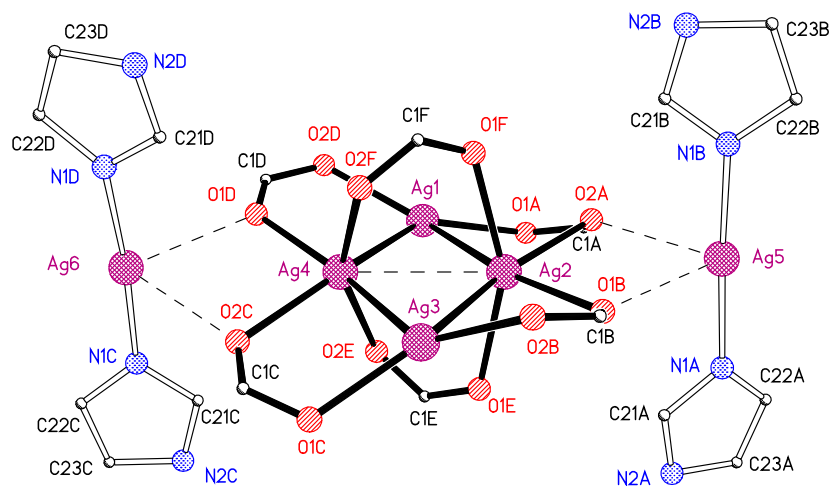


Figure 64. Structure of $[\text{Ag}(\text{1-Bu-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$ with the anthracene rings and alkyl chains removed for clarity.

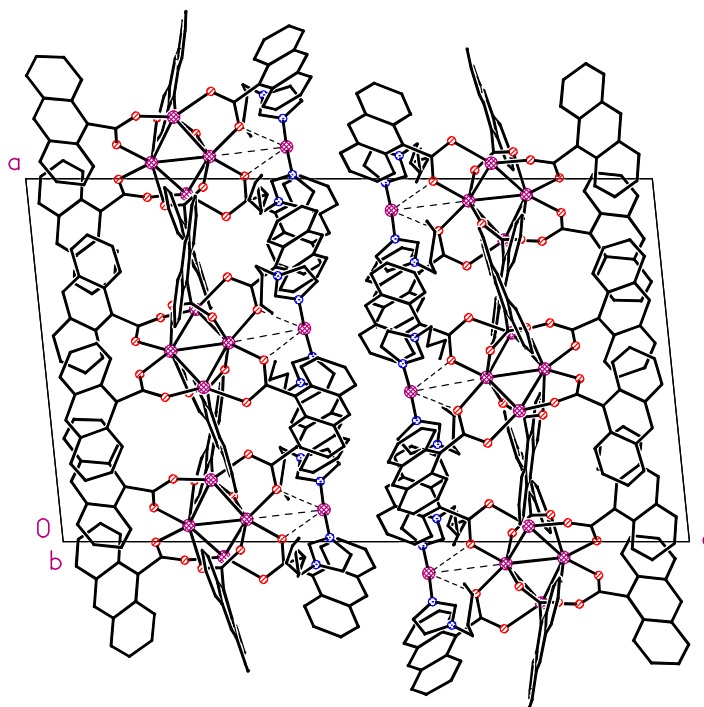


Figure 65. Packing diagram for $[\text{Ag}(\text{1-Bu-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$.

Table 8. Selected bond lengths and bond angles for $[\text{Ag}(\text{1-Bu-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$.

| Bond | Bond Length (Å) | Bond | Bond Angle (°) |
|----------------|-----------------|--|----------------|
| Ag(1)-Ag(2) | 2.903 | Ag(1)-Ag(2)-Ag(3) Ag(3)-Ag(4)-Ag(1) | 120.83 |
| Ag(2)-Ag(3) | 2.877 | Ag(2)-Ag(3)-Ag(4) Ag(4)-Ag(1)-Ag(2) | 58.87 |
| Ag(3)-Ag(4) | 2.895 | O(2A)-Ag(2)-O(1B) | 93.86 |
| Ag(4)-Ag(1) | 2.875 | O(1D)-Ag(4)-O(2C) | 89.46 |
| Ag(2)-Ag(4) | 2.837 | O(1A)-Ag(1)-Ag(2) | 83.96 |
| Ag(5)-N(1A/1B) | 2.116 | N(1A)-Ag(5)-N(1B) | 176.98 |
| Ag(6)-N(1C/1D) | 2.131 | N(1C)-Ag(6)-N(1D) | 175.10 |
| Ag(5)-O(2A/1B) | 2.696/2.809 | O(2C)-Ag(4)-O(2E) | 102.37 |
| Ag(6)-O(1D/2C) | 2.603/2.756 | O(2C)-Ag(4)-O(2F) | 93.00 |

[Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆] contains two-, four- and six-coordinate silver(I) ions (Figure 64). Two of the metals are coordinated approximately linearly to the imine nitrogen atoms of two 1-Bu-imid ligands (bond angles of 175° and 177°), with an average Ag-N bond length of 2.124 Å. There are also longer interactions of these silver ions with carboxylate oxygen atoms at the central core of the molecule (Ag(6)-O(2C) and Ag(6)-O(1D) bond lengths of 2.756 and 2.603 Å, respectively).

Within the central [Ag₄(9-aca)₆]²⁻ core there are five Ag-Ag bonds, with lengths ranging from 2.837 to 2.903 Å. All of the anthracene ligands use both of their carboxylate oxygen atoms to coordinate to two different silver ions in a syn-syn binding mode. There are no intramolecular or intermolecular π-π interactions between either the anthracene or the imidazole rings. The structure of [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆] is very similar to that of [Ag(1-Me-imid)₂]₂[Ag₄(9-aca)₆] which was discussed previously. In this instance, the change in the length of the alkyl chain (from methyl to butyl) on the imidazole ring does not appear to affect the core structure of the product.

The IR spectrum of [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆] contains bands for the anthracene ring system at 1622, 759 and 732 cm⁻¹ ^{144,160}. The band representing the C-N stretching vibration of the 1-Bu-imid ligands occur at 1085 cm⁻¹. The ν_(OCO)_{asym} and ν_(OCO)_{sym} vibrations appear at 1565 and 1427 cm⁻¹, respectively, giving a Δ_(OCO) value of 138 cm⁻¹. This indicates that the carboxylate ligands are coordinated in either a chelating or a bridging mode¹⁴³.

The ¹H NMR spectrum of [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆] shows that the aromatic protons of the 1-Bu-imid have become deshielded compared to that of uncoordinated 1-Bu-imid. These peaks now appear further downfield (8.06 (H in the 2-position) and 7.47 (H in the 4-position) and 7.13 ppm (H in the 5-position)). The peaks for the aromatic anthracene protons are present at 8.44 (H₁₀), 8.20 (H_{1,8}), 8.06 (H_{4,5}) and 7.47 ppm (H_{2,3,6,7}) whilst peaks for the protons of the butyl chain remain unchanged compared to the free ligand and occur at

4.06 (CH₂, triplet), 1.73 (CH₂, quintet), 1.23 (CH₂, sextet) and 0.90 ppm (CH₃, triplet). Peak integration gives a ligand ratio of 3:2 (9-aca:1-Bu-imid).

3.1.9 [Ag₂(1-Bu-imid)₂(9-aca)₂]

[Ag₂(1-Bu-imid)₂(9-aca)₂] was synthesised from [Ag₂(9-aca)₂] and 1-butylimidazole in good yield (71%) (Scheme 9). Unlike [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆], [Ag₂(1-Bu-imid)₂(9-aca)₂] was not recrystallised from ethanol and it is this somewhat minor variation in reaction conditions that has prompted a major change in the product formulation.



Scheme 9. Synthesis of [Ag₂(1-Bu-imid)₂(9-aca)₂].

The IR spectrum of [Ag₂(1-Bu-imid)₂(9-aca)₂] displays bands at 1611, 758 and 737 cm⁻¹ for the stretching vibrations of the anthracene ring system^{144,160}. A band is present at 1086 cm⁻¹ for the C-N stretching vibration of the imidazole ring. The $\nu_{(\text{OCO})\text{asym}}$ and $\nu_{(\text{OCO})\text{sym}}$ vibrations occur at 1567 and 1429 cm⁻¹, respectively, giving a $\Delta_{(\text{OCO})}$ value of 138 cm⁻¹. This value suggests that the carboxylate ligands are coordinated to the metal centre in either a bridging or a chelating mode¹⁴³.

The ¹H NMR spectrum of [Ag₂(1-Bu-imid)₂(9-aca)₂] shows the aromatic anthracene protons at 8.43 (H₁₀), 8.17 (H_{1,8}), 8.04 (H_{4,5}), and 7.47 ppm (H_{2,3,6,7}). The aromatic protons of the imidazole ring appear at 8.00 (H_{2a}), 7.40 (H_{4a}) and 7.10 ppm (H_{5a}) (Figure 66), and are more shielded in comparison to those observed for [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆]. The proton peaks associated with the butyl chain are present in the same positions as those seen in the spectra of [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆] and the free ligand (4.05 (H_{6a}, triplet), 1.72 (H_{7a}, quintet), 1.25 (H_{8a}, sextet) and 0.90 ppm (H_{9a}, triplet)). Peak integration gives a 9-aca:1-Bu-imid ratio of 1:1 and the microanalytical data confirms the ratio of Ag:9-aca:1-butyl-imid as 1:1:1.

A tentative structure for $[\text{Ag}_2(1\text{-Me-imid})_2(9\text{-aca})_2]$ is given in Figure 66. This structure is very similar to that proposed for $[\text{Ag}_2(1\text{-Me-imidH})_2(9\text{-aca})_2]$, with the carboxylate ligands bridging two silver(I) ions. The 1-Bu-imid ligands are coordinated through the imine nitrogen atom and there is a possibility of some Ag-Ag interactions.

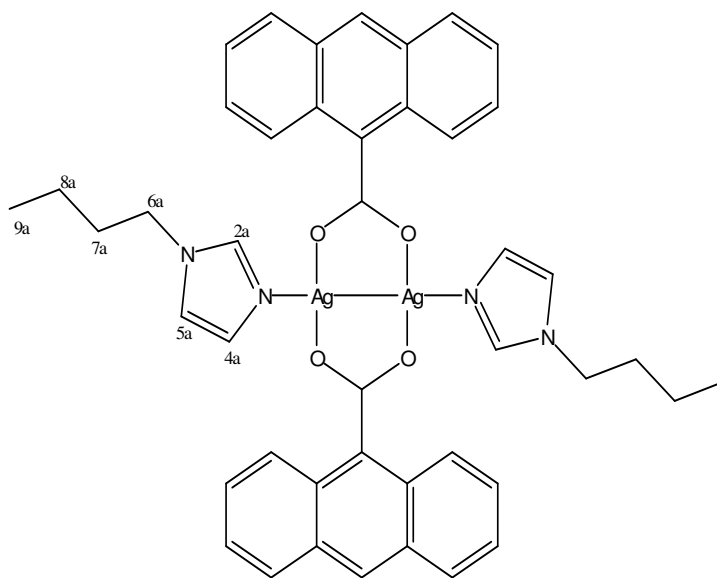


Figure 66. Tentative structure for $[\text{Ag}_2(1\text{-Bu-imid})_2(9\text{-aca})_2]$.

3.1.10 $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$

$[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$ was synthesised from $[\text{Ag}_2(9\text{-aca})_2]_n$ and 1-(3-aminopropyl)-imidazole (apim) in acetonitrile giving a product yield of 82% (Scheme 15). The complex was recrystallised from a mixture of ethanol and methanol (9:1) and the X-ray crystal structure was obtained (Figures 67-72). Selected bond lengths and angle are listed in Table 9.



Scheme 10. Synthesis of $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$.

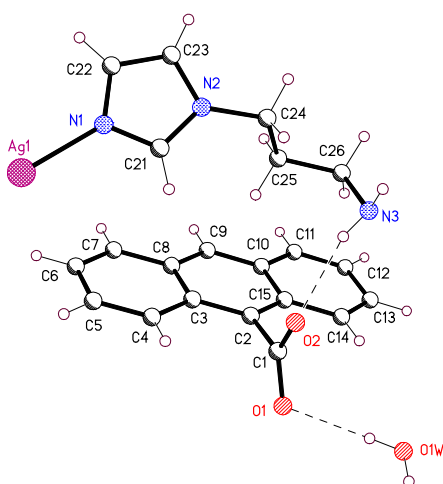


Figure 67. Structure of one asymmetric unit of $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$.

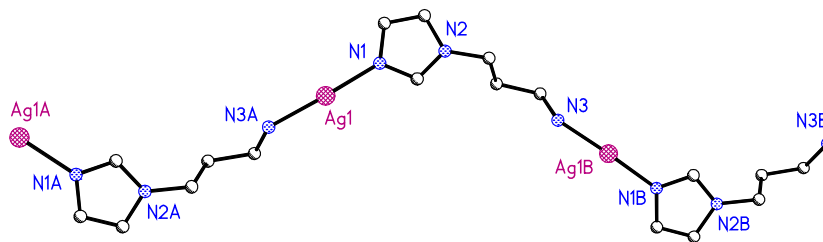


Figure 68. Polymeric cationic chains of $[\text{Ag}(\text{apim})]_n^{n+}$.

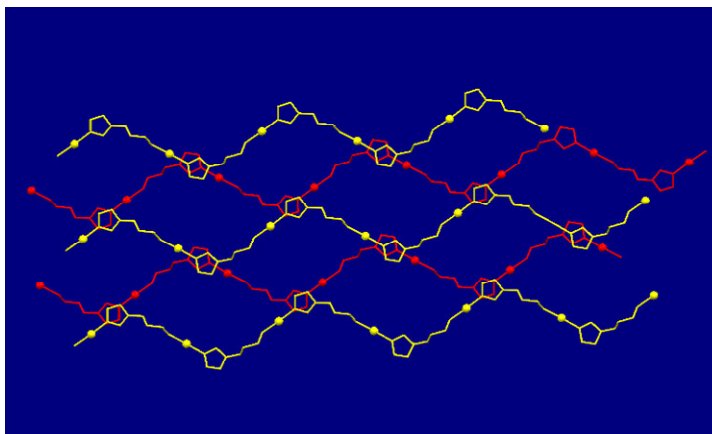


Figure 69. π - π stacking interactions of the imidazole rings in $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$.

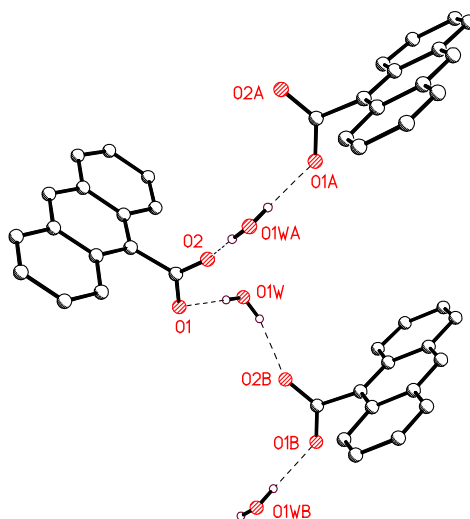


Figure 70. Section of H-bonded polymeric chain of 9-aca⁻ anions and H₂O.

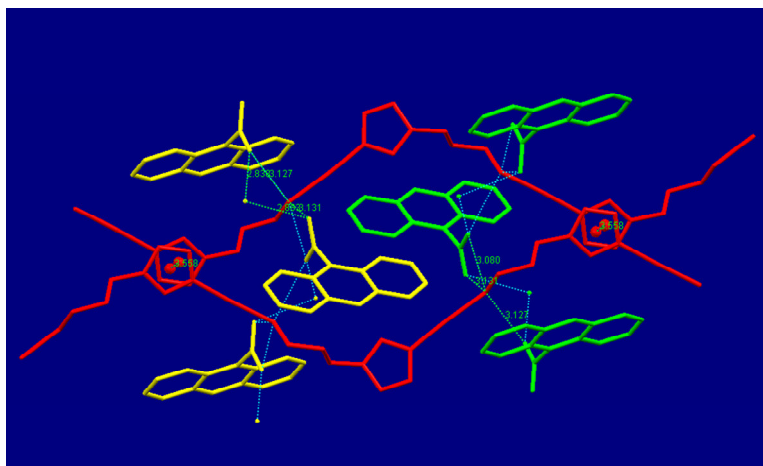


Figure 71. Packing of the polymeric cationic and anionic chains in [Ag(apim)](9-aca)·H₂O.

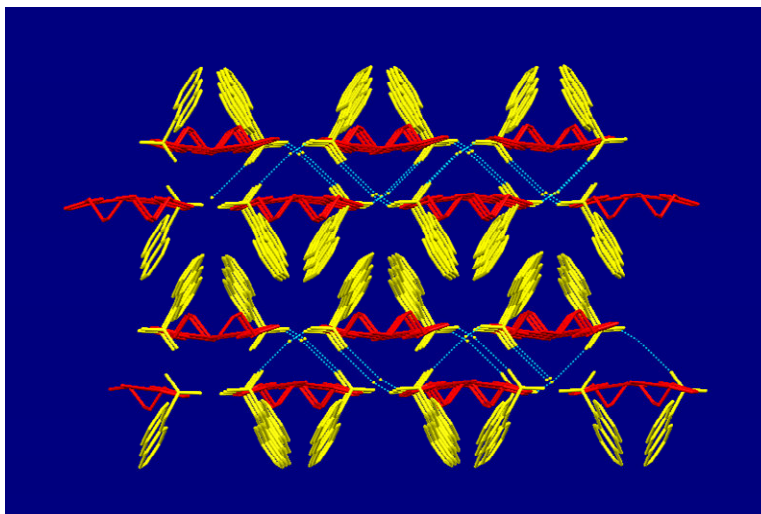


Figure 72. Packing diagram for $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$.

Table 9. Selected bond lengths and bond angles for $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$.

| Bond | Bond Length (Å) | Bond | Bond Angle (°) |
|-------------|-----------------|------------------|----------------|
| Ag(1)-N(1) | 2.084 | N(1)-Ag(1)-N(3A) | 177.76 |
| Ag(1)-N(3A) | 2.107 | Ag(1)-N(1)-C(22) | 129.35 |

In $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$, the metal is bonded to the imine nitrogen of the imidazole ring with an Ag(1)-N(1) bond length of 2.084 Å. The silver and imidazole form 1-D zig-zag polymeric chains with the silver being coordinated approximately linearly to the imine nitrogen of one imidazole and the amine (NH_2) nitrogen of another imidazole (N(1)-Ag(1)-N(3A) bond angle of 178°) (Figure 68). π - π Stacking interactions are also observed between the imidazole rings creating 2-D sheets with a centroid distance of 3.558 Å (Figure 69).

The water molecules in $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$ link up with the anionic 9-aca units through H-bonds (Figure 70) forming polymeric chains which zig-zag in-and-out through the spaces in the $[\text{Ag}(\text{apim})]_n^{n+}$ sheets (Figure 71). The H-bonds in this chain are relatively strong and there are also longer, weaker interactions linking the carboxylate oxygen to the hydrogen of the pendant amine group.

Due to the relatively long distance between the sheets, there are no π - π interactions involving the anthracene rings. The structurally similar complex, $[\text{Ag}(\text{apim})]\text{ClO}_4$ ¹²⁶, also shows the same type of zig-zag arrangement of polymeric $[\text{Ag}(\text{apim})]_n^{n+}$ chains but this complex has weak metal-anion interactions which are not present in $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$.

The IR spectrum of $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$ contains a band at 3427 cm^{-1} corresponding to the apim NH_2 stretching vibration and a band at 1089 cm^{-1} for the C-N stretching vibration of the imidazole ring. Two bands are present at 761 and 735 cm^{-1} for the stretching vibrations of the anthracene ring system^{144,160}, but the third band, which is usually located at approximately 1625 cm^{-1} , is masked by the strong $\nu_{(\text{OCO})\text{asym}}$ stretching band centred at 1568 cm^{-1} . The $\nu_{(\text{OCO})\text{sym}}$ stretching vibration occurs at 1426 cm^{-1} , thus giving a $\Delta_{(\text{OCO})}$ value of 142 cm^{-1} . Although this value implies that the carboxylate is either chelating or bridging¹⁴³, it is evident from the X-ray crystal structure of the complex that this is not the case. Thus, it must be stressed that coordination mode assignments based on $\Delta_{(\text{OCO})}$ values can indeed be quite tentative.

The ^1H NMR spectrum of $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$ shows peaks for the aromatic anthracene protons at 8.39 (H_{10}), 8.15 ($\text{H}_{1,8}$), 8.01 ($\text{H}_{4,5}$) and 7.44 ppm ($\text{H}_{2,3,6,7}$). The aromatic imidazole protons appear as singlets at 7.87, 7.33 and 7.01 ppm. Although the ^1H NMR spectrum does not show any coupling between the protons on the imidazole ring, a COSY NMR spectrum provided evidence that coupling does occur. The protons in the propyl chain appear at 4.11 (triplet), 2.61 (triplet) and 1.93 (quintet) ppm with the amine protons being masked by the residual peak for the DMSO solvent at 2.55 ppm.

3.1.11 [Ag(2-Ph-imid)]

$[\text{Ag}(2\text{-Ph-imid})]$ was made in a 79% yield from $[\text{Ag}_2(9\text{-aca})_2]_n$ and 2-phenylimidazole (2-Ph-imidH) in acetonitrile (Scheme 11).



Scheme 11. Synthesis of [Ag(2-Ph-imid)].

The IR spectrum of [Ag(2-Ph-imid)] shows bands for the C=C and C=N stretching vibrations of the imidazole ring at 1601 and 1578 cm^{-1} , respectively. These bands are masked in previous complexes by the $\nu_{(\text{OCO})_{\text{asym}}}$ band of the carboxylate moiety. The strong band for the C=O stretching of the carboxylate group is absent. The aromatic C=C stretching band of the 2-Ph-imidH occurs as a strong band at 1458 cm^{-1} and there is also a band at 1074 cm^{-1} for the C-N stretching vibration of the imidazole ring. The distinctive band for the stretching vibration of the anthracene ring system, at *ca.* 1625 cm^{-1} , is also absent.

The ^1H NMR spectrum of [Ag(2-Ph-imid)] shows only peaks associated with the protons for the 2-Ph-imid ligand at 7.92 ($\text{H}_{6,10}$), 7.41 ($\text{H}_{7,9}$), 7.33 (H_8), 7.24 (H_4) and 7.02 ppm (H_5) (Figure 73). The microanalytical data indicates a ratio of silver:2-Ph-imid of 1:1. Thus, in this reaction the 9-aca ligands in the $[\text{Ag}_2(9\text{-aca})_2]_n$ starting complex have been replaced by the anionic 2-Ph-imid $^-$ ligands. Deprotonation of the 2-Ph-imidH is thought to be assisted by the ability of the phenyl substituent to delocalise electron density from the resulting N $^-$ atom on the imidazole ring.

It is believed that [Ag(2-Ph-imid)] will form polymeric chains in which the silver is coordinated to the deprotonated amine N of one 2-Ph-imid ligand and the imine nitrogen of a neighbouring 2-Ph-imid ligand (Figure 73(b)). Similar polymeric chains have been reported for the silver(I)-4-nitroimidazole complex, [Ag(4-NO $_2$ -imid)]¹⁶⁴, and also for metal-imidazolate complexes of Ni(II), Cu(II), Zn(II) and Ag(I)¹⁰².

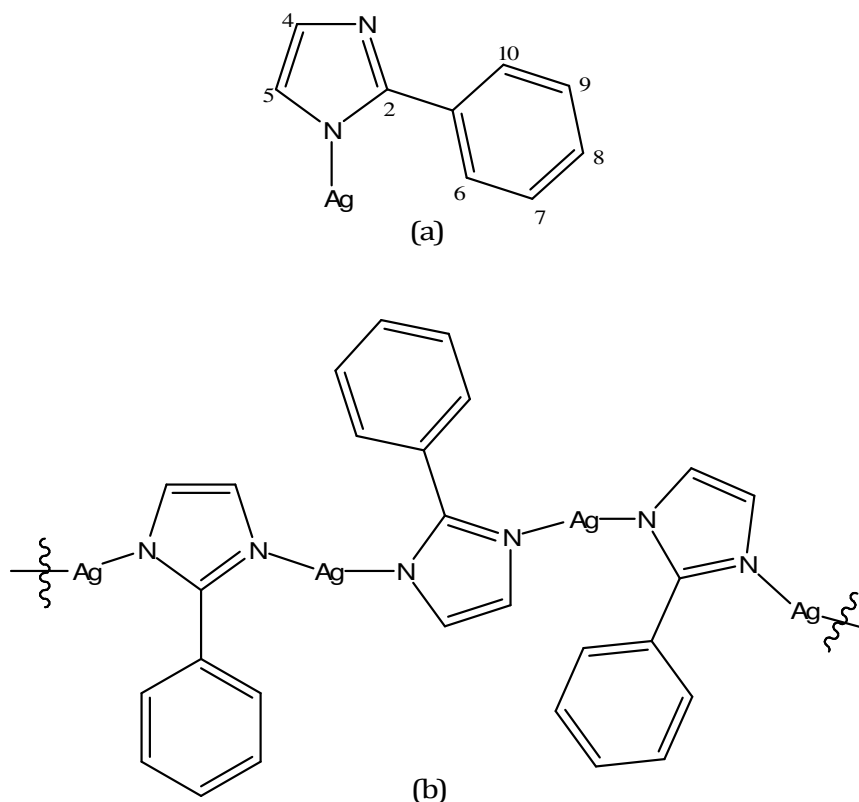


Figure 73. Proposed structure for (a) an isolated unit and (b) polymeric chain of [Ag(2-Ph-imid)].

3.1.12 [Ag(4-Ph-imidH)₂(9-aca)]

[Ag(4-Ph-imidH)₂(9-aca)] was synthesised from [Ag₂(9-aca)₂]_n and 4-phenylimidazole (4-Ph-imidH) in good yield (81%) (Scheme 12). Although the synthesis conditions are very similar to those used in reactions involving 2-Ph-imidH, the products obtained are very different. The 9-aca⁻ anion was absent in the product involving 2-Ph-imidH whereas the carboxylate was retained in the product where the 4-Ph-imidH was employed as a reactant.



Scheme 12. Synthesis of [Ag(4-Ph-imidH)₂(9-aca)].

The IR spectrum of [Ag(4-Ph-imidH)₂(9-aca)] contains bands at 1614, 755 and 732 cm⁻¹ for the anthracene ring stretching vibrations^{144,160}. Bands are also

present at 3129 and 1073 cm^{-1} for the N-H and C-N stretching vibrations of the imidazole ring, respectively. The $\nu_{(\text{OCO})\text{asym}}$ and $\nu_{(\text{OCO})\text{sym}}$ vibrations occur at 1553 and 1424 cm^{-1} , respectively, giving a $\Delta_{(\text{OCO})}$ value of 129 cm^{-1} . This value suggests that the carboxylate is coordinated in either a chelating or a bridging mode¹⁴³.

The ^1H NMR spectrum of $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$ indicates that the ratio of 9-aca:4-Ph-imid is 1:2. The aromatic anthracene protons give rise to peaks at 8.47 (H_{10}), 8.14 ($\text{H}_{1,8}$), 8.06 ($\text{H}_{4,5}$) and 7.48 ppm ($\text{H}_{2,3,6,7}$). Peaks for the 4-Ph-imid protons occur at 7.88 (H_{2a}), 7.83 ($\text{H}_{7a,11a}$), 7.59 (H_{9a}), 7.39 ($\text{H}_{8a,10a}$) and 7.25 ppm (H_{5a}) (Figure 74). The anthracene peaks are not shifted significantly when compared to those in the spectrum of the starting material $[\text{Ag}_2(9\text{-aca})_2]_n$, while the 4-Ph-imid peaks are shifted downfield in comparison to those observed in the spectrum of the free ligand.

It is thought that $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$ may have a similar structure to $[\text{Ag}(2\text{-Me-imidH})_2(9\text{-aca})]$, with the silver coordinated to the imine nitrogen of the imidazole ring (Figure 74). This approximately linear alignment of the imidazole ligands is a common arrangement in silver(I) imidazole complexes as observed in complexes previously discussed. The IR spectrum of $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$ indicates that the carboxylate may be in either a bridging or a chelating mode of coordination which may indicate either the presence of H-bonding or an interaction of the carboxylate oxygen with the silver(I) ion.

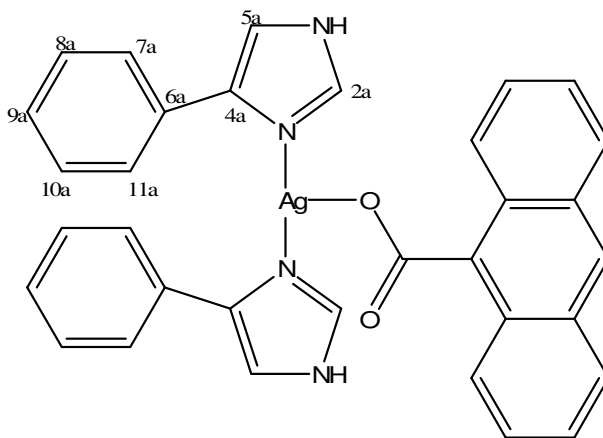
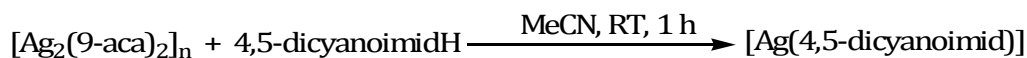


Figure 74. Proposed structure of $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$.

3.1.13 [Ag(4,5-dicyanoimid)]

[Ag(4,5-dicyanoimid)] was synthesised from [Ag₂(9-aca)₂]_n and 4,5-dicyanoimidazole in acetonitrile with a yield of 70% (Scheme 13).



Scheme 13. Synthesis of [Ag(4,5-dicyanoimid)].

The IR spectrum of [Ag(4,5-dicyanoimid)] contains a strong band at 2227 cm⁻¹ for the C≡N stretching vibration of the cyanoimidazole ligand. The characteristic bands for the anthracene ring system at approximately 1620 and 750 cm⁻¹, along with the ν_{OCO} stretching vibrations of the carboxylate ligand are absent. Also, the N-H stretching vibration at 3100 cm⁻¹ is not present, indicating that the 4,5-dicyanoimidazole has been deprotonated forming an anion. It is expected that the electron-withdrawing cyano substituents on the imidazole ring helps stabilise the negatively charged imidazolate ion.

As a consequence of insolubility, it was not possible to obtain a solution ¹H NMR spectrum of [Ag(4,5-dicyanoimid)]. The microanalytical data for [Ag(4,5-dicyanoimid)] indicates a ratio of Ag:4,5-dicyanoimid of 1:1 and a tentative structure of the complex is shown in Figure 75. The imidazole is deprotonated at the amine nitrogen and it is likely that the lone pair of electrons on the imine nitrogen will also interact with the silver of another molecule forming a polymeric chain similar to that postulated for [Ag(2-Ph-imid)] (Figure 75(b)).

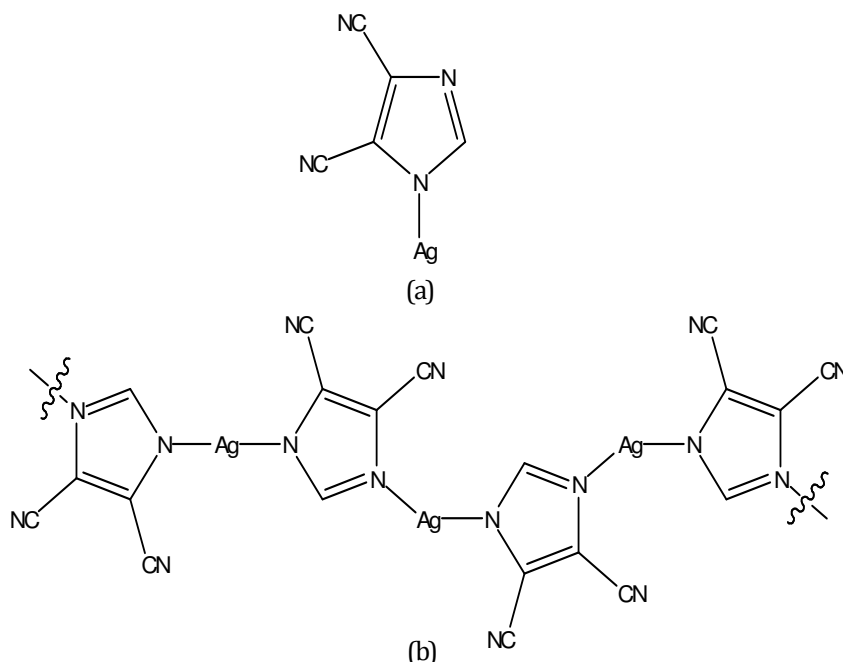


Figure 75. Proposed structure of [Ag(4,5-dicyanoimid)]: (a) an isolated unit and (b) a polymeric chain.

3.1.14 [Ag(Benz-imid)]

[Ag(Benz-imid)] was synthesised from [Ag₂(9-aca)₂]_n and benzimidazole (Benz-imidH) in methanol with a yield of 68% (Scheme 14).



Scheme 14. Synthesis of [Ag(Benz-imid)].

The IR spectrum of [Ag(Benz-imid)] contains bands for the C=C and C=N stretching vibrations of the imidazole ring at 1609 and 1584 cm⁻¹, respectively, along with a strong band at 1463 cm⁻¹ for the C=C stretching vibration of the aromatic benzene ring system. The band for the stretching vibration of the carboxylate group is absent, as well as the band at *ca.* 1625 cm⁻¹ for the stretching of the anthracene ring system.

As a result of insolubility, it was not possible to obtain a ¹H NMR spectrum of [Ag(Benz-imid)]. However, the microanalytical data for the complex indicates

that the ratio of Ag:Benzimid is 1:1 and a tentative structure for the complex is given in Figure 76. The silver is coordinated to the amine nitrogen of the deprotonated imidazole ring. As indicated previously for [Ag(2-Ph-imid)] and [Ag(4,5-dicyanoimid)], there is a possibility that [Ag(Benz-imid)] may form polymeric chains by the coordination of the silver(I) ion to the imine nitrogen of a neighbouring molecule (Figure 76(b)).

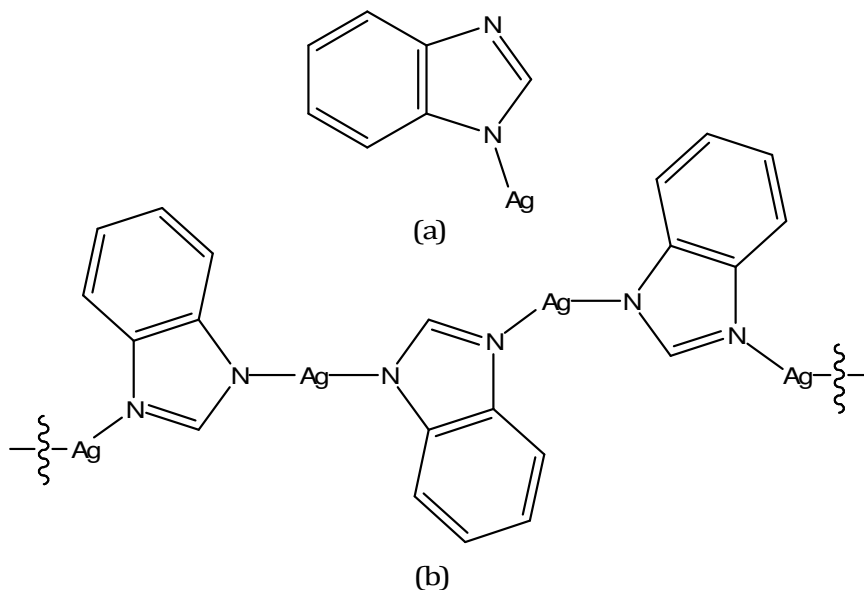
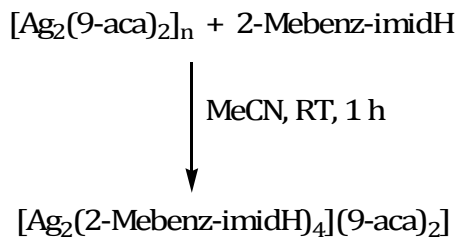


Figure 76. Tentative structure of [Ag(Benz-imid)]: (a) and isolated unit and (b) a polymeric chain.

3.1.15 [Ag₂(2-Mebenz-imidH)₄](9-aca)₂

[Ag₂(2-Mebenz-imidH)₄](9-aca)₂ was synthesised from [Ag₂(9-aca)₂]_n and 2-methylbenzimidazole (2-Mebenz-imidH) in acetonitrile and the product formed in excellent yield (87%) (Scheme 15).



Scheme 15. Synthesis of [Ag₂(2-Mebenz-imidH)₄](9-aca)₂.

The IR spectrum of $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ shows the N-H stretching vibrations at 3446 cm^{-1} along with the C=C ring vibration of the benzimidazole at 1599 cm^{-1} . The bands at 1625 , 764 and 728 cm^{-1} correspond to the stretching vibrations of the anthracene ring system^{144,160}. There is a broad band centred at 2524 cm^{-1} which indicates the presence of H-bonding¹⁴⁴, possibly between the carboxylate oxygen atoms and the amine hydrogen of the imidazole ring. The $\nu_{(\text{OCO})\text{asym}}$ and $\nu_{(\text{OCO})\text{sym}}$ vibrations occur at 1558 and 1427 cm^{-1} , respectively, giving a $\Delta_{(\text{OCO})}$ value of 131 cm^{-1} . This value suggests that the carboxylate group may have a chelating or a bridging mode of coordination¹⁴³.

Peak integrations in the ^1H NMR spectrum of $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ indicates a ratio of 9-aca:2-Mebenz-imidH of 2:3. However, this is not consistent with the microanalytical data (discussed below). $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ is very insoluble in common solvents and a good quality ^1H NMR spectrum could not be obtained (even in hot DMSO). There is a possibility that, due to the large amount of heat required to dissolve some of the sample prior to running the ^1H NMR spectrum, the complex undergoes changes and is not representative of the formula of the solid form. Such changes were observed previously for $[\text{Ag}_2(1\text{-Me-imidH})_2(9\text{-aca})_2]$ which were ultimately overcome by using an alternate NMR solvent. Unfortunately, a change of solvent was not an option in this case due to insolubility. The poor quality spectrum shows the aromatic protons of the anthracene ring at 8.63 (H₁₀), 8.09 (H_{1,8}), 8.03 (H_{4,5}) and 7.49 ppm (H_{2,3,6,7}). The protons of the benzene ring appear as multiplets at 7.56 and 7.15 ppm, while the peak for the protons of the methyl group is masked by the DMSO residual peak at 2.50 ppm.

Microanalytical data for the complex indicate a ratio of Ag:9-aca:2-Mebenz-imidH of 1:1:2 and a tentative structure for $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ is given in Figure 77. This proposed structure is similar to that of the known complex, $[\text{Ag}_2(\text{imidH})_4](\text{salH})_2$ ¹²⁶, with the silver being coordinated to the imine nitrogen of the imidazole ring and the carboxylate acting as a counterion.

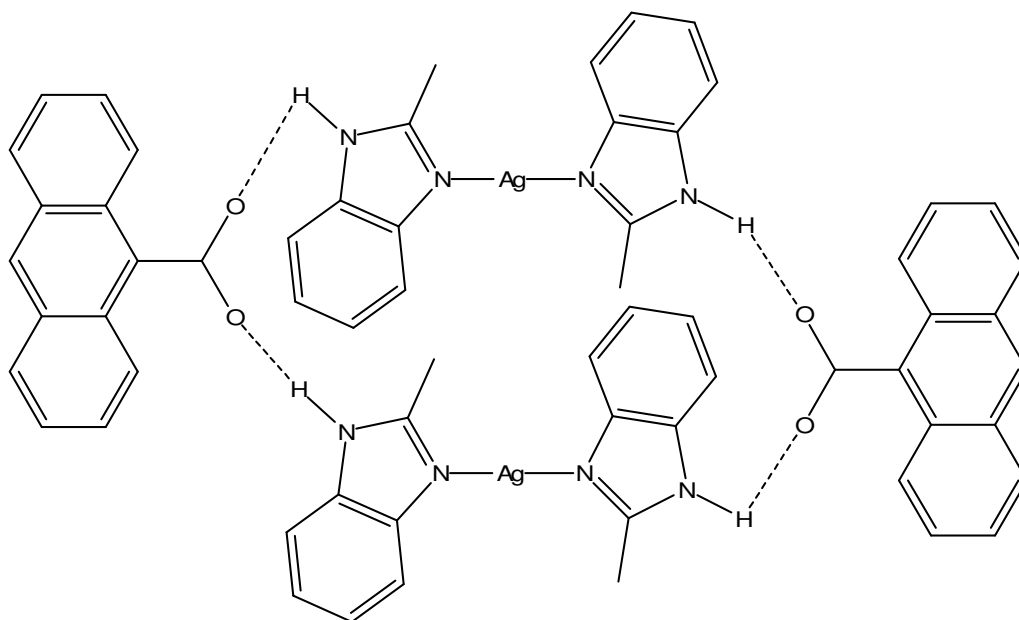


Figure 77. Proposed structure of $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$.

In an attempt to recrystallise $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ from ethanol the silver-free, monohydrate salt, $(2\text{-Mebenz-imidH}_2)(9\text{-aca})\cdot\text{H}_2\text{O}$, crystallised and was subsequently characterised using X-ray crystallography (Figures 78-80). Bond lengths and angles are listed in Tables 29 and 30 in the Appendix.

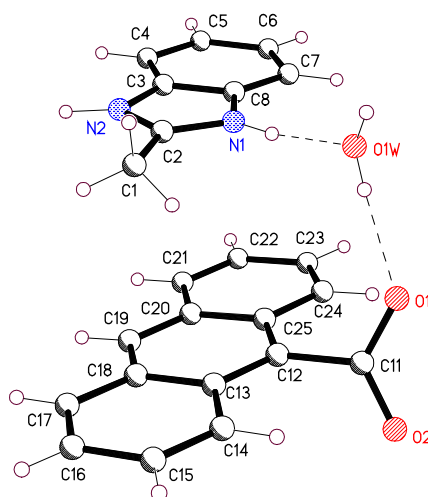


Figure 78. X-ray crystal structure of $(2\text{-Mebenz-imidH}_2)(9\text{-aca})\cdot\text{H}_2\text{O}$.

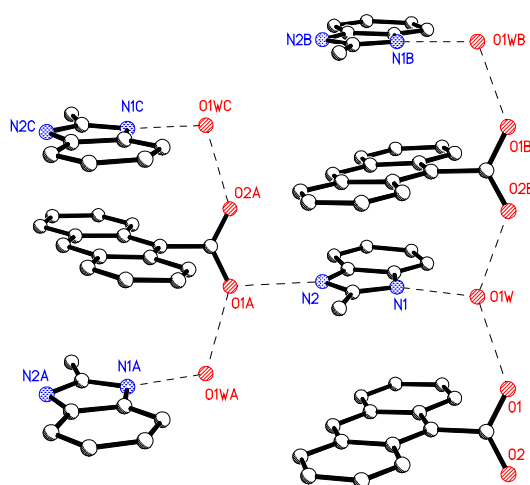


Figure 79. Chains of (2-Mebenz-imidH₂)(9-aca)·H₂O linked by H-bonds.

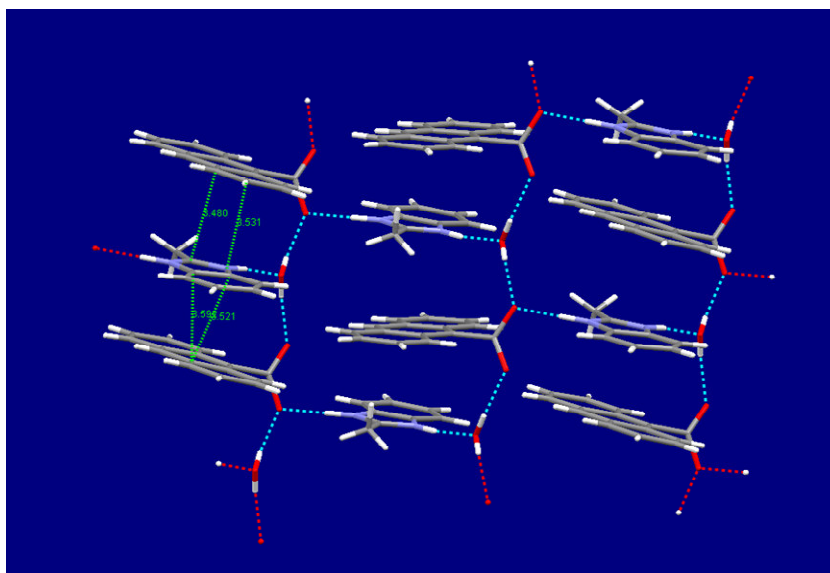


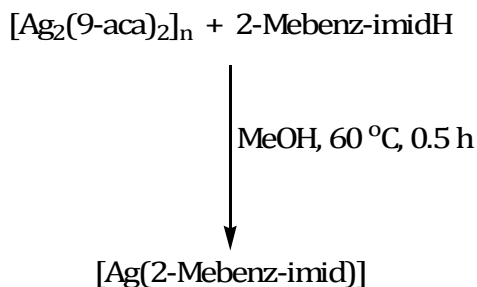
Figure 80. Packing diagram for (2-Mebenz-imidH₂)(9-aca)·H₂O showing hydrogen bonds between chains.

H-bonding links the 9-aca⁻ anions and the 2-Mebenz-imidH₂⁺ cations via the water molecule and this allows the structure to form chains (Figure 79). Inter-chain H-bonding is also observed in the structure of (2-Mebenz-imidH₂)(9-aca)·H₂O (Figure 80). Some π - π stacking interactions occur between the

cationic imidazolate and the anionic anthracene ring (centroid distance 3.480-3.592 Å) (Figure 3.1.14d).

3.1.16 [Ag(2-Mebenz-imid)]

[Ag(2-Mebenz-imid)] was synthesised from $[\text{Ag}_2(9\text{-aca})_2]_n$ and 2-methylbenzimidazole in methanol and the product formed in good yield (79%) (Scheme 16). The small changes in the reaction conditions, compared to the synthesis of $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ (methanol as opposed to acetonitrile and an increase in temperature), has led to a product that is structurally quite different with no 9-acaH present.



Scheme 16. Synthesis of [Ag(2-Mebenz-imid)].

In the IR spectrum of [Ag(2-Mebenz-imid)] bands are observed for the C=C and the C=N stretching vibrations of the imidazole ring at 1608 and 1579 cm^{-1} , respectively. These bands are masked in previous complexes (e.g. $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$ and $[\text{Ag}(1\text{-Me-imid})_2][\text{Ag}_4(9\text{-aca})_6]$) by the $\nu_{(\text{OCO})\text{asym}}$ band of the carboxylate group. The strong aromatic C=C stretching band occurs at 1448 cm^{-1} and a band is also present at 1076 cm^{-1} for the C-N stretching vibration of the imidazole ring. The absence of the distinctive bands for the anthracene ring stretching vibrations at approximately 1625 and 750 cm^{-1} confirms the omission of the 9-acaH in the complex.

As a consequence of its insolubility, it was not possible to obtain a solution ^1H NMR spectrum of [Ag(2-Mebenz-imid)]. However, the microanalytical data indicates the ratio of silver:2-Mebenz-imid to be 1:1. It is thought that the silver

bonds to the amine nitrogen of the deprotonated imidazole ring (Figure 81(a)). This complex, as suggested for [Ag(2-Ph-imid)] and [Ag(4,5-dicyanoimid)], may possibly form a polymeric chain through interaction of the silver(I) with the lone pair of electrons on the imine nitrogen of another molecule of [Ag(2-Mebenz-imid)] (Figure 81(b)).

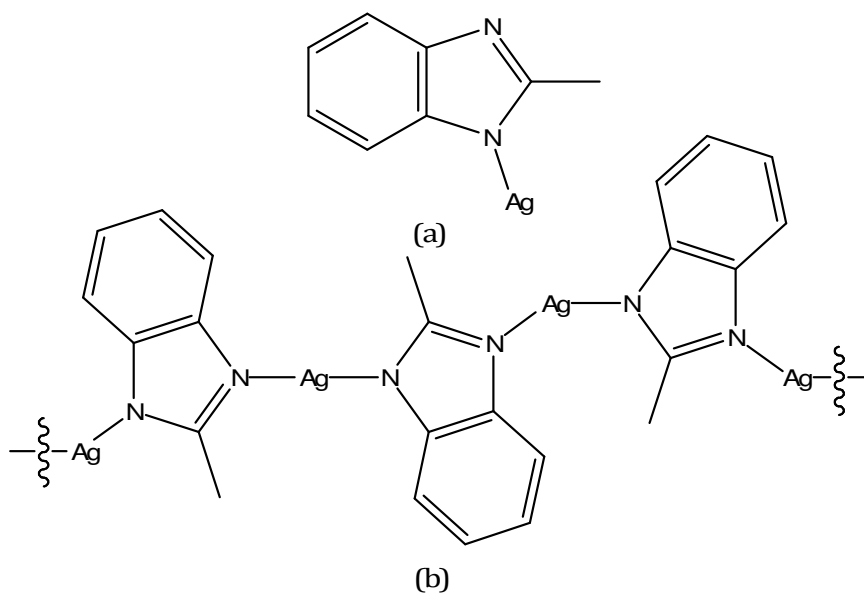
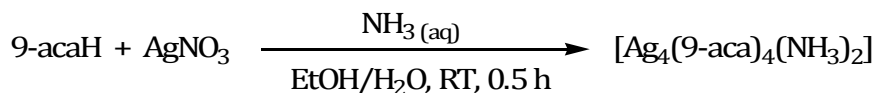


Figure 81. Tentative structure of [Ag(2-Mebenz-imid)]: (a) one unit and (b) polymeric chain.

3.1.17 [Ag₄(9-aca)₄(NH₃)₂]

[Ag₄(9-aca)₄(NH₃)₂] was synthesised from 9-anthracenecarboxylic acid and silver nitrate in an ethanol/water mixture (4:1) to give the product with a yield of 45% (Scheme 17). The aqueous ammonia was used to prevent the precipitation of insoluble silver(I) oxide.



Scheme 17. Synthesis of [Ag₄(9-aca)₄(NH₃)₂].

Crystals suitable for X-ray crystallographic analysis were grown from the reaction filtrate and the structure of $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ is shown in Figures 82-85. Selected bond lengths and angles are listed in Table 10.

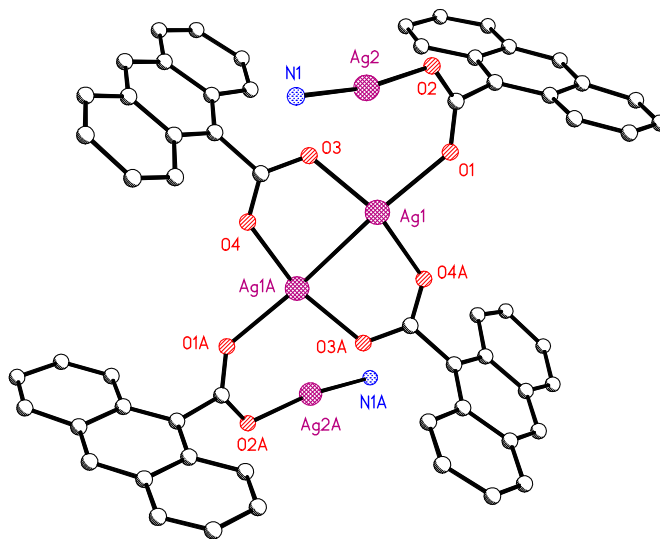


Figure 82. X-ray crystal structure of $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$.

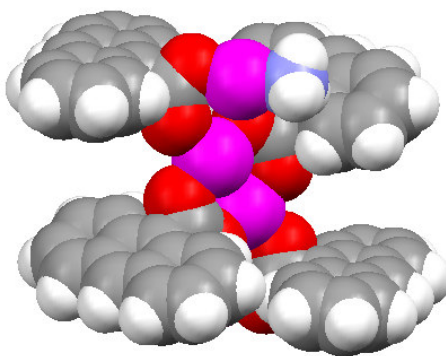


Figure 83. Space-filled structural diagram for $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ (Ag = purple, O = red, N = blue, C = grey, H = white).

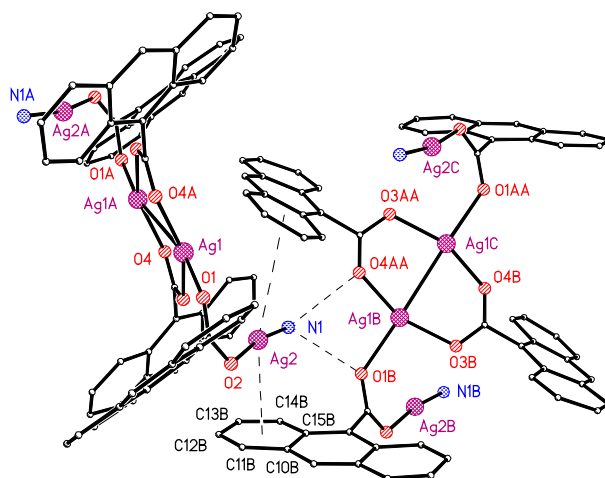


Figure 84. Intermolecular π - and H-bonding interactions in [Ag₄(9-aca)₄(NH₃)₂].

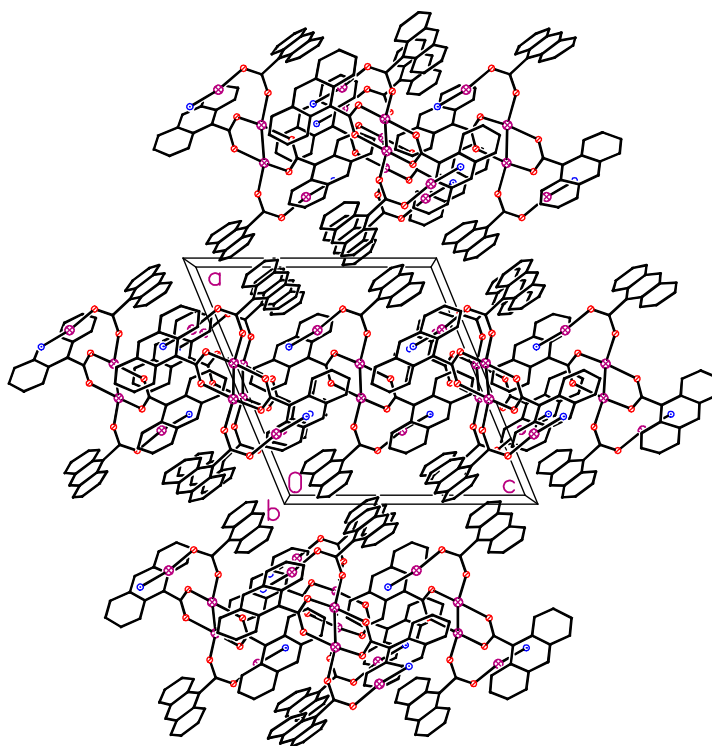


Figure 85. Packing diagram for [Ag₄(9-aca)₄(NH₃)₂].

Table 10. Selected bond lengths and bond angles for $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$.

| Bond | Bond Length (Å) | Bond | Bond Angle (°) |
|--------------|-----------------|--------------------|----------------|
| Ag(1)-Ag(1A) | 2.939 | O(1)-Ag(1)-Ag(1A) | 164.17 |
| Ag(1)-O(1) | 2.329 | O(3)-Ag(1)-O(4A) | 155.63 |
| Ag(1)-O(3) | 2.192 | O(3)-Ag(1)-Ag(1A) | 85.15 |
| Ag(1)-O(4A) | 2.261 | N(1)-Ag(2)-O(2) | 170.60 |
| Ag(2)-O(2) | 2.135 | O(3)-Ag(1)-O(1) | 100.39 |
| Ag(2)-N(1) | 2.148 | O(4A)-Ag(1)-Ag(1A) | 75.23 |

$[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ is dimeric and centrosymmetric, containing two four-coordinate silver(I) ions and two two-coordinate silver(I) ions. The Ag(1)-Ag(1A) distance is 2.939 Å. The two carboxylates that are linked to the metal-metal bimetallic core are syn-syn bridging. The two carboxylates in the equatorial plane are in the syn-anti configuration, being coordinated to one silver of the bimetallic core and a second, non-core silver (Ag2). A space-filled structural diagram for $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ shows it to resemble a sandwich complex with the bimetallic core at the centre encased by the carboxylate ligands (Figure 83).

In $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$, Ag(2) is coordinated approximately linearly by ammonia and carboxylate ligands, and this metal also interacts with the anthracene π -systems of a neighbouring molecule (Figure 84). This interaction is supported by two long H-bonds from the hydrogens of the ammonia ligand to the carboxylate oxygen atoms of the same neighbouring molecule. These interactions lead to the packing arrangement illustrated in Figure 85.

The IR spectrum of $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ contains a band at 3370 cm^{-1} for the N-H stretching vibration of the ammonia ligand. Bands are also present at 1620,

764 and 736 cm^{-1} for the stretching vibrations of the anthracene ring system^{144,160}. The $\nu_{(\text{OCO})\text{asym}}$ and $\nu_{(\text{OCO})\text{sym}}$ vibrations occur at 1551 and 1424 cm^{-1} , respectively, giving a $\Delta_{(\text{OCO})}$ value of 127 cm^{-1} . This value is consistent with the carboxylate ligands being in a bridging coordination mode¹⁴³.

The ^1H NMR spectrum of $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ is very similar to that of $[\text{Ag}_2(9\text{-aca})_2]_n$, with the anthracene aromatic proton peaks occurring at 8.41 (H_{10}), 8.15 ($\text{H}_{1,8}$), 8.03 ($\text{H}_{4,5}$) and 7.47 ppm ($\text{H}_{2,3,6,7}$). There is also a singlet at 3.01 ppm for the protons of the NH_3 ligands. The presence of the silver(I) ions and amine groups have caused a shielding of anthracene protons, shifting them slightly upfield in comparison to those in the spectrum of the uncomplexed, free carboxylic acid.

3.2 Fluorescence of Silver(I) Complexes

The fluorescence properties of uncomplexed 9-anthracenecarboxylic acid have been of interest to research groups for over thirty years¹⁵⁴. Some preliminary fluorescence studies were carried out on a selection of the current silver(I) anthracene complexes in order to investigate the effect that coordination to silver(I) metal centres has on the fluorescence of the free ligands. The UV-Vis absorption spectrum was recorded to identify the maximum absorption wavelength of each complex and 9-acaH (Figures 86, 88, 90, 92, 94, 96, 98, 100, and 102). The four peaks at *ca.* 365 nm in the absorption spectrum are assigned to vibrational levels of the $^1\text{L}_a$ state while the peak at *ca.* 260 nm are assigned to the $^1\text{B}_b$ state^{153,165}. These absorptions arise from the excitation of electrons into the π^* orbital of the anthracene moiety from various levels within the ground state. Fluorescence spectra were then recorded and compared to that of metal-free 9-acaH (Figures 87, 89, 91, 93, 95, 97, 99, 101 and 103). The broad fluorescence band of 9-acaH centred at *ca.* 450 nm is thought to arise the presence of H-bonded dimers in the solutions^{154,155}. UV-Vis and fluorescence data are listed in Tables 33-35 in the Appendix.

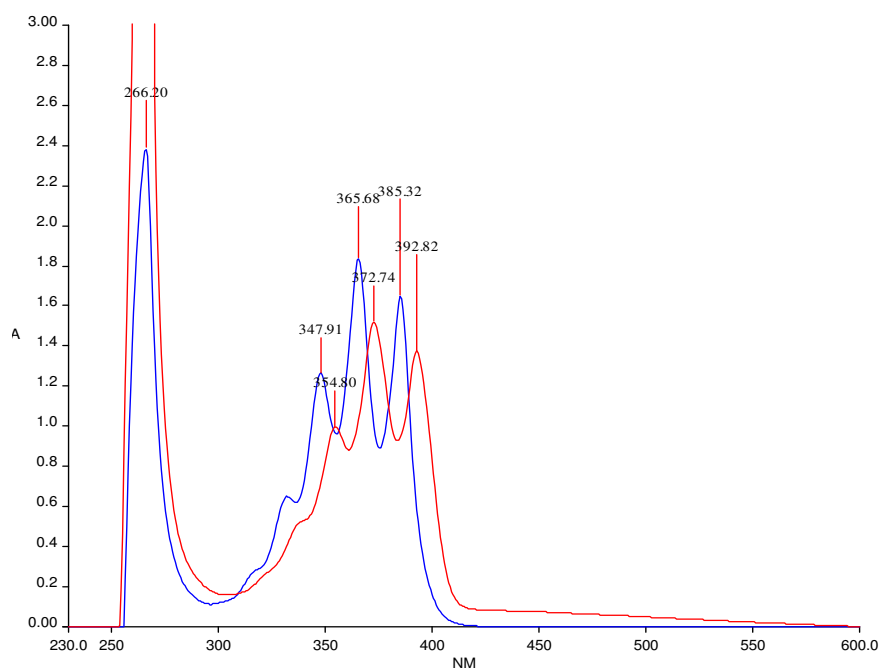


Figure 86. UV-Vis absorption spectra of $[Ag_2(9-aca)_2]_n$ (red) and 9-acaH (blue).

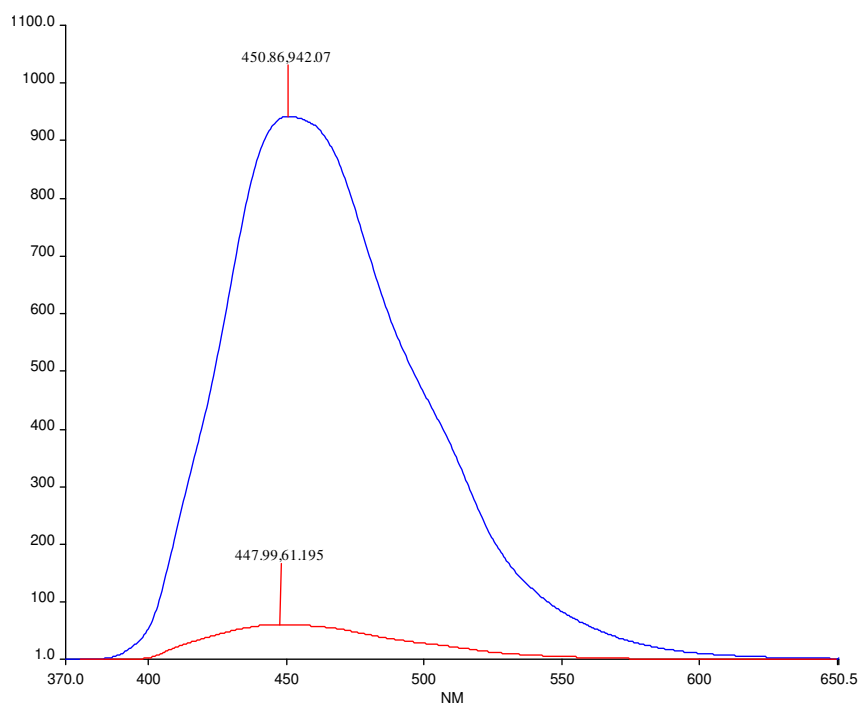


Figure 87. Fluorescence spectra of $[Ag_2(9-aca)_2]_n$ (red) and 9-acaH (blue).

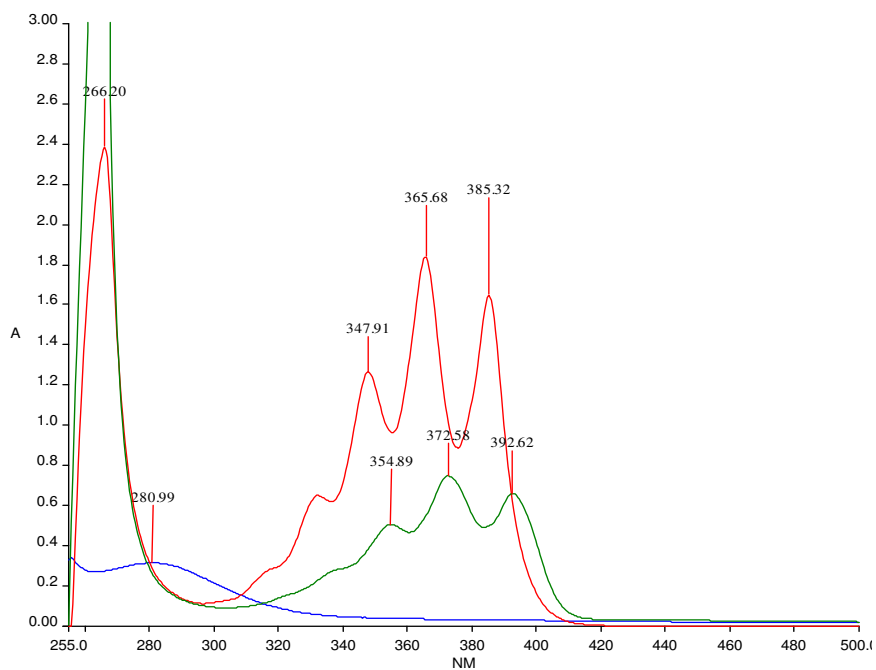


Figure 88. UV-Vis absorption spectra of [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca) (green), 9-acaH (red) and imidH (blue).

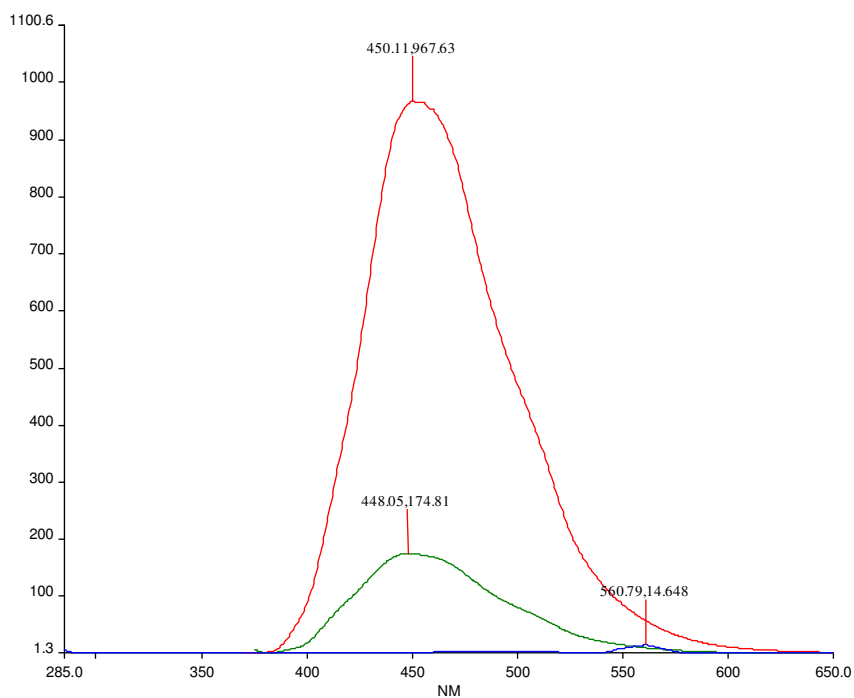


Figure 89. Fluorescence spectra of [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca) (green), 9-acaH (red) and imidH (blue).

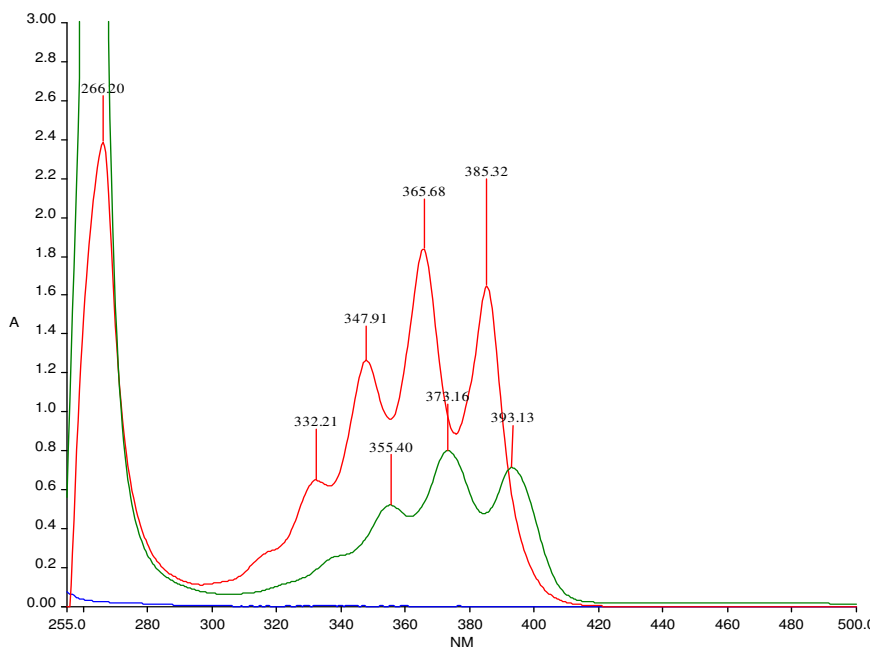


Figure 90. UV-Vis absorption spectra of [Ag(apim)](9-aca)·H₂O (green), 9-acaH (red) and apim (blue).

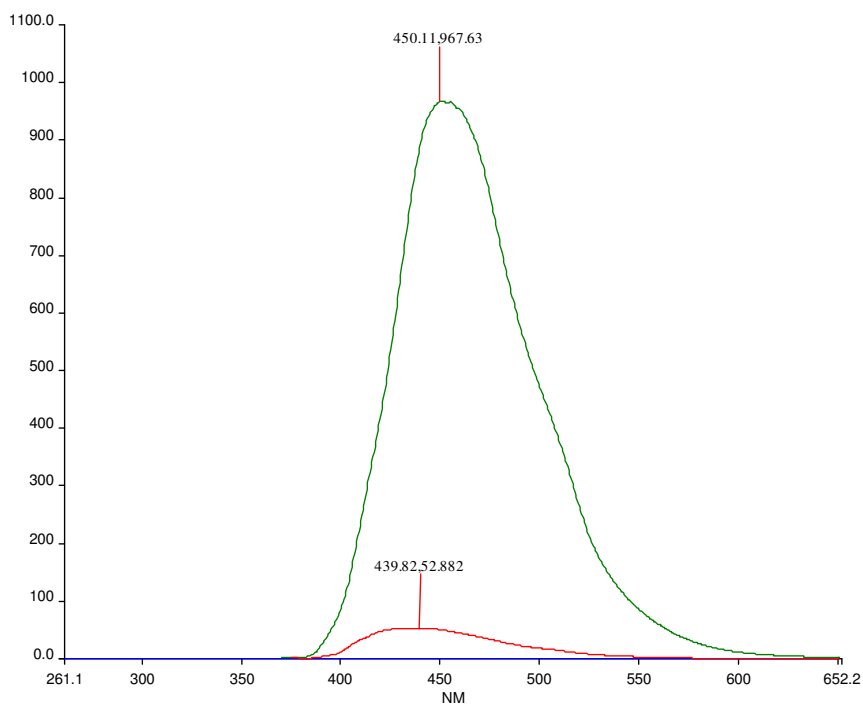


Figure 91. Fluorescence spectra of [Ag(apim)](9-aca)·H₂O (red), 9-acaH (green) and apim (blue).

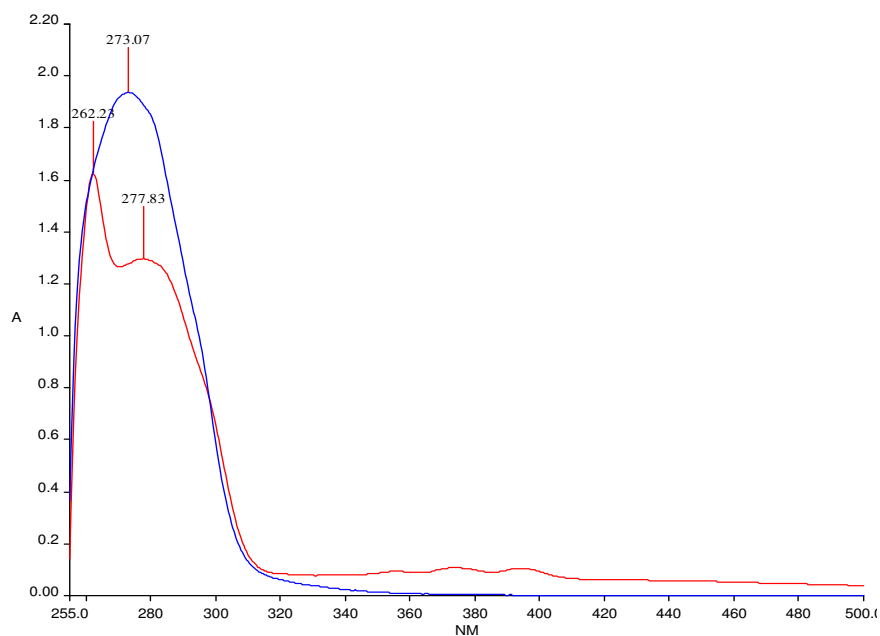


Figure 92. UV-Vis absorption spectra of [Ag(2-Ph-imid)] (blue) and 2-Ph-imidH (red).

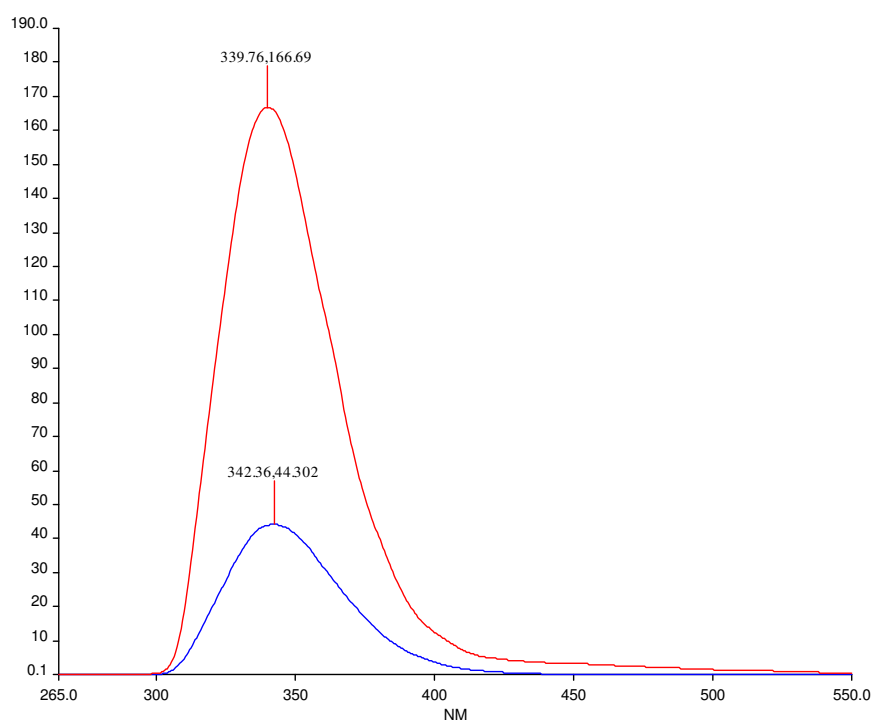


Figure 93. Fluorescence spectra of [Ag(2-Ph-imid)] (blue) and 2-Ph-imidH (red).

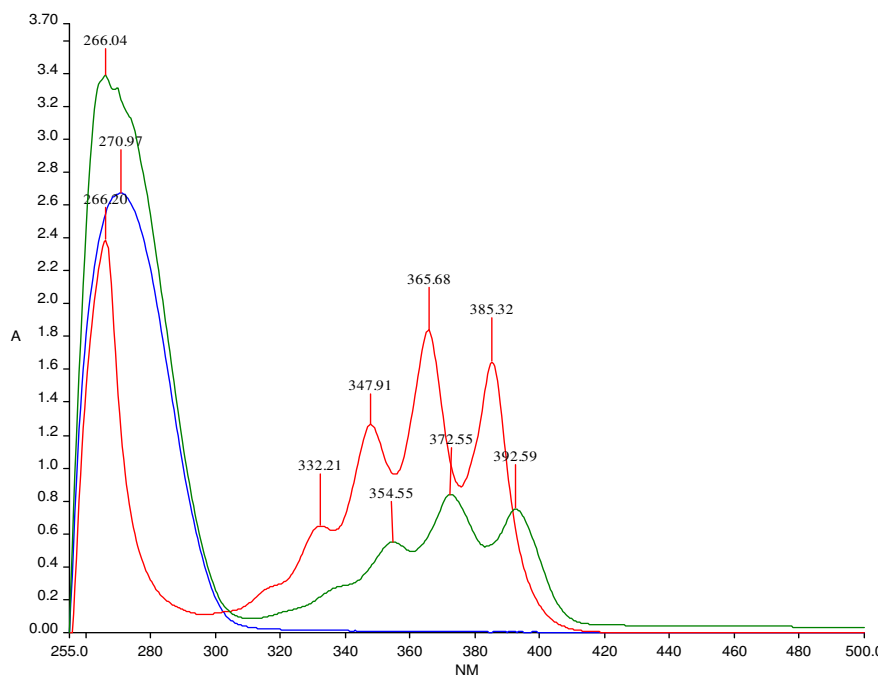


Figure 94. UV-Vis absorption spectra of [Ag(4-Ph-imidH)₂(9-aca)] (green), 9-acaH (red) and 4-Ph-imidH (blue).

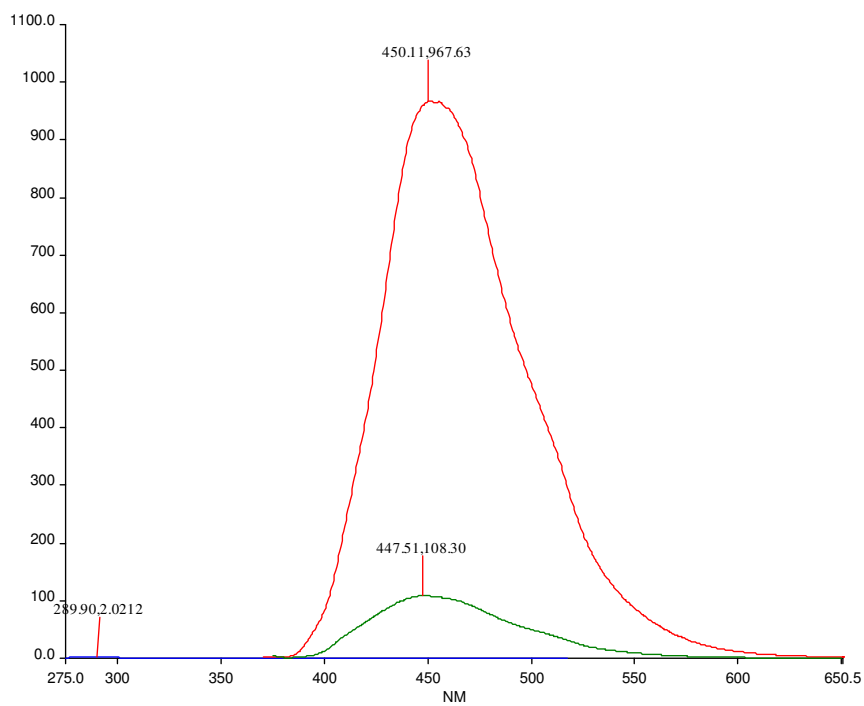


Figure 95. Fluorescence spectra of [Ag(4-Ph-imidH)₂(9-aca)] (green), 9-acaH (red) and 4-Ph-imidH (blue).

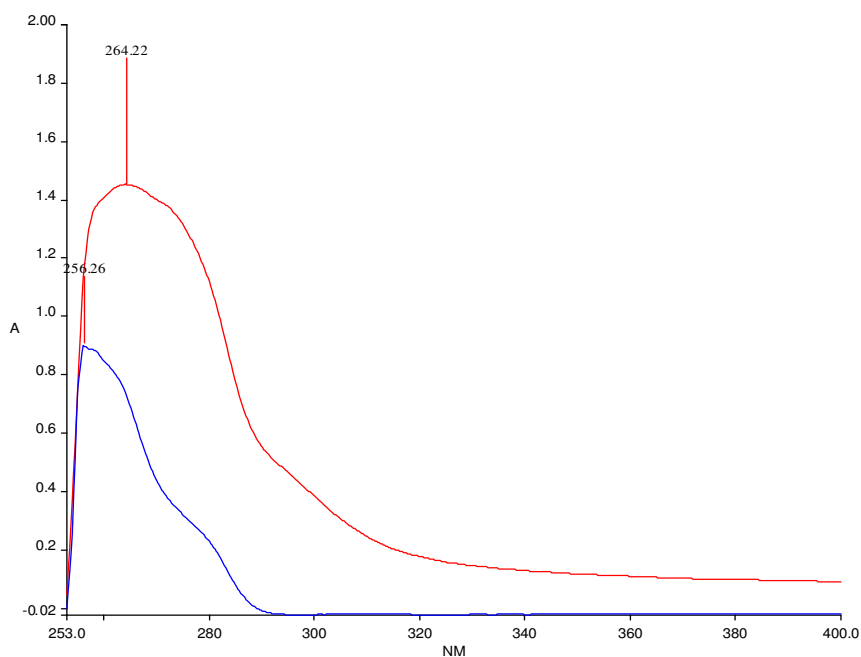


Figure 96. UV-Vis absorption spectra of [Ag(4,5-dicyanoimid)] (red) and 4,5-dicyanoimidH (blue).

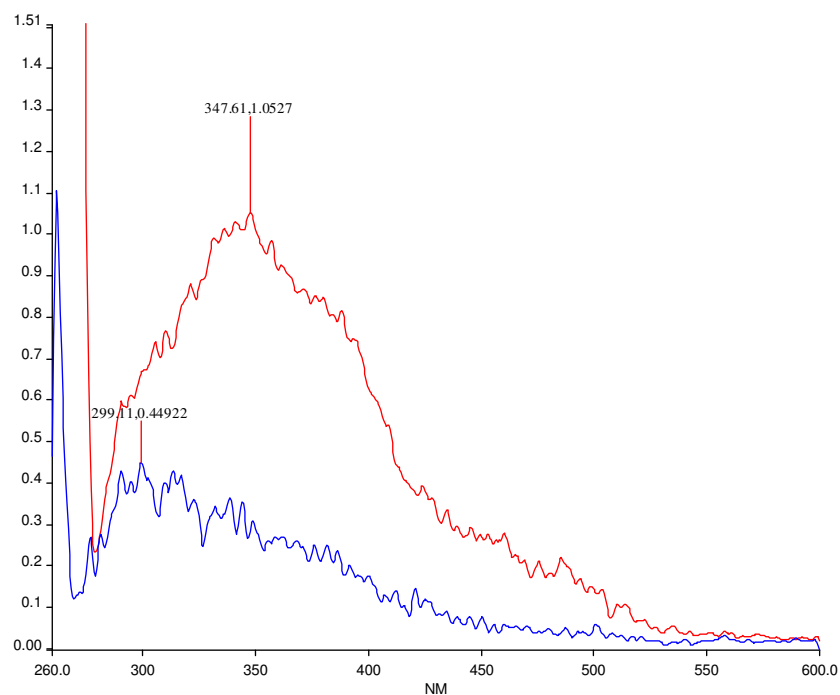


Figure 97. Fluorescence spectra of [Ag(4,5-dicyanoimid)] (red) and 4,5-dicyanoimidH (blue).

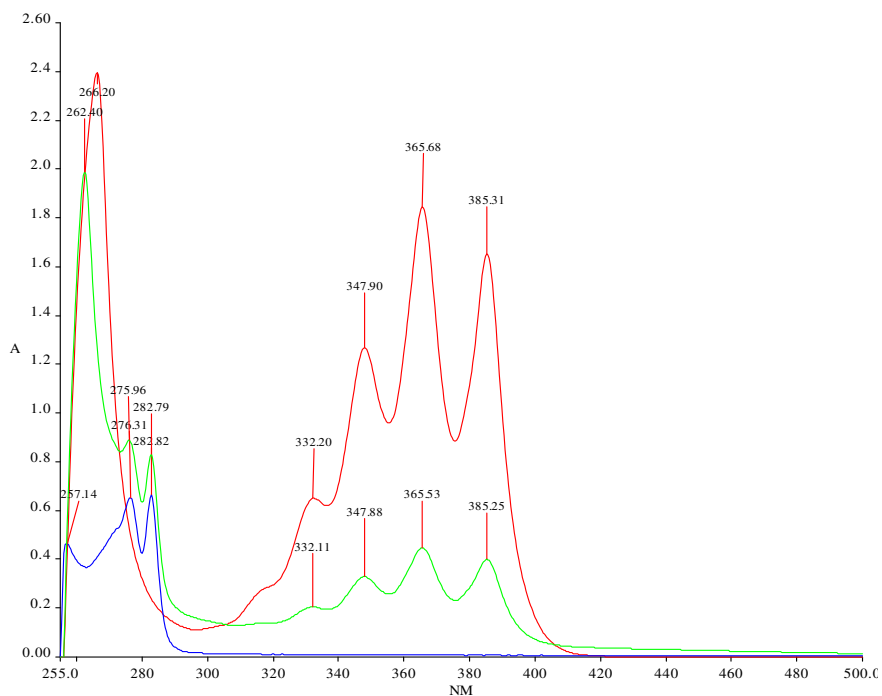


Figure 98. UV-Vis absorption spectra of $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ (green), 9-acaH (red) and 2-MebenzimidH (blue).

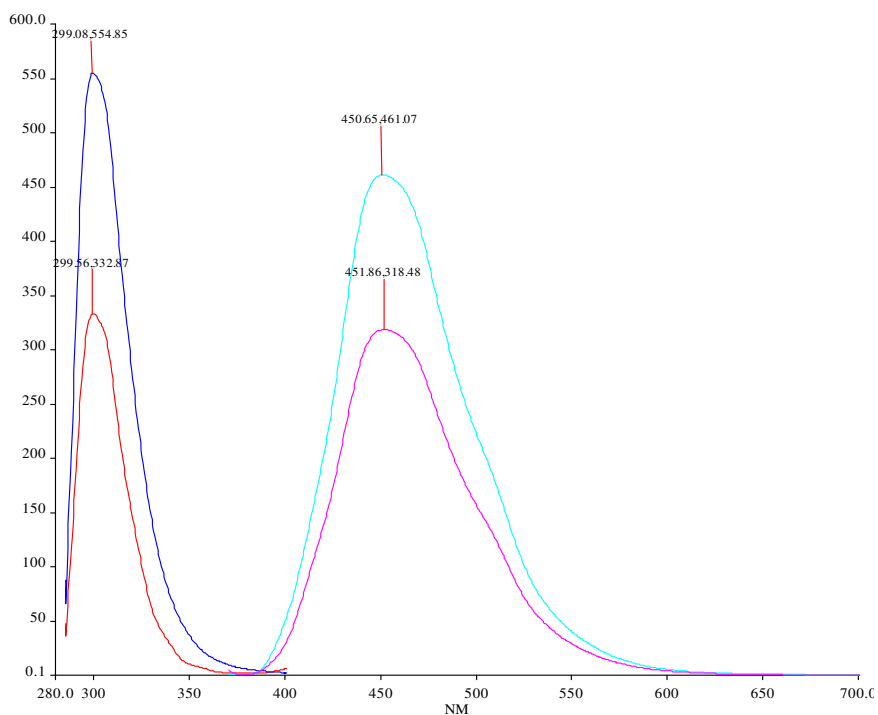


Figure 99. Fluorescence spectra of $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ (red, excited at 283 nm), $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ (pink, excited at 366 nm), 2-Mebenz-imidH (blue) and 9-acaH (light blue).

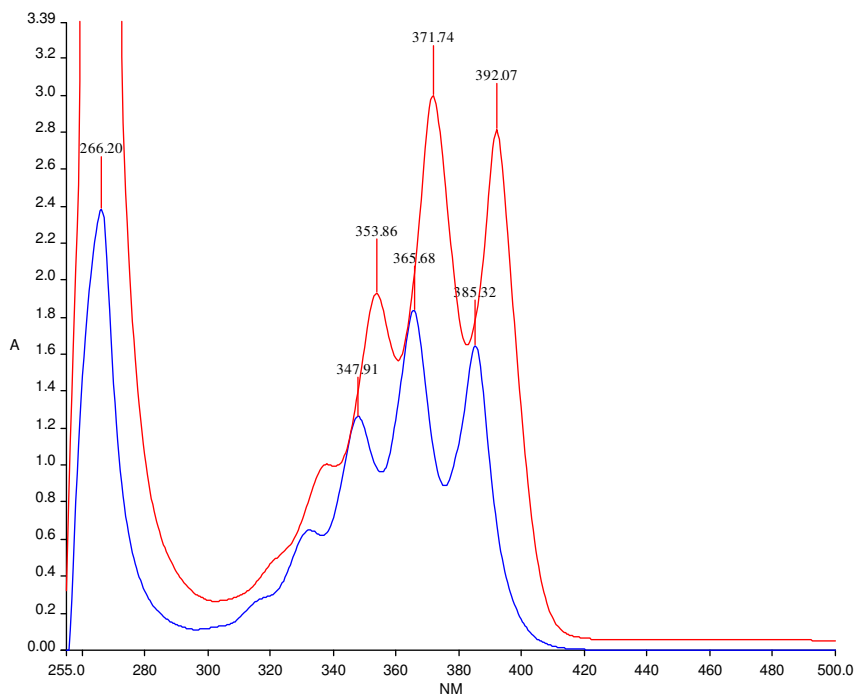


Figure 100. UV-Vis absorption spectra of $[Ag_4(9-aca)_4(NH_3)_2]$ (red) and 9-acaH (blue).

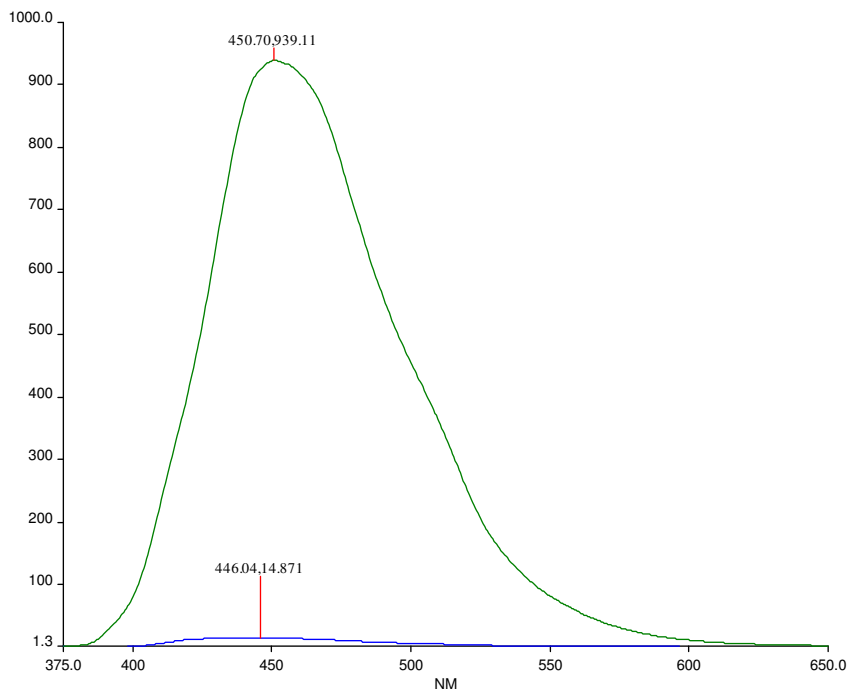


Figure 101. Fluorescence spectra of $[Ag_4(9-aca)_4(NH_3)_2]$ (blue) and 9-acaH (green).

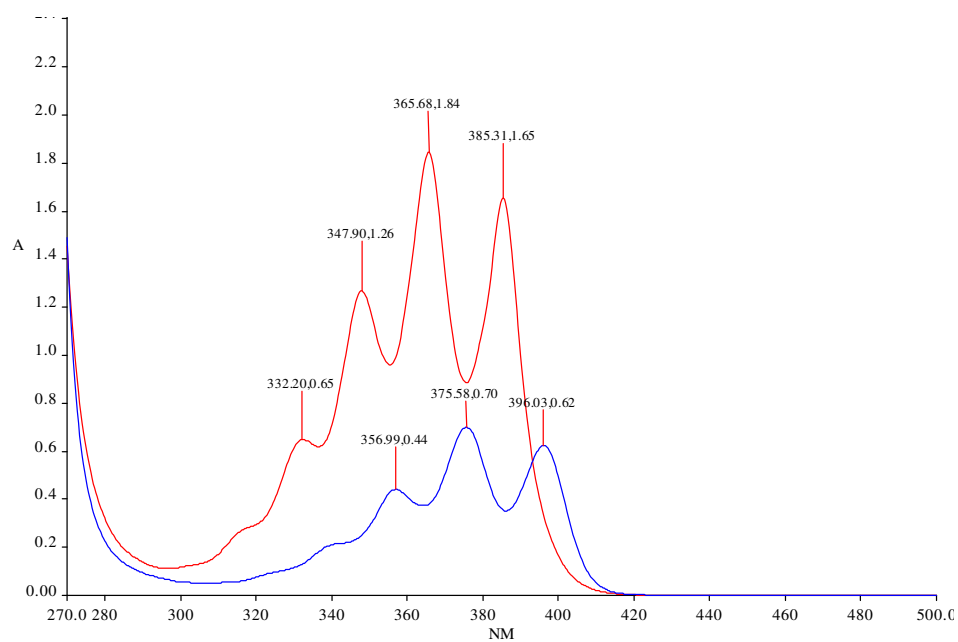


Figure 102. UV-Vis absorption spectra of [Na(9-aca)] (blue) and 9-acaH (red).

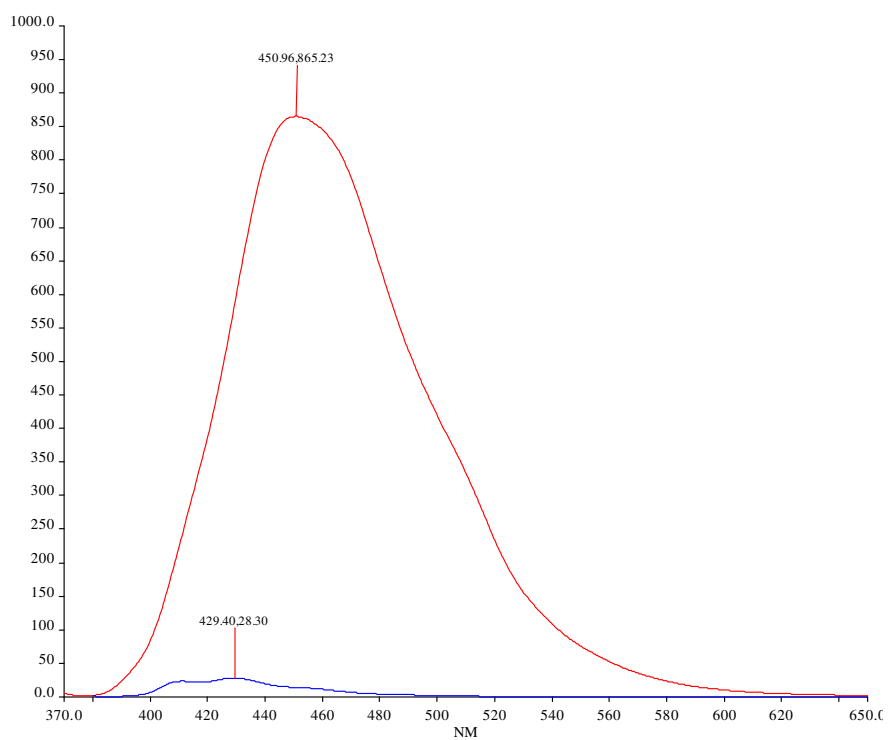


Figure 103. Fluorescence spectra of [Na(9-aca)] (blue) and 9-acaH (red).

For all of the silver(I) complexes containing the 9-aca⁻ anion and also the simple sodium salt, Na⁺9-aca⁻, fluorescence decreases dramatically with respect to that for free 9-acaH. [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca) caused the biggest reduction in fluorescence, quenching the fluorescence of 9-acaH by a factor of *ca.* 63. With the exception of [Ag(4,5-dicyanoimid)], all of the silver(I) imidazolate complexes (9-aca⁻ absent) fluoresce with a higher intensity than that of the corresponding free imidazole ligand. In the case of [Ag(4,5-dicyanoimid)], coordination to the silver(I) ion and deprotonation of the imidazole causes a reduction in fluorescence intensity when compared to that of the free 4,5-dicyanoimidH.

The ability of the silver(I) complexes to reduce the fluorescence of 9-acaH may be useful in identifying the manner in which the silver(I) carboxylate complexes interact with microbial or cancer cells. An increase in the fluorescence of the compounds within the cells could possibly indicate dissociation of the complex with subsequent protonation of the free 9-aca⁻ ligand.

Discussion 2:
Biological Activity

4.1 Antimicrobial Growth

The growth of fungal and bacterial cells can be divided into four phases:

- (i) *Lag Phase.* Growth is slow at first while the cells acclimatise to the new environmental conditions to which they have been introduced (pH, temperature, nutrients, etc.). There is no significant increase in cell numbers with time.
- (ii) *Exponential phase.* Once the cells are accustomed to their surroundings they begin to multiply exponentially, doubling every few minutes.
- (iii) *Stationary phase.* The rapid growth ceases due to limited supply of food, nutrients and space. There is no significant increase or decrease in cell numbers with time.
- (iv) *Death phase.* Toxic waste products build up, nutrient supplies are depleted and cells begin to die.

Typical growth curves for healthy microbial (control cells) and drug-treated cells are illustrated in Figure 104.

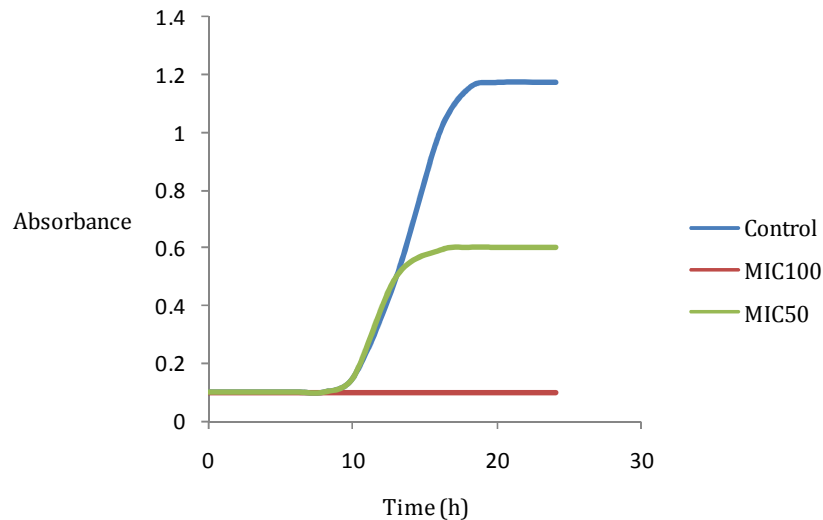


Figure 104. Growth curve for non-drug treated (control) and drug-treated (MIC₁₀₀, MIC₅₀) fungal or bacterial cells (death phase not included).

4.2 *In vitro* Antifungal Screening

The silver(I) complexes, simple silver(I) compounds (silver nitrate, silver perchlorate and silver oxide) and the prescription antifungal drug, Ketoconazole, were screened *in vitro* for their ability to inhibit the growth of *C. albicans*. MIC₁₀₀ values for these compounds are given in Table 11 and Figure 105. All of the test solutions were made by dissolving the complex in DMSO (1 cm³) and diluting with water to yield the required concentration. The maximum DMSO concentration in any sample was 0.5% v/v, and at this level the DMSO does not inhibit the growth of *C. albicans* cells. The metal-free ligands were also screened for their biological activity and all proved to be inactive at a concentration of 100 µg cm⁻³. The activity of the complexes, relative to the quantity (µM) of Ag⁺ ion present, is also given in Table 11.

Of the silver-containing samples tested in this work, all but three were more active than Ketoconazole. The simple silver(I) compounds (silver nitrate, silver perchlorate and silver oxide) were all more cytotoxic than Ketoconazole (MIC₁₀₀ values of 1.83, 1.50, 0.67 and 4.70, respectively). Interestingly, the water-insoluble Ag₂O was more active than water-soluble AgNO₃ and AgClO₄, suggesting that lipophilicity might be a desirable property.

The most effective silver(I) complex at inhibiting the growth of *C. albicans* cells was [Ag₄(9-aca)₄(NH₃)₂]. The MIC₁₀₀ value for the complex (0.14 µM) showed that it was *ca.* 32 times more cytotoxic than Ketoconazole (4.70 µM). This anthracene complex was also more active than the three simple silver(I) compounds. A similar high level of activity was also reported for the structurally related complex, [Ag₂(salH)₂(NH₃)₂] (0.50 µM)¹²⁴. Both complexes contain silver(I) ions coordinated to carboxylate and ammonia ligands, although the carboxylate binding mode in each is different. The carboxylates in [Ag₄(9-aca)₄(NH₃)₂] have syn-syn and syn-anti bridging conformations, while the salicylates of [Ag₂(salH)₂(NH₃)₂] are monodentate. In both complexes, the ammonia ligands are coordinated to the silver(I) in an approximately linear arrangement. It has previously been reported that the presence of this Ag-N

Table 11. Minimum inhibitory concentrations (MIC₁₀₀) of silver(I) complexes against *C. albicans*.

| Complex (#poor solubility) | MIC ₁₀₀ ($\mu\text{g cm}^{-3}$) | MIC ₁₀₀ (μM) | MIC ₁₀₀ ($\mu\text{M Ag}^+$) |
|--|---|---|--|
| Ketoconazole [#] | 2.50 | 4.70 | n/a |
| AgNO ₃ | 0.31 | 1.83 | 1.83 |
| AgClO ₄ | 0.31 | 1.50 | 1.50 |
| Ag ₂ O [#] | 0.16 | 0.67 | 1.34 |
| [Ag ₂ (9-aca) ₂] _n | 0.63 | 0.95 | 1.90 |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | 0.78 | 0.96 | 1.92 |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | 0.20 | 0.38 | 0.38 |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | 1.25 | 0.54 | 3.24 |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | 0.78 | 0.34 | 2.04 |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | 1.00 | 1.22 | 2.44 |
| [Ag(2-Me-imidH) ₂ (9-aca)] | 0.78 | 1.58 | 1.58 |
| [Ag(1-Bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | 0.78 | 0.32 | 1.92 |
| [Ag ₂ (1-Bu-imid) ₂ (9-aca) ₂] | 0.78 | 0.86 | 1.72 |
| [Ag(apim)](9-aca)·H ₂ O | 0.20 | 0.43 | 0.43 |
| [Ag(2-Ph-imid)] [#] | 1.56 | 6.21 | 6.21 |
| [Ag(4-Ph-imidH) ₂ (9-aca)] | 1.56 | 2.53 | 2.53 |
| [Ag(4,5-dicyanoimid)] [#] | 0.39 | 1.73 | 1.73 |
| [Ag(Benz-imid)] [#] | 1.56 | 6.93 | 6.93 |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ | 1.56 | 1.31 | 2.62 |
| [Ag(2-Mebenz-imid)] [#] | 3.13 | 13.07 | 13.07 |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] | 0.19 | 0.14 | 0.56 |

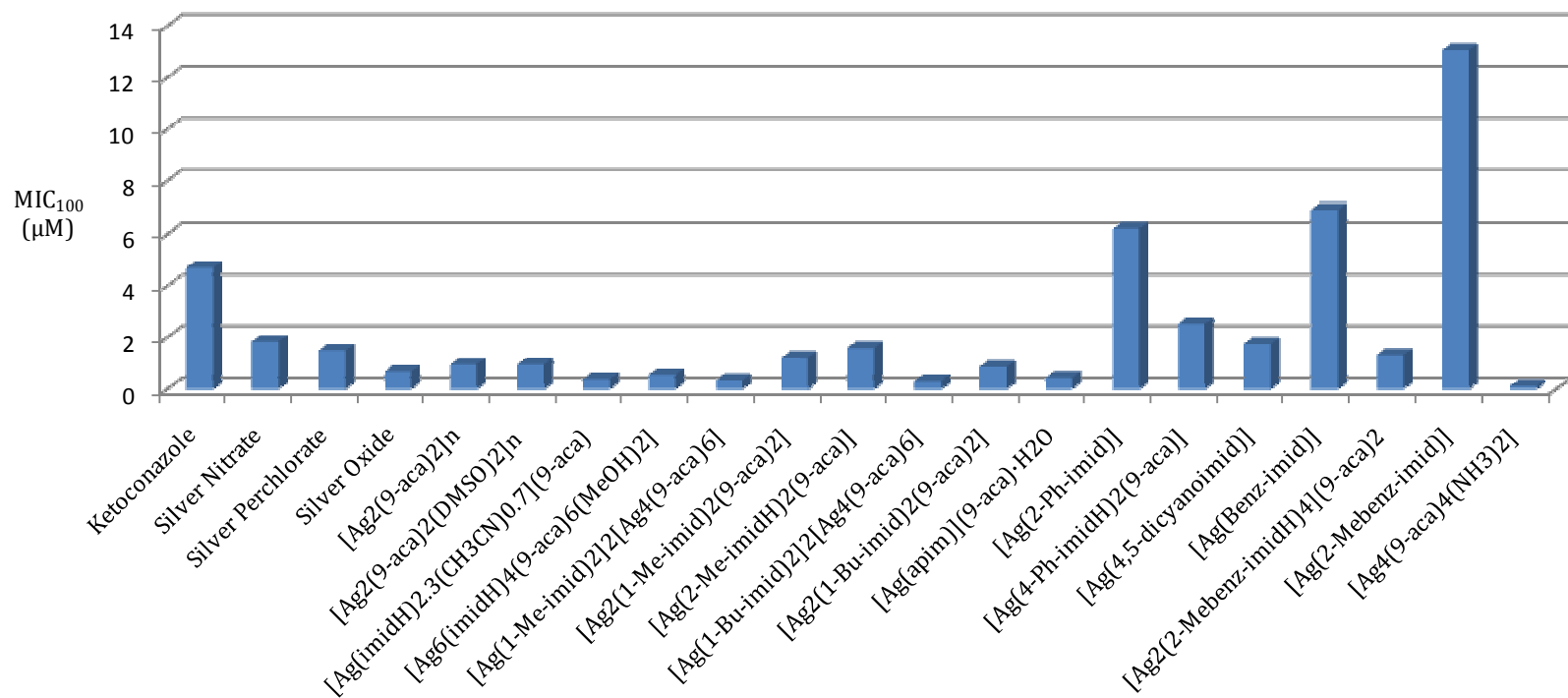


Figure 105. MIC₁₀₀ values (µM) of silver(I) complexes and reference standards.

bond allows for good antimicrobial activity and this may be related to the relatively weak strength of the Ag-N bond and the release of Ag(I) ions from the molecule⁸⁵. A comparison of the relative activity of these two complexes in terms of the concentration of Ag⁺ ions clearly shows that [Ag₄(9-aca)₄(NH₃)₂] is almost twice as active as [Ag₂(salH)₂(NH₃)₂].

Although [Ag₄(9-aca)₄(NH₃)₂] is the most active of the silver(I) complexes on a molecular level, the most active complex per mole of silver(I) present is [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca) (MIC₁₀₀ = 0.38 μM Ag⁺). This complex is 1.5 times more active per Ag⁺ than [Ag₄(9-aca)₄(NH₃)₂] (MIC₁₀₀ = 0.56 μM Ag⁺) and 4-5 times more active than AgNO₃ and AgClO₄ (MIC₁₀₀ = 1.83 and 1.50 μM Ag⁺, respectively).

The anthracene complex, [Ag₂(9-aca)₂]_n (MIC₁₀₀ = 0.95 μM), was *ca.* 7 times less active than [Ag₄(9-aca)₄(NH₃)₂], suggesting again that the presence of NH₃ ligands has a significant influence on bioactivity. However, [Ag₂(9-aca)₂]_n was still *ca.* 5 times more active than its salicylate relative, [Ag₂(salH)₂] (5.00 μM)¹²⁴. [Ag₂(9-aca)₂(DMSO)₂]_n (MIC₁₀₀ = 0.96 μM) displayed similar activity to [Ag₂(9-aca)₂]_n.

The most active of the imidazole-containing complexes was the complex salt, [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆] (MIC₁₀₀ = 0.32 μM). This salt was 15 times more cytotoxic than Ketoconazole and it was also more active than its precursor, [Ag₂(1-Bu-imid)₂(9-aca)₂] (0.86 μM). However, a comparison of activities in terms of Ag⁺ content reveals that [Ag₂(1-Bu-imid)₂(9-aca)₂] is slightly more active than [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆] (1.72 and 1.92 μM Ag⁺, respectively). The activities of the 1-Bu-imid pair of complexes, [Ag₂(1-Bu-imid)₂(9-aca)₂] and [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆], were superior to that of the related 1-Me-imid pair, [Ag₂(1-Me-imid)₂(9-aca)₂] and [Ag(1-Me-imid)₂]₂[Ag₄(9-aca)₆] (MIC₁₀₀ = 1.22 and 0.34 μM, respectively). This suggests that a longer alkyl substituent (butyl vs. methyl) on the imidazole ring enhances activity. The large butyl group is expected to confer greater lipid solubility and this may be an important attribute in the penetration of the cell membrane.

The 2-Me-imidH derivative, $[\text{Ag}(\text{2-Me-imidH})_2(\text{9-aca})]$ ($\text{MIC}_{100} = 1.58 \mu\text{M}$), was *ca.* 3 times more active than Ketoconazole ($\text{MIC}_{100} = 4.70 \mu\text{M}$). This complex was less active than its 1-Me-imid counterparts, yet when a comparison is made in terms of the quantity of Ag^+ present per molecule, the 2-Me-imidH complex had the greater cytotoxicity towards *C. albicans* cells ($\text{MIC}_{100} = 1.58, 2.04$ and $2.44 \mu\text{M Ag}^+$ for $[\text{Ag}(\text{2-Me-imidH})_2(\text{9-aca})]$, $[\text{Ag}(\text{1-Me-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$ and $[\text{Ag}_2(\text{1-Me-imid})_2(\text{9-aca})_2]$, respectively).

The unsubstituted imidazole complex, $[\text{Ag}_6(\text{imidH})_4(\text{9-aca})_6(\text{MeOH})_2]$ ($\text{MIC}_{100} = 0.54 \mu\text{M}$), had a cytotoxicity 9 times greater than Ketoconazole. Although this complex contains silver(I) coordinated approximately linearly by two imidazole ligands in a similar manner to that in $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](\text{9-aca})$, it was less active per Ag^+ ion present ($\text{MIC}_{100} = 0.38$ and $3.24 \mu\text{M Ag}^+$, respectively). This finding may be related to the quantity of silver(I) which can readily be released from the complexes. It is possible that the metal ions are more tightly bound in the hexanuclear core of $[\text{Ag}_6(\text{imidH})_4(\text{9-aca})_6(\text{MeOH})_2]$ than in $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](\text{9-aca})$.

Although $[\text{Ag}(\text{4-Ph-imidH})_2(\text{9-aca})]$ ($\text{MIC}_{100} = 2.53 \mu\text{M}$) was almost twice as active at inhibiting the growth of *C. albicans* as Ketoconazole, it was not as cytotoxic as the three simple silver compounds. Whereas $[\text{Ag}_2(\text{2-Mebenz-imidH})_4](\text{9-aca})_2$ ($\text{MIC}_{100} = 1.31 \mu\text{M}$) was less cytotoxic than all of the previously discussed silver(I) complexes, it was still 3.5 times more active than Ketoconazole. $[\text{Ag}_2(\text{2-Mebenz-imidH})_4](\text{9-aca})_2$ is structurally similar to the silver salicylate complex, $[\text{Ag}_2(\text{imidH})_4](\text{salH})_2^{126}$ ($\text{MIC}_{100} = 0.10 \mu\text{M}$) yet $[\text{Ag}_2(\text{imidH})_4](\text{salH})_2$ was *ca.* 13 times more cytotoxic towards *C. albicans* cells. This suggests that the combination of the 9-aca counterion with the bulkier and more aromatic imidazole ligand is important to how $[\text{Ag}_2(\text{2-Mebenz-imidH})_4](\text{9-aca})_2$ interacts with the fungal cells.

$[\text{Ag}(\text{apim})](\text{9-aca})\cdot\text{H}_2\text{O}$ ($\text{MIC}_{100} = 0.43 \mu\text{M}$) was *ca.* 11 times more active than Ketoconazole and *ca.* 4 times more active than AgNO_3 at inhibiting the growth of *C. albicans*. This complex is structurally very similar to the known biologically

active complex, [Ag(apim)]ClO₄¹²⁶ (MIC₁₀₀ = 1.80 μM), although the presence of the 9-aca⁻ as the counterion (as opposed to the perchlorate counterion) appears to have increased the cytotoxicity 4-fold. However, this interpretation is somewhat contradicted by the fact that the salts, K⁺9-aca⁻ and Na⁺ClO₄⁻, are both inactive at inhibiting the growth of *C. albicans*.

Three silver(I) imidazolate complexes that did not contain the anthracene carboxylate ligand were also screened for their inhibitory activity. [Ag(4,5-dicyanoimid)] (MIC₁₀₀ = 1.734 μM) had a similar activity profile to AgNO₃ and was *ca.* 3 times more active than Ketoconazole. [Ag(2-Ph-imid)], [Ag(Benz-imid)] and [Ag(2-Mebenz-imid)] (MIC₁₀₀ = 6.214, 6.930 and 13.073 μM, respectively) were all less cytotoxic towards *C. albicans* cells than Ketoconazole. Each of these three complexes contain anionic imidazolate ligands (deprotonated amine nitrogen) and most likely are polymeric. Bonding of the silver(I) to the N⁻ atom of the imidazole is likely to be quite strong and this may retard the release of the silver(I) ions from the complex.

4.3 *In vivo* Antifungal Screening

In vivo antifungal screening was carried out using the *G. mellonella* insect model. *G. mellonella* larvae were administered test solutions by injection directly into the haemocoel through the last pro-leg (Figure 106). Survival was monitored every 24 h and death was assessed by the lack of movement in response to stimulus together with discolouration of the cuticle (Figure 107).

The toxicity of all complexes was assessed at three different concentrations: 100 μg cm⁻³, 10 μg cm⁻³ and twice their MIC₁₀₀ value. The simple silver(I) salts, silver nitrate and silver perchlorate, and the prescription antifungal drug, Ketoconazole, were used as reference standards. It was found that the survival of the larvae was not affected by Ketoconazole, AgNO₃, AgClO₄ or any of the silver(I) complexes.



Figure 106. Injection of test solutions into the haemocoel of *G. mellonella* through the last pro-leg.

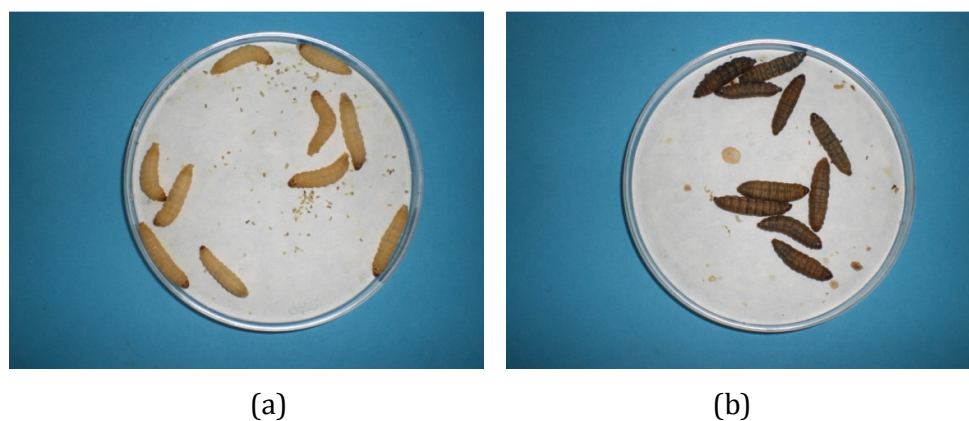


Figure 107. *G. mellonella* after 72 h incubation at 30 °C: (a) healthy control specimens and (b) specimens treated with a lethal dose of *C. albicans*.

The two types of antifungal screening conducted were prophylactic treatment and the treatment of infection (pre-infected larvae). A lethal dose of *C. albicans* was pre-determined to be 2×10^6 cells administered in 20 μl of PBS solution (1×10^8 cells cm^{-3}). Each of the test compounds was screened at three concentrations; 100 $\mu\text{g cm}^{-3}$, 10 $\mu\text{g cm}^{-3}$ and twice their MIC_{100} value. The prophylactic dose of complex was administered 1 h prior to infection with *C. albicans* cells, while in treatment form the complex was administered 1 h after infection. Survival was analysed at 24, 48 and 72 h intervals and significance was determined using the log rank (Mantel-Cox) method. Positive results were placed into one of three categories: * = $p < 0.05$, ** = $p < 0.01$ and *** = $p < 0.001$.

Results for prophylactic treatment are illustrated in Figures 108-110 and those for the treatment of infection are illustrated in Figures 111-113. These data, along with significant p categories and values, are listed in Tables 36-39 in the Appendix.

Ketoconazole, administered prophylactically at a concentration of $100 \mu\text{g cm}^{-3}$, significantly increased the survival rate of *G. mellonella* larvae 48 h ($p = 0.0285$) and 72 h ($p = 0.0076$) after infection with *C. albicans* cells. At the lower concentrations (10 and $5 \mu\text{g cm}^{-3}$) the increased survival was not deemed to be statistically significant. A similar pattern was observed for the treatment of *C. albicans* with Ketoconazole in pre-infected larvae (at $100 \mu\text{g cm}^{-3}$, $p = 0.0076$ after 48 and 72 h). Silver nitrate proved to be more effective than Ketoconazole at increasing the survival of *G. mellonella* larvae, both prophylactically and in the treatment of infection. AgNO_3 improved survival rates after 48 h and 72 h at an administered concentration of $10 \mu\text{g cm}^{-3}$ prophylactically ($p = 0.0285$ and 0.0076 , respectively), and after 72 h at $0.625 \mu\text{g cm}^{-3}$ when treating the pre-infected larvae ($p = 0.0223$).

The best silver(I) complex for increasing the survival rate of *C. albicans* infected *G. mellonella* larvae was $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$. Prophylactically, it significantly increased the survival rate after 48 h and 72 h at a concentration of $10 \mu\text{g cm}^{-3}$ ($p = 0.0285$ and 0.0076 , respectively). Furthermore, the complex was also very effective after 72 h at a concentration of twice its MIC_{100} value ($0.390 \mu\text{g cm}^{-3}$) ($p = 0.0223$). The concentrations of Ketoconazole and AgNO_3 required to effect the same degree of survival were found to be substantially greater (100 and $10 \mu\text{g cm}^{-3}$, respectively). $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ was not as effective at treating pre-infected larvae, requiring a dose of $100 \mu\text{g cm}^{-3}$ to significantly increase survival ($p = 0.0223$).

The remaining silver(I) complexes, although not as effective as $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$, also increased the survival rate of *G. mellonella* larvae infected with *C. albicans* and their activities are summarised below.

When administered prophylactically at a concentration of $100 \mu\text{g cm}^{-3}$, $[\text{Ag}_2(9\text{-aca})_2]_n$, $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$, $[\text{Ag}(4,5\text{-dicyanoimid})]$ and $[\text{Ag}(\text{Benzimid})]$ all significantly increased the survival rate of larvae subsequently infected with *C. albicans* ($p = 0.0223$ for each complex). $[\text{Ag}_2(1\text{-Bu-imid})_2(9\text{-aca})_2]$, $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$ and $[\text{Ag}(2\text{-Ph-imid})]$ improved the survival rate after 48 and 72 h at $100 \mu\text{g cm}^{-3}$ prophylactically ($p = 0.0285$ and 0.0076 , respectively). Although the activity of the latter three complexes was similar to that of Ketoconazole, they were not as effective as silver nitrate. $[\text{Ag}(1\text{-Bu-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ and AgNO_3 were found to be substantially more efficient than Ketoconazole as prophylactics, requiring only a concentration of $10 \mu\text{g cm}^{-3}$ (as opposed to $100 \mu\text{g cm}^{-3}$) to promote the same degree of survival.

In general, the treatment of *G. mellonella* larvae pre-infected with *C. albicans* was not as good as those treated prophylactically. The most effective silver(I) complex at increasing the survival rate of pre-infected larvae was $[\text{Ag}(2\text{-Me-imidH})_2(9\text{-aca})]$. This complex significantly increased the survival rate when administered at a concentration of $10 \mu\text{g cm}^{-3}$ ($p = 0.0223$). A Ketoconazole concentration of $100 \mu\text{g cm}^{-3}$ was required to maintain the same survival rate.

$[\text{Ag}_2(1\text{-Bu-imid})_2(9\text{-aca})_2]$ and $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$, at a concentration of $100 \mu\text{g cm}^{-3}$, both significantly increased the larval survival rate 48 h and 72 h after pre-infection ($p = 0.0285$ and 0.0223 for $[\text{Ag}_2(1\text{-Bu-imid})_2(9\text{-aca})_2]$ and $p = 0.0076$ for $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$). Treatment of pre-infected larvae with $[\text{Ag}(4,5\text{-dicyanoimid})]$ at $100 \mu\text{g cm}^{-3}$ also promoted an increased survival rate. Thus, the latter three complexes were equally effective when administered either prophylactically or to pre-infected larvae.

When treating pre-infected larvae at $100 \mu\text{g cm}^{-3}$, $[\text{Ag}(2\text{-Ph-imid})]$ only increased the survival rate after a 72 h period ($p = 0.0223$), whereas with prophylactic dosing a beneficial effect was observed after 48 h ($p = 0.0285$). The opposite trend was seen for $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$. This complex did not significantly increase the survival rate of *G. mellonella* larvae at any time point when administered prophylactically, but when the pre-existing infection

was treated with $[\text{Ag}(\text{1-Me-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$ ($100 \mu\text{g cm}^{-3}$) the survival rate significantly increased ($p = 0.0223$).

In summary, the prophylactic method of administering the silver(I) complexes proved more effective at increasing the survival rate of *G. mellonella* infected with *C. albicans*. This may be attributed not only to the efficacy of the complexes but also to the anticipated increase in the number of haemocytes, antimicrobial peptides and proteins produced by the innate immune system of the larvae in response to the presence of the foreign substance⁵⁰.

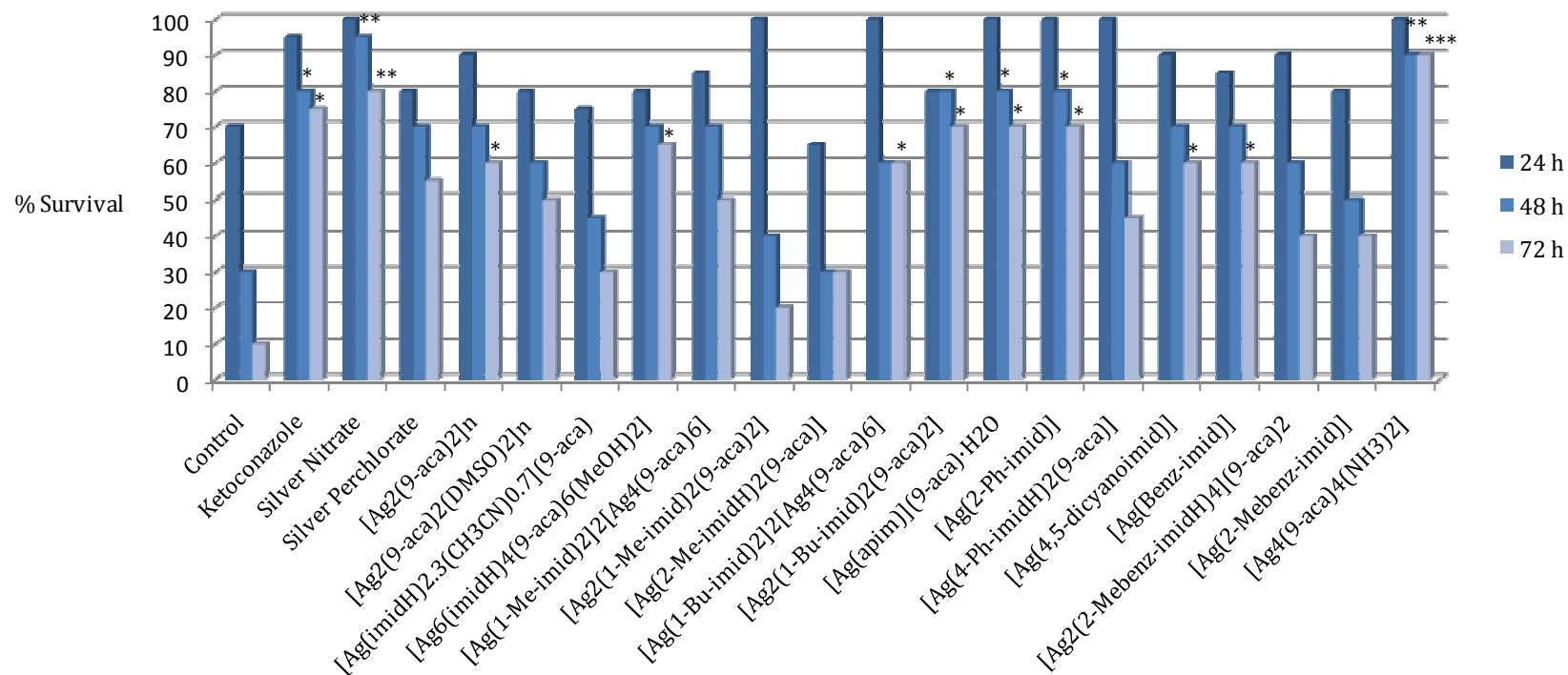


Figure 108. Percentage survival of *G. mellonella* larvae inoculated with complexes ($100 \mu\text{g cm}^{-3}$) one hour prior to infection with *C. albicans* (* = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$).

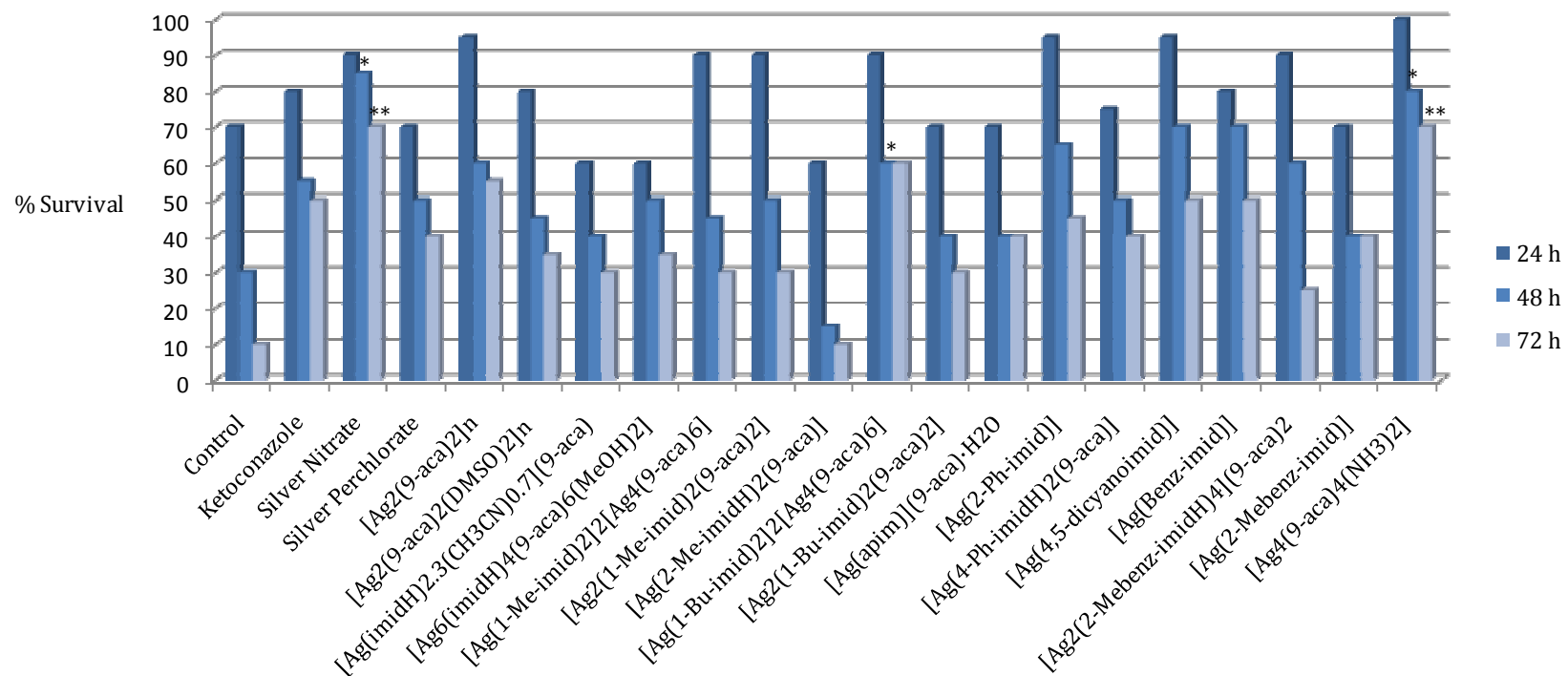


Figure 109. Percentage survival of *G. mellonella* larvae inoculated with complexes ($10 \mu\text{g cm}^{-3}$) one hour prior to infection with *C. albicans* (* = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$).

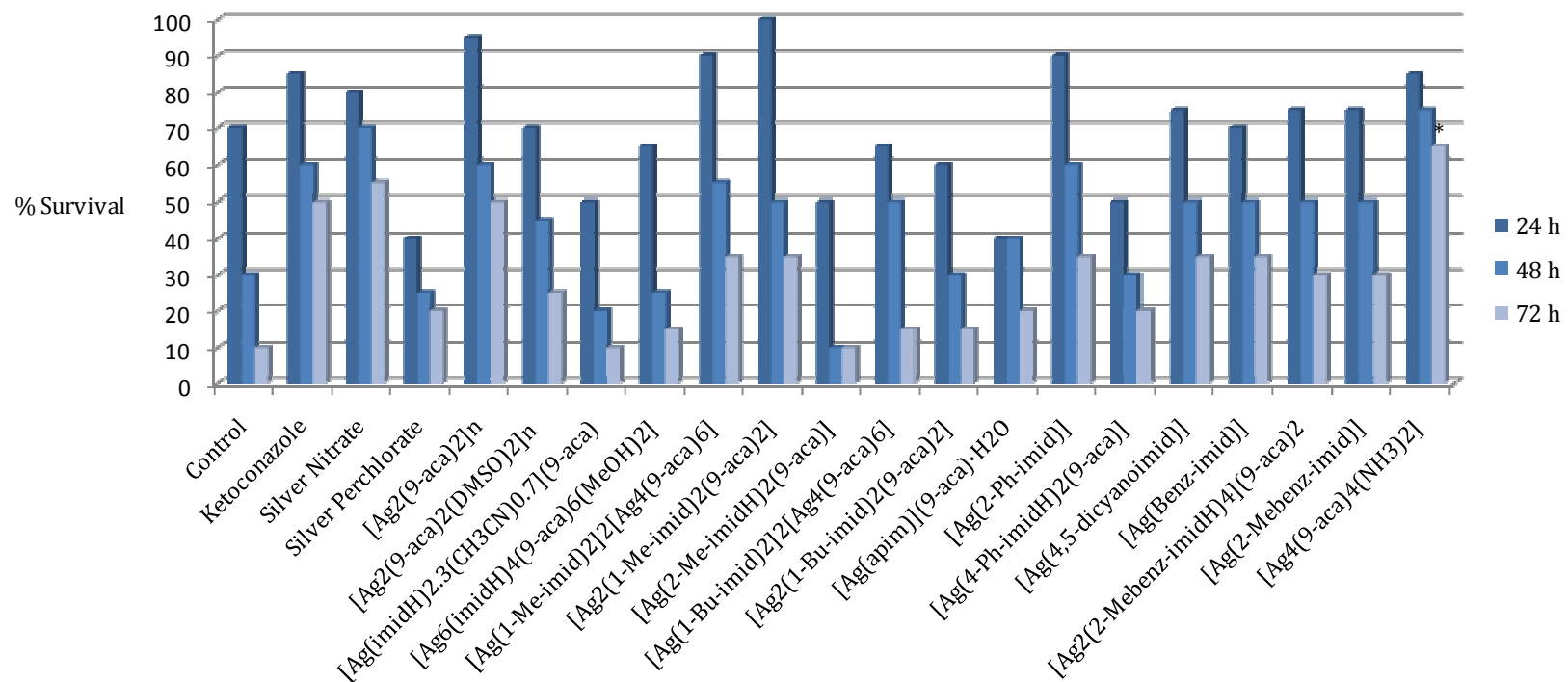


Figure 110. Percentage survival of *G. mellonella* larvae inoculated with complexes (concentration twice the MIC₁₀₀ value) one hour prior to infection with *C. albicans* (* = p<0.05, ** = p<0.01, *** = p<0.001).

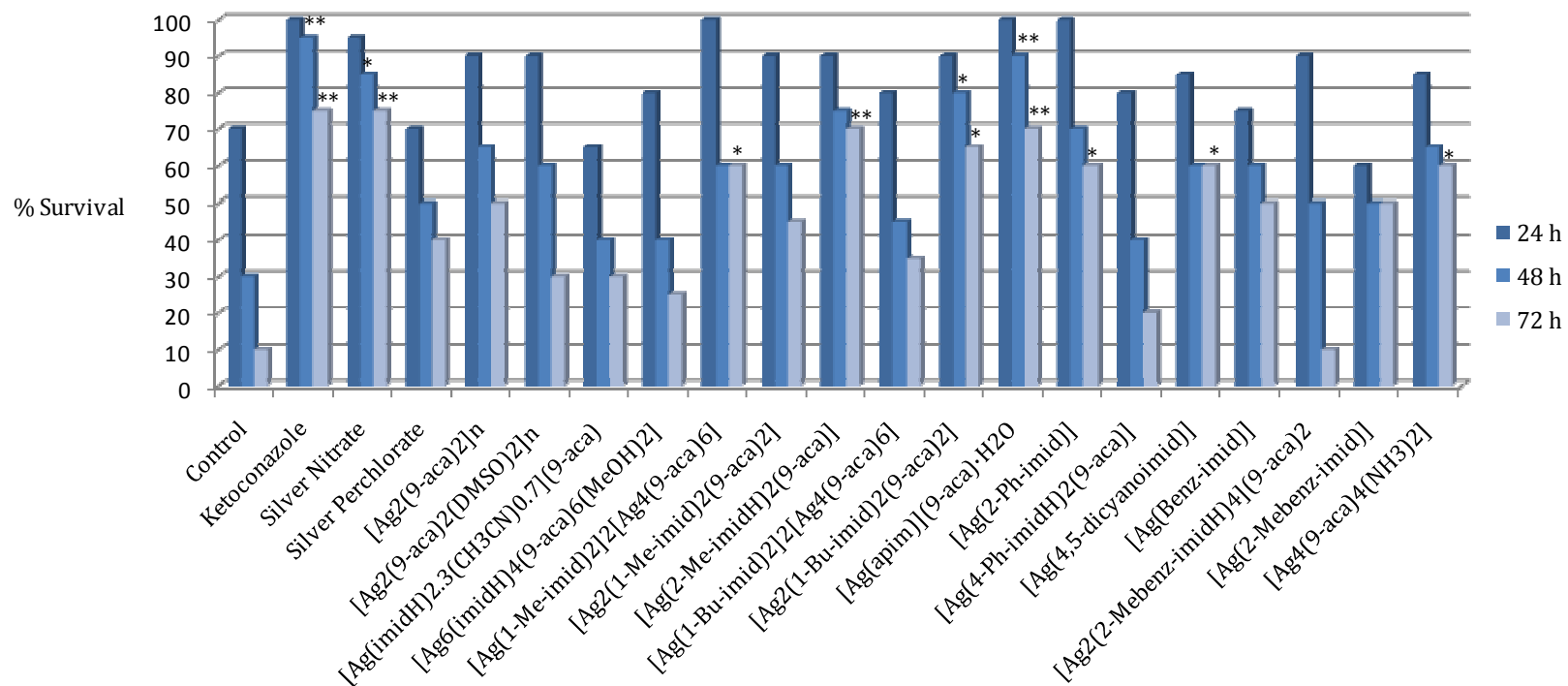


Figure 111. Percentage survival of *G. mellonella* larvae inoculated with complexes ($100 \mu\text{g cm}^{-3}$) one hour after infection with *C. albicans* (* = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$).

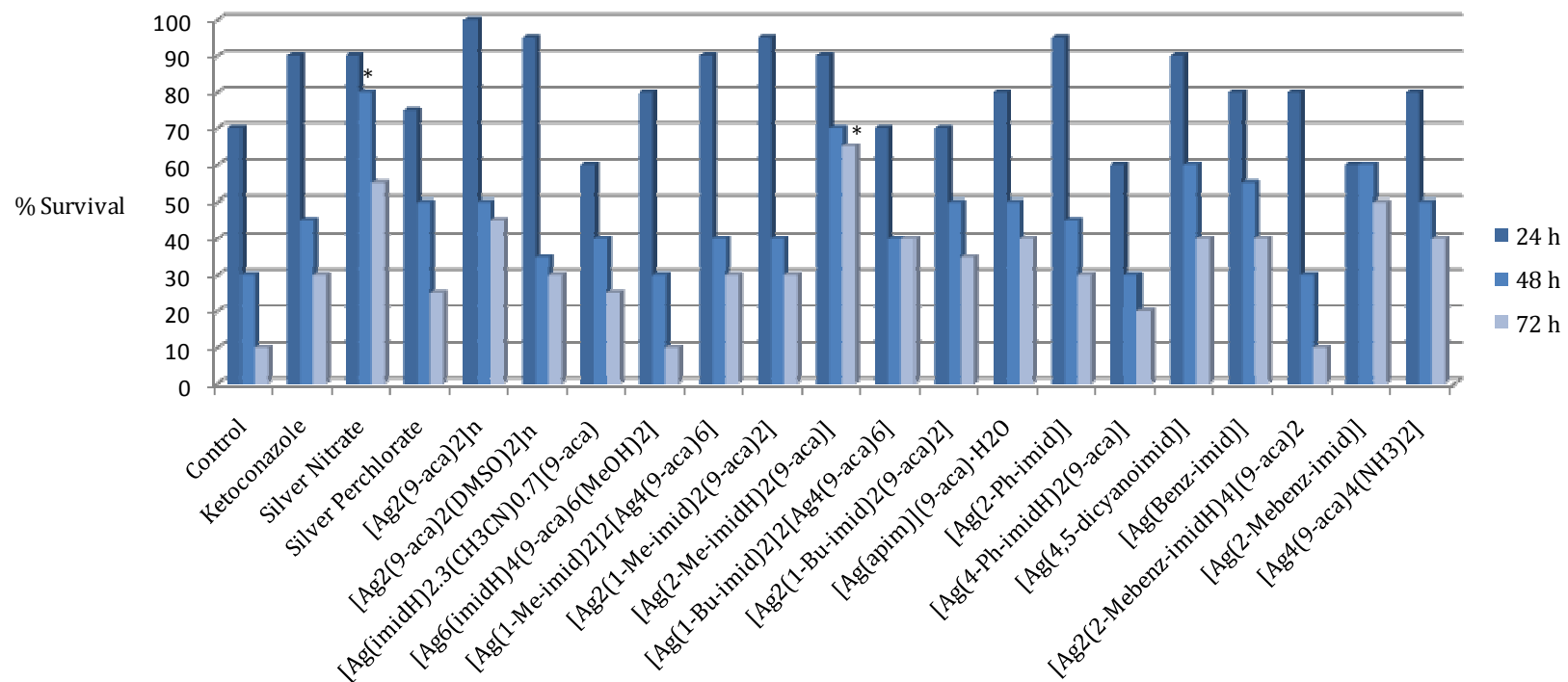


Figure 112. Percentage survival of *G. mellonella* larvae inoculated with complexes ($10 \mu\text{g cm}^{-3}$) one hour after infection with *C. albicans* (* = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$).

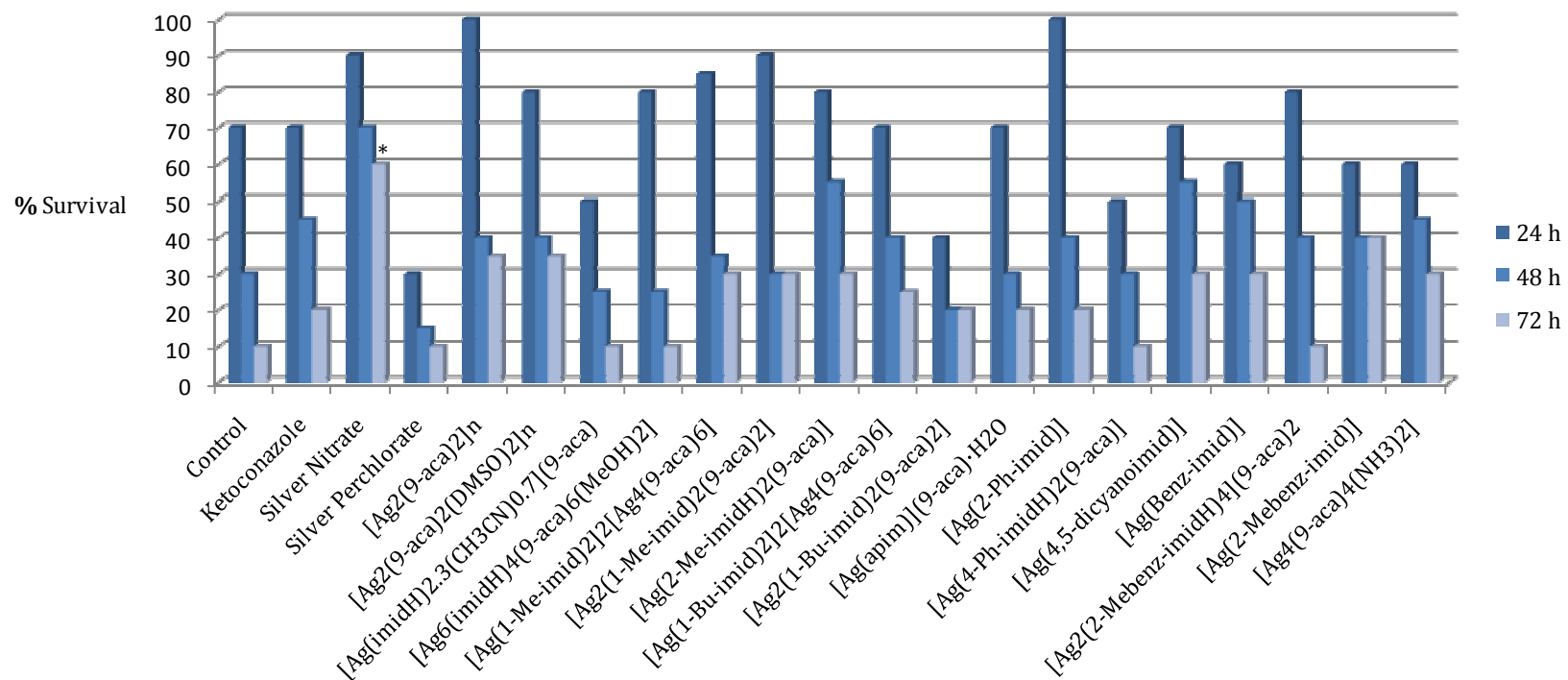


Figure 113. Percentage survival of *G. mellonella* larvae inoculated with complexes (concentration twice the MIC₁₀₀ value) one hour after infection with *C. albicans* (* = p<0.05, ** = p<0.01, *** = p<0.001).

4.4 *In vitro* Antibacterial Screening

In a similar manner to that described for fungal growth, bacterial growth can be divided into four phases: the lag phase, exponential phase, stationary phase and death phase (Figure 104). Bacterial cells replicate faster than fungal cells so the exponential and stationary phases are reached more quickly.

Silver(I) complexes, the simple salts silver nitrate and silver perchlorate, and the commercial reference standard, silver(I) sulfadiazine, were screened for their ability to inhibit the growth of Gram-negative *E. coli* and Gram-positive MRSA. All test solutions were made by dissolving the complex in DMSO (1 cm⁻³) and diluting with water to yield the required concentration. The maximum DMSO concentration in any sample was 0.5% v/v, a concentration which does not inhibit the growth of the bacterial cells. The metal-free ligands were also screened for their antibacterial activity and all proved to be inactive at a concentration of 100 µg cm⁻³. The MIC₅₀ value was calculated for all test solutions and results are shown in Tables 12 and 13, and Figure 114.

Of the silver(I) complexes that were screened against *E. coli*, all but three were more active than silver sulfadiazine (MIC₅₀ = 73.05 µM). When tested against MRSA, five of the silver(I) complexes proved less cytotoxic than silver sulfadiazine. The simple silver salts, AgNO₃ and AgClO₄, were more cytotoxic than silver sulfadiazine against both strains of bacteria (MIC₅₀ = 65.19 and 51.95 µM for *E. coli* and MIC₅₀ = 34.32 and 37.09 µM for MRSA, respectively).

The most effective of the silver(I) complexes at inhibiting the growth of *E. coli* was [Ag₆(imidH)₄(9-aca)₆(MeOH)₂] (1.87 µM). The complex was *ca.* 39 times more active than silver sulfadiazine and *ca.* 27 times more active than AgNO₃ and AgClO₄. When activity per Ag⁺ ion was examined, [Ag₆(imidH)₄(9-aca)₆(MeOH)₂] was still the most cytotoxic towards *E. coli* (MIC₅₀ = 11.22 µM). This complex also exhibited good activity against MRSA (MIC₅₀ = 5.85 µM), exhibiting cytotoxicity over 8 times greater than that of silver sulfadiazine and *ca.* 6 times more active than AgNO₃ (MIC₅₀ = 50.20 and 34.32 µM, respectively).

The ammonia-containing complex, $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$, proved to be the most effective silver(I) complex at inhibiting the growth of MRSA at both μM concentration of complex and μM concentration of Ag^+ levels ($\text{MIC}_{50} = 5.44 \mu\text{M}$, $21.76 \mu\text{M Ag}^+$). This complex has an MIC_{50} value *ca.* 9 times greater than that of silver sulfadiazine ($\text{MIC}_{50} = 73.05 \mu\text{M}$). A similar high level of activity was observed against *E. coli* ($\text{MIC}_{50} = 8.51 \mu\text{M}$).

The structurally similar complex salts, $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ and $[\text{Ag}(1\text{-Bu-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$, had similar antibacterial properties. Against both *E. coli* and MRSA, $[\text{Ag}(1\text{-Bu-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ proved more cytotoxic than $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ ($\text{MIC}_{50} = 7.04$ and $8.64 \mu\text{M}$ for *E. coli*, $\text{MIC}_{50} = 6.16$ and $8.10 \mu\text{M}$ for MRSA, respectively). $[\text{Ag}(1\text{-Bu-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ was also *ca.* 10 times more active against *E. coli* and *ca.* 7 times more cytotoxic against MRSA than silver sulfadiazine.

The other 1-Me-imid- and 1-Bu-imid-containing compounds, $[\text{Ag}_2(1\text{-Me-imid})_2(9\text{-aca})_2]$ and $[\text{Ag}_2(1\text{-Bu-imid})_2(9\text{-aca})_2]$, were also active at inhibiting bacterial growth (MIC_{50} of $[\text{Ag}_2(1\text{-Me-imid})_2(9\text{-aca})_2] = 16.82$ and $35.22 \mu\text{M}$, MIC_{50} of $[\text{Ag}_2(1\text{-Bu-imid})_2(9\text{-aca})_2] = 13.89$ and $16.98 \mu\text{M}$, against *E. coli* and MRSA, respectively). Both of these complexes were more active than silver sulfadiazine, AgNO_3 and AgClO_4 , and, as observed for $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ and $[\text{Ag}(1\text{-Bu-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$, the 1-Bu-imid complex showed greater antibacterial activity than the 1-Me-imid complex. This would appear to confirm earlier suggestions that the length of the alkyl chain may influence the mode of interaction of these molecules with the microorganism.

The imidazole-free silver(I) complexes, $[\text{Ag}_2(9\text{-aca})_2]_n$ and $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$, proved to be cytotoxic towards both *E. coli* and MRSA. Against *E. coli*, $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ was twice as active as $[\text{Ag}_2(9\text{-aca})_2]_n$ ($\text{MIC}_{50} = 11.06$ and $22.44 \mu\text{M}$, respectively) and both were more active towards the two bacterial pathogens than silver sulfadiazine, AgNO_3 and AgClO_4 ($\text{MIC}_{50} = 73.05$,

Table 12. Minimum inhibitory concentrations (MIC₅₀) of silver(I) complexes against *E. coli*.

| Complex (#poor solubility) | MIC ₅₀ (μg cm ⁻³) | MIC ₅₀ (μM) | MIC ₅₀ (μM Ag ⁺) |
|--|---|---------------------------|--|
| Silver sulfadiazine [#] | 26.09 | 73.05 | 73.05 |
| AgNO ₃ | 11.08 | 65.19 | 65.19 |
| AgClO ₄ | 10.77 | 51.95 | 51.95 |
| [Ag ₂ (9-aca) ₂] _n | 14.77 | 22.44 | 44.88 |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | 9.01 | 11.06 | 22.12 |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | 10.63 | 20.66 | 20.66 |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | 4.32 | 1.87 | 11.22 |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | 19.89 | 8.64 | 51.84 |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | 13.83 | 16.82 | 33.64 |
| [Ag(2-Me-imidH) ₂ (9-aca)] | 11.28 | 22.87 | 22.87 |
| [Ag(1-Bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | 17.39 | 7.04 | 42.24 |
| [Ag ₂ (1-Bu-imid) ₂ (9-aca) ₂] | 12.59 | 13.89 | 27.78 |
| [Ag(apim)](9-aca)·H ₂ O | 14.23 | 30.13 | 30.13 |
| [Ag(2-Ph-imid)] [#] | 37.60 | 149.77 | 149.77 |
| [Ag(4-Ph-imidH) ₂ (9-aca)] | 31.00 | 50.21 | 50.21 |
| [Ag(4,5-dicyanoimid)] [#] | 28.75 | 127.22 | 127.22 |
| [Ag(Benz-imid)] [#] | 31.26 | 138.93 | 138.93 |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ | 15.40 | 12.98 | 25.96 |
| [Ag(2-Mebenz-imid)] [#] | 8.64 | 36.14 | 36.14 |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] | 11.49 | 8.51 | 34.04 |

Table 13. Minimum inhibitory concentrations (MIC₅₀) of silver(I) complexes against MRSA.

| Complex (#poor solubility) | MIC ₅₀ (μg cm ⁻³) | MIC ₅₀ (μM) | MIC ₅₀ (μM Ag ⁺) |
|--|---|---------------------------|--|
| Silver sulfadiazine [#] | 17.93 | 50.20 | 50.20 |
| AgNO ₃ | 5.83 | 34.32 | 34.32 |
| AgClO ₄ | 7.69 | 37.09 | 37.09 |
| [Ag ₂ (9-aca) ₂] _n | 7.48 | 11.36 | 22.72 |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | 18.23 | 22.38 | 44.76 |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | 34.50 | 67.07 | 67.07 |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | 13.53 | 5.85 | 35.10 |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | 18.65 | 8.10 | 48.60 |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | 28.97 | 35.22 | 70.44 |
| [Ag(2-Me-imidH) ₂ (9-aca)] | 17.04 | 34.54 | 34.54 |
| [Ag(1-Bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | 15.23 | 6.16 | 36.96 |
| [Ag ₂ (1-Bu-imid) ₂ (9-aca) ₂] | 15.39 | 16.98 | 33.96 |
| [Ag(apim)](9-aca)·H ₂ O | 12.99 | 27.50 | 27.50 |
| [Ag(2-Ph-imid)] [#] | 19.10 | 76.08 | 76.08 |
| [Ag(4-Ph-imidH) ₂ (9-aca)] | 30.40 | 49.23 | 49.23 |
| [Ag(4,5-dicyanoimid)] [#] | 55.25 | 244.49 | 244.49 |
| [Ag(Benz-imid)] [#] | 38.64 | 171.73 | 171.73 |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ | 17.70 | 14.91 | 29.82 |
| [Ag(2-Mebenz-imid)] [#] | 12.48 | 52.21 | 52.21 |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] | 7.34 | 5.44 | 21.76 |

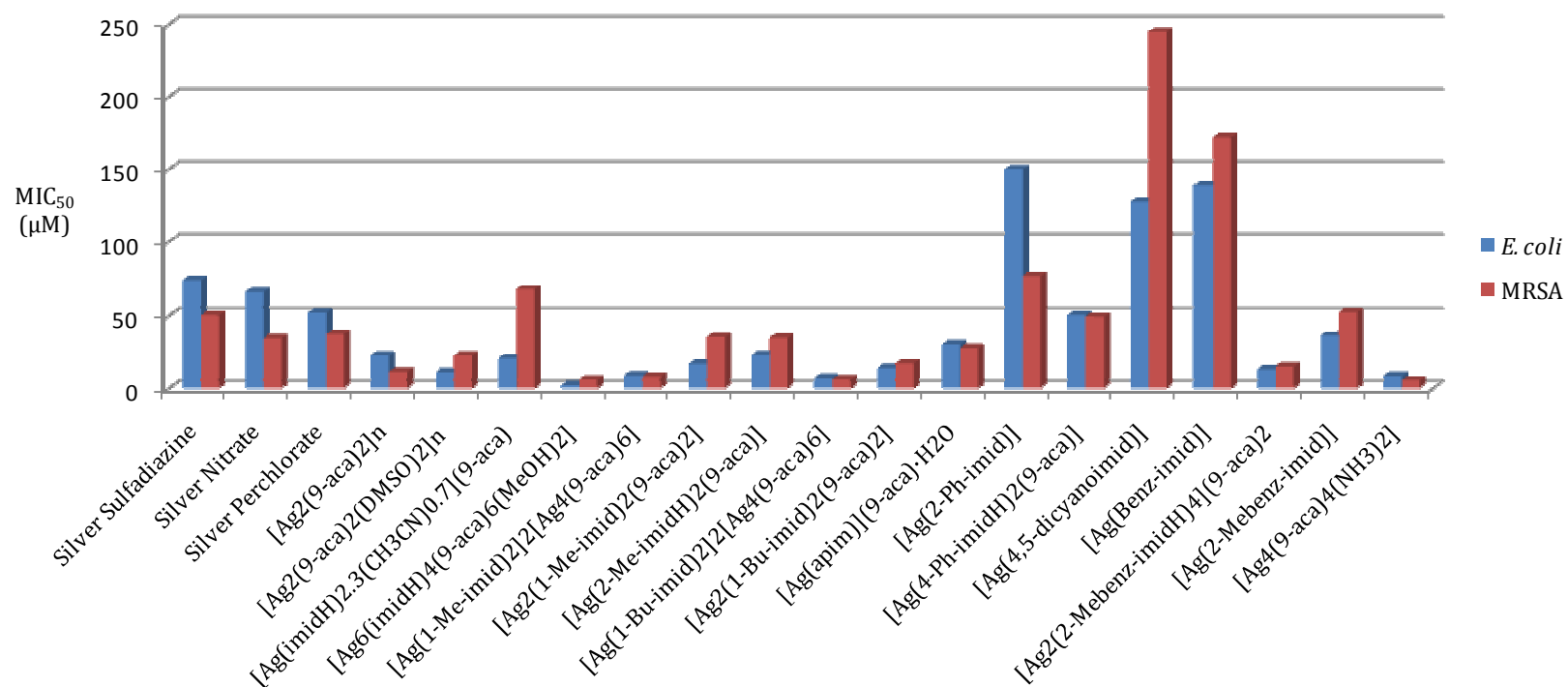


Figure 114. MIC₅₀ values of silver complexes against *E. coli* and MRSA.

65.19 and 51.95 μM , respectively). The reverse trend was observed for the activity of these two complexes against MRSA, with $[\text{Ag}_2(9\text{-aca})_2]_n$ being *ca.* 2 times more cytotoxic than $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ (MIC_{50} of 11.36 and 22.38 μM , respectively). The reasons for this difference in activity towards these bacterial strains have yet to be uncovered, but they may be linked to the difference in the structure of their cell walls. *E. coli* is a Gram-negative bacterium whose cell wall consists of a few layers of peptidoglycan and an outer membrane of various lipid complexes. MRSA, a Gram-positive bacterium, has a cell wall containing many layers of peptidoglycan and no lipid outer membrane. The presence or absence of this lipid membrane may significantly influence the absorbance of the drug molecules into the cell.

$[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$ ($\text{MIC}_{50} = 20.66 \mu\text{M}$) was *ca.* 3 times more active than silver sulfadiazine against *E. coli*. However, the complex was substantially less cytotoxic towards MRSA ($\text{MIC}_{50} = 67.07 \mu\text{M}$), with AgNO_3 and AgClO_4 being approximately twice as active. $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$ also proved to be twice as active as silver sulfadiazine at inhibiting the growth of both *E. coli* and MRSA ($\text{MIC}_{50} = 30.13$ and $27.50 \mu\text{M}$ against *E. coli* and MRSA, respectively).

The 2-Mebenz-imidH complexes, $(\text{Ag}_2(2\text{-Mebenz-imidH})_4)(9\text{-aca})_2$ and $[\text{Ag}(2\text{-Mebenz-imidH})]_2(9\text{-aca})_2$, both exhibited good antibacterial properties when screened against *E. coli*, with the anthracene complex proving to be more active ($\text{MIC}_{50} = 12.98$ and $36.14 \mu\text{M}$, respectively). The same trend was observed in tests against MRSA ($\text{MIC}_{50} = 14.91$ and $52.21 \mu\text{M}$, respectively). This superior antibacterial activity of $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ over $[\text{Ag}(2\text{-Mebenz-imidH})]_2(9\text{-aca})_2$ may be due to its greater solubility and thus the ease of release of Ag^+ from the complex.

$[\text{Ag}(2\text{-Me-imidH})_2(9\text{-aca})]$ contains a three-coordinate silver(I) ion and although it is thought that this coordination is also present in $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$, the two complexes show varied antibacterial properties. Against *E. coli*, $[\text{Ag}(2\text{-Me-imidH})_2(9\text{-aca})]$ is *ca.* 3 times more active than silver sulfadiazine and is twice as cytotoxic as $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$ ($\text{MIC}_{50} =$

22.87 and 50.21 μM , respectively). These two compounds are also effective at inhibiting the growth of MRSA (MIC_{50} of 34.54 and 49.23 μM , respectively) and are as active as silver sulfadiazine, AgNO_3 and AgClO_4 (MIC_{50} of 50.20, 34.32 and 37.09 μM , respectively).

The imidazolate complexes, $[\text{Ag}(2\text{-Ph-imid})]$, $[\text{Ag}(4,5\text{-dicyanoimid})]$ and $[\text{Ag}(\text{Benz-imid})]$, which all contain deprotonated imidazole rings, exhibit similar antibacterial activities. Against *E. coli*, all three complexes have MIC_{50} values in excess of 125 μM (149.77, 127.22 and 138.93 μM for $[\text{Ag}(2\text{-Ph-imid})]$, $[\text{Ag}(4,5\text{-dicyanoimid})]$ and $[\text{Ag}(\text{Benz-imid})]$, respectively). This activity is significantly less than that of silver sulfadiazine, AgNO_3 and AgClO_4 . A similar trend was observed against MRSA (MIC_{50} of 76.08, 244.49 and 171.73 μM for $[\text{Ag}(2\text{-Ph-imid})]$, $[\text{Ag}(4,5\text{-dicyanoimid})]$ and $[\text{Ag}(\text{Benz-imid})]$, respectively). It is thought that these complexes, with their proposed polymeric structures, may be reluctant to release their bioactive Ag^+ ions.

4.5 *In vitro* Anticancer Screening

In vitro anticancer screening was carried out using selected silver(I) complexes on:

- (i) MCF-7, human breast adenocarcinoma cell line.
- (ii) HT-29, human colon adenocarcinoma cell line.
- (iii) Hep-G₂, human hepatocellular carcinoma cell line.
- (iv) A-498, human kidney adenocarcinoma cell line.

The results of these studies are presented in Tables 14-16 and Figures 115 and 116.

All of the silver(I) complexes, the simple silver salt AgNO_3 , the metal-based anticancer drug Cisplatin and the anthracene-containing anticancer drug Mitoxantrone were screened against the MCF-7 and HT-29 cancer cell lines.

Cisplatin did not stop the proliferation of MCF-7 and HT-29 cells at a concentration of 100 μM . Mitoxantrone and the simple silver(I) salt, AgNO_3 , was moderately active against MCF-7 and HT-29 cells (Mitoxantrone $\text{IC}_{50} = 44.10$ and $76.90 \mu\text{M}$, AgNO_3 $\text{IC}_{50} = 49.00$ and $55.60 \mu\text{M}$, for MCF-7 and HT-29, respectively). The metal-free ligands were all inactive at a concentration of 100 μM .

Although all of the new silver(I) complexes decreased the growth of the MCF-7 cell line, the most active were $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$, $[\text{Ag}(1\text{-Bu-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$, $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$ and $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ (IC_{50} value of 6.30, 6.30, 6.50 and $7.16 \mu\text{M}$, respectively). These four complexes were *ca.* 7 times more active than Mitoxantrone and *ca.* 8 times more active than AgNO_3 . $[\text{Ag}_2(1\text{-Bu-imid})_2(9\text{-aca})_2]$ and $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$ ($\text{IC}_{50} = 19.08$ and $17.27 \mu\text{M}$, respectively) were also found to be active, but a decrease in activity was observed for the methyl-substituted imidazole complexes, $[\text{Ag}_2(1\text{-Me-imid})_2(9\text{-aca})_2]$ and $[\text{Ag}(2\text{-Me-imidH})_2(9\text{-aca})]$ ($\text{IC}_{50} = 59.70$ and $64.80 \mu\text{M}$, respectively) and also the imidazole-free silver(I) carboxylate complexes, $[\text{Ag}_2(9\text{-aca})_2]_n$ and $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ (IC_{50} value of 57.33, $54.70 \mu\text{M}$, respectively). $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$, $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$ and $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ ($\text{IC}_{50} = 62.20$, 64.00 and $51.30 \mu\text{M}$) were also less active than Mitoxantrone and AgNO_3 ($\text{IC}_{50} = 44.10$ and $49.00 \mu\text{M}$, respectively) against MCF-7 cells.

The polymeric imidazolate complexes $[\text{Ag}(4,5\text{-dicyanoimid})]$ and $[\text{Ag}(\text{Benz-imid})]$, were found to have activities similar to the silver(I) complexes mentioned above ($\text{IC}_{50} = 62.80$ and $64.60 \mu\text{M}$, respectively), while the other two polymeric imidazolate complexes, $[\text{Ag}(2\text{-Ph-imid})]$ and $[\text{Ag}(2\text{-Mebenz-imid})]$ ($\text{IC}_{50} = 40.80$ and $47.40 \mu\text{M}$, respectively), were found to be marginally more cytotoxic towards MCF-7 cells with an IC_{50} comparable to that of Mitoxantrone.

Table 14. Minimum inhibitory concentrations (IC₅₀) of silver(I) complexes against MCF-7 cell line.

| Complex (#poor solubility) | IC ₅₀ ($\mu\text{g cm}^{-3}$) | IC ₅₀ (μM) | IC ₅₀ ($\mu\text{M Ag}^+$) |
|--|---|---------------------------------------|--|
| Cisplatin | N/A | >100 | N/A |
| Mitoxantrone | 19.47 (± 1.15) | 44.10 (± 2.60) | N/A |
| AgNO ₃ | 8.32 (± 2.50) | 49.00 (± 14.70) | 49.00 |
| [Ag ₂ (9-aca) ₂] _n | 37.73 (± 0.72) | 57.33 (± 1.09) | 114.66 |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | 44.55 (± 4.40) | 54.70 (± 5.40) | 109.40 |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | 32.00 (± 2.01) | 62.20 (± 3.90) | 62.20 |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | 14.56 (± 1.39) | 6.30 (± 0.60) | 37.80 |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | 14.97 (± 0.67) | 6.50 (± 0.29) | 39.00 |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | 49.10 (± 2.06) | 59.70 (± 2.50) | 119.40 |
| [Ag(2-Me-imidH) ₂ (9-aca)] | 31.97 (± 2.47) | 64.80 (± 5.00) | 64.80 |
| [Ag(1-Bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | 15.57 (± 0.74) | 6.30 (± 0.30) | 37.80 |
| [Ag ₂ (1-Bu-imid) ₂ (9-aca) ₂] | 17.30 (± 2.47) | 19.08 (± 1.10) | 38.16 |
| [Ag(apim)](9-aca)·H ₂ O | 30.23 (± 3.02) | 64.00 (± 6.40) | 64.00 |
| [Ag(2-Ph-imid)] [#] | 10.24 (± 1.86) | 40.80 (± 7.40) | 40.80 |
| [Ag(4-Ph-imidH) ₂ (9-aca)] | 10.66 (± 1.25) | 17.27 (± 2.02) | 17.27 |
| [Ag(4,5-dicyanoimid)] [#] | 14.13 (± 1.51) | 62.80 (± 6.70) | 62.80 |
| [Ag(Benz-imid)] [#] | 14.54 (± 0.90) | 64.60 (± 4.00) | 64.60 |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ | 60.87 (± 5.22) | 51.30 (± 4.40) | 102.60 |
| [Ag(2-Mebenz-imid)] [#] | 11.33 (± 0.54) | 47.40 (± 2.26) | 47.40 |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] | 9.67 (± 0.59) | 7.16 (± 0.44) | 28.64 |

Table 15. Minimum inhibitory concentrations (IC₅₀) of silver(I) complexes against HT-29 cell line.

| Complex (#poor solubility) | IC ₅₀ ($\mu\text{g cm}^{-3}$) | IC ₅₀ (μM) | IC ₅₀ ($\mu\text{M Ag}^+$) |
|--|---|---------------------------------------|--|
| Cisplatin | N/A | >100 | N/A |
| Mitoxantrone | 33.95 (± 2.47) | 76.90 (± 5.60) | N/A |
| AgNO ₃ | 9.45 (± 0.31) | 55.60 (± 1.80) | 55.60 |
| [Ag ₂ (9-aca) ₂] _n | 36.86 (± 0.05) | 56.00 (± 0.76) | 112.00 |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | 43.82 (± 1.82) | 53.80 (± 2.24) | 107.60 |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | 35.29 (± 0.93) | 68.60 (± 1.80) | 68.60 |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | 108.62 (± 18.72) | 47.00 (± 8.10) | 282.00 |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | 135.49 (± 10.00) | 58.83 (± 4.34) | 352.98 |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | 48.20 (± 0.49) | 58.60 (± 0.60) | 117.20 |
| [Ag(2-Me-imidH) ₂ (9-aca)] | 33.35 (± 0.92) | 67.60 (± 1.86) | 67.60 |
| [Ag(1-Bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | 150.26 (± 7.66) | 60.80 (± 3.10) | 364.80 |
| [Ag ₂ (1-Bu-imid) ₂ (9-aca) ₂] | 135.92 (± 4.20) | 149.93 (± 1.88) | 299.86 |
| [Ag(apim)](9-aca)·H ₂ O | 25.27 (± 2.49) | 53.50 (± 5.27) | 53.50 |
| [Ag(2-Ph-imid)] [#] | 14.18 (± 1.05) | 56.50 (± 4.20) | 56.50 |
| [Ag(4-Ph-imidH) ₂ (9-aca)] | 9.71 (± 0.11) | 15.73 (± 0.18) | 15.73 |
| [Ag(4,5-dicyanoimid)] [#] | 15.75 (± 2.47) | 70.00 (± 11.00) | 70.00 |
| [Ag(Benz-imid)] [#] | 13.21 (± 0.14) | 58.70 (± 0.60) | 58.70 |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ | 74.77 (± 1.31) | 63.00 (± 1.10) | 126.00 |
| [Ag(2-Mebenz-imid)] [#] | 102.70 (± 2.55) | 429.64 (± 10.67) | 429.64 |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] | 79.22 (± 3.15) | 58.66 (± 2.33) | 234.64 |

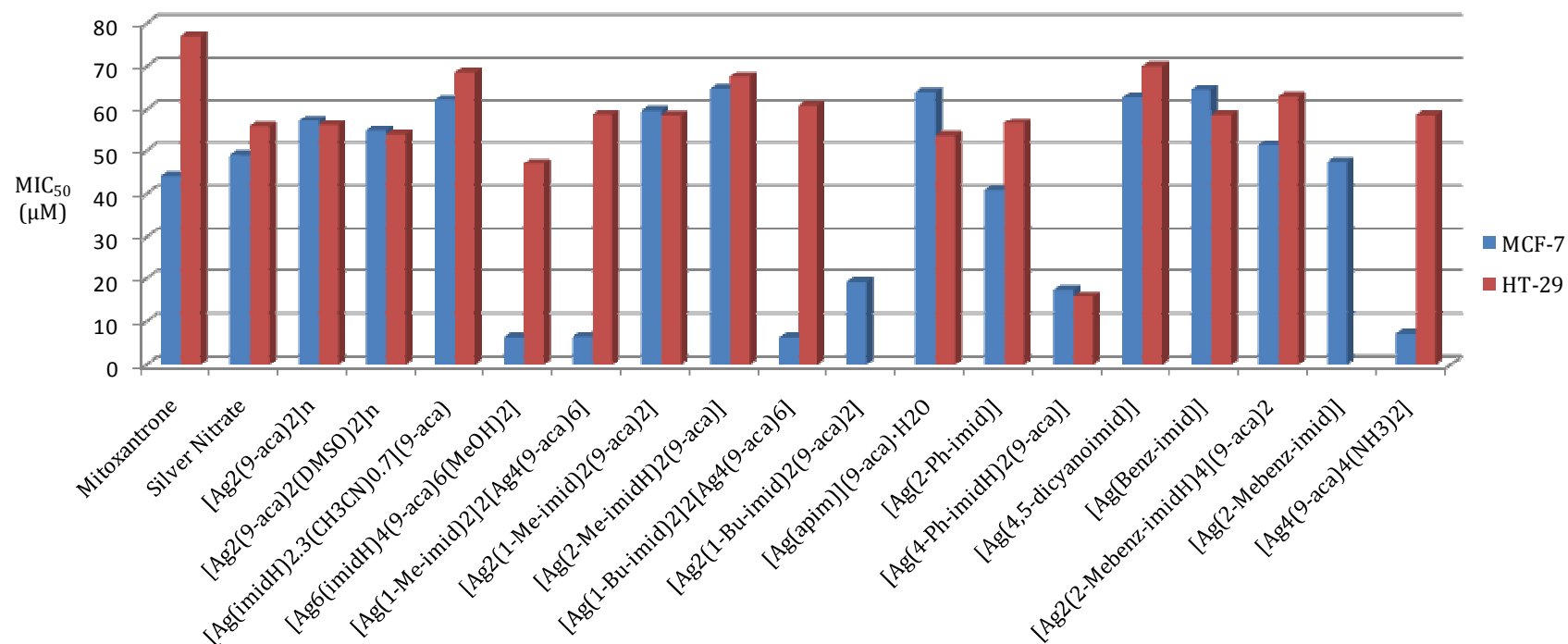


Figure 115. IC₅₀ values of silver(I) complexes against MCF-7 and HT-29 cell lines (HT-29 values of [Ag₂(1-Bu-imid)₂(9-aca)₂] and [Ag(2-Mebenz-imid)] not shown as >100 µM).

Although most of the silver(I) complexes were more active than Cisplatin against HT-29 cells only [Ag(4-Ph-imidH)₂(9-aca)] (IC₅₀ = 15.73 μM) was significantly more active than AgNO₃ (IC₅₀ = 55.60 μM). [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆] and [Ag(2-Mebenz-imid)] had the lowest activity (IC₅₀ = 149.93 and 429.64 μM, respectively). The remaining silver(I) complexes had IC₅₀ values similar to AgNO₃ (IC₅₀ ≈ 55 μM).

Overall, [Ag₆(imidH)₄(9-aca)₆(MeOH)₂] was the most active of the silver(I) complexes against both MCF-7 and HT-29 cell lines (IC₅₀ = 6.30 and 47.00 μM, respectively) and it exhibited a higher selectivity towards MCF-7 cells.

Cisplatin, [Ag₂(9-aca)₂]_n and [Ag₄(9-aca)₄(NH₃)₂] were also screened against Hep-G₂ and A-498 cell lines (Table 16 and Figure 116). The metal-free ligand, 9-acaH, was found to be inactive at the 100 μM concentration level. While both of the silver-containing complexes decreased the proliferation of the Hep-G₂ and A-498 cell lines, [Ag₄(9-aca)₄(NH₃)₂] was the most active (IC₅₀ = 3.60 and 5.50 μM for Hep-G₂ and A-498 cell lines, respectively). This ammonia-containing complex was 4 times more active than Cisplatin against Hep-G₂ cells and over twice as active against A-498 cells. [Ag₂(9-aca)₂]_n (IC₅₀ = 27.80 and 30.00 μM for the Hep-G₂ and A-498 cell lines, respectively) was less active than Cisplatin against both cell lines.

Table 16. IC₅₀ values of [Ag₂(9-aca)₂]_n and [Ag₄(9-aca)₄(NH₃)₂] against Hep-G₂ and A-498 cell lines.

| Complex (#poor solubility) | Hep-G ₂ IC ₅₀ (μg cm ⁻³) | Hep-G ₂ IC ₅₀ (μM) | A-498 IC ₅₀ (μg cm ⁻³) | A-498 IC ₅₀ (μM) |
|---|--|--|---|-----------------------------------|
| Cisplatin | 4.50 | 15.00 | 4.20 | 14.00 |
| [Ag ₂ (9-aca) ₂] _n | 18.30 | 27.80 | 19.75 | 30.00 |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] | 4.86 | 3.60 | 7.43 | 5.50 |

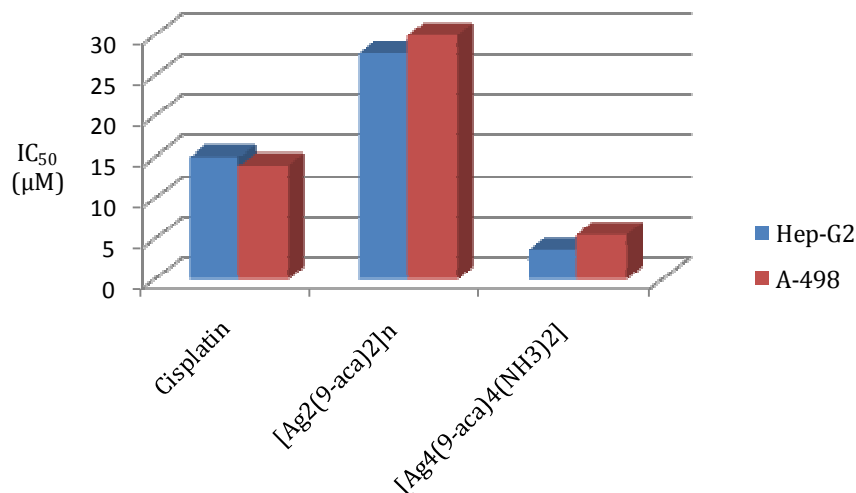


Figure 116. IC₅₀ values of [Ag₂(9-aca)₂]_n and [Ag₄(9-aca)₄(NH₃)₂] against Hep-G₂ and A-498 cell lines.

4.6 Summary of Biological Activity

The majority of the silver(I) complexes synthesised during this research exhibited very good antimicrobial and anticancer activities. In many cases, these complexes performed better than the current prescription drugs. While many complexes were shown to exhibit both excellent antifungal and antibacterial activities (e.g. [Ag₄(9-aca)₄(NH₃)₂]), others were more selective (e.g. [Ag(apim)](9-aca)·H₂O was highly cytotoxic towards fungal cells but not as active against bacterial cells).

In tests against cancer cell lines it was found that, in general, the silver(I) complexes were more cytotoxic towards breast cancer cells than colon cancer cells, thus showing some degree of selectivity. One notable exception to this trend was [Ag(4-Ph-imidH)₂(9-aca)], which was equally active against both MCF-7 and HT-29 cell lines. The varied activity of the silver(I) complexes indicates that the presence of the silver(I) ion alone does not necessarily guarantee good antimicrobial and anticancer activity, but that the nature of the ligands coordinated to the metal also influences activity. It would appear that

the bioactivity is attributable to the complex as a whole, rather than to the individual constituents acting independently of each other.

To date, the mechanisms of action of the silver(I) complexes prepared in the present work have not been examined. However, it is thought that these complexes may have similar modes of action as other silver(I) complexes studied by our group. For example, treating *C. albicans* with $[\text{Ag}_2(\text{phen})_3(\text{mal})]\cdot 2\text{H}_2\text{O}$ (phen = 1,10-phenanthroline, malH₂ = malonic acid) resulted in DNA degradation and induced extensive changes to the internal structure of the yeast cells, including retraction of the cytoplasm, nuclear fragmentation and disruption of the mitochondrion¹²³. This complex was also shown to reduce the levels of cytochromes b and c, as well as the concentration of ergosterol within the cell¹⁶⁶. $[\text{Ag}(\text{phendio})_2]\text{ClO}_4$ (phendio = 1,10-phenanthroline-5,6-dione) also caused extensive, non-specific DNA cleavage, induced gross distortions in fungal cell morphology and disrupted cell division¹²⁷.

Silver(I)-coumarin complexes have also been reported to reduce respiration, lower the ergosterol content of *C. albicans* cells and increase the trans-membrane leakage of amino acids from the cell¹³⁰. Silver(I) has been reported to accumulate in the cell wall of *C. albicans* cells, with complexes, such as $[\text{Ag}(\text{apim})]\text{ClO}_4$, depositing *ca.* 7 times more Ag⁺ than the simple silver salts AgNO₃ and AgClO₄¹⁶⁷. Recently, silver(0) nano-particles have been reported to exert antifungal activity by disrupting the structure of the cell membrane, inhibiting the normal budding process of *C. albicans* and these effects contributed to the destruction of the membrane integrity¹⁶⁸.

Investigations into the effect of silver(I) on bacterial cells revealed that it interacts with the respiratory chain of bacterial cells¹⁶⁹. Silver(I) has also been reported to react with nucleophilic portions of amino acids and cause denaturing of the proteins and, ultimately, leads to cell death¹³⁹. Electron microscopy and X-ray microanalysis have shown that silver builds up as granules in the cell wall and in the cytoplasm of *E. coli* and *S. aureus*^{170,171}. This

causes damage to the RNA and DNA, and proteins are deactivated within the cell. The mode of action of silver(I) complexes against human cancer cells has also been studied. $[\text{Ag}_2(\text{phen})_3(\text{mal})] \cdot 2\text{H}_2\text{O}$ and silver(I)-coumarin complexes were shown to inhibit DNA synthesis without intercalating with it and cell death occurred primarily in the form of apoptosis^{72,79,80,172,173}.

Concluding Remarks

This research project has shown that silver(I) complexes containing 9-anthracenecarboxylic acid and imidazoles are readily synthesised from widely available starting materials. By varying the reaction conditions and functional groups on the starting materials it is possible to obtain a range of silver(I) complexes with a wide variety of structures, ranging from mononuclear to hexanuclear, and from complex salts to polymeric chains.

The silver(I) complexes possess antimicrobial and anticancer properties, and in many cases they perform better than the currently prescribed drugs. The silver(I) complex, $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$, exhibited the broadest spectrum of *in vitro* biological activity. It was cytotoxic towards fungal cells, bacterial cells and human cancer cells. The complex also displayed excellent *in vivo* activity when tested on the insect model, *G. mellonella*. It is thought that the complexes have a mode of action distinct from that of current antimicrobial and anticancer drugs, an attribute that could prove extremely useful when combating drug-resistant cells.

Although much has been reported in this thesis, there remains much scope for further research in this area. Future work would include detailed mode of action studies. This would provide valuable information regarding the specific cellular targets that the complexes are reaching and could lead to the design and synthesis of even more efficient silver(I) complexes

Appendix

X-ray Crystal Data for [Ag₂(9-aca)₂]_n

| | |
|-----------------------------------|--|
| Identification code | [Ag ₂ (9-aca) ₂] _n |
| Empirical formula | C ₃₀ H ₁₈ Ag ₂ O ₄ |
| Formula weight | 658.18 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | a = 14.813(3) Å α = 90°. b = 5.6055(12) Å β = 95.250(3)°. c = 27.413(6) Å γ = 90°. |
| Volume | 2266.6(8) Å ³ |
| Z | 4 |
| Density (calculated) | 1.929 Mg/m ³ |
| Absorption coefficient | 1.766 mm ⁻¹ |
| F(000) | 1296 |
| Crystal size | 0.57 x 0.05 x 0.02 mm ³ |
| Crystal description | yellow rod |
| Theta range for data collection | 1.94 to 25.00°. |
| Index ranges | -17 ≤ h ≤ 17, -6 ≤ k ≤ 6, -32 ≤ l ≤ 32 |
| Reflections collected | 16694 |
| Independent reflections | 3991 [R(int) = 0.0520] |
| Completeness to theta = 25.00° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9655 and 0.4326 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 3991 / 0 / 325 |
| Goodness-of-fit on F ² | 1.020 |
| Final R indices [I > 2σ(I)] | R1 = 0.0374, wR2 = 0.0854 |
| R indices (all data) | R1 = 0.0610, wR2 = 0.0979 |
| Largest diff. peak and hole | 0.913 and -0.917 e.Å ⁻³ |

Table 17: Bond lengths [Å] and angles [°] for [Ag₂(9-aca)₂]_n.

| | | | |
|----------------------|------------|-----------------|-----------|
| Ag(1)-O(1) | 2.170(3) | Ag(2)-O(3) | 2.190(3) |
| Ag(1)-O(2)#1 | 2.190(3) | Ag(2)-O(4)#4 | 2.243(3) |
| Ag(1)-O(2)#2 | 2.473(4) | Ag(2)-O(4)#3 | 2.381(4) |
| Ag(1)-Ag(1)#1 | 2.8508(9) | Ag(2)-Ag(2)#4 | 2.8643(9) |
| O(1)-C(1) | 1.242(6) | O(3)-C(16) | 1.239(6) |
| O(2)-C(1) | 1.267(6) | O(4)-C(16) | 1.257(6) |
| O(2)-Ag(1)#1 | 2.190(3) | O(4)-Ag(2)#4 | 2.243(3) |
| O(2)-Ag(1)#3 | 2.473(4) | O(4)-Ag(2)#2 | 2.381(4) |
| C(1)-C(2) | 1.504(7) | C(16)-C(17) | 1.526(6) |
| C(2)-C(3) | 1.407(7) | C(17)-C(18) | 1.385(7) |
| C(2)-C(15) | 1.411(6) | C(17)-C(30) | 1.412(7) |
| C(3)-C(8) | 1.434(7) | C(18)-C(19) | 1.420(7) |
| C(3)-C(4) | 1.442(6) | C(18)-C(23) | 1.446(7) |
| C(4)-C(5) | 1.350(7) | C(19)-C(20) | 1.351(7) |
| C(5)-C(6) | 1.417(7) | C(20)-C(21) | 1.416(8) |
| C(6)-C(7) | 1.355(7) | C(21)-C(22) | 1.341(8) |
| C(7)-C(8) | 1.416(7) | C(22)-C(23) | 1.421(7) |
| C(8)-C(9) | 1.395(7) | C(23)-C(24) | 1.387(7) |
| C(9)-C(10) | 1.379(7) | C(24)-C(25) | 1.387(7) |
| C(10)-C(11) | 1.437(6) | C(25)-C(26) | 1.421(7) |
| C(10)-C(15) | 1.440(7) | C(25)-C(30) | 1.447(7) |
| C(11)-C(12) | 1.338(8) | C(26)-C(27) | 1.339(8) |
| C(12)-C(13) | 1.428(8) | C(27)-C(28) | 1.418(8) |
| C(13)-C(14) | 1.364(7) | C(28)-C(29) | 1.363(8) |
| C(14)-C(15) | 1.424(7) | C(29)-C(30) | 1.423(7) |
| | | O(1)-C(1)-O(2) | 126.1(5) |
| O(1)-Ag(1)-O(2)#1 | 162.20(13) | | |
| O(1)-Ag(1)-O(2)#2 | 116.66(12) | O(1)-C(1)-C(2) | 119.3(4) |
| O(2)#1-Ag(1)-O(2)#2 | 76.88(13) | O(2)-C(1)-C(2) | 114.6(4) |
| O(1)-Ag(1)-Ag(1)#1 | 84.41(9) | C(3)-C(2)-C(15) | 120.3(4) |
| O(2)#1-Ag(1)-Ag(1)#1 | 79.04(9) | C(3)-C(2)-C(1) | 118.3(4) |
| O(2)#2-Ag(1)-Ag(1)#1 | 150.72(8) | C(15)-C(2)-C(1) | 121.4(4) |
| C(1)-O(1)-Ag(1) | 120.3(3) | C(2)-C(3)-C(8) | 120.3(4) |
| C(1)-O(2)-Ag(1)#1 | 126.7(3) | C(2)-C(3)-C(4) | 123.2(4) |
| C(1)-O(2)-Ag(1)#3 | 127.6(3) | C(8)-C(3)-C(4) | 116.5(4) |
| Ag(1)#1-O(2)-Ag(1)#3 | 103.12(13) | C(5)-C(4)-C(3) | 121.3(5) |

| | | | |
|----------------------|------------|-------------------|----------|
| C(4)-C(5)-C(6) | 121.4(5) | O(3)-C(16)-O(4) | 126.1(5) |
| C(7)-C(6)-C(5) | 119.3(5) | O(3)-C(16)-C(17) | 118.6(4) |
| C(6)-C(7)-C(8) | 121.5(5) | O(4)-C(16)-C(17) | 115.2(4) |
| C(9)-C(8)-C(7) | 121.6(5) | C(18)-C(17)-C(30) | 121.5(5) |
| C(9)-C(8)-C(3) | 118.5(4) | C(18)-C(17)-C(16) | 120.1(4) |
| C(7)-C(8)-C(3) | 119.8(4) | C(30)-C(17)-C(16) | 118.2(4) |
| C(10)-C(9)-C(8) | 121.8(5) | C(17)-C(18)-C(19) | 123.5(5) |
| C(9)-C(10)-C(11) | 120.8(5) | C(17)-C(18)-C(23) | 119.4(5) |
| C(9)-C(10)-C(15) | 120.4(4) | C(19)-C(18)-C(23) | 117.1(4) |
| C(11)-C(10)-C(15) | 118.8(5) | C(20)-C(19)-C(18) | 121.9(5) |
| C(12)-C(11)-C(10) | 120.9(5) | C(19)-C(20)-C(21) | 120.3(5) |
| C(11)-C(12)-C(13) | 121.0(5) | C(22)-C(21)-C(20) | 120.6(5) |
| C(14)-C(13)-C(12) | 119.9(5) | C(21)-C(22)-C(23) | 121.1(5) |
| C(13)-C(14)-C(15) | 121.5(5) | C(24)-C(23)-C(22) | 122.6(5) |
| C(2)-C(15)-C(14) | 123.7(5) | C(24)-C(23)-C(18) | 118.4(5) |
| C(2)-C(15)-C(10) | 118.4(4) | C(22)-C(23)-C(18) | 119.0(5) |
| C(14)-C(15)-C(10) | 117.9(4) | C(25)-C(24)-C(23) | 123.1(5) |
| O(3)-Ag(2)-O(4)#4 | 163.19(13) | C(24)-C(25)-C(26) | 123.1(5) |
| O(3)-Ag(2)-O(4)#3 | 119.35(12) | C(24)-C(25)-C(30) | 118.5(5) |
| O(4)#4-Ag(2)-O(4)#3 | 77.20(13) | C(26)-C(25)-C(30) | 118.4(5) |
| O(3)-Ag(2)-Ag(2)#4 | 84.01(9) | C(27)-C(26)-C(25) | 121.9(5) |
| O(4)#4-Ag(2)-Ag(2)#4 | 79.39(9) | C(26)-C(27)-C(28) | 120.3(5) |
| O(4)#3-Ag(2)-Ag(2)#4 | 156.59(8) | C(29)-C(28)-C(27) | 120.3(5) |
| C(16)-O(3)-Ag(2) | 123.7(3) | C(28)-C(29)-C(30) | 121.3(5) |
| C(16)-O(4)-Ag(2)#4 | 126.6(3) | C(17)-C(30)-C(29) | 123.7(5) |
| C(16)-O(4)-Ag(2)#2 | 130.5(3) | C(17)-C(30)-C(25) | 118.6(5) |
| Ag(2)#4-O(4)-Ag(2)#2 | 102.80(13) | C(29)-C(30)-C(25) | 117.6(5) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z #2 x,y+1,z #3 x,y-1,z #4 -x,-y+2,-z+1

X-ray Crystal Data for $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$

| | |
|---------------------------------------|---|
| Identification code | $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$ |
| Empirical formula | $\text{C}_{34} \text{H}_{30} \text{Ag}_2 \text{O}_6 \text{S}_2$ |
| Formula weight | 814.44 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | $P2(1)/c$ |
| Unit cell dimensions | $a = 9.1304(7) \text{ Å}$ $\alpha = 90^\circ$. $b = 19.5875(14) \text{ Å}$ $\beta = 99.2280(10)^\circ$. $c = 18.0502(13) \text{ Å}$ $\gamma = 90^\circ$. |
| Volume | $3186.3(4) \text{ Å}^3$ |
| Z | 4 |
| Density (calculated) | 1.698 Mg/m^3 |
| Absorption coefficient | 1.405 mm^{-1} |
| F(000) | 1632 |
| Crystal size | $0.41 \times 0.09 \times 0.08 \text{ mm}^3$ |
| Crystal description | yellow rod |
| Theta range for data collection | 1.55 to 27.50° . |
| Index ranges | $-11 \leq h \leq 11$, $-25 \leq k \leq 25$, $-23 \leq l \leq 23$ |
| Reflections collected | 30770 |
| Independent reflections | 7311 [R(int) = 0.0426] |
| Completeness to theta = 27.50° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8959 and 0.5967 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 7311 / 904 / 527 |
| Goodness-of-fit on F^2 | 1.026 |
| Final R indices [$I > 2\sigma(I)$] | $R1 = 0.0317$, $wR2 = 0.0701$ |
| R indices (all data) | $R1 = 0.0463$, $wR2 = 0.0769$ |
| Largest diff. peak and hole | 0.817 and -0.673 e.Å^{-3} |

Table 18: Selected bond lengths [Å] and angles [°] for [Ag₂(9-aca)₂(DMSO)₂]_n.

| | | | |
|---------------------|------------|---------------------|------------|
| Ag(1)-O(11) | 2.3576(19) | Ag(1)-Ag(1)#1 | 3.1467(5) |
| Ag(1)-O(31) | 2.384(2) | Ag(2)-O(12) | 2.357(2) |
| Ag(1)-O(11)#1 | 2.421(2) | Ag(2)-O(2)#2 | 2.4005(19) |
| Ag(1)-O(1) | 2.428(2) | Ag(2)-O(32) | 2.421(2) |
| Ag(1)-O(32) | 2.598(2) | Ag(2)-O(2) | 2.4674(19) |
| Ag(1)-Ag(2) | 2.9144(3) | Ag(2)-O(1)#1 | 2.500(2) |
| O(11)-Ag(1)-O(31) | 110.86(9) | O(12)-Ag(2)-O(2) | 165.34(7) |
| O(11)-Ag(1)-O(11)#1 | 97.65(6) | O(2)#2-Ag(2)-O(2) | 81.12(7) |
| O(31)-Ag(1)-O(11)#1 | 151.23(8) | O(32)-Ag(2)-O(2) | 80.90(7) |
| O(11)-Ag(1)-O(1) | 90.51(7) | O(12)-Ag(2)-O(1)#1 | 83.66(8) |
| O(31)-Ag(1)-O(1) | 99.46(7) | O(2)#2-Ag(2)-O(1)#1 | 108.51(7) |
| O(11)#1-Ag(1)-O(1) | 83.58(7) | O(32)-Ag(2)-O(1)#1 | 139.17(7) |
| O(11)-Ag(1)-O(32) | 117.64(7) | O(2)-Ag(2)-O(1)#1 | 81.83(7) |
| O(31)-Ag(1)-O(32) | 52.25(7) | Ag(1)-O(1)-Ag(2)#1 | 104.22(8) |
| O(1)-Ag(1)-O(32) | 144.60(7) | Ag(2)#2-O(2)-Ag(2) | 98.88(7) |
| O(12)-Ag(2)-O(2)#2 | 101.61(7) | Ag(1)-O(11)-Ag(1)#1 | 82.35(6) |
| O(12)-Ag(2)-O(32) | 111.83(7) | Ag(2)-O(32)-Ag(1) | 70.90(5) |
| O(2)#2-Ag(2)-O(32) | 104.95(7) | | |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+1

X-ray Crystal Data for [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca)

| | |
|-----------------------------------|---|
| Identification code | [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) |
| Empirical formula | C _{23.30} H _{20.30} Ag N _{5.30} O ₂ |
| Formula weight | 514.42 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/n |
| Unit cell dimensions | a = 9.7905(5) Å α = 90°. b = 14.2012(7) Å β = 101.8640(10)°. c = 16.3251(9) Å γ = 90°. |
| Volume | 2221.3(2) Å ³ |
| Z | 4 |
| Density (calculated) | 1.538 Mg/m ³ |
| Absorption coefficient | 0.938 mm ⁻¹ |
| F(000) | 1041 |
| Crystal size | 0.33 x 0.22 x 0.21 mm ³ |
| Crystal description | colourless block |
| Theta range for data collection | 1.92 to 26.00°. |
| Index ranges | -12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20 |
| Reflections collected | 19005 |
| Independent reflections | 4361 [R(int) = 0.0326] |
| Completeness to theta = 25.00° | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8273 and 0.7471 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 4361 / 23 / 326 |
| Goodness-of-fit on F ² | 1.049 |
| Final R indices [I > 2σ(I)] | R1 = 0.0347, wR2 = 0.0730 |
| R indices (all data) | R1 = 0.0460, wR2 = 0.0782 |
| Largest diff. peak and hole | 0.936 and -1.192 e.Å ⁻³ |

Table 19: Bond lengths [Å] and angles [°] for [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca).

| | | | |
|--------------------|------------|------------------|-----------|
| Ag(1)-N(21) | 2.126(2) | C(12)-C(13) | 1.414(5) |
| Ag(1)-N(31) | 2.126(2) | C(13)-C(14) | 1.355(4) |
| Ag(1)-N(41) | 2.588(17) | C(14)-C(15) | 1.426(4) |
| Ag(1)-N(51) | 2.713(8) | N(21)-C(21) | 1.319(4) |
| Ag(1)-O(2)#1 | 3.009(2) | N(21)-C(22) | 1.377(4) |
| O(1)-C(1) | 1.253(3) | C(21)-N(22) | 1.329(4) |
| O(2)-C(1) | 1.251(3) | N(22)-C(23) | 1.357(4) |
| C(1)-C(2) | 1.519(3) | C(23)-C(22) | 1.349(4) |
| C(2)-C(3) | 1.397(4) | N(31)-C(31) | 1.323(4) |
| C(2)-C(15) | 1.398(4) | N(31)-C(33) | 1.370(4) |
| C(3)-C(4) | 1.428(4) | C(31)-N(32) | 1.329(4) |
| C(3)-C(8) | 1.433(4) | N(32)-C(32) | 1.359(4) |
| C(4)-C(5) | 1.351(5) | C(32)-C(33) | 1.350(4) |
| C(5)-C(6) | 1.403(6) | N(51)-C(52) | 1.132(9) |
| C(6)-C(7) | 1.357(6) | C(52)-C(53) | 1.468(10) |
| C(7)-C(8) | 1.436(5) | N(41)-C(41) | 1.301(15) |
| C(8)-C(9) | 1.388(5) | N(41)-C(43) | 1.366(16) |
| C(9)-C(10) | 1.385(4) | C(41)-N(42) | 1.334(15) |
| C(10)-C(11) | 1.422(5) | N(42)-C(42) | 1.339(17) |
| C(10)-C(15) | 1.438(4) | C(42)-C(43) | 1.373(17) |
| C(11)-C(12) | 1.334(5) | | |
| N(21)-Ag(1)-N(31) | 168.51(10) | C(3)-C(2)-C(1) | 119.2(2) |
| N(21)-Ag(1)-N(41) | 96.1(6) | C(15)-C(2)-C(1) | 119.8(2) |
| N(31)-Ag(1)-N(41) | 94.7(6) | C(2)-C(3)-C(4) | 121.9(3) |
| N(21)-Ag(1)-N(51) | 93.7(3) | C(2)-C(3)-C(8) | 119.5(3) |
| N(31)-Ag(1)-N(51) | 96.0(3) | C(4)-C(3)-C(8) | 118.6(3) |
| N(41)-Ag(1)-N(51) | 12.4(4) | C(5)-C(4)-C(3) | 120.9(4) |
| N(21)-Ag(1)-O(2)#1 | 93.98(8) | C(4)-C(5)-C(6) | 121.0(4) |
| N(31)-Ag(1)-O(2)#1 | 92.38(7) | C(7)-C(6)-C(5) | 120.5(3) |
| N(41)-Ag(1)-O(2)#1 | 76.5(3) | C(6)-C(7)-C(8) | 121.1(4) |
| N(51)-Ag(1)-O(2)#1 | 88.78(18) | C(9)-C(8)-C(3) | 119.2(3) |
| O(2)-C(1)-O(1) | 125.3(2) | C(9)-C(8)-C(7) | 123.0(3) |
| O(2)-C(1)-C(2) | 117.1(2) | C(3)-C(8)-C(7) | 117.8(3) |
| O(1)-C(1)-C(2) | 117.6(2) | C(10)-C(9)-C(8) | 121.9(3) |
| C(3)-C(2)-C(15) | 121.0(2) | C(9)-C(10)-C(11) | 122.3(3) |

| | | | |
|-------------------|----------|-------------------|-----------|
| C(9)-C(10)-C(15) | 119.3(3) | C(31)-N(31)-C(33) | 105.2(2) |
| C(11)-C(10)-C(15) | 118.5(3) | C(31)-N(31)-Ag(1) | 127.1(2) |
| C(12)-C(11)-C(10) | 121.5(3) | C(33)-N(31)-Ag(1) | 127.8(2) |
| C(11)-C(12)-C(13) | 120.7(3) | N(31)-C(31)-N(32) | 111.6(3) |
| C(14)-C(13)-C(12) | 120.5(3) | C(31)-N(32)-C(32) | 107.2(3) |
| C(13)-C(14)-C(15) | 121.0(3) | C(33)-C(32)-N(32) | 106.7(3) |
| C(2)-C(15)-C(14) | 123.0(2) | C(32)-C(33)-N(31) | 109.3(3) |
| C(2)-C(15)-C(10) | 119.2(3) | C(52)-N(51)-Ag(1) | 142.3(7) |
| C(14)-C(15)-C(10) | 117.9(3) | N(51)-C(52)-C(53) | 178.4(9) |
| C(21)-N(21)-C(22) | 105.5(3) | C(41)-N(41)-C(43) | 104.0(14) |
| C(21)-N(21)-Ag(1) | 123.7(2) | C(41)-N(41)-Ag(1) | 129.5(14) |
| C(22)-N(21)-Ag(1) | 130.2(2) | C(43)-N(41)-Ag(1) | 126.0(9) |
| N(21)-C(21)-N(22) | 111.2(3) | N(41)-C(41)-N(42) | 113.2(15) |
| C(21)-N(22)-C(23) | 107.6(3) | C(41)-N(42)-C(42) | 107.1(12) |
| C(22)-C(23)-N(22) | 106.7(3) | N(42)-C(42)-C(43) | 105.7(14) |
| C(23)-C(22)-N(21) | 109.0(3) | N(41)-C(43)-C(42) | 109.9(13) |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1/2, y-1/2, -z+1/2$

Table 20: Hydrogen bonds for $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$ [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | $\angle(\text{DHA})$ |
|----------------------|--------|----------|-----------|----------------------|
| N(22)-H(22)...O(1)#2 | 0.88 | 1.87 | 2.745(3) | 178.3 |
| N(32)-H(32)...O(2) | 0.88 | 1.89 | 2.752(3) | 165.5 |
| N(42)-H(42)...O(1)#3 | 0.88 | 1.86 | 2.734(10) | 174.8 |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1/2, y-1/2, -z+1/2$ #2 $x, y-1, z$ #3 $-x+3/2, y-1/2, -z+1/2$

X-ray Crystal Data for [Ag₆(imidH)₄(9-aca)₆(MeOH)₂]

| | |
|-----------------------------------|--|
| Identification code | [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] |
| Empirical formula | C ₁₀₄ H ₇₈ Ag ₆ N ₈ O ₁₄ |
| Formula weight | 2310.96 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | Pbcn |
| Unit cell dimensions | a = 20.6935(8) Å α = 90°. b = 18.2786(7) Å β = 90°. c = 23.6859(10) Å γ = 90°. |
| Volume | 8959.1(6) Å ³ |
| Z | 4 |
| Density (calculated) | 1.713 Mg/m ³ |
| Absorption coefficient | 1.358 mm ⁻¹ |
| F(000) | 4608 |
| Crystal size | 0.23 x 0.15 x 0.12 mm ³ |
| Crystal description | Pale yellow block |
| Theta range for data collection | 1.72 to 27.00°. |
| Index ranges | -26 ≤ h ≤ 26, -23 ≤ k ≤ 23, -30 ≤ l ≤ 30 |
| Reflections collected | 80667 |
| Independent reflections | 9793 [R(int) = 0.0580] |
| Completeness to theta = 27.00° | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8540 and 0.7453 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 9793 / 0 / 599 |
| Goodness-of-fit on F ² | 1.025 |
| Final R indices [I > 2σ(I)] | R1 = 0.0316, wR2 = 0.0695 |
| R indices (all data) | R1 = 0.0475, wR2 = 0.0765 |
| Largest diff. peak and hole | 0.487 and -0.788 e.Å ⁻³ |

Table 21: Bond lengths [Å] and angles [°] for [Ag₆(imidH)₄(9-aca)₆(MeOH)₂].

| | | | |
|---------------|-----------|---------------|------------|
| Ag(1)-N(21) | 2.088(2) | O(2B)-C(1B) | 1.253(3) |
| Ag(1)-N(31) | 2.089(2) | O(2B)-Ag(3) | 2.789(2) |
| Ag(1)-Ag(2) | 3.0651(4) | C(1B)-C(2B) | 1.520(4) |
| N(21)-C(21) | 1.325(4) | C(2B)-C(15B) | 1.396(4) |
| N(21)-C(23) | 1.363(4) | C(2B)-C(3B) | 1.403(4) |
| C(21)-N(22) | 1.336(4) | C(3B)-C(4B) | 1.426(4) |
| N(22)-C(22) | 1.360(4) | C(3B)-C(8B) | 1.442(4) |
| C(22)-C(23) | 1.363(4) | C(4B)-C(5B) | 1.357(4) |
| N(31)-C(31) | 1.330(4) | C(5B)-C(6B) | 1.418(4) |
| N(31)-C(33) | 1.379(4) | C(6B)-C(7B) | 1.354(5) |
| C(31)-N(32) | 1.334(4) | C(7B)-C(8B) | 1.432(4) |
| N(32)-C(32) | 1.363(4) | C(8B)-C(9B) | 1.393(4) |
| C(32)-C(33) | 1.353(4) | C(9B)-C(10B) | 1.388(4) |
| Ag(2)-O(1B) | 2.218(2) | C(10B)-C(11B) | 1.424(4) |
| Ag(2)-O(1A) | 2.416(2) | C(10B)-C(15B) | 1.437(4) |
| Ag(2)-O(2A) | 2.424(2) | C(11B)-C(12B) | 1.352(4) |
| O(1A)-C(1A) | 1.254(3) | C(12B)-C(13B) | 1.420(4) |
| O(2A)-C(1A) | 1.254(3) | C(13B)-C(14B) | 1.359(4) |
| C(1A)-C(2A) | 1.510(4) | C(14B)-C(15B) | 1.427(4) |
| C(2A)-C(15A) | 1.400(4) | Ag(3)-O(1D) | 2.1574(19) |
| C(2A)-C(3A) | 1.404(4) | Ag(3)-O(1C) | 2.1681(19) |
| C(3A)-C(4A) | 1.427(4) | Ag(3)-O(41) | 2.467(2) |
| C(3A)-C(8A) | 1.434(4) | Ag(3)-Ag(3)#1 | 2.8818(5) |
| C(4A)-C(5A) | 1.352(4) | O(1C)-C(1C) | 1.248(3) |
| C(5A)-C(6A) | 1.415(4) | C(1C)-O(1C)#1 | 1.248(3) |
| C(6A)-C(7A) | 1.360(5) | C(1C)-C(2C) | 1.494(5) |
| C(7A)-C(8A) | 1.425(4) | C(2C)-C(3C)#1 | 1.398(4) |
| C(8A)-C(9A) | 1.387(4) | C(2C)-C(3C) | 1.398(4) |
| C(9A)-C(10A) | 1.396(4) | C(3C)-C(4C) | 1.432(5) |
| C(10A)-C(11A) | 1.422(4) | C(3C)-C(8C) | 1.443(4) |
| C(10A)-C(15A) | 1.438(4) | C(4C)-C(5C) | 1.356(5) |
| C(11A)-C(12A) | 1.351(4) | C(5C)-C(6C) | 1.426(5) |
| C(12A)-C(13A) | 1.419(5) | C(6C)-C(7C) | 1.349(5) |
| C(13A)-C(14A) | 1.349(4) | C(7C)-C(8C) | 1.426(5) |
| C(14A)-C(15A) | 1.427(4) | C(8C)-C(9C) | 1.388(4) |
| O(1B)-C(1B) | 1.258(3) | C(9C)-C(8C)#1 | 1.388(4) |

| | | | |
|--------------------|------------|----------------------|------------|
| O(1D)-C(1D) | 1.246(3) | C(1D)-O(1D)#1 | 1.246(3) |
| C(1D)-C(2D) | 1.512(5) | C(5D)-C(6D) | 1.424(4) |
| C(2D)-C(3D) | 1.402(3) | C(6D)-C(7D) | 1.346(4) |
| C(2D)-C(3D)#1 | 1.402(3) | C(7D)-C(8D) | 1.418(4) |
| C(3D)-C(4D) | 1.430(4) | C(8D)-C(9D) | 1.393(3) |
| C(3D)-C(8D) | 1.439(4) | C(9D)-C(8D)#1 | 1.393(3) |
| C(4D)-C(5D) | 1.351(4) | O(41)-C(41) | 1.448(4) |
| N(21)-Ag(1)-N(31) | 174.33(10) | C(3A)-C(2A)-C(1A) | 117.6(2) |
| N(21)-Ag(1)-Ag(2) | 111.93(7) | C(2A)-C(3A)-C(4A) | 122.9(3) |
| N(31)-Ag(1)-Ag(2) | 73.35(7) | C(2A)-C(3A)-C(8A) | 118.6(3) |
| C(21)-N(21)-C(23) | 105.7(3) | C(4A)-C(3A)-C(8A) | 118.5(3) |
| C(21)-N(21)-Ag(1) | 128.9(2) | C(5A)-C(4A)-C(3A) | 121.2(3) |
| C(23)-N(21)-Ag(1) | 125.4(2) | C(4A)-C(5A)-C(6A) | 120.6(3) |
| N(21)-C(21)-N(22) | 111.0(3) | C(7A)-C(6A)-C(5A) | 120.1(3) |
| C(21)-N(22)-C(22) | 107.9(3) | C(6A)-C(7A)-C(8A) | 121.4(3) |
| N(22)-C(22)-C(23) | 105.9(3) | C(9A)-C(8A)-C(7A) | 121.8(3) |
| C(22)-C(23)-N(21) | 109.7(3) | C(9A)-C(8A)-C(3A) | 120.0(3) |
| C(31)-N(31)-C(33) | 105.9(2) | C(7A)-C(8A)-C(3A) | 118.2(3) |
| C(31)-N(31)-Ag(1) | 127.9(2) | C(8A)-C(9A)-C(10A) | 121.4(3) |
| C(33)-N(31)-Ag(1) | 126.1(2) | C(9A)-C(10A)-C(11A) | 122.0(3) |
| N(31)-C(31)-N(32) | 110.3(3) | C(9A)-C(10A)-C(15A) | 119.3(3) |
| C(31)-N(32)-C(32) | 108.4(3) | C(11A)-C(10A)-C(15A) | 118.7(3) |
| C(33)-C(32)-N(32) | 106.2(3) | C(12A)-C(11A)-C(10A) | 121.1(3) |
| C(32)-C(33)-N(31) | 109.1(3) | C(11A)-C(12A)-C(13A) | 120.1(3) |
| O(1B)-Ag(2)-O(1A) | 143.97(7) | C(14A)-C(13A)-C(12A) | 121.0(3) |
| O(1B)-Ag(2)-O(2A) | 154.09(7) | C(13A)-C(14A)-C(15A) | 121.0(3) |
| O(1A)-Ag(2)-O(2A) | 54.34(7) | C(2A)-C(15A)-C(14A) | 123.0(3) |
| O(1B)-Ag(2)-Ag(1) | 78.07(6) | C(2A)-C(15A)-C(10A) | 119.0(3) |
| O(1A)-Ag(2)-Ag(1) | 75.58(5) | C(14A)-C(15A)-C(10A) | 118.0(3) |
| O(2A)-Ag(2)-Ag(1) | 96.64(5) | C(1B)-O(1B)-Ag(2) | 113.00(18) |
| C(1A)-O(1A)-Ag(2) | 91.21(17) | C(1B)-O(2B)-Ag(3) | 123.03(18) |
| C(1A)-O(2A)-Ag(2) | 90.86(17) | O(2B)-C(1B)-O(1B) | 125.8(3) |
| O(2A)-C(1A)-O(1A) | 123.6(3) | O(2B)-C(1B)-C(2B) | 118.0(2) |
| O(2A)-C(1A)-C(2A) | 117.8(3) | O(1B)-C(1B)-C(2B) | 116.1(2) |
| O(1A)-C(1A)-C(2A) | 118.5(3) | C(15B)-C(2B)-C(3B) | 121.8(3) |
| C(15A)-C(2A)-C(3A) | 121.6(3) | C(15B)-C(2B)-C(1B) | 117.5(2) |
| C(15A)-C(2A)-C(1A) | 120.7(2) | C(3B)-C(2B)-C(1B) | 120.7(2) |

| | | | |
|----------------------|------------|---------------------|------------|
| C(2B)-C(3B)-C(4B) | 123.6(3) | C(2B)-C(3B)-C(8B) | 118.4(3) |
| C(4B)-C(3B)-C(8B) | 118.0(3) | C(3C)#1-C(2C)-C(3C) | 121.7(4) |
| C(5B)-C(4B)-C(3B) | 121.2(3) | C(3C)#1-C(2C)-C(1C) | 119.14(19) |
| C(4B)-C(5B)-C(6B) | 121.0(3) | C(3C)-C(2C)-C(1C) | 119.14(19) |
| C(7B)-C(6B)-C(5B) | 120.1(3) | C(2C)-C(3C)-C(4C) | 123.4(3) |
| C(6B)-C(7B)-C(8B) | 121.2(3) | C(2C)-C(3C)-C(8C) | 119.0(3) |
| C(9B)-C(8B)-C(7B) | 122.0(3) | C(4C)-C(3C)-C(8C) | 117.6(3) |
| C(9B)-C(8B)-C(3B) | 119.5(3) | C(5C)-C(4C)-C(3C) | 121.8(3) |
| C(7B)-C(8B)-C(3B) | 118.6(3) | C(4C)-C(5C)-C(6C) | 120.1(4) |
| C(10B)-C(9B)-C(8B) | 121.8(3) | C(7C)-C(6C)-C(5C) | 120.2(3) |
| C(9B)-C(10B)-C(11B) | 122.2(3) | C(6C)-C(7C)-C(8C) | 121.8(3) |
| C(9B)-C(10B)-C(15B) | 119.3(3) | C(9C)-C(8C)-C(7C) | 122.9(3) |
| C(11B)-C(10B)-C(15B) | 118.6(3) | C(9C)-C(8C)-C(3C) | 118.8(3) |
| C(12B)-C(11B)-C(10B) | 121.2(3) | C(7C)-C(8C)-C(3C) | 118.3(3) |
| C(11B)-C(12B)-C(13B) | 120.7(3) | C(8C)-C(9C)-C(8C)#1 | 122.7(4) |
| C(14B)-C(13B)-C(12B) | 119.9(3) | C(1D)-O(1D)-Ag(3) | 124.1(2) |
| C(13B)-C(14B)-C(15B) | 121.6(3) | O(1D)-C(1D)-O(1D)#1 | 128.7(4) |
| C(2B)-C(15B)-C(14B) | 122.8(3) | O(1D)-C(1D)-C(2D) | 115.66(18) |
| C(2B)-C(15B)-C(10B) | 119.1(3) | O(1D)#1-C(1D)-C(2D) | 115.66(18) |
| C(14B)-C(15B)-C(10B) | 118.0(3) | C(3D)-C(2D)-C(3D)#1 | 121.9(3) |
| O(1D)-Ag(3)-O(1C) | 162.45(8) | C(3D)-C(2D)-C(1D) | 119.06(17) |
| O(1D)-Ag(3)-O(41) | 102.11(7) | C(3D)#1-C(2D)-C(1D) | 119.06(17) |
| O(1C)-Ag(3)-O(41) | 92.58(8) | C(2D)-C(3D)-C(4D) | 122.2(3) |
| O(1D)-Ag(3)-O(2B) | 94.62(7) | C(2D)-C(3D)-C(8D) | 118.7(3) |
| O(1C)-Ag(3)-O(2B) | 95.22(7) | C(4D)-C(3D)-C(8D) | 119.2(2) |
| O(41)-Ag(3)-O(2B) | 88.95(7) | C(5D)-C(4D)-C(3D) | 120.8(3) |
| O(1D)-Ag(3)-Ag(3)#1 | 81.52(6) | C(4D)-C(5D)-C(6D) | 120.0(3) |
| O(1C)-Ag(3)-Ag(3)#1 | 81.10(6) | C(7D)-C(6D)-C(5D) | 120.8(3) |
| O(41)-Ag(3)-Ag(3)#1 | 138.73(5) | C(6D)-C(7D)-C(8D) | 121.9(3) |
| O(2B)-Ag(3)-Ag(3)#1 | 132.10(4) | C(9D)-C(8D)-C(7D) | 123.1(3) |
| C(1C)-O(1C)-Ag(3) | 125.6(2) | C(9D)-C(8D)-C(3D) | 119.5(3) |
| O(1C)#1-C(1C)-O(1C) | 125.7(4) | C(7D)-C(8D)-C(3D) | 117.4(3) |
| O(1C)#1-C(1C)-C(2C) | 117.13(19) | C(8D)#1-C(9D)-C(8D) | 121.7(4) |
| O(1C)-C(1C)-C(2C) | 117.13(19) | C(41)-O(41)-Ag(3) | 115.5(2) |

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

Table 22: Hydrogen bonds for [Ag₆(imidH)₄(9-aca)₆(MeOH)₂] [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|----------------------------|--------|----------|----------|--------|
| N(22)- H(22N)...O(2A)#2 | 0.88 | 1.92 | 2.796(3) | 176.3 |
| N(32)- H(32N)...O(2B)#3 | 0.88 | 1.94 | 2.815(3) | 170.4 |
| O(41)-H(41)...O(1A) | 0.94 | 1.92 | 2.782(3) | 150.9 |

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2 #2 -x+1/2,y-1/2,z #3 -x+1/2,y+1/2,z

X-ray Crystal Data for [Ag(1-Me-imid)₂]₂[Ag₄(9-aca)₆]

| | |
|-----------------------------------|--|
| Identification code | [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] |
| Empirical formula | C ₁₀₆ H ₇₈ Ag ₆ N ₈ O ₁₂ |
| Formula weight | 2302.98 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | a = 11.7251(17) Å α = 111.403(2)°. b = 17.908(3) Å β = 90.095(2)°. c = 23.464(3) Å γ = 101.710(2)°. |
| Volume | 4476.2(11) Å ³ |
| Z | 2 |
| Density (calculated) | 1.709 Mg/m ³ |
| Absorption coefficient | 1.357 mm ⁻¹ |
| F(000) | 2296 |
| Crystal size | 0.43 x 0.32 x 0.06 mm ³ |
| Crystal description | colourless plate |
| Theta range for data collection | 1.78 to 25.00°. |
| Index ranges | -13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -27 ≤ l ≤ 27 |
| Reflections collected | 35083 |
| Independent reflections | 15686 [R(int) = 0.0421] |
| Completeness to theta = 25.00° | 99.5 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9230 and 0.5930 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 15686 / 0 / 1224 |
| Goodness-of-fit on F ² | 1.046 |
| Final R indices [I > 2σ(I)] | R1 = 0.0512, wR2 = 0.1262 |
| R indices (all data) | R1 = 0.0706, wR2 = 0.1370 |
| Largest diff. peak and hole | 1.787 and -1.037 e.Å ⁻³ |

Table 23. Bond lengths [Å] and angles [°] for [Ag(1-Me-imid)₂]₂[Ag₄(9-aca)₆].

| | | | |
|----------------|------------|----------------|-----------|
| Ag(1)-O(12C)#1 | 2.248(4) | C(12B)-C(13B) | 1.414(9) |
| Ag(1)-O(11C) | 2.270(4) | C(13B)-C(18B) | 1.420(9) |
| Ag(1)-O(11A) | 2.314(5) | C(13B)-C(14B) | 1.435(9) |
| Ag(1)-O(11B) | 2.383(4) | C(14B)-C(15B) | 1.358(9) |
| Ag(1)-Ag(1)#1 | 2.7860(10) | C(15B)-C(16B) | 1.408(10) |
| Ag(1)-Ag(2)#1 | 2.9621(7) | C(16B)-C(17B) | 1.366(11) |
| Ag(1)-Ag(2) | 3.0085(7) | C(17B)-C(18B) | 1.419(10) |
| Ag(2)-O(12A) | 2.188(4) | C(18B)-C(19B) | 1.399(10) |
| Ag(2)-O(12B)#1 | 2.190(4) | C(19B)-C(20B) | 1.389(10) |
| Ag(2)-Ag(1)#1 | 2.9621(7) | C(20B)-C(21B) | 1.419(10) |
| O(11A)-C(11A) | 1.241(8) | C(20B)-C(25B) | 1.443(9) |
| O(11A)-Ag(5) | 2.713(5) | C(21B)-C(22B) | 1.346(11) |
| O(12A)-C(11A) | 1.262(8) | C(22B)-C(23B) | 1.424(11) |
| C(11A)-C(12A) | 1.523(9) | C(23B)-C(24B) | 1.349(10) |
| C(12A)-C(13A) | 1.409(10) | C(24B)-C(25B) | 1.416(9) |
| C(12A)-C(25A) | 1.414(9) | O(11C)-C(11C) | 1.246(8) |
| C(13A)-C(14A) | 1.414(10) | O(12C)-C(11C) | 1.242(8) |
| C(13A)-C(18A) | 1.428(9) | O(12C)-Ag(1)#1 | 2.248(4) |
| C(14A)-C(15A) | 1.356(11) | C(11C)-C(12C) | 1.512(8) |
| C(15A)-C(16A) | 1.411(11) | C(12C)-C(13C) | 1.381(9) |
| C(16A)-C(17A) | 1.344(11) | C(12C)-C(25C) | 1.409(9) |
| C(17A)-C(18A) | 1.440(10) | C(13C)-C(18C) | 1.435(9) |
| C(18A)-C(19A) | 1.386(10) | C(13C)-C(14C) | 1.441(9) |
| C(19A)-C(20A) | 1.394(10) | C(14C)-C(15C) | 1.349(9) |
| C(20A)-C(21A) | 1.429(10) | C(15C)-C(16C) | 1.427(9) |
| C(20A)-C(25A) | 1.440(9) | C(16C)-C(17C) | 1.371(10) |
| C(21A)-C(22A) | 1.348(12) | C(17C)-C(18C) | 1.435(9) |
| C(22A)-C(23A) | 1.356(11) | C(18C)-C(19C) | 1.390(9) |
| C(23A)-C(24A) | 1.396(10) | C(19C)-C(20C) | 1.388(9) |
| C(24A)-C(25A) | 1.421(10) | C(20C)-C(21C) | 1.430(9) |
| O(11B)-C(11B) | 1.264(8) | C(20C)-C(25C) | 1.448(9) |
| O(11B)-Ag(5) | 2.629(4) | C(21C)-C(22C) | 1.366(10) |
| O(12B)-C(11B) | 1.259(8) | C(22C)-C(23C) | 1.419(10) |
| O(12B)-Ag(2)#1 | 2.190(4) | C(23C)-C(24C) | 1.380(9) |
| C(11B)-C(12B) | 1.513(9) | C(24C)-C(25C) | 1.417(9) |
| C(12B)-C(25B) | 1.407(9) | Ag(3)-O(11E) | 2.228(5) |

| | | | |
|----------------|------------|---------------|-----------|
| Ag(3)-O(12E)#2 | 2.248(5) | Ag(3)-O(11F) | 2.318(5) |
| Ag(3)-O(11D) | 2.392(4) | C(15E)-C(16E) | 1.419(10) |
| Ag(3)-Ag(3)#2 | 2.7892(10) | C(16E)-C(17E) | 1.382(10) |
| Ag(3)-Ag(4)#2 | 2.9493(7) | C(17E)-C(18E) | 1.431(9) |
| Ag(3)-Ag(4) | 2.9843(8) | C(18E)-C(19E) | 1.394(10) |
| Ag(4)-O(12F) | 2.183(4) | C(19E)-C(20E) | 1.395(10) |
| Ag(4)-O(12D)#2 | 2.183(4) | C(20E)-C(21E) | 1.422(10) |
| Ag(4)-Ag(3)#2 | 2.9493(7) | C(20E)-C(25E) | 1.452(9) |
| O(11D)-C(11D) | 1.241(7) | C(21E)-C(22E) | 1.354(10) |
| O(11D)-Ag(6) | 2.607(4) | C(22E)-C(23E) | 1.432(10) |
| O(12D)-C(11D) | 1.260(7) | C(23E)-C(24E) | 1.360(10) |
| O(12D)-Ag(4)#2 | 2.183(4) | C(24E)-C(25E) | 1.427(9) |
| C(11D)-C(12D) | 1.514(8) | O(11F)-C(11F) | 1.257(8) |
| C(12D)-C(25D) | 1.408(9) | O(11F)-Ag(6) | 2.790(5) |
| C(12D)-C(13D) | 1.412(9) | O(12F)-C(11F) | 1.248(8) |
| C(13D)-C(18D) | 1.431(9) | C(11F)-C(12F) | 1.518(9) |
| C(13D)-C(14D) | 1.437(9) | C(12F)-C(13F) | 1.405(9) |
| C(14D)-C(15D) | 1.352(10) | C(12F)-C(25F) | 1.417(9) |
| C(15D)-C(16D) | 1.429(11) | C(13F)-C(18F) | 1.424(9) |
| C(16D)-C(17D) | 1.371(11) | C(13F)-C(14F) | 1.426(10) |
| C(17D)-C(18D) | 1.418(10) | C(14F)-C(15F) | 1.361(10) |
| C(18D)-C(19D) | 1.386(10) | C(15F)-C(16F) | 1.422(10) |
| C(19D)-C(20D) | 1.389(10) | C(16F)-C(17F) | 1.358(11) |
| C(20D)-C(25D) | 1.428(9) | C(17F)-C(18F) | 1.437(10) |
| C(20D)-C(21D) | 1.430(10) | C(18F)-C(19F) | 1.393(10) |
| C(21D)-C(22D) | 1.353(10) | C(19F)-C(20F) | 1.371(11) |
| C(22D)-C(23D) | 1.413(10) | C(20F)-C(21F) | 1.440(10) |
| C(23D)-C(24D) | 1.366(9) | C(20F)-C(25F) | 1.445(9) |
| C(24D)-C(25D) | 1.438(9) | C(21F)-C(22F) | 1.358(12) |
| O(11E)-C(11E) | 1.254(8) | C(22F)-C(23F) | 1.407(12) |
| O(12E)-C(11E) | 1.229(8) | C(23F)-C(24F) | 1.359(11) |
| O(12E)-Ag(3)#2 | 2.248(4) | C(24F)-C(25F) | 1.429(10) |
| C(11E)-C(12E) | 1.515(8) | Ag(5)-N(1B) | 2.125(7) |
| C(12E)-C(25E) | 1.392(9) | Ag(5)-N(1A) | 2.141(7) |
| C(12E)-C(13E) | 1.402(9) | C(1A)-N(1A) | 1.296(10) |
| C(13E)-C(18E) | 1.428(9) | C(1A)-N(2A) | 1.354(10) |
| C(13E)-C(14E) | 1.440(9) | N(1A)-C(2A) | 1.398(10) |
| C(14E)-C(15E) | 1.375(9) | C(2A)-C(3A) | 1.343(12) |

| | | | |
|------------------------|------------|------------------------|------------|
| C(3A)-N(2A) | 1.357(10) | N(2A)-C(4A) | 1.468(10) |
| C(1B)-N(2B) | 1.316(9) | Ag(11)-Ag(13)#3 | 2.94(2) |
| C(1B)-N(1B) | 1.334(10) | Ag(11)-Ag(12) | 3.019(19) |
| N(1B)-C(2B) | 1.391(10) | Ag(12)-Ag(11)#3 | 2.361(19) |
| C(2B)-C(3B) | 1.336(13) | Ag(12)-Ag(13) | 2.596(19) |
| C(3B)-N(2B) | 1.356(11) | Ag(12)-Ag(13)#3 | 2.791(19) |
| N(2B)-C(4B) | 1.464(11) | Ag(12)-Ag(14)#3 | 2.947(19) |
| Ag(6)-N(1C) | 2.127(7) | Ag(13)-Ag(12)#3 | 2.791(19) |
| Ag(6)-N(1D) | 2.143(7) | Ag(13)-Ag(11)#3 | 2.94(2) |
| C(1C)-N(1C) | 1.323(10) | Ag(13)-Ag(14) | 3.03(2) |
| C(1C)-N(2C) | 1.330(10) | Ag(14)-Ag(12)#3 | 2.947(19) |
| N(1C)-C(2C) | 1.381(9) | Ag(15)-Ag(16)#4 | 2.403(19) |
| C(2C)-C(3C) | 1.342(12) | Ag(15)-Ag(18)#4 | 2.57(2) |
| C(3C)-N(2C) | 1.375(10) | Ag(15)-Ag(18) | 2.79(2) |
| N(2C)-C(4C) | 1.430(10) | Ag(15)-Ag(17) | 2.951(19) |
| C(1D)-N(1D) | 1.298(10) | Ag(15)-Ag(16) | 3.003(19) |
| C(1D)-N(2D) | 1.344(9) | Ag(16)-Ag(15)#4 | 2.403(19) |
| N(1D)-C(2D) | 1.366(11) | Ag(16)-Ag(18)#4 | 2.46(2) |
| C(2D)-C(3D) | 1.356(13) | Ag(16)-Ag(17)#4 | 2.597(19) |
| C(3D)-N(2D) | 1.369(10) | Ag(16)-Ag(18) | 2.96(2) |
| N(2D)-C(4D) | 1.455(11) | Ag(17)-Ag(16)#4 | 2.597(19) |
| Ag(11)-Ag(12)#3 | 2.360(19) | Ag(17)-Ag(18) | 3.01(2) |
| Ag(11)-Ag(14) | 2.606(19) | Ag(18)-Ag(16)#4 | 2.46(2) |
| Ag(11)-Ag(13) | 2.639(19) | Ag(18)-Ag(15)#4 | 2.57(2) |
| O(12C)#1-Ag(1)-O(11C) | 156.54(18) | O(11B)-Ag(1)-Ag(2)#1 | 75.58(11) |
| O(12C)#1-Ag(1)-O(11A) | 100.79(18) | Ag(1)#1-Ag(1)-Ag(2)#1 | 63.03(2) |
| O(11C)-Ag(1)-O(11A) | 102.66(18) | O(12C)#1-Ag(1)-Ag(2) | 78.27(13) |
| O(12C)#1-Ag(1)-O(11B) | 93.57(16) | O(11C)-Ag(1)-Ag(2) | 107.63(12) |
| O(11C)-Ag(1)-O(11B) | 87.81(16) | O(11A)-Ag(1)-Ag(2) | 74.06(12) |
| O(11A)-Ag(1)-O(11B) | 88.22(16) | O(11B)-Ag(1)-Ag(2) | 158.49(11) |
| O(12C)#1-Ag(1)-Ag(1)#1 | 81.43(12) | Ag(1)#1-Ag(1)-Ag(2) | 61.34(2) |
| O(11C)-Ag(1)-Ag(1)#1 | 81.86(12) | Ag(2)#1-Ag(1)-Ag(2) | 124.37(2) |
| O(11A)-Ag(1)-Ag(1)#1 | 134.03(13) | O(12A)-Ag(2)-O(12B)#1 | 140.38(17) |
| O(11B)-Ag(1)-Ag(1)#1 | 137.71(11) | O(12A)-Ag(2)-Ag(1)#1 | 135.98(12) |
| O(12C)#1-Ag(1)-Ag(2)#1 | 93.80(13) | O(12B)#1-Ag(2)-Ag(1)#1 | 80.33(11) |
| O(11C)-Ag(1)-Ag(2)#1 | 63.84(13) | O(12A)-Ag(2)-Ag(1) | 81.70(12) |
| O(11A)-Ag(1)-Ag(2)#1 | 158.86(12) | O(12B)#1-Ag(2)-Ag(1) | 124.95(11) |

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| Ag(1)#1-Ag(2)-Ag(1) | 55.62(2) | C(11A)-O(11A)-Ag(1) | 124.5(4) |
| C(11A)-O(11A)-Ag(5) | 117.9(4) | C(25B)-C(12B)-C(13B) | 120.6(6) |
| Ag(1)-O(11A)-Ag(5) | 97.72(18) | C(25B)-C(12B)-C(11B) | 120.0(6) |
| C(11A)-O(12A)-Ag(2) | 120.4(4) | C(13B)-C(12B)-C(11B) | 119.4(6) |
| O(11A)-C(11A)-O(12A) | 126.4(6) | C(12B)-C(13B)-C(18B) | 120.1(6) |
| O(11A)-C(11A)-C(12A) | 116.7(6) | C(12B)-C(13B)-C(14B) | 122.0(6) |
| O(12A)-C(11A)-C(12A) | 116.8(6) | C(18B)-C(13B)-C(14B) | 117.8(6) |
| C(13A)-C(12A)-C(25A) | 121.4(6) | C(15B)-C(14B)-C(13B) | 120.2(6) |
| C(13A)-C(12A)-C(11A) | 119.5(6) | C(14B)-C(15B)-C(16B) | 121.7(7) |
| C(25A)-C(12A)-C(11A) | 119.0(6) | C(17B)-C(16B)-C(15B) | 119.8(7) |
| C(12A)-C(13A)-C(14A) | 123.2(6) | C(16B)-C(17B)-C(18B) | 120.4(7) |
| C(12A)-C(13A)-C(18A) | 118.6(6) | C(19B)-C(18B)-C(17B) | 121.3(6) |
| C(14A)-C(13A)-C(18A) | 118.2(6) | C(19B)-C(18B)-C(13B) | 118.7(6) |
| C(15A)-C(14A)-C(13A) | 121.7(7) | C(17B)-C(18B)-C(13B) | 120.0(6) |
| C(14A)-C(15A)-C(16A) | 120.0(8) | C(20B)-C(19B)-C(18B) | 122.3(6) |
| C(17A)-C(16A)-C(15A) | 121.1(7) | C(19B)-C(20B)-C(21B) | 121.4(6) |
| C(16A)-C(17A)-C(18A) | 120.5(7) | C(19B)-C(20B)-C(25B) | 119.3(6) |
| C(19A)-C(18A)-C(13A) | 120.2(7) | C(21B)-C(20B)-C(25B) | 119.2(6) |
| C(19A)-C(18A)-C(17A) | 121.3(7) | C(22B)-C(21B)-C(20B) | 121.5(7) |
| C(13A)-C(18A)-C(17A) | 118.5(7) | C(21B)-C(22B)-C(23B) | 119.4(7) |
| C(18A)-C(19A)-C(20A) | 121.8(6) | C(24B)-C(23B)-C(22B) | 120.9(7) |
| C(19A)-C(20A)-C(21A) | 121.7(7) | C(23B)-C(24B)-C(25B) | 122.0(7) |
| C(19A)-C(20A)-C(25A) | 119.3(6) | C(12B)-C(25B)-C(24B) | 124.3(6) |
| C(21A)-C(20A)-C(25A) | 119.0(7) | C(12B)-C(25B)-C(20B) | 118.8(6) |
| C(22A)-C(21A)-C(20A) | 120.6(7) | C(24B)-C(25B)-C(20B) | 116.9(6) |
| C(21A)-C(22A)-C(23A) | 121.4(7) | C(11C)-O(11C)-Ag(1) | 119.3(4) |
| C(22A)-C(23A)-C(24A) | 121.2(7) | C(11C)-O(12C)-Ag(1)#1 | 123.1(4) |
| C(23A)-C(24A)-C(25A) | 120.2(7) | O(12C)-C(11C)-O(11C) | 126.8(6) |
| C(12A)-C(25A)-C(24A) | 124.0(6) | O(12C)-C(11C)-C(12C) | 115.7(5) |
| C(12A)-C(25A)-C(20A) | 118.6(6) | O(11C)-C(11C)-C(12C) | 117.5(6) |
| C(24A)-C(25A)-C(20A) | 117.3(6) | C(13C)-C(12C)-C(25C) | 121.9(6) |
| C(11B)-O(11B)-Ag(1) | 114.6(4) | C(13C)-C(12C)-C(11C) | 119.0(6) |
| C(11B)-O(11B)-Ag(5) | 133.6(4) | C(25C)-C(12C)-C(11C) | 119.1(6) |
| Ag(1)-O(11B)-Ag(5) | 98.32(15) | C(12C)-C(13C)-C(18C) | 119.2(6) |
| C(11B)-O(12B)-Ag(2)#1 | 123.8(4) | C(12C)-C(13C)-C(14C) | 122.8(6) |
| O(12B)-C(11B)-O(11B) | 125.4(6) | C(18C)-C(13C)-C(14C) | 118.0(6) |
| O(12B)-C(11B)-C(12B) | 116.1(6) | C(15C)-C(14C)-C(13C) | 120.8(6) |
| O(11B)-C(11B)-C(12B) | 118.5(6) | C(14C)-C(15C)-C(16C) | 122.1(7) |

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| C(17C)-C(16C)-C(15C) | 118.7(6) | O(12F)-Ag(4)-Ag(3)#2 | 136.97(12) |
| C(16C)-C(17C)-C(18C) | 121.5(6) | O(12D)#2-Ag(4)-Ag(3)#2 | 80.28(11) |
| C(19C)-C(18C)-C(17C) | 121.3(6) | O(12F)-Ag(4)-Ag(3) | 82.40(12) |
| C(19C)-C(18C)-C(13C) | 119.9(6) | O(12D)#2-Ag(4)-Ag(3) | 126.81(12) |
| C(17C)-C(18C)-C(13C) | 118.8(6) | Ag(3)#2-Ag(4)-Ag(3) | 56.07(2) |
| C(20C)-C(19C)-C(18C) | 120.9(6) | C(11D)-O(11D)-Ag(3) | 114.9(4) |
| C(19C)-C(20C)-C(21C) | 121.8(6) | C(11D)-O(11D)-Ag(6) | 127.3(4) |
| C(19C)-C(20C)-C(25C) | 120.0(6) | Ag(3)-O(11D)-Ag(6) | 100.84(15) |
| C(21C)-C(20C)-C(25C) | 118.2(6) | C(11D)-O(12D)-Ag(4)#2 | 124.1(4) |
| C(22C)-C(21C)-C(20C) | 121.3(6) | O(11D)-C(11D)-O(12D) | 125.8(6) |
| C(21C)-C(22C)-C(23C) | 120.4(6) | O(11D)-C(11D)-C(12D) | 118.2(5) |
| C(24C)-C(23C)-C(22C) | 120.3(6) | O(12D)-C(11D)-C(12D) | 116.0(5) |
| C(23C)-C(24C)-C(25C) | 121.0(6) | C(25D)-C(12D)-C(13D) | 120.6(6) |
| C(12C)-C(25C)-C(24C) | 123.3(6) | C(25D)-C(12D)-C(11D) | 119.4(6) |
| C(12C)-C(25C)-C(20C) | 117.9(6) | C(13D)-C(12D)-C(11D) | 120.0(5) |
| C(24C)-C(25C)-C(20C) | 118.8(6) | C(12D)-C(13D)-C(18D) | 119.1(6) |
| O(11E)-Ag(3)-O(12E)#2 | 158.78(19) | C(12D)-C(13D)-C(14D) | 123.1(6) |
| O(11E)-Ag(3)-O(11F) | 99.6(2) | C(18D)-C(13D)-C(14D) | 117.6(6) |
| O(12E)#2-Ag(3)-O(11F) | 101.5(2) | C(15D)-C(14D)-C(13D) | 121.1(6) |
| O(11E)-Ag(3)-O(11D) | 94.71(17) | C(14D)-C(15D)-C(16D) | 121.2(7) |
| O(12E)#2-Ag(3)-O(11D) | 88.40(16) | C(17D)-C(16D)-C(15D) | 119.3(7) |
| O(11F)-Ag(3)-O(11D) | 86.84(17) | C(16D)-C(17D)-C(18D) | 121.1(7) |
| O(11E)-Ag(3)-Ag(3)#2 | 81.66(13) | C(19D)-C(18D)-C(17D) | 121.3(6) |
| O(12E)#2-Ag(3)-Ag(3)#2 | 81.99(12) | C(19D)-C(18D)-C(13D) | 119.0(6) |
| O(11F)-Ag(3)-Ag(3)#2 | 135.26(14) | C(17D)-C(18D)-C(13D) | 119.7(6) |
| O(11D)-Ag(3)-Ag(3)#2 | 137.86(11) | C(18D)-C(19D)-C(20D) | 122.8(6) |
| O(11E)-Ag(3)-Ag(4)#2 | 92.74(14) | C(19D)-C(20D)-C(25D) | 118.7(6) |
| O(12E)#2-Ag(3)-Ag(4)#2 | 67.65(14) | C(19D)-C(20D)-C(21D) | 121.5(6) |
| O(11F)-Ag(3)-Ag(4)#2 | 159.46(13) | C(25D)-C(20D)-C(21D) | 119.9(6) |
| O(11D)-Ag(3)-Ag(4)#2 | 75.77(10) | C(22D)-C(21D)-C(20D) | 119.6(6) |
| Ag(3)#2-Ag(3)-Ag(4)#2 | 62.60(2) | C(21D)-C(22D)-C(23D) | 122.1(7) |
| O(11E)-Ag(3)-Ag(4) | 79.46(14) | C(24D)-C(23D)-C(22D) | 119.6(7) |
| O(12E)#2-Ag(3)-Ag(4) | 104.22(13) | C(23D)-C(24D)-C(25D) | 121.2(6) |
| O(11F)-Ag(3)-Ag(4) | 74.84(13) | C(12D)-C(25D)-C(20D) | 119.7(6) |
| O(11D)-Ag(3)-Ag(4) | 159.39(11) | C(12D)-C(25D)-C(24D) | 122.7(6) |
| Ag(3)#2-Ag(3)-Ag(4) | 61.330(19) | C(20D)-C(25D)-C(24D) | 117.6(6) |
| Ag(4)#2-Ag(3)-Ag(4) | 123.93(2) | C(11E)-O(11E)-Ag(3) | 123.6(4) |
| O(12F)-Ag(4)-O(12D)#2 | 140.72(16) | C(11E)-O(12E)-Ag(3)#2 | 121.3(4) |

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| O(12E)-C(11E)-O(11E) | 126.4(6) | C(12F)-C(13F)-C(14F) | 121.8(6) |
| O(12E)-C(11E)-C(12E) | 117.5(5) | C(18F)-C(13F)-C(14F) | 118.6(6) |
| O(11E)-C(11E)-C(12E) | 116.1(5) | C(15F)-C(14F)-C(13F) | 121.2(7) |
| C(25E)-C(12E)-C(13E) | 122.2(6) | C(14F)-C(15F)-C(16F) | 120.0(7) |
| C(25E)-C(12E)-C(11E) | 118.0(5) | C(17F)-C(16F)-C(15F) | 120.9(7) |
| C(13E)-C(12E)-C(11E) | 119.7(5) | C(16F)-C(17F)-C(18F) | 120.4(7) |
| C(12E)-C(13E)-C(18E) | 118.6(6) | C(19F)-C(18F)-C(13F) | 119.9(7) |
| C(12E)-C(13E)-C(14E) | 122.4(6) | C(19F)-C(18F)-C(17F) | 121.2(7) |
| C(18E)-C(13E)-C(14E) | 119.0(6) | C(13F)-C(18F)-C(17F) | 118.9(7) |
| C(15E)-C(14E)-C(13E) | 120.2(6) | C(20F)-C(19F)-C(18F) | 121.4(7) |
| C(14E)-C(15E)-C(16E) | 120.7(6) | C(19F)-C(20F)-C(21F) | 121.8(7) |
| C(17E)-C(16E)-C(15E) | 120.8(6) | C(19F)-C(20F)-C(25F) | 120.3(7) |
| C(16E)-C(17E)-C(18E) | 120.1(7) | C(21F)-C(20F)-C(25F) | 117.9(7) |
| C(19E)-C(18E)-C(13E) | 119.3(6) | C(22F)-C(21F)-C(20F) | 120.8(7) |
| C(19E)-C(18E)-C(17E) | 121.3(6) | C(21F)-C(22F)-C(23F) | 121.0(8) |
| C(13E)-C(18E)-C(17E) | 119.4(6) | C(24F)-C(23F)-C(22F) | 120.7(8) |
| C(18E)-C(19E)-C(20E) | 122.8(6) | C(23F)-C(24F)-C(25F) | 121.0(7) |
| C(19E)-C(20E)-C(21E) | 123.1(6) | C(12F)-C(25F)-C(24F) | 123.0(6) |
| C(19E)-C(20E)-C(25E) | 117.8(6) | C(12F)-C(25F)-C(20F) | 118.5(6) |
| C(21E)-C(20E)-C(25E) | 119.1(6) | C(24F)-C(25F)-C(20F) | 118.5(6) |
| C(22E)-C(21E)-C(20E) | 121.0(7) | N(1B)-Ag(5)-N(1A) | 171.1(2) |
| C(21E)-C(22E)-C(23E) | 120.5(7) | N(1B)-Ag(5)-O(11B) | 90.5(2) |
| C(24E)-C(23E)-C(22E) | 120.2(7) | N(1A)-Ag(5)-O(11B) | 95.8(2) |
| C(23E)-C(24E)-C(25E) | 121.7(6) | N(1B)-Ag(5)-O(11A) | 100.8(2) |
| C(12E)-C(25E)-C(24E) | 123.3(6) | N(1A)-Ag(5)-O(11A) | 86.8(2) |
| C(12E)-C(25E)-C(20E) | 119.3(6) | O(11B)-Ag(5)-O(11A) | 75.46(14) |
| C(24E)-C(25E)-C(20E) | 117.5(6) | N(1A)-C(1A)-N(2A) | 111.3(7) |
| C(11F)-O(11F)-Ag(3) | 124.2(5) | C(1A)-N(1A)-C(2A) | 105.8(7) |
| C(11F)-O(11F)-Ag(6) | 120.0(4) | C(1A)-N(1A)-Ag(5) | 123.8(5) |
| Ag(3)-O(11F)-Ag(6) | 97.57(18) | C(2A)-N(1A)-Ag(5) | 130.0(6) |
| C(11F)-O(12F)-Ag(4) | 120.8(4) | C(3A)-C(2A)-N(1A) | 108.8(8) |
| O(12F)-C(11F)-O(11F) | 126.9(6) | C(2A)-C(3A)-N(2A) | 106.9(7) |
| O(12F)-C(11F)-C(12F) | 118.3(6) | C(1A)-N(2A)-C(3A) | 107.2(7) |
| O(11F)-C(11F)-C(12F) | 114.8(6) | C(1A)-N(2A)-C(4A) | 126.5(7) |
| C(13F)-C(12F)-C(25F) | 120.4(6) | C(3A)-N(2A)-C(4A) | 126.2(7) |
| C(13F)-C(12F)-C(11F) | 121.1(6) | N(2B)-C(1B)-N(1B) | 111.7(7) |
| C(25F)-C(12F)-C(11F) | 118.6(6) | C(1B)-N(1B)-C(2B) | 103.4(7) |
| C(12F)-C(13F)-C(18F) | 119.6(6) | C(1B)-N(1B)-Ag(5) | 125.1(5) |

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| C(2B)-N(1B)-Ag(5) | 130.7(6) | Ag(13)-Ag(11)-Ag(12) | 54.1(5) |
| C(3B)-C(2B)-N(1B) | 110.5(8) | Ag(13)#3-Ag(11)-Ag(12) | 55.8(4) |
| C(2B)-C(3B)-N(2B) | 105.9(8) | Ag(11)#3-Ag(12)-Ag(13) | 72.6(6) |
| C(1B)-N(2B)-C(3B) | 108.5(8) | Ag(11)#3-Ag(12)-Ag(13)#3 | 61.0(5) |
| C(1B)-N(2B)-C(4B) | 125.8(7) | Ag(13)-Ag(12)-Ag(13)#3 | 93.6(6) |
| C(3B)-N(2B)-C(4B) | 125.7(7) | Ag(11)#3-Ag(12)-Ag(14)#3 | 57.5(5) |
| N(1C)-Ag(6)-N(1D) | 171.5(2) | Ag(13)-Ag(12)-Ag(14)#3 | 130.1(7) |
| N(1C)-Ag(6)-O(11D) | 91.7(2) | Ag(13)#3-Ag(12)-Ag(14)#3 | 63.6(5) |
| N(1D)-Ag(6)-O(11D) | 95.22(19) | Ag(11)#3-Ag(12)-Ag(11) | 94.3(6) |
| N(1C)-Ag(6)-O(11F) | 84.0(2) | Ag(13)-Ag(12)-Ag(11) | 55.4(5) |
| N(1D)-Ag(6)-O(11F) | 102.7(2) | Ag(13)#3-Ag(12)-Ag(11) | 60.6(5) |
| O(11D)-Ag(6)-O(11F) | 73.62(13) | Ag(14)#3-Ag(12)-Ag(11) | 124.3(6) |
| N(1C)-C(1C)-N(2C) | 113.1(7) | Ag(12)-Ag(13)-Ag(11) | 70.4(5) |
| C(1C)-N(1C)-C(2C) | 104.2(7) | Ag(12)-Ag(13)-Ag(12)#3 | 86.4(6) |
| C(1C)-N(1C)-Ag(6) | 124.2(5) | Ag(11)-Ag(13)-Ag(12)#3 | 51.4(5) |
| C(2C)-N(1C)-Ag(6) | 131.3(5) | Ag(12)-Ag(13)-Ag(11)#3 | 50.0(5) |
| C(3C)-C(2C)-N(1C) | 109.7(7) | Ag(11)-Ag(13)-Ag(11)#3 | 90.6(6) |
| C(2C)-C(3C)-N(2C) | 107.1(7) | Ag(12)#3-Ag(13)-Ag(11)#3 | 63.5(5) |
| C(1C)-N(2C)-C(3C) | 105.9(7) | Ag(12)-Ag(13)-Ag(14) | 124.7(6) |
| C(1C)-N(2C)-C(4C) | 128.2(7) | Ag(11)-Ag(13)-Ag(14) | 54.2(5) |
| C(3C)-N(2C)-C(4C) | 125.9(7) | Ag(12)#3-Ag(13)-Ag(14) | 60.7(5) |
| N(1D)-C(1D)-N(2D) | 111.8(7) | Ag(11)#3-Ag(13)-Ag(14) | 124.2(6) |
| C(1D)-N(1D)-C(2D) | 106.9(7) | Ag(11)-Ag(14)-Ag(12)#3 | 49.9(5) |
| C(1D)-N(1D)-Ag(6) | 123.3(5) | Ag(11)-Ag(14)-Ag(13) | 55.3(5) |
| C(2D)-N(1D)-Ag(6) | 129.7(6) | Ag(12)#3-Ag(14)-Ag(13) | 55.7(4) |
| C(3D)-C(2D)-N(1D) | 108.0(8) | Ag(16)#4-Ag(15)-Ag(18)#4 | 73.0(6) |
| C(2D)-C(3D)-N(2D) | 107.4(8) | Ag(16)#4-Ag(15)-Ag(18) | 56.0(5) |
| C(1D)-N(2D)-C(3D) | 105.8(7) | Ag(18)#4-Ag(15)-Ag(18) | 90.1(6) |
| C(1D)-N(2D)-C(4D) | 127.7(7) | Ag(16)#4-Ag(15)-Ag(17) | 56.9(5) |
| C(3D)-N(2D)-C(4D) | 126.3(7) | Ag(18)#4-Ag(15)-Ag(17) | 129.9(7) |
| Ag(12)#3-Ag(11)-Ag(14) | 72.6(6) | Ag(18)-Ag(15)-Ag(17) | 63.1(5) |
| Ag(12)#3-Ag(11)-Ag(13) | 67.6(6) | Ag(16)#4-Ag(15)-Ag(16) | 91.8(6) |
| Ag(14)-Ag(11)-Ag(13) | 70.5(5) | Ag(18)#4-Ag(15)-Ag(16) | 51.7(5) |
| Ag(12)#3-Ag(11)-Ag(13)#3 | 57.4(5) | Ag(18)-Ag(15)-Ag(16) | 61.3(5) |
| Ag(14)-Ag(11)-Ag(13)#3 | 130.0(7) | Ag(17)-Ag(15)-Ag(16) | 124.4(6) |
| Ag(13)-Ag(11)-Ag(13)#3 | 89.4(6) | Ag(15)#4-Ag(16)-Ag(18)#4 | 69.9(6) |
| Ag(12)#3-Ag(11)-Ag(12) | 85.7(6) | Ag(15)#4-Ag(16)-Ag(17)#4 | 72.2(6) |
| Ag(14)-Ag(11)-Ag(12) | 124.6(6) | Ag(18)#4-Ag(16)-Ag(17)#4 | 72.9(6) |

| | | | |
|------------------------|----------|--------------------------|----------|
| Ag(15)#4-Ag(16)-Ag(18) | 56.1(5) | Ag(16)#4-Ag(18)-Ag(15)#4 | 73.2(6) |
| Ag(18)#4-Ag(16)-Ag(18) | 88.4(6) | Ag(16)#4-Ag(18)-Ag(15) | 54.0(5) |
| Ag(17)#4-Ag(16)-Ag(18) | 128.3(6) | Ag(15)#4-Ag(18)-Ag(15) | 89.9(6) |
| Ag(15)#4-Ag(16)-Ag(15) | 88.2(6) | Ag(16)#4-Ag(18)-Ag(16) | 91.6(6) |
| Ag(18)#4-Ag(16)-Ag(15) | 55.0(5) | Ag(15)#4-Ag(18)-Ag(16) | 50.9(5) |
| Ag(17)#4-Ag(16)-Ag(15) | 127.9(6) | Ag(15)-Ag(18)-Ag(16) | 62.9(5) |
| Ag(18)-Ag(16)-Ag(15) | 55.8(4) | Ag(16)#4-Ag(18)-Ag(17) | 55.6(5) |
| Ag(16)#4-Ag(17)-Ag(15) | 50.9(5) | Ag(15)#4-Ag(18)-Ag(17) | 128.9(6) |
| Ag(16)#4-Ag(17)-Ag(18) | 51.5(5) | Ag(15)-Ag(18)-Ag(17) | 61.1(5) |
| Ag(15)-Ag(17)-Ag(18) | 55.8(4) | Ag(16)-Ag(18)-Ag(17) | 124.0(6) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 -x+2,-y,-z+1 #3 -x+2,-y,-z #4 -x+1,-y,-z+1

X-ray Crystal Data for [Ag(2-Me-imidH)₂(9-aca)]

| | |
|-----------------------------------|---|
| Identification code | [Ag(2-Me-imidH) ₂ (9-aca)] |
| Empirical formula | C ₂₃ H ₂₁ Ag N ₄ O ₂ |
| Formula weight | 493.31 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | a = 19.8374(17) Å α = 90°. b = 15.2507(13) Å β = 110.140(1)°. c = 14.4941(13) Å γ = 90°. |
| Volume | 4116.8(6) Å ³ |
| Z | 8 |
| Density (calculated) | 1.592 Mg/m ³ |
| Absorption coefficient | 1.007 mm ⁻¹ |
| F(000) | 2000 |
| Crystal size | 0.28 x 0.14 x 0.13 mm ³ |
| Crystal description | colourless pyramid |
| Theta range for data collection | 1.73 to 28.35°. |
| Index ranges | -26 ≤ h ≤ 26, -20 ≤ k ≤ 20, -19 ≤ l ≤ 19 |
| Reflections collected | 20857 |
| Independent reflections | 5142 [R(int) = 0.0541] |
| Completeness to theta = 28.35° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8803 and 0.7658 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 5142 / 0 / 273 |
| Goodness-of-fit on F ² | 1.030 |
| Final R indices [I > 2σ(I)] | R1 = 0.0345, wR2 = 0.0715 |
| R indices (all data) | R1 = 0.0541, wR2 = 0.0787 |
| Largest diff. peak and hole | 0.680 and -0.407 e.Å ⁻³ |

Table 24. Bond lengths [Å] and angles [°] for [Ag(2-Me-imidH)₂(9-aca)].

| | | | |
|---------------------|------------|-------------------|----------|
| Ag(1)-N(31) | 2.111(2) | C(10)-C(15) | 1.441(4) |
| Ag(1)-N(21) | 2.115(2) | C(11)-C(12) | 1.346(5) |
| Ag(1)-O(1) | 2.4941(19) | C(12)-C(13) | 1.423(4) |
| Ag(1) ... Ag(1)#1 | 4.1930(5) | C(13)-C(14) | 1.364(4) |
| O(1)-C(1) | 1.239(3) | C(14)-C(15) | 1.424(4) |
| O(2)-C(1) | 1.261(3) | N(21)-C(21) | 1.327(3) |
| C(1)-C(2) | 1.520(4) | N(21)-C(24) | 1.372(3) |
| C(2)-C(15) | 1.403(4) | C(21)-N(22) | 1.344(3) |
| C(2)-C(3) | 1.408(4) | C(21)-C(22) | 1.487(4) |
| C(3)-C(4) | 1.421(4) | N(22)-C(23) | 1.363(4) |
| C(3)-C(8) | 1.430(4) | C(23)-C(24) | 1.355(4) |
| C(4)-C(5) | 1.357(5) | N(31)-C(31) | 1.329(3) |
| C(5)-C(6) | 1.420(5) | N(31)-C(34) | 1.388(3) |
| C(6)-C(7) | 1.350(5) | C(31)-N(32) | 1.344(3) |
| C(7)-C(8) | 1.424(5) | C(31)-C(32) | 1.478(4) |
| C(8)-C(9) | 1.390(5) | N(32)-C(33) | 1.370(4) |
| C(9)-C(10) | 1.387(4) | C(33)-C(34) | 1.353(4) |
| C(10)-C(11) | 1.423(4) | | |
| N(31)-Ag(1)-N(21) | 162.07(9) | C(4)-C(5)-C(6) | 120.8(3) |
| N(31)-Ag(1)-O(1) | 96.93(8) | C(7)-C(6)-C(5) | 119.7(4) |
| N(21)-Ag(1)-O(1) | 101.00(8) | C(6)-C(7)-C(8) | 121.5(3) |
| N(31)-Ag(1)-Ag(1)#1 | 72.16(6) | C(9)-C(8)-C(7) | 121.9(3) |
| N(21)-Ag(1)-Ag(1)#1 | 95.26(6) | C(9)-C(8)-C(3) | 119.2(3) |
| O(1)-Ag(1)-Ag(1)#1 | 132.01(5) | C(7)-C(8)-C(3) | 118.8(3) |
| C(1)-O(1)-Ag(1) | 130.54(17) | C(10)-C(9)-C(8) | 122.1(3) |
| O(1)-C(1)-O(2) | 124.7(2) | C(9)-C(10)-C(11) | 122.1(3) |
| O(1)-C(1)-C(2) | 118.6(2) | C(9)-C(10)-C(15) | 119.2(3) |
| O(2)-C(1)-C(2) | 116.7(2) | C(11)-C(10)-C(15) | 118.7(3) |
| C(15)-C(2)-C(3) | 120.8(3) | C(12)-C(11)-C(10) | 121.9(3) |
| C(15)-C(2)-C(1) | 119.5(3) | C(11)-C(12)-C(13) | 119.9(3) |
| C(3)-C(2)-C(1) | 119.7(3) | C(14)-C(13)-C(12) | 120.3(3) |
| C(2)-C(3)-C(4) | 122.6(3) | C(13)-C(14)-C(15) | 121.7(3) |
| C(2)-C(3)-C(8) | 119.5(3) | C(2)-C(15)-C(14) | 123.4(3) |
| C(4)-C(3)-C(8) | 117.9(3) | C(2)-C(15)-C(10) | 119.1(3) |
| C(5)-C(4)-C(3) | 121.3(3) | C(14)-C(15)-C(10) | 117.5(3) |

| | | | |
|-------------------|------------|-------------------|------------|
| C(21)-N(21)-C(24) | 106.4(2) | C(21)-N(21)-Ag(1) | 126.10(18) |
| C(24)-N(21)-Ag(1) | 127.13(19) | C(31)-N(31)-Ag(1) | 126.98(19) |
| N(21)-C(21)-N(22) | 109.9(2) | C(34)-N(31)-Ag(1) | 126.72(18) |
| N(21)-C(21)-C(22) | 124.8(2) | N(31)-C(31)-N(32) | 110.4(2) |
| N(22)-C(21)-C(22) | 125.3(3) | N(31)-C(31)-C(32) | 125.9(2) |
| C(21)-N(22)-C(23) | 108.4(2) | N(32)-C(31)-C(32) | 123.7(2) |
| C(24)-C(23)-N(22) | 106.0(3) | C(31)-N(32)-C(33) | 107.9(2) |
| C(23)-C(24)-N(21) | 109.4(3) | C(34)-C(33)-N(32) | 106.7(2) |
| C(31)-N(31)-C(34) | 106.2(2) | C(33)-C(34)-N(31) | 108.8(2) |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y, -z+2$

Table 25. Hydrogen bonds for [Ag(2-Me-imidH)₂(9-aca)] [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|----------------------|--------|----------|----------|--------|
| N(22)-H(22)...O(2)#2 | 0.88 | 1.97 | 2.764(3) | 149.1 |
| N(32)-H(32)...O(2)#3 | 0.88 | 1.91 | 2.779(3) | 168.8 |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y, -z+2$ #2 $x+1/2, -y+1/2, z+1/2$ #3 $x, -y, z+1/2$

X-ray Crystal Data for [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆]

| | |
|-----------------------------------|--|
| Identification code | [Ag(1-Bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] |
| Empirical formula | C ₁₁₈ H ₁₀₂ Ag ₆ N ₈ O ₁₂ |
| Formula weight | 2471.30 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | a = 17.6333(7) Å α = 96.019(1)°. b = 19.3853(8) Å β = 95.831(1)°. c = 30.4753(13) Å γ = 90.237(1)°. |
| Volume | 10305.1(7) Å ³ |
| Z | 4 |
| Density (calculated) | 1.593 Mg/m ³ |
| Absorption coefficient | 1.185 mm ⁻¹ |
| F(000) | 4976 |
| Crystal size | 0.32 x 0.19 x 0.12 mm ³ |
| Crystal description | Colourless block |
| Theta range for data collection | 0.68 to 26.00°. |
| Index ranges | -21 ≤ h ≤ 21, -23 ≤ k ≤ 23, -37 ≤ l ≤ 37 |
| Reflections collected | 89958 |
| Independent reflections | 40407 [R(int) = 0.0422] |
| Completeness to theta = 26.00° | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.4311 and 0.3430 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 40407 / 3021 / 2665 |
| Goodness-of-fit on F ² | 1.068 |
| Final R indices [I > 2σ(I)] | R1 = 0.0505, wR2 = 0.1130 |
| R indices (all data) | R1 = 0.0739, wR2 = 0.1229 |
| Largest diff. peak and hole | 1.703 and -0.977 e.Å ⁻³ |

Table 26. Bond lengths [Å] and angles [°] for [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆].

| | | | |
|---------------|-----------|---------------|-----------|
| Ag(1)-O(1A) | 2.207(4) | C(14A)-C(15A) | 1.430(8) |
| Ag(1)-O(2D) | 2.217(4) | O(1B)-C(1B) | 1.249(6) |
| Ag(1)-Ag(4) | 2.8750(6) | O(1B)-Ag(5) | 2.809(4) |
| Ag(1)-Ag(2) | 2.9028(6) | O(2B)-C(1B) | 1.248(7) |
| Ag(2)-O(1E) | 2.222(4) | C(1B)-C(2B) | 1.505(7) |
| Ag(2)-O(1F) | 2.226(4) | C(2B)-C(3B) | 1.389(8) |
| Ag(2)-O(2A) | 2.335(4) | C(2B)-C(15B) | 1.413(8) |
| Ag(2)-O(1B) | 2.357(4) | C(3B)-C(4B) | 1.433(8) |
| Ag(2)-Ag(4) | 2.8365(5) | C(3B)-C(8B) | 1.449(8) |
| Ag(2)-Ag(3) | 2.8770(6) | C(4B)-C(5B) | 1.359(9) |
| Ag(3)-O(1C) | 2.174(4) | C(5B)-C(6B) | 1.403(10) |
| Ag(3)-O(2B) | 2.192(4) | C(6B)-C(7B) | 1.347(10) |
| Ag(3)-Ag(4) | 2.8949(6) | C(7B)-C(8B) | 1.435(9) |
| Ag(4)-O(1D) | 2.275(4) | C(8B)-C(9B) | 1.372(8) |
| Ag(4)-O(2C) | 2.304(4) | C(9B)-C(10B) | 1.414(8) |
| Ag(4)-O(2F) | 2.354(4) | C(10B)-C(11B) | 1.397(8) |
| Ag(4)-O(2E) | 2.355(4) | C(10B)-C(15B) | 1.423(7) |
| O(1A)-C(1A) | 1.266(6) | C(11B)-C(12B) | 1.347(9) |
| O(2A)-C(1A) | 1.247(6) | C(12B)-C(13B) | 1.423(9) |
| O(2A)-Ag(5) | 2.696(4) | C(13B)-C(14B) | 1.360(8) |
| C(1A)-C(2A) | 1.516(7) | C(14B)-C(15B) | 1.423(8) |
| C(2A)-C(15A) | 1.410(8) | O(1C)-C(1C) | 1.269(7) |
| C(2A)-C(3A) | 1.416(8) | O(2C)-C(1C) | 1.220(7) |
| C(3A)-C(4A) | 1.416(8) | O(2C)-Ag(6) | 2.756(4) |
| C(3A)-C(8A) | 1.436(8) | C(1C)-C(2C) | 1.522(7) |
| C(4A)-C(5A) | 1.347(9) | C(2C)-C(3C) | 1.392(8) |
| C(5A)-C(6A) | 1.420(9) | C(2C)-C(15C) | 1.402(8) |
| C(6A)-C(7A) | 1.349(10) | C(3C)-C(8C) | 1.429(8) |
| C(7A)-C(8A) | 1.422(9) | C(3C)-C(4C) | 1.430(8) |
| C(8A)-C(9A) | 1.394(9) | C(4C)-C(5C) | 1.342(9) |
| C(9A)-C(10A) | 1.388(8) | C(5C)-C(6C) | 1.421(9) |
| C(10A)-C(11A) | 1.422(8) | C(6C)-C(7C) | 1.352(10) |
| C(10A)-C(15A) | 1.431(8) | C(7C)-C(8C) | 1.430(9) |
| C(11A)-C(12A) | 1.334(9) | C(8C)-C(9C) | 1.403(9) |
| C(12A)-C(13A) | 1.411(9) | C(9C)-C(10C) | 1.377(9) |
| C(13A)-C(14A) | 1.373(9) | C(10C)-C(15C) | 1.438(8) |

| | | | |
|---------------|-----------|---------------|-----------|
| C(10C)-C(11C) | 1.444(9) | C(10E)-C(11E) | 1.430(9) |
| C(11C)-C(12C) | 1.324(10) | C(10E)-C(15E) | 1.431(8) |
| C(12C)-C(13C) | 1.397(10) | C(11E)-C(12E) | 1.358(10) |
| C(13C)-C(14C) | 1.363(9) | C(12E)-C(13E) | 1.402(10) |
| C(14C)-C(15C) | 1.428(9) | C(13E)-C(14E) | 1.373(9) |
| O(1D)-C(1D) | 1.230(7) | C(14E)-C(15E) | 1.424(9) |
| O(1D)-Ag(6) | 2.603(4) | O(1F)-C(1F) | 1.224(7) |
| O(2D)-C(1D) | 1.235(7) | O(2F)-C(1F) | 1.265(6) |
| C(1D)-C(2D) | 1.511(7) | O(2F)-Ag(12) | 14.267(4) |
| C(2D)-C(15D) | 1.398(8) | C(1F)-C(2F) | 1.529(8) |
| C(2D)-C(3D) | 1.404(8) | C(2F)-C(15F) | 1.388(9) |
| C(3D)-C(8D) | 1.422(8) | C(2F)-C(3F) | 1.410(9) |
| C(3D)-C(4D) | 1.421(9) | C(3F)-C(4F) | 1.400(10) |
| C(4D)-C(5D) | 1.338(9) | C(3F)-C(8F) | 1.460(9) |
| C(5D)-C(6D) | 1.415(11) | C(4F)-C(5F) | 1.360(10) |
| C(6D)-C(7D) | 1.359(12) | C(5F)-C(6F) | 1.406(12) |
| C(7D)-C(8D) | 1.432(10) | C(6F)-C(7F) | 1.327(13) |
| C(8D)-C(9D) | 1.359(10) | C(7F)-C(8F) | 1.455(12) |
| C(9D)-C(10D) | 1.401(10) | C(8F)-C(9F) | 1.373(12) |
| C(10D)-C(11D) | 1.413(10) | C(9F)-C(10F) | 1.376(12) |
| C(10D)-C(15D) | 1.446(9) | C(10F)-C(11F) | 1.427(12) |
| C(11D)-C(12D) | 1.323(12) | C(10F)-C(15F) | 1.456(9) |
| C(12D)-C(13D) | 1.403(12) | C(11F)-C(12F) | 1.330(14) |
| C(13D)-C(14D) | 1.384(10) | C(12F)-C(13F) | 1.397(13) |
| C(14D)-C(15D) | 1.434(9) | C(13F)-C(14F) | 1.380(10) |
| O(1E)-C(1E) | 1.271(6) | C(14F)-C(15F) | 1.405(10) |
| O(2E)-C(1E) | 1.227(7) | Ag(5)-N(1A) | 2.116(5) |
| C(1E)-C(2E) | 1.516(7) | Ag(5)-N(1B) | 2.117(5) |
| C(2E)-C(3E) | 1.398(8) | Ag(5)-O(2A) | 2.696(4) |
| C(2E)-C(15E) | 1.410(8) | ag(5)-O(1B) | 2.809(4) |
| C(3E)-C(4E) | 1.417(8) | C(21A)-N(1A) | 1.327(7) |
| C(3E)-C(8E) | 1.457(8) | C(21A)-N(2A) | 1.335(7) |
| C(4E)-C(5E) | 1.373(9) | N(1A)-C(22A) | 1.372(7) |
| C(5E)-C(6E) | 1.429(10) | C(22A)-C(23A) | 1.323(8) |
| C(6E)-C(7E) | 1.348(10) | C(23A)-N(2A) | 1.377(7) |
| C(7E)-C(8E) | 1.441(9) | N(2A)-C(24A) | 1.474(8) |
| C(8E)-C(9E) | 1.376(9) | C(24A)-C(25A) | 1.589(12) |
| C(9E)-C(10E) | 1.386(9) | C(25A)-C(26A) | 1.425(11) |

| | | | |
|---------------|-----------|---------------|-----------|
| C(26A)-C(27A) | 1.483(13) | Ag(8)-O(1K) | 2.217(4) |
| C(21B)-N(1B) | 1.314(7) | Ag(8)-O(2L) | 2.257(4) |
| C(21B)-N(2B) | 1.338(7) | Ag(8)-O(2G) | 2.301(4) |
| N(1B)-C(22B) | 1.376(7) | Ag(8)-O(1H) | 2.382(4) |
| C(22B)-C(23B) | 1.346(8) | Ag(8)-Ag(10) | 2.8165(6) |
| C(23B)-N(2B) | 1.374(7) | Ag(8)-Ag(9) | 2.8544(6) |
| N(2B)-C(24B) | 1.462(8) | Ag(9)-O(1I) | 2.178(4) |
| C(24B)-C(25B) | 1.514(9) | Ag(9)-O(2H) | 2.203(4) |
| C(25B)-C(26B) | 1.488(9) | Ag(9)-Ag(10) | 2.9511(6) |
| C(26B)-C(27B) | 1.535(10) | Ag(10)-O(2I) | 2.286(4) |
| Ag(6)-N(1D) | 2.131(5) | Ag(10)-O(1J) | 2.305(4) |
| Ag(6)-N(1C) | 2.131(5) | Ag(10)-O(2K) | 2.309(4) |
| Ag(6)-O(1D) | 2.603(4) | Ag(10)-O(1L) | 2.374(4) |
| Ag(6)-O(2C) | 2.756(4) | O(1G)-C(1G) | 1.245(6) |
| C(21C)-N(1C) | 1.326(8) | O(2G)-C(1G) | 1.233(6) |
| C(21C)-N(2C) | 1.346(8) | O(2G)-Ag(11) | 2.847(4) |
| N(1C)-C(22C) | 1.372(8) | C(1G)-C(2G) | 1.519(7) |
| C(22C)-C(23C) | 1.340(9) | C(2G)-C(15G) | 1.400(8) |
| C(23C)-N(2C) | 1.378(8) | C(2G)-C(3G) | 1.403(8) |
| N(2C)-C(24C) | 1.462(8) | C(3G)-C(4G) | 1.413(8) |
| C(24C)-C(25C) | 1.484(11) | C(3G)-C(8G) | 1.447(7) |
| C(25C)-C(26C) | 1.395(18) | C(4G)-C(5G) | 1.352(8) |
| C(26C)-C(27C) | 1.52(4) | C(5G)-C(6G) | 1.420(8) |
| C(26X)-C(27X) | 1.57(4) | C(6G)-C(7G) | 1.353(9) |
| C(21D)-N(1D) | 1.306(8) | C(7G)-C(8G) | 1.420(8) |
| C(21D)-N(2D) | 1.345(8) | C(8G)-C(9G) | 1.380(8) |
| N(1D)-C(22D) | 1.374(8) | C(9G)-C(10G) | 1.379(8) |
| C(22D)-C(23D) | 1.350(9) | C(10G)-C(11G) | 1.415(8) |
| C(23D)-N(2D) | 1.375(8) | C(10G)-C(15G) | 1.454(8) |
| N(2D)-C(24D) | 1.442(8) | C(11G)-C(12G) | 1.362(10) |
| C(24D)-C(25D) | 1.538(9) | C(12G)-C(13G) | 1.412(10) |
| C(25D)-C(26D) | 1.503(9) | C(13G)-C(14G) | 1.359(9) |
| C(26D)-C(27D) | 1.533(10) | C(14G)-C(15G) | 1.409(8) |
| Ag(7)-O(1G) | 2.196(4) | O(1H)-C(1H) | 1.243(7) |
| Ag(7)-O(2J) | 2.202(4) | O(1H)-Ag(11) | 2.678(4) |
| Ag(7)-O(1L) | 2.564(4) | O(2H)-C(1H) | 1.257(7) |
| Ag(7)-Ag(10) | 2.8760(6) | C(1H)-C(2H) | 1.519(7) |
| Ag(7)-Ag(8) | 2.9646(6) | C(2H)-C(15H) | 1.395(8) |

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| C(2H)-C(3H) | 1.417(8) | C(2J)-C(15J) | 1.404(9) |
| C(3H)-C(4H) | 1.424(8) | C(2J)-C(3J) | 1.420(8) |
| C(3H)-C(8H) | 1.427(8) | C(3J)-C(4J) | 1.417(8) |
| C(4H)-C(5H) | 1.359(9) | C(3J)-C(8J) | 1.430(8) |
| C(5H)-C(6H) | 1.423(9) | C(4J)-C(5J) | 1.356(9) |
| C(6H)-C(7H) | 1.343(10) | C(5J)-C(6J) | 1.415(11) |
| C(7H)-C(8H) | 1.434(9) | C(6J)-C(7J) | 1.332(11) |
| C(8H)-C(9H) | 1.392(9) | C(7J)-C(8J) | 1.454(9) |
| C(9H)-C(10H) | 1.389(9) | C(8J)-C(9J) | 1.370(9) |
| C(10H)-C(11H) | 1.425(9) | C(9J)-C(10J) | 1.389(10) |
| C(10H)-C(15H) | 1.439(8) | C(10J)-C(11J) | 1.419(9) |
| C(11H)-C(12H) | 1.345(10) | C(10J)-C(15J) | 1.461(9) |
| C(12H)-C(13H) | 1.424(9) | C(11J)-C(12J) | 1.331(12) |
| C(13H)-C(14H) | 1.362(9) | C(12J)-C(13J) | 1.403(13) |
| C(14H)-C(15H) | 1.433(9) | C(13J)-C(14J) | 1.407(11) |
| O(1I)-C(1I) | 1.261(7) | C(14J)-C(15J) | 1.419(10) |
| O(2I)-C(1I) | 1.236(7) | O(1K)-C(1K) | 1.250(7) |
| C(1I)-C(2I) | 1.512(7) | O(2K)-C(1K) | 1.262(7) |
| C(2I)-C(3I) | 1.388(8) | C(1K)-C(2K) | 1.500(8) |
| C(2I)-C(15I) | 1.401(8) | C(2K)-C(15K) | 1.388(9) |
| C(3I)-C(4I) | 1.424(8) | C(2K)-C(3K) | 1.417(9) |
| C(3I)-C(8I) | 1.447(8) | C(3K)-C(4K) | 1.396(10) |
| C(4I)-C(5I) | 1.351(9) | C(3K)-C(8K) | 1.445(9) |
| C(5I)-C(6I) | 1.427(10) | C(4K)-C(5K) | 1.387(10) |
| C(6I)-C(7I) | 1.325(10) | C(5K)-C(6K) | 1.393(12) |
| C(7I)-C(8I) | 1.427(9) | C(6K)-C(7K) | 1.348(13) |
| C(8I)-C(9I) | 1.391(9) | C(7K)-C(8K) | 1.425(11) |
| C(9I)-C(10I) | 1.386(9) | C(8K)-C(9K) | 1.387(11) |
| C(10I)-C(15I) | 1.435(8) | C(9K)-C(10K) | 1.365(11) |
| C(10I)-C(11I) | 1.445(9) | C(10K)-C(15K) | 1.438(9) |
| C(11I)-C(12I) | 1.339(10) | C(10K)-C(11K) | 1.449(11) |
| C(12I)-C(13I) | 1.394(10) | C(11K)-C(12K) | 1.321(12) |
| C(13I)-C(14I) | 1.375(9) | C(12K)-C(13K) | 1.411(11) |
| C(14I)-C(15I) | 1.415(9) | C(13K)-C(14K) | 1.346(10) |
| O(1J)-C(1J) | 1.226(7) | C(14K)-C(15K) | 1.430(9) |
| O(1J)-Ag(12) | 2.624(4) | O(1L)-C(1L) | 1.231(6) |
| O(2J)-C(1J) | 1.244(7) | O(2L)-C(1L) | 1.269(6) |
| C(1J)-C(2J) | 1.508(8) | C(1L)-C(2L) | 1.525(7) |

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| C(2L)-C(3L) | 1.389(8) | C(21F)-N(2F) | 1.338(7) |
| C(2L)-C(15L) | 1.417(8) | N(1F)-C(22F) | 1.365(7) |
| C(3L)-C(8L) | 1.435(8) | C(22F)-C(23F) | 1.336(9) |
| C(3L)-C(4L) | 1.438(9) | C(23F)-N(2F) | 1.376(7) |
| C(4L)-C(5L) | 1.354(9) | N(2F)-C(24F) | 1.473(7) |
| C(5L)-C(6L) | 1.411(11) | C(24F)-C(25F) | 1.512(9) |
| C(6L)-C(7L) | 1.362(11) | C(25F)-C(26F) | 1.500(9) |
| C(7L)-C(8L) | 1.445(9) | C(26F)-C(27F) | 1.517(10) |
| C(8L)-C(9L) | 1.362(9) | Ag(12)-N(1H) | 2.122(5) |
| C(9L)-C(10L) | 1.416(9) | Ag(12)-N(1G) | 2.124(5) |
| C(10L)-C(11L) | 1.412(9) | Ag(12)-O(1J) | 2.624(4) |
| C(10L)-C(15L) | 1.454(8) | Ag(12)-O(2F) | 2.740(4) |
| C(11L)-C(12L) | 1.341(11) | C(21G)-N(1G) | 1.314(8) |
| C(12L)-C(13L) | 1.439(10) | C(21G)-N(2G) | 1.328(8) |
| C(13L)-C(14L) | 1.365(9) | N(1G)-C(22G) | 1.381(8) |
| C(14L)-C(15L) | 1.395(9) | C(22G)-C(23G) | 1.353(9) |
| Ag(11)-N(1E) | 2.112(5) | C(23G)-N(2G) | 1.371(8) |
| Ag(11)-N(1F) | 2.113(5) | N(2G)-C(24G) | 1.463(9) |
| Ag(11)-O(1H) | 2.678(4) | C(24G)-C(25G) | 1.549(10) |
| Ag(11)-O(2G) | 2.847(4) | C(25G)-C(26G) | 1.501(10) |
| C(21E)-N(1E) | 1.315(8) | C(26G)-C(27G) | 1.504(11) |
| C(21E)-N(2E) | 1.334(8) | C(21H)-N(1H) | 1.318(8) |
| N(1E)-C(22E) | 1.371(7) | C(21H)-N(2H) | 1.361(8) |
| C(22E)-C(23E) | 1.338(9) | N(1H)-C(22H) | 1.366(8) |
| C(23E)-N(2E) | 1.365(8) | C(22H)-C(23H) | 1.353(9) |
| N(2E)-C(24E) | 1.456(9) | C(23H)-N(2H) | 1.372(8) |
| C(24E)-C(25E) | 1.607(16) | N(2H)-C(24H) | 1.463(8) |
| C(25E)-C(26Y) | 1.521(17) | C(24H)-C(25H) | 1.56(2) |
| C(26Y)-C(27E) | 1.49(2) | C(25H)-C(26H) | 1.48(3) |
| C(25Y)-C(26E) | 1.34(3) | C(26H)-C(27H) | 1.52(3) |
| C(26E)-C(27Y) | 1.61(3) | C(25Z)-C(26Z) | 1.52(2) |
| C(21F)-N(1F) | 1.329(7) | C(26Z)-C(27Z) | 1.52(3) |
| O(1A)-Ag(1)-O(2D) | 132.81(16) | Ag(4)-Ag(1)-Ag(2) | 58.801(14) |
| O(1A)-Ag(1)-Ag(4) | 140.04(10) | O(1E)-Ag(2)-O(1F) | 154.83(15) |
| O(2D)-Ag(1)-Ag(4) | 87.07(12) | O(1E)-Ag(2)-O(2A) | 108.55(15) |
| O(1A)-Ag(1)-Ag(2) | 83.96(10) | O(1F)-Ag(2)-O(2A) | 91.25(14) |
| O(2D)-Ag(1)-Ag(2) | 140.64(14) | O(1E)-Ag(2)-O(1B) | 94.95(15) |

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| O(1F)-Ag(2)-O(1B) | 99.15(16) | O(1D)-Ag(4)-Ag(3) | 162.13(12) |
| O(2A)-Ag(2)-O(1B) | 93.86(14) | O(2C)-Ag(4)-Ag(3) | 77.92(10) |
| O(1E)-Ag(2)-Ag(4) | 79.05(10) | O(2F)-Ag(4)-Ag(3) | 61.65(10) |
| O(1F)-Ag(2)-Ag(4) | 76.00(10) | O(2E)-Ag(4)-Ag(3) | 102.95(10) |
| O(2A)-Ag(2)-Ag(4) | 133.76(10) | Ag(2)-Ag(4)-Ag(3) | 60.250(14) |
| O(1B)-Ag(2)-Ag(4) | 131.69(10) | Ag(1)-Ag(4)-Ag(3) | 121.175(18) |
| O(1E)-Ag(2)-Ag(3) | 77.51(12) | C(1A)-O(1A)-Ag(1) | 118.7(4) |
| O(1F)-Ag(2)-Ag(3) | 87.50(11) | C(1A)-O(2A)-Ag(2) | 122.1(3) |
| O(2A)-Ag(2)-Ag(3) | 164.34(10) | C(1A)-O(2A)-Ag(5) | 124.1(3) |
| O(1B)-Ag(2)-Ag(3) | 70.97(10) | Ag(2)-O(2A)-Ag(5) | 96.20(13) |
| Ag(4)-Ag(2)-Ag(3) | 60.881(14) | O(2A)-C(1A)-O(1A) | 126.1(5) |
| O(1E)-Ag(2)-Ag(1) | 87.73(11) | O(2A)-C(1A)-C(2A) | 116.9(5) |
| O(1F)-Ag(2)-Ag(1) | 82.71(12) | O(1A)-C(1A)-C(2A) | 117.0(5) |
| O(2A)-Ag(2)-Ag(1) | 74.40(10) | C(15A)-C(2A)-C(3A) | 120.9(5) |
| O(1B)-Ag(2)-Ag(1) | 168.19(10) | C(15A)-C(2A)-C(1A) | 119.6(5) |
| Ag(4)-Ag(2)-Ag(1) | 60.110(14) | C(3A)-C(2A)-C(1A) | 119.5(5) |
| Ag(3)-Ag(2)-Ag(1) | 120.829(18) | C(4A)-C(3A)-C(2A) | 123.2(5) |
| O(1C)-Ag(3)-O(2B) | 135.29(16) | C(4A)-C(3A)-C(8A) | 118.2(6) |
| O(1C)-Ag(3)-Ag(2) | 134.20(11) | C(2A)-C(3A)-C(8A) | 118.6(5) |
| O(2B)-Ag(3)-Ag(2) | 88.77(11) | C(5A)-C(4A)-C(3A) | 121.1(6) |
| O(1C)-Ag(3)-Ag(4) | 83.61(11) | C(4A)-C(5A)-C(6A) | 121.0(7) |
| O(2B)-Ag(3)-Ag(4) | 139.39(12) | C(7A)-C(6A)-C(5A) | 119.9(7) |
| Ag(2)-Ag(3)-Ag(4) | 58.869(14) | C(6A)-C(7A)-C(8A) | 121.2(6) |
| O(1D)-Ag(4)-O(2C) | 89.46(15) | C(9A)-C(8A)-C(7A) | 121.9(6) |
| O(1D)-Ag(4)-O(2F) | 107.09(18) | C(9A)-C(8A)-C(3A) | 119.5(6) |
| O(2C)-Ag(4)-O(2F) | 93.00(15) | C(7A)-C(8A)-C(3A) | 118.6(6) |
| O(1D)-Ag(4)-O(2E) | 92.01(17) | C(10A)-C(9A)-C(8A) | 122.4(5) |
| O(2C)-Ag(4)-O(2E) | 102.37(15) | C(9A)-C(10A)-C(11A) | 121.6(5) |
| O(2F)-Ag(4)-O(2E) | 155.64(13) | C(9A)-C(10A)-C(15A) | 118.8(5) |
| O(1D)-Ag(4)-Ag(2) | 134.30(11) | C(11A)-C(10A)-C(15A) | 119.6(6) |
| O(2C)-Ag(4)-Ag(2) | 136.04(10) | C(12A)-C(11A)-C(10A) | 120.7(6) |
| O(2F)-Ag(4)-Ag(2) | 79.41(9) | C(11A)-C(12A)-C(13A) | 121.4(6) |
| O(2E)-Ag(4)-Ag(2) | 76.40(10) | C(14A)-C(13A)-C(12A) | 120.0(6) |
| O(1D)-Ag(4)-Ag(1) | 74.98(11) | C(13A)-C(14A)-C(15A) | 120.9(6) |
| O(2C)-Ag(4)-Ag(1) | 154.24(11) | C(2A)-C(15A)-C(14A) | 122.8(5) |
| O(2F)-Ag(4)-Ag(1) | 110.99(10) | C(2A)-C(15A)-C(10A) | 119.8(5) |
| O(2E)-Ag(4)-Ag(1) | 58.77(10) | C(14A)-C(15A)-C(10A) | 117.4(5) |
| Ag(2)-Ag(4)-Ag(1) | 61.088(14) | C(1B)-O(1B)-Ag(2) | 128.8(4) |

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| C(1B)-O(1B)-Ag(5) | 130.0(4) | C(3C)-C(2C)-C(1C) | 116.4(5) |
| Ag(2)-O(1B)-Ag(5) | 92.72(13) | C(15C)-C(2C)-C(1C) | 121.3(5) |
| C(1B)-O(2B)-Ag(3) | 114.2(4) | C(2C)-C(3C)-C(8C) | 119.0(5) |
| O(2B)-C(1B)-O(1B) | 125.9(5) | C(2C)-C(3C)-C(4C) | 122.9(5) |
| O(2B)-C(1B)-C(2B) | 117.9(5) | C(8C)-C(3C)-C(4C) | 118.0(6) |
| O(1B)-C(1B)-C(2B) | 116.2(5) | C(5C)-C(4C)-C(3C) | 121.7(6) |
| C(3B)-C(2B)-C(15B) | 120.7(5) | C(4C)-C(5C)-C(6C) | 120.5(6) |
| C(3B)-C(2B)-C(1B) | 121.4(5) | C(7C)-C(6C)-C(5C) | 119.9(6) |
| C(15B)-C(2B)-C(1B) | 117.9(5) | C(6C)-C(7C)-C(8C) | 121.6(6) |
| C(2B)-C(3B)-C(4B) | 122.8(5) | C(9C)-C(8C)-C(3C) | 119.0(6) |
| C(2B)-C(3B)-C(8B) | 118.6(5) | C(9C)-C(8C)-C(7C) | 122.8(6) |
| C(4B)-C(3B)-C(8B) | 118.5(5) | C(3C)-C(8C)-C(7C) | 118.2(6) |
| C(5B)-C(4B)-C(3B) | 120.5(6) | C(10C)-C(9C)-C(8C) | 121.8(5) |
| C(4B)-C(5B)-C(6B) | 121.0(7) | C(9C)-C(10C)-C(15C) | 120.0(6) |
| C(7B)-C(6B)-C(5B) | 121.0(7) | C(9C)-C(10C)-C(11C) | 123.3(6) |
| C(6B)-C(7B)-C(8B) | 121.4(6) | C(15C)-C(10C)-C(11C) | 116.7(6) |
| C(9B)-C(8B)-C(7B) | 122.1(6) | C(12C)-C(11C)-C(10C) | 122.0(7) |
| C(9B)-C(8B)-C(3B) | 120.4(5) | C(11C)-C(12C)-C(13C) | 121.1(7) |
| C(7B)-C(8B)-C(3B) | 117.5(6) | C(14C)-C(13C)-C(12C) | 120.9(7) |
| C(8B)-C(9B)-C(10B) | 121.3(5) | C(13C)-C(14C)-C(15C) | 120.1(6) |
| C(11B)-C(10B)-C(9B) | 122.5(5) | C(2C)-C(15C)-C(14C) | 122.9(5) |
| C(11B)-C(10B)-C(15B) | 118.9(5) | C(2C)-C(15C)-C(10C) | 118.0(6) |
| C(9B)-C(10B)-C(15B) | 118.5(5) | C(14C)-C(15C)-C(10C) | 119.0(6) |
| C(12B)-C(11B)-C(10B) | 122.1(6) | C(1D)-O(1D)-Ag(4) | 132.1(4) |
| C(11B)-C(12B)-C(13B) | 119.5(6) | C(1D)-O(1D)-Ag(6) | 126.3(4) |
| C(14B)-C(13B)-C(12B) | 120.6(6) | Ag(4)-O(1D)-Ag(6) | 100.77(16) |
| C(13B)-C(14B)-C(15B) | 120.3(6) | C(1D)-O(2D)-Ag(1) | 118.6(4) |
| C(2B)-C(15B)-C(10B) | 120.2(5) | O(1D)-C(1D)-O(2D) | 125.5(5) |
| C(2B)-C(15B)-C(14B) | 121.2(5) | O(1D)-C(1D)-C(2D) | 115.9(5) |
| C(10B)-C(15B)-C(14B) | 118.5(5) | O(2D)-C(1D)-C(2D) | 118.6(5) |
| C(1C)-O(1C)-Ag(3) | 118.6(4) | C(15D)-C(2D)-C(3D) | 120.4(5) |
| C(1C)-O(2C)-Ag(4) | 123.8(4) | C(15D)-C(2D)-C(1D) | 120.4(5) |
| C(1C)-O(2C)-Ag(6) | 139.3(4) | C(3D)-C(2D)-C(1D) | 119.0(5) |
| Ag(4)-O(2C)-Ag(6) | 95.73(14) | C(2D)-C(3D)-C(8D) | 119.7(6) |
| O(2C)-C(1C)-O(1C) | 127.6(5) | C(2D)-C(3D)-C(4D) | 122.3(5) |
| O(2C)-C(1C)-C(2C) | 117.0(5) | C(8D)-C(3D)-C(4D) | 118.0(6) |
| O(1C)-C(1C)-C(2C) | 115.3(5) | C(5D)-C(4D)-C(3D) | 122.7(7) |
| C(3C)-C(2C)-C(15C) | 122.2(5) | C(4D)-C(5D)-C(6D) | 119.6(8) |

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| C(7D)-C(6D)-C(5D) | 120.5(7) | C(12E)-C(11E)-C(10E) | 121.1(7) |
| C(6D)-C(7D)-C(8D) | 120.9(7) | C(11E)-C(12E)-C(13E) | 120.6(7) |
| C(9D)-C(8D)-C(3D) | 119.8(6) | C(14E)-C(13E)-C(12E) | 120.7(7) |
| C(9D)-C(8D)-C(7D) | 121.9(6) | C(13E)-C(14E)-C(15E) | 120.5(7) |
| C(3D)-C(8D)-C(7D) | 118.2(7) | C(2E)-C(15E)-C(14E) | 122.3(6) |
| C(8D)-C(9D)-C(10D) | 122.5(6) | C(2E)-C(15E)-C(10E) | 119.0(6) |
| C(9D)-C(10D)-C(11D) | 122.7(7) | C(14E)-C(15E)-C(10E) | 118.6(6) |
| C(9D)-C(10D)-C(15D) | 118.1(6) | C(1F)-O(1F)-Ag(2) | 122.5(4) |
| C(11D)-C(10D)-C(15D) | 119.1(7) | C(1F)-O(2F)-Ag(4) | 109.6(4) |
| C(12D)-C(11D)-C(10D) | 121.8(8) | C(1F)-O(2F)-Ag(12) | 77.1(3) |
| C(11D)-C(12D)-C(13D) | 120.7(8) | Ag(4)-O(2F)-Ag(12) | 59.91(9) |
| C(14D)-C(13D)-C(12D) | 121.3(8) | O(1F)-C(1F)-O(2F) | 127.8(5) |
| C(13D)-C(14D)-C(15D) | 119.5(8) | O(1F)-C(1F)-C(2F) | 115.6(5) |
| C(2D)-C(15D)-C(14D) | 123.1(6) | O(2F)-C(1F)-C(2F) | 116.6(5) |
| C(2D)-C(15D)-C(10D) | 119.5(6) | C(15F)-C(2F)-C(3F) | 122.5(6) |
| C(14D)-C(15D)-C(10D) | 117.5(6) | C(15F)-C(2F)-C(1F) | 120.8(6) |
| C(1E)-O(1E)-Ag(2) | 118.4(4) | C(3F)-C(2F)-C(1F) | 116.6(6) |
| C(1E)-O(2E)-Ag(4) | 113.3(3) | C(4F)-C(3F)-C(2F) | 124.1(6) |
| O(2E)-C(1E)-O(1E) | 127.1(5) | C(4F)-C(3F)-C(8F) | 117.9(7) |
| O(2E)-C(1E)-C(2E) | 118.5(5) | C(2F)-C(3F)-C(8F) | 117.9(7) |
| O(1E)-C(1E)-C(2E) | 114.4(5) | C(5F)-C(4F)-C(3F) | 122.5(8) |
| C(3E)-C(2E)-C(15E) | 121.4(5) | C(4F)-C(5F)-C(6F) | 120.3(9) |
| C(3E)-C(2E)-C(1E) | 118.5(5) | C(7F)-C(6F)-C(5F) | 120.3(9) |
| C(15E)-C(2E)-C(1E) | 120.1(5) | C(6F)-C(7F)-C(8F) | 122.6(8) |
| C(2E)-C(3E)-C(4E) | 123.4(5) | C(9F)-C(8F)-C(7F) | 124.6(7) |
| C(2E)-C(3E)-C(8E) | 118.3(5) | C(9F)-C(8F)-C(3F) | 119.0(7) |
| C(4E)-C(3E)-C(8E) | 118.2(6) | C(7F)-C(8F)-C(3F) | 116.4(8) |
| C(5E)-C(4E)-C(3E) | 121.9(6) | C(10F)-C(9F)-C(8F) | 123.0(7) |
| C(4E)-C(5E)-C(6E) | 119.7(7) | C(9F)-C(10F)-C(11F) | 123.2(8) |
| C(7E)-C(6E)-C(5E) | 120.7(7) | C(9F)-C(10F)-C(15F) | 119.5(7) |
| C(6E)-C(7E)-C(8E) | 121.6(7) | C(11F)-C(10F)-C(15F) | 117.3(9) |
| C(9E)-C(8E)-C(7E) | 122.8(6) | C(12F)-C(11F)-C(10F) | 122.2(9) |
| C(9E)-C(8E)-C(3E) | 119.4(6) | C(11F)-C(12F)-C(13F) | 120.6(9) |
| C(7E)-C(8E)-C(3E) | 117.8(6) | C(14F)-C(13F)-C(12F) | 120.9(10) |
| C(8E)-C(9E)-C(10E) | 122.3(6) | C(13F)-C(14F)-C(15F) | 120.4(8) |
| C(9E)-C(10E)-C(11E) | 122.1(6) | C(2F)-C(15F)-C(14F) | 123.3(6) |
| C(9E)-C(10E)-C(15E) | 119.4(6) | C(2F)-C(15F)-C(10F) | 118.1(7) |
| C(11E)-C(10E)-C(15E) | 118.4(6) | C(14F)-C(15F)-C(10F) | 118.6(7) |

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| N(1A)-Ag(5)-N(1B) | 176.98(18) | C(21C)-N(1C)-Ag(6) | 125.3(4) |
| N(1A)-Ag(5)-O(2A) | 93.44(15) | C(22C)-N(1C)-Ag(6) | 128.2(4) |
| N(1B)-Ag(5)-O(2A) | 89.43(15) | C(23C)-C(22C)-N(1C) | 110.2(6) |
| N(1A)-Ag(5)-O(1B) | 89.53(16) | C(22C)-C(23C)-N(2C) | 106.4(6) |
| N(1B)-Ag(5)-O(1B) | 92.03(16) | C(21C)-N(2C)-C(23C) | 106.9(5) |
| O(2A)-Ag(5)-O(1B) | 76.98(11) | C(21C)-N(2C)-C(24C) | 126.7(5) |
| N(1A)-C(21A)-N(2A) | 110.9(5) | C(23C)-N(2C)-C(24C) | 126.4(5) |
| C(21A)-N(1A)-C(22A) | 105.5(5) | N(2C)-C(24C)-C(25C) | 113.8(6) |
| C(21A)-N(1A)-Ag(5) | 119.8(4) | C(26C)-C(25C)-C(24C) | 127.4(10) |
| C(22A)-N(1A)-Ag(5) | 134.2(4) | C(25C)-C(26C)-C(27C) | 119.8(17) |
| C(23A)-C(22A)-N(1A) | 109.9(6) | N(1D)-C(21D)-N(2D) | 112.6(5) |
| C(22A)-C(23A)-N(2A) | 107.0(5) | C(21D)-N(1D)-C(22D) | 105.2(5) |
| C(21A)-N(2A)-C(23A) | 106.8(5) | C(21D)-N(1D)-Ag(6) | 121.9(4) |
| C(21A)-N(2A)-C(24A) | 124.9(6) | C(22D)-N(1D)-Ag(6) | 132.8(5) |
| C(23A)-N(2A)-C(24A) | 128.2(5) | C(23D)-C(22D)-N(1D) | 109.6(6) |
| N(2A)-C(24A)-C(25A) | 110.0(6) | C(22D)-C(23D)-N(2D) | 106.7(6) |
| C(26A)-C(25A)-C(24A) | 115.8(8) | C(21D)-N(2D)-C(23D) | 105.9(5) |
| C(25A)-C(26A)-C(27A) | 112.4(9) | C(21D)-N(2D)-C(24D) | 126.3(5) |
| N(1B)-C(21B)-N(2B) | 111.4(5) | C(23D)-N(2D)-C(24D) | 127.6(6) |
| C(21B)-N(1B)-C(22B) | 105.9(5) | N(2D)-C(24D)-C(25D) | 111.5(6) |
| C(21B)-N(1B)-Ag(5) | 124.7(4) | C(26D)-C(25D)-C(24D) | 112.3(6) |
| C(22B)-N(1B)-Ag(5) | 129.3(4) | C(25D)-C(26D)-C(27D) | 111.2(7) |
| C(23B)-C(22B)-N(1B) | 109.1(5) | O(1G)-Ag(7)-O(2J) | 132.37(16) |
| C(22B)-C(23B)-N(2B) | 106.7(5) | O(1G)-Ag(7)-O(1L) | 105.07(14) |
| C(21B)-N(2B)-C(23B) | 106.8(5) | O(2J)-Ag(7)-O(1L) | 105.68(16) |
| C(21B)-N(2B)-C(24B) | 126.8(5) | O(1G)-Ag(7)-Ag(10) | 137.51(11) |
| C(23B)-N(2B)-C(24B) | 126.3(5) | O(2J)-Ag(7)-Ag(10) | 90.08(12) |
| N(2B)-C(24B)-C(25B) | 112.0(5) | O(1L)-Ag(7)-Ag(10) | 51.36(9) |
| C(26B)-C(25B)-C(24B) | 114.0(6) | O(1G)-Ag(7)-Ag(8) | 83.06(10) |
| C(25B)-C(26B)-C(27B) | 112.8(6) | O(2J)-Ag(7)-Ag(8) | 140.98(14) |
| N(1D)-Ag(6)-N(1C) | 175.1(2) | O(1L)-Ag(7)-Ag(8) | 72.61(9) |
| N(1D)-Ag(6)-O(1D) | 90.55(19) | Ag(10)-Ag(7)-Ag(8) | 57.638(14) |
| N(1C)-Ag(6)-O(1D) | 94.19(19) | O(1K)-Ag(8)-O(2L) | 153.12(15) |
| N(1D)-Ag(6)-O(2C) | 97.24(17) | O(1K)-Ag(8)-O(2G) | 99.71(16) |
| N(1C)-Ag(6)-O(2C) | 85.17(16) | O(2L)-Ag(8)-O(2G) | 104.46(16) |
| O(1D)-Ag(6)-O(2C) | 73.86(12) | O(1K)-Ag(8)-O(1H) | 104.54(16) |
| N(1C)-C(21C)-N(2C) | 111.1(5) | O(2L)-Ag(8)-O(1H) | 85.64(14) |
| C(21C)-N(1C)-C(22C) | 105.4(5) | O(2G)-Ag(8)-O(1H) | 93.64(14) |

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| O(1K)-Ag(8)-Ag(10) | 78.51(11) | O(2K)-Ag(10)-Ag(9) | 66.73(12) |
| O(2L)-Ag(8)-Ag(10) | 76.28(10) | O(1L)-Ag(10)-Ag(9) | 98.89(10) |
| O(2G)-Ag(8)-Ag(10) | 134.13(10) | Ag(8)-Ag(10)-Ag(9) | 59.271(14) |
| O(1H)-Ag(8)-Ag(10) | 131.58(10) | Ag(7)-Ag(10)-Ag(9) | 120.788(18) |
| O(1K)-Ag(8)-Ag(9) | 90.79(11) | C(1G)-O(1G)-Ag(7) | 120.3(4) |
| O(2L)-Ag(8)-Ag(9) | 69.42(11) | C(1G)-O(2G)-Ag(8) | 125.9(4) |
| O(2G)-Ag(8)-Ag(9) | 161.55(11) | C(1G)-O(2G)-Ag(11) | 127.1(4) |
| O(1H)-Ag(8)-Ag(9) | 68.90(10) | Ag(8)-O(2G)-Ag(11) | 93.69(13) |
| Ag(10)-Ag(8)-Ag(9) | 62.715(14) | O(2G)-C(1G)-O(1G) | 126.8(5) |
| O(1K)-Ag(8)-Ag(7) | 89.04(13) | O(2G)-C(1G)-C(2G) | 115.9(5) |
| O(2L)-Ag(8)-Ag(7) | 86.22(10) | O(1G)-C(1G)-C(2G) | 117.3(5) |
| O(2G)-Ag(8)-Ag(7) | 74.59(10) | C(15G)-C(2G)-C(3G) | 121.7(5) |
| O(1H)-Ag(8)-Ag(7) | 163.52(10) | C(15G)-C(2G)-C(1G) | 120.3(5) |
| Ag(10)-Ag(8)-Ag(7) | 59.603(14) | C(3G)-C(2G)-C(1G) | 118.0(5) |
| Ag(9)-Ag(8)-Ag(7) | 121.069(18) | C(2G)-C(3G)-C(4G) | 123.3(5) |
| O(1I)-Ag(9)-O(2H) | 135.17(16) | C(2G)-C(3G)-C(8G) | 119.1(5) |
| O(1I)-Ag(9)-Ag(8) | 134.99(11) | C(4G)-C(3G)-C(8G) | 117.6(5) |
| O(2H)-Ag(9)-Ag(8) | 89.72(11) | C(5G)-C(4G)-C(3G) | 122.4(5) |
| O(1I)-Ag(9)-Ag(10) | 81.06(11) | C(4G)-C(5G)-C(6G) | 119.5(6) |
| O(2H)-Ag(9)-Ag(10) | 140.35(12) | C(7G)-C(6G)-C(5G) | 121.1(6) |
| Ag(8)-Ag(9)-Ag(10) | 58.015(14) | C(6G)-C(7G)-C(8G) | 120.8(6) |
| O(2I)-Ag(10)-O(1J) | 88.66(15) | C(9G)-C(8G)-C(7G) | 122.9(5) |
| O(2I)-Ag(10)-O(2K) | 95.31(16) | C(9G)-C(8G)-C(3G) | 118.4(5) |
| O(1J)-Ag(10)-O(2K) | 109.95(17) | C(7G)-C(8G)-C(3G) | 118.6(5) |
| O(2I)-Ag(10)-O(1L) | 99.16(15) | C(10G)-C(9G)-C(8G) | 123.4(5) |
| O(1J)-Ag(10)-O(1L) | 87.68(16) | C(9G)-C(10G)-C(11G) | 123.2(5) |
| O(2K)-Ag(10)-O(1L) | 157.45(14) | C(9G)-C(10G)-C(15G) | 118.9(5) |
| O(2I)-Ag(10)-Ag(8) | 137.57(11) | C(11G)-C(10G)-C(15G) | 117.9(6) |
| O(1J)-Ag(10)-Ag(8) | 132.93(10) | C(12G)-C(11G)-C(10G) | 121.6(6) |
| O(2K)-Ag(10)-Ag(8) | 79.52(10) | C(11G)-C(12G)-C(13G) | 120.2(6) |
| O(1L)-Ag(10)-Ag(8) | 78.13(9) | C(14G)-C(13G)-C(12G) | 120.5(6) |
| O(2I)-Ag(10)-Ag(7) | 149.04(11) | C(13G)-C(14G)-C(15G) | 121.4(6) |
| O(1J)-Ag(10)-Ag(7) | 71.70(10) | C(2G)-C(15G)-C(14G) | 123.2(5) |
| O(2K)-Ag(10)-Ag(7) | 113.59(11) | C(2G)-C(15G)-C(10G) | 118.4(5) |
| O(1L)-Ag(10)-Ag(7) | 57.51(9) | C(14G)-C(15G)-C(10G) | 118.4(5) |
| Ag(8)-Ag(10)-Ag(7) | 62.759(14) | C(1H)-O(1H)-Ag(8) | 126.0(4) |
| O(2I)-Ag(10)-Ag(9) | 79.84(10) | C(1H)-O(1H)-Ag(11) | 124.6(3) |
| O(1J)-Ag(10)-Ag(9) | 167.51(10) | Ag(8)-O(1H)-Ag(11) | 96.29(14) |

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| C(1H)-O(2H)-Ag(9) | 111.6(4) | C(4I)-C(3I)-C(8I) | 117.7(6) |
| O(1H)-C(1H)-O(2H) | 125.9(5) | C(5I)-C(4I)-C(3I) | 122.3(6) |
| O(1H)-C(1H)-C(2H) | 116.8(5) | C(4I)-C(5I)-C(6I) | 119.2(7) |
| O(2H)-C(1H)-C(2H) | 117.3(5) | C(7I)-C(6I)-C(5I) | 121.0(7) |
| C(15H)-C(2H)-C(3H) | 120.9(5) | C(6I)-C(7I)-C(8I) | 122.2(6) |
| C(15H)-C(2H)-C(1H) | 119.3(5) | C(9I)-C(8I)-C(7I) | 123.3(6) |
| C(3H)-C(2H)-C(1H) | 119.8(5) | C(9I)-C(8I)-C(3I) | 119.0(6) |
| C(2H)-C(3H)-C(4H) | 122.8(5) | C(7I)-C(8I)-C(3I) | 117.6(6) |
| C(2H)-C(3H)-C(8H) | 118.7(6) | C(8I)-C(9I)-C(10I) | 121.8(6) |
| C(4H)-C(3H)-C(8H) | 118.5(6) | C(9I)-C(10I)-C(15I) | 119.7(6) |
| C(5H)-C(4H)-C(3H) | 121.2(6) | C(9I)-C(10I)-C(11I) | 122.6(6) |
| C(4H)-C(5H)-C(6H) | 120.1(7) | C(15I)-C(10I)-C(11I) | 117.7(6) |
| C(7H)-C(6H)-C(5H) | 120.6(7) | C(12I)-C(11I)-C(10I) | 121.2(6) |
| C(6H)-C(7H)-C(8H) | 121.2(6) | C(11I)-C(12I)-C(13I) | 120.6(7) |
| C(9H)-C(8H)-C(3H) | 120.0(6) | C(14I)-C(13I)-C(12I) | 121.5(7) |
| C(9H)-C(8H)-C(7H) | 121.7(6) | C(13I)-C(14I)-C(15I) | 119.9(6) |
| C(3H)-C(8H)-C(7H) | 118.3(6) | C(2I)-C(15I)-C(14I) | 122.4(5) |
| C(10H)-C(9H)-C(8H) | 121.7(6) | C(2I)-C(15I)-C(10I) | 118.6(6) |
| C(9H)-C(10H)-C(11H) | 121.7(6) | C(14I)-C(15I)-C(10I) | 119.0(6) |
| C(9H)-C(10H)-C(15H) | 119.0(6) | C(1J)-O(1J)-Ag(10) | 134.7(4) |
| C(11H)-C(10H)-C(15H) | 119.3(6) | C(1J)-O(1J)-Ag(12) | 124.8(4) |
| C(12H)-C(11H)-C(10H) | 120.3(6) | Ag(10)-O(1J)-Ag(12) | 100.23(15) |
| C(11H)-C(12H)-C(13H) | 121.9(7) | C(1J)-O(2J)-Ag(7) | 115.0(4) |
| C(14H)-C(13H)-C(12H) | 119.0(7) | O(1J)-C(1J)-O(2J) | 125.5(6) |
| C(13H)-C(14H)-C(15H) | 121.9(6) | O(1J)-C(1J)-C(2J) | 116.3(5) |
| C(2H)-C(15H)-C(14H) | 123.0(5) | O(2J)-C(1J)-C(2J) | 118.2(5) |
| C(2H)-C(15H)-C(10H) | 119.7(6) | C(15J)-C(2J)-C(3J) | 121.1(5) |
| C(14H)-C(15H)-C(10H) | 117.4(6) | C(15J)-C(2J)-C(1J) | 120.8(5) |
| C(1I)-O(1I)-Ag(9) | 124.4(4) | C(3J)-C(2J)-C(1J) | 118.0(5) |
| C(1I)-O(2I)-Ag(10) | 122.9(4) | C(4J)-C(3J)-C(2J) | 121.9(5) |
| O(2I)-C(1I)-O(1I) | 126.8(5) | C(4J)-C(3J)-C(8J) | 119.4(6) |
| O(2I)-C(1I)-C(2I) | 116.8(5) | C(2J)-C(3J)-C(8J) | 118.7(5) |
| O(1I)-C(1I)-C(2I) | 116.4(5) | C(5J)-C(4J)-C(3J) | 121.7(6) |
| C(3I)-C(2I)-C(15I) | 121.9(5) | C(4J)-C(5J)-C(6J) | 118.8(7) |
| C(3I)-C(2I)-C(1I) | 117.2(5) | C(7J)-C(6J)-C(5J) | 122.4(7) |
| C(15I)-C(2I)-C(1I) | 120.8(5) | C(6J)-C(7J)-C(8J) | 120.7(7) |
| C(2I)-C(3I)-C(4I) | 123.5(5) | C(9J)-C(8J)-C(3J) | 120.4(6) |
| C(2I)-C(3I)-C(8I) | 118.9(5) | C(9J)-C(8J)-C(7J) | 122.7(6) |

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| C(3J)-C(8J)-C(7J) | 116.8(6) | C(2K)-C(15K)-C(14K) | 123.4(6) |
| C(8J)-C(9J)-C(10J) | 122.2(6) | C(2K)-C(15K)-C(10K) | 118.9(7) |
| C(9J)-C(10J)-C(11J) | 121.7(7) | C(14K)-C(15K)-C(10K) | 117.7(7) |
| C(9J)-C(10J)-C(15J) | 119.0(6) | C(1L)-O(1L)-Ag(10) | 111.1(3) |
| C(11J)-C(10J)-C(15J) | 119.2(7) | C(1L)-O(1L)-Ag(7) | 115.0(3) |
| C(12J)-C(11J)-C(10J) | 121.0(8) | Ag(10)-O(1L)-Ag(7) | 71.13(10) |
| C(11J)-C(12J)-C(13J) | 121.1(8) | C(1L)-O(2L)-Ag(8) | 118.7(3) |
| C(12J)-C(13J)-C(14J) | 121.4(8) | O(1L)-C(1L)-O(2L) | 126.9(5) |
| C(13J)-C(14J)-C(15J) | 118.7(8) | O(1L)-C(1L)-C(2L) | 119.0(5) |
| C(2J)-C(15J)-C(14J) | 123.2(7) | O(2L)-C(1L)-C(2L) | 114.1(5) |
| C(2J)-C(15J)-C(10J) | 118.5(6) | C(3L)-C(2L)-C(15L) | 123.0(5) |
| C(14J)-C(15J)-C(10J) | 118.3(6) | C(3L)-C(2L)-C(1L) | 119.1(5) |
| C(1K)-O(1K)-Ag(8) | 123.1(4) | C(15L)-C(2L)-C(1L) | 118.0(5) |
| C(1K)-O(2K)-Ag(10) | 114.5(4) | C(2L)-C(3L)-C(8L) | 118.6(6) |
| O(1K)-C(1K)-O(2K) | 125.2(5) | C(2L)-C(3L)-C(4L) | 123.5(5) |
| O(1K)-C(1K)-C(2K) | 115.9(5) | C(8L)-C(3L)-C(4L) | 117.9(6) |
| O(2K)-C(1K)-C(2K) | 118.9(5) | C(5L)-C(4L)-C(3L) | 121.3(7) |
| C(15K)-C(2K)-C(3K) | 121.6(6) | C(4L)-C(5L)-C(6L) | 120.9(8) |
| C(15K)-C(2K)-C(1K) | 118.1(6) | C(7L)-C(6L)-C(5L) | 120.6(7) |
| C(3K)-C(2K)-C(1K) | 120.3(6) | C(6L)-C(7L)-C(8L) | 120.6(7) |
| C(4K)-C(3K)-C(2K) | 123.0(6) | C(9L)-C(8L)-C(3L) | 120.0(6) |
| C(4K)-C(3K)-C(8K) | 118.9(7) | C(9L)-C(8L)-C(7L) | 121.3(6) |
| C(2K)-C(3K)-C(8K) | 118.1(7) | C(3L)-C(8L)-C(7L) | 118.7(7) |
| C(5K)-C(4K)-C(3K) | 121.9(8) | C(8L)-C(9L)-C(10L) | 122.4(6) |
| C(6K)-C(5K)-C(4K) | 118.8(9) | C(11L)-C(10L)-C(9L) | 122.9(6) |
| C(7K)-C(6K)-C(5K) | 121.5(8) | C(11L)-C(10L)-C(15L) | 118.4(6) |
| C(6K)-C(7K)-C(8K) | 121.8(8) | C(9L)-C(10L)-C(15L) | 118.7(6) |
| C(9K)-C(8K)-C(7K) | 124.1(8) | C(12L)-C(11L)-C(10L) | 120.7(7) |
| C(9K)-C(8K)-C(3K) | 118.8(7) | C(11L)-C(12L)-C(13L) | 121.8(7) |
| C(7K)-C(8K)-C(3K) | 117.0(8) | C(14L)-C(13L)-C(12L) | 118.3(7) |
| C(10K)-C(9K)-C(8K) | 122.8(7) | C(13L)-C(14L)-C(15L) | 122.2(6) |
| C(9K)-C(10K)-C(15K) | 119.6(7) | C(14L)-C(15L)-C(2L) | 124.2(5) |
| C(9K)-C(10K)-C(11K) | 122.8(7) | C(14L)-C(15L)-C(10L) | 118.6(6) |
| C(15K)-C(10K)-C(11K) | 117.6(8) | C(2L)-C(15L)-C(10L) | 117.2(5) |
| C(12K)-C(11K)-C(10K) | 121.1(8) | N(1E)-Ag(11)-N(1F) | 176.84(19) |
| C(11K)-C(12K)-C(13K) | 121.9(9) | N(1E)-Ag(11)-O(1H) | 93.65(16) |
| C(14K)-C(13K)-C(12K) | 119.6(8) | N(1F)-Ag(11)-O(1H) | 89.24(16) |
| C(13K)-C(14K)-C(15K) | 122.0(7) | N(1E)-Ag(11)-O(2G) | 87.63(16) |

| | | | |
|----------------------|-----------|----------------------|------------|
| N(1F)-Ag(11)-O(2G) | 94.29(16) | N(1G)-Ag(12)-O(1J) | 90.14(18) |
| O(1H)-Ag(11)-O(2G) | 76.30(11) | N(1H)-Ag(12)-O(2F) | 16.37(13) |
| N(1E)-C(21E)-N(2E) | 110.9(6) | N(1G)-Ag(12)-O(2F) | 167.86(14) |
| C(21E)-N(1E)-C(22E) | 105.5(5) | O(1J)-Ag(12)-O(2F) | 82.46(11) |
| C(21E)-N(1E)-Ag(11) | 120.4(4) | N(1G)-C(21G)-N(2G) | 112.3(6) |
| C(22E)-N(1E)-Ag(11) | 133.4(4) | C(21G)-N(1G)-C(22G) | 105.0(6) |
| C(23E)-C(22E)-N(1E) | 109.9(6) | C(21G)-N(1G)-Ag(12) | 122.0(4) |
| C(22E)-C(23E)-N(2E) | 106.1(5) | C(22G)-N(1G)-Ag(12) | 132.8(5) |
| C(21E)-N(2E)-C(23E) | 107.6(5) | C(23G)-C(22G)-N(1G) | 109.4(6) |
| C(21E)-N(2E)-C(24E) | 125.1(6) | C(22G)-C(23G)-N(2G) | 106.2(6) |
| C(23E)-N(2E)-C(24E) | 127.1(6) | C(21G)-N(2G)-C(23G) | 107.1(6) |
| N(2E)-C(24E)-C(25E) | 104.9(8) | C(21G)-N(2G)-C(24G) | 126.1(5) |
| C(26Y)-C(25E)-C(24E) | 114.6(12) | C(23G)-N(2G)-C(24G) | 126.7(6) |
| C(27E)-C(26Y)-C(25E) | 115.7(14) | N(2G)-C(24G)-C(25G) | 111.0(6) |
| C(25Y)-C(26E)-C(27Y) | 112.7(19) | C(26G)-C(25G)-C(24G) | 112.3(7) |
| N(1F)-C(21F)-N(2F) | 110.3(5) | C(27G)-C(26G)-C(25G) | 111.9(7) |
| C(21F)-N(1F)-C(22F) | 105.7(5) | N(1H)-C(21H)-N(2H) | 111.4(5) |
| C(21F)-N(1F)-Ag(11) | 123.9(4) | C(21H)-N(1H)-C(22H) | 105.7(6) |
| C(22F)-N(1F)-Ag(11) | 130.3(4) | C(21H)-N(1H)-Ag(12) | 124.8(4) |
| C(23F)-C(22F)-N(1F) | 110.4(6) | C(22H)-N(1H)-Ag(12) | 128.6(4) |
| C(22F)-C(23F)-N(2F) | 106.0(5) | C(23H)-C(22H)-N(1H) | 110.0(6) |
| C(21F)-N(2F)-C(23F) | 107.6(5) | C(22H)-C(23H)-N(2H) | 106.6(6) |
| C(21F)-N(2F)-C(24F) | 126.7(5) | C(21H)-N(2H)-C(23H) | 106.2(5) |
| C(23F)-N(2F)-C(24F) | 125.7(5) | C(21H)-N(2H)-C(24H) | 127.4(5) |
| N(2F)-C(24F)-C(25F) | 112.9(5) | C(23H)-N(2H)-C(24H) | 126.3(6) |
| C(26F)-C(25F)-C(24F) | 114.6(5) | N(2H)-C(24H)-C(25H) | 110.3(10) |
| C(25F)-C(26F)-C(27F) | 113.5(6) | C(26H)-C(25H)-C(24H) | 115.0(15) |
| N(1H)-Ag(12)-N(1G) | 175.0(2) | C(25H)-C(26H)-C(27H) | 113.7(16) |
| N(1H)-Ag(12)-O(1J) | 94.68(18) | C(27Z)-C(26Z)-C(25Z) | 115(2) |

X-ray Crystal Data for [Ag(apim)](9-aca)·H₂O

| | | |
|-----------------------------------|--|----------|
| Identification code | [Ag(apim)](9-aca)·H ₂ O | |
| Empirical formula | C ₂₁ H ₂₂ Ag N ₃ O ₃ | |
| Formula weight | 472.29 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pbca | |
| Unit cell dimensions | a = 9.6450(6) Å | α = 90°. |
| | b = 19.0589(11) Å | β = 90°. |
| | c = 21.2920(12) Å | γ = 90°. |
| Volume | 3914.0(4) Å ³ | |
| Z | 8 | |
| Density (calculated) | 1.603 Mg/m ³ | |
| Absorption coefficient | 1.057 mm ⁻¹ | |
| F(000) | 1920 | |
| Crystal size | 0.20 x 0.17 x 0.07 mm ³ | |
| Crystal description | colourless plate | |
| Theta range for data collection | 1.91 to 28.35°. | |
| Index ranges | -12 ≤ h ≤ 12, -25 ≤ k ≤ 25, -28 ≤ l ≤ 28 | |
| Reflections collected | 37907 | |
| Independent reflections | 4890 [R(int) = 0.0398] | |
| Completeness to theta = 26.00° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9297 and 0.8164 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 4890 / 6 / 265 | |
| Goodness-of-fit on F ² | 1.027 | |
| Final R indices [I > 2σ(I)] | R1 = 0.0280, wR2 = 0.0665 | |
| R indices (all data) | R1 = 0.0410, wR2 = 0.0723 | |
| Largest diff. peak and hole | 0.447 and -0.546 e.Å ⁻³ | |

Table 27. Bond lengths [Å] and angles [°] for [Ag(apim)](9-aca)·H₂O.

| | | | |
|--------------------|------------|-------------------|------------|
| Ag(1)-N(1) | 2.0841(18) | C(2)-C(3) | 1.409(3) |
| Ag(1)-N(3)#1 | 2.1069(18) | C(3)-C(4) | 1.431(3) |
| C(21)-N(1) | 1.321(3) | C(3)-C(8) | 1.434(3) |
| C(21)-N(2) | 1.336(3) | C(4)-C(5) | 1.368(3) |
| N(1)-C(22) | 1.376(3) | C(5)-C(6) | 1.415(4) |
| C(22)-C(23) | 1.354(3) | C(6)-C(7) | 1.348(4) |
| C(23)-N(2) | 1.371(3) | C(7)-C(8) | 1.436(3) |
| N(2)-C(24) | 1.470(3) | C(8)-C(9) | 1.391(3) |
| C(24)-C(25) | 1.518(3) | C(9)-C(10) | 1.395(3) |
| C(25)-C(26) | 1.520(3) | C(10)-C(11) | 1.429(3) |
| C(26)-N(3) | 1.483(3) | C(10)-C(15) | 1.432(3) |
| N(3)-Ag(1)#2 | 2.1069(18) | C(11)-C(12) | 1.358(4) |
| O(1)-C(1) | 1.246(3) | C(12)-C(13) | 1.425(3) |
| O(2)-C(1) | 1.253(3) | C(13)-C(14) | 1.362(3) |
| C(1)-C(2) | 1.513(3) | C(14)-C(15) | 1.432(3) |
| C(2)-C(15) | 1.404(3) | | |
| N(1)-Ag(1)-N(3)#1 | 177.76(7) | C(3)-C(2)-C(1) | 119.82(18) |
| N(1)-C(21)-N(2) | 111.4(2) | C(2)-C(3)-C(4) | 122.3(2) |
| C(21)-N(1)-C(22) | 105.78(18) | C(2)-C(3)-C(8) | 119.2(2) |
| C(21)-N(1)-Ag(1) | 124.86(16) | C(4)-C(3)-C(8) | 118.5(2) |
| C(22)-N(1)-Ag(1) | 129.35(15) | C(5)-C(4)-C(3) | 120.7(2) |
| C(23)-C(22)-N(1) | 109.1(2) | C(4)-C(5)-C(6) | 120.4(2) |
| C(22)-C(23)-N(2) | 106.5(2) | C(7)-C(6)-C(5) | 120.9(2) |
| C(21)-N(2)-C(23) | 107.22(18) | C(6)-C(7)-C(8) | 121.1(2) |
| C(21)-N(2)-C(24) | 125.68(19) | C(9)-C(8)-C(3) | 119.5(2) |
| C(23)-N(2)-C(24) | 127.09(18) | C(9)-C(8)-C(7) | 122.1(2) |
| N(2)-C(24)-C(25) | 110.51(17) | C(3)-C(8)-C(7) | 118.4(2) |
| C(24)-C(25)-C(26) | 112.97(18) | C(8)-C(9)-C(10) | 121.5(2) |
| N(3)-C(26)-C(25) | 113.36(17) | C(9)-C(10)-C(11) | 121.8(2) |
| C(26)-N(3)-Ag(1)#2 | 116.60(13) | C(9)-C(10)-C(15) | 119.6(2) |
| O(1)-C(1)-O(2) | 125.4(2) | C(11)-C(10)-C(15) | 118.6(2) |
| O(1)-C(1)-C(2) | 117.9(2) | C(12)-C(11)-C(10) | 121.2(2) |
| O(2)-C(1)-C(2) | 116.69(18) | C(11)-C(12)-C(13) | 120.3(2) |
| C(15)-C(2)-C(3) | 120.92(19) | C(14)-C(13)-C(12) | 120.4(2) |
| C(15)-C(2)-C(1) | 119.24(18) | C(13)-C(14)-C(15) | 121.1(2) |

| | | | |
|------------------|------------|-------------------|------------|
| C(2)-C(15)-C(14) | 122.39(19) | C(14)-C(15)-C(10) | 118.40(19) |
| C(2)-C(15)-C(10) | 119.20(19) | | |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1/2, y+1/2, z$ #2 $-x+1/2, y-1/2, z$

Table 28. Hydrogen bonds for [Ag(apim)](9-aca)·H₂O [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|--------------------------|-----------|-----------|----------|--------|
| N(3)-H(1N)...O(2) | 0.857(16) | 2.291(17) | 3.128(3) | 165(3) |
| N(3)-H(2N)...O(2)#3 | 0.852(16) | 2.274(17) | 3.080(2) | 158(2) |
| N(3)-H(2N)...O(2)#3 | 0.852(16) | 2.40(2) | 3.131(2) | 144(2) |
| O(1W)-H(1W)...O(1) | 0.810(17) | 2.072(18) | 2.883(3) | 179(4) |
| O(1W)- H(2W)...O(2)#4 | 0.832(17) | 2.04(2) | 2.838(3) | 162(3) |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1/2, y+1/2, z$ #2 $-x+1/2, y-1/2, z$ #3 $x+1/2, -y-1/2, -z+1$ #4 $x-1/2, -y-1/2, -z+1$

X-ray Crystal Data for (2-Mebenz-imidH)(9-aca)·H₂O

| | | |
|-----------------------------------|---|----------|
| Identification code | (2-Mebenz-imidH)(9-aca)·H ₂ O | |
| Empirical formula | C ₂₃ H ₂₀ N ₂ O ₃ | |
| Formula weight | 372.41 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P2(1)2(1)2(1) | |
| Unit cell dimensions | a = 6.9251(8) Å | α = 90°. |
| | b = 14.8341(17) Å | β = 90°. |
| | c = 18.522(2) Å | γ = 90°. |
| Volume | 1902.7(4) Å ³ | |
| Z | 4 | |
| Density (calculated) | 1.300 Mg/m ³ | |
| Absorption coefficient | 0.087 mm ⁻¹ | |
| F(000) | 784 | |
| Crystal size | 0.41 x 0.08 x 0.08 mm ³ | |
| Crystal description | colourless rod | |
| Theta range for data collection | 1.76 to 26.35°. | |
| Index ranges | -8<=h<=8, -18<=k<=18, -23<=l<=23 | |
| Reflections collected | 16919 | |
| Independent reflections | 2241 [R(int) = 0.0507] | |
| Completeness to theta = 26.35° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9931 and 0.9652 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 2241 / 0 / 260 | |
| Goodness-of-fit on F ² | 1.046 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0365, wR2 = 0.0853 | |
| R indices (all data) | R1 = 0.0482, wR2 = 0.0917 | |
| Largest diff. peak and hole | 0.308 and -0.355 e.Å ⁻³ | |

Table 29. Bond lengths [Å] and angles [°] for (2-Mebenz-imidH)(9-aca)·H₂O.

| | | | |
|-------------------|----------|-------------------|----------|
| N(1)-C(2) | 1.331(3) | C(12)-C(25) | 1.409(3) |
| N(1)-C(8) | 1.385(3) | C(13)-C(14) | 1.432(4) |
| C(1)-C(2) | 1.489(4) | C(13)-C(18) | 1.440(3) |
| C(2)-N(2) | 1.329(3) | C(14)-C(15) | 1.354(4) |
| N(2)-C(3) | 1.385(3) | C(15)-C(16) | 1.419(4) |
| C(3)-C(4) | 1.389(3) | C(16)-C(17) | 1.355(4) |
| C(3)-C(8) | 1.395(3) | C(17)-C(18) | 1.430(4) |
| C(4)-C(5) | 1.374(4) | C(18)-C(19) | 1.390(3) |
| C(5)-C(6) | 1.398(4) | C(19)-C(20) | 1.392(3) |
| C(6)-C(7) | 1.377(4) | C(20)-C(21) | 1.428(3) |
| C(7)-C(8) | 1.390(4) | C(20)-C(25) | 1.440(3) |
| O(1)-C(11) | 1.276(3) | C(21)-C(22) | 1.353(4) |
| O(2)-C(11) | 1.240(3) | C(22)-C(23) | 1.419(4) |
| C(11)-C(12) | 1.514(3) | C(23)-C(24) | 1.360(4) |
| C(12)-C(13) | 1.401(3) | C(24)-C(25) | 1.427(3) |
| C(2)-N(1)-C(8) | 108.7(2) | C(25)-C(12)-C(11) | 118.6(2) |
| N(2)-C(2)-N(1) | 109.9(2) | C(12)-C(13)-C(14) | 123.1(2) |
| N(2)-C(2)-C(1) | 125.4(2) | C(12)-C(13)-C(18) | 119.2(2) |
| N(1)-C(2)-C(1) | 124.7(2) | C(14)-C(13)-C(18) | 117.7(2) |
| C(2)-N(2)-C(3) | 108.5(2) | C(15)-C(14)-C(13) | 121.4(2) |
| N(2)-C(3)-C(4) | 131.6(2) | C(14)-C(15)-C(16) | 120.9(3) |
| N(2)-C(3)-C(8) | 106.6(2) | C(17)-C(16)-C(15) | 120.0(3) |
| C(4)-C(3)-C(8) | 121.8(2) | C(16)-C(17)-C(18) | 121.4(3) |
| C(5)-C(4)-C(3) | 116.7(2) | C(19)-C(18)-C(17) | 121.7(2) |
| C(4)-C(5)-C(6) | 121.7(3) | C(19)-C(18)-C(13) | 119.7(2) |
| C(7)-C(6)-C(5) | 121.8(2) | C(17)-C(18)-C(13) | 118.7(2) |
| C(6)-C(7)-C(8) | 116.8(2) | C(18)-C(19)-C(20) | 121.6(2) |
| N(1)-C(8)-C(7) | 132.6(2) | C(19)-C(20)-C(21) | 121.9(2) |
| N(1)-C(8)-C(3) | 106.2(2) | C(19)-C(20)-C(25) | 119.3(2) |
| C(7)-C(8)-C(3) | 121.2(2) | C(21)-C(20)-C(25) | 118.7(2) |
| O(2)-C(11)-O(1) | 124.5(2) | C(22)-C(21)-C(20) | 121.3(2) |
| O(2)-C(11)-C(12) | 119.1(2) | C(21)-C(22)-C(23) | 120.2(2) |
| O(1)-C(11)-C(12) | 116.4(2) | C(24)-C(23)-C(22) | 120.7(3) |
| C(13)-C(12)-C(25) | 120.8(2) | C(23)-C(24)-C(25) | 121.2(2) |
| C(13)-C(12)-C(11) | 120.6(2) | C(12)-C(25)-C(24) | 122.7(2) |

C(12)-C(25)-C(20) 119.4(2) C(24)-C(25)-C(20) 117.9(2)

Table 30. Hydrogen bonds for (2-Mebenz-imidH)(9-aca)·H₂O [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------------------------|---------|----------|----------|--------|
| N(1)-H(1N)...O(1W) | 0.90(3) | 1.75(3) | 2.654(3) | 172(3) |
| N(2)-H(2N)...O(1)#1 | 0.99(3) | 1.67(3) | 2.651(3) | 178(2) |
| O(1W)- H(1WA)...O(2)#2 | 0.86 | 1.89 | 2.724(3) | 162.8 |
| O(1W)-H(1WB)...O(1) | 0.86 | 1.91 | 2.731(3) | 158.9 |

Symmetry transformations used to generate equivalent atoms:

#1 -x,y-1/2,-z+3/2 #2 x-1,y,z

X-ray Crystal Data for [Ag₄(9-aca)₄(NH₃)₂]

| | |
|-----------------------------------|---|
| Identification code | [Ag ₄ (9-aca) ₄ (NH ₃) ₂] |
| Empirical formula | C ₆₀ H ₄₂ Ag ₄ N ₂ O ₈ |
| Formula weight | 1350.44 |
| Temperature | 150(2) K |
| Wavelength | 0.84620 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | a = 16.837(3) Å α = 90°. b = 9.8639(16) Å β = 112.383(2)°. c = 16.035(3) Å γ = 90°. |
| Volume | 2462.4(7) Å ³ |
| Z | 2 |
| Density (calculated) | 1.821 Mg/m ³ |
| Absorption coefficient | 1.629 mm ⁻¹ |
| F(000) | 1336 |
| Crystal size | 0.09 x 0.07 x 0.01 mm ³ |
| Crystal description | Colourless plate |
| Theta range for data collection | 3.82 to 27.50°. |
| Index ranges | -18<=h<=18, -10<=k<=10, -17<=l<=17 |
| Reflections collected | 12821 |
| Independent reflections | 3344 [R(int) = 0.0853] |
| Completeness to theta = 27.50° | 99.6 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.0000 and 0.641332 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 3344 / 0 / 336 |
| Goodness-of-fit on F ² | 1.010 |
| Final R indices [I>2sigma(I)] | R1 = 0.0475, wR2 = 0.0987 |
| R indices (all data) | R1 = 0.0684, wR2 = 0.1079 |
| Extinction coefficient | 0.0021(2) |
| Largest diff. peak and hole | 0.604 and -0.648 e.Å ⁻³ |

Table 31. Bond lengths [Å] and angles [°] for [Ag₄(9-aca)₄(NH₃)₂].

| | | | |
|----------------------|------------|-----------------|-----------|
| Ag(1)-O(3) | 2.192(4) | C(13)-C(14) | 1.366(10) |
| Ag(1)-O(4)#1 | 2.261(4) | C(14)-C(15) | 1.416(10) |
| Ag(1)-O(1) | 2.329(6) | O(3)-C(16) | 1.273(8) |
| Ag(1)-Ag(1)#1 | 2.9390(12) | O(4)-C(16) | 1.249(8) |
| Ag(2)-O(2) | 2.135(5) | O(4)-Ag(1)#1 | 2.261(4) |
| Ag(2)-N(1) | 2.148(5) | C(16)-C(17) | 1.516(9) |
| O(1)-C(1) | 1.259(9) | C(17)-C(30) | 1.400(9) |
| O(2)-C(1) | 1.247(9) | C(17)-C(18) | 1.411(9) |
| C(1)-C(2) | 1.513(10) | C(18)-C(19) | 1.438(10) |
| C(2)-C(15) | 1.415(10) | C(18)-C(23) | 1.446(9) |
| C(2)-C(3) | 1.415(10) | C(19)-C(20) | 1.347(10) |
| C(3)-C(8) | 1.429(11) | C(20)-C(21) | 1.406(10) |
| C(3)-C(4) | 1.436(11) | C(21)-C(22) | 1.358(10) |
| C(4)-C(5) | 1.381(12) | C(22)-C(23) | 1.409(10) |
| C(5)-C(6) | 1.406(16) | C(23)-C(24) | 1.409(9) |
| C(6)-C(7) | 1.328(15) | C(24)-C(25) | 1.385(9) |
| C(7)-C(8) | 1.426(12) | C(25)-C(30) | 1.418(9) |
| C(8)-C(9) | 1.387(12) | C(25)-C(26) | 1.423(9) |
| C(9)-C(10) | 1.377(11) | C(26)-C(27) | 1.355(10) |
| C(10)-C(11) | 1.431(12) | C(27)-C(28) | 1.435(10) |
| C(10)-C(15) | 1.433(10) | C(28)-C(29) | 1.358(9) |
| C(11)-C(12) | 1.337(13) | C(29)-C(30) | 1.430(9) |
| C(12)-C(13) | 1.420(13) | | |
| O(3)-Ag(1)-O(4)#1 | 155.63(17) | C(1)-O(2)-Ag(2) | 121.9(5) |
| O(3)-Ag(1)-O(1) | 100.39(19) | O(2)-C(1)-O(1) | 127.1(7) |
| O(4)#1-Ag(1)-O(1) | 95.19(18) | O(2)-C(1)-C(2) | 118.6(7) |
| O(3)-Ag(1)-Ag(1)#1 | 85.15(13) | O(1)-C(1)-C(2) | 114.3(7) |
| O(4)#1-Ag(1)-Ag(1)#1 | 75.23(13) | C(15)-C(2)-C(3) | 120.4(7) |
| O(1)-Ag(1)-Ag(1)#1 | 164.17(15) | C(15)-C(2)-C(1) | 119.6(6) |
| O(2)-Ag(2)-N(1) | 170.6(2) | C(3)-C(2)-C(1) | 119.7(7) |
| C(1)-O(1)-Ag(1) | 136.0(5) | C(2)-C(3)-C(8) | 119.7(8) |
| C(2)-C(3)-C(4) | 121.6(7) | C(7)-C(6)-C(5) | 120.6(10) |
| C(8)-C(3)-C(4) | 118.6(8) | C(6)-C(7)-C(8) | 122.2(11) |
| C(5)-C(4)-C(3) | 119.6(9) | C(9)-C(8)-C(7) | 123.4(10) |
| C(4)-C(5)-C(6) | 120.8(11) | C(9)-C(8)-C(3) | 118.4(8) |

| | | | |
|--------------------|-----------|-------------------|----------|
| C(7)-C(8)-C(3) | 118.1(10) | C(10)-C(9)-C(8) | 123.3(8) |
| C(9)-C(10)-C(11) | 123.3(8) | C(17)-C(18)-C(23) | 118.3(6) |
| C(9)-C(10)-C(15) | 119.2(8) | C(19)-C(18)-C(23) | 117.0(7) |
| C(11)-C(10)-C(15) | 117.3(8) | C(20)-C(19)-C(18) | 120.8(7) |
| C(12)-C(11)-C(10) | 122.3(9) | C(19)-C(20)-C(21) | 121.5(7) |
| C(11)-C(12)-C(13) | 119.7(9) | C(22)-C(21)-C(20) | 120.3(7) |
| C(14)-C(13)-C(12) | 120.9(9) | C(21)-C(22)-C(23) | 120.8(7) |
| C(13)-C(14)-C(15) | 120.3(8) | C(22)-C(23)-C(24) | 122.3(6) |
| C(2)-C(15)-C(14) | 121.9(7) | C(22)-C(23)-C(18) | 119.5(6) |
| C(2)-C(15)-C(10) | 118.9(7) | C(24)-C(23)-C(18) | 118.2(7) |
| C(14)-C(15)-C(10) | 119.1(7) | C(25)-C(24)-C(23) | 122.2(6) |
| C(16)-O(3)-Ag(1) | 119.7(4) | C(24)-C(25)-C(30) | 119.8(6) |
| C(16)-O(4)-Ag(1)#1 | 128.2(4) | C(24)-C(25)-C(26) | 121.2(6) |
| O(4)-C(16)-O(3) | 126.0(6) | C(30)-C(25)-C(26) | 119.0(6) |
| O(4)-C(16)-C(17) | 116.6(7) | C(27)-C(26)-C(25) | 121.8(6) |
| O(3)-C(16)-C(17) | 117.5(7) | C(26)-C(27)-C(28) | 118.8(7) |
| C(30)-C(17)-C(18) | 122.0(6) | C(29)-C(28)-C(27) | 121.1(7) |
| C(30)-C(17)-C(16) | 119.7(6) | C(28)-C(29)-C(30) | 120.7(6) |
| C(18)-C(17)-C(16) | 118.3(6) | C(17)-C(30)-C(25) | 119.0(6) |
| C(17)-C(18)-C(19) | 124.7(6) | C(17)-C(30)-C(29) | 122.7(6) |
| C(25)-C(30)-C(29) | 118.4(6) | | |

Table 32. Hydrogen bonds for [Ag₄(9-aca)₄(NH₃)₂] [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------------------|--------|----------|----------|--------|
| N(1)-H(1A)...O(1)#2 | 0.91 | 2.42 | 3.222(8) | 146.5 |
| N(1)-H(1B)...O(4)#3 | 0.91 | 2.32 | 3.103(7) | 143.4 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 x,-y+1/2,z+1/2 #3 -x+1,y+1/2,-z+1/2

UV-Vis and Fluorescence Spectral Data

Table 33. Complex and ligand UV-Vis maxima.

| Complex | Absorbance max (nm) | Ligand 1 max (nm) | Ligand 2 max (nm) |
|---|---------------------|-------------------|-------------------|
| $[\text{Ag}_2(9\text{-aca})_2]_n$ | 373 | 366 (7) | N/A |
| $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$ | 373 | 366 (7) | 280 (1) |
| $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$ | 373 | 366 (7) | no maximum |
| $[\text{Ag}(2\text{-Ph-imid})]$ | 273 | 262(6) | N/A |
| $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$ | 373 | 366 (7) | 271 (5) |
| $[\text{Ag}(4,5\text{-dicyanoimid})]$ | 264 | 256 (4) | N/A |
| $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ | 366 | 366 (7) | 283 (2) |
| $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ | 372 | 366 (7) | N/A |

Table 34. Complex and ligand 1 fluorescence data (^a excited at 366 nm, ^b excited at 283 nm).

| Complex | Emission max (nm) | Emission intensity (AU) | Ligand 1 Emission max (nm) | Ligand 1 Emission intensity (AU) |
|---|--------------------------------------|-------------------------|----------------------------|----------------------------------|
| $[\text{Ag}_2(9\text{-aca})_2]_n$ | 448 | 61 | 451 (7) | 942 (7) |
| $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$ | 448 | 175 | 450 (7) | 968 (7) |
| $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$ | 440 | 53 | 450 (7) | 968 (7) |
| $[\text{Ag}(2\text{-Ph-imid})]$ | 342 | 44 | 340 (6) | 167 (6) |
| $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$ | 448 | 108 | 450 (7) | 968 (7) |
| $[\text{Ag}(4,5\text{-dicyanoimid})]$ | 347 | 1 | 299 (4) | 0.5 (4) |
| $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ | 451 ^a 299 ^b | 318 333 | 451 (7) | 461 (7) |
| $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ | 446 | 15 | 451 (7) | 939 (7) |

Table 35. Complex and ligand 2 fluorescence data (^a excited at 366 nm, ^b excited at 283 nm).

| Complex | Emission max (nm) | Emission intensity (AU) | Ligand 2 Emission max (nm) | Ligand 2 Emission intensity (AU) |
|---|--------------------------------------|-------------------------|----------------------------|----------------------------------|
| [Ag ₂ (9-aca) ₂] _n | 448 | 61 | N/A | N/A |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | 448 | 175 | 561 (1) | 15 (1) |
| [Ag(apim)](9-aca)·H ₂ O | 440 | 53 | 0 (4) | 0 (4) |
| [Ag(2-Ph-imid)] | 342 | 44 | N/A | N/A |
| [Ag(4-Ph-imidH) ₂](9-aca)] | 448 | 108 | 290 (5) | 2 (5) |
| [Ag(4,5-dicyanoimid)] | 347 | 1 | N/A | N/A |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ | 451 ^a 299 ^b | 318 333 | 299 (2) | 554 (2) |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] | 446 | 15 | N/A | N/A |

In vivo* Data*Table 36.** Survival of *G. mellonella* larvae after prophylactic treatment with silver(I) compounds and infection with a lethal dose of *C. albicans*.

| Complex Concentration (#poor solubility) | % Survival after 24 h. | % Survival after 48 h | % Survival after 72 h |
|--|------------------------------|-----------------------------|-----------------------------|
| Control (1×10^8 cells cm^{-3}) | 70 | 30 | 10 |
| Ketoconazole# | | | |
| 100 $\mu\text{g cm}^{-3}$ | 95 | 80 | 75 |
| 10 $\mu\text{g cm}^{-3}$ | 80 | 55 | 50 |
| 5 $\mu\text{g cm}^{-3}$ | 85 | 60 | 50 |
| AgNO ₃ | | | |
| 100 $\mu\text{g cm}^{-3}$ | 100 | 95 | 80 |
| 10 $\mu\text{g cm}^{-3}$ | 90 | 85 | 70 |
| 0.625 $\mu\text{g cm}^{-3}$ | 80 | 70 | 55 |
| AgClO ₄ | | | |
| 100 $\mu\text{g cm}^{-3}$ | 80 | 70 | 55 |
| 10 $\mu\text{g cm}^{-3}$ | 70 | 50 | 40 |
| 0.625 $\mu\text{g cm}^{-3}$ | 40 | 25 | 20 |
| [Ag ₂ (9-aca) ₂] _n | | | |
| 100 $\mu\text{g cm}^{-3}$ | 90 | 70 | 60 |
| 10 $\mu\text{g cm}^{-3}$ | 95 | 60 | 55 |
| 1.250 $\mu\text{g cm}^{-3}$ | 95 | 60 | 50 |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | | | |
| 100 $\mu\text{g cm}^{-3}$ | 80 | 60 | 50 |
| 10 $\mu\text{g cm}^{-3}$ | 80 | 45 | 35 |
| 1.560 $\mu\text{g cm}^{-3}$ | 70 | 45 | 25 |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | | | |
| 100 $\mu\text{g cm}^{-3}$ | 75 | 45 | 30 |
| 10 $\mu\text{g cm}^{-3}$ | 60 | 40 | 30 |
| 0.390 $\mu\text{g cm}^{-3}$ | 50 | 20 | 10 |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | | | |
| 100 $\mu\text{g cm}^{-3}$ | 80 | 70 | 65 |
| 10 $\mu\text{g cm}^{-3}$ | 60 | 50 | 35 |
| 2.5 $\mu\text{g cm}^{-3}$ | 65 | 25 | 15 |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | | | |
| 100 $\mu\text{g cm}^{-3}$ | 85 | 70 | 50 |
| 10 $\mu\text{g cm}^{-3}$ | 90 | 45 | 30 |
| 1.560 $\mu\text{g cm}^{-3}$ | 90 | 55 | 35 |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | | | |
| 100 $\mu\text{g cm}^{-3}$ | 100 | 40 | 20 |
| 10 $\mu\text{g cm}^{-3}$ | 90 | 50 | 30 |
| 2 $\mu\text{g cm}^{-3}$ | 100 | 50 | 35 |

| Complex Concentration (#poor solubility) | % Survival after 24 h. | % Survival after 48 h | % Survival after 72 h |
|--|------------------------------|-----------------------------|-----------------------------|
| [Ag(2-Me-imidH) ₂ (9-aca)] | | | |
| 100 µg cm ⁻³ | 65 | 30 | 30 |
| 10 µg cm ⁻³ | 60 | 15 | 10 |
| 1.560 µg cm ⁻³ | 50 | 10 | 10 |
| [Ag(1-Bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | | | |
| 100 µg cm ⁻³ | 100 | 60 | 60 |
| 10 µg cm ⁻³ | 90 | 60 | 60 |
| 1.560 µg cm ⁻³ | 65 | 50 | 15 |
| [Ag ₂ (1-Bu-imid) ₂ (9-aca) ₂] | | | |
| 100 µg cm ⁻³ | 80 | 80 | 70 |
| 10 µg cm ⁻³ | 70 | 40 | 30 |
| 1.560 µg cm ⁻³ | 60 | 30 | 15 |
| [Ag(apim)](9-aca)·H ₂ O | | | |
| 100 µg cm ⁻³ | 100 | 80 | 70 |
| 10 µg cm ⁻³ | 70 | 40 | 40 |
| 0.400 µg cm ⁻³ | 40 | 40 | 20 |
| [Ag(2-Ph-imid)] [#] | | | |
| 100 µg cm ⁻³ | 100 | 80 | 70 |
| 10 µg cm ⁻³ | 95 | 65 | 45 |
| 3.125 µg cm ⁻³ | 90 | 60 | 35 |
| [Ag(4-Ph-imidH) ₂ (9-aca)] | | | |
| 100 µg cm ⁻³ | 100 | 60 | 45 |
| 10 µg cm ⁻³ | 75 | 50 | 40 |
| 3.125 µg cm ⁻³ | 50 | 30 | 20 |
| [Ag(4,5-dicyanoimid)] [#] | | | |
| 100 µg cm ⁻³ | 90 | 70 | 60 |
| 10 µg cm ⁻³ | 95 | 70 | 50 |
| 0.780 µg cm ⁻³ | 75 | 50 | 35 |
| [Ag(Benz-imid)] [#] | | | |
| 100 µg cm ⁻³ | 85 | 70 | 60 |
| 10 µg cm ⁻³ | 80 | 70 | 50 |
| 3.125 µg cm ⁻³ | 70 | 50 | 35 |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ | | | |
| 100 µg cm ⁻³ | 90 | 60 | 40 |
| 10 µg cm ⁻³ | 90 | 60 | 25 |
| 3.125 µg cm ⁻³ | 75 | 50 | 30 |
| [Ag(2-Mebenz-imid)] [#] | | | |
| 100 µg cm ⁻³ | 80 | 50 | 40 |
| 10 µg cm ⁻³ | 70 | 40 | 40 |
| 6.250 µg cm ⁻³ | 75 | 50 | 30 |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] | | | |
| 100 µg cm ⁻³ | 100 | 90 | 90 |
| 10 µg cm ⁻³ | 100 | 80 | 70 |
| 0.390 µg cm ⁻³ | 85 | 75 | 65 |

Table 37. Survival of *G. mellonella* larvae after infection with a lethal dose of *C. albicans* and treatment with silver(I) compounds.

| Complex Concentration (#poor solubility) | % Survival after 24 h. | % Survival after 48 h | % Survival after 72 h |
|--|------------------------|-----------------------|-----------------------|
| Control (1×10 ⁸ cells cm ⁻³) | 70 | 30 | 10 |
| Ketoconazole [#] | | | |
| 100 µg cm ⁻³ | 100 | 95 | 75 |
| 10 µg cm ⁻³ | 90 | 45 | 30 |
| 5 µg cm ⁻³ | 70 | 45 | 20 |
| AgNO ₃ | | | |
| 100 µg cm ⁻³ | 95 | 85 | 75 |
| 10 µg cm ⁻³ | 95 | 80 | 55 |
| 0.625 µg cm ⁻³ | 90 | 70 | 60 |
| AgClO ₄ | | | |
| 100 µg cm ⁻³ | 70 | 50 | 40 |
| 10 µg cm ⁻³ | 75 | 50 | 25 |
| 0.625 µg cm ⁻³ | 30 | 15 | 10 |
| [Ag ₂ (9-aca) ₂] _n | | | |
| 100 µg cm ⁻³ | 90 | 65 | 50 |
| 10 µg cm ⁻³ | 100 | 50 | 45 |
| 1.25 µg cm ⁻³ | 100 | 40 | 35 |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | | | |
| 100 µg cm ⁻³ | 90 | 60 | 30 |
| 10 µg cm ⁻³ | 95 | 35 | 30 |
| 1.560 µg cm ⁻³ | 80 | 40 | 35 |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | | | |
| 100 µg cm ⁻³ | 65 | 40 | 30 |
| 10 µg cm ⁻³ | 60 | 40 | 25 |
| 0.390 µg cm ⁻³ | 50 | 25 | 10 |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | | | |
| 100 µg cm ⁻³ | 80 | 40 | 25 |
| 10 µg cm ⁻³ | 80 | 30 | 10 |
| 2.5 µg cm ⁻³ | 80 | 25 | 10 |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | | | |
| 100 µg cm ⁻³ | 100 | 60 | 60 |
| 10 µg cm ⁻³ | 90 | 40 | 30 |
| 1.560 µg cm ⁻³ | 85 | 35 | 30 |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | | | |
| 100 µg cm ⁻³ | 90 | 60 | 45 |
| 10 µg cm ⁻³ | 95 | 40 | 30 |
| 2 µg cm ⁻³ | 90 | 30 | 30 |
| [Ag(2-Me-imidH) ₂ (9-aca)] | | | |
| 100 µg cm ⁻³ | 90 | 75 | 70 |
| 10 µg cm ⁻³ | 90 | 70 | 65 |
| 1.560 µg cm ⁻³ | 80 | 55 | 30 |

| Complex Concentration (#poor solubility) | % Survival after 24 h. | % Survival after 48 h | % Survival after 72 h |
|---|------------------------|-----------------------|-----------------------|
| [Ag(1-Bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] 100 µg cm ⁻³ | 80 | 45 | 35 |
| 10 µg cm ⁻³ | 70 | 40 | 40 |
| 1.560 µg cm ⁻³ | 70 | 40 | 25 |
| [Ag ₂ (1-Bu-imid) ₂ (9-aca) ₂] 100 µg cm ⁻³ | 90 | 80 | 65 |
| 10 µg cm ⁻³ | 70 | 50 | 35 |
| 1.560 µg cm ⁻³ | 40 | 20 | 20 |
| [Ag(apim)](9-aca)·H ₂ O 100 µg cm ⁻³ | 100 | 90 | 70 |
| 10 µg cm ⁻³ | 80 | 50 | 40 |
| 0.400 µg cm ⁻³ | 70 | 30 | 20 |
| [Ag(2-Ph-imid)]# 100 µg cm ⁻³ | 100 | 70 | 60 |
| 10 µg cm ⁻³ | 95 | 45 | 30 |
| 3.125 µg cm ⁻³ | 100 | 40 | 20 |
| [Ag(4-Ph-imidH) ₂ (9-aca)] 100 µg cm ⁻³ | 80 | 40 | 20 |
| 10 µg cm ⁻³ | 60 | 30 | 20 |
| 3.125 µg cm ⁻³ | 50 | 30 | 10 |
| [Ag(4,5-dicyanoimid)]# 100 µg cm ⁻³ | 85 | 60 | 60 |
| 10 µg cm ⁻³ | 90 | 60 | 40 |
| 0.780 µg cm ⁻³ | 70 | 55 | 30 |
| [Ag(Benz-imid)]# 100 µg cm ⁻³ | 75 | 60 | 50 |
| 10 µg cm ⁻³ | 80 | 55 | 40 |
| 3.125 µg cm ⁻³ | 60 | 50 | 30 |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ 100 µg cm ⁻³ | 90 | 50 | 10 |
| 10 µg cm ⁻³ | 80 | 30 | 10 |
| 3.125 µg cm ⁻³ | 80 | 40 | 10 |
| [Ag(2-Mebenz-imid)]# 100 µg cm ⁻³ | 60 | 50 | 50 |
| 10 µg cm ⁻³ | 60 | 60 | 50 |
| 0.625 µg cm ⁻³ | 60 | 40 | 40 |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] 100 µg cm ⁻³ | 85 | 65 | 60 |
| 10 µg cm ⁻³ | 80 | 50 | 40 |
| 0.390 µg cm ⁻³ | 60 | 45 | 30 |

Table 38. Significance of prophylactic treatment (categories and p values).

| Complex Concentration (#poor solubility) | Significant after 24 h. (p value) | Significant after 48 h (p value) | Significant after 72 h (p value) |
|--|-----------------------------------|----------------------------------|----------------------------------|
| Ketoconazole [#] | | | |
| 100 µg cm ⁻³ | No (0.2758) | Yes* (0.0285) | Yes** (0.0076) |
| 10 µg cm ⁻³ | No (0.6147) | No (0.3736) | No (0.0571) |
| 5 µg cm ⁻³ | No (0.6147) | No (0.1888) | No (0.0571) |
| AgNO ₃ | | | |
| 100 µg cm ⁻³ | No (0.9671) | Yes** (0.0076) | Yes** (0.0022) |
| 10 µg cm ⁻³ | No (0.2758) | Yes* (0.0285) | Yes** (0.0076) |
| 0.625 µg cm ⁻³ | No (0.6147) | No (0.0812) | No (0.0571) |
| AgClO ₄ | | | |
| 100 µg cm ⁻³ | No (0.6147) | No (0.0812) | No (0.0571) |
| 10 µg cm ⁻³ | No (1.000) | No (0.3736) | No (0.1311) |
| 0.625 µg cm ⁻³ | No (0.1888) | No (0.6147) | No (0.5416) |
| [Ag ₂ (9-aca) ₂] _n | | | |
| 100 µg cm ⁻³ | No (0.2758) | No (0.0812) | Yes* (0.0223) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.1888) | No (0.0571) |
| 1.250 µg cm ⁻³ | No (0.2758) | No (0.1888) | No (0.0571) |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | | | |
| 100 µg cm ⁻³ | No (0.6174) | No (0.1888) | No (0.0571) |
| 10 µg cm ⁻³ | No (0.6147) | No (0.6477) | No (0.2758) |
| 1.560 µg cm ⁻³ | No (1.000) | No (0.6477) | No (0.5416) |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | | | |
| 100 µg cm ⁻³ | No (1.000) | No (0.6477) | No (0.2758) |
| 10 µg cm ⁻³ | No (0.6477) | No (0.6477) | No (0.2758) |
| 0.390 µg cm ⁻³ | No (0.3736) | No (0.6147) | No (1.000) |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | | | |
| 100 µg cm ⁻³ | No (0.6147) | No (0.0812) | Yes* (0.0223) |
| 10 µg cm ⁻³ | No (0.6477) | No (0.3736) | No (0.2758) |
| 2.5 µg cm ⁻³ | No (0.6477) | No (0.6147) | No (1.000) |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | | | |
| 100 µg cm ⁻³ | No (0.6147) | No (0.0812) | No (0.0571) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.6477) | No (0.2758) |
| 1.560 µg cm ⁻³ | No (0.2758) | No (0.3736) | No (0.2758) |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | | | |
| 100 µg cm ⁻³ | No (0.0671) | No (0.6477) | No (0.5416) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.3736) | No (0.2758) |
| 2 µg cm ⁻³ | No (0.0671) | No (0.3736) | No (0.2758) |
| [Ag(2-Me-imidH) ₂ (9-aca)] | | | |
| 100 µg cm ⁻³ | No (0.6477) | No (1.000) | No (0.2758) |
| 10 µg cm ⁻³ | No (0.6477) | No (0.2758) | No (1.000) |
| 1.560 µg cm ⁻³ | No (0.3736) | No (0.2758) | No (1.000) |

| Complex Concentration (#poor solubility) | Significant after 24 h. (p value) | Significant after 48 h (p value) | Significant after 72 h (p value) |
|--|---|--|--|
| [Ag(1-bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] 100 µg cm ⁻³ 10 µg cm ⁻³ 1.560 µg cm ⁻³ | No (0.0671) No (0.2758) No (0.6477) | No (0.1888) No (0.1888) No (0.3736) | Yes* (0.0223) Yes* (0.0223) No (1.000) |
| [Ag ₂ (1-bu-imid) ₂ (9-aca) ₂] 100 µg cm ⁻³ 10 µg cm ⁻³ 1.560 µg cm ⁻³ | No (0.6147) No (1.000) No (0.6477) | Yes* (0.0285) No (0.6477) No (0.3736) | Yes** (0.0076) No (0.2758) No (1.000) |
| [Ag(apim)](9-aca)·H ₂ O 100 µg cm ⁻³ 10 µg cm ⁻³ 0.400 µg cm ⁻³ | No (0.0671) No (1.000) No (0.1888) | Yes* (0.0285) No (0.6477) No (0.6477) | Yes** (0.0076) No (0.1311) No (0.5416) |
| [Ag(2-Ph-imid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.0671) No (0.2758) No (0.2758) | Yes* (0.0285) No (0.1888) No (0.1888) | Yes** (0.0076) No (0.1311) No (0.2758) |
| [Ag(4-Ph-imidH) ₂ (9-aca)] 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.0671) No (1.000) No (0.3736) | No (0.1888) No (0.3736) No (1.000) | No (0.1311) No (0.1311) No (0.5416) |
| [Ag(4,5-dicyanoimid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 0.780 µg cm ⁻³ | No (0.2758) No (0.2758) No (1.000) | No (0.0812) No (0.0812) No (0.3736) | Yes* (0.0223) No (0.0571) No (0.2758) |
| [Ag(Benz-imid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.6147) No (0.6147) No (1.000) | No (0.0812) No (0.0812) No (0.3736) | Yes* (0.0223) No (0.0571) No (0.2758) |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.2758) No (0.2758) No (1.000) | No (0.1888) No (0.1888) No (0.3736) | No (0.1311) No (0.5416) No (0.2758) |
| [Ag(2-Mebenz-imid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 6.250 µg cm ⁻³ | No (0.6147) No (1.000) No (1.000) | No (0.3736) No (0.6477) No (0.3736) | No (0.1311) No (0.1311) No (0.2758) |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] 100 µg cm ⁻³ 10 µg cm ⁻³ 0.390 µg cm ⁻³ | No (0.0671) No (0.0671) No (0.6147) | Yes** (0.0076) Yes* (0.0285) No (0.0812) | Yes*** (0.0005) Yes** (0.0076) Yes* (0.0223) |

Table 39. Significance of treatment of infection (categories and p values).

| Complex Concentration (#poor solubility) | Significant after 24 h (p value) | Significant after 48 h (p value) | Significant after 72 h (p value) |
|--|----------------------------------|----------------------------------|----------------------------------|
| Ketoconazole [#] | | | |
| 100 µg cm ⁻³ | No (0.0671) | Yes** (0.0076) | Yes** (0.0076) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.6477) | No (0.2758) |
| 5 µg cm ⁻³ | No (1.000) | No (0.6477) | No (0.5416) |
| AgNO ₃ | | | |
| 100 µg cm ⁻³ | No (0.2758) | Yes * (0.0285) | Yes** (0.0076) |
| 10 µg cm ⁻³ | No (0.2758) | Yes* (0.0285) | No (0.0571) |
| 0.625 µg cm ⁻³ | No (0.2758) | No (0.0812) | Yes* (0.0223) |
| AgClO ₄ | | | |
| 100 µg cm ⁻³ | No (1.000) | No (0.3736) | No (0.1311) |
| 10 µg cm ⁻³ | No (1.000) | No (0.3736) | No (0.5416) |
| 0.625 µg cm ⁻³ | No (0.0812) | No (0.2758) | No (1.000) |
| [Ag ₂ (9-aca) ₂] _n | | | |
| 100 µg cm ⁻³ | No (0.2758) | No (0.1888) | No (0.0571) |
| 10 µg cm ⁻³ | No (0.0671) | No (0.3736) | No (0.1311) |
| 1.250 µg cm ⁻³ | No (0.0671) | No (0.6477) | No (0.2758) |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | | | |
| 100 µg cm ⁻³ | No (0.2758) | No (0.1888) | No (0.2758) |
| 10 µg cm ⁻³ | No (0.2758) | No (1.000) | No (0.2758) |
| 1.560 µg cm ⁻³ | No (0.6147) | No (0.6477) | No (0.2758) |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | | | |
| 100 µg cm ⁻³ | No (0.6477) | No (0.6477) | No (0.2758) |
| 10 µg cm ⁻³ | No (0.6477) | No (0.6477) | No (0.5416) |
| 0.390 µg cm ⁻³ | No (0.3736) | No (0.6147) | No (1.000) |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | | | |
| 100 µg cm ⁻³ | No (0.6147) | No (0.6477) | No (0.5416) |
| 10 µg cm ⁻³ | No (0.6147) | No (1.000) | No (1.000) |
| 2.5 µg cm ⁻³ | No (0.6147) | No (0.6147) | No (1.000) |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | | | |
| 100 µg cm ⁻³ | No (0.0671) | No (0.1888) | Yes* (0.0223) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.6477) | No (0.2758) |
| 1.560 µg cm ⁻³ | No (0.6147) | No (1.000) | No (0.2758) |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | | | |
| 100 µg cm ⁻³ | No (0.2758) | No (0.1888) | No (0.1311) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.6477) | No (0.2758) |
| 2 µg cm ⁻³ | No (0.2758) | No (1.000) | No (0.2758) |
| [Ag(2-Me-imidH) ₂ (9-aca)] | | | |
| 100 µg cm ⁻³ | No (0.2758) | No (0.0812) | Yes** (0.0076) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.0812) | Yes* (0.0223) |
| 1.560 µg cm ⁻³ | No (0.6147) | No (0.3736) | No (0.2758) |

| Complex Concentration (#poor solubility) | Significant after 24 h. (p value) | Significant after 48 h (p value) | Significant after 72 h (p value) |
|--|---|---|--|
| [Ag(1-bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] 100 µg cm ⁻³ 10 µg cm ⁻³ 1.560 µg cm ⁻³ | No (0.6147) No (1.000) No (1.000) | No (0.6477) No (0.6477) No (0.6477) | No (0.2758) No (0.1311) No (0.5416) |
| [Ag ₂ (1-bu-imid) ₂ (9-aca) ₂] 100 µg cm ⁻³ 10 µg cm ⁻³ 1.560 µg cm ⁻³ | No (0.2758) No (1.000) No (0.1888) | Yes* (0.0285) No (0.3736) No (0.6147) | Yes* (0.0223) No (0.2758) No (0.5416) |
| [Ag(apim)](9-aca)·H ₂ O 100 µg cm ⁻³ 10 µg cm ⁻³ 0.400 µg cm ⁻³ | No (0.0671) No (0.6147) No (1.000) | Yes** (0.0076) No (0.3736) No (1.000) | Yes** (0.0076) No (0.1311) No (0.5416) |
| [Ag(2-Ph-imid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.0671) No (0.2758) No (0.0671) | No (0.0812) No (0.6477) No (0.6477) | Yes* (0.0223) No (0.2758) No (0.5416) |
| [Ag(4-Ph-imidH) ₂ (9-aca)] 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.6147) No (0.6477) No (0.3736) | No (0.6477) No (1.000) No (1.000) | No (0.5416) No (0.5416) No (1.000) |
| [Ag(4,5-dicyanoimid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 0.780 µg cm ⁻³ | No (0.6147) No (0.2758) No (1.000) | No (0.1888) No (0.1888) No (0.3736) | Yes* (0.0223) No (0.1311) No (0.2758) |
| [Ag(Benz-imid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (1.000) No (0.6147) No (0.6477) | No (0.1888) No (0.3736) No (0.3736) | No (0.0571) No (0.1311) No (0.2758) |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.2758) No (0.6147) No (0.6147) | No (0.3736) No (1.000) No (0.6477) | No (1.000) No (1.000) No (1.000) |
| [Ag(2-Mebenz-imid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 6.250 µg cm ⁻³ | No (0.6477) No (0.6477) No (0.6477) | No (0.3736) No (0.1888) No (0.6477) | No (0.0571) No (0.0571) No (0.1311) |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] 100 µg cm ⁻³ 10 µg cm ⁻³ 0.390 µg cm ⁻³ | No (0.6147) No (0.6147) No (0.6477) | No (0.1888) No (0.3736) No (0.6477) | Yes* (0.0223) No (0.1311) No (0.2758) |

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X-ray Crystal Data for [Ag₂(9-aca)₂]_n

| | |
|-----------------------------------|--|
| Identification code | [Ag ₂ (9-aca) ₂] _n |
| Empirical formula | C ₃₀ H ₁₈ Ag ₂ O ₄ |
| Formula weight | 658.18 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | a = 14.813(3) Å α = 90°. b = 5.6055(12) Å β = 95.250(3)°. c = 27.413(6) Å γ = 90°. |
| Volume | 2266.6(8) Å ³ |
| Z | 4 |
| Density (calculated) | 1.929 Mg/m ³ |
| Absorption coefficient | 1.766 mm ⁻¹ |
| F(000) | 1296 |
| Crystal size | 0.57 x 0.05 x 0.02 mm ³ |
| Crystal description | yellow rod |
| Theta range for data collection | 1.94 to 25.00°. |
| Index ranges | -17 ≤ h ≤ 17, -6 ≤ k ≤ 6, -32 ≤ l ≤ 32 |
| Reflections collected | 16694 |
| Independent reflections | 3991 [R(int) = 0.0520] |
| Completeness to theta = 25.00° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9655 and 0.4326 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 3991 / 0 / 325 |
| Goodness-of-fit on F ² | 1.020 |
| Final R indices [I > 2σ(I)] | R1 = 0.0374, wR2 = 0.0854 |
| R indices (all data) | R1 = 0.0610, wR2 = 0.0979 |
| Largest diff. peak and hole | 0.913 and -0.917 e.Å ⁻³ |

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}_2(9\text{-aca})_2]_n$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|-------|----------|-----------|---------|-------|
| Ag(1) | 4611(1) | 7083(1) | 193(1) | 28(1) |
| O(1) | 4213(2) | 4684(6) | 757(1) | 26(1) |
| O(2) | 4681(2) | 1377(6) | 400(1) | 25(1) |
| C(1) | 4215(3) | 2493(9) | 691(2) | 18(1) |
| C(2) | 3628(3) | 933(9) | 978(2) | 19(1) |
| C(3) | 3054(3) | -726(9) | 720(2) | 19(1) |
| C(4) | 2917(3) | -808(9) | 192(2) | 23(1) |
| C(5) | 2418(3) | -2547(9) | -42(2) | 28(1) |
| C(6) | 2005(3) | -4364(10) | 221(2) | 27(1) |
| C(7) | 2063(3) | -4263(10) | 716(2) | 27(1) |
| C(8) | 2578(3) | -2475(9) | 979(2) | 21(1) |
| C(9) | 2666(3) | -2418(9) | 1490(2) | 23(1) |
| C(10) | 3179(3) | -703(9) | 1748(2) | 22(1) |
| C(11) | 3229(4) | -618(11) | 2274(2) | 32(1) |
| C(12) | 3694(4) | 1106(11) | 2523(2) | 34(1) |
| C(13) | 4184(4) | 2861(10) | 2276(2) | 34(1) |
| C(14) | 4172(3) | 2807(10) | 1778(2) | 27(1) |
| C(15) | 3674(3) | 1043(9) | 1493(2) | 19(1) |
| Ag(2) | 220(1) | 7887(1) | 4742(1) | 27(1) |
| O(3) | 605(2) | 10405(6) | 4187(1) | 27(1) |
| O(4) | 334(2) | 13714(6) | 4597(1) | 29(1) |
| C(16) | 604(3) | 12600(9) | 4240(2) | 20(1) |
| C(17) | 1001(3) | 14151(9) | 3855(2) | 21(1) |
| C(18) | 452(3) | 15730(9) | 3576(2) | 20(1) |
| C(19) | -507(4) | 15753(9) | 3568(2) | 27(1) |
| C(20) | -1024(4) | 17285(10) | 3282(2) | 31(1) |
| C(21) | -615(4) | 18972(10) | 2988(2) | 35(1) |
| C(22) | 289(4) | 19049(10) | 2982(2) | 30(1) |
| C(23) | 859(4) | 17441(9) | 3268(2) | 23(1) |
| C(24) | 1795(4) | 17450(9) | 3266(2) | 28(1) |
| C(25) | 2353(4) | 15795(10) | 3519(2) | 25(1) |
| C(26) | 3308(4) | 15728(11) | 3498(2) | 31(1) |

| | | | | |
|-------|---------|-----------|---------|-------|
| C(27) | 3827(4) | 14065(11) | 3734(2) | 34(1) |
| C(28) | 3431(4) | 12270(11) | 4010(2) | 34(1) |
| C(29) | 2522(4) | 12277(10) | 4054(2) | 28(1) |
| C(30) | 1943(3) | 14025(9) | 3814(2) | 19(1) |

Table 2. Bond lengths [\AA] and angles [$^\circ$] for $[\text{Ag}_2(9\text{-aca})_2]_n$.

| | | | |
|----------------------|------------|----------------------|------------|
| Ag(1)-O(1) | 2.170(3) | Ag(2)-O(3) | 2.190(3) |
| Ag(1)-O(2)#1 | 2.190(3) | Ag(2)-O(4)#4 | 2.243(3) |
| Ag(1)-O(2)#2 | 2.473(4) | Ag(2)-O(4)#3 | 2.381(4) |
| Ag(1)-Ag(1)#1 | 2.8508(9) | Ag(2)-Ag(2)#4 | 2.8643(9) |
| O(1)-C(1) | 1.242(6) | O(3)-C(16) | 1.239(6) |
| O(2)-C(1) | 1.267(6) | O(4)-C(16) | 1.257(6) |
| O(2)-Ag(1)#1 | 2.190(3) | O(4)-Ag(2)#4 | 2.243(3) |
| O(2)-Ag(1)#3 | 2.473(4) | O(4)-Ag(2)#2 | 2.381(4) |
| C(1)-C(2) | 1.504(7) | C(16)-C(17) | 1.526(6) |
| C(2)-C(3) | 1.407(7) | C(17)-C(18) | 1.385(7) |
| C(2)-C(15) | 1.411(6) | C(17)-C(30) | 1.412(7) |
| C(3)-C(8) | 1.434(7) | C(18)-C(19) | 1.420(7) |
| C(3)-C(4) | 1.442(6) | C(18)-C(23) | 1.446(7) |
| C(4)-C(5) | 1.350(7) | C(19)-C(20) | 1.351(7) |
| C(5)-C(6) | 1.417(7) | C(20)-C(21) | 1.416(8) |
| C(6)-C(7) | 1.355(7) | C(21)-C(22) | 1.341(8) |
| C(7)-C(8) | 1.416(7) | C(22)-C(23) | 1.421(7) |
| C(8)-C(9) | 1.395(7) | C(23)-C(24) | 1.387(7) |
| C(9)-C(10) | 1.379(7) | C(24)-C(25) | 1.387(7) |
| C(10)-C(11) | 1.437(6) | C(25)-C(26) | 1.421(7) |
| C(10)-C(15) | 1.440(7) | C(25)-C(30) | 1.447(7) |
| C(11)-C(12) | 1.338(8) | C(26)-C(27) | 1.339(8) |
| C(12)-C(13) | 1.428(8) | C(27)-C(28) | 1.418(8) |
| C(13)-C(14) | 1.364(7) | C(28)-C(29) | 1.363(8) |
| C(14)-C(15) | 1.424(7) | C(29)-C(30) | 1.423(7) |
| O(1)-Ag(1)-O(2)#1 | 162.20(13) | O(2)#2-Ag(1)-Ag(1)#1 | 150.72(8) |
| O(1)-Ag(1)-O(2)#2 | 116.66(12) | C(1)-O(1)-Ag(1) | 120.3(3) |
| O(2)#1-Ag(1)-O(2)#2 | 76.88(13) | C(1)-O(2)-Ag(1)#1 | 126.7(3) |
| O(1)-Ag(1)-Ag(1)#1 | 84.41(9) | C(1)-O(2)-Ag(1)#3 | 127.6(3) |
| O(2)#1-Ag(1)-Ag(1)#1 | 79.04(9) | Ag(1)#1-O(2)-Ag(1)#3 | 103.12(13) |

| | | | |
|----------------------|------------|----------------------|------------|
| O(1)-C(1)-O(2) | 126.1(5) | O(4)#3-Ag(2)-Ag(2)#4 | 156.59(8) |
| O(1)-C(1)-C(2) | 119.3(4) | C(16)-O(3)-Ag(2) | 123.7(3) |
| O(2)-C(1)-C(2) | 114.6(4) | C(16)-O(4)-Ag(2)#4 | 126.6(3) |
| C(3)-C(2)-C(15) | 120.3(4) | C(16)-O(4)-Ag(2)#2 | 130.5(3) |
| C(3)-C(2)-C(1) | 118.3(4) | Ag(2)#4-O(4)-Ag(2)#2 | 102.80(13) |
| C(15)-C(2)-C(1) | 121.4(4) | O(3)-C(16)-O(4) | 126.1(5) |
| C(2)-C(3)-C(8) | 120.3(4) | O(3)-C(16)-C(17) | 118.6(4) |
| C(2)-C(3)-C(4) | 123.2(4) | O(4)-C(16)-C(17) | 115.2(4) |
| C(8)-C(3)-C(4) | 116.5(4) | C(18)-C(17)-C(30) | 121.5(5) |
| C(5)-C(4)-C(3) | 121.3(5) | C(18)-C(17)-C(16) | 120.1(4) |
| C(4)-C(5)-C(6) | 121.4(5) | C(30)-C(17)-C(16) | 118.2(4) |
| C(7)-C(6)-C(5) | 119.3(5) | C(17)-C(18)-C(19) | 123.5(5) |
| C(6)-C(7)-C(8) | 121.5(5) | C(17)-C(18)-C(23) | 119.4(5) |
| C(9)-C(8)-C(7) | 121.6(5) | C(19)-C(18)-C(23) | 117.1(4) |
| C(9)-C(8)-C(3) | 118.5(4) | C(20)-C(19)-C(18) | 121.9(5) |
| C(7)-C(8)-C(3) | 119.8(4) | C(19)-C(20)-C(21) | 120.3(5) |
| C(10)-C(9)-C(8) | 121.8(5) | C(22)-C(21)-C(20) | 120.6(5) |
| C(9)-C(10)-C(11) | 120.8(5) | C(21)-C(22)-C(23) | 121.1(5) |
| C(9)-C(10)-C(15) | 120.4(4) | C(24)-C(23)-C(22) | 122.6(5) |
| C(11)-C(10)-C(15) | 118.8(5) | C(24)-C(23)-C(18) | 118.4(5) |
| C(12)-C(11)-C(10) | 120.9(5) | C(22)-C(23)-C(18) | 119.0(5) |
| C(11)-C(12)-C(13) | 121.0(5) | C(25)-C(24)-C(23) | 123.1(5) |
| C(14)-C(13)-C(12) | 119.9(5) | C(24)-C(25)-C(26) | 123.1(5) |
| C(13)-C(14)-C(15) | 121.5(5) | C(24)-C(25)-C(30) | 118.5(5) |
| C(2)-C(15)-C(14) | 123.7(5) | C(26)-C(25)-C(30) | 118.4(5) |
| C(2)-C(15)-C(10) | 118.4(4) | C(27)-C(26)-C(25) | 121.9(5) |
| C(14)-C(15)-C(10) | 117.9(4) | C(26)-C(27)-C(28) | 120.3(5) |
| O(3)-Ag(2)-O(4)#4 | 163.19(13) | C(29)-C(28)-C(27) | 120.3(5) |
| O(3)-Ag(2)-O(4)#3 | 119.35(12) | C(28)-C(29)-C(30) | 121.3(5) |
| O(4)#4-Ag(2)-O(4)#3 | 77.20(13) | C(17)-C(30)-C(29) | 123.7(5) |
| O(3)-Ag(2)-Ag(2)#4 | 84.01(9) | C(17)-C(30)-C(25) | 118.6(5) |
| O(4)#4-Ag(2)-Ag(2)#4 | 79.39(9) | C(29)-C(30)-C(25) | 117.6(5) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z #2 x,y+1,z #3 x,y-1,z #4 -x,-y+2,-z+1

Table 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}_2(9\text{-aca})_2]_n$.
The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U^{11} | U^{22} | U^{33} | U^{23} | U^{13} | U^{12} |
|-------|----------|----------|----------|----------|----------|----------|
| Ag(1) | 41(1) | 18(1) | 30(1) | 3(1) | 24(1) | -1(1) |
| O(1) | 36(2) | 16(2) | 28(2) | 4(2) | 20(2) | 0(2) |
| O(2) | 37(2) | 19(2) | 23(2) | 2(2) | 22(2) | 3(2) |
| C(1) | 20(2) | 19(3) | 16(2) | 3(2) | 1(2) | 2(2) |
| C(2) | 29(3) | 14(3) | 16(2) | 1(2) | 8(2) | 7(2) |
| C(3) | 23(3) | 18(3) | 19(2) | 4(2) | 10(2) | 5(2) |
| C(4) | 28(3) | 27(3) | 16(2) | 4(2) | 14(2) | 3(2) |
| C(5) | 36(3) | 30(3) | 18(3) | 6(2) | 5(2) | 0(2) |
| C(6) | 27(3) | 29(3) | 27(3) | -4(2) | 7(2) | -4(2) |
| C(7) | 25(3) | 32(3) | 25(3) | 2(2) | 10(2) | -3(2) |
| C(8) | 21(2) | 25(3) | 18(2) | 2(2) | 7(2) | 2(2) |
| C(9) | 25(3) | 24(3) | 24(3) | 5(2) | 15(2) | -2(2) |
| C(10) | 28(3) | 27(3) | 13(2) | 6(2) | 14(2) | 2(2) |
| C(11) | 41(3) | 37(4) | 19(3) | 6(2) | 15(2) | -2(3) |
| C(12) | 47(4) | 40(4) | 17(3) | -3(3) | 13(2) | -2(3) |
| C(13) | 42(3) | 32(3) | 28(3) | -8(3) | 5(2) | -1(3) |
| C(14) | 33(3) | 25(3) | 24(3) | 2(2) | 11(2) | -1(2) |
| C(15) | 19(2) | 19(3) | 20(3) | 1(2) | 9(2) | 0(2) |
| Ag(2) | 45(1) | 17(1) | 23(1) | 3(1) | 19(1) | -2(1) |
| O(3) | 48(2) | 18(2) | 20(2) | -1(2) | 17(2) | -1(2) |
| O(4) | 52(2) | 21(2) | 17(2) | 1(2) | 26(2) | -5(2) |
| C(16) | 26(3) | 20(3) | 16(2) | 1(2) | 10(2) | 2(2) |
| C(17) | 32(3) | 20(3) | 13(2) | -4(2) | 14(2) | -6(2) |
| C(18) | 31(3) | 15(3) | 15(2) | -6(2) | 11(2) | 1(2) |
| C(19) | 39(3) | 23(3) | 23(3) | -2(2) | 19(2) | -2(2) |
| C(20) | 36(3) | 31(3) | 26(3) | -5(2) | 11(2) | 2(3) |
| C(21) | 54(4) | 28(3) | 23(3) | 6(2) | 5(3) | 9(3) |
| C(22) | 51(4) | 23(3) | 19(3) | 4(2) | 16(2) | 0(3) |
| C(23) | 42(3) | 16(3) | 13(2) | -1(2) | 13(2) | -4(2) |
| C(24) | 48(3) | 19(3) | 20(3) | 1(2) | 20(2) | -10(2) |
| C(25) | 37(3) | 27(3) | 13(2) | -2(2) | 12(2) | -6(2) |
| C(26) | 32(3) | 40(4) | 22(3) | -5(3) | 16(2) | -11(3) |

| | | | | | | |
|-------|-------|-------|-------|-------|-------|--------|
| C(27) | 31(3) | 47(4) | 25(3) | -5(3) | 13(2) | -11(3) |
| C(28) | 34(3) | 45(4) | 24(3) | -6(3) | 6(2) | 3(3) |
| C(29) | 36(3) | 31(3) | 17(2) | 1(2) | 7(2) | -2(2) |
| C(30) | 27(3) | 23(3) | 9(2) | -7(2) | 9(2) | -4(2) |

Table 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}_2(9\text{-aca})_2]_n$.

| | x | y | z | U(eq) |
|-------|-------|-------|------|-------|
| H(4) | 3184 | 385 | 5 | 27 |
| H(5) | 2341 | -2554 | -390 | 33 |
| H(6) | 1691 | -5638 | 51 | 33 |
| H(7) | 1752 | -5418 | 891 | 32 |
| H(9) | 2364 | -3591 | 1666 | 28 |
| H(11) | 2928 | -1802 | 2446 | 38 |
| H(12) | 3699 | 1164 | 2870 | 41 |
| H(13) | 4516 | 4064 | 2459 | 41 |
| H(14) | 4505 | 3972 | 1618 | 32 |
| H(19) | -795 | 14659 | 3768 | 33 |
| H(20) | -1666 | 17229 | 3279 | 37 |
| H(21) | -984 | 20060 | 2793 | 42 |
| H(22) | 552 | 20196 | 2783 | 36 |
| H(24) | 2067 | 18646 | 3082 | 33 |
| H(26) | 3585 | 16897 | 3309 | 37 |
| H(27) | 4465 | 14088 | 3718 | 40 |
| H(28) | 3801 | 11055 | 4166 | 41 |
| H(29) | 2269 | 11092 | 4248 | 33 |

X-ray Crystal Data for [Ag₂(9-aca)₂(DMSO)₂]_n

| | |
|-----------------------------------|--|
| Identification code | [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n |
| Empirical formula | C ₃₄ H ₃₀ Ag ₂ O ₆ S ₂ |
| Formula weight | 814.44 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | a = 9.1304(7) Å α = 90°. b = 19.5875(14) Å β = 99.2280(10)°. c = 18.0502(13) Å γ = 90°. |
| Volume | 3186.3(4) Å ³ |
| Z | 4 |
| Density (calculated) | 1.698 Mg/m ³ |
| Absorption coefficient | 1.405 mm ⁻¹ |
| F(000) | 1632 |
| Crystal size | 0.41 x 0.09 x 0.08 mm ³ |
| Crystal description | yellow rod |
| Theta range for data collection | 1.55 to 27.50°. |
| Index ranges | -11 ≤ h ≤ 11, -25 ≤ k ≤ 25, -23 ≤ l ≤ 23 |
| Reflections collected | 30770 |
| Independent reflections | 7311 [R(int) = 0.0426] |
| Completeness to theta = 27.50° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8959 and 0.5967 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 7311 / 904 / 527 |
| Goodness-of-fit on F ² | 1.026 |
| Final R indices [I > 2σ(I)] | R1 = 0.0317, wR2 = 0.0701 |
| R indices (all data) | R1 = 0.0463, wR2 = 0.0769 |
| Largest diff. peak and hole | 0.817 and -0.673 e.Å ⁻³ |

Table 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|--------|----------|----------|----------|--------|
| Ag(1) | 4461(1) | 5722(1) | 4686(1) | 34(1) |
| Ag(2) | 1637(1) | 5000(1) | 4515(1) | 33(1) |
| O(1) | 7081(2) | 5992(1) | 4789(1) | 44(1) |
| S(1) | 7744(1) | 6306(1) | 4151(1) | 59(1) |
| C(1) | 7050(4) | 7157(2) | 4104(3) | 81(1) |
| C(2) | 6680(4) | 5996(2) | 3310(2) | 64(1) |
| O(2) | 970(2) | 5245(1) | 5760(1) | 35(1) |
| S(2) | 1625(1) | 5864(1) | 6198(1) | 39(1) |
| C(3) | 1220(4) | 5729(2) | 7120(2) | 51(1) |
| C(4) | 363(4) | 6546(2) | 5941(2) | 45(1) |
| O(11) | 4822(2) | 4701(1) | 4048(1) | 35(1) |
| O(12) | 2502(2) | 4504(1) | 3477(1) | 42(1) |
| C(10) | 3763(14) | 4422(9) | 3550(9) | 34(3) |
| C(11) | 4511(7) | 3894(4) | 3104(5) | 37(2) |
| C(12) | 4847(8) | 4102(4) | 2406(4) | 49(2) |
| C(13) | 4573(7) | 4782(5) | 2113(4) | 60(2) |
| C(14) | 4950(9) | 4971(5) | 1442(4) | 87(2) |
| C(15) | 5641(10) | 4507(5) | 1012(4) | 100(3) |
| C(16) | 5881(9) | 3854(5) | 1258(4) | 94(3) |
| C(17) | 5521(9) | 3621(5) | 1962(4) | 66(2) |
| C(18) | 5857(12) | 2973(5) | 2254(5) | 69(3) |
| C(19) | 5571(18) | 2774(6) | 2948(5) | 60(2) |
| C(20) | 5956(19) | 2111(6) | 3254(6) | 87(3) |
| C(21) | 5664(13) | 1929(5) | 3929(6) | 89(3) |
| C(22) | 4996(12) | 2388(5) | 4372(6) | 68(3) |
| C(23) | 4584(13) | 3024(5) | 4101(6) | 43(2) |
| C(24) | 4860(20) | 3246(5) | 3392(7) | 43(2) |
| C(10') | 3973(19) | 4404(13) | 3581(13) | 26(3) |
| C(11') | 4479(12) | 3959(7) | 2978(7) | 38(3) |
| C(12') | 4451(12) | 4160(6) | 2241(6) | 50(3) |
| C(13') | 3895(14) | 4808(6) | 1981(6) | 63(3) |
| C(14') | 3804(18) | 4979(6) | 1249(6) | 102(4) |

| | | | | |
|--------|----------|---------|---------|--------|
| C(15') | 4340(20) | 4537(7) | 757(7) | 124(5) |
| C(16') | 5073(19) | 3971(8) | 997(7) | 111(5) |
| C(17') | 5096(16) | 3733(6) | 1742(6) | 67(3) |
| C(18') | 5649(17) | 3106(7) | 1973(7) | 56(3) |
| C(19') | 5570(20) | 2868(7) | 2678(7) | 43(3) |
| C(20') | 6120(20) | 2217(7) | 2940(8) | 61(3) |
| C(21') | 6100(20) | 2010(8) | 3640(8) | 71(4) |
| C(22') | 5443(18) | 2418(8) | 4150(8) | 60(3) |
| C(23') | 4910(20) | 3047(8) | 3920(9) | 43(3) |
| C(24') | 4990(30) | 3304(8) | 3200(9) | 36(3) |
| O(31) | 3461(2) | 6591(1) | 3826(2) | 61(1) |
| O(32) | 1801(2) | 6233(1) | 4498(1) | 42(1) |
| C(30) | 2189(3) | 6577(2) | 3985(2) | 37(1) |
| C(31) | 1026(3) | 7009(2) | 3506(2) | 35(1) |
| C(32) | 638(3) | 7649(2) | 3761(2) | 40(1) |
| C(33) | 1207(4) | 7899(2) | 4488(2) | 52(1) |
| C(34) | 775(5) | 8519(2) | 4724(2) | 70(1) |
| C(35) | -238(5) | 8923(2) | 4243(3) | 77(1) |
| C(36) | -797(4) | 8713(2) | 3550(3) | 65(1) |
| C(37) | -404(3) | 8064(2) | 3281(2) | 47(1) |
| C(38) | -1036(3) | 7819(2) | 2587(2) | 51(1) |
| C(39) | -705(3) | 7173(2) | 2339(2) | 48(1) |
| C(40) | -1391(4) | 6899(2) | 1636(2) | 66(1) |
| C(41) | -1069(5) | 6270(2) | 1415(2) | 75(1) |
| C(42) | -15(5) | 5859(2) | 1879(2) | 66(1) |
| C(43) | 685(4) | 6091(2) | 2552(2) | 48(1) |
| C(44) | 366(3) | 6758(2) | 2808(2) | 39(1) |

Table 6. Selected bond lengths [\AA] and angles [$^\circ$] for $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$.

| | | | |
|-------------------|------------|---------------------|------------|
| Ag(1)-O(11) | 2.3576(19) | Ag(1)-Ag(1)#1 | 3.1467(5) |
| Ag(1)-O(31) | 2.384(2) | Ag(2)-O(12) | 2.357(2) |
| Ag(1)-O(11)#1 | 2.421(2) | Ag(2)-O(2)#2 | 2.4005(19) |
| Ag(1)-O(1) | 2.428(2) | Ag(2)-O(32) | 2.421(2) |
| Ag(1)-O(32) | 2.598(2) | Ag(2)-O(2) | 2.4674(19) |
| Ag(1)-Ag(2) | 2.9144(3) | Ag(2)-O(1)#1 | 2.500(2) |
| O(11)-Ag(1)-O(31) | 110.86(9) | O(11)-Ag(1)-O(11)#1 | 97.65(6) |

| | | | |
|---------------------|-----------|---------------------|-----------|
| O(31)-Ag(1)-O(11)#1 | 151.23(8) | O(2)#2-Ag(2)-O(2) | 81.12(7) |
| O(11)-Ag(1)-O(1) | 90.51(7) | O(32)-Ag(2)-O(2) | 80.90(7) |
| O(31)-Ag(1)-O(1) | 99.46(7) | O(12)-Ag(2)-O(1)#1 | 83.66(8) |
| O(11)#1-Ag(1)-O(1) | 83.58(7) | O(2)#2-Ag(2)-O(1)#1 | 108.51(7) |
| O(11)-Ag(1)-O(32) | 117.64(7) | O(32)-Ag(2)-O(1)#1 | 139.17(7) |
| O(31)-Ag(1)-O(32) | 52.25(7) | O(2)-Ag(2)-O(1)#1 | 81.83(7) |
| O(1)-Ag(1)-O(32) | 144.60(7) | Ag(1)-O(1)-Ag(2)#1 | 104.22(8) |
| O(12)-Ag(2)-O(2)#2 | 101.61(7) | Ag(2)#2-O(2)-Ag(2) | 98.88(7) |
| O(12)-Ag(2)-O(32) | 111.83(7) | Ag(1)-O(11)-Ag(1)#1 | 82.35(6) |
| O(2)#2-Ag(2)-O(32) | 104.95(7) | Ag(2)-O(32)-Ag(1) | 70.90(5) |
| O(12)-Ag(2)-O(2) | 165.34(7) | | |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+1

Table 7. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$. The anisotropic displacement factor exponent takes the form: - $2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U ¹¹ | U ²² | U ³³ | U ²³ | U ¹³ | U ¹² |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ag(1) | 24(1) | 31(1) | 44(1) | 2(1) | 0(1) | 1(1) |
| Ag(2) | 24(1) | 36(1) | 40(1) | -1(1) | 11(1) | -2(1) |
| O(1) | 25(1) | 56(1) | 51(1) | 15(1) | 6(1) | 0(1) |
| S(1) | 24(1) | 82(1) | 71(1) | 33(1) | 10(1) | -2(1) |
| C(1) | 56(2) | 71(3) | 117(4) | 43(3) | 14(2) | -15(2) |
| C(2) | 45(2) | 101(3) | 49(2) | 26(2) | 16(2) | 11(2) |
| O(2) | 27(1) | 37(1) | 41(1) | -5(1) | 9(1) | -4(1) |
| S(2) | 25(1) | 46(1) | 46(1) | -10(1) | 6(1) | -7(1) |
| C(3) | 48(2) | 62(2) | 41(2) | -6(2) | 3(2) | 2(2) |
| C(4) | 49(2) | 38(2) | 52(2) | -7(2) | 16(2) | -1(1) |
| O(11) | 32(1) | 37(1) | 35(1) | -7(1) | 5(1) | -2(1) |
| O(12) | 24(1) | 56(1) | 47(1) | -11(1) | 7(1) | 2(1) |
| C(10) | 40(6) | 33(4) | 31(4) | -9(4) | 9(4) | -3(4) |
| C(11) | 18(3) | 53(4) | 42(4) | -26(3) | 7(2) | -9(2) |
| C(12) | 23(3) | 77(4) | 43(4) | -27(3) | -2(3) | 2(3) |
| C(13) | 43(4) | 98(5) | 36(4) | -17(3) | 3(3) | 12(4) |
| C(14) | 81(5) | 144(7) | 37(4) | 3(4) | 17(4) | 21(5) |
| C(15) | 73(5) | 186(8) | 46(4) | -21(5) | 24(4) | 19(6) |

| | | | | | | |
|--------|---------|---------|---------|--------|--------|--------|
| C(16) | 61(5) | 172(7) | 48(4) | -44(4) | 3(4) | 37(5) |
| C(17) | 31(4) | 108(5) | 55(4) | -51(4) | -5(3) | 11(4) |
| C(18) | 33(4) | 108(6) | 62(7) | -63(4) | -3(5) | 15(4) |
| C(19) | 36(4) | 73(5) | 66(6) | -51(4) | -8(5) | 4(4) |
| C(20) | 83(8) | 70(6) | 101(10) | -60(5) | -12(8) | 22(6) |
| C(21) | 87(8) | 44(5) | 130(8) | -32(5) | -2(6) | 16(5) |
| C(22) | 65(7) | 40(4) | 96(7) | -14(4) | 2(5) | 0(4) |
| C(23) | 30(5) | 35(3) | 63(5) | -17(3) | 3(3) | -3(3) |
| C(24) | 23(4) | 46(4) | 57(6) | -30(3) | 5(5) | -5(4) |
| C(10') | 3(4) | 38(6) | 38(6) | 3(5) | 3(3) | 1(4) |
| C(12') | 46(7) | 69(6) | 37(5) | -14(4) | 10(5) | -22(5) |
| C(13') | 80(9) | 62(6) | 45(5) | -8(4) | 0(6) | -26(6) |
| C(14') | 163(12) | 90(8) | 55(6) | 12(5) | 25(8) | -41(8) |
| C(15') | 189(14) | 130(10) | 63(7) | 7(6) | 51(8) | -40(9) |
| C(16') | 155(14) | 145(10) | 43(7) | -23(6) | 48(8) | -18(9) |
| C(17') | 81(10) | 77(6) | 49(6) | -26(4) | 23(6) | -29(6) |
| C(18') | 50(8) | 81(7) | 40(6) | -46(4) | 14(6) | -30(6) |
| C(19') | 27(5) | 54(5) | 48(8) | -38(5) | 5(8) | -5(4) |
| C(20') | 42(6) | 63(6) | 75(8) | -39(5) | 1(7) | 6(5) |
| C(21') | 60(9) | 54(7) | 96(11) | -13(7) | 5(9) | 20(6) |
| C(22') | 66(9) | 49(6) | 65(7) | -1(5) | 13(5) | -2(6) |
| C(23') | 33(8) | 43(5) | 54(7) | -18(5) | 13(6) | 2(5) |
| C(24') | 21(6) | 50(5) | 39(6) | -20(4) | 6(5) | -10(4) |
| O(31) | 29(1) | 67(2) | 90(2) | 41(1) | 14(1) | 11(1) |
| O(32) | 48(1) | 38(1) | 41(1) | 12(1) | 10(1) | 5(1) |
| C(30) | 30(2) | 34(2) | 45(2) | 7(1) | 4(1) | 3(1) |
| C(31) | 23(1) | 40(2) | 45(2) | 18(1) | 9(1) | 1(1) |
| C(32) | 31(2) | 38(2) | 53(2) | 15(1) | 14(1) | 1(1) |
| C(33) | 54(2) | 47(2) | 58(2) | 9(2) | 16(2) | 0(2) |
| C(34) | 90(3) | 53(2) | 71(3) | 1(2) | 29(2) | -1(2) |
| C(35) | 96(3) | 48(2) | 97(3) | 10(2) | 46(3) | 19(2) |
| C(36) | 58(2) | 47(2) | 96(3) | 27(2) | 33(2) | 19(2) |
| C(37) | 32(2) | 45(2) | 66(2) | 22(2) | 20(2) | 8(1) |
| C(38) | 30(2) | 55(2) | 70(2) | 31(2) | 9(2) | 7(2) |
| C(39) | 30(2) | 61(2) | 51(2) | 23(2) | 4(1) | -4(2) |
| C(40) | 51(2) | 85(3) | 57(2) | 21(2) | -7(2) | -12(2) |
| C(41) | 79(3) | 93(3) | 47(2) | 6(2) | -2(2) | -24(3) |
| C(42) | 75(3) | 61(2) | 63(3) | -2(2) | 15(2) | -13(2) |

| | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|
| C(43) | 47(2) | 47(2) | 52(2) | 8(2) | 14(2) | -4(2) |
| C(44) | 27(2) | 46(2) | 46(2) | 14(1) | 9(1) | -2(1) |

Table 8. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}_2(9\text{-aca})_2(\text{DMSO})_2]_n$.

| | x | y | z | U(eq) |
|--------|------|------|------|-------|
| H(1A) | 7536 | 7415 | 4540 | 122 |
| H(1B) | 5976 | 7149 | 4103 | 122 |
| H(1C) | 7255 | 7375 | 3643 | 122 |
| H(2A) | 6931 | 5516 | 3239 | 96 |
| H(2B) | 6900 | 6266 | 2884 | 96 |
| H(2C) | 5622 | 6034 | 3342 | 96 |
| H(3A) | 1835 | 5355 | 7359 | 77 |
| H(3B) | 169 | 5611 | 7091 | 77 |
| H(3C) | 1433 | 6147 | 7416 | 77 |
| H(4A) | 429 | 6694 | 5429 | 68 |
| H(4B) | 614 | 6929 | 6288 | 68 |
| H(4C) | -649 | 6392 | 5965 | 68 |
| H(13) | 4119 | 5106 | 2395 | 71 |
| H(14) | 4744 | 5422 | 1262 | 104 |
| H(15) | 5935 | 4648 | 554 | 120 |
| H(16) | 6304 | 3539 | 953 | 113 |
| H(18) | 6304 | 2654 | 1962 | 83 |
| H(20) | 6429 | 1794 | 2972 | 105 |
| H(21) | 5912 | 1482 | 4112 | 107 |
| H(22) | 4830 | 2257 | 4858 | 82 |
| H(23) | 4102 | 3324 | 4398 | 52 |
| H(13') | 3585 | 5124 | 2324 | 76 |
| H(14') | 3371 | 5402 | 1073 | 122 |
| H(15') | 4186 | 4641 | 237 | 148 |
| H(16') | 5587 | 3724 | 666 | 133 |
| H(18') | 6095 | 2831 | 1637 | 68 |
| H(20') | 6518 | 1922 | 2605 | 73 |
| H(21') | 6520 | 1582 | 3801 | 85 |
| H(22') | 5380 | 2257 | 4640 | 72 |

| | | | | |
|--------|-------|------|------|----|
| H(23') | 4468 | 3321 | 4258 | 51 |
| H(33) | 1897 | 7632 | 4816 | 63 |
| H(34) | 1159 | 8677 | 5214 | 83 |
| H(35) | -530 | 9353 | 4413 | 92 |
| H(36) | -1464 | 9000 | 3233 | 78 |
| H(38) | -1717 | 8099 | 2269 | 62 |
| H(40) | -2093 | 7168 | 1316 | 79 |
| H(41) | -1549 | 6098 | 946 | 89 |
| H(42) | 203 | 5415 | 1715 | 79 |
| H(43) | 1388 | 5809 | 2854 | 58 |

X-ray Crystal Data for [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca)

| | |
|-----------------------------------|---|
| Identification code | [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) |
| Empirical formula | C _{23.30} H _{20.30} Ag N _{5.30} O ₂ |
| Formula weight | 514.42 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/n |
| Unit cell dimensions | a = 9.7905(5) Å α = 90°. b = 14.2012(7) Å β = 101.8640(10)°. c = 16.3251(9) Å γ = 90°. |
| Volume | 2221.3(2) Å ³ |
| Z | 4 |
| Density (calculated) | 1.538 Mg/m ³ |
| Absorption coefficient | 0.938 mm ⁻¹ |
| F(000) | 1041 |
| Crystal size | 0.33 x 0.22 x 0.21 mm ³ |
| Crystal description | colourless block |
| Theta range for data collection | 1.92 to 26.00°. |
| Index ranges | -12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20 |
| Reflections collected | 19005 |
| Independent reflections | 4361 [R(int) = 0.0326] |
| Completeness to theta = 25.00° | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8273 and 0.7471 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 4361 / 23 / 326 |
| Goodness-of-fit on F ² | 1.049 |
| Final R indices [I > 2σ(I)] | R1 = 0.0347, wR2 = 0.0730 |
| R indices (all data) | R1 = 0.0460, wR2 = 0.0782 |
| Largest diff. peak and hole | 0.936 and -1.192 e.Å ⁻³ |

Table 9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|-------|----------|----------|----------|-------|
| Ag(1) | 2421(1) | 8163(1) | 1512(1) | 50(1) |
| O(1) | 5308(2) | 13838(1) | 1704(2) | 44(1) |
| O(2) | 3509(2) | 12945(1) | 1853(1) | 36(1) |
| C(1) | 4781(3) | 13083(2) | 1887(2) | 29(1) |
| C(2) | 5761(3) | 12262(2) | 2163(2) | 28(1) |
| C(3) | 6311(3) | 12131(2) | 3015(2) | 33(1) |
| C(4) | 6059(3) | 12786(2) | 3632(2) | 44(1) |
| C(5) | 6609(4) | 12649(3) | 4452(2) | 62(1) |
| C(6) | 7434(4) | 11857(4) | 4724(3) | 74(1) |
| C(7) | 7710(4) | 11215(3) | 4165(2) | 62(1) |
| C(8) | 7171(3) | 11328(2) | 3284(2) | 42(1) |
| C(9) | 7445(3) | 10695(2) | 2689(2) | 47(1) |
| C(10) | 6927(3) | 10826(2) | 1842(2) | 38(1) |
| C(11) | 7215(4) | 10188(2) | 1228(3) | 56(1) |
| C(12) | 6751(4) | 10342(2) | 412(3) | 60(1) |
| C(13) | 5933(4) | 11145(2) | 132(2) | 49(1) |
| C(14) | 5598(3) | 11767(2) | 688(2) | 37(1) |
| C(15) | 6077(3) | 11637(2) | 1567(2) | 29(1) |
| N(21) | 2503(3) | 6688(2) | 1303(2) | 41(1) |
| C(21) | 3655(3) | 6183(2) | 1498(2) | 43(1) |
| N(22) | 3386(3) | 5269(2) | 1393(2) | 40(1) |
| C(23) | 1986(3) | 5171(2) | 1122(2) | 45(1) |
| C(22) | 1441(3) | 6046(2) | 1064(2) | 44(1) |
| N(31) | 2061(2) | 9640(2) | 1483(2) | 36(1) |
| C(31) | 2977(3) | 10309(2) | 1769(2) | 39(1) |
| N(32) | 2400(3) | 11159(2) | 1671(2) | 38(1) |
| C(32) | 1035(3) | 11039(2) | 1303(2) | 45(1) |
| C(33) | 834(3) | 10105(2) | 1185(2) | 42(1) |
| N(51) | 5098(8) | 8252(8) | 2377(5) | 73(2) |
| C(52) | 5748(6) | 8377(4) | 3026(4) | 51(1) |
| C(53) | 6625(9) | 8530(12) | 3860(5) | 56(2) |
| N(41) | 4729(15) | 8257(19) | 2617(12) | 62(4) |

| | | | | |
|-------|----------|----------|----------|-------|
| C(41) | 6000(13) | 8369(10) | 2512(10) | 62(3) |
| N(42) | 6917(10) | 8515(7) | 3226(8) | 62(3) |
| C(42) | 6206(19) | 8500(30) | 3844(13) | 70(5) |
| C(43) | 4845(12) | 8317(9) | 3464(10) | 75(4) |

Table 10. Selected bond lengths [\AA] and angles [$^\circ$] for $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$.

| | | | |
|-------------------|------------|--------------------|-----------|
| Ag(1)-N(21) | 2.126(2) | Ag(1)-N(51) | 2.713(8) |
| Ag(1)-N(31) | 2.126(2) | Ag(1)-O(2)#1 | 3.009(2) |
| Ag(1)-N(41) | 2.588(17) | | |
| N(21)-Ag(1)-N(31) | 168.51(10) | N(21)-Ag(1)-O(2)#1 | 93.98(8) |
| N(21)-Ag(1)-N(41) | 96.1(6) | N(31)-Ag(1)-O(2)#1 | 92.38(7) |
| N(31)-Ag(1)-N(41) | 94.7(6) | N(41)-Ag(1)-O(2)#1 | 76.5(3) |
| N(21)-Ag(1)-N(51) | 93.7(3) | N(51)-Ag(1)-O(2)#1 | 88.78(18) |
| N(31)-Ag(1)-N(51) | 96.0(3) | | |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1/2, y-1/2, -z+1/2$

Table 11. Bond lengths [\AA] and angles [$^\circ$] for $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$.

| | | | |
|--------------|-----------|-------------|----------|
| Ag(1)-N(21) | 2.126(2) | C(9)-C(10) | 1.385(4) |
| Ag(1)-N(31) | 2.126(2) | C(10)-C(11) | 1.422(5) |
| Ag(1)-N(41) | 2.588(17) | C(10)-C(15) | 1.438(4) |
| Ag(1)-N(51) | 2.713(8) | C(11)-C(12) | 1.334(5) |
| Ag(1)-O(2)#1 | 3.009(2) | C(12)-C(13) | 1.414(5) |
| O(1)-C(1) | 1.253(3) | C(13)-C(14) | 1.355(4) |
| O(2)-C(1) | 1.251(3) | C(14)-C(15) | 1.426(4) |
| C(1)-C(2) | 1.519(3) | N(21)-C(21) | 1.319(4) |
| C(2)-C(3) | 1.397(4) | N(21)-C(22) | 1.377(4) |
| C(2)-C(15) | 1.398(4) | C(21)-N(22) | 1.329(4) |
| C(3)-C(4) | 1.428(4) | N(22)-C(23) | 1.357(4) |
| C(3)-C(8) | 1.433(4) | C(23)-C(22) | 1.349(4) |
| C(4)-C(5) | 1.351(5) | N(31)-C(31) | 1.323(4) |
| C(5)-C(6) | 1.403(6) | N(31)-C(33) | 1.370(4) |
| C(6)-C(7) | 1.357(6) | C(31)-N(32) | 1.329(4) |
| C(7)-C(8) | 1.436(5) | N(32)-C(32) | 1.359(4) |
| C(8)-C(9) | 1.388(5) | C(32)-C(33) | 1.350(4) |

| | | | |
|--------------------|------------|-------------------|-----------|
| N(51)-C(52) | 1.132(9) | C(41)-N(42) | 1.334(15) |
| C(52)-C(53) | 1.468(10) | N(42)-C(42) | 1.339(17) |
| N(41)-C(41) | 1.301(15) | C(42)-C(43) | 1.373(17) |
| N(41)-C(43) | 1.366(16) | | |
| N(21)-Ag(1)-N(31) | 168.51(10) | C(12)-C(11)-C(10) | 121.5(3) |
| N(21)-Ag(1)-N(41) | 96.1(6) | C(11)-C(12)-C(13) | 120.7(3) |
| N(31)-Ag(1)-N(41) | 94.7(6) | C(14)-C(13)-C(12) | 120.5(3) |
| N(21)-Ag(1)-N(51) | 93.7(3) | C(13)-C(14)-C(15) | 121.0(3) |
| N(31)-Ag(1)-N(51) | 96.0(3) | C(2)-C(15)-C(14) | 123.0(2) |
| N(41)-Ag(1)-N(51) | 12.4(4) | C(2)-C(15)-C(10) | 119.2(3) |
| N(21)-Ag(1)-O(2)#1 | 93.98(8) | C(14)-C(15)-C(10) | 117.9(3) |
| N(31)-Ag(1)-O(2)#1 | 92.38(7) | C(21)-N(21)-C(22) | 105.5(3) |
| N(41)-Ag(1)-O(2)#1 | 76.5(3) | C(21)-N(21)-Ag(1) | 123.7(2) |
| N(51)-Ag(1)-O(2)#1 | 88.78(18) | C(22)-N(21)-Ag(1) | 130.2(2) |
| O(2)-C(1)-O(1) | 125.3(2) | N(21)-C(21)-N(22) | 111.2(3) |
| O(2)-C(1)-C(2) | 117.1(2) | C(21)-N(22)-C(23) | 107.6(3) |
| O(1)-C(1)-C(2) | 117.6(2) | C(22)-C(23)-N(22) | 106.7(3) |
| C(3)-C(2)-C(15) | 121.0(2) | C(23)-C(22)-N(21) | 109.0(3) |
| C(3)-C(2)-C(1) | 119.2(2) | C(31)-N(31)-C(33) | 105.2(2) |
| C(15)-C(2)-C(1) | 119.8(2) | C(31)-N(31)-Ag(1) | 127.1(2) |
| C(2)-C(3)-C(4) | 121.9(3) | C(33)-N(31)-Ag(1) | 127.8(2) |
| C(2)-C(3)-C(8) | 119.5(3) | N(31)-C(31)-N(32) | 111.6(3) |
| C(4)-C(3)-C(8) | 118.6(3) | C(31)-N(32)-C(32) | 107.2(3) |
| C(5)-C(4)-C(3) | 120.9(4) | C(33)-C(32)-N(32) | 106.7(3) |
| C(4)-C(5)-C(6) | 121.0(4) | C(32)-C(33)-N(31) | 109.3(3) |
| C(7)-C(6)-C(5) | 120.5(3) | C(52)-N(51)-Ag(1) | 142.3(7) |
| C(6)-C(7)-C(8) | 121.1(4) | N(51)-C(52)-C(53) | 178.4(9) |
| C(9)-C(8)-C(3) | 119.2(3) | C(41)-N(41)-C(43) | 104.0(14) |
| C(9)-C(8)-C(7) | 123.0(3) | C(41)-N(41)-Ag(1) | 129.5(14) |
| C(3)-C(8)-C(7) | 117.8(3) | C(43)-N(41)-Ag(1) | 126.0(9) |
| C(10)-C(9)-C(8) | 121.9(3) | N(41)-C(41)-N(42) | 113.2(15) |
| C(9)-C(10)-C(11) | 122.3(3) | C(41)-N(42)-C(42) | 107.1(12) |
| C(9)-C(10)-C(15) | 119.3(3) | N(42)-C(42)-C(43) | 105.7(14) |
| C(11)-C(10)-C(15) | 118.5(3) | N(41)-C(43)-C(42) | 109.9(13) |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1/2, y-1/2, -z+1/2$

Table 12. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U^{11} | U^{22} | U^{33} | U^{23} | U^{13} | U^{12} |
|-------|----------|----------|----------|----------|----------|----------|
| Ag(1) | 52(1) | 29(1) | 74(1) | 4(1) | 25(1) | 8(1) |
| O(1) | 32(1) | 24(1) | 75(2) | 4(1) | 11(1) | 3(1) |
| O(2) | 28(1) | 30(1) | 50(1) | 2(1) | 8(1) | 4(1) |
| C(1) | 32(2) | 24(1) | 31(1) | -4(1) | 5(1) | 6(1) |
| C(2) | 26(1) | 23(1) | 34(2) | 0(1) | 3(1) | 0(1) |
| C(3) | 28(1) | 35(2) | 34(2) | 2(1) | 0(1) | -8(1) |
| C(4) | 50(2) | 46(2) | 36(2) | -5(1) | 11(1) | -22(2) |
| C(5) | 78(3) | 73(3) | 36(2) | -7(2) | 10(2) | -49(2) |
| C(6) | 70(3) | 99(3) | 44(2) | 21(2) | -11(2) | -56(3) |
| C(7) | 41(2) | 73(3) | 60(2) | 38(2) | -16(2) | -24(2) |
| C(8) | 26(2) | 47(2) | 45(2) | 18(2) | -7(1) | -11(1) |
| C(9) | 27(2) | 37(2) | 75(3) | 22(2) | 6(2) | 8(1) |
| C(10) | 27(1) | 30(2) | 60(2) | 5(1) | 16(1) | 5(1) |
| C(11) | 50(2) | 33(2) | 94(3) | -2(2) | 40(2) | 10(2) |
| C(12) | 67(2) | 42(2) | 82(3) | -21(2) | 46(2) | -5(2) |
| C(13) | 53(2) | 55(2) | 45(2) | -14(2) | 21(2) | -13(2) |
| C(14) | 34(2) | 39(2) | 38(2) | -4(1) | 7(1) | -1(1) |
| C(15) | 25(1) | 26(1) | 36(2) | -1(1) | 5(1) | 1(1) |
| N(21) | 45(2) | 34(1) | 45(2) | 2(1) | 13(1) | 12(1) |
| C(21) | 41(2) | 33(2) | 55(2) | 0(1) | 12(2) | 8(1) |
| N(22) | 39(1) | 32(1) | 51(2) | 0(1) | 10(1) | 12(1) |
| C(23) | 43(2) | 36(2) | 56(2) | -15(2) | 7(2) | 3(1) |
| C(22) | 40(2) | 44(2) | 45(2) | -8(1) | 3(1) | 11(1) |
| N(31) | 39(1) | 31(1) | 40(1) | 6(1) | 10(1) | 4(1) |
| C(31) | 34(2) | 37(2) | 44(2) | 6(1) | 7(1) | 5(1) |
| N(32) | 44(2) | 29(1) | 43(2) | 4(1) | 12(1) | 1(1) |
| C(32) | 37(2) | 37(2) | 63(2) | 13(2) | 13(2) | 7(1) |
| C(33) | 37(2) | 38(2) | 50(2) | 11(1) | 9(1) | 0(1) |
| N(51) | 42(4) | 69(4) | 98(5) | -4(4) | -7(4) | -2(5) |
| C(52) | 33(3) | 42(3) | 81(4) | -3(3) | 17(3) | 0(2) |
| C(53) | 52(5) | 60(5) | 59(4) | 0(4) | 19(3) | 5(5) |
| N(41) | 28(6) | 44(7) | 121(10) | 5(9) | 28(6) | 8(6) |

| | | | | | | |
|-------|-------|--------|---------|---------|-------|--------|
| C(41) | 28(7) | 55(8) | 106(9) | 10(9) | 17(6) | 0(6) |
| N(42) | 41(6) | 35(5) | 110(9) | 1(6) | 16(5) | 1(4) |
| C(42) | 43(9) | 52(10) | 122(10) | -22(11) | 32(7) | -8(10) |
| C(43) | 52(6) | 50(7) | 130(10) | -19(8) | 37(7) | -6(6) |

Table 13. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$.

| | x | y | z | U(eq) |
|--------|------|-------|------|-------|
| H(4) | 5497 | 13325 | 3462 | 52 |
| H(5) | 6435 | 13097 | 4851 | 75 |
| H(6) | 7802 | 11770 | 5305 | 89 |
| H(7) | 8270 | 10682 | 4360 | 74 |
| H(9) | 8003 | 10157 | 2869 | 57 |
| H(11) | 7751 | 9639 | 1402 | 67 |
| H(12) | 6972 | 9909 | 15 | 71 |
| H(13) | 5616 | 11249 | -451 | 59 |
| H(14) | 5036 | 12298 | 490 | 44 |
| H(21) | 4561 | 6440 | 1690 | 51 |
| H(22) | 4003 | 4810 | 1482 | 48 |
| H(23) | 1488 | 4597 | 998 | 54 |
| H(22A) | 480 | 6196 | 886 | 53 |
| H(31) | 3930 | 10195 | 2014 | 46 |
| H(32) | 2823 | 11698 | 1816 | 46 |
| H(32A) | 354 | 11520 | 1158 | 54 |
| H(33) | -25 | 9814 | 933 | 50 |
| H(53A) | 7596 | 8622 | 3809 | 84 |
| H(53B) | 6563 | 7981 | 4213 | 84 |
| H(53C) | 6300 | 9091 | 4114 | 84 |
| H(41) | 6251 | 8349 | 1980 | 75 |
| H(42) | 7821 | 8607 | 3281 | 74 |
| H(42A) | 6567 | 8586 | 4425 | 84 |
| H(43) | 4096 | 8245 | 3748 | 89 |

Table 14. Hydrogen bonds for [Ag(imidH)_{2.3}(CH₃CN)_{0.7}](9-aca) [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|----------------------|--------|----------|-----------|--------|
| N(22)-H(22)...O(1)#2 | 0.88 | 1.87 | 2.745(3) | 178.3 |
| N(32)-H(32)...O(2) | 0.88 | 1.89 | 2.752(3) | 165.5 |
| N(42)-H(42)...O(1)#3 | 0.88 | 1.86 | 2.734(10) | 174.8 |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1/2, y-1/2, -z+1/2$ #2 $x, y-1, z$ #3 $-x+3/2, y-1/2, -z+1/2$

X-ray Crystal Data for [Ag₆(imidH)₄(9-aca)₆(MeOH)₂]

| | |
|-----------------------------------|--|
| Identification code | [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] |
| Empirical formula | C ₁₀₄ H ₇₈ Ag ₆ N ₈ O ₁₄ |
| Formula weight | 2310.96 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | Pbcn |
| Unit cell dimensions | a = 20.6935(8) Å α = 90°. b = 18.2786(7) Å β = 90°. c = 23.6859(10) Å γ = 90°. |
| Volume | 8959.1(6) Å ³ |
| Z | 4 |
| Density (calculated) | 1.713 Mg/m ³ |
| Absorption coefficient | 1.358 mm ⁻¹ |
| F(000) | 4608 |
| Crystal size | 0.23 x 0.15 x 0.12 mm ³ |
| Crystal description | Pale yellow block |
| Theta range for data collection | 1.72 to 27.00°. |
| Index ranges | -26 ≤ h ≤ 26, -23 ≤ k ≤ 23, -30 ≤ l ≤ 30 |
| Reflections collected | 80667 |
| Independent reflections | 9793 [R(int) = 0.0580] |
| Completeness to theta = 27.00° | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8540 and 0.7453 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 9793 / 0 / 599 |
| Goodness-of-fit on F ² | 1.025 |
| Final R indices [I > 2σ(I)] | R1 = 0.0316, wR2 = 0.0695 |
| R indices (all data) | R1 = 0.0475, wR2 = 0.0765 |
| Largest diff. peak and hole | 0.487 and -0.788 e.Å ⁻³ |

Table 15. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|--------|---------|---------|---------|-------|
| Ag(1) | 3180(1) | 3749(1) | 2564(1) | 33(1) |
| N(21) | 3367(1) | 2768(1) | 2143(1) | 35(1) |
| C(21) | 3206(2) | 2092(2) | 2290(1) | 33(1) |
| N(22) | 3428(1) | 1607(1) | 1916(1) | 35(1) |
| C(22) | 3748(2) | 1981(2) | 1506(2) | 45(1) |
| C(23) | 3707(2) | 2701(2) | 1653(2) | 43(1) |
| N(31) | 3086(1) | 4761(1) | 2964(1) | 29(1) |
| C(31) | 3244(2) | 5417(2) | 2764(1) | 31(1) |
| N(32) | 3143(1) | 5930(1) | 3155(1) | 31(1) |
| C(32) | 2913(2) | 5598(2) | 3630(1) | 34(1) |
| C(33) | 2878(2) | 4876(2) | 3510(1) | 33(1) |
| Ag(2) | 1728(1) | 4058(1) | 2655(1) | 37(1) |
| O(1A) | 1934(1) | 4005(1) | 1652(1) | 34(1) |
| O(2A) | 1709(1) | 5091(1) | 2013(1) | 33(1) |
| C(1A) | 1856(1) | 4683(2) | 1607(1) | 27(1) |
| C(2A) | 1981(1) | 5038(2) | 1042(1) | 24(1) |
| C(3A) | 2626(1) | 5101(2) | 865(1) | 25(1) |
| C(4A) | 3156(1) | 4820(2) | 1183(1) | 30(1) |
| C(5A) | 3772(2) | 4897(2) | 1001(1) | 34(1) |
| C(6A) | 3907(2) | 5260(2) | 487(1) | 38(1) |
| C(7A) | 3416(2) | 5538(2) | 170(1) | 38(1) |
| C(8A) | 2760(2) | 5476(2) | 346(1) | 30(1) |
| C(9A) | 2258(2) | 5776(2) | 34(1) | 32(1) |
| C(10A) | 1616(1) | 5712(2) | 209(1) | 28(1) |
| C(11A) | 1098(2) | 6024(2) | -104(1) | 34(1) |
| C(12A) | 480(2) | 5956(2) | 72(2) | 39(1) |
| C(13A) | 336(2) | 5563(2) | 573(1) | 38(1) |
| C(14A) | 811(1) | 5263(2) | 887(1) | 32(1) |
| C(15A) | 1472(1) | 5329(2) | 724(1) | 25(1) |
| O(1B) | 1931(1) | 3516(1) | 3474(1) | 33(1) |
| O(2B) | 1792(1) | 2458(1) | 3016(1) | 31(1) |

| | | | | |
|--------|----------|----------|---------|-------|
| C(1B) | 1860(1) | 2833(2) | 3455(1) | 24(1) |
| C(2B) | 1831(1) | 2442(1) | 4021(1) | 23(1) |
| C(3B) | 2394(1) | 2324(1) | 4338(1) | 24(1) |
| C(4B) | 3017(2) | 2579(2) | 4172(1) | 29(1) |
| C(5B) | 3548(2) | 2437(2) | 4489(1) | 34(1) |
| C(6B) | 3501(2) | 2032(2) | 4998(1) | 40(1) |
| C(7B) | 2920(2) | 1778(2) | 5174(1) | 37(1) |
| C(8B) | 2343(2) | 1920(2) | 4859(1) | 29(1) |
| C(9B) | 1739(2) | 1682(2) | 5042(1) | 33(1) |
| C(10B) | 1179(1) | 1835(2) | 4742(1) | 28(1) |
| C(11B) | 556(2) | 1631(2) | 4943(1) | 36(1) |
| C(12B) | 15(2) | 1807(2) | 4652(1) | 37(1) |
| C(13B) | 54(2) | 2186(2) | 4130(1) | 34(1) |
| C(14B) | 640(2) | 2376(2) | 3918(1) | 30(1) |
| C(15B) | 1225(1) | 2216(1) | 4212(1) | 26(1) |
| Ag(3) | 676(1) | 2496(1) | 2356(1) | 31(1) |
| O(1C) | 532(1) | 3666(1) | 2435(1) | 37(1) |
| C(1C) | 0 | 3978(2) | 2500 | 28(1) |
| C(2C) | 0 | 4795(2) | 2500 | 30(1) |
| C(3C) | -385(2) | 5168(2) | 2109(1) | 33(1) |
| C(4C) | -770(2) | 4807(2) | 1691(1) | 35(1) |
| C(5C) | -1173(2) | 5183(2) | 1346(2) | 43(1) |
| C(6C) | -1204(2) | 5961(2) | 1378(2) | 48(1) |
| C(7C) | -819(2) | 6328(2) | 1740(2) | 47(1) |
| C(8C) | -395(2) | 5957(2) | 2119(2) | 38(1) |
| C(9C) | 0 | 6321(2) | 2500 | 44(1) |
| O(1D) | 525(1) | 1329(1) | 2379(1) | 34(1) |
| C(1D) | 0 | 1034(2) | 2500 | 24(1) |
| C(2D) | 0 | 207(2) | 2500 | 22(1) |
| C(3D) | -183(1) | -166(1) | 2008(1) | 22(1) |
| C(4D) | -373(1) | 211(2) | 1506(1) | 26(1) |
| C(5D) | -547(1) | -163(2) | 1038(1) | 30(1) |
| C(6D) | -533(2) | -942(2) | 1039(1) | 32(1) |
| C(7D) | -357(2) | -1315(2) | 1504(1) | 31(1) |
| C(8D) | -178(1) | -953(2) | 2011(1) | 24(1) |
| C(9D) | 0 | -1325(2) | 2500 | 27(1) |
| O(4I) | 1363(1) | 2639(1) | 1511(1) | 36(1) |
| C(4I) | 1810(2) | 2046(2) | 1403(2) | 55(1) |

Table 16. Bond lengths [Å] and angles [°] for [Ag₆(imidH)₄(9-aca)₆(MeOH)₂].

| | | | |
|---------------|-----------|---------------|------------|
| Ag(1)-N(21) | 2.088(2) | O(2B)-Ag(3) | 2.789(2) |
| Ag(1)-N(31) | 2.089(2) | C(1B)-C(2B) | 1.520(4) |
| Ag(1)-Ag(2) | 3.0651(4) | C(2B)-C(15B) | 1.396(4) |
| N(21)-C(21) | 1.325(4) | C(2B)-C(3B) | 1.403(4) |
| N(21)-C(23) | 1.363(4) | C(3B)-C(4B) | 1.426(4) |
| C(21)-N(22) | 1.336(4) | C(3B)-C(8B) | 1.442(4) |
| N(22)-C(22) | 1.360(4) | C(4B)-C(5B) | 1.357(4) |
| C(22)-C(23) | 1.363(4) | C(5B)-C(6B) | 1.418(4) |
| N(31)-C(31) | 1.330(4) | C(6B)-C(7B) | 1.354(5) |
| N(31)-C(33) | 1.379(4) | C(7B)-C(8B) | 1.432(4) |
| C(31)-N(32) | 1.334(4) | C(8B)-C(9B) | 1.393(4) |
| N(32)-C(32) | 1.363(4) | C(9B)-C(10B) | 1.388(4) |
| C(32)-C(33) | 1.353(4) | C(10B)-C(11B) | 1.424(4) |
| Ag(2)-O(1B) | 2.218(2) | C(10B)-C(15B) | 1.437(4) |
| Ag(2)-O(1A) | 2.416(2) | C(11B)-C(12B) | 1.352(4) |
| Ag(2)-O(2A) | 2.424(2) | C(12B)-C(13B) | 1.420(4) |
| O(1A)-C(1A) | 1.254(3) | C(13B)-C(14B) | 1.359(4) |
| O(2A)-C(1A) | 1.254(3) | C(14B)-C(15B) | 1.427(4) |
| C(1A)-C(2A) | 1.510(4) | Ag(3)-O(1D) | 2.1574(19) |
| C(2A)-C(15A) | 1.400(4) | Ag(3)-O(1C) | 2.1681(19) |
| C(2A)-C(3A) | 1.404(4) | Ag(3)-O(41) | 2.467(2) |
| C(3A)-C(4A) | 1.427(4) | Ag(3)-Ag(3)#1 | 2.8818(5) |
| C(3A)-C(8A) | 1.434(4) | O(1C)-C(1C) | 1.248(3) |
| C(4A)-C(5A) | 1.352(4) | C(1C)-O(1C)#1 | 1.248(3) |
| C(5A)-C(6A) | 1.415(4) | C(1C)-C(2C) | 1.494(5) |
| C(6A)-C(7A) | 1.360(5) | C(2C)-C(3C)#1 | 1.398(4) |
| C(7A)-C(8A) | 1.425(4) | C(2C)-C(3C) | 1.398(4) |
| C(8A)-C(9A) | 1.387(4) | C(3C)-C(4C) | 1.432(5) |
| C(9A)-C(10A) | 1.396(4) | C(3C)-C(8C) | 1.443(4) |
| C(10A)-C(11A) | 1.422(4) | C(4C)-C(5C) | 1.356(5) |
| C(10A)-C(15A) | 1.438(4) | C(5C)-C(6C) | 1.426(5) |
| C(11A)-C(12A) | 1.351(4) | C(6C)-C(7C) | 1.349(5) |
| C(12A)-C(13A) | 1.419(5) | C(7C)-C(8C) | 1.426(5) |
| C(13A)-C(14A) | 1.349(4) | C(8C)-C(9C) | 1.388(4) |
| C(14A)-C(15A) | 1.427(4) | C(9C)-C(8C)#1 | 1.388(4) |
| O(1B)-C(1B) | 1.258(3) | O(1D)-C(1D) | 1.246(3) |
| O(2B)-C(1B) | 1.253(3) | C(1D)-O(1D)#1 | 1.246(3) |

| | | | |
|--------------------|------------|----------------------|------------|
| C(1D)-C(2D) | 1.512(5) | C(5D)-C(6D) | 1.424(4) |
| C(2D)-C(3D) | 1.402(3) | C(6D)-C(7D) | 1.346(4) |
| C(2D)-C(3D)#1 | 1.402(3) | C(7D)-C(8D) | 1.418(4) |
| C(3D)-C(4D) | 1.430(4) | C(8D)-C(9D) | 1.393(3) |
| C(3D)-C(8D) | 1.439(4) | C(9D)-C(8D)#1 | 1.393(3) |
| C(4D)-C(5D) | 1.351(4) | O(41)-C(41) | 1.448(4) |
| N(21)-Ag(1)-N(31) | 174.33(10) | C(2A)-C(3A)-C(4A) | 122.9(3) |
| N(21)-Ag(1)-Ag(2) | 111.93(7) | C(2A)-C(3A)-C(8A) | 118.6(3) |
| N(31)-Ag(1)-Ag(2) | 73.35(7) | C(4A)-C(3A)-C(8A) | 118.5(3) |
| C(21)-N(21)-C(23) | 105.7(3) | C(5A)-C(4A)-C(3A) | 121.2(3) |
| C(21)-N(21)-Ag(1) | 128.9(2) | C(4A)-C(5A)-C(6A) | 120.6(3) |
| C(23)-N(21)-Ag(1) | 125.4(2) | C(7A)-C(6A)-C(5A) | 120.1(3) |
| N(21)-C(21)-N(22) | 111.0(3) | C(6A)-C(7A)-C(8A) | 121.4(3) |
| C(21)-N(22)-C(22) | 107.9(3) | C(9A)-C(8A)-C(7A) | 121.8(3) |
| N(22)-C(22)-C(23) | 105.9(3) | C(9A)-C(8A)-C(3A) | 120.0(3) |
| C(22)-C(23)-N(21) | 109.7(3) | C(7A)-C(8A)-C(3A) | 118.2(3) |
| C(31)-N(31)-C(33) | 105.9(2) | C(8A)-C(9A)-C(10A) | 121.4(3) |
| C(31)-N(31)-Ag(1) | 127.9(2) | C(9A)-C(10A)-C(11A) | 122.0(3) |
| C(33)-N(31)-Ag(1) | 126.1(2) | C(9A)-C(10A)-C(15A) | 119.3(3) |
| N(31)-C(31)-N(32) | 110.3(3) | C(11A)-C(10A)-C(15A) | 118.7(3) |
| C(31)-N(32)-C(32) | 108.4(3) | C(12A)-C(11A)-C(10A) | 121.1(3) |
| C(33)-C(32)-N(32) | 106.2(3) | C(11A)-C(12A)-C(13A) | 120.1(3) |
| C(32)-C(33)-N(31) | 109.1(3) | C(14A)-C(13A)-C(12A) | 121.0(3) |
| O(1B)-Ag(2)-O(1A) | 143.97(7) | C(13A)-C(14A)-C(15A) | 121.0(3) |
| O(1B)-Ag(2)-O(2A) | 154.09(7) | C(2A)-C(15A)-C(14A) | 123.0(3) |
| O(1A)-Ag(2)-O(2A) | 54.34(7) | C(2A)-C(15A)-C(10A) | 119.0(3) |
| O(1B)-Ag(2)-Ag(1) | 78.07(6) | C(14A)-C(15A)-C(10A) | 118.0(3) |
| O(1A)-Ag(2)-Ag(1) | 75.58(5) | C(1B)-O(1B)-Ag(2) | 113.00(18) |
| O(2A)-Ag(2)-Ag(1) | 96.64(5) | C(1B)-O(2B)-Ag(3) | 123.03(18) |
| C(1A)-O(1A)-Ag(2) | 91.21(17) | O(2B)-C(1B)-O(1B) | 125.8(3) |
| C(1A)-O(2A)-Ag(2) | 90.86(17) | O(2B)-C(1B)-C(2B) | 118.0(2) |
| O(2A)-C(1A)-O(1A) | 123.6(3) | O(1B)-C(1B)-C(2B) | 116.1(2) |
| O(2A)-C(1A)-C(2A) | 117.8(3) | C(15B)-C(2B)-C(3B) | 121.8(3) |
| O(1A)-C(1A)-C(2A) | 118.5(3) | C(15B)-C(2B)-C(1B) | 117.5(2) |
| C(15A)-C(2A)-C(3A) | 121.6(3) | C(3B)-C(2B)-C(1B) | 120.7(2) |
| C(15A)-C(2A)-C(1A) | 120.7(2) | C(2B)-C(3B)-C(4B) | 123.6(3) |
| C(3A)-C(2A)-C(1A) | 117.6(2) | C(2B)-C(3B)-C(8B) | 118.4(3) |

| | | | |
|----------------------|------------|---------------------|------------|
| C(4B)-C(3B)-C(8B) | 118.0(3) | C(3C)#1-C(2C)-C(3C) | 121.7(4) |
| C(5B)-C(4B)-C(3B) | 121.2(3) | C(3C)#1-C(2C)-C(1C) | 119.14(19) |
| C(4B)-C(5B)-C(6B) | 121.0(3) | C(3C)-C(2C)-C(1C) | 119.14(19) |
| C(7B)-C(6B)-C(5B) | 120.1(3) | C(2C)-C(3C)-C(4C) | 123.4(3) |
| C(6B)-C(7B)-C(8B) | 121.2(3) | C(2C)-C(3C)-C(8C) | 119.0(3) |
| C(9B)-C(8B)-C(7B) | 122.0(3) | C(4C)-C(3C)-C(8C) | 117.6(3) |
| C(9B)-C(8B)-C(3B) | 119.5(3) | C(5C)-C(4C)-C(3C) | 121.8(3) |
| C(7B)-C(8B)-C(3B) | 118.6(3) | C(4C)-C(5C)-C(6C) | 120.1(4) |
| C(10B)-C(9B)-C(8B) | 121.8(3) | C(7C)-C(6C)-C(5C) | 120.2(3) |
| C(9B)-C(10B)-C(11B) | 122.2(3) | C(6C)-C(7C)-C(8C) | 121.8(3) |
| C(9B)-C(10B)-C(15B) | 119.3(3) | C(9C)-C(8C)-C(7C) | 122.9(3) |
| C(11B)-C(10B)-C(15B) | 118.6(3) | C(9C)-C(8C)-C(3C) | 118.8(3) |
| C(12B)-C(11B)-C(10B) | 121.2(3) | C(7C)-C(8C)-C(3C) | 118.3(3) |
| C(11B)-C(12B)-C(13B) | 120.7(3) | C(8C)-C(9C)-C(8C)#1 | 122.7(4) |
| C(14B)-C(13B)-C(12B) | 119.9(3) | C(1D)-O(1D)-Ag(3) | 124.1(2) |
| C(13B)-C(14B)-C(15B) | 121.6(3) | O(1D)-C(1D)-O(1D)#1 | 128.7(4) |
| C(2B)-C(15B)-C(14B) | 122.8(3) | O(1D)-C(1D)-C(2D) | 115.66(18) |
| C(2B)-C(15B)-C(10B) | 119.1(3) | O(1D)#1-C(1D)-C(2D) | 115.66(18) |
| C(14B)-C(15B)-C(10B) | 118.0(3) | C(3D)-C(2D)-C(3D)#1 | 121.9(3) |
| O(1D)-Ag(3)-O(1C) | 162.45(8) | C(3D)-C(2D)-C(1D) | 119.06(17) |
| O(1D)-Ag(3)-O(41) | 102.11(7) | C(3D)#1-C(2D)-C(1D) | 119.06(17) |
| O(1C)-Ag(3)-O(41) | 92.58(8) | C(2D)-C(3D)-C(4D) | 122.2(3) |
| O(1D)-Ag(3)-O(2B) | 94.62(7) | C(2D)-C(3D)-C(8D) | 118.7(3) |
| O(1C)-Ag(3)-O(2B) | 95.22(7) | C(4D)-C(3D)-C(8D) | 119.2(2) |
| O(41)-Ag(3)-O(2B) | 88.95(7) | C(5D)-C(4D)-C(3D) | 120.8(3) |
| O(1D)-Ag(3)-Ag(3)#1 | 81.52(6) | C(4D)-C(5D)-C(6D) | 120.0(3) |
| O(1C)-Ag(3)-Ag(3)#1 | 81.10(6) | C(7D)-C(6D)-C(5D) | 120.8(3) |
| O(41)-Ag(3)-Ag(3)#1 | 138.73(5) | C(6D)-C(7D)-C(8D) | 121.9(3) |
| O(2B)-Ag(3)-Ag(3)#1 | 132.10(4) | C(9D)-C(8D)-C(7D) | 123.1(3) |
| C(1C)-O(1C)-Ag(3) | 125.6(2) | C(9D)-C(8D)-C(3D) | 119.5(3) |
| O(1C)#1-C(1C)-O(1C) | 125.7(4) | C(7D)-C(8D)-C(3D) | 117.4(3) |
| O(1C)#1-C(1C)-C(2C) | 117.13(19) | C(8D)#1-C(9D)-C(8D) | 121.7(4) |
| O(1C)-C(1C)-C(2C) | 117.13(19) | C(41)-O(41)-Ag(3) | 115.5(2) |

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

Table 17. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U ¹¹ | U ²² | U ³³ | U ²³ | U ¹³ | U ¹² |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ag(1) | 42(1) | 20(1) | 36(1) | -6(1) | 1(1) | 2(1) |
| N(21) | 44(2) | 23(1) | 38(2) | -8(1) | 2(1) | 0(1) |
| C(21) | 39(2) | 24(2) | 36(2) | -4(1) | -1(1) | 1(1) |
| N(22) | 43(2) | 22(1) | 39(2) | -4(1) | -4(1) | 2(1) |
| C(22) | 56(2) | 33(2) | 45(2) | -12(2) | 10(2) | 0(2) |
| C(23) | 52(2) | 31(2) | 45(2) | -5(2) | 10(2) | -6(2) |
| N(31) | 33(1) | 22(1) | 33(1) | -5(1) | 0(1) | 0(1) |
| C(31) | 38(2) | 23(2) | 32(2) | -2(1) | 1(1) | -2(1) |
| N(32) | 37(2) | 16(1) | 40(2) | -2(1) | -4(1) | -2(1) |
| C(32) | 38(2) | 27(2) | 39(2) | -6(1) | 6(1) | -1(1) |
| C(33) | 38(2) | 27(2) | 35(2) | -3(1) | 4(1) | -2(1) |
| Ag(2) | 36(1) | 44(1) | 31(1) | 17(1) | -2(1) | -8(1) |
| O(1A) | 47(1) | 22(1) | 34(1) | 6(1) | 6(1) | -3(1) |
| O(2A) | 46(1) | 28(1) | 23(1) | 1(1) | 7(1) | -1(1) |
| C(1A) | 26(2) | 28(2) | 26(2) | 3(1) | 1(1) | -5(1) |
| C(2A) | 34(2) | 18(1) | 22(1) | -2(1) | 3(1) | -6(1) |
| C(3A) | 33(2) | 21(1) | 22(1) | -3(1) | 4(1) | -3(1) |
| C(4A) | 40(2) | 24(2) | 25(2) | 1(1) | 2(1) | -3(1) |
| C(5A) | 33(2) | 33(2) | 37(2) | -3(1) | -3(1) | -2(1) |
| C(6A) | 30(2) | 41(2) | 43(2) | 1(2) | 12(1) | -5(1) |
| C(7A) | 39(2) | 39(2) | 36(2) | 6(2) | 14(2) | -5(2) |
| C(8A) | 36(2) | 24(2) | 29(2) | 1(1) | 6(1) | -3(1) |
| C(9A) | 42(2) | 29(2) | 26(2) | 6(1) | 6(1) | -4(1) |
| C(10A) | 38(2) | 21(1) | 25(2) | 0(1) | 2(1) | -1(1) |
| C(11A) | 43(2) | 27(2) | 33(2) | 6(1) | -1(1) | 0(1) |
| C(12A) | 40(2) | 36(2) | 43(2) | 0(2) | -8(2) | 6(2) |
| C(13A) | 28(2) | 41(2) | 45(2) | 0(2) | 3(1) | -1(1) |
| C(14A) | 33(2) | 31(2) | 31(2) | 2(1) | 5(1) | -3(1) |
| C(15A) | 33(2) | 20(1) | 23(1) | -1(1) | 2(1) | -1(1) |
| O(1B) | 55(1) | 20(1) | 25(1) | 5(1) | -4(1) | -6(1) |
| O(2B) | 48(1) | 24(1) | 21(1) | -2(1) | -1(1) | 2(1) |

| | | | | | | |
|--------|-------|-------|-------|-------|--------|-------|
| C(1B) | 29(2) | 19(1) | 24(1) | 3(1) | 1(1) | 0(1) |
| C(2B) | 39(2) | 12(1) | 19(1) | -2(1) | 2(1) | 0(1) |
| C(3B) | 36(2) | 16(1) | 22(1) | -2(1) | -1(1) | -1(1) |
| C(4B) | 40(2) | 20(1) | 26(2) | -1(1) | 4(1) | -2(1) |
| C(5B) | 36(2) | 29(2) | 38(2) | -3(1) | -1(1) | -5(1) |
| C(6B) | 41(2) | 36(2) | 44(2) | 0(2) | -13(2) | -3(2) |
| C(7B) | 50(2) | 33(2) | 29(2) | 6(1) | -7(2) | -3(2) |
| C(8B) | 43(2) | 22(2) | 23(2) | 2(1) | -4(1) | -3(1) |
| C(9B) | 46(2) | 27(2) | 25(2) | 7(1) | 1(1) | -5(1) |
| C(10B) | 38(2) | 21(1) | 25(2) | 2(1) | 4(1) | -2(1) |
| C(11B) | 43(2) | 33(2) | 33(2) | 5(1) | 7(2) | -5(1) |
| C(12B) | 37(2) | 35(2) | 40(2) | -1(1) | 9(2) | -4(1) |
| C(13B) | 36(2) | 30(2) | 36(2) | -2(1) | -3(1) | 1(1) |
| C(14B) | 38(2) | 26(2) | 25(2) | 1(1) | -1(1) | 1(1) |
| C(15B) | 38(2) | 15(1) | 24(1) | -1(1) | 2(1) | 0(1) |
| Ag(3) | 41(1) | 16(1) | 37(1) | -1(1) | 6(1) | 0(1) |
| O(1C) | 30(1) | 17(1) | 65(2) | -5(1) | 8(1) | -1(1) |
| C(1C) | 32(2) | 16(2) | 36(2) | 0 | 7(2) | 0 |
| C(2C) | 37(2) | 14(2) | 40(2) | 0 | 13(2) | 0 |
| C(3C) | 34(2) | 20(2) | 46(2) | 5(1) | 18(1) | 1(1) |
| C(4C) | 38(2) | 22(2) | 46(2) | 5(1) | 12(2) | 2(1) |
| C(5C) | 37(2) | 40(2) | 51(2) | 7(2) | 15(2) | 4(2) |
| C(6C) | 48(2) | 37(2) | 60(2) | 16(2) | 12(2) | 11(2) |
| C(7C) | 53(2) | 23(2) | 64(3) | 11(2) | 20(2) | 7(2) |
| C(8C) | 44(2) | 19(2) | 51(2) | 7(1) | 19(2) | 4(1) |
| C(9C) | 51(3) | 16(2) | 63(3) | 0 | 19(3) | 0 |
| O(1D) | 34(1) | 16(1) | 51(1) | 3(1) | 5(1) | -1(1) |
| C(1D) | 35(2) | 19(2) | 18(2) | 0 | -5(2) | 0 |
| C(2D) | 22(2) | 17(2) | 28(2) | 0 | 0(2) | 0 |
| C(3D) | 25(1) | 18(1) | 24(1) | -2(1) | 0(1) | 0(1) |
| C(4D) | 28(2) | 23(1) | 27(2) | 2(1) | -1(1) | 0(1) |
| C(5D) | 30(2) | 32(2) | 27(2) | 2(1) | -4(1) | 3(1) |
| C(6D) | 38(2) | 31(2) | 28(2) | -9(1) | -4(1) | 3(1) |
| C(7D) | 39(2) | 21(2) | 34(2) | -6(1) | -4(1) | 4(1) |
| C(8D) | 25(1) | 19(1) | 29(2) | -3(1) | 1(1) | 1(1) |
| C(9D) | 36(2) | 11(2) | 34(2) | 0 | -1(2) | 0 |
| O(41) | 38(1) | 33(1) | 39(1) | -5(1) | 6(1) | -8(1) |
| C(41) | 46(2) | 61(3) | 59(3) | 0(2) | 3(2) | 15(2) |

Table 18. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$.

| | x | y | z | U(eq) |
|--------|-------|------|------|-------|
| H(21) | 2965 | 1970 | 2618 | 40 |
| H(22N) | 3377 | 1129 | 1931 | 41 |
| H(22) | 3957 | 1783 | 1183 | 54 |
| H(23) | 3887 | 3096 | 1445 | 51 |
| H(31) | 3407 | 5508 | 2396 | 37 |
| H(32N) | 3212 | 6402 | 3114 | 37 |
| H(32) | 2800 | 5828 | 3976 | 41 |
| H(33) | 2732 | 4506 | 3762 | 40 |
| H(4A) | 3075 | 4575 | 1529 | 36 |
| H(5A) | 4117 | 4706 | 1221 | 41 |
| H(6A) | 4341 | 5310 | 362 | 46 |
| H(7A) | 3513 | 5778 | -175 | 46 |
| H(9A) | 2353 | 6030 | -306 | 39 |
| H(11A) | 1188 | 6283 | -442 | 41 |
| H(12A) | 140 | 6172 | -141 | 47 |
| H(13A) | -101 | 5510 | 689 | 46 |
| H(14A) | 703 | 5005 | 1222 | 38 |
| H(4B) | 3061 | 2852 | 3833 | 35 |
| H(5B) | 3958 | 2613 | 4369 | 41 |
| H(6B) | 3878 | 1937 | 5215 | 48 |
| H(7B) | 2895 | 1501 | 5513 | 45 |
| H(9B) | 1710 | 1408 | 5382 | 39 |
| H(11B) | 520 | 1368 | 5287 | 44 |
| H(12B) | -396 | 1675 | 4800 | 45 |
| H(13B) | -329 | 2306 | 3930 | 41 |
| H(14B) | 662 | 2621 | 3564 | 36 |
| H(4C) | -741 | 4290 | 1655 | 42 |
| H(5C) | -1435 | 4927 | 1082 | 51 |
| H(6C) | -1497 | 6222 | 1144 | 58 |
| H(7C) | -831 | 6847 | 1743 | 56 |
| H(9C) | 0 | 6841 | 2500 | 52 |
| H(4D) | -377 | 730 | 1501 | 31 |
| H(5D) | -679 | 93 | 709 | 36 |

| | | | | |
|--------|------|-------|------|----|
| H(6D) | -650 | -1202 | 707 | 39 |
| H(7D) | -351 | -1834 | 1493 | 37 |
| H(9D) | 0 | -1844 | 2500 | 32 |
| H(41) | 1683 | 3006 | 1534 | 44 |
| H(41A) | 2035 | 1919 | 1754 | 83 |
| H(41B) | 2126 | 2199 | 1119 | 83 |
| H(41C) | 1572 | 1619 | 1265 | 83 |

Table 19. Hydrogen bonds for $[\text{Ag}_6(\text{imidH})_4(9\text{-aca})_6(\text{MeOH})_2]$ [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | $\angle(\text{DHA})$ |
|------------------------|--------|----------|----------|----------------------|
| N(22)-H(22N)...O(2A)#2 | 0.88 | 1.92 | 2.796(3) | 176.3 |
| N(32)-H(32N)...O(2B)#3 | 0.88 | 1.94 | 2.815(3) | 170.4 |
| O(41)-H(41)...O(1A) | 0.94 | 1.92 | 2.782(3) | 150.9 |

Symmetry transformations used to generate equivalent atoms:

#1 $-x, y, -z+1/2$ #2 $-x+1/2, y-1/2, z$ #3 $-x+1/2, y+1/2, z$

X-ray Crystal Data for [Ag(1-Me-imid)₂]₂[Ag₄(9-aca)₆]

| | |
|-----------------------------------|--|
| Identification code | [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] |
| Empirical formula | C ₁₀₆ H ₇₈ Ag ₆ N ₈ O ₁₂ |
| Formula weight | 2302.98 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | a = 11.7251(17) Å α = 111.403(2)°. b = 17.908(3) Å β = 90.095(2)°. c = 23.464(3) Å γ = 101.710(2)°. |
| Volume | 4476.2(11) Å ³ |
| Z | 2 |
| Density (calculated) | 1.709 Mg/m ³ |
| Absorption coefficient | 1.357 mm ⁻¹ |
| F(000) | 2296 |
| Crystal size | 0.43 x 0.32 x 0.06 mm ³ |
| Crystal description | colourless plate |
| Theta range for data collection | 1.78 to 25.00°. |
| Index ranges | -13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -27 ≤ l ≤ 27 |
| Reflections collected | 35083 |
| Independent reflections | 15686 [R(int) = 0.0421] |
| Completeness to theta = 25.00° | 99.5 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9230 and 0.5930 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 15686 / 0 / 1224 |
| Goodness-of-fit on F ² | 1.046 |
| Final R indices [I > 2σ(I)] | R1 = 0.0512, wR2 = 0.1262 |
| R indices (all data) | R1 = 0.0706, wR2 = 0.1370 |
| Largest diff. peak and hole | 1.787 and -1.037 e.Å ⁻³ |

Table 20. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|--------|---------|---------|----------|-------|
| Ag(1) | 5320(1) | 854(1) | 268(1) | 19(1) |
| Ag(2) | 3367(1) | -33(1) | 769(1) | 27(1) |
| O(11A) | 4961(4) | 1820(3) | 1181(2) | 36(1) |
| O(12A) | 3128(4) | 1219(3) | 1249(2) | 28(1) |
| C(11A) | 3989(6) | 1823(4) | 1389(3) | 26(2) |
| C(12A) | 3842(6) | 2622(4) | 1886(3) | 25(2) |
| C(13A) | 4587(6) | 2964(4) | 2432(3) | 24(1) |
| C(14A) | 5469(7) | 2594(4) | 2551(3) | 34(2) |
| C(15A) | 6173(7) | 2941(5) | 3081(4) | 42(2) |
| C(16A) | 6045(7) | 3695(5) | 3527(4) | 44(2) |
| C(17A) | 5214(7) | 4072(5) | 3443(3) | 41(2) |
| C(18A) | 4442(6) | 3718(4) | 2889(3) | 31(2) |
| C(19A) | 3600(6) | 4108(4) | 2788(3) | 33(2) |
| C(20A) | 2873(6) | 3785(4) | 2244(3) | 32(2) |
| C(21A) | 2020(7) | 4196(5) | 2136(4) | 43(2) |
| C(22A) | 1349(7) | 3884(5) | 1600(4) | 44(2) |
| C(23A) | 1412(7) | 3151(4) | 1163(4) | 39(2) |
| C(24A) | 2251(6) | 2727(4) | 1225(3) | 32(2) |
| C(25A) | 2986(6) | 3019(4) | 1778(3) | 28(2) |
| O(11B) | 6478(4) | 1952(3) | 40(2) | 25(1) |
| O(12B) | 6613(4) | 1156(3) | -938(2) | 24(1) |
| C(11B) | 6508(5) | 1820(4) | -526(3) | 22(1) |
| C(12B) | 6410(5) | 2508(4) | -740(3) | 21(1) |
| C(13B) | 5553(5) | 2362(4) | -1215(3) | 21(1) |
| C(14B) | 4713(6) | 1597(4) | -1474(3) | 24(1) |
| C(15B) | 3882(6) | 1489(5) | -1918(3) | 32(2) |
| C(16B) | 3816(6) | 2113(5) | -2139(3) | 35(2) |
| C(17B) | 4591(6) | 2853(5) | -1899(3) | 35(2) |
| C(18B) | 5471(6) | 2994(4) | -1433(3) | 26(2) |
| C(19B) | 6268(6) | 3750(4) | -1178(3) | 30(2) |
| C(20B) | 7106(6) | 3913(4) | -704(3) | 29(2) |
| C(21B) | 7878(7) | 4694(4) | -437(3) | 35(2) |

| | | | | |
|--------|----------|----------|---------|-------|
| C(22B) | 8641(7) | 4870(5) | 48(4) | 42(2) |
| C(23B) | 8716(7) | 4249(5) | 280(4) | 41(2) |
| C(24B) | 8024(6) | 3490(4) | 25(3) | 28(2) |
| C(25B) | 7172(5) | 3283(4) | -467(3) | 21(1) |
| O(11C) | 7010(4) | 574(3) | 522(2) | 30(1) |
| O(12C) | 6234(4) | -740(3) | 345(2) | 31(1) |
| C(11C) | 6982(5) | -91(4) | 585(3) | 20(1) |
| C(12C) | 7946(5) | -123(4) | 998(3) | 22(1) |
| C(13C) | 7885(5) | 196(4) | 1627(3) | 22(1) |
| C(14C) | 6969(5) | 596(4) | 1909(3) | 25(2) |
| C(15C) | 6931(6) | 885(4) | 2525(3) | 29(2) |
| C(16C) | 7766(6) | 792(4) | 2922(3) | 31(2) |
| C(17C) | 8641(6) | 403(4) | 2669(3) | 29(2) |
| C(18C) | 8745(5) | 106(4) | 2019(3) | 24(1) |
| C(19C) | 9655(6) | -263(4) | 1766(3) | 26(2) |
| C(20C) | 9754(5) | -544(4) | 1137(3) | 25(2) |
| C(21C) | 10697(6) | -911(4) | 870(3) | 31(2) |
| C(22C) | 10776(6) | -1195(4) | 249(3) | 31(2) |
| C(23C) | 9910(6) | -1138(4) | -147(3) | 30(2) |
| C(24C) | 8977(6) | -797(4) | 90(3) | 26(2) |
| C(25C) | 8869(5) | -489(4) | 732(3) | 23(1) |
| Ag(3) | 10314(1) | 856(1) | 5225(1) | 19(1) |
| Ag(4) | 8434(1) | -5(1) | 4201(1) | 28(1) |
| O(11D) | 11491(4) | 1942(3) | 6072(2) | 24(1) |
| O(12D) | 11589(4) | 1131(3) | 6591(2) | 25(1) |
| C(11D) | 11523(5) | 1806(4) | 6554(3) | 18(1) |
| C(12D) | 11470(5) | 2500(4) | 7155(3) | 19(1) |
| C(13D) | 12309(6) | 3248(4) | 7327(3) | 22(1) |
| C(14D) | 13242(6) | 3392(4) | 6958(3) | 28(2) |
| C(15D) | 14058(7) | 4104(5) | 7154(3) | 39(2) |
| C(16D) | 14040(7) | 4731(5) | 7741(4) | 45(2) |
| C(17D) | 13160(7) | 4616(4) | 8105(3) | 38(2) |
| C(18D) | 12277(6) | 3883(4) | 7910(3) | 27(2) |
| C(19D) | 11382(6) | 3766(4) | 8274(3) | 31(2) |
| C(20D) | 10530(6) | 3044(4) | 8108(3) | 27(2) |
| C(21D) | 9613(6) | 2943(4) | 8492(3) | 31(2) |
| C(22D) | 8802(6) | 2229(5) | 8314(3) | 34(2) |
| C(23D) | 8826(6) | 1571(4) | 7754(3) | 29(2) |

| | | | | |
|--------|----------|---------|---------|-------|
| C(24D) | 9687(6) | 1652(4) | 7376(3) | 25(1) |
| C(25D) | 10581(5) | 2392(4) | 7539(3) | 20(1) |
| O(11E) | 8759(4) | 720(3) | 5753(2) | 38(1) |
| O(12E) | 8036(4) | -602(3) | 5218(2) | 35(1) |
| C(11E) | 8026(5) | 56(4) | 5635(3) | 20(1) |
| C(12E) | 7053(5) | 73(4) | 6061(3) | 20(1) |
| C(13E) | 6120(5) | 428(4) | 6001(3) | 23(1) |
| C(14E) | 6018(6) | 753(4) | 5530(3) | 25(1) |
| C(15E) | 5077(6) | 1086(4) | 5487(3) | 29(2) |
| C(16E) | 4196(6) | 1112(4) | 5903(3) | 30(2) |
| C(17E) | 4270(6) | 814(4) | 6365(3) | 33(2) |
| C(18E) | 5236(6) | 462(4) | 6423(3) | 25(2) |
| C(19E) | 5343(6) | 168(4) | 6890(3) | 30(2) |
| C(20E) | 6273(6) | -178(4) | 6960(3) | 28(2) |
| C(21E) | 6394(6) | -472(5) | 7439(3) | 35(2) |
| C(22E) | 7288(6) | -833(4) | 7474(3) | 34(2) |
| C(23E) | 8147(6) | -911(4) | 7035(3) | 30(2) |
| C(24E) | 8076(6) | -618(4) | 6580(3) | 26(2) |
| C(25E) | 7152(5) | -235(4) | 6520(3) | 22(1) |
| O(11F) | 9953(4) | 1868(3) | 4899(3) | 42(1) |
| O(12F) | 8162(4) | 1238(3) | 4428(2) | 27(1) |
| C(11F) | 8988(6) | 1848(4) | 4654(3) | 26(2) |
| C(12F) | 8833(6) | 2669(4) | 4653(3) | 24(1) |
| C(13F) | 7977(6) | 3053(4) | 4984(3) | 25(2) |
| C(14F) | 7210(6) | 2688(4) | 5327(3) | 31(2) |
| C(15F) | 6416(6) | 3082(5) | 5665(3) | 34(2) |
| C(16F) | 6316(7) | 3860(5) | 5665(3) | 38(2) |
| C(17F) | 7028(7) | 4232(4) | 5346(3) | 35(2) |
| C(18F) | 7876(6) | 3833(4) | 4986(3) | 31(2) |
| C(19F) | 8633(6) | 4214(4) | 4667(3) | 34(2) |
| C(20F) | 9453(6) | 3840(4) | 4329(3) | 33(2) |
| C(21F) | 10220(7) | 4219(5) | 3986(3) | 38(2) |
| C(22F) | 11059(7) | 3852(5) | 3675(4) | 47(2) |
| C(23F) | 11174(7) | 3079(5) | 3661(4) | 43(2) |
| C(24F) | 10468(6) | 2689(5) | 3972(3) | 35(2) |
| C(25F) | 9581(6) | 3048(4) | 4316(3) | 26(2) |
| Ag(5) | 6087(1) | 3184(1) | 996(1) | 38(1) |
| C(1A) | 7975(7) | 2597(5) | 1516(4) | 39(2) |

| | | | | |
|---------|-----------|----------|---------|-------|
| N(1A) | 7507(6) | 3219(4) | 1587(3) | 40(2) |
| C(2A) | 8024(8) | 3830(6) | 2144(4) | 51(2) |
| C(3A) | 8800(7) | 3544(5) | 2383(4) | 48(2) |
| N(2A) | 8768(6) | 2764(4) | 1990(3) | 39(2) |
| C(4A) | 9488(8) | 2216(5) | 2058(4) | 52(2) |
| C(1B) | 3948(7) | 2747(5) | 72(4) | 37(2) |
| N(1B) | 4765(6) | 3350(4) | 462(3) | 40(2) |
| C(2B) | 4632(9) | 4040(5) | 351(5) | 56(2) |
| C(3B) | 3755(8) | 3842(5) | -78(5) | 57(3) |
| N(2B) | 3329(6) | 3022(4) | -245(3) | 39(2) |
| C(4B) | 2339(8) | 2530(6) | -695(4) | 55(2) |
| Ag(6) | 10995(1) | 3224(1) | 5936(1) | 39(1) |
| C(1C) | 12817(7) | 2674(5) | 5025(4) | 39(2) |
| N(1C) | 12409(5) | 3310(4) | 5379(3) | 39(2) |
| C(2C) | 13026(7) | 3963(5) | 5248(4) | 39(2) |
| C(3C) | 13785(7) | 3705(5) | 4832(4) | 47(2) |
| N(2C) | 13644(5) | 2873(4) | 4686(3) | 38(2) |
| C(4C) | 14282(7) | 2348(5) | 4260(4) | 48(2) |
| C(1D) | 8800(7) | 2719(5) | 6524(3) | 35(2) |
| N(1D) | 9631(6) | 3334(4) | 6548(3) | 40(2) |
| C(2D) | 9474(9) | 3999(5) | 7038(5) | 63(3) |
| C(3D) | 8537(8) | 3751(5) | 7314(5) | 55(2) |
| N(2D) | 8105(6) | 2932(4) | 6985(3) | 38(2) |
| C(4D) | 7059(7) | 2423(6) | 7093(4) | 51(2) |
| *Ag(11) | 11649(12) | 53(8) | 238(6) | 30 |
| *Ag(12) | 9686(12) | -836(8) | -763(6) | 30 |
| *Ag(13) | 9657(12) | -875(8) | 332(7) | 30 |
| *Ag(14) | 11623(12) | 16(8) | 1337(6) | 30 |
| *Ag(15) | 5283(12) | 858(8) | 4693(6) | 30 |
| *Ag(16) | 3412(12) | -7(8) | 5250(6) | 30 |
| *Ag(17) | 6546(12) | 17(8) | 3647(6) | 30 |
| *Ag(18) | 4699(13) | -856(9) | 4212(7) | 30 |
| *Ag(19) | 5969(12) | 3237(9) | 5277(6) | 30 |
| *Ag(20) | 8908(12) | -3192(8) | -185(6) | 30 |

* 4% site occupancy

Table 21. Bond lengths [\AA] and angles [$^\circ$] for $[\text{Ag}(1\text{-Me-imid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$.

| | | | |
|----------------|------------|----------------|-----------|
| Ag(1)-O(12C)#1 | 2.248(4) | C(12B)-C(13B) | 1.414(9) |
| Ag(1)-O(11C) | 2.270(4) | C(13B)-C(18B) | 1.420(9) |
| Ag(1)-O(11A) | 2.314(5) | C(13B)-C(14B) | 1.435(9) |
| Ag(1)-O(11B) | 2.383(4) | C(14B)-C(15B) | 1.358(9) |
| Ag(1)-Ag(1)#1 | 2.7860(10) | C(15B)-C(16B) | 1.408(10) |
| Ag(1)-Ag(2)#1 | 2.9621(7) | C(16B)-C(17B) | 1.366(11) |
| Ag(1)-Ag(2) | 3.0085(7) | C(17B)-C(18B) | 1.419(10) |
| Ag(2)-O(12A) | 2.188(4) | C(18B)-C(19B) | 1.399(10) |
| Ag(2)-O(12B)#1 | 2.190(4) | C(19B)-C(20B) | 1.389(10) |
| Ag(2)-Ag(1)#1 | 2.9621(7) | C(20B)-C(21B) | 1.419(10) |
| O(11A)-C(11A) | 1.241(8) | C(20B)-C(25B) | 1.443(9) |
| O(11A)-Ag(5) | 2.713(5) | C(21B)-C(22B) | 1.346(11) |
| O(12A)-C(11A) | 1.262(8) | C(22B)-C(23B) | 1.424(11) |
| C(11A)-C(12A) | 1.523(9) | C(23B)-C(24B) | 1.349(10) |
| C(12A)-C(13A) | 1.409(10) | C(24B)-C(25B) | 1.416(9) |
| C(12A)-C(25A) | 1.414(9) | O(11C)-C(11C) | 1.246(8) |
| C(13A)-C(14A) | 1.414(10) | O(12C)-C(11C) | 1.242(8) |
| C(13A)-C(18A) | 1.428(9) | O(12C)-Ag(1)#1 | 2.248(4) |
| C(14A)-C(15A) | 1.356(11) | C(11C)-C(12C) | 1.512(8) |
| C(15A)-C(16A) | 1.411(11) | C(12C)-C(13C) | 1.381(9) |
| C(16A)-C(17A) | 1.344(11) | C(12C)-C(25C) | 1.409(9) |
| C(17A)-C(18A) | 1.440(10) | C(13C)-C(18C) | 1.435(9) |
| C(18A)-C(19A) | 1.386(10) | C(13C)-C(14C) | 1.441(9) |
| C(19A)-C(20A) | 1.394(10) | C(14C)-C(15C) | 1.349(9) |
| C(20A)-C(21A) | 1.429(10) | C(15C)-C(16C) | 1.427(9) |
| C(20A)-C(25A) | 1.440(9) | C(16C)-C(17C) | 1.371(10) |
| C(21A)-C(22A) | 1.348(12) | C(17C)-C(18C) | 1.435(9) |
| C(22A)-C(23A) | 1.356(11) | C(18C)-C(19C) | 1.390(9) |
| C(23A)-C(24A) | 1.396(10) | C(19C)-C(20C) | 1.388(9) |
| C(24A)-C(25A) | 1.421(10) | C(20C)-C(21C) | 1.430(9) |
| O(11B)-C(11B) | 1.264(8) | C(20C)-C(25C) | 1.448(9) |
| O(11B)-Ag(5) | 2.629(4) | C(21C)-C(22C) | 1.366(10) |
| O(12B)-C(11B) | 1.259(8) | C(22C)-C(23C) | 1.419(10) |
| O(12B)-Ag(2)#1 | 2.190(4) | C(23C)-C(24C) | 1.380(9) |
| C(11B)-C(12B) | 1.513(9) | C(24C)-C(25C) | 1.417(9) |
| C(12B)-C(25B) | 1.407(9) | Ag(3)-O(11E) | 2.228(5) |
| Ag(3)-O(12E)#2 | 2.248(5) | Ag(3)-O(11F) | 2.318(5) |

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| Ag(3)-O(11D) | 2.392(4) | C(16E)-C(17E) | 1.382(10) |
| Ag(3)-Ag(3)#2 | 2.7892(10) | C(17E)-C(18E) | 1.431(9) |
| Ag(3)-Ag(4)#2 | 2.9493(7) | C(18E)-C(19E) | 1.394(10) |
| Ag(3)-Ag(4) | 2.9843(8) | C(19E)-C(20E) | 1.395(10) |
| Ag(4)-O(12F) | 2.183(4) | C(20E)-C(21E) | 1.422(10) |
| Ag(4)-O(12D)#2 | 2.183(4) | C(20E)-C(25E) | 1.452(9) |
| Ag(4)-Ag(3)#2 | 2.9493(7) | C(21E)-C(22E) | 1.354(10) |
| O(11D)-C(11D) | 1.241(7) | C(22E)-C(23E) | 1.432(10) |
| O(11D)-Ag(6) | 2.607(4) | C(23E)-C(24E) | 1.360(10) |
| O(12D)-C(11D) | 1.260(7) | C(24E)-C(25E) | 1.427(9) |
| O(12D)-Ag(4)#2 | 2.183(4) | O(11F)-C(11F) | 1.257(8) |
| C(11D)-C(12D) | 1.514(8) | O(11F)-Ag(6) | 2.790(5) |
| C(12D)-C(25D) | 1.408(9) | O(12F)-C(11F) | 1.248(8) |
| C(12D)-C(13D) | 1.412(9) | C(11F)-C(12F) | 1.518(9) |
| C(13D)-C(18D) | 1.431(9) | C(12F)-C(13F) | 1.405(9) |
| C(13D)-C(14D) | 1.437(9) | C(12F)-C(25F) | 1.417(9) |
| C(14D)-C(15D) | 1.352(10) | C(13F)-C(18F) | 1.424(9) |
| C(15D)-C(16D) | 1.429(11) | C(13F)-C(14F) | 1.426(10) |
| C(16D)-C(17D) | 1.371(11) | C(14F)-C(15F) | 1.361(10) |
| C(17D)-C(18D) | 1.418(10) | C(15F)-C(16F) | 1.422(10) |
| C(18D)-C(19D) | 1.386(10) | C(16F)-C(17F) | 1.358(11) |
| C(19D)-C(20D) | 1.389(10) | C(17F)-C(18F) | 1.437(10) |
| C(20D)-C(25D) | 1.428(9) | C(18F)-C(19F) | 1.393(10) |
| C(20D)-C(21D) | 1.430(10) | C(19F)-C(20F) | 1.371(11) |
| C(21D)-C(22D) | 1.353(10) | C(20F)-C(21F) | 1.440(10) |
| C(22D)-C(23D) | 1.413(10) | C(20F)-C(25F) | 1.445(9) |
| C(23D)-C(24D) | 1.366(9) | C(21F)-C(22F) | 1.358(12) |
| C(24D)-C(25D) | 1.438(9) | C(22F)-C(23F) | 1.407(12) |
| O(11E)-C(11E) | 1.254(8) | C(23F)-C(24F) | 1.359(11) |
| O(12E)-C(11E) | 1.229(8) | C(24F)-C(25F) | 1.429(10) |
| O(12E)-Ag(3)#2 | 2.248(4) | Ag(5)-N(1B) | 2.125(7) |
| C(11E)-C(12E) | 1.515(8) | Ag(5)-N(1A) | 2.141(7) |
| C(12E)-C(25E) | 1.392(9) | C(1A)-N(1A) | 1.296(10) |
| C(12E)-C(13E) | 1.402(9) | C(1A)-N(2A) | 1.354(10) |
| C(13E)-C(18E) | 1.428(9) | N(1A)-C(2A) | 1.398(10) |
| C(13E)-C(14E) | 1.440(9) | C(2A)-C(3A) | 1.343(12) |
| C(14E)-C(15E) | 1.375(9) | C(3A)-N(2A) | 1.357(10) |
| C(15E)-C(16E) | 1.419(10) | N(2A)-C(4A) | 1.468(10) |

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| C(1B)-N(2B) | 1.316(9) | Ag(11)-Ag(13)#3 | 2.94(2) |
| C(1B)-N(1B) | 1.334(10) | Ag(11)-Ag(12) | 3.019(19) |
| N(1B)-C(2B) | 1.391(10) | Ag(12)-Ag(11)#3 | 2.361(19) |
| C(2B)-C(3B) | 1.336(13) | Ag(12)-Ag(13) | 2.596(19) |
| C(3B)-N(2B) | 1.356(11) | Ag(12)-Ag(13)#3 | 2.791(19) |
| N(2B)-C(4B) | 1.464(11) | Ag(12)-Ag(14)#3 | 2.947(19) |
| Ag(6)-N(1C) | 2.127(7) | Ag(13)-Ag(12)#3 | 2.791(19) |
| Ag(6)-N(1D) | 2.143(7) | Ag(13)-Ag(11)#3 | 2.94(2) |
| C(1C)-N(1C) | 1.323(10) | Ag(13)-Ag(14) | 3.03(2) |
| C(1C)-N(2C) | 1.330(10) | Ag(14)-Ag(12)#3 | 2.947(19) |
| N(1C)-C(2C) | 1.381(9) | Ag(15)-Ag(16)#4 | 2.403(19) |
| C(2C)-C(3C) | 1.342(12) | Ag(15)-Ag(18)#4 | 2.57(2) |
| C(3C)-N(2C) | 1.375(10) | Ag(15)-Ag(18) | 2.79(2) |
| N(2C)-C(4C) | 1.430(10) | Ag(15)-Ag(17) | 2.951(19) |
| C(1D)-N(1D) | 1.298(10) | Ag(15)-Ag(16) | 3.003(19) |
| C(1D)-N(2D) | 1.344(9) | Ag(16)-Ag(15)#4 | 2.403(19) |
| N(1D)-C(2D) | 1.366(11) | Ag(16)-Ag(18)#4 | 2.46(2) |
| C(2D)-C(3D) | 1.356(13) | Ag(16)-Ag(17)#4 | 2.597(19) |
| C(3D)-N(2D) | 1.369(10) | Ag(16)-Ag(18) | 2.96(2) |
| N(2D)-C(4D) | 1.455(11) | Ag(17)-Ag(16)#4 | 2.597(19) |
| Ag(11)-Ag(12)#3 | 2.360(19) | Ag(17)-Ag(18) | 3.01(2) |
| Ag(11)-Ag(14) | 2.606(19) | Ag(18)-Ag(16)#4 | 2.46(2) |
| Ag(11)-Ag(13) | 2.639(19) | Ag(18)-Ag(15)#4 | 2.57(2) |
| O(12C)#1-Ag(1)-O(11C) | 156.54(18) | O(11B)-Ag(1)-Ag(2)#1 | 75.58(11) |
| O(12C)#1-Ag(1)-O(11A) | 100.79(18) | Ag(1)#1-Ag(1)-Ag(2)#1 | 63.03(2) |
| O(11C)-Ag(1)-O(11A) | 102.66(18) | O(12C)#1-Ag(1)-Ag(2) | 78.27(13) |
| O(12C)#1-Ag(1)-O(11B) | 93.57(16) | O(11C)-Ag(1)-Ag(2) | 107.63(12) |
| O(11C)-Ag(1)-O(11B) | 87.81(16) | O(11A)-Ag(1)-Ag(2) | 74.06(12) |
| O(11A)-Ag(1)-O(11B) | 88.22(16) | O(11B)-Ag(1)-Ag(2) | 158.49(11) |
| O(12C)#1-Ag(1)-Ag(1)#1 | 81.43(12) | Ag(1)#1-Ag(1)-Ag(2) | 61.34(2) |
| O(11C)-Ag(1)-Ag(1)#1 | 81.86(12) | Ag(2)#1-Ag(1)-Ag(2) | 124.37(2) |
| O(11A)-Ag(1)-Ag(1)#1 | 134.03(13) | O(12A)-Ag(2)-O(12B)#1 | 140.38(17) |
| O(11B)-Ag(1)-Ag(1)#1 | 137.71(11) | O(12A)-Ag(2)-Ag(1)#1 | 135.98(12) |
| O(12C)#1-Ag(1)-Ag(2)#1 | 93.80(13) | O(12B)#1-Ag(2)-Ag(1)#1 | 80.33(11) |
| O(11C)-Ag(1)-Ag(2)#1 | 63.84(13) | O(12A)-Ag(2)-Ag(1) | 81.70(12) |
| O(11A)-Ag(1)-Ag(2)#1 | 158.86(12) | O(12B)#1-Ag(2)-Ag(1) | 124.95(11) |
| Ag(1)#1-Ag(2)-Ag(1) | 55.62(2) | C(11A)-O(11A)-Ag(1) | 124.5(4) |

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| C(11A)-O(11A)-Ag(5) | 117.9(4) | C(25B)-C(12B)-C(13B) | 120.6(6) |
| Ag(1)-O(11A)-Ag(5) | 97.72(18) | C(25B)-C(12B)-C(11B) | 120.0(6) |
| C(11A)-O(12A)-Ag(2) | 120.4(4) | C(13B)-C(12B)-C(11B) | 119.4(6) |
| O(11A)-C(11A)-O(12A) | 126.4(6) | C(12B)-C(13B)-C(18B) | 120.1(6) |
| O(11A)-C(11A)-C(12A) | 116.7(6) | C(12B)-C(13B)-C(14B) | 122.0(6) |
| O(12A)-C(11A)-C(12A) | 116.8(6) | C(18B)-C(13B)-C(14B) | 117.8(6) |
| C(13A)-C(12A)-C(25A) | 121.4(6) | C(15B)-C(14B)-C(13B) | 120.2(6) |
| C(13A)-C(12A)-C(11A) | 119.5(6) | C(14B)-C(15B)-C(16B) | 121.7(7) |
| C(25A)-C(12A)-C(11A) | 119.0(6) | C(17B)-C(16B)-C(15B) | 119.8(7) |
| C(12A)-C(13A)-C(14A) | 123.2(6) | C(16B)-C(17B)-C(18B) | 120.4(7) |
| C(12A)-C(13A)-C(18A) | 118.6(6) | C(19B)-C(18B)-C(17B) | 121.3(6) |
| C(14A)-C(13A)-C(18A) | 118.2(6) | C(19B)-C(18B)-C(13B) | 118.7(6) |
| C(15A)-C(14A)-C(13A) | 121.7(7) | C(17B)-C(18B)-C(13B) | 120.0(6) |
| C(14A)-C(15A)-C(16A) | 120.0(8) | C(20B)-C(19B)-C(18B) | 122.3(6) |
| C(17A)-C(16A)-C(15A) | 121.1(7) | C(19B)-C(20B)-C(21B) | 121.4(6) |
| C(16A)-C(17A)-C(18A) | 120.5(7) | C(19B)-C(20B)-C(25B) | 119.3(6) |
| C(19A)-C(18A)-C(13A) | 120.2(7) | C(21B)-C(20B)-C(25B) | 119.2(6) |
| C(19A)-C(18A)-C(17A) | 121.3(7) | C(22B)-C(21B)-C(20B) | 121.5(7) |
| C(13A)-C(18A)-C(17A) | 118.5(7) | C(21B)-C(22B)-C(23B) | 119.4(7) |
| C(18A)-C(19A)-C(20A) | 121.8(6) | C(24B)-C(23B)-C(22B) | 120.9(7) |
| C(19A)-C(20A)-C(21A) | 121.7(7) | C(23B)-C(24B)-C(25B) | 122.0(7) |
| C(19A)-C(20A)-C(25A) | 119.3(6) | C(12B)-C(25B)-C(24B) | 124.3(6) |
| C(21A)-C(20A)-C(25A) | 119.0(7) | C(12B)-C(25B)-C(20B) | 118.8(6) |
| C(22A)-C(21A)-C(20A) | 120.6(7) | C(24B)-C(25B)-C(20B) | 116.9(6) |
| C(21A)-C(22A)-C(23A) | 121.4(7) | C(11C)-O(11C)-Ag(1) | 119.3(4) |
| C(22A)-C(23A)-C(24A) | 121.2(7) | C(11C)-O(12C)-Ag(1)#1 | 123.1(4) |
| C(23A)-C(24A)-C(25A) | 120.2(7) | O(12C)-C(11C)-O(11C) | 126.8(6) |
| C(12A)-C(25A)-C(24A) | 124.0(6) | O(12C)-C(11C)-C(12C) | 115.7(5) |
| C(12A)-C(25A)-C(20A) | 118.6(6) | O(11C)-C(11C)-C(12C) | 117.5(6) |
| C(24A)-C(25A)-C(20A) | 117.3(6) | C(13C)-C(12C)-C(25C) | 121.9(6) |
| C(11B)-O(11B)-Ag(1) | 114.6(4) | C(13C)-C(12C)-C(11C) | 119.0(6) |
| C(11B)-O(11B)-Ag(5) | 133.6(4) | C(25C)-C(12C)-C(11C) | 119.1(6) |
| Ag(1)-O(11B)-Ag(5) | 98.32(15) | C(12C)-C(13C)-C(18C) | 119.2(6) |
| C(11B)-O(12B)-Ag(2)#1 | 123.8(4) | C(12C)-C(13C)-C(14C) | 122.8(6) |
| O(12B)-C(11B)-O(11B) | 125.4(6) | C(18C)-C(13C)-C(14C) | 118.0(6) |
| O(12B)-C(11B)-C(12B) | 116.1(6) | C(15C)-C(14C)-C(13C) | 120.8(6) |
| O(11B)-C(11B)-C(12B) | 118.5(6) | C(14C)-C(15C)-C(16C) | 122.1(7) |
| C(17C)-C(16C)-C(15C) | 118.7(6) | C(16C)-C(17C)-C(18C) | 121.5(6) |

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| C(19C)-C(18C)-C(17C) | 121.3(6) | O(12D)#2-Ag(4)-Ag(3)#2 | 80.28(11) |
| C(19C)-C(18C)-C(13C) | 119.9(6) | O(12F)-Ag(4)-Ag(3) | 82.40(12) |
| C(17C)-C(18C)-C(13C) | 118.8(6) | O(12D)#2-Ag(4)-Ag(3) | 126.81(12) |
| C(20C)-C(19C)-C(18C) | 120.9(6) | Ag(3)#2-Ag(4)-Ag(3) | 56.07(2) |
| C(19C)-C(20C)-C(21C) | 121.8(6) | C(11D)-O(11D)-Ag(3) | 114.9(4) |
| C(19C)-C(20C)-C(25C) | 120.0(6) | C(11D)-O(11D)-Ag(6) | 127.3(4) |
| C(21C)-C(20C)-C(25C) | 118.2(6) | Ag(3)-O(11D)-Ag(6) | 100.84(15) |
| C(22C)-C(21C)-C(20C) | 121.3(6) | C(11D)-O(12D)-Ag(4)#2 | 124.1(4) |
| C(21C)-C(22C)-C(23C) | 120.4(6) | O(11D)-C(11D)-O(12D) | 125.8(6) |
| C(24C)-C(23C)-C(22C) | 120.3(6) | O(11D)-C(11D)-C(12D) | 118.2(5) |
| C(23C)-C(24C)-C(25C) | 121.0(6) | O(12D)-C(11D)-C(12D) | 116.0(5) |
| C(12C)-C(25C)-C(24C) | 123.3(6) | C(25D)-C(12D)-C(13D) | 120.6(6) |
| C(12C)-C(25C)-C(20C) | 117.9(6) | C(25D)-C(12D)-C(11D) | 119.4(6) |
| C(24C)-C(25C)-C(20C) | 118.8(6) | C(13D)-C(12D)-C(11D) | 120.0(5) |
| O(11E)-Ag(3)-O(12E)#2 | 158.78(19) | C(12D)-C(13D)-C(18D) | 119.1(6) |
| O(11E)-Ag(3)-O(11F) | 99.6(2) | C(12D)-C(13D)-C(14D) | 123.1(6) |
| O(12E)#2-Ag(3)-O(11F) | 101.5(2) | C(18D)-C(13D)-C(14D) | 117.6(6) |
| O(11E)-Ag(3)-O(11D) | 94.71(17) | C(15D)-C(14D)-C(13D) | 121.1(6) |
| O(12E)#2-Ag(3)-O(11D) | 88.40(16) | C(14D)-C(15D)-C(16D) | 121.2(7) |
| O(11F)-Ag(3)-O(11D) | 86.84(17) | C(17D)-C(16D)-C(15D) | 119.3(7) |
| O(11E)-Ag(3)-Ag(3)#2 | 81.66(13) | C(16D)-C(17D)-C(18D) | 121.1(7) |
| O(12E)#2-Ag(3)-Ag(3)#2 | 81.99(12) | C(19D)-C(18D)-C(17D) | 121.3(6) |
| O(11F)-Ag(3)-Ag(3)#2 | 135.26(14) | C(19D)-C(18D)-C(13D) | 119.0(6) |
| O(11D)-Ag(3)-Ag(3)#2 | 137.86(11) | C(17D)-C(18D)-C(13D) | 119.7(6) |
| O(11E)-Ag(3)-Ag(4)#2 | 92.74(14) | C(18D)-C(19D)-C(20D) | 122.8(6) |
| O(12E)#2-Ag(3)-Ag(4)#2 | 67.65(14) | C(19D)-C(20D)-C(25D) | 118.7(6) |
| O(11F)-Ag(3)-Ag(4)#2 | 159.46(13) | C(19D)-C(20D)-C(21D) | 121.5(6) |
| O(11D)-Ag(3)-Ag(4)#2 | 75.77(10) | C(25D)-C(20D)-C(21D) | 119.9(6) |
| Ag(3)#2-Ag(3)-Ag(4)#2 | 62.60(2) | C(22D)-C(21D)-C(20D) | 119.6(6) |
| O(11E)-Ag(3)-Ag(4) | 79.46(14) | C(21D)-C(22D)-C(23D) | 122.1(7) |
| O(12E)#2-Ag(3)-Ag(4) | 104.22(13) | C(24D)-C(23D)-C(22D) | 119.6(7) |
| O(11F)-Ag(3)-Ag(4) | 74.84(13) | C(23D)-C(24D)-C(25D) | 121.2(6) |
| O(11D)-Ag(3)-Ag(4) | 159.39(11) | C(12D)-C(25D)-C(20D) | 119.7(6) |
| Ag(3)#2-Ag(3)-Ag(4) | 61.330(19) | C(12D)-C(25D)-C(24D) | 122.7(6) |
| Ag(4)#2-Ag(3)-Ag(4) | 123.93(2) | C(20D)-C(25D)-C(24D) | 117.6(6) |
| O(12F)-Ag(4)-O(12D)#2 | 140.72(16) | C(11E)-O(11E)-Ag(3) | 123.6(4) |
| O(12F)-Ag(4)-Ag(3)#2 | 136.97(12) | C(11E)-O(12E)-Ag(3)#2 | 121.3(4) |
| O(12E)-C(11E)-O(11E) | 126.4(6) | O(12E)-C(11E)-C(12E) | 117.5(5) |

| | | | |
|----------------------|-----------|----------------------|-----------|
| O(11E)-C(11E)-C(12E) | 116.1(5) | C(18F)-C(13F)-C(14F) | 118.6(6) |
| C(25E)-C(12E)-C(13E) | 122.2(6) | C(15F)-C(14F)-C(13F) | 121.2(7) |
| C(25E)-C(12E)-C(11E) | 118.0(5) | C(14F)-C(15F)-C(16F) | 120.0(7) |
| C(13E)-C(12E)-C(11E) | 119.7(5) | C(17F)-C(16F)-C(15F) | 120.9(7) |
| C(12E)-C(13E)-C(18E) | 118.6(6) | C(16F)-C(17F)-C(18F) | 120.4(7) |
| C(12E)-C(13E)-C(14E) | 122.4(6) | C(19F)-C(18F)-C(13F) | 119.9(7) |
| C(18E)-C(13E)-C(14E) | 119.0(6) | C(19F)-C(18F)-C(17F) | 121.2(7) |
| C(15E)-C(14E)-C(13E) | 120.2(6) | C(13F)-C(18F)-C(17F) | 118.9(7) |
| C(14E)-C(15E)-C(16E) | 120.7(6) | C(20F)-C(19F)-C(18F) | 121.4(7) |
| C(17E)-C(16E)-C(15E) | 120.8(6) | C(19F)-C(20F)-C(21F) | 121.8(7) |
| C(16E)-C(17E)-C(18E) | 120.1(7) | C(19F)-C(20F)-C(25F) | 120.3(7) |
| C(19E)-C(18E)-C(13E) | 119.3(6) | C(21F)-C(20F)-C(25F) | 117.9(7) |
| C(19E)-C(18E)-C(17E) | 121.3(6) | C(22F)-C(21F)-C(20F) | 120.8(7) |
| C(13E)-C(18E)-C(17E) | 119.4(6) | C(21F)-C(22F)-C(23F) | 121.0(8) |
| C(18E)-C(19E)-C(20E) | 122.8(6) | C(24F)-C(23F)-C(22F) | 120.7(8) |
| C(19E)-C(20E)-C(21E) | 123.1(6) | C(23F)-C(24F)-C(25F) | 121.0(7) |
| C(19E)-C(20E)-C(25E) | 117.8(6) | C(12F)-C(25F)-C(24F) | 123.0(6) |
| C(21E)-C(20E)-C(25E) | 119.1(6) | C(12F)-C(25F)-C(20F) | 118.5(6) |
| C(22E)-C(21E)-C(20E) | 121.0(7) | C(24F)-C(25F)-C(20F) | 118.5(6) |
| C(21E)-C(22E)-C(23E) | 120.5(7) | N(1B)-Ag(5)-N(1A) | 171.1(2) |
| C(24E)-C(23E)-C(22E) | 120.2(7) | N(1B)-Ag(5)-O(11B) | 90.5(2) |
| C(23E)-C(24E)-C(25E) | 121.7(6) | N(1A)-Ag(5)-O(11B) | 95.8(2) |
| C(12E)-C(25E)-C(24E) | 123.3(6) | N(1B)-Ag(5)-O(11A) | 100.8(2) |
| C(12E)-C(25E)-C(20E) | 119.3(6) | N(1A)-Ag(5)-O(11A) | 86.8(2) |
| C(24E)-C(25E)-C(20E) | 117.5(6) | O(11B)-Ag(5)-O(11A) | 75.46(14) |
| C(11F)-O(11F)-Ag(3) | 124.2(5) | N(1A)-C(1A)-N(2A) | 111.3(7) |
| C(11F)-O(11F)-Ag(6) | 120.0(4) | C(1A)-N(1A)-C(2A) | 105.8(7) |
| Ag(3)-O(11F)-Ag(6) | 97.57(18) | C(1A)-N(1A)-Ag(5) | 123.8(5) |
| C(11F)-O(12F)-Ag(4) | 120.8(4) | C(2A)-N(1A)-Ag(5) | 130.0(6) |
| O(12F)-C(11F)-O(11F) | 126.9(6) | C(3A)-C(2A)-N(1A) | 108.8(8) |
| O(12F)-C(11F)-C(12F) | 118.3(6) | C(2A)-C(3A)-N(2A) | 106.9(7) |
| O(11F)-C(11F)-C(12F) | 114.8(6) | C(1A)-N(2A)-C(3A) | 107.2(7) |
| C(13F)-C(12F)-C(25F) | 120.4(6) | C(1A)-N(2A)-C(4A) | 126.5(7) |
| C(13F)-C(12F)-C(11F) | 121.1(6) | C(3A)-N(2A)-C(4A) | 126.2(7) |
| C(25F)-C(12F)-C(11F) | 118.6(6) | N(2B)-C(1B)-N(1B) | 111.7(7) |
| C(12F)-C(13F)-C(18F) | 119.6(6) | C(1B)-N(1B)-C(2B) | 103.4(7) |
| C(12F)-C(13F)-C(14F) | 121.8(6) | C(1B)-N(1B)-Ag(5) | 125.1(5) |
| C(2B)-N(1B)-Ag(5) | 130.7(6) | C(3B)-C(2B)-N(1B) | 110.5(8) |

| | | | |
|--------------------------|-----------|--------------------------|----------|
| C(2B)-C(3B)-N(2B) | 105.9(8) | Ag(13)#3-Ag(11)-Ag(12) | 55.8(4) |
| C(1B)-N(2B)-C(3B) | 108.5(8) | Ag(11)#3-Ag(12)-Ag(13) | 72.6(6) |
| C(1B)-N(2B)-C(4B) | 125.8(7) | Ag(11)#3-Ag(12)-Ag(13)#3 | 61.0(5) |
| C(3B)-N(2B)-C(4B) | 125.7(7) | Ag(13)-Ag(12)-Ag(13)#3 | 93.6(6) |
| N(1C)-Ag(6)-N(1D) | 171.5(2) | Ag(11)#3-Ag(12)-Ag(14)#3 | 57.5(5) |
| N(1C)-Ag(6)-O(11D) | 91.7(2) | Ag(13)-Ag(12)-Ag(14)#3 | 130.1(7) |
| N(1D)-Ag(6)-O(11D) | 95.22(19) | Ag(13)#3-Ag(12)-Ag(14)#3 | 63.6(5) |
| N(1C)-Ag(6)-O(11F) | 84.0(2) | Ag(11)#3-Ag(12)-Ag(11) | 94.3(6) |
| N(1D)-Ag(6)-O(11F) | 102.7(2) | Ag(13)-Ag(12)-Ag(11) | 55.4(5) |
| O(11D)-Ag(6)-O(11F) | 73.62(13) | Ag(13)#3-Ag(12)-Ag(11) | 60.6(5) |
| N(1C)-C(1C)-N(2C) | 113.1(7) | Ag(14)#3-Ag(12)-Ag(11) | 124.3(6) |
| C(1C)-N(1C)-C(2C) | 104.2(7) | Ag(12)-Ag(13)-Ag(11) | 70.4(5) |
| C(1C)-N(1C)-Ag(6) | 124.2(5) | Ag(12)-Ag(13)-Ag(12)#3 | 86.4(6) |
| C(2C)-N(1C)-Ag(6) | 131.3(5) | Ag(11)-Ag(13)-Ag(12)#3 | 51.4(5) |
| C(3C)-C(2C)-N(1C) | 109.7(7) | Ag(12)-Ag(13)-Ag(11)#3 | 50.0(5) |
| C(2C)-C(3C)-N(2C) | 107.1(7) | Ag(11)-Ag(13)-Ag(11)#3 | 90.6(6) |
| C(1C)-N(2C)-C(3C) | 105.9(7) | Ag(12)#3-Ag(13)-Ag(11)#3 | 63.5(5) |
| C(1C)-N(2C)-C(4C) | 128.2(7) | Ag(12)-Ag(13)-Ag(14) | 124.7(6) |
| C(3C)-N(2C)-C(4C) | 125.9(7) | Ag(11)-Ag(13)-Ag(14) | 54.2(5) |
| N(1D)-C(1D)-N(2D) | 111.8(7) | Ag(12)#3-Ag(13)-Ag(14) | 60.7(5) |
| C(1D)-N(1D)-C(2D) | 106.9(7) | Ag(11)#3-Ag(13)-Ag(14) | 124.2(6) |
| C(1D)-N(1D)-Ag(6) | 123.3(5) | Ag(11)-Ag(14)-Ag(12)#3 | 49.9(5) |
| C(2D)-N(1D)-Ag(6) | 129.7(6) | Ag(11)-Ag(14)-Ag(13) | 55.3(5) |
| C(3D)-C(2D)-N(1D) | 108.0(8) | Ag(12)#3-Ag(14)-Ag(13) | 55.7(4) |
| C(2D)-C(3D)-N(2D) | 107.4(8) | Ag(16)#4-Ag(15)-Ag(18)#4 | 73.0(6) |
| C(1D)-N(2D)-C(3D) | 105.8(7) | Ag(16)#4-Ag(15)-Ag(18) | 56.0(5) |
| C(1D)-N(2D)-C(4D) | 127.7(7) | Ag(18)#4-Ag(15)-Ag(18) | 90.1(6) |
| C(3D)-N(2D)-C(4D) | 126.3(7) | Ag(16)#4-Ag(15)-Ag(17) | 56.9(5) |
| Ag(12)#3-Ag(11)-Ag(14) | 72.6(6) | Ag(18)#4-Ag(15)-Ag(17) | 129.9(7) |
| Ag(12)#3-Ag(11)-Ag(13) | 67.6(6) | Ag(18)-Ag(15)-Ag(17) | 63.1(5) |
| Ag(14)-Ag(11)-Ag(13) | 70.5(5) | Ag(16)#4-Ag(15)-Ag(16) | 91.8(6) |
| Ag(12)#3-Ag(11)-Ag(13)#3 | 57.4(5) | Ag(18)#4-Ag(15)-Ag(16) | 51.7(5) |
| Ag(14)-Ag(11)-Ag(13)#3 | 130.0(7) | Ag(18)-Ag(15)-Ag(16) | 61.3(5) |
| Ag(13)-Ag(11)-Ag(13)#3 | 89.4(6) | Ag(17)-Ag(15)-Ag(16) | 124.4(6) |
| Ag(12)#3-Ag(11)-Ag(12) | 85.7(6) | Ag(15)#4-Ag(16)-Ag(18)#4 | 69.9(6) |
| Ag(14)-Ag(11)-Ag(12) | 124.6(6) | Ag(15)#4-Ag(16)-Ag(17)#4 | 72.2(6) |
| Ag(13)-Ag(11)-Ag(12) | 54.1(5) | Ag(18)#4-Ag(16)-Ag(17)#4 | 72.9(6) |
| Ag(15)#4-Ag(16)-Ag(18) | 56.1(5) | Ag(18)#4-Ag(16)-Ag(18) | 88.4(6) |

| | | | |
|--------------------------|----------|------------------------|----------|
| Ag(17)#4-Ag(16)-Ag(18) | 128.3(6) | Ag(16)#4-Ag(18)-Ag(15) | 54.0(5) |
| Ag(15)#4-Ag(16)-Ag(15) | 88.2(6) | Ag(15)#4-Ag(18)-Ag(15) | 89.9(6) |
| Ag(18)#4-Ag(16)-Ag(15) | 55.0(5) | Ag(16)#4-Ag(18)-Ag(16) | 91.6(6) |
| Ag(17)#4-Ag(16)-Ag(15) | 127.9(6) | Ag(15)#4-Ag(18)-Ag(16) | 50.9(5) |
| Ag(18)-Ag(16)-Ag(15) | 55.8(4) | Ag(15)-Ag(18)-Ag(16) | 62.9(5) |
| Ag(16)#4-Ag(17)-Ag(15) | 50.9(5) | Ag(16)#4-Ag(18)-Ag(17) | 55.6(5) |
| Ag(16)#4-Ag(17)-Ag(18) | 51.5(5) | Ag(15)#4-Ag(18)-Ag(17) | 128.9(6) |
| Ag(15)-Ag(17)-Ag(18) | 55.8(4) | Ag(15)-Ag(18)-Ag(17) | 61.1(5) |
| Ag(16)#4-Ag(18)-Ag(15)#4 | 73.2(6) | Ag(16)-Ag(18)-Ag(17) | 124.0(6) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 -x+2,-y,-z+1 #3 -x+2,-y,-z #4 -x+1,-y,-z+1

Table 22. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(1\text{-Meimid})_2]_2[\text{Ag}_4(9\text{-aca})_6]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U^{11} | U^{22} | U^{33} | U^{23} | U^{13} | U^{12} |
|--------|----------|----------|----------|----------|----------|----------|
| Ag(1) | 17(1) | 20(1) | 20(1) | 7(1) | 1(1) | 6(1) |
| Ag(2) | 31(1) | 21(1) | 32(1) | 9(1) | 8(1) | 10(1) |
| O(11A) | 28(3) | 30(3) | 35(3) | -3(2) | 8(2) | 6(2) |
| O(12A) | 29(3) | 19(2) | 33(3) | 7(2) | 8(2) | 4(2) |
| C(11A) | 31(4) | 20(3) | 24(4) | 4(3) | 3(3) | 7(3) |
| C(12A) | 30(4) | 21(3) | 23(3) | 7(3) | 13(3) | 4(3) |
| C(13A) | 23(3) | 19(3) | 28(4) | 6(3) | 15(3) | 4(3) |
| C(14A) | 40(4) | 27(4) | 31(4) | 5(3) | 6(3) | 9(3) |
| C(15A) | 45(5) | 34(4) | 42(5) | 8(4) | -3(4) | 9(4) |
| C(16A) | 47(5) | 35(5) | 37(5) | 2(4) | -9(4) | 4(4) |
| C(17A) | 50(5) | 30(4) | 26(4) | -7(3) | 3(4) | 3(4) |
| C(18A) | 30(4) | 23(4) | 35(4) | 7(3) | 5(3) | 0(3) |
| C(19A) | 35(4) | 18(3) | 34(4) | -3(3) | 6(3) | 7(3) |
| C(20A) | 28(4) | 26(4) | 39(4) | 8(3) | 10(3) | 7(3) |
| C(21A) | 41(5) | 30(4) | 54(5) | 5(4) | 11(4) | 19(4) |
| C(22A) | 37(5) | 41(5) | 62(6) | 22(4) | 9(4) | 19(4) |
| C(23A) | 50(5) | 23(4) | 43(5) | 13(3) | -18(4) | 8(3) |
| C(24A) | 37(4) | 28(4) | 26(4) | 5(3) | 7(3) | 7(3) |

| | | | | | | |
|--------|-------|-------|-------|-------|--------|-------|
| C(25A) | 32(4) | 22(4) | 31(4) | 7(3) | 12(3) | 12(3) |
| O(11B) | 29(3) | 25(2) | 24(3) | 13(2) | 4(2) | 7(2) |
| O(12B) | 24(2) | 22(2) | 27(2) | 8(2) | 2(2) | 8(2) |
| C(11B) | 12(3) | 24(4) | 32(4) | 11(3) | 1(3) | 3(3) |
| C(12B) | 18(3) | 22(3) | 24(3) | 7(3) | 6(3) | 7(3) |
| C(13B) | 20(3) | 28(4) | 21(3) | 11(3) | 8(3) | 12(3) |
| C(14B) | 26(4) | 24(4) | 25(3) | 10(3) | 2(3) | 9(3) |
| C(15B) | 22(4) | 34(4) | 36(4) | 9(3) | -5(3) | 4(3) |
| C(16B) | 31(4) | 43(5) | 36(4) | 16(4) | -1(3) | 17(4) |
| C(17B) | 37(4) | 40(4) | 33(4) | 16(4) | 0(3) | 17(4) |
| C(18B) | 33(4) | 27(4) | 23(4) | 12(3) | 6(3) | 11(3) |
| C(19B) | 42(4) | 22(4) | 32(4) | 15(3) | 7(3) | 11(3) |
| C(20B) | 35(4) | 19(3) | 32(4) | 12(3) | 4(3) | 3(3) |
| C(21B) | 46(5) | 22(4) | 39(4) | 15(3) | 2(4) | 5(3) |
| C(22B) | 42(5) | 28(4) | 46(5) | 10(4) | 6(4) | -7(3) |
| C(23B) | 33(4) | 46(5) | 37(4) | 16(4) | -4(3) | -4(4) |
| C(24B) | 21(3) | 34(4) | 29(4) | 15(3) | 2(3) | 1(3) |
| C(25B) | 22(3) | 23(3) | 19(3) | 5(3) | 9(3) | 8(3) |
| O(11C) | 25(3) | 27(3) | 41(3) | 17(2) | -10(2) | 3(2) |
| O(12C) | 29(3) | 28(3) | 38(3) | 14(2) | -12(2) | 6(2) |
| C(11C) | 17(3) | 26(4) | 18(3) | 9(3) | -3(3) | 6(3) |
| C(12C) | 16(3) | 26(4) | 26(4) | 15(3) | -2(3) | 2(3) |
| C(13C) | 14(3) | 24(3) | 29(4) | 12(3) | -1(3) | 5(3) |
| C(14C) | 16(3) | 32(4) | 34(4) | 20(3) | -2(3) | 4(3) |
| C(15C) | 23(4) | 36(4) | 27(4) | 12(3) | 1(3) | 5(3) |
| C(16C) | 32(4) | 38(4) | 22(4) | 12(3) | 2(3) | 2(3) |
| C(17C) | 22(4) | 40(4) | 28(4) | 19(3) | -4(3) | -1(3) |
| C(18C) | 17(3) | 27(4) | 28(4) | 9(3) | -4(3) | 2(3) |
| C(19C) | 17(3) | 31(4) | 29(4) | 13(3) | -5(3) | 1(3) |
| C(20C) | 14(3) | 30(4) | 34(4) | 16(3) | 2(3) | 5(3) |
| C(21C) | 16(3) | 39(4) | 40(4) | 18(4) | -1(3) | 5(3) |
| C(22C) | 20(4) | 35(4) | 44(4) | 17(4) | 8(3) | 11(3) |
| C(23C) | 26(4) | 36(4) | 25(4) | 5(3) | 7(3) | 12(3) |
| C(24C) | 18(3) | 32(4) | 32(4) | 16(3) | -2(3) | 9(3) |
| C(25C) | 15(3) | 24(3) | 28(4) | 11(3) | 1(3) | 1(3) |
| Ag(3) | 18(1) | 21(1) | 19(1) | 5(1) | 3(1) | 6(1) |
| Ag(4) | 32(1) | 21(1) | 28(1) | 2(1) | -3(1) | 11(1) |
| O(11D) | 32(3) | 20(2) | 15(2) | 4(2) | -1(2) | 3(2) |

| | | | | | | |
|--------|-------|-------|-------|-------|--------|-------|
| O(12D) | 28(3) | 22(2) | 22(2) | 4(2) | 0(2) | 9(2) |
| C(11D) | 12(3) | 20(3) | 17(3) | 2(3) | 0(2) | 0(2) |
| C(12D) | 20(3) | 23(3) | 17(3) | 8(3) | 1(3) | 10(3) |
| C(13D) | 26(3) | 18(3) | 19(3) | 3(3) | -2(3) | 7(3) |
| C(14D) | 30(4) | 29(4) | 24(4) | 8(3) | 6(3) | 6(3) |
| C(15D) | 48(5) | 37(4) | 26(4) | 13(3) | 7(3) | -7(4) |
| C(16D) | 46(5) | 31(4) | 48(5) | 9(4) | 8(4) | -5(4) |
| C(17D) | 43(5) | 21(4) | 32(4) | -5(3) | 6(3) | -5(3) |
| C(18D) | 32(4) | 27(4) | 23(4) | 10(3) | 1(3) | 5(3) |
| C(19D) | 33(4) | 27(4) | 25(4) | -1(3) | 4(3) | 10(3) |
| C(20D) | 29(4) | 28(4) | 25(4) | 9(3) | 2(3) | 11(3) |
| C(21D) | 35(4) | 29(4) | 24(4) | 0(3) | 10(3) | 12(3) |
| C(22D) | 28(4) | 41(4) | 34(4) | 11(4) | 14(3) | 10(3) |
| C(23D) | 28(4) | 32(4) | 29(4) | 13(3) | 8(3) | 8(3) |
| C(24D) | 27(4) | 27(4) | 22(3) | 7(3) | 4(3) | 12(3) |
| C(25D) | 19(3) | 17(3) | 21(3) | 4(3) | -1(3) | 8(3) |
| O(11E) | 32(3) | 26(3) | 43(3) | 2(2) | 20(2) | 3(2) |
| O(12E) | 28(3) | 27(3) | 35(3) | -2(2) | 16(2) | 2(2) |
| C(11E) | 17(3) | 22(3) | 21(3) | 9(3) | 5(3) | 1(3) |
| C(12E) | 18(3) | 18(3) | 14(3) | -1(3) | 0(2) | 0(3) |
| C(13E) | 15(3) | 24(3) | 21(3) | 0(3) | 3(3) | 4(3) |
| C(14E) | 22(3) | 25(4) | 24(4) | 5(3) | 9(3) | 5(3) |
| C(15E) | 34(4) | 29(4) | 30(4) | 16(3) | -4(3) | 11(3) |
| C(16E) | 19(3) | 33(4) | 35(4) | 8(3) | 3(3) | 6(3) |
| C(17E) | 21(4) | 31(4) | 39(4) | 7(3) | 6(3) | 4(3) |
| C(18E) | 18(3) | 25(4) | 29(4) | 6(3) | 3(3) | 4(3) |
| C(19E) | 25(4) | 36(4) | 26(4) | 8(3) | 9(3) | 5(3) |
| C(20E) | 24(4) | 35(4) | 20(3) | 8(3) | 7(3) | 3(3) |
| C(21E) | 30(4) | 43(5) | 31(4) | 16(4) | 5(3) | 3(3) |
| C(22E) | 33(4) | 35(4) | 31(4) | 15(3) | -6(3) | -1(3) |
| C(23E) | 25(4) | 34(4) | 30(4) | 11(3) | -2(3) | 6(3) |
| C(24E) | 21(3) | 28(4) | 28(4) | 9(3) | 6(3) | 5(3) |
| C(25E) | 19(3) | 20(3) | 23(3) | 4(3) | 3(3) | 0(3) |
| O(11F) | 34(3) | 35(3) | 64(4) | 27(3) | -14(3) | 5(2) |
| O(12F) | 30(3) | 17(2) | 29(3) | 3(2) | -7(2) | 5(2) |
| C(11F) | 29(4) | 34(4) | 18(3) | 11(3) | 2(3) | 13(3) |
| C(12F) | 28(4) | 19(3) | 24(3) | 5(3) | -5(3) | 7(3) |
| C(13F) | 30(4) | 17(3) | 27(4) | 6(3) | -7(3) | 3(3) |

| | | | | | | |
|--------|-------|-------|-------|-------|--------|-------|
| C(14F) | 38(4) | 26(4) | 30(4) | 12(3) | 2(3) | 9(3) |
| C(15F) | 32(4) | 37(4) | 35(4) | 13(3) | 8(3) | 13(3) |
| C(16F) | 38(4) | 40(5) | 35(4) | 10(4) | 9(3) | 17(4) |
| C(17F) | 40(4) | 21(4) | 41(4) | 3(3) | -2(4) | 14(3) |
| C(18F) | 29(4) | 26(4) | 35(4) | 8(3) | -6(3) | 4(3) |
| C(19F) | 41(4) | 24(4) | 40(4) | 15(3) | -11(3) | 9(3) |
| C(20F) | 32(4) | 28(4) | 37(4) | 13(3) | -10(3) | 0(3) |
| C(21F) | 46(5) | 36(4) | 34(4) | 21(4) | -8(4) | -1(4) |
| C(22F) | 42(5) | 47(5) | 45(5) | 17(4) | 3(4) | -8(4) |
| C(23F) | 38(5) | 57(6) | 33(4) | 18(4) | 0(4) | 3(4) |
| C(24F) | 33(4) | 41(4) | 36(4) | 19(4) | 4(3) | 9(3) |
| C(25F) | 23(3) | 28(4) | 26(4) | 11(3) | -3(3) | 4(3) |
| Ag(5) | 35(1) | 29(1) | 41(1) | 5(1) | 4(1) | 6(1) |
| C(1A) | 43(5) | 33(4) | 35(4) | 10(4) | 9(4) | 5(4) |
| N(1A) | 40(4) | 33(4) | 36(4) | 7(3) | -1(3) | -1(3) |
| C(2A) | 53(5) | 41(5) | 49(5) | 8(4) | -4(4) | 3(4) |
| C(3A) | 45(5) | 44(5) | 41(5) | 5(4) | -10(4) | -2(4) |
| N(2A) | 36(4) | 34(4) | 44(4) | 16(3) | 0(3) | -1(3) |
| C(4A) | 48(5) | 49(5) | 61(6) | 28(5) | 1(4) | 3(4) |
| C(1B) | 38(4) | 33(4) | 50(5) | 23(4) | 15(4) | 15(4) |
| N(1B) | 40(4) | 33(4) | 51(4) | 15(3) | 20(3) | 17(3) |
| C(2B) | 58(6) | 30(5) | 85(7) | 26(5) | 10(5) | 14(4) |
| C(3B) | 60(6) | 41(5) | 87(7) | 35(5) | 27(6) | 30(5) |
| N(2B) | 43(4) | 48(4) | 43(4) | 26(3) | 19(3) | 26(3) |
| C(4B) | 61(6) | 69(7) | 46(5) | 30(5) | 12(5) | 24(5) |
| Ag(6) | 36(1) | 34(1) | 51(1) | 18(1) | 1(1) | 10(1) |
| C(1C) | 41(5) | 28(4) | 51(5) | 19(4) | 3(4) | 2(3) |
| N(1C) | 36(4) | 36(4) | 46(4) | 18(3) | -4(3) | 4(3) |
| C(2C) | 41(5) | 27(4) | 53(5) | 18(4) | 1(4) | 6(3) |
| C(3C) | 35(5) | 44(5) | 68(6) | 31(5) | -3(4) | 4(4) |
| N(2C) | 32(3) | 33(4) | 44(4) | 14(3) | -2(3) | 1(3) |
| C(4C) | 47(5) | 42(5) | 43(5) | 10(4) | -1(4) | -8(4) |
| C(1D) | 37(4) | 31(4) | 35(4) | 6(3) | -2(3) | 13(4) |
| N(1D) | 38(4) | 31(4) | 49(4) | 10(3) | -1(3) | 14(3) |
| C(2D) | 69(7) | 22(4) | 81(7) | -3(5) | 6(6) | 16(4) |
| C(3D) | 58(6) | 32(5) | 66(6) | 3(4) | 19(5) | 19(4) |
| N(2D) | 41(4) | 31(4) | 41(4) | 7(3) | 4(3) | 16(3) |
| C(4D) | 34(5) | 57(6) | 57(6) | 15(5) | -4(4) | 7(4) |

Table 23. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(\text{1-Me-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$.

| | x | y | z | U(eq) |
|--------|-------|-------|-------|-------|
| H(14A) | 5572 | 2091 | 2252 | 41 |
| H(15A) | 6752 | 2676 | 3153 | 50 |
| H(16A) | 6556 | 3941 | 3892 | 53 |
| H(17A) | 5135 | 4575 | 3752 | 49 |
| H(19A) | 3515 | 4609 | 3097 | 39 |
| H(21A) | 1923 | 4694 | 2445 | 51 |
| H(22A) | 823 | 4185 | 1527 | 53 |
| H(23A) | 874 | 2921 | 808 | 46 |
| H(24A) | 2330 | 2241 | 896 | 38 |
| H(14B) | 4739 | 1164 | -1334 | 29 |
| H(15B) | 3332 | 979 | -2083 | 39 |
| H(16B) | 3234 | 2019 | -2454 | 42 |
| H(17B) | 4540 | 3276 | -2044 | 41 |
| H(19B) | 6236 | 4166 | -1335 | 36 |
| H(21B) | 7857 | 5101 | -604 | 42 |
| H(22B) | 9126 | 5405 | 233 | 50 |
| H(23B) | 9260 | 4370 | 619 | 49 |
| H(24B) | 8111 | 3082 | 181 | 33 |
| H(14C) | 6384 | 657 | 1659 | 30 |
| H(15C) | 6329 | 1160 | 2699 | 34 |
| H(16C) | 7717 | 995 | 3354 | 38 |
| H(17C) | 9191 | 327 | 2930 | 35 |
| H(19C) | 10218 | -325 | 2028 | 31 |
| H(21C) | 11279 | -959 | 1128 | 37 |
| H(22C) | 11414 | -1431 | 82 | 38 |
| H(23C) | 9973 | -1335 | -578 | 36 |
| H(24C) | 8398 | -769 | -180 | 31 |
| H(14D) | 13285 | 2980 | 6569 | 34 |
| H(15D) | 14653 | 4189 | 6896 | 47 |
| H(16D) | 14632 | 5221 | 7879 | 54 |
| H(17D) | 13142 | 5034 | 8494 | 45 |
| H(19D) | 11349 | 4198 | 8654 | 37 |

| | | | | |
|--------|-------|-------|-------|----|
| H(21D) | 9574 | 3375 | 8871 | 38 |
| H(23D) | 8197 | 2167 | 8572 | 41 |
| H(23D) | 8247 | 1075 | 7642 | 35 |
| H(24D) | 9695 | 1210 | 6998 | 30 |
| H(14E) | 6601 | 738 | 5248 | 30 |
| H(14E) | 5018 | 1300 | 5176 | 35 |
| H(16E) | 3546 | 1337 | 5864 | 36 |
| H(18E) | 3680 | 842 | 6644 | 39 |
| H(19E) | 4759 | 204 | 7173 | 36 |
| H(22E) | 5840 | -415 | 7738 | 42 |
| H(21E) | 7345 | -1036 | 7792 | 41 |
| H(23E) | 8768 | -1167 | 7063 | 36 |
| H(24E) | 8657 | -671 | 6294 | 32 |
| H(14F) | 7253 | 2161 | 5319 | 37 |
| H(15F) | 5929 | 2837 | 5901 | 40 |
| H(16F) | 5743 | 4123 | 5892 | 45 |
| H(17F) | 6964 | 4759 | 5360 | 42 |
| H(19F) | 8580 | 4744 | 4684 | 41 |
| H(21F) | 10139 | 4732 | 3977 | 46 |
| H(22F) | 11575 | 4122 | 3464 | 57 |
| H(23F) | 11751 | 2826 | 3430 | 52 |
| H(24F) | 10567 | 2171 | 3962 | 42 |
| H(1A) | 7785 | 2090 | 1175 | 46 |
| H(2A) | 7855 | 4360 | 2323 | 62 |
| H(3A) | 9280 | 3833 | 2757 | 58 |
| H(4A1) | 9307 | 2100 | 2429 | 78 |
| H(4A2) | 10317 | 2480 | 2092 | 78 |
| H(4A3) | 9321 | 1700 | 1698 | 78 |
| H(1B) | 3828 | 2187 | 27 | 44 |
| H(2B) | 5099 | 4578 | 552 | 67 |
| H(3B) | 3486 | 4200 | -235 | 68 |
| H(4B1) | 2365 | 1948 | -833 | 82 |
| H(4B2) | 2382 | 2701 | -1048 | 82 |
| H(4B3) | 1606 | 2612 | -506 | 82 |
| H(1C) | 12548 | 2131 | 5014 | 47 |
| H(2C) | 12927 | 4513 | 5426 | 47 |
| H(3C) | 14320 | 4034 | 4669 | 56 |
| H(4C1) | 14009 | 2256 | 3839 | 73 |

| | | | | |
|--------|-------|------|------|----|
| H(4C2) | 14157 | 1820 | 4313 | 73 |
| H(4C3) | 15117 | 2607 | 4334 | 73 |
| H(2D) | 8695 | 2182 | 6217 | 42 |
| H(2D) | 9940 | 4541 | 7163 | 76 |
| H(3D) | 8235 | 4084 | 7671 | 66 |
| H(4D1) | 7051 | 1843 | 6862 | 77 |
| H(4D2) | 6365 | 2561 | 6958 | 77 |
| H(4D3) | 7055 | 2524 | 7533 | 77 |

X-ray Crystal Data for [Ag(2-Me-imidH)₂(9-aca)]

| | |
|-----------------------------------|---|
| Identification code | [Ag(2-Me-imidH) ₂ (9-aca)] |
| Empirical formula | C ₂₃ H ₂₁ Ag N ₄ O ₂ |
| Formula weight | 493.31 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | a = 19.8374(17) Å α = 90°. b = 15.2507(13) Å β = 110.140(1)°. c = 14.4941(13) Å γ = 90°. |
| Volume | 4116.8(6) Å ³ |
| Z | 8 |
| Density (calculated) | 1.592 Mg/m ³ |
| Absorption coefficient | 1.007 mm ⁻¹ |
| F(000) | 2000 |
| Crystal size | 0.28 x 0.14 x 0.13 mm ³ |
| Crystal description | colourless pyramid |
| Theta range for data collection | 1.73 to 28.35°. |
| Index ranges | -26 ≤ h ≤ 26, -20 ≤ k ≤ 20, -19 ≤ l ≤ 19 |
| Reflections collected | 20857 |
| Independent reflections | 5142 [R(int) = 0.0541] |
| Completeness to theta = 28.35° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8803 and 0.7658 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 5142 / 0 / 273 |
| Goodness-of-fit on F ² | 1.030 |
| Final R indices [I > 2σ(I)] | R1 = 0.0345, wR2 = 0.0715 |
| R indices (all data) | R1 = 0.0541, wR2 = 0.0787 |
| Largest diff. peak and hole | 0.680 and -0.407 e.Å ⁻³ |

Table 24. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(2\text{-Me-imidH})_2(9\text{-aca})]$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|-------|---------|---------|----------|-------|
| Ag(1) | 4366(1) | 1099(1) | 9399(1) | 27(1) |
| O(1) | 3649(1) | 1507(1) | 7673(1) | 37(1) |
| O(2) | 2646(1) | 1832(1) | 6455(1) | 36(1) |
| C(1) | 3066(2) | 1893(2) | 7332(2) | 28(1) |
| C(2) | 2840(2) | 2505(2) | 8000(2) | 29(1) |
| C(3) | 3217(2) | 3293(2) | 8323(2) | 33(1) |
| C(4) | 3833(2) | 3527(2) | 8089(2) | 40(1) |
| C(5) | 4195(2) | 4282(2) | 8428(3) | 50(1) |
| C(6) | 3963(2) | 4869(2) | 9018(3) | 54(1) |
| C(7) | 3378(2) | 4672(2) | 9250(2) | 48(1) |
| C(8) | 2985(2) | 3883(2) | 8920(2) | 37(1) |
| C(9) | 2396(2) | 3660(2) | 9182(2) | 39(1) |
| C(10) | 2020(2) | 2884(2) | 8878(2) | 36(1) |
| C(11) | 1418(2) | 2656(2) | 9148(2) | 41(1) |
| C(12) | 1056(2) | 1901(2) | 8852(2) | 47(1) |
| C(13) | 1268(2) | 1310(2) | 8244(2) | 42(1) |
| C(14) | 1842(2) | 1501(2) | 7965(2) | 36(1) |
| C(15) | 2240(2) | 2292(2) | 8260(2) | 30(1) |
| N(21) | 5238(1) | 1981(1) | 9699(2) | 26(1) |
| C(21) | 5729(1) | 2136(2) | 10573(2) | 27(1) |
| C(22) | 5707(2) | 1782(2) | 11519(2) | 36(1) |
| N(22) | 6242(1) | 2665(2) | 10476(2) | 30(1) |
| C(23) | 6081(2) | 2847(2) | 9502(2) | 34(1) |
| C(24) | 5457(2) | 2423(2) | 9028(2) | 35(1) |
| N(31) | 3679(1) | 96(1) | 9552(2) | 26(1) |
| C(31) | 3689(1) | -284(2) | 10383(2) | 24(1) |
| C(32) | 4207(2) | -99(2) | 11375(2) | 32(1) |
| N(32) | 3147(1) | -861(2) | 10203(2) | 28(1) |
| C(33) | 2774(2) | -857(2) | 9212(2) | 32(1) |
| C(34) | 3100(1) | -266(2) | 8811(2) | 29(1) |

Table 25. Bond lengths [Å] and angles [°] for [Ag(2-Me-imidH)₂(9-aca)].

| | | | |
|---------------------|------------|-------------------|------------|
| Ag(1)-N(31) | 2.111(2) | C(10)-C(15) | 1.441(4) |
| Ag(1)-N(21) | 2.115(2) | C(11)-C(12) | 1.346(5) |
| Ag(1)-O(1) | 2.4941(19) | C(12)-C(13) | 1.423(4) |
| Ag(1) ... Ag(1)#1 | 4.1930(5) | C(13)-C(14) | 1.364(4) |
| O(1)-C(1) | 1.239(3) | C(14)-C(15) | 1.424(4) |
| O(2)-C(1) | 1.261(3) | N(21)-C(21) | 1.327(3) |
| C(1)-C(2) | 1.520(4) | N(21)-C(24) | 1.372(3) |
| C(2)-C(15) | 1.403(4) | C(21)-N(22) | 1.344(3) |
| C(2)-C(3) | 1.408(4) | C(21)-C(22) | 1.487(4) |
| C(3)-C(4) | 1.421(4) | N(22)-C(23) | 1.363(4) |
| C(3)-C(8) | 1.430(4) | C(23)-C(24) | 1.355(4) |
| C(4)-C(5) | 1.357(5) | N(31)-C(31) | 1.329(3) |
| C(5)-C(6) | 1.420(5) | N(31)-C(34) | 1.388(3) |
| C(6)-C(7) | 1.350(5) | C(31)-N(32) | 1.344(3) |
| C(7)-C(8) | 1.424(5) | C(31)-C(32) | 1.478(4) |
| C(8)-C(9) | 1.390(5) | N(32)-C(33) | 1.370(4) |
| C(9)-C(10) | 1.387(4) | C(33)-C(34) | 1.353(4) |
| C(10)-C(11) | 1.423(4) | | |
| N(31)-Ag(1)-N(21) | 162.07(9) | C(7)-C(6)-C(5) | 119.7(4) |
| N(31)-Ag(1)-O(1) | 96.93(8) | C(6)-C(7)-C(8) | 121.5(3) |
| N(21)-Ag(1)-O(1) | 101.00(8) | C(9)-C(8)-C(7) | 121.9(3) |
| N(31)-Ag(1)-Ag(1)#1 | 72.16(6) | C(9)-C(8)-C(3) | 119.2(3) |
| N(21)-Ag(1)-Ag(1)#1 | 95.26(6) | C(7)-C(8)-C(3) | 118.8(3) |
| O(1)-Ag(1)-Ag(1)#1 | 132.01(5) | C(10)-C(9)-C(8) | 122.1(3) |
| C(1)-O(1)-Ag(1) | 130.54(17) | C(9)-C(10)-C(11) | 122.1(3) |
| O(1)-C(1)-O(2) | 124.7(2) | C(9)-C(10)-C(15) | 119.2(3) |
| O(1)-C(1)-C(2) | 118.6(2) | C(11)-C(10)-C(15) | 118.7(3) |
| O(2)-C(1)-C(2) | 116.7(2) | C(12)-C(11)-C(10) | 121.9(3) |
| C(15)-C(2)-C(3) | 120.8(3) | C(11)-C(12)-C(13) | 119.9(3) |
| C(15)-C(2)-C(1) | 119.5(3) | C(14)-C(13)-C(12) | 120.3(3) |
| C(3)-C(2)-C(1) | 119.7(3) | C(13)-C(14)-C(15) | 121.7(3) |
| C(2)-C(3)-C(4) | 122.6(3) | C(2)-C(15)-C(14) | 123.4(3) |
| C(2)-C(3)-C(8) | 119.5(3) | C(2)-C(15)-C(10) | 119.1(3) |
| C(4)-C(3)-C(8) | 117.9(3) | C(14)-C(15)-C(10) | 117.5(3) |
| C(5)-C(4)-C(3) | 121.3(3) | C(21)-N(21)-C(24) | 106.4(2) |
| C(4)-C(5)-C(6) | 120.8(3) | C(21)-N(21)-Ag(1) | 126.10(18) |

| | | | |
|-------------------|------------|-------------------|------------|
| C(24)-N(21)-Ag(1) | 127.13(19) | C(31)-N(31)-Ag(1) | 126.98(19) |
| N(21)-C(21)-N(22) | 109.9(2) | C(34)-N(31)-Ag(1) | 126.72(18) |
| N(21)-C(21)-C(22) | 124.8(2) | N(31)-C(31)-N(32) | 110.4(2) |
| N(22)-C(21)-C(22) | 125.3(3) | N(31)-C(31)-C(32) | 125.9(2) |
| C(21)-N(22)-C(23) | 108.4(2) | N(32)-C(31)-C(32) | 123.7(2) |
| C(24)-C(23)-N(22) | 106.0(3) | C(31)-N(32)-C(33) | 107.9(2) |
| C(23)-C(24)-N(21) | 109.4(3) | C(34)-C(33)-N(32) | 106.7(2) |
| C(31)-N(31)-C(34) | 106.2(2) | C(33)-C(34)-N(31) | 108.8(2) |

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+2

Table 26. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(\text{2-Me-imidH})_2(\text{9-aca})]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U^{11} | U^{22} | U^{33} | U^{23} | U^{13} | U^{12} |
|-------|----------|----------|----------|----------|----------|----------|
| Ag(1) | 25(1) | 32(1) | 24(1) | -2(1) | 9(1) | -5(1) |
| O(1) | 36(1) | 50(1) | 23(1) | 1(1) | 7(1) | 21(1) |
| O(2) | 32(1) | 49(1) | 22(1) | -5(1) | 4(1) | 14(1) |
| C(1) | 29(2) | 35(2) | 21(1) | 2(1) | 11(1) | 9(1) |
| C(2) | 29(2) | 37(2) | 17(1) | 4(1) | 4(1) | 16(1) |
| C(3) | 38(2) | 37(2) | 21(1) | 3(1) | 6(1) | 14(1) |
| C(4) | 40(2) | 43(2) | 35(2) | 1(2) | 12(2) | 9(2) |
| C(5) | 46(2) | 46(2) | 53(2) | 9(2) | 13(2) | 4(2) |
| C(6) | 59(2) | 40(2) | 54(2) | 1(2) | 7(2) | 6(2) |
| C(7) | 61(2) | 40(2) | 39(2) | -3(2) | 11(2) | 10(2) |
| C(8) | 41(2) | 38(2) | 26(2) | -1(1) | 5(1) | 15(2) |
| C(9) | 48(2) | 42(2) | 25(2) | 1(1) | 11(1) | 23(2) |
| C(10) | 39(2) | 47(2) | 20(1) | 5(1) | 10(1) | 21(2) |
| C(11) | 48(2) | 51(2) | 26(2) | 5(2) | 17(2) | 19(2) |
| C(12) | 41(2) | 65(2) | 40(2) | 16(2) | 21(2) | 19(2) |
| C(13) | 41(2) | 45(2) | 40(2) | 5(2) | 16(2) | 9(2) |
| C(14) | 37(2) | 42(2) | 30(2) | 4(1) | 12(1) | 13(2) |
| C(15) | 34(2) | 37(2) | 16(1) | 2(1) | 5(1) | 14(1) |
| N(21) | 23(1) | 31(1) | 22(1) | 0(1) | 5(1) | -4(1) |
| C(21) | 24(2) | 29(2) | 26(1) | -2(1) | 8(1) | -1(1) |

| | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|
| C(22) | 38(2) | 44(2) | 23(2) | 0(1) | 7(1) | -7(2) |
| N(22) | 26(1) | 34(1) | 27(1) | -2(1) | 6(1) | -6(1) |
| C(23) | 32(2) | 38(2) | 33(2) | 6(1) | 13(1) | -4(1) |
| C(24) | 31(2) | 47(2) | 25(2) | 7(1) | 7(1) | -2(1) |
| N(31) | 25(1) | 26(1) | 26(1) | 2(1) | 9(1) | -1(1) |
| C(31) | 25(1) | 24(1) | 24(1) | 1(1) | 8(1) | 1(1) |
| C(32) | 36(2) | 35(2) | 23(2) | 1(1) | 9(1) | -7(1) |
| N(32) | 28(1) | 31(1) | 26(1) | 4(1) | 11(1) | -2(1) |
| C(33) | 26(2) | 37(2) | 29(2) | -3(1) | 6(1) | -7(1) |
| C(34) | 27(2) | 35(2) | 25(2) | 1(1) | 6(1) | -1(1) |

Table 27. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(2\text{-Me-imidH})_2(9\text{-aca})]$.

| | x | y | z | U(eq) |
|--------|------|-------|-------|-------|
| H(4) | 3993 | 3149 | 7687 | 48 |
| H(5) | 4609 | 4420 | 8269 | 59 |
| H(6) | 4219 | 5397 | 9249 | 65 |
| H(7) | 3224 | 5069 | 9643 | 58 |
| H(9) | 2246 | 4051 | 9584 | 46 |
| H(11) | 1267 | 3048 | 9548 | 49 |
| H(12) | 658 | 1763 | 9050 | 56 |
| H(13) | 1009 | 780 | 8031 | 50 |
| H(14) | 1979 | 1096 | 7564 | 44 |
| H(22A) | 5533 | 2237 | 11859 | 54 |
| H(22B) | 6191 | 1600 | 11932 | 54 |
| H(22C) | 5384 | 1276 | 11389 | 54 |
| H(22) | 6618 | 2860 | 10958 | 36 |
| H(23) | 6351 | 3200 | 9215 | 41 |
| H(24) | 5210 | 2431 | 8338 | 42 |
| H(32A) | 4697 | -160 | 11369 | 48 |
| H(32B) | 4132 | -514 | 11846 | 48 |
| H(32C) | 4135 | 501 | 11566 | 48 |
| H(32) | 3049 | -1184 | 10643 | 33 |
| H(33) | 2365 | -1203 | 8873 | 38 |
| H(34) | 2956 | -121 | 8133 | 35 |

Table 28. Hydrogen bonds for [Ag(2-Me-imidH)₂(9-aca)] [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|----------------------|--------|----------|----------|--------|
| N(22)-H(22)...O(2)#2 | 0.88 | 1.97 | 2.764(3) | 149.1 |
| N(32)-H(32)...O(2)#3 | 0.88 | 1.91 | 2.779(3) | 168.8 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+2 #2 x+1/2,-y+1/2,z+1/2 #3 x,-y,z+1/2

X-ray Crystal Data for [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆]

| | |
|-----------------------------------|--|
| Identification code | [Ag(1-Bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] |
| Empirical formula | C ₁₁₈ H ₁₀₂ Ag ₆ N ₈ O ₁₂ |
| Formula weight | 2471.30 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | a = 17.6333(7) Å α = 96.019(1)°. b = 19.3853(8) Å β = 95.831(1)°. c = 30.4753(13) Å γ = 90.237(1)°. |
| Volume | 10305.1(7) Å ³ |
| Z | 4 |
| Density (calculated) | 1.593 Mg/m ³ |
| Absorption coefficient | 1.185 mm ⁻¹ |
| F(000) | 4976 |
| Crystal size | 0.32 x 0.19 x 0.12 mm ³ |
| Crystal description | Colourless block |
| Theta range for data collection | 0.68 to 26.00°. |
| Index ranges | -21 ≤ h ≤ 21, -23 ≤ k ≤ 23, -37 ≤ l ≤ 37 |
| Reflections collected | 89958 |
| Independent reflections | 40407 [R(int) = 0.0422] |
| Completeness to theta = 26.00° | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.4311 and 0.3430 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 40407 / 3021 / 2665 |
| Goodness-of-fit on F ² | 1.068 |
| Final R indices [I > 2σ(I)] | R1 = 0.0505, wR2 = 0.1130 |
| R indices (all data) | R1 = 0.0739, wR2 = 0.1229 |
| Largest diff. peak and hole | 1.703 and -0.977 e.Å ⁻³ |

Table 29. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(\text{1-Bu-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|--------|---------|----------|---------|-------|
| Ag(1) | 5749(1) | -404(1) | 7502(1) | 41(1) |
| Ag(2) | 4521(1) | 304(1) | 7031(1) | 22(1) |
| Ag(3) | 3603(1) | 1295(1) | 7500(1) | 38(1) |
| Ag(4) | 4754(1) | 511(1) | 7971(1) | 24(1) |
| O(1A) | 6167(2) | -593(2) | 6842(1) | 39(1) |
| O(2A) | 4998(2) | -483(2) | 6497(1) | 34(1) |
| C(1A) | 5691(3) | -608(3) | 6501(2) | 29(1) |
| C(2A) | 5994(3) | -783(3) | 6055(2) | 27(1) |
| C(3A) | 6551(3) | -344(3) | 5920(2) | 31(1) |
| C(4A) | 6865(3) | 250(3) | 6189(2) | 37(1) |
| C(5A) | 7411(4) | 640(4) | 6052(2) | 48(2) |
| C(6A) | 7676(4) | 479(4) | 5629(2) | 53(2) |
| C(7A) | 7373(4) | -68(4) | 5356(2) | 47(2) |
| C(8A) | 6802(4) | -500(3) | 5488(2) | 37(1) |
| C(9A) | 6504(3) | -1082(3) | 5217(2) | 36(1) |
| C(10A) | 5978(3) | -1529(3) | 5351(2) | 33(1) |
| C(11A) | 5692(4) | -2127(3) | 5073(2) | 39(1) |
| C(12A) | 5198(4) | -2559(3) | 5212(2) | 47(2) |
| C(13A) | 4939(4) | -2436(3) | 5635(2) | 49(2) |
| C(14A) | 5184(4) | -1855(3) | 5911(2) | 38(1) |
| C(15A) | 5712(3) | -1375(3) | 5778(2) | 32(1) |
| O(1B) | 3611(2) | 750(2) | 6518(1) | 41(1) |
| O(2B) | 2713(2) | 1137(2) | 6941(1) | 44(1) |
| C(1B) | 2958(3) | 966(3) | 6575(2) | 29(1) |
| C(2B) | 2436(3) | 1045(3) | 6161(2) | 27(1) |
| C(3B) | 1881(3) | 547(3) | 5998(2) | 32(1) |
| C(4B) | 1723(3) | -38(3) | 6227(2) | 39(1) |
| C(5B) | 1174(4) | -511(4) | 6052(3) | 53(2) |
| C(6B) | 764(4) | -450(4) | 5639(3) | 60(2) |
| C(7B) | 892(4) | 87(4) | 5408(2) | 50(2) |
| C(8B) | 1443(3) | 621(3) | 5577(2) | 34(1) |
| C(9B) | 1556(3) | 1187(3) | 5355(2) | 37(1) |

| | | | | |
|--------|---------|----------|---------|-------|
| C(10B) | 2085(3) | 1719(3) | 5534(2) | 32(1) |
| C(11B) | 2189(4) | 2315(3) | 5324(2) | 39(1) |
| C(12B) | 2684(4) | 2824(3) | 5501(2) | 43(2) |
| C(13B) | 3120(4) | 2759(3) | 5913(2) | 43(2) |
| C(14B) | 3057(3) | 2178(3) | 6123(2) | 38(1) |
| C(15B) | 2531(3) | 1640(3) | 5941(2) | 28(1) |
| O(1C) | 3830(2) | 2059(2) | 8074(1) | 38(1) |
| O(2C) | 4483(2) | 1367(2) | 8513(1) | 41(1) |
| C(1C) | 4061(3) | 1850(3) | 8445(2) | 32(1) |
| C(2C) | 3742(3) | 2233(3) | 8846(2) | 32(1) |
| C(3C) | 3011(3) | 2037(3) | 8925(2) | 31(1) |
| C(4C) | 2564(3) | 1521(3) | 8642(2) | 38(1) |
| C(5C) | 1863(4) | 1338(4) | 8726(2) | 47(2) |
| C(6C) | 1548(4) | 1645(4) | 9111(2) | 50(2) |
| C(7C) | 1950(4) | 2135(4) | 9389(2) | 48(2) |
| C(8C) | 2692(3) | 2358(3) | 9307(2) | 34(1) |
| C(9C) | 3127(4) | 2857(3) | 9593(2) | 39(1) |
| C(10C) | 3854(4) | 3042(3) | 9518(2) | 38(1) |
| C(11C) | 4332(5) | 3527(3) | 9817(2) | 51(2) |
| C(12C) | 5036(5) | 3684(4) | 9742(2) | 58(2) |
| C(13C) | 5349(4) | 3384(3) | 9365(2) | 53(2) |
| C(14C) | 4940(4) | 2920(3) | 9065(2) | 46(2) |
| C(15C) | 4182(3) | 2727(3) | 9134(2) | 34(1) |
| O(1D) | 5393(3) | -72(2) | 8500(1) | 57(1) |
| O(2D) | 6025(3) | -870(3) | 8132(1) | 67(2) |
| C(1D) | 5835(3) | -560(3) | 8478(2) | 32(1) |
| C(2D) | 6150(3) | -799(3) | 8916(2) | 30(1) |
| C(3D) | 5688(3) | -1211(3) | 9136(2) | 34(1) |
| C(4D) | 4965(4) | -1475(3) | 8941(2) | 45(2) |
| C(5D) | 4537(4) | -1894(4) | 9140(3) | 61(2) |
| C(6D) | 4788(5) | -2064(4) | 9571(3) | 73(2) |
| C(7D) | 5469(5) | -1818(4) | 9778(3) | 62(2) |
| C(8D) | 5950(4) | -1388(3) | 9566(2) | 43(2) |
| C(9D) | 6651(4) | -1168(4) | 9757(2) | 49(2) |
| C(10D) | 7137(4) | -765(3) | 9548(2) | 45(2) |
| C(11D) | 7861(4) | -525(4) | 9749(3) | 64(2) |
| C(12D) | 8318(5) | -157(4) | 9541(3) | 73(2) |
| C(13D) | 8094(5) | 15(4) | 9112(3) | 74(2) |

| | | | | |
|--------|---------|----------|---------|-------|
| C(14D) | 7383(4) | -177(4) | 8897(3) | 56(2) |
| C(15D) | 6872(3) | -576(3) | 9112(2) | 35(1) |
| O(1E) | 5261(2) | 1249(2) | 7133(1) | 41(1) |
| O(2E) | 5898(2) | 923(2) | 7748(1) | 36(1) |
| C(1E) | 5797(3) | 1296(3) | 7447(2) | 29(1) |
| C(2E) | 6360(3) | 1885(3) | 7435(2) | 32(1) |
| C(3E) | 6119(3) | 2566(3) | 7527(2) | 32(1) |
| C(4E) | 5403(4) | 2735(3) | 7678(2) | 41(1) |
| C(5E) | 5207(4) | 3407(4) | 7800(2) | 52(2) |
| C(6E) | 5723(4) | 3961(4) | 7757(3) | 60(2) |
| C(7E) | 6408(4) | 3830(4) | 7609(3) | 54(2) |
| C(8E) | 6652(4) | 3131(3) | 7496(2) | 40(1) |
| C(9E) | 7367(4) | 2980(3) | 7372(2) | 43(2) |
| C(10E) | 7616(4) | 2305(4) | 7295(2) | 42(1) |
| C(11E) | 8381(4) | 2151(4) | 7205(2) | 54(2) |
| C(12E) | 8624(4) | 1487(4) | 7156(2) | 59(2) |
| C(13E) | 8128(4) | 933(4) | 7192(2) | 56(2) |
| C(14E) | 7383(4) | 1051(4) | 7268(2) | 45(2) |
| C(15E) | 7110(3) | 1740(3) | 7333(2) | 36(1) |
| O(1F) | 3811(2) | -525(2) | 7248(1) | 39(1) |
| O(2F) | 3492(2) | 78(2) | 7867(1) | 36(1) |
| C(1F) | 3434(3) | -423(3) | 7563(2) | 32(1) |
| C(2F) | 2822(4) | -973(3) | 7592(2) | 38(1) |
| C(3F) | 3081(4) | -1638(3) | 7678(2) | 42(1) |
| C(4F) | 3848(4) | -1800(4) | 7776(2) | 54(2) |
| C(5F) | 4076(6) | -2446(4) | 7861(3) | 70(2) |
| C(6F) | 3539(7) | -2990(5) | 7839(3) | 85(3) |
| C(7F) | 2803(7) | -2875(4) | 7742(3) | 82(2) |
| C(8F) | 2513(5) | -2194(4) | 7659(2) | 61(2) |
| C(9F) | 1757(5) | -2048(5) | 7561(3) | 70(2) |
| C(10F) | 1504(4) | -1395(5) | 7490(2) | 60(2) |
| C(11F) | 719(5) | -1241(6) | 7388(3) | 81(2) |
| C(12F) | 486(5) | -604(7) | 7325(3) | 93(3) |
| C(13F) | 1013(5) | -61(6) | 7337(3) | 78(2) |
| C(14F) | 1784(4) | -167(4) | 7427(2) | 53(2) |
| C(15F) | 2054(4) | -829(4) | 7504(2) | 48(2) |
| Ag(5) | 4130(1) | -67(1) | 5795(1) | 37(1) |
| C(21A) | 5073(3) | 1236(3) | 6045(2) | 38(1) |

| | | | | |
|--------|----------|----------|---------|--------|
| N(1A) | 4899(3) | 740(3) | 5715(2) | 35(1) |
| C(22A) | 5372(3) | 855(3) | 5398(2) | 36(1) |
| C(23A) | 5806(3) | 1411(3) | 5533(2) | 37(1) |
| N(2A) | 5622(3) | 1655(3) | 5949(2) | 38(1) |
| C(24A) | 5916(5) | 2282(4) | 6231(2) | 64(2) |
| C(25A) | 5384(6) | 2922(4) | 6140(3) | 84(3) |
| C(26A) | 5545(6) | 3539(5) | 6433(3) | 88(3) |
| C(27A) | 5040(6) | 4117(5) | 6317(4) | 98(3) |
| C(21B) | 3230(3) | -1143(3) | 6207(2) | 35(1) |
| N(1B) | 3335(3) | -870(2) | 5841(2) | 34(1) |
| C(22B) | 2823(4) | -1204(3) | 5516(2) | 40(2) |
| C(23B) | 2422(4) | -1676(3) | 5694(2) | 41(2) |
| N(2B) | 2680(3) | -1631(3) | 6137(2) | 39(1) |
| C(24B) | 2415(4) | -2050(3) | 6465(2) | 46(2) |
| C(25B) | 2641(4) | -2801(3) | 6384(2) | 48(2) |
| C(26B) | 3478(4) | -2911(4) | 6448(2) | 54(2) |
| C(27B) | 3703(5) | -3651(4) | 6286(3) | 66(2) |
| Ag(6) | 5148(1) | 719(1) | 9215(1) | 41(1) |
| C(21C) | 6323(3) | 1599(3) | 8820(2) | 38(1) |
| N(1C) | 6101(3) | 1387(3) | 9187(2) | 42(1) |
| C(22C) | 6512(4) | 1785(4) | 9529(2) | 48(2) |
| C(23C) | 6974(4) | 2227(4) | 9370(2) | 49(2) |
| N(2C) | 6853(3) | 2109(3) | 8915(2) | 43(1) |
| C(24C) | 7250(4) | 2453(4) | 8597(2) | 53(2) |
| C(25C) | 8016(5) | 2170(6) | 8532(3) | 85(3) |
| C(26C) | 8500(10) | 1840(10) | 8833(7) | 79(5) |
| C(27C) | 9180(20) | 1436(19) | 8674(9) | 90(10) |
| C(25X) | 8016(5) | 2170(6) | 8532(3) | 85(3) |
| C(26X) | 8176(9) | 1521(9) | 8448(5) | 60(3) |
| C(27X) | 9040(20) | 1340(20) | 8448(8) | 94(9) |
| C(21D) | 3678(4) | -111(3) | 8970(2) | 40(1) |
| N(1D) | 4190(3) | 92(3) | 9300(2) | 42(1) |
| C(22D) | 3971(4) | -212(3) | 9656(2) | 45(2) |
| C(23D) | 3320(4) | -581(4) | 9533(2) | 45(2) |
| N(2D) | 3137(3) | -525(3) | 9089(2) | 42(1) |
| C(24D) | 2467(4) | -795(4) | 8812(2) | 52(2) |
| C(25D) | 1737(4) | -461(4) | 8967(2) | 50(2) |
| C(26D) | 1050(4) | -636(4) | 8640(3) | 59(2) |

| | | | | |
|--------|----------|----------|---------|-------|
| C(27D) | 342(4) | -262(5) | 8790(3) | 74(2) |
| Ag(7) | 8305(1) | -5328(1) | 7538(1) | 40(1) |
| Ag(8) | 9389(1) | -4645(1) | 7032(1) | 23(1) |
| Ag(9) | 10424(1) | -3586(1) | 7457(1) | 41(1) |
| Ag(10) | 9561(1) | -4475(1) | 7966(1) | 24(1) |
| O(1G) | 7596(2) | -5428(2) | 6898(1) | 39(1) |
| O(2G) | 8564(2) | -5279(2) | 6506(1) | 42(1) |
| C(1G) | 7896(3) | -5431(3) | 6546(2) | 26(1) |
| C(2G) | 7402(3) | -5662(3) | 6118(2) | 26(1) |
| C(3G) | 7509(3) | -6329(3) | 5909(2) | 26(1) |
| C(4G) | 8014(3) | -6811(3) | 6094(2) | 34(1) |
| C(5G) | 8095(4) | -7459(3) | 5892(2) | 40(1) |
| C(6G) | 7687(4) | -7658(3) | 5472(2) | 44(2) |
| C(7G) | 7195(3) | -7221(3) | 5278(2) | 37(1) |
| C(8G) | 7077(3) | -6547(3) | 5487(2) | 31(1) |
| C(9G) | 6579(3) | -6084(3) | 5303(2) | 34(1) |
| C(10G) | 6455(3) | -5430(3) | 5506(2) | 35(1) |
| C(11G) | 5928(3) | -4964(4) | 5322(2) | 45(2) |
| C(12G) | 5788(4) | -4338(4) | 5544(3) | 56(2) |
| C(13G) | 6173(4) | -4139(3) | 5968(2) | 49(2) |
| C(14G) | 6704(3) | -4558(3) | 6153(2) | 39(1) |
| C(15G) | 6867(3) | -5211(3) | 5936(2) | 29(1) |
| O(1H) | 9931(2) | -4027(2) | 6501(1) | 37(1) |
| O(2H) | 11043(3) | -3653(2) | 6862(1) | 48(1) |
| C(1H) | 10610(3) | -3841(3) | 6516(2) | 31(1) |
| C(2H) | 10940(3) | -3835(3) | 6075(2) | 31(1) |
| C(3H) | 10686(3) | -3340(3) | 5784(2) | 32(1) |
| C(4H) | 10152(4) | -2817(3) | 5894(2) | 41(2) |
| C(5H) | 9925(4) | -2348(4) | 5608(2) | 50(2) |
| C(6H) | 10212(4) | -2380(4) | 5186(2) | 51(2) |
| C(7H) | 10707(4) | -2872(4) | 5067(2) | 44(2) |
| C(8H) | 10973(3) | -3370(3) | 5361(2) | 36(1) |
| C(9H) | 11497(3) | -3873(3) | 5244(2) | 40(1) |
| C(10H) | 11776(3) | -4340(3) | 5535(2) | 38(1) |
| C(11H) | 12348(4) | -4827(4) | 5426(2) | 48(2) |
| C(12H) | 12629(4) | -5252(4) | 5722(2) | 50(2) |
| C(13H) | 12342(4) | -5263(3) | 6141(2) | 50(2) |
| C(14H) | 11782(4) | -4815(3) | 6251(2) | 41(1) |

| | | | | |
|--------|----------|----------|---------|-------|
| C(15H) | 11484(3) | -4324(3) | 5960(2) | 34(1) |
| O(1I) | 10515(2) | -2937(2) | 8089(1) | 40(1) |
| O(2I) | 10023(3) | -3648(2) | 8520(1) | 45(1) |
| C(1I) | 10430(3) | -3155(3) | 8457(2) | 31(1) |
| C(2I) | 10899(3) | -2791(3) | 8858(2) | 29(1) |
| C(3I) | 11650(3) | -2995(3) | 8938(2) | 33(1) |
| C(4I) | 11995(4) | -3512(3) | 8659(2) | 39(1) |
| C(5I) | 12727(4) | -3702(4) | 8745(2) | 47(2) |
| C(6I) | 13171(4) | -3381(4) | 9131(3) | 56(2) |
| C(7I) | 12875(4) | -2903(4) | 9404(2) | 49(2) |
| C(8I) | 12113(4) | -2668(3) | 9324(2) | 38(1) |
| C(9I) | 11789(4) | -2169(3) | 9606(2) | 44(2) |
| C(10I) | 11033(4) | -1981(3) | 9531(2) | 39(1) |
| C(11I) | 10679(5) | -1483(3) | 9829(2) | 54(2) |
| C(12I) | 9942(5) | -1327(4) | 9754(2) | 60(2) |
| C(13I) | 9502(4) | -1624(4) | 9375(3) | 58(2) |
| C(14I) | 9800(4) | -2099(3) | 9074(2) | 44(2) |
| C(15I) | 10571(4) | -2294(3) | 9146(2) | 36(1) |
| O(1J) | 9065(3) | -5065(2) | 8493(1) | 50(1) |
| O(2J) | 8275(3) | -5862(3) | 8139(2) | 66(2) |
| C(1J) | 8622(3) | -5558(3) | 8481(2) | 36(1) |
| C(2J) | 8486(3) | -5800(3) | 8921(2) | 32(1) |
| C(3J) | 9040(3) | -6231(3) | 9120(2) | 31(1) |
| C(4J) | 9661(4) | -6496(3) | 8897(2) | 40(1) |
| C(5J) | 10165(4) | -6938(4) | 9079(3) | 58(2) |
| C(6J) | 10083(4) | -7117(4) | 9510(3) | 65(2) |
| C(7J) | 9526(4) | -6869(4) | 9743(2) | 57(2) |
| C(8J) | 8953(4) | -6417(3) | 9555(2) | 41(1) |
| C(9J) | 8347(4) | -6182(3) | 9772(2) | 46(2) |
| C(10J) | 7782(4) | -5778(3) | 9580(2) | 48(2) |
| C(11J) | 7157(5) | -5536(4) | 9809(3) | 64(2) |
| C(12J) | 6630(5) | -5137(4) | 9624(4) | 79(2) |
| C(13J) | 6656(5) | -4967(4) | 9189(4) | 80(3) |
| C(14J) | 7271(4) | -5161(4) | 8946(3) | 66(2) |
| C(15J) | 7852(4) | -5574(3) | 9138(2) | 42(1) |
| O(1K) | 10232(2) | -5455(2) | 7182(1) | 44(1) |
| O(2K) | 10740(2) | -4910(2) | 7827(1) | 44(1) |
| C(1K) | 10721(4) | -5389(3) | 7511(2) | 39(1) |

| | | | | |
|--------|----------|----------|---------|-------|
| C(2K) | 11336(3) | -5922(3) | 7517(2) | 41(1) |
| C(3K) | 12085(4) | -5743(4) | 7434(2) | 47(2) |
| C(4K) | 12308(4) | -5068(4) | 7381(2) | 55(2) |
| C(5K) | 13041(4) | -4909(5) | 7292(3) | 69(2) |
| C(6K) | 13570(5) | -5439(6) | 7261(3) | 85(3) |
| C(7K) | 13374(5) | -6104(6) | 7292(3) | 80(2) |
| C(8K) | 12634(4) | -6291(5) | 7394(2) | 58(2) |
| C(9K) | 12418(5) | -6959(4) | 7459(3) | 67(2) |
| C(10K) | 11709(5) | -7121(4) | 7564(2) | 58(2) |
| C(11K) | 11498(6) | -7809(4) | 7658(3) | 76(2) |
| C(12K) | 10811(6) | -7943(4) | 7768(3) | 75(2) |
| C(13K) | 10249(5) | -7429(4) | 7796(2) | 61(2) |
| C(14K) | 10410(4) | -6781(4) | 7707(2) | 47(2) |
| C(15K) | 11145(4) | -6589(3) | 7597(2) | 42(1) |
| O(1L) | 8325(2) | -4028(2) | 7804(1) | 34(1) |
| O(2L) | 8762(2) | -3657(2) | 7205(1) | 37(1) |
| C(1L) | 8317(3) | -3642(3) | 7508(2) | 27(1) |
| C(2L) | 7737(3) | -3061(3) | 7496(2) | 31(1) |
| C(3L) | 6971(3) | -3230(3) | 7383(2) | 35(1) |
| C(4L) | 6679(4) | -3930(4) | 7309(2) | 45(2) |
| C(5L) | 5924(4) | -4068(4) | 7212(3) | 59(2) |
| C(6L) | 5398(4) | -3527(5) | 7168(3) | 71(2) |
| C(7L) | 5639(4) | -2852(5) | 7226(2) | 59(2) |
| C(8L) | 6437(4) | -2678(4) | 7341(2) | 43(1) |
| C(9L) | 6685(4) | -2005(4) | 7415(2) | 50(2) |
| C(10L) | 7457(4) | -1820(3) | 7551(2) | 39(1) |
| C(11L) | 7712(5) | -1125(4) | 7654(3) | 59(2) |
| C(12L) | 8440(5) | -976(4) | 7807(3) | 60(2) |
| C(13L) | 8993(4) | -1511(4) | 7865(2) | 52(2) |
| C(14L) | 8762(4) | -2186(3) | 7756(2) | 42(1) |
| C(15L) | 8011(3) | -2368(3) | 7596(2) | 33(1) |
| Ag(11) | 9125(1) | -4682(1) | 5785(1) | 37(1) |
| C(21E) | 10069(4) | -5868(3) | 6077(2) | 43(2) |
| N(1E) | 9887(3) | -5518(3) | 5735(2) | 37(1) |
| C(22E) | 10362(3) | -5753(3) | 5425(2) | 40(1) |
| C(23E) | 10815(3) | -6243(3) | 5580(2) | 40(1) |
| N(2E) | 10633(3) | -6306(3) | 5998(2) | 41(1) |
| C(24E) | 10942(5) | -6797(4) | 6297(3) | 72(2) |

| | | | | |
|--------|-----------|-----------|----------|-------|
| C(25E) | 10421(10) | -7485(7) | 6167(5) | 69(4) |
| C(26Y) | 10582(9) | -8053(7) | 6470(5) | 67(3) |
| C(27E) | 10110(11) | -8698(8) | 6355(7) | 78(5) |
| C(24Y) | 10942(5) | -6797(4) | 6297(3) | 72(2) |
| C(25Y) | 10897(13) | -7552(8) | 6298(8) | 72(5) |
| C(26E) | 10152(13) | -7674(12) | 6319(8) | 68(5) |
| C(27Y) | 9924(15) | -8486(13) | 6220(10) | 70(6) |
| C(21F) | 8237(3) | -3441(3) | 6160(2) | 34(1) |
| N(1F) | 8342(3) | -3860(3) | 5798(2) | 35(1) |
| C(22F) | 7856(4) | -3638(3) | 5465(2) | 44(2) |
| C(23F) | 7453(4) | -3103(3) | 5622(2) | 43(2) |
| N(2F) | 7694(3) | -2981(3) | 6068(2) | 34(1) |
| C(24F) | 7409(4) | -2437(3) | 6381(2) | 41(1) |
| C(25F) | 7697(4) | -1720(3) | 6323(2) | 44(2) |
| C(26F) | 8537(4) | -1605(4) | 6446(2) | 52(2) |
| C(27F) | 8826(5) | -912(4) | 6335(3) | 72(2) |
| Ag(12) | 9596(1) | -4289(1) | 9218(1) | 41(1) |
| C(21G) | 10945(4) | -5134(3) | 8941(2) | 40(1) |
| N(1G) | 10568(3) | -4929(3) | 9281(2) | 43(1) |
| C(22G) | 10915(4) | -5253(3) | 9629(2) | 45(2) |
| C(23G) | 11504(4) | -5633(4) | 9489(2) | 47(2) |
| N(2G) | 11512(3) | -5553(3) | 9048(2) | 42(1) |
| C(24G) | 12072(4) | -5832(4) | 8757(2) | 55(2) |
| C(25G) | 12879(4) | -5531(4) | 8918(2) | 56(2) |
| C(26G) | 13432(5) | -5685(4) | 8579(3) | 68(2) |
| C(27G) | 14198(5) | -5346(5) | 8725(3) | 79(3) |
| C(21H) | 8283(4) | -3407(3) | 8853(2) | 39(1) |
| N(1H) | 8651(3) | -3615(3) | 9213(2) | 43(1) |
| C(22H) | 8385(4) | -3219(4) | 9561(2) | 52(2) |
| C(23H) | 7857(4) | -2774(4) | 9409(2) | 50(2) |
| N(2H) | 7790(3) | -2890(3) | 8955(2) | 42(1) |
| C(24H) | 7259(4) | -2552(4) | 8647(2) | 55(2) |
| C(25H) | 6519(13) | -3002(11) | 8522(7) | 58(4) |
| C(26H) | 6112(8) | -3160(7) | 8901(5) | 52(3) |
| C(27H) | 5357(15) | -3540(14) | 8766(7) | 75(6) |
| C(24Z) | 7259(4) | -2552(4) | 8647(2) | 55(2) |
| C(25Z) | 6460(13) | -2729(10) | 8637(8) | 59(4) |
| C(26Z) | 6283(11) | -3496(9) | 8502(6) | 70(4) |

C(27Z) 5456(17) -3709(17) 8516(8) 107(11)

Table 30. Selected bond lengths [Å] and angles [°] for [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆].

| | | | |
|-------------|-----------|--------------|-----------|
| Ag(1)-O(1A) | 2.207(4) | Ag(7)-O(1G) | 2.196(4) |
| Ag(1)-O(2D) | 2.217(4) | Ag(7)-O(2J) | 2.202(4) |
| Ag(1)-Ag(4) | 2.8750(6) | Ag(7)-Ag(10) | 2.8760(6) |
| Ag(1)-Ag(2) | 2.9028(6) | Ag(7)-Ag(8) | 2.9646(6) |
| Ag(2)-O(1E) | 2.222(4) | Ag(8)-O(1K) | 2.217(4) |
| Ag(2)-O(1F) | 2.226(4) | Ag(8)-O(2L) | 2.257(4) |
| Ag(2)-O(2A) | 2.335(4) | Ag(8)-O(2G) | 2.301(4) |
| Ag(2)-O(1B) | 2.357(4) | Ag(8)-O(1H) | 2.382(4) |
| Ag(2)-Ag(4) | 2.8365(5) | Ag(8)-Ag(10) | 2.8165(6) |
| Ag(2)-Ag(3) | 2.8770(6) | Ag(8)-Ag(9) | 2.8544(6) |
| Ag(3)-O(1C) | 2.174(4) | Ag(9)-O(1I) | 2.178(4) |
| Ag(3)-O(2B) | 2.192(4) | Ag(9)-O(2H) | 2.203(4) |
| Ag(3)-Ag(4) | 2.8949(6) | Ag(9)-Ag(10) | 2.9511(6) |
| Ag(4)-O(1D) | 2.275(4) | Ag(10)-O(2I) | 2.286(4) |
| Ag(4)-O(2C) | 2.304(4) | Ag(10)-O(1J) | 2.305(4) |
| Ag(4)-O(2F) | 2.354(4) | Ag(10)-O(2K) | 2.309(4) |
| Ag(4)-O(2E) | 2.355(4) | Ag(10)-O(1L) | 2.374(4) |
| Ag(5)-N(1A) | 2.116(5) | Ag(11)-N(1E) | 2.112(5) |
| Ag(5)-N(1B) | 2.117(5) | Ag(11)-N(1F) | 2.113(5) |
| Ag(5)-O(2A) | 2.696(4) | Ag(11)-O(1H) | 2.678(4) |
| Ag(5)-O(1B) | 2.809(4) | Ag(11)-O(2G) | 2.847(4) |
| Ag(6)-N(1D) | 2.131(5) | Ag(12)-N(1H) | 2.122(5) |
| Ag(6)-N(1C) | 2.131(5) | Ag(12)-N(1G) | 2.124(5) |
| Ag(6)-O(1D) | 2.603(4) | Ag(12)-O(1J) | 2.624(4) |
| Ag(6)-O(2C) | 2.756(4) | Ag(12)-O(2F) | 2.740(4) |

Table 31. Bond lengths [Å] and angles [°] for [Ag(1-Bu-imid)₂]₂[Ag₄(9-aca)₆].

| | | | |
|-------------|-----------|-------------|----------|
| Ag(1)-O(1A) | 2.207(4) | Ag(2)-O(1E) | 2.222(4) |
| Ag(1)-O(2D) | 2.217(4) | Ag(2)-O(1F) | 2.226(4) |
| Ag(1)-Ag(4) | 2.8750(6) | Ag(2)-O(2A) | 2.335(4) |
| Ag(1)-Ag(2) | 2.9028(6) | Ag(2)-O(1B) | 2.357(4) |

| | | | |
|---------------|-----------|---------------|-----------|
| Ag(2)-Ag(4) | 2.8365(5) | C(5B)-C(6B) | 1.403(10) |
| Ag(2)-Ag(3) | 2.8770(6) | C(6B)-C(7B) | 1.347(10) |
| Ag(3)-O(1C) | 2.174(4) | C(7B)-C(8B) | 1.435(9) |
| Ag(3)-O(2B) | 2.192(4) | C(8B)-C(9B) | 1.372(8) |
| Ag(3)-Ag(4) | 2.8949(6) | C(9B)-C(10B) | 1.414(8) |
| Ag(4)-O(1D) | 2.275(4) | C(10B)-C(11B) | 1.397(8) |
| Ag(4)-O(2C) | 2.304(4) | C(10B)-C(15B) | 1.423(7) |
| Ag(4)-O(2F) | 2.354(4) | C(11B)-C(12B) | 1.347(9) |
| Ag(4)-O(2E) | 2.355(4) | C(12B)-C(13B) | 1.423(9) |
| O(1A)-C(1A) | 1.266(6) | C(13B)-C(14B) | 1.360(8) |
| O(2A)-C(1A) | 1.247(6) | C(14B)-C(15B) | 1.423(8) |
| O(2A)-Ag(5) | 2.696(4) | O(1C)-C(1C) | 1.269(7) |
| C(1A)-C(2A) | 1.516(7) | O(2C)-C(1C) | 1.220(7) |
| C(2A)-C(15A) | 1.410(8) | O(2C)-Ag(6) | 2.756(4) |
| C(2A)-C(3A) | 1.416(8) | C(1C)-C(2C) | 1.522(7) |
| C(3A)-C(4A) | 1.416(8) | C(2C)-C(3C) | 1.392(8) |
| C(3A)-C(8A) | 1.436(8) | C(2C)-C(15C) | 1.402(8) |
| C(4A)-C(5A) | 1.347(9) | C(3C)-C(8C) | 1.429(8) |
| C(5A)-C(6A) | 1.420(9) | C(3C)-C(4C) | 1.430(8) |
| C(6A)-C(7A) | 1.349(10) | C(4C)-C(5C) | 1.342(9) |
| C(7A)-C(8A) | 1.422(9) | C(5C)-C(6C) | 1.421(9) |
| C(8A)-C(9A) | 1.394(9) | C(6C)-C(7C) | 1.352(10) |
| C(9A)-C(10A) | 1.388(8) | C(7C)-C(8C) | 1.430(9) |
| C(10A)-C(11A) | 1.422(8) | C(8C)-C(9C) | 1.403(9) |
| C(10A)-C(15A) | 1.431(8) | C(9C)-C(10C) | 1.377(9) |
| C(11A)-C(12A) | 1.334(9) | C(10C)-C(15C) | 1.438(8) |
| C(12A)-C(13A) | 1.411(9) | C(10C)-C(11C) | 1.444(9) |
| C(13A)-C(14A) | 1.373(9) | C(11C)-C(12C) | 1.324(10) |
| C(14A)-C(15A) | 1.430(8) | C(12C)-C(13C) | 1.397(10) |
| O(1B)-C(1B) | 1.249(6) | C(13C)-C(14C) | 1.363(9) |
| O(1B)-Ag(5) | 2.809(4) | C(14C)-C(15C) | 1.428(9) |
| O(2B)-C(1B) | 1.248(7) | O(1D)-C(1D) | 1.230(7) |
| C(1B)-C(2B) | 1.505(7) | O(1D)-Ag(6) | 2.603(4) |
| C(2B)-C(3B) | 1.389(8) | O(2D)-C(1D) | 1.235(7) |
| C(2B)-C(15B) | 1.413(8) | C(1D)-C(2D) | 1.511(7) |
| C(3B)-C(4B) | 1.433(8) | C(2D)-C(15D) | 1.398(8) |
| C(3B)-C(8B) | 1.449(8) | C(2D)-C(3D) | 1.404(8) |
| C(4B)-C(5B) | 1.359(9) | C(3D)-C(8D) | 1.422(8) |

| | | | |
|---------------|-----------|---------------|-----------|
| C(3D)-C(4D) | 1.421(9) | C(3F)-C(4F) | 1.400(10) |
| C(4D)-C(5D) | 1.338(9) | C(3F)-C(8F) | 1.460(9) |
| C(5D)-C(6D) | 1.415(11) | C(4F)-C(5F) | 1.360(10) |
| C(6D)-C(7D) | 1.359(12) | C(5F)-C(6F) | 1.406(12) |
| C(7D)-C(8D) | 1.432(10) | C(6F)-C(7F) | 1.327(13) |
| C(8D)-C(9D) | 1.359(10) | C(7F)-C(8F) | 1.455(12) |
| C(9D)-C(10D) | 1.401(10) | C(8F)-C(9F) | 1.373(12) |
| C(10D)-C(11D) | 1.413(10) | C(9F)-C(10F) | 1.376(12) |
| C(10D)-C(15D) | 1.446(9) | C(10F)-C(11F) | 1.427(12) |
| C(11D)-C(12D) | 1.323(12) | C(10F)-C(15F) | 1.456(9) |
| C(12D)-C(13D) | 1.403(12) | C(11F)-C(12F) | 1.330(14) |
| C(13D)-C(14D) | 1.384(10) | C(12F)-C(13F) | 1.397(13) |
| C(14D)-C(15D) | 1.434(9) | C(13F)-C(14F) | 1.380(10) |
| O(1E)-C(1E) | 1.271(6) | C(14F)-C(15F) | 1.405(10) |
| O(2E)-C(1E) | 1.227(7) | Ag(5)-N(1A) | 2.116(5) |
| C(1E)-C(2E) | 1.516(7) | Ag(5)-N(1B) | 2.117(5) |
| C(2E)-C(3E) | 1.398(8) | Ag(5)-O(2A) | 2.696(4) |
| C(2E)-C(15E) | 1.410(8) | ag(5)-O(1B) | 2.809(4) |
| C(3E)-C(4E) | 1.417(8) | C(21A)-N(1A) | 1.327(7) |
| C(3E)-C(8E) | 1.457(8) | C(21A)-N(2A) | 1.335(7) |
| C(4E)-C(5E) | 1.373(9) | N(1A)-C(22A) | 1.372(7) |
| C(5E)-C(6E) | 1.429(10) | C(22A)-C(23A) | 1.323(8) |
| C(6E)-C(7E) | 1.348(10) | C(23A)-N(2A) | 1.377(7) |
| C(7E)-C(8E) | 1.441(9) | N(2A)-C(24A) | 1.474(8) |
| C(8E)-C(9E) | 1.376(9) | C(24A)-C(25A) | 1.589(12) |
| C(9E)-C(10E) | 1.386(9) | C(25A)-C(26A) | 1.425(11) |
| C(10E)-C(11E) | 1.430(9) | C(26A)-C(27A) | 1.483(13) |
| C(10E)-C(15E) | 1.431(8) | C(21B)-N(1B) | 1.314(7) |
| C(11E)-C(12E) | 1.358(10) | C(21B)-N(2B) | 1.338(7) |
| C(12E)-C(13E) | 1.402(10) | N(1B)-C(22B) | 1.376(7) |
| C(13E)-C(14E) | 1.373(9) | C(22B)-C(23B) | 1.346(8) |
| C(14E)-C(15E) | 1.424(9) | C(23B)-N(2B) | 1.374(7) |
| O(1F)-C(1F) | 1.224(7) | N(2B)-C(24B) | 1.462(8) |
| O(2F)-C(1F) | 1.265(6) | C(24B)-C(25B) | 1.514(9) |
| O(2F)-Ag(12) | 14.267(4) | C(25B)-C(26B) | 1.488(9) |
| C(1F)-C(2F) | 1.529(8) | C(26B)-C(27B) | 1.535(10) |
| C(2F)-C(15F) | 1.388(9) | Ag(6)-N(1D) | 2.131(5) |
| C(2F)-C(3F) | 1.410(9) | Ag(6)-N(1C) | 2.131(5) |

| | | | |
|---------------|-----------|---------------|-----------|
| Ag(6)-O(1D) | 2.603(4) | Ag(10)-O(1L) | 2.374(4) |
| Ag(6)-O(2C) | 2.756(4) | O(1G)-C(1G) | 1.245(6) |
| C(21C)-N(1C) | 1.326(8) | O(2G)-C(1G) | 1.233(6) |
| C(21C)-N(2C) | 1.346(8) | O(2G)-Ag(11) | 2.847(4) |
| N(1C)-C(22C) | 1.372(8) | C(1G)-C(2G) | 1.519(7) |
| C(22C)-C(23C) | 1.340(9) | C(2G)-C(15G) | 1.400(8) |
| C(23C)-N(2C) | 1.378(8) | C(2G)-C(3G) | 1.403(8) |
| N(2C)-C(24C) | 1.462(8) | C(3G)-C(4G) | 1.413(8) |
| C(24C)-C(25C) | 1.484(11) | C(3G)-C(8G) | 1.447(7) |
| C(25C)-C(26C) | 1.395(18) | C(4G)-C(5G) | 1.352(8) |
| C(26C)-C(27C) | 1.52(4) | C(5G)-C(6G) | 1.420(8) |
| C(26X)-C(27X) | 1.57(4) | C(6G)-C(7G) | 1.353(9) |
| C(21D)-N(1D) | 1.306(8) | C(7G)-C(8G) | 1.420(8) |
| C(21D)-N(2D) | 1.345(8) | C(8G)-C(9G) | 1.380(8) |
| N(1D)-C(22D) | 1.374(8) | C(9G)-C(10G) | 1.379(8) |
| C(22D)-C(23D) | 1.350(9) | C(10G)-C(11G) | 1.415(8) |
| C(23D)-N(2D) | 1.375(8) | C(10G)-C(15G) | 1.454(8) |
| N(2D)-C(24D) | 1.442(8) | C(11G)-C(12G) | 1.362(10) |
| C(24D)-C(25D) | 1.538(9) | C(12G)-C(13G) | 1.412(10) |
| C(25D)-C(26D) | 1.503(9) | C(13G)-C(14G) | 1.359(9) |
| C(26D)-C(27D) | 1.533(10) | C(14G)-C(15G) | 1.409(8) |
| Ag(7)-O(1G) | 2.196(4) | O(1H)-C(1H) | 1.243(7) |
| Ag(7)-O(2J) | 2.202(4) | O(1H)-Ag(11) | 2.678(4) |
| Ag(7)-O(1L) | 2.564(4) | O(2H)-C(1H) | 1.257(7) |
| Ag(7)-Ag(10) | 2.8760(6) | C(1H)-C(2H) | 1.519(7) |
| Ag(7)-Ag(8) | 2.9646(6) | C(2H)-C(15H) | 1.395(8) |
| Ag(8)-O(1K) | 2.217(4) | C(2H)-C(3H) | 1.417(8) |
| Ag(8)-O(2L) | 2.257(4) | C(3H)-C(4H) | 1.424(8) |
| Ag(8)-O(2G) | 2.301(4) | C(3H)-C(8H) | 1.427(8) |
| Ag(8)-O(1H) | 2.382(4) | C(4H)-C(5H) | 1.359(9) |
| Ag(8)-Ag(10) | 2.8165(6) | C(5H)-C(6H) | 1.423(9) |
| Ag(8)-Ag(9) | 2.8544(6) | C(6H)-C(7H) | 1.343(10) |
| Ag(9)-O(1I) | 2.178(4) | C(7H)-C(8H) | 1.434(9) |
| Ag(9)-O(2H) | 2.203(4) | C(8H)-C(9H) | 1.392(9) |
| Ag(9)-Ag(10) | 2.9511(6) | C(9H)-C(10H) | 1.389(9) |
| Ag(10)-O(2I) | 2.286(4) | C(10H)-C(11H) | 1.425(9) |
| Ag(10)-O(1J) | 2.305(4) | C(10H)-C(15H) | 1.439(8) |
| Ag(10)-O(2K) | 2.309(4) | C(11H)-C(12H) | 1.345(10) |

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| C(12H)-C(13H) | 1.424(9) | C(11J)-C(12J) | 1.331(12) |
| C(13H)-C(14H) | 1.362(9) | C(12J)-C(13J) | 1.403(13) |
| C(14H)-C(15H) | 1.433(9) | C(13J)-C(14J) | 1.407(11) |
| O(1I)-C(1I) | 1.261(7) | C(14J)-C(15J) | 1.419(10) |
| O(2I)-C(1I) | 1.236(7) | O(1K)-C(1K) | 1.250(7) |
| C(1I)-C(2I) | 1.512(7) | O(2K)-C(1K) | 1.262(7) |
| C(2I)-C(3I) | 1.388(8) | C(1K)-C(2K) | 1.500(8) |
| C(2I)-C(15I) | 1.401(8) | C(2K)-C(15K) | 1.388(9) |
| C(3I)-C(4I) | 1.424(8) | C(2K)-C(3K) | 1.417(9) |
| C(3I)-C(8I) | 1.447(8) | C(3K)-C(4K) | 1.396(10) |
| C(4I)-C(5I) | 1.351(9) | C(3K)-C(8K) | 1.445(9) |
| C(5I)-C(6I) | 1.427(10) | C(4K)-C(5K) | 1.387(10) |
| C(6I)-C(7I) | 1.325(10) | C(5K)-C(6K) | 1.393(12) |
| C(7I)-C(8I) | 1.427(9) | C(6K)-C(7K) | 1.348(13) |
| C(8I)-C(9I) | 1.391(9) | C(7K)-C(8K) | 1.425(11) |
| C(9I)-C(10I) | 1.386(9) | C(8K)-C(9K) | 1.387(11) |
| C(10I)-C(15I) | 1.435(8) | C(9K)-C(10K) | 1.365(11) |
| C(10I)-C(11I) | 1.445(9) | C(10K)-C(15K) | 1.438(9) |
| C(11I)-C(12I) | 1.339(10) | C(10K)-C(11K) | 1.449(11) |
| C(12I)-C(13I) | 1.394(10) | C(11K)-C(12K) | 1.321(12) |
| C(13I)-C(14I) | 1.375(9) | C(12K)-C(13K) | 1.411(11) |
| C(14I)-C(15I) | 1.415(9) | C(13K)-C(14K) | 1.346(10) |
| O(1J)-C(1J) | 1.226(7) | C(14K)-C(15K) | 1.430(9) |
| O(1J)-Ag(12) | 2.624(4) | O(1L)-C(1L) | 1.231(6) |
| O(2J)-C(1J) | 1.244(7) | O(2L)-C(1L) | 1.269(6) |
| C(1J)-C(2J) | 1.508(8) | C(1L)-C(2L) | 1.525(7) |
| C(2J)-C(15J) | 1.404(9) | C(2L)-C(3L) | 1.389(8) |
| C(2J)-C(3J) | 1.420(8) | C(2L)-C(15L) | 1.417(8) |
| C(3J)-C(4J) | 1.417(8) | C(3L)-C(8L) | 1.435(8) |
| C(3J)-C(8J) | 1.430(8) | C(3L)-C(4L) | 1.438(9) |
| C(4J)-C(5J) | 1.356(9) | C(4L)-C(5L) | 1.354(9) |
| C(5J)-C(6J) | 1.415(11) | C(5L)-C(6L) | 1.411(11) |
| C(6J)-C(7J) | 1.332(11) | C(6L)-C(7L) | 1.362(11) |
| C(7J)-C(8J) | 1.454(9) | C(7L)-C(8L) | 1.445(9) |
| C(8J)-C(9J) | 1.370(9) | C(8L)-C(9L) | 1.362(9) |
| C(9J)-C(10J) | 1.389(10) | C(9L)-C(10L) | 1.416(9) |
| C(10J)-C(11J) | 1.419(9) | C(10L)-C(11L) | 1.412(9) |
| C(10J)-C(15J) | 1.461(9) | C(10L)-C(15L) | 1.454(8) |

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| C(11L)-C(12L) | 1.341(11) | C(25F)-C(26F) | 1.500(9) |
| C(12L)-C(13L) | 1.439(10) | C(26F)-C(27F) | 1.517(10) |
| C(13L)-C(14L) | 1.365(9) | Ag(12)-N(1H) | 2.122(5) |
| C(14L)-C(15L) | 1.395(9) | Ag(12)-N(1G) | 2.124(5) |
| Ag(11)-N(1E) | 2.112(5) | Ag(12)-O(1J) | 2.624(4) |
| Ag(11)-N(1F) | 2.113(5) | Ag(12)-O(2F) | 2.740(4) |
| Ag(11)-O(1H) | 2.678(4) | C(21G)-N(1G) | 1.314(8) |
| Ag(11)-O(2G) | 2.847(4) | C(21G)-N(2G) | 1.328(8) |
| C(21E)-N(1E) | 1.315(8) | N(1G)-C(22G) | 1.381(8) |
| C(21E)-N(2E) | 1.334(8) | C(22G)-C(23G) | 1.353(9) |
| N(1E)-C(22E) | 1.371(7) | C(23G)-N(2G) | 1.371(8) |
| C(22E)-C(23E) | 1.338(9) | N(2G)-C(24G) | 1.463(9) |
| C(23E)-N(2E) | 1.365(8) | C(24G)-C(25G) | 1.549(10) |
| N(2E)-C(24E) | 1.456(9) | C(25G)-C(26G) | 1.501(10) |
| C(24E)-C(25E) | 1.607(16) | C(26G)-C(27G) | 1.504(11) |
| C(25E)-C(26Y) | 1.521(17) | C(21H)-N(1H) | 1.318(8) |
| C(26Y)-C(27E) | 1.49(2) | C(21H)-N(2H) | 1.361(8) |
| C(25Y)-C(26E) | 1.34(3) | N(1H)-C(22H) | 1.366(8) |
| C(26E)-C(27Y) | 1.61(3) | C(22H)-C(23H) | 1.353(9) |
| C(21F)-N(1F) | 1.329(7) | C(23H)-N(2H) | 1.372(8) |
| C(21F)-N(2F) | 1.338(7) | N(2H)-C(24H) | 1.463(8) |
| N(1F)-C(22F) | 1.365(7) | C(24H)-C(25H) | 1.56(2) |
| C(22F)-C(23F) | 1.336(9) | C(25H)-C(26H) | 1.48(3) |
| C(23F)-N(2F) | 1.376(7) | C(26H)-C(27H) | 1.52(3) |
| N(2F)-C(24F) | 1.473(7) | C(25Z)-C(26Z) | 1.52(2) |
| C(24F)-C(25F) | 1.512(9) | C(26Z)-C(27Z) | 1.52(3) |
| O(1A)-Ag(1)-O(2D) | 132.81(16) | O(2A)-Ag(2)-O(1B) | 93.86(14) |
| O(1A)-Ag(1)-Ag(4) | 140.04(10) | O(1E)-Ag(2)-Ag(4) | 79.05(10) |
| O(2D)-Ag(1)-Ag(4) | 87.07(12) | O(1F)-Ag(2)-Ag(4) | 76.00(10) |
| O(1A)-Ag(1)-Ag(2) | 83.96(10) | O(2A)-Ag(2)-Ag(4) | 133.76(10) |
| O(2D)-Ag(1)-Ag(2) | 140.64(14) | O(1B)-Ag(2)-Ag(4) | 131.69(10) |
| Ag(4)-Ag(1)-Ag(2) | 58.801(14) | O(1E)-Ag(2)-Ag(3) | 77.51(12) |
| O(1E)-Ag(2)-O(1F) | 154.83(15) | O(1F)-Ag(2)-Ag(3) | 87.50(11) |
| O(1E)-Ag(2)-O(2A) | 108.55(15) | O(2A)-Ag(2)-Ag(3) | 164.34(10) |
| O(1F)-Ag(2)-O(2A) | 91.25(14) | O(1B)-Ag(2)-Ag(3) | 70.97(10) |
| O(1E)-Ag(2)-O(1B) | 94.95(15) | Ag(4)-Ag(2)-Ag(3) | 60.881(14) |
| O(1F)-Ag(2)-O(1B) | 99.15(16) | O(1E)-Ag(2)-Ag(1) | 87.73(11) |

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| O(1F)-Ag(2)-Ag(1) | 82.71(12) | O(1A)-C(1A)-C(2A) | 117.0(5) |
| O(2A)-Ag(2)-Ag(1) | 74.40(10) | C(15A)-C(2A)-C(3A) | 120.9(5) |
| O(1B)-Ag(2)-Ag(1) | 168.19(10) | C(15A)-C(2A)-C(1A) | 119.6(5) |
| Ag(4)-Ag(2)-Ag(1) | 60.110(14) | C(3A)-C(2A)-C(1A) | 119.5(5) |
| Ag(3)-Ag(2)-Ag(1) | 120.829(18) | C(4A)-C(3A)-C(2A) | 123.2(5) |
| O(1C)-Ag(3)-O(2B) | 135.29(16) | C(4A)-C(3A)-C(8A) | 118.2(6) |
| O(1C)-Ag(3)-Ag(2) | 134.20(11) | C(2A)-C(3A)-C(8A) | 118.6(5) |
| O(2B)-Ag(3)-Ag(2) | 88.77(11) | C(5A)-C(4A)-C(3A) | 121.1(6) |
| O(1C)-Ag(3)-Ag(4) | 83.61(11) | C(4A)-C(5A)-C(6A) | 121.0(7) |
| O(2B)-Ag(3)-Ag(4) | 139.39(12) | C(7A)-C(6A)-C(5A) | 119.9(7) |
| Ag(2)-Ag(3)-Ag(4) | 58.869(14) | C(6A)-C(7A)-C(8A) | 121.2(6) |
| O(1D)-Ag(4)-O(2C) | 89.46(15) | C(9A)-C(8A)-C(7A) | 121.9(6) |
| O(1D)-Ag(4)-O(2F) | 107.09(18) | C(9A)-C(8A)-C(3A) | 119.5(6) |
| O(2C)-Ag(4)-O(2F) | 93.00(15) | C(7A)-C(8A)-C(3A) | 118.6(6) |
| O(1D)-Ag(4)-O(2E) | 92.01(17) | C(10A)-C(9A)-C(8A) | 122.4(5) |
| O(2C)-Ag(4)-O(2E) | 102.37(15) | C(9A)-C(10A)-C(11A) | 121.6(5) |
| O(2F)-Ag(4)-O(2E) | 155.64(13) | C(9A)-C(10A)-C(15A) | 118.8(5) |
| O(1D)-Ag(4)-Ag(2) | 134.30(11) | C(11A)-C(10A)-C(15A) | 119.6(6) |
| O(2C)-Ag(4)-Ag(2) | 136.04(10) | C(12A)-C(11A)-C(10A) | 120.7(6) |
| O(2F)-Ag(4)-Ag(2) | 79.41(9) | C(11A)-C(12A)-C(13A) | 121.4(6) |
| O(2E)-Ag(4)-Ag(2) | 76.40(10) | C(14A)-C(13A)-C(12A) | 120.0(6) |
| O(1D)-Ag(4)-Ag(1) | 74.98(11) | C(13A)-C(14A)-C(15A) | 120.9(6) |
| O(2C)-Ag(4)-Ag(1) | 154.24(11) | C(2A)-C(15A)-C(14A) | 122.8(5) |
| O(2F)-Ag(4)-Ag(1) | 110.99(10) | C(2A)-C(15A)-C(10A) | 119.8(5) |
| O(2E)-Ag(4)-Ag(1) | 58.77(10) | C(14A)-C(15A)-C(10A) | 117.4(5) |
| Ag(2)-Ag(4)-Ag(1) | 61.088(14) | C(1B)-O(1B)-Ag(2) | 128.8(4) |
| O(1D)-Ag(4)-Ag(3) | 162.13(12) | C(1B)-O(1B)-Ag(5) | 130.0(4) |
| O(2C)-Ag(4)-Ag(3) | 77.92(10) | Ag(2)-O(1B)-Ag(5) | 92.72(13) |
| O(2F)-Ag(4)-Ag(3) | 61.65(10) | C(1B)-O(2B)-Ag(3) | 114.2(4) |
| O(2E)-Ag(4)-Ag(3) | 102.95(10) | O(2B)-C(1B)-O(1B) | 125.9(5) |
| Ag(2)-Ag(4)-Ag(3) | 60.250(14) | O(2B)-C(1B)-C(2B) | 117.9(5) |
| Ag(1)-Ag(4)-Ag(3) | 121.175(18) | O(1B)-C(1B)-C(2B) | 116.2(5) |
| C(1A)-O(1A)-Ag(1) | 118.7(4) | C(3B)-C(2B)-C(15B) | 120.7(5) |
| C(1A)-O(2A)-Ag(2) | 122.1(3) | C(3B)-C(2B)-C(1B) | 121.4(5) |
| C(1A)-O(2A)-Ag(5) | 124.1(3) | C(15B)-C(2B)-C(1B) | 117.9(5) |
| Ag(2)-O(2A)-Ag(5) | 96.20(13) | C(2B)-C(3B)-C(4B) | 122.8(5) |
| O(2A)-C(1A)-O(1A) | 126.1(5) | C(2B)-C(3B)-C(8B) | 118.6(5) |
| O(2A)-C(1A)-C(2A) | 116.9(5) | C(4B)-C(3B)-C(8B) | 118.5(5) |

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| C(5B)-C(4B)-C(3B) | 120.5(6) | C(10C)-C(9C)-C(8C) | 121.8(5) |
| C(4B)-C(5B)-C(6B) | 121.0(7) | C(9C)-C(10C)-C(15C) | 120.0(6) |
| C(7B)-C(6B)-C(5B) | 121.0(7) | C(9C)-C(10C)-C(11C) | 123.3(6) |
| C(6B)-C(7B)-C(8B) | 121.4(6) | C(15C)-C(10C)-C(11C) | 116.7(6) |
| C(9B)-C(8B)-C(7B) | 122.1(6) | C(12C)-C(11C)-C(10C) | 122.0(7) |
| C(9B)-C(8B)-C(3B) | 120.4(5) | C(11C)-C(12C)-C(13C) | 121.1(7) |
| C(7B)-C(8B)-C(3B) | 117.5(6) | C(14C)-C(13C)-C(12C) | 120.9(7) |
| C(8B)-C(9B)-C(10B) | 121.3(5) | C(13C)-C(14C)-C(15C) | 120.1(6) |
| C(11B)-C(10B)-C(9B) | 122.5(5) | C(2C)-C(15C)-C(14C) | 122.9(5) |
| C(11B)-C(10B)-C(15B) | 118.9(5) | C(2C)-C(15C)-C(10C) | 118.0(6) |
| C(9B)-C(10B)-C(15B) | 118.5(5) | C(14C)-C(15C)-C(10C) | 119.0(6) |
| C(12B)-C(11B)-C(10B) | 122.1(6) | C(1D)-O(1D)-Ag(4) | 132.1(4) |
| C(11B)-C(12B)-C(13B) | 119.5(6) | C(1D)-O(1D)-Ag(6) | 126.3(4) |
| C(14B)-C(13B)-C(12B) | 120.6(6) | Ag(4)-O(1D)-Ag(6) | 100.77(16) |
| C(13B)-C(14B)-C(15B) | 120.3(6) | C(1D)-O(2D)-Ag(1) | 118.6(4) |
| C(2B)-C(15B)-C(10B) | 120.2(5) | O(1D)-C(1D)-O(2D) | 125.5(5) |
| C(2B)-C(15B)-C(14B) | 121.2(5) | O(1D)-C(1D)-C(2D) | 115.9(5) |
| C(10B)-C(15B)-C(14B) | 118.5(5) | O(2D)-C(1D)-C(2D) | 118.6(5) |
| C(1C)-O(1C)-Ag(3) | 118.6(4) | C(15D)-C(2D)-C(3D) | 120.4(5) |
| C(1C)-O(2C)-Ag(4) | 123.8(4) | C(15D)-C(2D)-C(1D) | 120.4(5) |
| C(1C)-O(2C)-Ag(6) | 139.3(4) | C(3D)-C(2D)-C(1D) | 119.0(5) |
| Ag(4)-O(2C)-Ag(6) | 95.73(14) | C(2D)-C(3D)-C(8D) | 119.7(6) |
| O(2C)-C(1C)-O(1C) | 127.6(5) | C(2D)-C(3D)-C(4D) | 122.3(5) |
| O(2C)-C(1C)-C(2C) | 117.0(5) | C(8D)-C(3D)-C(4D) | 118.0(6) |
| O(1C)-C(1C)-C(2C) | 115.3(5) | C(5D)-C(4D)-C(3D) | 122.7(7) |
| C(3C)-C(2C)-C(15C) | 122.2(5) | C(4D)-C(5D)-C(6D) | 119.6(8) |
| C(3C)-C(2C)-C(1C) | 116.4(5) | C(7D)-C(6D)-C(5D) | 120.5(7) |
| C(15C)-C(2C)-C(1C) | 121.3(5) | C(6D)-C(7D)-C(8D) | 120.9(7) |
| C(2C)-C(3C)-C(8C) | 119.0(5) | C(9D)-C(8D)-C(3D) | 119.8(6) |
| C(2C)-C(3C)-C(4C) | 122.9(5) | C(9D)-C(8D)-C(7D) | 121.9(6) |
| C(8C)-C(3C)-C(4C) | 118.0(6) | C(3D)-C(8D)-C(7D) | 118.2(7) |
| C(5C)-C(4C)-C(3C) | 121.7(6) | C(8D)-C(9D)-C(10D) | 122.5(6) |
| C(4C)-C(5C)-C(6C) | 120.5(6) | C(9D)-C(10D)-C(11D) | 122.7(7) |
| C(7C)-C(6C)-C(5C) | 119.9(6) | C(9D)-C(10D)-C(15D) | 118.1(6) |
| C(6C)-C(7C)-C(8C) | 121.6(6) | C(11D)-C(10D)-C(15D) | 119.1(7) |
| C(9C)-C(8C)-C(3C) | 119.0(6) | C(12D)-C(11D)-C(10D) | 121.8(8) |
| C(9C)-C(8C)-C(7C) | 122.8(6) | C(11D)-C(12D)-C(13D) | 120.7(8) |
| C(3C)-C(8C)-C(7C) | 118.2(6) | C(14D)-C(13D)-C(12D) | 121.3(8) |

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| C(13D)-C(14D)-C(15D) | 119.5(8) | O(1F)-C(1F)-C(2F) | 115.6(5) |
| C(2D)-C(15D)-C(14D) | 123.1(6) | O(2F)-C(1F)-C(2F) | 116.6(5) |
| C(2D)-C(15D)-C(10D) | 119.5(6) | C(15F)-C(2F)-C(3F) | 122.5(6) |
| C(14D)-C(15D)-C(10D) | 117.5(6) | C(15F)-C(2F)-C(1F) | 120.8(6) |
| C(1E)-O(1E)-Ag(2) | 118.4(4) | C(3F)-C(2F)-C(1F) | 116.6(6) |
| C(1E)-O(2E)-Ag(4) | 113.3(3) | C(4F)-C(3F)-C(2F) | 124.1(6) |
| O(2E)-C(1E)-O(1E) | 127.1(5) | C(4F)-C(3F)-C(8F) | 117.9(7) |
| O(2E)-C(1E)-C(2E) | 118.5(5) | C(2F)-C(3F)-C(8F) | 117.9(7) |
| O(1E)-C(1E)-C(2E) | 114.4(5) | C(5F)-C(4F)-C(3F) | 122.5(8) |
| C(3E)-C(2E)-C(15E) | 121.4(5) | C(4F)-C(5F)-C(6F) | 120.3(9) |
| C(3E)-C(2E)-C(1E) | 118.5(5) | C(7F)-C(6F)-C(5F) | 120.3(9) |
| C(15E)-C(2E)-C(1E) | 120.1(5) | C(6F)-C(7F)-C(8F) | 122.6(8) |
| C(2E)-C(3E)-C(4E) | 123.4(5) | C(9F)-C(8F)-C(7F) | 124.6(7) |
| C(2E)-C(3E)-C(8E) | 118.3(5) | C(9F)-C(8F)-C(3F) | 119.0(7) |
| C(4E)-C(3E)-C(8E) | 118.2(6) | C(7F)-C(8F)-C(3F) | 116.4(8) |
| C(5E)-C(4E)-C(3E) | 121.9(6) | C(10F)-C(9F)-C(8F) | 123.0(7) |
| C(4E)-C(5E)-C(6E) | 119.7(7) | C(9F)-C(10F)-C(11F) | 123.2(8) |
| C(7E)-C(6E)-C(5E) | 120.7(7) | C(9F)-C(10F)-C(15F) | 119.5(7) |
| C(6E)-C(7E)-C(8E) | 121.6(7) | C(11F)-C(10F)-C(15F) | 117.3(9) |
| C(9E)-C(8E)-C(7E) | 122.8(6) | C(12F)-C(11F)-C(10F) | 122.2(9) |
| C(9E)-C(8E)-C(3E) | 119.4(6) | C(11F)-C(12F)-C(13F) | 120.6(9) |
| C(7E)-C(8E)-C(3E) | 117.8(6) | C(14F)-C(13F)-C(12F) | 120.9(10) |
| C(8E)-C(9E)-C(10E) | 122.3(6) | C(13F)-C(14F)-C(15F) | 120.4(8) |
| C(9E)-C(10E)-C(11E) | 122.1(6) | C(2F)-C(15F)-C(14F) | 123.3(6) |
| C(9E)-C(10E)-C(15E) | 119.4(6) | C(2F)-C(15F)-C(10F) | 118.1(7) |
| C(11E)-C(10E)-C(15E) | 118.4(6) | C(14F)-C(15F)-C(10F) | 118.6(7) |
| C(12E)-C(11E)-C(10E) | 121.1(7) | N(1A)-Ag(5)-N(1B) | 176.98(18) |
| C(11E)-C(12E)-C(13E) | 120.6(7) | N(1A)-Ag(5)-O(2A) | 93.44(15) |
| C(14E)-C(13E)-C(12E) | 120.7(7) | N(1B)-Ag(5)-O(2A) | 89.43(15) |
| C(13E)-C(14E)-C(15E) | 120.5(7) | N(1A)-Ag(5)-O(1B) | 89.53(16) |
| C(2E)-C(15E)-C(14E) | 122.3(6) | N(1B)-Ag(5)-O(1B) | 92.03(16) |
| C(2E)-C(15E)-C(10E) | 119.0(6) | O(2A)-Ag(5)-O(1B) | 76.98(11) |
| C(14E)-C(15E)-C(10E) | 118.6(6) | N(1A)-C(21A)-N(2A) | 110.9(5) |
| C(1F)-O(1F)-Ag(2) | 122.5(4) | C(21A)-N(1A)-C(22A) | 105.5(5) |
| C(1F)-O(2F)-Ag(4) | 109.6(4) | C(21A)-N(1A)-Ag(5) | 119.8(4) |
| C(1F)-O(2F)-Ag(12) | 77.1(3) | C(22A)-N(1A)-Ag(5) | 134.2(4) |
| Ag(4)-O(2F)-Ag(12) | 59.91(9) | C(23A)-C(22A)-N(1A) | 109.9(6) |
| O(1F)-C(1F)-O(2F) | 127.8(5) | C(22A)-C(23A)-N(2A) | 107.0(5) |

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| C(21A)-N(2A)-C(23A) | 106.8(5) | C(21D)-N(1D)-Ag(6) | 121.9(4) |
| C(21A)-N(2A)-C(24A) | 124.9(6) | C(22D)-N(1D)-Ag(6) | 132.8(5) |
| C(23A)-N(2A)-C(24A) | 128.2(5) | C(23D)-C(22D)-N(1D) | 109.6(6) |
| N(2A)-C(24A)-C(25A) | 110.0(6) | C(22D)-C(23D)-N(2D) | 106.7(6) |
| C(26A)-C(25A)-C(24A) | 115.8(8) | C(21D)-N(2D)-C(23D) | 105.9(5) |
| C(25A)-C(26A)-C(27A) | 112.4(9) | C(21D)-N(2D)-C(24D) | 126.3(5) |
| N(1B)-C(21B)-N(2B) | 111.4(5) | C(23D)-N(2D)-C(24D) | 127.6(6) |
| C(21B)-N(1B)-C(22B) | 105.9(5) | N(2D)-C(24D)-C(25D) | 111.5(6) |
| C(21B)-N(1B)-Ag(5) | 124.7(4) | C(26D)-C(25D)-C(24D) | 112.3(6) |
| C(22B)-N(1B)-Ag(5) | 129.3(4) | C(25D)-C(26D)-C(27D) | 111.2(7) |
| C(23B)-C(22B)-N(1B) | 109.1(5) | O(1G)-Ag(7)-O(2J) | 132.37(16) |
| C(22B)-C(23B)-N(2B) | 106.7(5) | O(1G)-Ag(7)-O(1L) | 105.07(14) |
| C(21B)-N(2B)-C(23B) | 106.8(5) | O(2J)-Ag(7)-O(1L) | 105.68(16) |
| C(21B)-N(2B)-C(24B) | 126.8(5) | O(1G)-Ag(7)-Ag(10) | 137.51(11) |
| C(23B)-N(2B)-C(24B) | 126.3(5) | O(2J)-Ag(7)-Ag(10) | 90.08(12) |
| N(2B)-C(24B)-C(25B) | 112.0(5) | O(1L)-Ag(7)-Ag(10) | 51.36(9) |
| C(26B)-C(25B)-C(24B) | 114.0(6) | O(1G)-Ag(7)-Ag(8) | 83.06(10) |
| C(25B)-C(26B)-C(27B) | 112.8(6) | O(2J)-Ag(7)-Ag(8) | 140.98(14) |
| N(1D)-Ag(6)-N(1C) | 175.1(2) | O(1L)-Ag(7)-Ag(8) | 72.61(9) |
| N(1D)-Ag(6)-O(1D) | 90.55(19) | Ag(10)-Ag(7)-Ag(8) | 57.638(14) |
| N(1C)-Ag(6)-O(1D) | 94.19(19) | O(1K)-Ag(8)-O(2L) | 153.12(15) |
| N(1D)-Ag(6)-O(2C) | 97.24(17) | O(1K)-Ag(8)-O(2G) | 99.71(16) |
| N(1C)-Ag(6)-O(2C) | 85.17(16) | O(2L)-Ag(8)-O(2G) | 104.46(16) |
| O(1D)-Ag(6)-O(2C) | 73.86(12) | O(1K)-Ag(8)-O(1H) | 104.54(16) |
| N(1C)-C(21C)-N(2C) | 111.1(5) | O(2L)-Ag(8)-O(1H) | 85.64(14) |
| C(21C)-N(1C)-C(22C) | 105.4(5) | O(2G)-Ag(8)-O(1H) | 93.64(14) |
| C(21C)-N(1C)-Ag(6) | 125.3(4) | O(1K)-Ag(8)-Ag(10) | 78.51(11) |
| C(22C)-N(1C)-Ag(6) | 128.2(4) | O(2L)-Ag(8)-Ag(10) | 76.28(10) |
| C(23C)-C(22C)-N(1C) | 110.2(6) | O(2G)-Ag(8)-Ag(10) | 134.13(10) |
| C(22C)-C(23C)-N(2C) | 106.4(6) | O(1H)-Ag(8)-Ag(10) | 131.58(10) |
| C(21C)-N(2C)-C(23C) | 106.9(5) | O(1K)-Ag(8)-Ag(9) | 90.79(11) |
| C(21C)-N(2C)-C(24C) | 126.7(5) | O(2L)-Ag(8)-Ag(9) | 69.42(11) |
| C(23C)-N(2C)-C(24C) | 126.4(5) | O(2G)-Ag(8)-Ag(9) | 161.55(11) |
| N(2C)-C(24C)-C(25C) | 113.8(6) | O(1H)-Ag(8)-Ag(9) | 68.90(10) |
| C(26C)-C(25C)-C(24C) | 127.4(10) | Ag(10)-Ag(8)-Ag(9) | 62.715(14) |
| C(25C)-C(26C)-C(27C) | 119.8(17) | O(1K)-Ag(8)-Ag(7) | 89.04(13) |
| N(1D)-C(21D)-N(2D) | 112.6(5) | O(2L)-Ag(8)-Ag(7) | 86.22(10) |
| C(21D)-N(1D)-C(22D) | 105.2(5) | O(2G)-Ag(8)-Ag(7) | 74.59(10) |

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| O(1H)-Ag(8)-Ag(7) | 163.52(10) | C(15G)-C(2G)-C(1G) | 120.3(5) |
| Ag(10)-Ag(8)-Ag(7) | 59.603(14) | C(3G)-C(2G)-C(1G) | 118.0(5) |
| Ag(9)-Ag(8)-Ag(7) | 121.069(18) | C(2G)-C(3G)-C(4G) | 123.3(5) |
| O(1I)-Ag(9)-O(2H) | 135.17(16) | C(2G)-C(3G)-C(8G) | 119.1(5) |
| O(1I)-Ag(9)-Ag(8) | 134.99(11) | C(4G)-C(3G)-C(8G) | 117.6(5) |
| O(2H)-Ag(9)-Ag(8) | 89.72(11) | C(5G)-C(4G)-C(3G) | 122.4(5) |
| O(1I)-Ag(9)-Ag(10) | 81.06(11) | C(4G)-C(5G)-C(6G) | 119.5(6) |
| O(2H)-Ag(9)-Ag(10) | 140.35(12) | C(7G)-C(6G)-C(5G) | 121.1(6) |
| Ag(8)-Ag(9)-Ag(10) | 58.015(14) | C(6G)-C(7G)-C(8G) | 120.8(6) |
| O(2I)-Ag(10)-O(1J) | 88.66(15) | C(9G)-C(8G)-C(7G) | 122.9(5) |
| O(2I)-Ag(10)-O(2K) | 95.31(16) | C(9G)-C(8G)-C(3G) | 118.4(5) |
| O(1J)-Ag(10)-O(2K) | 109.95(17) | C(7G)-C(8G)-C(3G) | 118.6(5) |
| O(2I)-Ag(10)-O(1L) | 99.16(15) | C(10G)-C(9G)-C(8G) | 123.4(5) |
| O(1J)-Ag(10)-O(1L) | 87.68(16) | C(9G)-C(10G)-C(11G) | 123.2(5) |
| O(2K)-Ag(10)-O(1L) | 157.45(14) | C(9G)-C(10G)-C(15G) | 118.9(5) |
| O(2I)-Ag(10)-Ag(8) | 137.57(11) | C(11G)-C(10G)-C(15G) | 117.9(6) |
| O(1J)-Ag(10)-Ag(8) | 132.93(10) | C(12G)-C(11G)-C(10G) | 121.6(6) |
| O(2K)-Ag(10)-Ag(8) | 79.52(10) | C(11G)-C(12G)-C(13G) | 120.2(6) |
| O(1L)-Ag(10)-Ag(8) | 78.13(9) | C(14G)-C(13G)-C(12G) | 120.5(6) |
| O(2I)-Ag(10)-Ag(7) | 149.04(11) | C(13G)-C(14G)-C(15G) | 121.4(6) |
| O(1J)-Ag(10)-Ag(7) | 71.70(10) | C(2G)-C(15G)-C(14G) | 123.2(5) |
| O(2K)-Ag(10)-Ag(7) | 113.59(11) | C(2G)-C(15G)-C(10G) | 118.4(5) |
| O(1L)-Ag(10)-Ag(7) | 57.51(9) | C(14G)-C(15G)-C(10G) | 118.4(5) |
| Ag(8)-Ag(10)-Ag(7) | 62.759(14) | C(1H)-O(1H)-Ag(8) | 126.0(4) |
| O(2I)-Ag(10)-Ag(9) | 79.84(10) | C(1H)-O(1H)-Ag(11) | 124.6(3) |
| O(1J)-Ag(10)-Ag(9) | 167.51(10) | Ag(8)-O(1H)-Ag(11) | 96.29(14) |
| O(2K)-Ag(10)-Ag(9) | 66.73(12) | C(1H)-O(2H)-Ag(9) | 111.6(4) |
| O(1L)-Ag(10)-Ag(9) | 98.89(10) | O(1H)-C(1H)-O(2H) | 125.9(5) |
| Ag(8)-Ag(10)-Ag(9) | 59.271(14) | O(1H)-C(1H)-C(2H) | 116.8(5) |
| Ag(7)-Ag(10)-Ag(9) | 120.788(18) | O(2H)-C(1H)-C(2H) | 117.3(5) |
| C(1G)-O(1G)-Ag(7) | 120.3(4) | C(15H)-C(2H)-C(3H) | 120.9(5) |
| C(1G)-O(2G)-Ag(8) | 125.9(4) | C(15H)-C(2H)-C(1H) | 119.3(5) |
| C(1G)-O(2G)-Ag(11) | 127.1(4) | C(3H)-C(2H)-C(1H) | 119.8(5) |
| Ag(8)-O(2G)-Ag(11) | 93.69(13) | C(2H)-C(3H)-C(4H) | 122.8(5) |
| O(2G)-C(1G)-O(1G) | 126.8(5) | C(2H)-C(3H)-C(8H) | 118.7(6) |
| O(2G)-C(1G)-C(2G) | 115.9(5) | C(4H)-C(3H)-C(8H) | 118.5(6) |
| O(1G)-C(1G)-C(2G) | 117.3(5) | C(5H)-C(4H)-C(3H) | 121.2(6) |
| C(15G)-C(2G)-C(3G) | 121.7(5) | C(4H)-C(5H)-C(6H) | 120.1(7) |

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| C(7H)-C(6H)-C(5H) | 120.6(7) | C(12I)-C(11I)-C(10I) | 121.2(6) |
| C(6H)-C(7H)-C(8H) | 121.2(6) | C(11I)-C(12I)-C(13I) | 120.6(7) |
| C(9H)-C(8H)-C(3H) | 120.0(6) | C(14I)-C(13I)-C(12I) | 121.5(7) |
| C(9H)-C(8H)-C(7H) | 121.7(6) | C(13I)-C(14I)-C(15I) | 119.9(6) |
| C(3H)-C(8H)-C(7H) | 118.3(6) | C(2I)-C(15I)-C(14I) | 122.4(5) |
| C(10H)-C(9H)-C(8H) | 121.7(6) | C(2I)-C(15I)-C(10I) | 118.6(6) |
| C(9H)-C(10H)-C(11H) | 121.7(6) | C(14I)-C(15I)-C(10I) | 119.0(6) |
| C(9H)-C(10H)-C(15H) | 119.0(6) | C(1J)-O(1J)-Ag(10) | 134.7(4) |
| C(11H)-C(10H)-C(15H) | 119.3(6) | C(1J)-O(1J)-Ag(12) | 124.8(4) |
| C(12H)-C(11H)-C(10H) | 120.3(6) | Ag(10)-O(1J)-Ag(12) | 100.23(15) |
| C(11H)-C(12H)-C(13H) | 121.9(7) | C(1J)-O(2J)-Ag(7) | 115.0(4) |
| C(14H)-C(13H)-C(12H) | 119.0(7) | O(1J)-C(1J)-O(2J) | 125.5(6) |
| C(13H)-C(14H)-C(15H) | 121.9(6) | O(1J)-C(1J)-C(2J) | 116.3(5) |
| C(2H)-C(15H)-C(14H) | 123.0(5) | O(2J)-C(1J)-C(2J) | 118.2(5) |
| C(2H)-C(15H)-C(10H) | 119.7(6) | C(15J)-C(2J)-C(3J) | 121.1(5) |
| C(14H)-C(15H)-C(10H) | 117.4(6) | C(15J)-C(2J)-C(1J) | 120.8(5) |
| C(1I)-O(1I)-Ag(9) | 124.4(4) | C(3J)-C(2J)-C(1J) | 118.0(5) |
| C(1I)-O(2I)-Ag(10) | 122.9(4) | C(4J)-C(3J)-C(2J) | 121.9(5) |
| O(2I)-C(1I)-O(1I) | 126.8(5) | C(4J)-C(3J)-C(8J) | 119.4(6) |
| O(2I)-C(1I)-C(2I) | 116.8(5) | C(2J)-C(3J)-C(8J) | 118.7(5) |
| O(1I)-C(1I)-C(2I) | 116.4(5) | C(5J)-C(4J)-C(3J) | 121.7(6) |
| C(3I)-C(2I)-C(15I) | 121.9(5) | C(4J)-C(5J)-C(6J) | 118.8(7) |
| C(3I)-C(2I)-C(1I) | 117.2(5) | C(7J)-C(6J)-C(5J) | 122.4(7) |
| C(15I)-C(2I)-C(1I) | 120.8(5) | C(6J)-C(7J)-C(8J) | 120.7(7) |
| C(2I)-C(3I)-C(4I) | 123.5(5) | C(9J)-C(8J)-C(3J) | 120.4(6) |
| C(2I)-C(3I)-C(8I) | 118.9(5) | C(9J)-C(8J)-C(7J) | 122.7(6) |
| C(4I)-C(3I)-C(8I) | 117.7(6) | C(3J)-C(8J)-C(7J) | 116.8(6) |
| C(5I)-C(4I)-C(3I) | 122.3(6) | C(8J)-C(9J)-C(10J) | 122.2(6) |
| C(4I)-C(5I)-C(6I) | 119.2(7) | C(9J)-C(10J)-C(11J) | 121.7(7) |
| C(7I)-C(6I)-C(5I) | 121.0(7) | C(9J)-C(10J)-C(15J) | 119.0(6) |
| C(6I)-C(7I)-C(8I) | 122.2(6) | C(11J)-C(10J)-C(15J) | 119.2(7) |
| C(9I)-C(8I)-C(7I) | 123.3(6) | C(12J)-C(11J)-C(10J) | 121.0(8) |
| C(9I)-C(8I)-C(3I) | 119.0(6) | C(11J)-C(12J)-C(13J) | 121.1(8) |
| C(7I)-C(8I)-C(3I) | 117.6(6) | C(12J)-C(13J)-C(14J) | 121.4(8) |
| C(8I)-C(9I)-C(10I) | 121.8(6) | C(13J)-C(14J)-C(15J) | 118.7(8) |
| C(9I)-C(10I)-C(15I) | 119.7(6) | C(2J)-C(15J)-C(14J) | 123.2(7) |
| C(9I)-C(10I)-C(11I) | 122.6(6) | C(2J)-C(15J)-C(10J) | 118.5(6) |
| C(15I)-C(10I)-C(11I) | 117.7(6) | C(14J)-C(15J)-C(10J) | 118.3(6) |

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| C(1K)-O(1K)-Ag(8) | 123.1(4) | C(15L)-C(2L)-C(1L) | 118.0(5) |
| C(1K)-O(2K)-Ag(10) | 114.5(4) | C(2L)-C(3L)-C(8L) | 118.6(6) |
| O(1K)-C(1K)-O(2K) | 125.2(5) | C(2L)-C(3L)-C(4L) | 123.5(5) |
| O(1K)-C(1K)-C(2K) | 115.9(5) | C(8L)-C(3L)-C(4L) | 117.9(6) |
| O(2K)-C(1K)-C(2K) | 118.9(5) | C(5L)-C(4L)-C(3L) | 121.3(7) |
| C(15K)-C(2K)-C(3K) | 121.6(6) | C(4L)-C(5L)-C(6L) | 120.9(8) |
| C(15K)-C(2K)-C(1K) | 118.1(6) | C(7L)-C(6L)-C(5L) | 120.6(7) |
| C(3K)-C(2K)-C(1K) | 120.3(6) | C(6L)-C(7L)-C(8L) | 120.6(7) |
| C(4K)-C(3K)-C(2K) | 123.0(6) | C(9L)-C(8L)-C(3L) | 120.0(6) |
| C(4K)-C(3K)-C(8K) | 118.9(7) | C(9L)-C(8L)-C(7L) | 121.3(6) |
| C(2K)-C(3K)-C(8K) | 118.1(7) | C(3L)-C(8L)-C(7L) | 118.7(7) |
| C(5K)-C(4K)-C(3K) | 121.9(8) | C(8L)-C(9L)-C(10L) | 122.4(6) |
| C(6K)-C(5K)-C(4K) | 118.8(9) | C(11L)-C(10L)-C(9L) | 122.9(6) |
| C(7K)-C(6K)-C(5K) | 121.5(8) | C(11L)-C(10L)-C(15L) | 118.4(6) |
| C(6K)-C(7K)-C(8K) | 121.8(8) | C(9L)-C(10L)-C(15L) | 118.7(6) |
| C(9K)-C(8K)-C(7K) | 124.1(8) | C(12L)-C(11L)-C(10L) | 120.7(7) |
| C(9K)-C(8K)-C(3K) | 118.8(7) | C(11L)-C(12L)-C(13L) | 121.8(7) |
| C(7K)-C(8K)-C(3K) | 117.0(8) | C(14L)-C(13L)-C(12L) | 118.3(7) |
| C(10K)-C(9K)-C(8K) | 122.8(7) | C(13L)-C(14L)-C(15L) | 122.2(6) |
| C(9K)-C(10K)-C(15K) | 119.6(7) | C(14L)-C(15L)-C(2L) | 124.2(5) |
| C(9K)-C(10K)-C(11K) | 122.8(7) | C(14L)-C(15L)-C(10L) | 118.6(6) |
| C(15K)-C(10K)-C(11K) | 117.6(8) | C(2L)-C(15L)-C(10L) | 117.2(5) |
| C(12K)-C(11K)-C(10K) | 121.1(8) | N(1E)-Ag(11)-N(1F) | 176.84(19) |
| C(11K)-C(12K)-C(13K) | 121.9(9) | N(1E)-Ag(11)-O(1H) | 93.65(16) |
| C(14K)-C(13K)-C(12K) | 119.6(8) | N(1F)-Ag(11)-O(1H) | 89.24(16) |
| C(13K)-C(14K)-C(15K) | 122.0(7) | N(1E)-Ag(11)-O(2G) | 87.63(16) |
| C(2K)-C(15K)-C(14K) | 123.4(6) | N(1F)-Ag(11)-O(2G) | 94.29(16) |
| C(2K)-C(15K)-C(10K) | 118.9(7) | O(1H)-Ag(11)-O(2G) | 76.30(11) |
| C(14K)-C(15K)-C(10K) | 117.7(7) | N(1E)-C(21E)-N(2E) | 110.9(6) |
| C(1L)-O(1L)-Ag(10) | 111.1(3) | C(21E)-N(1E)-C(22E) | 105.5(5) |
| C(1L)-O(1L)-Ag(7) | 115.0(3) | C(21E)-N(1E)-Ag(11) | 120.4(4) |
| Ag(10)-O(1L)-Ag(7) | 71.13(10) | C(22E)-N(1E)-Ag(11) | 133.4(4) |
| C(1L)-O(2L)-Ag(8) | 118.7(3) | C(23E)-C(22E)-N(1E) | 109.9(6) |
| O(1L)-C(1L)-O(2L) | 126.9(5) | C(22E)-C(23E)-N(2E) | 106.1(5) |
| O(1L)-C(1L)-C(2L) | 119.0(5) | C(21E)-N(2E)-C(23E) | 107.6(5) |
| O(2L)-C(1L)-C(2L) | 114.1(5) | C(21E)-N(2E)-C(24E) | 125.1(6) |
| C(3L)-C(2L)-C(15L) | 123.0(5) | C(23E)-N(2E)-C(24E) | 127.1(6) |
| C(3L)-C(2L)-C(1L) | 119.1(5) | N(2E)-C(24E)-C(25E) | 104.9(8) |

| | | | |
|----------------------|------------|----------------------|-----------|
| C(26Y)-C(25E)-C(24E) | 114.6(12) | C(21G)-N(1G)-Ag(12) | 122.0(4) |
| C(27E)-C(26Y)-C(25E) | 115.7(14) | C(22G)-N(1G)-Ag(12) | 132.8(5) |
| C(25Y)-C(26E)-C(27Y) | 112.7(19) | C(23G)-C(22G)-N(1G) | 109.4(6) |
| N(1F)-C(21F)-N(2F) | 110.3(5) | C(22G)-C(23G)-N(2G) | 106.2(6) |
| C(21F)-N(1F)-C(22F) | 105.7(5) | C(21G)-N(2G)-C(23G) | 107.1(6) |
| C(21F)-N(1F)-Ag(11) | 123.9(4) | C(21G)-N(2G)-C(24G) | 126.1(5) |
| C(22F)-N(1F)-Ag(11) | 130.3(4) | C(23G)-N(2G)-C(24G) | 126.7(6) |
| C(23F)-C(22F)-N(1F) | 110.4(6) | N(2G)-C(24G)-C(25G) | 111.0(6) |
| C(22F)-C(23F)-N(2F) | 106.0(5) | C(26G)-C(25G)-C(24G) | 112.3(7) |
| C(21F)-N(2F)-C(23F) | 107.6(5) | C(27G)-C(26G)-C(25G) | 111.9(7) |
| C(21F)-N(2F)-C(24F) | 126.7(5) | N(1H)-C(21H)-N(2H) | 111.4(5) |
| C(23F)-N(2F)-C(24F) | 125.7(5) | C(21H)-N(1H)-C(22H) | 105.7(6) |
| N(2F)-C(24F)-C(25F) | 112.9(5) | C(21H)-N(1H)-Ag(12) | 124.8(4) |
| C(26F)-C(25F)-C(24F) | 114.6(5) | C(22H)-N(1H)-Ag(12) | 128.6(4) |
| C(25F)-C(26F)-C(27F) | 113.5(6) | C(23H)-C(22H)-N(1H) | 110.0(6) |
| N(1H)-Ag(12)-N(1G) | 175.0(2) | C(22H)-C(23H)-N(2H) | 106.6(6) |
| N(1H)-Ag(12)-O(1J) | 94.68(18) | C(21H)-N(2H)-C(23H) | 106.2(5) |
| N(1G)-Ag(12)-O(1J) | 90.14(18) | C(21H)-N(2H)-C(24H) | 127.4(5) |
| N(1H)-Ag(12)-O(2F) | 16.37(13) | C(23H)-N(2H)-C(24H) | 126.3(6) |
| N(1G)-Ag(12)-O(2F) | 167.86(14) | N(2H)-C(24H)-C(25H) | 110.3(10) |
| O(1J)-Ag(12)-O(2F) | 82.46(11) | C(26H)-C(25H)-C(24H) | 115.0(15) |
| N(1G)-C(21G)-N(2G) | 112.3(6) | C(25H)-C(26H)-C(27H) | 113.7(16) |
| C(21G)-N(1G)-C(22G) | 105.0(6) | C(27Z)-C(26Z)-C(25Z) | 115(2) |

Table 32: Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(\text{1-Buimid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U^{11} | U^{22} | U^{33} | U^{23} | U^{13} | U^{12} |
|-------|----------|----------|----------|----------|----------|----------|
| Ag(1) | 58(1) | 45(1) | 22(1) | 7(1) | 9(1) | 25(1) |
| Ag(2) | 23(1) | 23(1) | 20(1) | 1(1) | 2(1) | -1(1) |
| Ag(3) | 47(1) | 42(1) | 22(1) | -3(1) | -3(1) | 15(1) |
| Ag(4) | 27(1) | 24(1) | 19(1) | 1(1) | 2(1) | 2(1) |
| O(1A) | 42(2) | 53(3) | 21(2) | 5(2) | 4(2) | 14(2) |
| O(2A) | 30(2) | 45(2) | 25(2) | -5(2) | 6(2) | 5(2) |
| C(1A) | 35(3) | 29(3) | 25(3) | 4(2) | 3(2) | 5(2) |

| | | | | | | |
|--------|-------|-------|-------|--------|--------|-------|
| C(2A) | 30(3) | 27(3) | 24(3) | 2(2) | 2(2) | 10(2) |
| C(3A) | 34(3) | 35(3) | 23(3) | 7(2) | 4(2) | 15(2) |
| C(4A) | 39(3) | 37(3) | 37(3) | 6(3) | 9(3) | 6(3) |
| C(5A) | 50(4) | 44(4) | 51(4) | 11(3) | 4(3) | -1(3) |
| C(6A) | 46(4) | 53(4) | 65(5) | 23(3) | 19(3) | 6(3) |
| C(7A) | 50(4) | 52(4) | 44(4) | 16(3) | 23(3) | 12(3) |
| C(8A) | 43(3) | 39(3) | 31(3) | 10(2) | 9(3) | 17(2) |
| C(9A) | 44(3) | 46(3) | 21(3) | 5(2) | 9(2) | 17(3) |
| C(10A) | 37(3) | 36(3) | 26(3) | 3(2) | 1(2) | 16(2) |
| C(11A) | 47(4) | 42(3) | 26(3) | -2(2) | -1(3) | 17(3) |
| C(12A) | 58(4) | 35(4) | 44(4) | -10(3) | 2(3) | 4(3) |
| C(13A) | 63(5) | 37(4) | 48(4) | 0(3) | 13(3) | -3(3) |
| C(14A) | 43(4) | 39(3) | 34(3) | 5(3) | 8(3) | 3(3) |
| C(15A) | 33(3) | 34(3) | 28(3) | 4(2) | 3(2) | 15(2) |
| O(1B) | 33(2) | 60(3) | 31(2) | 8(2) | -3(2) | 11(2) |
| O(2B) | 41(2) | 65(3) | 25(2) | -1(2) | -4(2) | 16(2) |
| C(1B) | 29(3) | 31(3) | 27(3) | 7(2) | 1(2) | 0(2) |
| C(2B) | 25(3) | 35(3) | 20(3) | -1(2) | 2(2) | 9(2) |
| C(3B) | 25(3) | 39(3) | 31(3) | -3(2) | 2(2) | 6(2) |
| C(4B) | 35(3) | 44(4) | 39(3) | 7(3) | 4(3) | 1(3) |
| C(5B) | 43(4) | 47(4) | 67(5) | 8(3) | -1(3) | -7(3) |
| C(6B) | 40(4) | 59(5) | 75(5) | 5(4) | -10(3) | -9(3) |
| C(7B) | 34(4) | 57(4) | 54(4) | 0(3) | -14(3) | -2(3) |
| C(8B) | 26(3) | 42(3) | 31(3) | -3(2) | 1(2) | 7(2) |
| C(9B) | 31(3) | 46(3) | 30(3) | 0(3) | -5(2) | 9(3) |
| C(10B) | 28(3) | 41(3) | 28(3) | 5(2) | 2(2) | 11(2) |
| C(11B) | 43(4) | 46(3) | 28(3) | 12(3) | 1(3) | 14(3) |
| C(12B) | 51(4) | 42(4) | 38(4) | 9(3) | 5(3) | 9(3) |
| C(13B) | 40(4) | 46(4) | 43(4) | 6(3) | 2(3) | -7(3) |
| C(14B) | 32(3) | 42(3) | 38(3) | 6(3) | -5(3) | 4(3) |
| C(15B) | 23(3) | 35(3) | 24(3) | 0(2) | 1(2) | 7(2) |
| O(1C) | 54(3) | 36(2) | 23(2) | -3(2) | 7(2) | 4(2) |
| O(2C) | 53(3) | 39(2) | 28(2) | -8(2) | 2(2) | 16(2) |
| C(1C) | 40(3) | 31(3) | 24(3) | -5(2) | 6(2) | -1(2) |
| C(2C) | 47(3) | 27(3) | 20(3) | 0(2) | 5(2) | 7(2) |
| C(3C) | 39(3) | 32(3) | 21(3) | 4(2) | 1(2) | 11(2) |
| C(4C) | 40(3) | 46(4) | 28(3) | 4(3) | 5(2) | 6(3) |
| C(5C) | 47(4) | 48(4) | 45(4) | 6(3) | -3(3) | -1(3) |

| | | | | | | |
|--------|--------|-------|--------|--------|--------|--------|
| C(6C) | 35(4) | 62(5) | 56(4) | 13(3) | 11(3) | 7(3) |
| C(7C) | 44(4) | 63(4) | 40(4) | 9(3) | 13(3) | 13(3) |
| C(8C) | 43(3) | 37(3) | 23(3) | 4(2) | 4(2) | 15(2) |
| C(9C) | 56(4) | 40(3) | 22(3) | 2(2) | 9(3) | 16(3) |
| C(10C) | 56(4) | 28(3) | 28(3) | -3(2) | 3(3) | 7(3) |
| C(11C) | 80(5) | 42(4) | 29(3) | -6(3) | -1(3) | 4(3) |
| C(12C) | 73(5) | 48(4) | 46(4) | -8(3) | -10(4) | -10(4) |
| C(13C) | 49(4) | 41(4) | 65(5) | -8(3) | -4(3) | -8(3) |
| C(14C) | 56(4) | 38(4) | 42(4) | -5(3) | 9(3) | 1(3) |
| C(15C) | 44(3) | 30(3) | 27(3) | 1(2) | 6(2) | 11(2) |
| O(1D) | 91(4) | 57(3) | 26(2) | 10(2) | 6(2) | 42(3) |
| O(2D) | 111(4) | 69(3) | 23(2) | 10(2) | 12(3) | 54(3) |
| C(1D) | 40(3) | 33(3) | 26(3) | 9(2) | 5(2) | 6(2) |
| C(2D) | 41(3) | 26(3) | 24(3) | 5(2) | 1(2) | 11(2) |
| C(3D) | 40(3) | 32(3) | 31(3) | 9(2) | 5(2) | 7(2) |
| C(4D) | 43(4) | 41(4) | 53(4) | 11(3) | 4(3) | 6(3) |
| C(5D) | 45(4) | 48(4) | 96(6) | 24(4) | 11(4) | 2(3) |
| C(6D) | 59(5) | 64(5) | 110(6) | 47(5) | 34(4) | 15(4) |
| C(7D) | 79(5) | 64(5) | 53(4) | 39(4) | 25(4) | 28(4) |
| C(8D) | 53(4) | 49(4) | 32(3) | 18(3) | 6(3) | 20(3) |
| C(9D) | 67(4) | 52(4) | 27(3) | 8(3) | -3(3) | 23(3) |
| C(10D) | 47(4) | 39(4) | 42(3) | -9(3) | -11(3) | 14(3) |
| C(11D) | 60(4) | 53(5) | 70(5) | -13(4) | -26(4) | 14(3) |
| C(12D) | 49(5) | 48(5) | 113(7) | -12(4) | -19(4) | 2(3) |
| C(13D) | 53(4) | 45(4) | 125(7) | 18(5) | 5(5) | -7(4) |
| C(14D) | 52(4) | 42(4) | 75(5) | 11(4) | 9(3) | 0(3) |
| C(15D) | 36(3) | 28(3) | 42(3) | 3(2) | 3(2) | 12(2) |
| O(1E) | 46(2) | 42(2) | 33(2) | 8(2) | -11(2) | -23(2) |
| O(2E) | 35(2) | 38(2) | 34(2) | 8(2) | -1(2) | -9(2) |
| C(1E) | 27(3) | 36(3) | 22(3) | -6(2) | 3(2) | -9(2) |
| C(2E) | 40(3) | 41(3) | 15(3) | 0(2) | 1(2) | -16(2) |
| C(3E) | 33(3) | 39(3) | 23(3) | -1(2) | -1(2) | -17(2) |
| C(4E) | 36(3) | 42(3) | 44(4) | 6(3) | -4(3) | -7(3) |
| C(5E) | 47(4) | 57(4) | 50(4) | -1(3) | 1(3) | -1(3) |
| C(6E) | 62(5) | 45(4) | 70(5) | -3(4) | 1(4) | -3(3) |
| C(7E) | 53(4) | 35(3) | 72(5) | 9(3) | -2(4) | -10(3) |
| C(8E) | 47(3) | 33(3) | 39(4) | 5(3) | -2(3) | -13(3) |
| C(9E) | 36(3) | 46(3) | 46(4) | 4(3) | 4(3) | -20(3) |

| | | | | | | |
|--------|--------|--------|--------|--------|-------|--------|
| C(10E) | 36(3) | 53(4) | 36(3) | -4(3) | 4(3) | -12(3) |
| C(11E) | 42(4) | 70(4) | 50(4) | 3(4) | 6(3) | -13(3) |
| C(12E) | 39(4) | 78(5) | 58(5) | -6(4) | 11(3) | 0(3) |
| C(13E) | 49(4) | 58(4) | 56(5) | -9(4) | 7(3) | 6(3) |
| C(14E) | 48(4) | 53(4) | 32(3) | -4(3) | 6(3) | -4(3) |
| C(15E) | 37(3) | 44(3) | 24(3) | -2(3) | 2(2) | -10(2) |
| O(1F) | 48(2) | 40(2) | 28(2) | -4(2) | 11(2) | -20(2) |
| O(2F) | 40(2) | 38(2) | 28(2) | -4(2) | 9(2) | -12(2) |
| C(1F) | 39(3) | 31(3) | 25(3) | 3(2) | -1(2) | -10(2) |
| C(2F) | 42(3) | 44(3) | 27(3) | -2(3) | 9(3) | -23(2) |
| C(3F) | 61(4) | 41(3) | 24(3) | 0(3) | 9(3) | -20(3) |
| C(4F) | 65(4) | 53(4) | 46(4) | 16(3) | 10(3) | -6(3) |
| C(5F) | 101(6) | 62(5) | 49(5) | 21(4) | 9(4) | 10(4) |
| C(6F) | 159(8) | 48(5) | 52(5) | 15(4) | 18(6) | -2(5) |
| C(7F) | 140(6) | 48(4) | 61(5) | 11(4) | 21(6) | -42(5) |
| C(8F) | 85(4) | 50(4) | 52(4) | 6(3) | 28(4) | -39(3) |
| C(9F) | 80(4) | 75(5) | 57(5) | -7(4) | 33(4) | -53(4) |
| C(10F) | 46(4) | 89(5) | 45(4) | -8(4) | 17(3) | -32(3) |
| C(11F) | 42(4) | 131(7) | 66(6) | -22(6) | 15(4) | -41(4) |
| C(12F) | 34(4) | 162(9) | 81(6) | 6(7) | 3(4) | -8(5) |
| C(13F) | 63(5) | 117(7) | 57(5) | 10(5) | 16(4) | 14(4) |
| C(14F) | 45(4) | 75(4) | 38(4) | 3(3) | 6(3) | -9(3) |
| C(15F) | 45(3) | 62(4) | 35(4) | 0(3) | 8(3) | -20(3) |
| Ag(5) | 41(1) | 39(1) | 30(1) | 4(1) | 2(1) | -9(1) |
| C(21A) | 39(3) | 48(4) | 29(3) | 8(3) | 10(3) | -7(3) |
| N(1A) | 35(3) | 40(3) | 33(3) | 10(2) | 4(2) | -4(2) |
| C(22A) | 40(3) | 39(3) | 31(3) | 9(2) | 9(3) | 3(3) |
| C(23A) | 31(3) | 49(4) | 32(3) | 8(3) | 8(2) | 3(3) |
| N(2A) | 38(3) | 42(3) | 34(3) | 12(2) | 4(2) | -6(2) |
| C(24A) | 85(6) | 59(4) | 46(4) | -4(3) | 8(4) | -28(4) |
| C(25A) | 123(8) | 53(4) | 74(6) | 7(4) | -5(5) | -21(5) |
| C(26A) | 102(7) | 77(6) | 82(7) | -6(5) | 18(6) | -14(5) |
| C(27A) | 87(7) | 99(7) | 108(8) | -1(6) | 26(6) | 14(6) |
| C(21B) | 41(3) | 39(3) | 25(3) | 0(2) | 2(2) | -2(3) |
| N(1B) | 38(3) | 33(3) | 30(3) | 0(2) | -1(2) | -6(2) |
| C(22B) | 50(4) | 47(4) | 21(3) | -2(3) | -1(3) | -11(3) |
| C(23B) | 44(4) | 45(4) | 31(3) | -4(3) | -2(3) | -13(3) |
| N(2B) | 45(3) | 42(3) | 29(3) | -2(2) | 7(2) | -10(2) |

| | | | | | | |
|--------|---------|---------|---------|--------|--------|--------|
| C(24B) | 50(4) | 50(4) | 39(4) | 4(3) | 8(3) | -14(3) |
| C(25B) | 56(4) | 47(4) | 40(4) | 4(3) | 8(3) | -16(3) |
| C(26B) | 60(4) | 47(4) | 53(4) | 8(3) | -5(4) | -13(3) |
| C(27B) | 74(5) | 50(4) | 73(6) | 6(4) | -4(4) | -4(4) |
| Ag(6) | 48(1) | 44(1) | 30(1) | 2(1) | 4(1) | -7(1) |
| C(21C) | 41(3) | 44(4) | 26(3) | 0(3) | -9(2) | -4(3) |
| N(1C) | 48(3) | 45(3) | 32(3) | 7(2) | -6(2) | -5(2) |
| C(22C) | 53(4) | 58(4) | 29(3) | 1(3) | -5(3) | -14(3) |
| C(23C) | 55(4) | 54(4) | 33(3) | 3(3) | -16(3) | -16(3) |
| N(2C) | 45(3) | 48(3) | 32(3) | 2(2) | -8(2) | -11(2) |
| C(24C) | 62(4) | 56(4) | 41(4) | 13(3) | -3(3) | -12(3) |
| C(25C) | 80(5) | 105(6) | 83(6) | 49(5) | 26(4) | 12(5) |
| C(26C) | 76(9) | 80(11) | 93(12) | 47(9) | 30(8) | 17(8) |
| C(27C) | 91(15) | 75(15) | 130(30) | 57(18) | 68(18) | 19(11) |
| C(25X) | 80(5) | 105(6) | 83(6) | 49(5) | 26(4) | 12(5) |
| C(26X) | 77(9) | 74(8) | 32(7) | 20(7) | 5(7) | -2(7) |
| C(27X) | 101(13) | 113(18) | 90(20) | 56(19) | 44(17) | 27(12) |
| C(21D) | 47(4) | 46(4) | 30(3) | 8(3) | 10(3) | 2(3) |
| N(1D) | 49(3) | 45(3) | 31(3) | 4(2) | 9(2) | 0(2) |
| C(22D) | 57(4) | 50(4) | 28(3) | 6(3) | 9(3) | 1(3) |
| C(23D) | 52(4) | 51(4) | 38(3) | 18(3) | 14(3) | 0(3) |
| N(2D) | 44(3) | 49(3) | 33(3) | 6(2) | 8(2) | 2(2) |
| C(24D) | 51(4) | 68(5) | 36(4) | 3(3) | 5(3) | -5(3) |
| C(25D) | 54(4) | 46(4) | 51(4) | 13(3) | 3(3) | -3(3) |
| C(26D) | 55(4) | 60(5) | 61(5) | 8(4) | 3(3) | -2(4) |
| C(27D) | 49(4) | 79(6) | 93(7) | 5(5) | 6(4) | 3(4) |
| Ag(7) | 53(1) | 41(1) | 23(1) | 7(1) | -7(1) | -20(1) |
| Ag(8) | 23(1) | 24(1) | 21(1) | 1(1) | 0(1) | 1(1) |
| Ag(9) | 53(1) | 47(1) | 22(1) | -6(1) | 9(1) | -22(1) |
| Ag(10) | 27(1) | 25(1) | 20(1) | 2(1) | 0(1) | -2(1) |
| O(1G) | 40(2) | 55(3) | 21(2) | 0(2) | 0(2) | -14(2) |
| O(2G) | 32(2) | 60(3) | 29(2) | -7(2) | -2(2) | -14(2) |
| C(1G) | 28(3) | 23(3) | 25(3) | -2(2) | -1(2) | -3(2) |
| C(2G) | 20(3) | 33(3) | 24(3) | -1(2) | 2(2) | -7(2) |
| C(3G) | 23(3) | 33(3) | 24(3) | 4(2) | 4(2) | -8(2) |
| C(4G) | 35(3) | 36(3) | 28(3) | 4(2) | 0(2) | -7(2) |
| C(5G) | 42(4) | 33(3) | 43(4) | -4(3) | -1(3) | 1(3) |
| C(6G) | 48(4) | 37(3) | 43(4) | -8(3) | 4(3) | -12(3) |

| | | | | | | |
|--------|-------|-------|-------|--------|--------|--------|
| C(7G) | 37(3) | 39(3) | 33(3) | -5(3) | 5(2) | -14(3) |
| C(8G) | 33(3) | 36(3) | 23(3) | 0(2) | 2(2) | -12(2) |
| C(9G) | 32(3) | 45(3) | 24(3) | 3(2) | -4(2) | -13(2) |
| C(10G) | 28(3) | 43(3) | 32(3) | 4(2) | -3(2) | -5(2) |
| C(11G) | 32(3) | 52(4) | 46(4) | 8(3) | -12(3) | 0(3) |
| C(12G) | 43(4) | 51(4) | 71(5) | 15(3) | -16(3) | 6(3) |
| C(13G) | 43(4) | 36(4) | 64(4) | 0(3) | -1(3) | 5(3) |
| C(14G) | 38(3) | 38(3) | 40(4) | -1(3) | 2(3) | -2(3) |
| C(15G) | 23(3) | 36(3) | 28(3) | 1(2) | 2(2) | -7(2) |
| O(1H) | 34(2) | 52(3) | 27(2) | 7(2) | 8(2) | -6(2) |
| O(2H) | 52(3) | 68(3) | 23(2) | -4(2) | 10(2) | -21(2) |
| C(1H) | 37(3) | 29(3) | 27(3) | 4(2) | 7(2) | -5(2) |
| C(2H) | 32(3) | 38(3) | 20(3) | -5(2) | 4(2) | -14(2) |
| C(3H) | 32(3) | 44(3) | 20(3) | -1(2) | 4(2) | -12(2) |
| C(4H) | 45(4) | 48(4) | 35(3) | 9(3) | 15(3) | 1(3) |
| C(5H) | 61(5) | 45(4) | 48(4) | 12(3) | 11(3) | 0(3) |
| C(6H) | 60(4) | 54(4) | 40(4) | 15(3) | 3(3) | -9(3) |
| C(7H) | 51(4) | 56(4) | 25(3) | 5(3) | 3(3) | -19(3) |
| C(8H) | 37(3) | 42(3) | 27(3) | 2(2) | 5(2) | -19(2) |
| C(9H) | 41(3) | 51(4) | 28(3) | -10(3) | 13(3) | -19(3) |
| C(10H) | 40(3) | 38(3) | 36(3) | -10(2) | 14(3) | -18(2) |
| C(11H) | 48(4) | 49(4) | 47(4) | -10(3) | 21(3) | -17(3) |
| C(12H) | 44(4) | 46(4) | 60(4) | -11(3) | 16(3) | -10(3) |
| C(13H) | 56(4) | 39(4) | 53(4) | 0(3) | 8(3) | -5(3) |
| C(14H) | 47(4) | 39(3) | 36(3) | -2(3) | 7(3) | -9(3) |
| C(15H) | 36(3) | 40(3) | 24(3) | -5(2) | 2(2) | -12(2) |
| O(1I) | 57(3) | 42(2) | 18(2) | -2(2) | 1(2) | -14(2) |
| O(2I) | 57(3) | 45(3) | 29(2) | -9(2) | 6(2) | -26(2) |
| C(1I) | 36(3) | 31(3) | 23(3) | -5(2) | -2(2) | -6(2) |
| C(2I) | 40(3) | 27(3) | 21(3) | 2(2) | 3(2) | -11(2) |
| C(3I) | 41(3) | 33(3) | 25(3) | 6(2) | -1(2) | -12(2) |
| C(4I) | 44(3) | 41(4) | 33(3) | 4(3) | 8(3) | -2(3) |
| C(5I) | 46(4) | 55(4) | 44(4) | 13(3) | 9(3) | -2(3) |
| C(6I) | 41(4) | 68(5) | 60(5) | 20(4) | -2(3) | -3(3) |
| C(7I) | 41(3) | 57(4) | 45(4) | 13(3) | -11(3) | -10(3) |
| C(8I) | 42(3) | 37(3) | 33(3) | 9(2) | -7(3) | -13(3) |
| C(9I) | 57(4) | 43(4) | 29(3) | 4(3) | -11(3) | -18(3) |
| C(10I) | 59(4) | 34(3) | 23(3) | 1(2) | -4(3) | -12(3) |

| | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|
| C(11I) | 84(5) | 40(4) | 34(4) | -10(3) | 2(3) | -9(3) |
| C(12I) | 92(5) | 41(4) | 46(4) | -8(3) | 16(4) | 6(4) |
| C(13I) | 61(4) | 42(4) | 67(5) | -9(3) | 8(3) | 6(3) |
| C(14I) | 52(4) | 38(4) | 40(4) | -7(3) | 5(3) | -7(3) |
| C(15I) | 50(3) | 28(3) | 28(3) | -1(2) | 0(2) | -13(3) |
| O(1J) | 72(3) | 50(3) | 28(2) | 12(2) | -4(2) | -31(2) |
| O(2J) | 101(4) | 66(3) | 30(2) | 18(2) | -14(2) | -47(3) |
| C(1J) | 41(3) | 37(3) | 30(3) | 9(2) | 1(2) | -4(3) |
| C(2J) | 40(3) | 27(3) | 30(3) | 10(2) | -2(2) | -10(2) |
| C(3J) | 39(3) | 29(3) | 24(3) | 4(2) | 2(2) | -5(2) |
| C(4J) | 42(4) | 32(3) | 48(4) | 12(3) | 11(3) | -4(3) |
| C(5J) | 48(4) | 51(4) | 79(5) | 23(4) | 10(4) | 0(3) |
| C(6J) | 51(4) | 65(5) | 82(5) | 30(4) | -8(4) | 8(4) |
| C(7J) | 67(5) | 65(5) | 42(4) | 30(4) | -10(3) | -4(4) |
| C(8J) | 52(4) | 40(4) | 31(3) | 9(3) | 0(3) | -12(3) |
| C(9J) | 66(4) | 44(4) | 27(3) | 3(3) | 11(3) | -19(3) |
| C(10J) | 53(4) | 37(4) | 55(4) | -8(3) | 26(3) | -15(3) |
| C(11J) | 80(5) | 40(4) | 76(5) | -4(4) | 39(4) | -6(3) |
| C(12J) | 70(5) | 52(5) | 121(7) | 0(5) | 44(5) | 0(4) |
| C(13J) | 62(5) | 45(5) | 139(7) | 23(5) | 20(5) | 13(4) |
| C(14J) | 51(4) | 47(4) | 104(6) | 26(4) | 13(4) | -1(3) |
| C(15J) | 46(4) | 25(3) | 56(4) | 4(3) | 9(3) | -5(3) |
| O(1K) | 52(3) | 40(2) | 35(2) | -4(2) | -11(2) | 21(2) |
| O(2K) | 37(2) | 55(3) | 35(2) | -6(2) | -5(2) | 16(2) |
| C(1K) | 42(3) | 47(4) | 30(3) | 6(3) | 4(3) | 18(3) |
| C(2K) | 35(3) | 52(3) | 34(3) | 2(3) | 0(3) | 18(3) |
| C(3K) | 42(3) | 66(4) | 32(3) | 4(3) | 0(3) | 15(3) |
| C(4K) | 39(4) | 79(5) | 44(4) | 6(4) | -3(3) | 8(3) |
| C(5K) | 47(4) | 104(6) | 56(5) | 8(5) | 5(4) | -8(4) |
| C(6K) | 31(4) | 132(7) | 91(7) | 7(6) | 8(4) | 4(4) |
| C(7K) | 44(4) | 124(6) | 68(6) | -5(6) | 6(4) | 28(4) |
| C(8K) | 41(4) | 86(5) | 49(4) | 8(4) | 4(3) | 30(3) |
| C(9K) | 70(5) | 72(5) | 60(5) | 9(4) | 2(4) | 43(4) |
| C(10K) | 73(4) | 59(4) | 41(4) | 6(3) | 6(4) | 34(3) |
| C(11K) | 107(6) | 57(4) | 66(5) | 14(4) | 8(5) | 40(4) |
| C(12K) | 111(7) | 52(5) | 61(5) | 13(4) | -4(5) | 13(4) |
| C(13K) | 85(5) | 61(4) | 40(4) | 18(4) | 1(4) | 7(4) |
| C(14K) | 57(4) | 53(4) | 33(3) | 14(3) | 0(3) | 8(3) |

| | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|
| C(15K) | 51(4) | 49(3) | 27(3) | 9(3) | -1(3) | 21(3) |
| O(1L) | 39(2) | 34(2) | 27(2) | 2(2) | 2(2) | 7(2) |
| O(2L) | 48(2) | 39(2) | 26(2) | 10(2) | 14(2) | 20(2) |
| C(1L) | 22(3) | 35(3) | 22(3) | 0(2) | 1(2) | 7(2) |
| C(2L) | 36(3) | 38(3) | 21(3) | 4(2) | 9(2) | 13(2) |
| C(3L) | 35(3) | 43(3) | 29(3) | 4(3) | 8(2) | 14(2) |
| C(4L) | 42(3) | 55(4) | 36(4) | -3(3) | 7(3) | 1(3) |
| C(5L) | 47(4) | 65(4) | 62(5) | -7(4) | 0(4) | -6(3) |
| C(6L) | 41(4) | 93(6) | 74(6) | -13(5) | 5(4) | 8(4) |
| C(7L) | 39(4) | 83(5) | 55(5) | 9(4) | 6(3) | 21(3) |
| C(8L) | 43(3) | 53(4) | 31(3) | 1(3) | 3(3) | 17(3) |
| C(9L) | 47(4) | 49(4) | 53(4) | 7(3) | 5(3) | 26(3) |
| C(10L) | 57(4) | 29(3) | 32(3) | 1(3) | 7(3) | 13(3) |
| C(11L) | 72(4) | 40(4) | 65(5) | 6(4) | 17(4) | 12(3) |
| C(12L) | 84(5) | 30(3) | 64(5) | -4(3) | 13(4) | -3(3) |
| C(13L) | 63(4) | 45(4) | 48(4) | -4(3) | 15(3) | -3(3) |
| C(14L) | 51(4) | 39(3) | 37(4) | 2(3) | 11(3) | 9(3) |
| C(15L) | 44(3) | 37(3) | 20(3) | 0(2) | 10(2) | 15(2) |
| Ag(11) | 39(1) | 41(1) | 31(1) | 1(1) | 3(1) | 9(1) |
| C(21E) | 41(4) | 44(4) | 42(4) | -4(3) | 10(3) | 6(3) |
| N(1E) | 36(3) | 38(3) | 35(3) | -3(2) | 7(2) | 1(2) |
| C(22E) | 33(3) | 51(4) | 35(3) | -7(3) | 7(3) | 1(3) |
| C(23E) | 36(3) | 43(4) | 40(3) | -13(3) | 10(3) | 6(3) |
| N(2E) | 37(3) | 43(3) | 44(3) | -1(2) | 9(2) | 8(2) |
| C(24E) | 85(6) | 72(4) | 69(5) | 24(4) | 30(4) | 36(4) |
| C(25E) | 87(10) | 72(7) | 61(9) | 43(6) | 34(7) | 28(7) |
| C(26Y) | 82(9) | 69(7) | 59(8) | 27(6) | 25(7) | 24(6) |
| C(27E) | 78(11) | 68(9) | 99(15) | 35(9) | 30(9) | 27(8) |
| C(24Y) | 85(6) | 72(4) | 69(5) | 24(4) | 30(4) | 36(4) |
| C(25Y) | 69(9) | 69(7) | 79(12) | 20(9) | -1(10) | 36(8) |
| C(26E) | 69(10) | 61(9) | 75(13) | 15(10) | 1(11) | 36(7) |
| C(27Y) | 74(15) | 70(11) | 74(17) | 31(12) | 23(13) | 25(11) |
| C(21F) | 36(3) | 37(3) | 29(3) | 9(2) | 3(2) | 7(2) |
| N(1F) | 35(3) | 40(3) | 29(3) | 4(2) | 2(2) | 4(2) |
| C(22F) | 57(4) | 53(4) | 21(3) | 3(3) | -6(3) | 13(3) |
| C(23F) | 51(4) | 51(4) | 26(3) | 7(3) | -2(3) | 12(3) |
| N(2F) | 37(3) | 41(3) | 25(2) | 10(2) | 6(2) | 10(2) |
| C(24F) | 45(4) | 48(4) | 31(3) | 4(3) | 13(3) | 14(3) |

| | | | | | | |
|--------|--------|---------|---------|--------|---------|---------|
| C(25F) | 49(4) | 44(3) | 38(4) | 3(3) | 7(3) | 17(3) |
| C(26F) | 52(4) | 52(4) | 52(4) | 5(3) | 5(3) | 14(3) |
| C(27F) | 75(6) | 47(4) | 94(7) | 3(4) | 9(5) | -2(4) |
| Ag(12) | 49(1) | 43(1) | 30(1) | 3(1) | 2(1) | 5(1) |
| C(21G) | 45(4) | 43(4) | 35(3) | 14(3) | 1(3) | -1(3) |
| N(1G) | 51(3) | 41(3) | 35(3) | 6(2) | -7(2) | 3(2) |
| C(22G) | 49(4) | 53(4) | 32(3) | 12(3) | -5(3) | -2(3) |
| C(23G) | 49(4) | 55(4) | 37(3) | 12(3) | -6(3) | 6(3) |
| N(2G) | 43(3) | 46(3) | 36(3) | 10(2) | -7(2) | 3(2) |
| C(24G) | 54(4) | 69(5) | 41(4) | 9(3) | 0(3) | 10(3) |
| C(25G) | 59(4) | 55(4) | 58(5) | 15(4) | 8(3) | 9(4) |
| C(26G) | 65(5) | 69(5) | 72(6) | 12(4) | 16(4) | 13(4) |
| C(27G) | 62(5) | 81(6) | 95(7) | 3(5) | 18(5) | 4(4) |
| C(21H) | 46(4) | 43(4) | 27(3) | -2(3) | 10(3) | 0(3) |
| N(1H) | 50(3) | 51(3) | 27(3) | 1(2) | 9(2) | 3(2) |
| C(22H) | 66(5) | 64(5) | 27(3) | 2(3) | 14(3) | 11(3) |
| C(23H) | 63(5) | 59(4) | 30(3) | 3(3) | 16(3) | 15(3) |
| N(2H) | 48(3) | 52(3) | 30(3) | 7(2) | 16(2) | 10(2) |
| C(24H) | 69(4) | 57(4) | 41(4) | 17(3) | 13(3) | 15(3) |
| C(25H) | 68(8) | 58(11) | 46(10) | 13(9) | -3(6) | 21(8) |
| C(26H) | 63(7) | 30(7) | 64(9) | 16(6) | 7(6) | 14(6) |
| C(27H) | 60(10) | 73(13) | 91(18) | 24(14) | -20(11) | 8(8) |
| C(24Z) | 69(4) | 57(4) | 41(4) | 17(3) | 13(3) | 15(3) |
| C(25Z) | 64(6) | 57(10) | 58(11) | 11(8) | 9(8) | 20(8) |
| C(26Z) | 89(10) | 58(9) | 65(10) | 21(8) | 3(9) | -4(7) |
| C(27Z) | 84(12) | 120(20) | 120(20) | 80(20) | -29(16) | -23(14) |

Table 33. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(\text{1-Bu-imid})_2]_2[\text{Ag}_4(\text{9-aca})_6]$.

| | x | y | z | U(eq) |
|-------|------|------|------|-------|
| H(4A) | 6688 | 374 | 6470 | 45 |
| H(5A) | 7621 | 1029 | 6242 | 57 |
| H(6A) | 8066 | 756 | 5539 | 63 |
| H(7A) | 7545 | -166 | 5071 | 56 |

| | | | | |
|--------|------|-------|-------|----|
| H(9A) | 6667 | -1175 | 4929 | 44 |
| H(11A) | 5853 | -2220 | 4784 | 47 |
| H(12A) | 5018 | -2959 | 5021 | 56 |
| H(13A) | 4595 | -2755 | 5730 | 59 |
| H(14A) | 5001 | -1772 | 6194 | 46 |
| H(4B) | 2003 | -95 | 6504 | 47 |
| H(5B) | 1066 | -888 | 6212 | 63 |
| H(6B) | 391 | -792 | 5520 | 72 |
| H(7B) | 611 | 113 | 5127 | 60 |
| H(9B) | 1273 | 1223 | 5076 | 44 |
| H(11B) | 1901 | 2362 | 5048 | 46 |
| H(12B) | 2742 | 3225 | 5351 | 52 |
| H(13B) | 3458 | 3124 | 6043 | 52 |
| H(14B) | 3367 | 2132 | 6392 | 46 |
| H(4C) | 2768 | 1301 | 8387 | 45 |
| H(5C) | 1574 | 1002 | 8528 | 56 |
| H(6C) | 1056 | 1505 | 9172 | 60 |
| H(7C) | 1735 | 2335 | 9645 | 58 |
| H(9C) | 2915 | 3074 | 9846 | 47 |
| H(11C) | 4136 | 3739 | 10077 | 61 |
| H(12C) | 5332 | 4005 | 9947 | 69 |
| H(13C) | 5854 | 3506 | 9318 | 64 |
| H(14C) | 5159 | 2725 | 8809 | 55 |
| H(4D) | 4777 | -1348 | 8657 | 54 |
| H(5D) | 4067 | -2078 | 8992 | 74 |
| H(6D) | 4479 | -2351 | 9716 | 88 |
| H(7D) | 5628 | -1933 | 10069 | 74 |
| H(9D) | 6819 | -1293 | 10044 | 59 |
| H(11D) | 8024 | -631 | 10041 | 77 |
| H(12D) | 8803 | -8 | 9685 | 88 |
| H(13D) | 8436 | 269 | 8966 | 88 |
| H(14D) | 7235 | -47 | 8609 | 67 |
| H(4E) | 5047 | 2372 | 7697 | 49 |
| H(5E) | 4731 | 3504 | 7912 | 62 |
| H(6E) | 5582 | 4427 | 7834 | 72 |
| H(7E) | 6738 | 4207 | 7579 | 65 |
| H(9E) | 7702 | 3352 | 7339 | 51 |
| H(11E) | 8724 | 2520 | 7179 | 65 |

| | | | | |
|--------|------|-------|------|-----|
| H(12E) | 9134 | 1396 | 7096 | 71 |
| H(13E) | 8310 | 472 | 7164 | 67 |
| H(14E) | 7047 | 669 | 7277 | 54 |
| H(4F) | 4223 | -1445 | 7783 | 64 |
| H(5F) | 4602 | -2530 | 7936 | 84 |
| H(6F) | 3704 | -3441 | 7895 | 102 |
| H(7F) | 2452 | -3251 | 7726 | 98 |
| H(9F) | 1393 | -2415 | 7541 | 84 |
| H(11F) | 351 | -1606 | 7363 | 98 |
| H(12F) | -44 | -518 | 7271 | 112 |
| H(13F) | 838 | 388 | 7282 | 94 |
| H(14F) | 2134 | 209 | 7437 | 63 |
| H(21A) | 4839 | 1286 | 6314 | 45 |
| H(22A) | 5385 | 577 | 5123 | 43 |
| H(23A) | 6175 | 1605 | 5373 | 44 |
| H(24A) | 6441 | 2387 | 6167 | 76 |
| H(24B) | 5934 | 2201 | 6547 | 76 |
| H(25A) | 5424 | 3031 | 5833 | 101 |
| H(25B) | 4849 | 2779 | 6158 | 101 |
| H(26A) | 6082 | 3682 | 6424 | 105 |
| H(26B) | 5483 | 3442 | 6740 | 105 |
| H(27A) | 5173 | 4529 | 6527 | 147 |
| H(27B) | 4508 | 3983 | 6333 | 147 |
| H(27C) | 5106 | 4222 | 6016 | 147 |
| H(21B) | 3509 | -1010 | 6487 | 43 |
| H(22B) | 2763 | -1116 | 5213 | 48 |
| H(23B) | 2035 | -1981 | 5543 | 49 |
| H(24C) | 1852 | -2024 | 6453 | 56 |
| H(24D) | 2632 | -1857 | 6765 | 56 |
| H(25C) | 2391 | -3073 | 6587 | 57 |
| H(25D) | 2449 | -2982 | 6077 | 57 |
| H(26C) | 3657 | -2814 | 6768 | 65 |
| H(26D) | 3739 | -2579 | 6287 | 65 |
| H(27D) | 4257 | -3695 | 6335 | 100 |
| H(27E) | 3537 | -3748 | 5968 | 100 |
| H(27F) | 3457 | -3983 | 6449 | 100 |
| H(21C) | 6133 | 1416 | 8528 | 46 |
| H(22C) | 6474 | 1751 | 9835 | 57 |

| | | | | |
|--------|------|-------|------|-----|
| H(23C) | 7317 | 2557 | 9539 | 59 |
| H(24E) | 7304 | 2953 | 8701 | 64 |
| H(24F) | 6933 | 2407 | 8308 | 64 |
| H(25E) | 7941 | 1839 | 8260 | 102 |
| H(25F) | 8318 | 2563 | 8454 | 102 |
| H(26E) | 8183 | 1517 | 8970 | 95 |
| H(26F) | 8702 | 2199 | 9072 | 95 |
| H(27G) | 9454 | 1237 | 8925 | 135 |
| H(27H) | 9515 | 1748 | 8550 | 135 |
| H(27I) | 8992 | 1062 | 8446 | 135 |
| H(25G) | 8196 | 2405 | 8288 | 102 |
| H(25H) | 8350 | 2341 | 8803 | 102 |
| H(26G) | 7914 | 1349 | 8154 | 72 |
| H(26H) | 7961 | 1261 | 8671 | 72 |
| H(27J) | 9101 | 842 | 8384 | 141 |
| H(27K) | 9313 | 1499 | 8740 | 141 |
| H(27L) | 9263 | 1582 | 8221 | 141 |
| H(21D) | 3687 | 21 | 8679 | 48 |
| H(22D) | 4238 | -168 | 9945 | 53 |
| H(23D) | 3043 | -831 | 9717 | 54 |
| H(24E) | 2433 | -1303 | 8820 | 62 |
| H(24F) | 2510 | -705 | 8502 | 62 |
| H(25E) | 1646 | -621 | 9256 | 60 |
| H(25F) | 1810 | 49 | 9013 | 60 |
| H(26E) | 956 | -1144 | 8607 | 71 |
| H(26F) | 1151 | -500 | 8346 | 71 |
| H(27G) | -97 | -387 | 8571 | 111 |
| H(27H) | 431 | 240 | 8816 | 111 |
| H(27I) | 238 | -401 | 9078 | 111 |
| H(4G) | 8307 | -6676 | 6368 | 40 |
| H(5G) | 8422 | -7777 | 6031 | 48 |
| H(6G) | 7761 | -8106 | 5325 | 52 |
| H(7G) | 6924 | -7367 | 4997 | 44 |
| H(9G) | 6307 | -6223 | 5023 | 41 |
| H(11G) | 5664 | -5091 | 5038 | 53 |
| H(12G) | 5430 | -4035 | 5414 | 67 |
| H(13G) | 6061 | -3708 | 6126 | 58 |
| H(14G) | 6970 | -4408 | 6434 | 47 |

| | | | | |
|--------|-------|-------|-------|-----|
| H(4H) | 9950 | -2796 | 6173 | 50 |
| H(5H) | 9575 | -1998 | 5689 | 60 |
| H(6H) | 10052 | -2050 | 4988 | 61 |
| H(7H) | 10884 | -2891 | 4782 | 53 |
| H(9H) | 11669 | -3899 | 4957 | 48 |
| H(11H) | 12532 | -4851 | 5142 | 57 |
| H(12H) | 13031 | -5554 | 5649 | 60 |
| H(13H) | 12538 | -5578 | 6341 | 60 |
| H(14H) | 11582 | -4829 | 6528 | 49 |
| H(4I) | 11700 | -3731 | 8404 | 47 |
| H(5I) | 12943 | -4045 | 8552 | 57 |
| H(6I) | 13686 | -3512 | 9193 | 67 |
| H(7I) | 13181 | -2710 | 9663 | 58 |
| H(9I) | 12094 | -1951 | 9858 | 53 |
| H(11I) | 10976 | -1261 | 10083 | 65 |
| H(12I) | 9716 | -1012 | 9961 | 72 |
| H(13I) | 8984 | -1495 | 9323 | 69 |
| H(14I) | 9489 | -2295 | 8818 | 53 |
| H(4J) | 9726 | -6360 | 8612 | 48 |
| H(5J) | 10566 | -7126 | 8919 | 70 |
| H(6J) | 10439 | -7424 | 9638 | 78 |
| H(7J) | 9503 | -6989 | 10036 | 69 |
| H(9J) | 8311 | -6299 | 10064 | 55 |
| H(11J) | 7115 | -5660 | 10099 | 77 |
| H(12J) | 6229 | -4965 | 9789 | 95 |
| H(13J) | 6249 | -4714 | 9057 | 96 |
| H(14J) | 7297 | -5020 | 8658 | 79 |
| H(4K) | 11948 | -4707 | 7406 | 65 |
| H(5K) | 13180 | -4447 | 7254 | 83 |
| H(6K) | 14081 | -5330 | 7216 | 102 |
| H(7K) | 13738 | -6457 | 7245 | 95 |
| H(9K) | 12778 | -7319 | 7428 | 81 |
| H(11K) | 11859 | -8171 | 7639 | 91 |
| H(12K) | 10692 | -8398 | 7831 | 90 |
| H(13K) | 9760 | -7539 | 7877 | 73 |
| H(14K) | 10023 | -6442 | 7718 | 57 |
| H(4L) | 7023 | -4304 | 7328 | 53 |
| H(5L) | 5745 | -4536 | 7174 | 71 |

| | | | | |
|--------|-------|-------|------|-----|
| H(6L) | 4871 | -3634 | 7096 | 85 |
| H(7L) | 5280 | -2493 | 7192 | 70 |
| H(9L) | 6326 | -1647 | 7374 | 59 |
| H(11L) | 7364 | -758 | 7614 | 70 |
| H(12L) | 8596 | -504 | 7880 | 71 |
| H(13L) | 9506 | -1398 | 7976 | 62 |
| H(14L) | 9124 | -2542 | 7789 | 50 |
| H(21E) | 9830 | -5816 | 6344 | 52 |
| H(22E) | 10369 | -5591 | 5141 | 48 |
| H(23E) | 11188 | -6497 | 5429 | 48 |
| H(24G) | 10909 | -6614 | 6610 | 87 |
| H(24H) | 11482 | -6895 | 6255 | 87 |
| H(25I) | 9879 | -7355 | 6169 | 83 |
| H(25J) | 10498 | -7674 | 5860 | 83 |
| H(26I) | 11126 | -8178 | 6469 | 80 |
| H(26J) | 10504 | -7863 | 6776 | 80 |
| H(27M) | 10264 | -9035 | 6564 | 117 |
| H(27N) | 10184 | -8897 | 6053 | 117 |
| H(27O) | 9571 | -8588 | 6371 | 117 |
| H(24I) | 10767 | -6619 | 6586 | 87 |
| H(24J) | 11497 | -6698 | 6329 | 87 |
| H(25K) | 11070 | -7792 | 6023 | 87 |
| H(25L) | 11209 | -7705 | 6558 | 87 |
| H(26K) | 9851 | -7413 | 6101 | 82 |
| H(26L) | 10019 | -7500 | 6618 | 82 |
| H(27P) | 9373 | -8544 | 6225 | 105 |
| H(27Q) | 10194 | -8742 | 6447 | 105 |
| H(27R) | 10067 | -8664 | 5927 | 105 |
| H(21F) | 8508 | -3464 | 6444 | 40 |
| H(22F) | 7810 | -3837 | 5165 | 53 |
| H(23F) | 7076 | -2855 | 5460 | 51 |
| H(24G) | 7567 | -2541 | 6688 | 49 |
| H(24H) | 6845 | -2444 | 6339 | 49 |
| H(25G) | 7575 | -1634 | 6010 | 52 |
| H(25H) | 7420 | -1375 | 6507 | 52 |
| H(26G) | 8815 | -1982 | 6289 | 62 |
| H(26H) | 8652 | -1633 | 6769 | 62 |
| H(27J) | 9376 | -869 | 6423 | 109 |

| | | | | |
|--------|-------|-------|------|-----|
| H(27K) | 8564 | -536 | 6496 | 109 |
| H(27L) | 8727 | -885 | 6015 | 109 |
| H(21G) | 10825 | -4998 | 8652 | 48 |
| H(22G) | 10764 | -5216 | 9921 | 54 |
| H(23G) | 11843 | -5901 | 9662 | 57 |
| H(24I) | 11922 | -5716 | 8451 | 66 |
| H(24J) | 12079 | -6344 | 8750 | 66 |
| H(25I) | 12847 | -5023 | 8988 | 68 |
| H(25J) | 13071 | -5729 | 9194 | 68 |
| H(26I) | 13495 | -6193 | 8525 | 81 |
| H(26J) | 13223 | -5518 | 8296 | 81 |
| H(27M) | 14540 | -5454 | 8494 | 118 |
| H(27N) | 14414 | -5521 | 9000 | 118 |
| H(27O) | 14139 | -4842 | 8775 | 118 |
| H(21H) | 8353 | -3594 | 8559 | 46 |
| H(22H) | 8547 | -3252 | 9865 | 62 |
| H(23H) | 7585 | -2444 | 9583 | 60 |
| H(24K) | 7504 | -2487 | 8376 | 65 |
| H(24L) | 7129 | -2090 | 8787 | 65 |
| H(25K) | 6167 | -2757 | 8319 | 69 |
| H(25L) | 6653 | -3445 | 8357 | 69 |
| H(26K) | 6019 | -2721 | 9083 | 62 |
| H(26L) | 6444 | -3447 | 9089 | 62 |
| H(27P) | 5111 | -3613 | 9032 | 113 |
| H(27Q) | 5447 | -3990 | 8602 | 113 |
| H(27R) | 5027 | -3263 | 8577 | 113 |
| H(24M) | 7319 | -2044 | 8722 | 65 |
| H(24N) | 7413 | -2664 | 8344 | 65 |
| H(25M) | 6162 | -2453 | 8426 | 71 |
| H(25N) | 6294 | -2600 | 8935 | 71 |
| H(26M) | 6422 | -3616 | 8196 | 84 |
| H(26N) | 6609 | -3771 | 8700 | 84 |
| H(27S) | 5395 | -4209 | 8431 | 160 |
| H(27T) | 5128 | -3459 | 8308 | 160 |
| H(27U) | 5312 | -3595 | 8817 | 160 |

X-ray Crystal Data for [Ag(apim)](9-aca)·H₂O

| | |
|-----------------------------------|---|
| Identification code | [Ag(apim)](9-aca)·H ₂ O |
| Empirical formula | C ₂₁ H ₂₂ Ag N ₃ O ₃ |
| Formula weight | 472.29 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | Pbca |
| Unit cell dimensions | a = 9.6450(6) Å α = 90°. b = 19.0589(11) Å β = 90°. c = 21.2920(12) Å γ = 90°. |
| Volume | 3914.0(4) Å ³ |
| Z | 8 |
| Density (calculated) | 1.603 Mg/m ³ |
| Absorption coefficient | 1.057 mm ⁻¹ |
| F(000) | 1920 |
| Crystal size | 0.20 x 0.17 x 0.07 mm ³ |
| Crystal description | colourless plate |
| Theta range for data collection | 1.91 to 28.35°. |
| Index ranges | -12 ≤ h ≤ 12, -25 ≤ k ≤ 25, -28 ≤ l ≤ 28 |
| Reflections collected | 37907 |
| Independent reflections | 4890 [R(int) = 0.0398] |
| Completeness to theta = 26.00° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9297 and 0.8164 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 4890 / 6 / 265 |
| Goodness-of-fit on F ² | 1.027 |
| Final R indices [I > 2σ(I)] | R1 = 0.0280, wR2 = 0.0665 |
| R indices (all data) | R1 = 0.0410, wR2 = 0.0723 |
| Largest diff. peak and hole | 0.447 and -0.546 e.Å ⁻³ |

Table 34. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|-------|----------|----------|---------|-------|
| Ag(1) | 3338(1) | 1127(1) | 4314(1) | 26(1) |
| C(21) | 4013(2) | -430(1) | 4348(1) | 28(1) |
| N(1) | 4502(2) | 208(1) | 4251(1) | 27(1) |
| C(22) | 5879(2) | 123(1) | 4101(1) | 28(1) |
| C(23) | 6193(2) | -570(1) | 4110(1) | 26(1) |
| N(2) | 4998(2) | -915(1) | 4270(1) | 23(1) |
| C(24) | 4806(2) | -1677(1) | 4333(1) | 25(1) |
| C(25) | 3976(2) | -1963(1) | 3784(1) | 23(1) |
| C(26) | 3679(2) | -2743(1) | 3840(1) | 23(1) |
| N(3) | 2765(2) | -2922(1) | 4377(1) | 23(1) |
| O(1) | -1841(2) | -2015(1) | 4164(1) | 33(1) |
| O(2) | 168(2) | -1996(1) | 4673(1) | 33(1) |
| C(1) | -563(2) | -1926(1) | 4190(1) | 22(1) |
| C(2) | 185(2) | -1729(1) | 3591(1) | 21(1) |
| C(3) | 537(2) | -1024(1) | 3476(1) | 24(1) |
| C(4) | 138(2) | -468(1) | 3891(1) | 30(1) |
| C(5) | 470(3) | 213(1) | 3757(1) | 38(1) |
| C(6) | 1247(3) | 378(1) | 3213(1) | 40(1) |
| C(7) | 1666(3) | -129(1) | 2815(1) | 38(1) |
| C(8) | 1318(2) | -851(1) | 2924(1) | 27(1) |
| C(9) | 1721(2) | -1383(1) | 2515(1) | 30(1) |
| C(10) | 1353(2) | -2081(1) | 2621(1) | 24(1) |
| C(11) | 1745(2) | -2628(1) | 2197(1) | 30(1) |
| C(12) | 1377(2) | -3305(1) | 2304(1) | 31(1) |
| C(13) | 576(2) | -3484(1) | 2843(1) | 28(1) |
| C(14) | 172(2) | -2978(1) | 3256(1) | 24(1) |
| C(15) | 552(2) | -2260(1) | 3164(1) | 21(1) |
| O(1W) | -2805(2) | -3415(1) | 4433(1) | 45(1) |

Table 35. Bond lengths [Å] and angles [°] for [Ag(apim)](9-aca)·H₂O.

| | | | |
|--------------------|------------|-------------------|------------|
| Ag(1)-N(1) | 2.0841(18) | C(2)-C(3) | 1.409(3) |
| Ag(1)-N(3)#1 | 2.1069(18) | C(3)-C(4) | 1.431(3) |
| C(21)-N(1) | 1.321(3) | C(3)-C(8) | 1.434(3) |
| C(21)-N(2) | 1.336(3) | C(4)-C(5) | 1.368(3) |
| N(1)-C(22) | 1.376(3) | C(5)-C(6) | 1.415(4) |
| C(22)-C(23) | 1.354(3) | C(6)-C(7) | 1.348(4) |
| C(23)-N(2) | 1.371(3) | C(7)-C(8) | 1.436(3) |
| N(2)-C(24) | 1.470(3) | C(8)-C(9) | 1.391(3) |
| C(24)-C(25) | 1.518(3) | C(9)-C(10) | 1.395(3) |
| C(25)-C(26) | 1.520(3) | C(10)-C(11) | 1.429(3) |
| C(26)-N(3) | 1.483(3) | C(10)-C(15) | 1.432(3) |
| N(3)-Ag(1)#2 | 2.1069(18) | C(11)-C(12) | 1.358(4) |
| O(1)-C(1) | 1.246(3) | C(12)-C(13) | 1.425(3) |
| O(2)-C(1) | 1.253(3) | C(13)-C(14) | 1.362(3) |
| C(1)-C(2) | 1.513(3) | C(14)-C(15) | 1.432(3) |
| C(2)-C(15) | 1.404(3) | | |
| N(1)-Ag(1)-N(3)#1 | 177.76(7) | C(2)-C(3)-C(4) | 122.3(2) |
| N(1)-C(21)-N(2) | 111.4(2) | C(2)-C(3)-C(8) | 119.2(2) |
| C(21)-N(1)-C(22) | 105.78(18) | C(4)-C(3)-C(8) | 118.5(2) |
| C(21)-N(1)-Ag(1) | 124.86(16) | C(5)-C(4)-C(3) | 120.7(2) |
| C(22)-N(1)-Ag(1) | 129.35(15) | C(4)-C(5)-C(6) | 120.4(2) |
| C(23)-C(22)-N(1) | 109.1(2) | C(7)-C(6)-C(5) | 120.9(2) |
| C(22)-C(23)-N(2) | 106.5(2) | C(6)-C(7)-C(8) | 121.1(2) |
| C(21)-N(2)-C(23) | 107.22(18) | C(9)-C(8)-C(3) | 119.5(2) |
| C(21)-N(2)-C(24) | 125.68(19) | C(9)-C(8)-C(7) | 122.1(2) |
| C(23)-N(2)-C(24) | 127.09(18) | C(3)-C(8)-C(7) | 118.4(2) |
| N(2)-C(24)-C(25) | 110.51(17) | C(8)-C(9)-C(10) | 121.5(2) |
| C(24)-C(25)-C(26) | 112.97(18) | C(9)-C(10)-C(11) | 121.8(2) |
| N(3)-C(26)-C(25) | 113.36(17) | C(9)-C(10)-C(15) | 119.6(2) |
| C(26)-N(3)-Ag(1)#2 | 116.60(13) | C(11)-C(10)-C(15) | 118.6(2) |
| O(1)-C(1)-O(2) | 125.4(2) | C(12)-C(11)-C(10) | 121.2(2) |
| O(1)-C(1)-C(2) | 117.9(2) | C(11)-C(12)-C(13) | 120.3(2) |
| O(2)-C(1)-C(2) | 116.69(18) | C(14)-C(13)-C(12) | 120.4(2) |
| C(15)-C(2)-C(3) | 120.92(19) | C(13)-C(14)-C(15) | 121.1(2) |
| C(15)-C(2)-C(1) | 119.24(18) | C(2)-C(15)-C(14) | 122.39(19) |
| C(3)-C(2)-C(1) | 119.82(18) | C(2)-C(15)-C(10) | 119.20(19) |

C(14)-C(15)-C(10) 118.40(19)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,z #2 -x+1/2,y-1/2,z

Table 36. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [Ag(apim)](9-aca)·H₂O. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U ¹¹ | U ²² | U ³³ | U ²³ | U ¹³ | U ¹² |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ag(1) | 27(1) | 20(1) | 31(1) | -1(1) | -1(1) | 5(1) |
| C(21) | 18(1) | 24(1) | 41(1) | 0(1) | -1(1) | 2(1) |
| N(1) | 26(1) | 21(1) | 33(1) | -1(1) | -3(1) | 1(1) |
| C(22) | 27(1) | 24(1) | 34(1) | 1(1) | 2(1) | -2(1) |
| C(23) | 19(1) | 25(1) | 34(1) | -2(1) | 2(1) | -1(1) |
| N(2) | 20(1) | 18(1) | 32(1) | -1(1) | -3(1) | 0(1) |
| C(24) | 20(1) | 18(1) | 38(1) | 3(1) | -6(1) | 0(1) |
| C(25) | 20(1) | 22(1) | 27(1) | 0(1) | 2(1) | 0(1) |
| C(26) | 21(1) | 20(1) | 28(1) | -3(1) | -1(1) | 0(1) |
| N(3) | 23(1) | 21(1) | 25(1) | 0(1) | -3(1) | -2(1) |
| O(1) | 20(1) | 45(1) | 34(1) | -3(1) | 5(1) | -2(1) |
| O(2) | 29(1) | 44(1) | 26(1) | 7(1) | -2(1) | 2(1) |
| C(1) | 21(1) | 18(1) | 27(1) | -2(1) | 4(1) | 1(1) |
| C(2) | 14(1) | 26(1) | 23(1) | 2(1) | -2(1) | 0(1) |
| C(3) | 17(1) | 27(1) | 29(1) | 4(1) | -4(1) | 2(1) |
| C(4) | 23(1) | 27(1) | 40(1) | -1(1) | -3(1) | 2(1) |
| C(5) | 35(1) | 26(1) | 53(2) | -1(1) | -11(1) | 0(1) |
| C(6) | 41(1) | 24(1) | 55(2) | 11(1) | -12(1) | -5(1) |
| C(7) | 40(1) | 35(1) | 40(1) | 15(1) | -6(1) | -7(1) |
| C(8) | 24(1) | 30(1) | 29(1) | 10(1) | -3(1) | -1(1) |
| C(9) | 26(1) | 39(1) | 23(1) | 9(1) | 0(1) | -3(1) |
| C(10) | 18(1) | 34(1) | 22(1) | 2(1) | -2(1) | 2(1) |
| C(11) | 22(1) | 48(1) | 21(1) | -1(1) | -1(1) | 8(1) |
| C(12) | 28(1) | 38(1) | 29(1) | -8(1) | -4(1) | 9(1) |
| C(13) | 24(1) | 28(1) | 33(1) | -4(1) | -5(1) | 2(1) |
| C(14) | 17(1) | 29(1) | 25(1) | 1(1) | -2(1) | 1(1) |

| | | | | | | |
|-------|-------|-------|-------|-------|-------|------|
| C(15) | 13(1) | 26(1) | 24(1) | 3(1) | -2(1) | 3(1) |
| O(1W) | 43(1) | 35(1) | 56(1) | -8(1) | 9(1) | 7(1) |

Table 37. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$.

| | x | y | z | U(eq) |
|--------|-----------|-----------|----------|-------|
| H(21) | 3080 | -531 | 4458 | 34 |
| H(22) | 6510 | 491 | 4006 | 34 |
| H(23) | 7069 | -775 | 4022 | 31 |
| H(24A) | 4315 | -1780 | 4730 | 30 |
| H(24B) | 5723 | -1910 | 4347 | 30 |
| H(25A) | 4494 | -1876 | 3390 | 28 |
| H(25B) | 3085 | -1706 | 3757 | 28 |
| H(26A) | 3237 | -2907 | 3447 | 27 |
| H(26B) | 4568 | -2998 | 3887 | 27 |
| H(1N) | 2140(20) | -2605(12) | 4430(11) | 34 |
| H(2N) | 3250(20) | -2970(13) | 4710(10) | 34 |
| H(4) | -364 | -574 | 4263 | 36 |
| H(5) | 178 | 578 | 4030 | 45 |
| H(6) | 1477 | 853 | 3127 | 48 |
| H(7) | 2200 | -7 | 2456 | 46 |
| H(9) | 2260 | -1268 | 2156 | 35 |
| H(11) | 2273 | -2515 | 1834 | 36 |
| H(12) | 1656 | -3661 | 2018 | 38 |
| H(13) | 322 | -3959 | 2914 | 34 |
| H(14) | -371 | -3105 | 3611 | 28 |
| H(1W) | -2530(40) | -3020(12) | 4363(15) | 67 |
| H(2W) | -3410(30) | -3389(17) | 4712(13) | 67 |

Table 38. Hydrogen bonds for [Ag(apim)](9-aca)·H₂O [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|----------------------|-----------|-----------|----------|--------|
| N(3)-H(1N)...O(2) | 0.857(16) | 2.291(17) | 3.128(3) | 165(3) |
| N(3)-H(2N)...O(2)#3 | 0.852(16) | 2.274(17) | 3.080(2) | 158(2) |
| N(3)-H(2N)...O(1)#3 | 0.852(16) | 2.40(2) | 3.131(2) | 144(2) |
| O(1W)-H(1W)...O(1) | 0.810(17) | 2.072(18) | 2.883(3) | 179(4) |
| O(1W)-H(2W)...O(2)#4 | 0.832(17) | 2.04(2) | 2.838(3) | 162(3) |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1/2, y+1/2, z$ #2 $-x+1/2, y-1/2, z$ #3 $x+1/2, -y-1/2, -z+1$ #4 $x-1/2, -y-1/2, -z+1$

X-ray Crystal Data for (2-Mebenz-imidH)(9-aca)·H₂O

| | | |
|-----------------------------------|---|----------|
| Identification code | (2-Mebenz-imidH)(9-aca)·H ₂ O | |
| Empirical formula | C ₂₃ H ₂₀ N ₂ O ₃ | |
| Formula weight | 372.41 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P2(1)2(1)2(1) | |
| Unit cell dimensions | a = 6.9251(8) Å | α = 90°. |
| | b = 14.8341(17) Å | β = 90°. |
| | c = 18.522(2) Å | γ = 90°. |
| Volume | 1902.7(4) Å ³ | |
| Z | 4 | |
| Density (calculated) | 1.300 Mg/m ³ | |
| Absorption coefficient | 0.087 mm ⁻¹ | |
| F(000) | 784 | |
| Crystal size | 0.41 x 0.08 x 0.08 mm ³ | |
| Crystal description | colourless rod | |
| Theta range for data collection | 1.76 to 26.35°. | |
| Index ranges | -8<=h<=8, -18<=k<=18, -23<=l<=23 | |
| Reflections collected | 16919 | |
| Independent reflections | 2241 [R(int) = 0.0507] | |
| Completeness to theta = 26.35° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9931 and 0.9652 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 2241 / 0 / 260 | |
| Goodness-of-fit on F ² | 1.046 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0365, wR2 = 0.0853 | |
| R indices (all data) | R1 = 0.0482, wR2 = 0.0917 | |
| Largest diff. peak and hole | 0.308 and -0.355 e.Å ⁻³ | |

Table 39. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (2-Mebenz-imidH)(9-aca) \cdot H₂O. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|-------|----------|----------|---------|-------|
| N(1) | -1873(3) | 9121(1) | 6908(1) | 29(1) |
| C(1) | -1130(4) | 7966(2) | 7850(1) | 42(1) |
| C(2) | -1688(3) | 8265(2) | 7112(1) | 29(1) |
| N(2) | -2067(3) | 7722(1) | 6558(1) | 27(1) |
| C(3) | -2545(3) | 8247(2) | 5966(1) | 25(1) |
| C(4) | -3088(4) | 8018(2) | 5268(1) | 31(1) |
| C(5) | -3461(4) | 8718(2) | 4803(1) | 38(1) |
| C(6) | -3287(4) | 9617(2) | 5019(2) | 37(1) |
| C(7) | -2763(4) | 9848(2) | 5712(2) | 33(1) |
| C(8) | -2411(3) | 9143(2) | 6188(1) | 26(1) |
| O(1) | 1873(2) | 10937(1) | 8433(1) | 33(1) |
| O(2) | 5080(2) | 10932(1) | 8514(1) | 31(1) |
| C(11) | 3522(3) | 10564(2) | 8366(1) | 24(1) |
| C(12) | 3535(3) | 9616(2) | 8061(1) | 23(1) |
| C(13) | 3967(3) | 8877(2) | 8504(1) | 25(1) |
| C(14) | 4437(4) | 8963(2) | 9254(1) | 32(1) |
| C(15) | 4839(4) | 8232(2) | 9665(2) | 39(1) |
| C(16) | 4794(4) | 7352(2) | 9366(2) | 40(1) |
| C(17) | 4356(4) | 7234(2) | 8660(2) | 33(1) |
| C(18) | 3958(3) | 7985(2) | 8198(1) | 26(1) |
| C(19) | 3596(3) | 7872(2) | 7466(1) | 28(1) |
| C(20) | 3168(3) | 8601(2) | 7020(1) | 24(1) |
| C(21) | 2776(4) | 8491(2) | 6269(1) | 29(1) |
| C(22) | 2352(4) | 9205(2) | 5843(1) | 34(1) |
| C(23) | 2307(4) | 10088(2) | 6139(1) | 32(1) |
| C(24) | 2671(4) | 10227(2) | 6852(1) | 28(1) |
| C(25) | 3115(3) | 9495(2) | 7323(1) | 24(1) |
| O(1W) | -1583(3) | 10497(2) | 7817(1) | 58(1) |

Table 40. Bond lengths [\AA] and angles [$^\circ$] for (2-Mebenz-imidH)(9-aca) \cdot H₂O.

| | | | |
|-------------------|----------|-------------------|----------|
| N(1)-C(2) | 1.331(3) | C(12)-C(25) | 1.409(3) |
| N(1)-C(8) | 1.385(3) | C(13)-C(14) | 1.432(4) |
| C(1)-C(2) | 1.489(4) | C(13)-C(18) | 1.440(3) |
| C(2)-N(2) | 1.329(3) | C(14)-C(15) | 1.354(4) |
| N(2)-C(3) | 1.385(3) | C(15)-C(16) | 1.419(4) |
| C(3)-C(4) | 1.389(3) | C(16)-C(17) | 1.355(4) |
| C(3)-C(8) | 1.395(3) | C(17)-C(18) | 1.430(4) |
| C(4)-C(5) | 1.374(4) | C(18)-C(19) | 1.390(3) |
| C(5)-C(6) | 1.398(4) | C(19)-C(20) | 1.392(3) |
| C(6)-C(7) | 1.377(4) | C(20)-C(21) | 1.428(3) |
| C(7)-C(8) | 1.390(4) | C(20)-C(25) | 1.440(3) |
| O(1)-C(11) | 1.276(3) | C(21)-C(22) | 1.353(4) |
| O(2)-C(11) | 1.240(3) | C(22)-C(23) | 1.419(4) |
| C(11)-C(12) | 1.514(3) | C(23)-C(24) | 1.360(4) |
| C(12)-C(13) | 1.401(3) | C(24)-C(25) | 1.427(3) |
| C(2)-N(1)-C(8) | 108.7(2) | C(12)-C(13)-C(14) | 123.1(2) |
| N(2)-C(2)-N(1) | 109.9(2) | C(12)-C(13)-C(18) | 119.2(2) |
| N(2)-C(2)-C(1) | 125.4(2) | C(14)-C(13)-C(18) | 117.7(2) |
| N(1)-C(2)-C(1) | 124.7(2) | C(15)-C(14)-C(13) | 121.4(2) |
| C(2)-N(2)-C(3) | 108.5(2) | C(14)-C(15)-C(16) | 120.9(3) |
| N(2)-C(3)-C(4) | 131.6(2) | C(17)-C(16)-C(15) | 120.0(3) |
| N(2)-C(3)-C(8) | 106.6(2) | C(16)-C(17)-C(18) | 121.4(3) |
| C(4)-C(3)-C(8) | 121.8(2) | C(19)-C(18)-C(17) | 121.7(2) |
| C(5)-C(4)-C(3) | 116.7(2) | C(19)-C(18)-C(13) | 119.7(2) |
| C(4)-C(5)-C(6) | 121.7(3) | C(17)-C(18)-C(13) | 118.7(2) |
| C(7)-C(6)-C(5) | 121.8(2) | C(18)-C(19)-C(20) | 121.6(2) |
| C(6)-C(7)-C(8) | 116.8(2) | C(19)-C(20)-C(21) | 121.9(2) |
| N(1)-C(8)-C(7) | 132.6(2) | C(19)-C(20)-C(25) | 119.3(2) |
| N(1)-C(8)-C(3) | 106.2(2) | C(21)-C(20)-C(25) | 118.7(2) |
| C(7)-C(8)-C(3) | 121.2(2) | C(22)-C(21)-C(20) | 121.3(2) |
| O(2)-C(11)-O(1) | 124.5(2) | C(21)-C(22)-C(23) | 120.2(2) |
| O(2)-C(11)-C(12) | 119.1(2) | C(24)-C(23)-C(22) | 120.7(3) |
| O(1)-C(11)-C(12) | 116.4(2) | C(23)-C(24)-C(25) | 121.2(2) |
| C(13)-C(12)-C(25) | 120.8(2) | C(12)-C(25)-C(24) | 122.7(2) |
| C(13)-C(12)-C(11) | 120.6(2) | C(12)-C(25)-C(20) | 119.4(2) |
| C(25)-C(12)-C(11) | 118.6(2) | C(24)-C(25)-C(20) | 117.9(2) |

Table 41. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (2-MebenzimidH)(9-aca)·H₂O. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U ¹¹ | U ²² | U ³³ | U ²³ | U ¹³ | U ¹² |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| N(1) | 23(1) | 31(1) | 34(1) | -8(1) | 2(1) | -5(1) |
| C(1) | 27(1) | 66(2) | 32(1) | 8(1) | -1(1) | -8(1) |
| C(2) | 17(1) | 40(2) | 31(1) | -1(1) | 2(1) | -5(1) |
| N(2) | 24(1) | 24(1) | 34(1) | 5(1) | 2(1) | -2(1) |
| C(3) | 21(1) | 26(1) | 29(1) | 1(1) | 6(1) | 0(1) |
| C(4) | 32(2) | 32(1) | 29(1) | -8(1) | 4(1) | 1(1) |
| C(5) | 39(2) | 46(2) | 28(1) | -1(1) | 6(1) | 4(1) |
| C(6) | 34(2) | 37(1) | 41(2) | 10(1) | 7(1) | 6(1) |
| C(7) | 29(1) | 22(1) | 49(2) | 1(1) | 7(1) | 0(1) |
| C(8) | 20(1) | 28(1) | 32(1) | -4(1) | 4(1) | -1(1) |
| O(1) | 20(1) | 29(1) | 50(1) | -16(1) | 3(1) | 1(1) |
| O(2) | 23(1) | 26(1) | 44(1) | -6(1) | -4(1) | -1(1) |
| C(11) | 22(1) | 24(1) | 25(1) | -1(1) | 1(1) | -1(1) |
| C(12) | 16(1) | 22(1) | 32(1) | -3(1) | 3(1) | -2(1) |
| C(13) | 18(1) | 26(1) | 32(1) | -3(1) | 3(1) | -1(1) |
| C(14) | 31(1) | 29(1) | 36(2) | -4(1) | 0(1) | 0(1) |
| C(15) | 42(2) | 42(2) | 34(2) | 1(1) | -2(1) | 2(1) |
| C(16) | 38(2) | 34(2) | 48(2) | 11(1) | 3(1) | 5(1) |
| C(17) | 28(1) | 25(1) | 47(2) | 1(1) | 8(1) | 0(1) |
| C(18) | 18(1) | 23(1) | 37(1) | -1(1) | 6(1) | 0(1) |
| C(19) | 19(1) | 23(1) | 41(1) | -10(1) | 7(1) | -2(1) |
| C(20) | 17(1) | 25(1) | 31(1) | -7(1) | 5(1) | -2(1) |
| C(21) | 25(1) | 30(1) | 32(1) | -12(1) | 4(1) | -4(1) |
| C(22) | 29(1) | 45(2) | 29(1) | -10(1) | 2(1) | -6(1) |
| C(23) | 29(1) | 37(1) | 30(1) | 0(1) | 1(1) | -3(1) |
| C(24) | 26(1) | 24(1) | 34(1) | -3(1) | 5(1) | -2(1) |
| C(25) | 15(1) | 24(1) | 31(1) | -5(1) | 5(1) | -2(1) |
| O(1W) | 27(1) | 84(2) | 63(1) | -47(1) | 1(1) | -4(1) |

Table 42. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (2-Mebenz-imidH)(9-aca) \cdot H₂O.

| | x | y | z | U(eq) |
|--------|-----------|----------|----------|-------|
| H(1N) | -1670(50) | 9573(19) | 7227(15) | 38 |
| H(1A) | -231 | 8403 | 8061 | 63 |
| H(1B) | -506 | 7374 | 7823 | 63 |
| H(1C) | -2287 | 7924 | 8153 | 63 |
| H(2N) | -2000(40) | 7059(18) | 6547(14) | 35 |
| H(4) | -3197 | 7407 | 5120 | 37 |
| H(5) | -3847 | 8587 | 4322 | 45 |
| H(6) | -3538 | 10081 | 4678 | 44 |
| H(7) | -2648 | 10460 | 5857 | 40 |
| H(14) | 4466 | 9545 | 9467 | 38 |
| H(15) | 5156 | 8310 | 10160 | 47 |
| H(16) | 5071 | 6844 | 9662 | 48 |
| H(17) | 4313 | 6641 | 8467 | 40 |
| H(19) | 3641 | 7283 | 7264 | 33 |
| H(21) | 2814 | 7904 | 6063 | 35 |
| H(22) | 2084 | 9116 | 5345 | 41 |
| H(23) | 2020 | 10586 | 5836 | 38 |
| H(24) | 2629 | 10823 | 7040 | 33 |
| H(1WA) | -2519 | 10594 | 8116 | 50 |
| H(1WB) | -632 | 10586 | 8109 | 50 |

Table 43. Hydrogen bonds for (2-Mebenz-imidH)(9-aca) \cdot H₂O [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | \angle (DHA) |
|-----------------------|---------|----------|----------|----------------|
| N(1)-H(1N)...O(1W) | 0.90(3) | 1.75(3) | 2.654(3) | 172(3) |
| N(2)-H(2N)...O(1)#1 | 0.99(3) | 1.67(3) | 2.651(3) | 178(2) |
| O(1W)-H(1WA)...O(2)#2 | 0.86 | 1.89 | 2.724(3) | 162.8 |
| O(1W)-H(1WB)...O(1) | 0.86 | 1.91 | 2.731(3) | 158.9 |

Symmetry transformations used to generate equivalent atoms: #1 -x,y-1/2,-z+3/2 #2 x-1,y,z

X-ray Crystal Data for [Ag₄(9-aca)₄(NH₃)₂]

| | |
|-----------------------------------|---|
| Identification code | [Ag ₄ (9-aca) ₄ (NH ₃) ₂] |
| Empirical formula | C ₆₀ H ₄₂ Ag ₄ N ₂ O ₈ |
| Formula weight | 1350.44 |
| Temperature | 150(2) K |
| Wavelength | 0.84620 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | a = 16.837(3) Å α = 90°. b = 9.8639(16) Å β = 112.383(2)°. c = 16.035(3) Å γ = 90°. |
| Volume | 2462.4(7) Å ³ |
| Z | 2 |
| Density (calculated) | 1.821 Mg/m ³ |
| Absorption coefficient | 1.629 mm ⁻¹ |
| F(000) | 1336 |
| Crystal size | 0.09 x 0.07 x 0.01 mm ³ |
| Crystal description | Colourless plate |
| Theta range for data collection | 3.82 to 27.50°. |
| Index ranges | -18<=h<=18, -10<=k<=10, -17<=l<=17 |
| Reflections collected | 12821 |
| Independent reflections | 3344 [R(int) = 0.0853] |
| Completeness to theta = 27.50° | 99.6 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.0000 and 0.641332 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 3344 / 0 / 336 |
| Goodness-of-fit on F ² | 1.010 |
| Final R indices [I>2sigma(I)] | R1 = 0.0475, wR2 = 0.0987 |
| R indices (all data) | R1 = 0.0684, wR2 = 0.1079 |
| Extinction coefficient | 0.0021(2) |
| Largest diff. peak and hole | 0.604 and -0.648 e.Å ⁻³ |

Table 44. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|-------|---------|-----------|-----------|-------|
| Ag(1) | 4274(1) | 951(1) | -262(1) | 35(1) |
| Ag(2) | 2883(1) | 1955(1) | 890(1) | 41(1) |
| O(1) | 3032(4) | 2171(6) | -1061(4) | 51(2) |
| O(2) | 2012(3) | 2141(5) | -480(3) | 42(1) |
| C(1) | 2265(5) | 2170(7) | -1116(5) | 34(2) |
| C(2) | 1603(5) | 2184(7) | -2071(5) | 28(2) |
| C(3) | 1110(5) | 1007(8) | -2429(5) | 37(2) |
| C(4) | 1183(6) | -184(8) | -1890(6) | 50(2) |
| C(5) | 722(7) | -1333(10) | -2280(9) | 75(4) |
| C(6) | 180(8) | -1349(13) | -3197(10) | 88(4) |
| C(7) | 97(6) | -256(13) | -3707(8) | 73(3) |
| C(8) | 554(5) | 968(10) | -3360(6) | 50(2) |
| C(9) | 524(5) | 2092(11) | -3891(6) | 52(3) |
| C(10) | 986(5) | 3260(9) | -3560(5) | 38(2) |
| C(11) | 986(6) | 4396(11) | -4115(6) | 57(3) |
| C(12) | 1423(6) | 5533(11) | -3776(7) | 62(3) |
| C(13) | 1929(6) | 5618(9) | -2839(6) | 55(3) |
| C(14) | 1981(5) | 4551(7) | -2278(5) | 34(2) |
| C(15) | 1540(5) | 3327(7) | -2626(5) | 31(2) |
| O(3) | 3822(3) | -285(5) | 605(3) | 31(1) |
| O(4) | 5094(3) | -1335(5) | 1257(3) | 29(1) |
| C(16) | 4334(5) | -1116(7) | 1160(5) | 27(2) |
| C(17) | 3996(5) | -1913(7) | 1764(4) | 24(2) |
| C(18) | 3313(5) | -2827(7) | 1356(5) | 28(2) |
| C(19) | 2851(5) | -2967(7) | 400(5) | 30(2) |
| C(20) | 2257(5) | -3948(8) | 64(5) | 36(2) |
| C(21) | 2067(5) | -4868(8) | 632(5) | 42(2) |
| C(22) | 2456(5) | -4748(8) | 1542(5) | 35(2) |
| C(23) | 3074(5) | -3730(7) | 1933(5) | 27(2) |
| C(24) | 3456(5) | -3530(7) | 2873(4) | 28(2) |
| C(25) | 4087(4) | -2564(6) | 3257(4) | 20(2) |
| C(26) | 4447(5) | -2355(7) | 4207(5) | 30(2) |

| | | | | |
|-------|---------|----------|---------|-------|
| C(27) | 5105(5) | -1483(7) | 4599(5) | 32(2) |
| C(28) | 5442(5) | -741(7) | 4036(5) | 32(2) |
| C(29) | 5098(5) | -878(7) | 3125(4) | 27(2) |
| C(30) | 4392(5) | -1778(7) | 2701(4) | 23(2) |
| N(1) | 3578(4) | 1820(6) | 2321(4) | 32(2) |

Table 45. Bond lengths [\AA] and angles [$^\circ$] for $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$.

| | | | |
|----------------------|------------|-----------------|-----------|
| Ag(1)-O(3) | 2.192(4) | C(13)-C(14) | 1.366(10) |
| Ag(1)-O(4)#1 | 2.261(4) | C(14)-C(15) | 1.416(10) |
| Ag(1)-O(1) | 2.329(6) | O(3)-C(16) | 1.273(8) |
| Ag(1)-Ag(1)#1 | 2.9390(12) | O(4)-C(16) | 1.249(8) |
| Ag(2)-O(2) | 2.135(5) | O(4)-Ag(1)#1 | 2.261(4) |
| Ag(2)-N(1) | 2.148(5) | C(16)-C(17) | 1.516(9) |
| O(1)-C(1) | 1.259(9) | C(17)-C(30) | 1.400(9) |
| O(2)-C(1) | 1.247(9) | C(17)-C(18) | 1.411(9) |
| C(1)-C(2) | 1.513(10) | C(18)-C(19) | 1.438(10) |
| C(2)-C(15) | 1.415(10) | C(18)-C(23) | 1.446(9) |
| C(2)-C(3) | 1.415(10) | C(19)-C(20) | 1.347(10) |
| C(3)-C(8) | 1.429(11) | C(20)-C(21) | 1.406(10) |
| C(3)-C(4) | 1.436(11) | C(21)-C(22) | 1.358(10) |
| C(4)-C(5) | 1.381(12) | C(22)-C(23) | 1.409(10) |
| C(5)-C(6) | 1.406(16) | C(23)-C(24) | 1.409(9) |
| C(6)-C(7) | 1.328(15) | C(24)-C(25) | 1.385(9) |
| C(7)-C(8) | 1.426(12) | C(25)-C(30) | 1.418(9) |
| C(8)-C(9) | 1.387(12) | C(25)-C(26) | 1.423(9) |
| C(9)-C(10) | 1.377(11) | C(26)-C(27) | 1.355(10) |
| C(10)-C(11) | 1.431(12) | C(27)-C(28) | 1.435(10) |
| C(10)-C(15) | 1.433(10) | C(28)-C(29) | 1.358(9) |
| C(11)-C(12) | 1.337(13) | C(29)-C(30) | 1.430(9) |
| C(12)-C(13) | 1.420(13) | | |
| O(3)-Ag(1)-O(4)#1 | 155.63(17) | O(2)-Ag(2)-N(1) | 170.6(2) |
| O(3)-Ag(1)-O(1) | 100.39(19) | C(1)-O(1)-Ag(1) | 136.0(5) |
| O(4)#1-Ag(1)-O(1) | 95.19(18) | C(1)-O(2)-Ag(2) | 121.9(5) |
| O(3)-Ag(1)-Ag(1)#1 | 85.15(13) | O(2)-C(1)-O(1) | 127.1(7) |
| O(4)#1-Ag(1)-Ag(1)#1 | 75.23(13) | O(2)-C(1)-C(2) | 118.6(7) |
| O(1)-Ag(1)-Ag(1)#1 | 164.17(15) | O(1)-C(1)-C(2) | 114.3(7) |

| | | | |
|-------------------|-----------|--------------------|----------|
| C(15)-C(2)-C(3) | 120.4(7) | C(3)-C(2)-C(1) | 119.7(7) |
| C(15)-C(2)-C(1) | 119.6(6) | C(2)-C(3)-C(8) | 119.7(8) |
| C(2)-C(3)-C(4) | 121.6(7) | C(14)-C(15)-C(10) | 119.1(7) |
| C(8)-C(3)-C(4) | 118.6(8) | C(16)-O(3)-Ag(1) | 119.7(4) |
| C(5)-C(4)-C(3) | 119.6(9) | C(16)-O(4)-Ag(1)#1 | 128.2(4) |
| C(4)-C(5)-C(6) | 120.8(11) | O(4)-C(16)-O(3) | 126.0(6) |
| C(7)-C(6)-C(5) | 120.6(10) | O(4)-C(16)-C(17) | 116.6(7) |
| C(6)-C(7)-C(8) | 122.2(11) | O(3)-C(16)-C(17) | 117.5(7) |
| C(9)-C(8)-C(7) | 123.4(10) | C(30)-C(17)-C(18) | 122.0(6) |
| C(9)-C(8)-C(3) | 118.4(8) | C(30)-C(17)-C(16) | 119.7(6) |
| C(7)-C(8)-C(3) | 118.1(10) | C(18)-C(17)-C(16) | 118.3(6) |
| C(10)-C(9)-C(8) | 123.3(8) | C(17)-C(18)-C(19) | 124.7(6) |
| C(9)-C(10)-C(11) | 123.3(8) | C(17)-C(18)-C(23) | 118.3(6) |
| C(9)-C(10)-C(15) | 119.2(8) | C(19)-C(18)-C(23) | 117.0(7) |
| C(11)-C(10)-C(15) | 117.3(8) | C(20)-C(19)-C(18) | 120.8(7) |
| C(12)-C(11)-C(10) | 122.3(9) | C(19)-C(20)-C(21) | 121.5(7) |
| C(11)-C(12)-C(13) | 119.7(9) | C(22)-C(21)-C(20) | 120.3(7) |
| C(14)-C(13)-C(12) | 120.9(9) | C(21)-C(22)-C(23) | 120.8(7) |
| C(13)-C(14)-C(15) | 120.3(8) | C(22)-C(23)-C(24) | 122.3(6) |
| C(2)-C(15)-C(14) | 121.9(7) | C(22)-C(23)-C(18) | 119.5(6) |
| C(2)-C(15)-C(10) | 118.9(7) | C(24)-C(23)-C(18) | 118.2(7) |
| C(25)-C(24)-C(23) | 122.2(6) | C(29)-C(28)-C(27) | 121.1(7) |
| C(24)-C(25)-C(30) | 119.8(6) | C(28)-C(29)-C(30) | 120.7(6) |
| C(24)-C(25)-C(26) | 121.2(6) | C(17)-C(30)-C(25) | 119.0(6) |
| C(30)-C(25)-C(26) | 119.0(6) | C(17)-C(30)-C(29) | 122.7(6) |
| C(27)-C(26)-C(25) | 121.8(6) | C(25)-C(30)-C(29) | 118.4(6) |
| C(26)-C(27)-C(28) | 118.8(7) | | |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z

Table 46. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U^{11} | U^{22} | U^{33} | U^{23} | U^{13} | U^{12} |
|-------|----------|----------|----------|----------|----------|----------|
| Ag(1) | 39(1) | 41(1) | 31(1) | 20(1) | 20(1) | 4(1) |
| Ag(2) | 53(1) | 50(1) | 21(1) | 0(1) | 16(1) | 3(1) |
| O(1) | 34(4) | 73(4) | 45(4) | 24(3) | 15(3) | 6(3) |
| O(2) | 53(4) | 52(4) | 25(3) | -2(3) | 18(3) | -1(3) |
| C(1) | 42(6) | 31(5) | 26(5) | 8(4) | 12(4) | -3(4) |
| C(2) | 28(4) | 36(5) | 21(4) | -5(4) | 12(3) | 4(4) |
| C(3) | 38(5) | 47(5) | 38(5) | -14(4) | 26(4) | -5(4) |
| C(4) | 61(6) | 43(6) | 69(6) | -4(5) | 49(5) | -6(5) |
| C(5) | 96(9) | 51(7) | 117(10) | -39(7) | 83(8) | -36(6) |
| C(6) | 89(9) | 93(10) | 121(12) | -71(9) | 84(9) | -60(8) |
| C(7) | 56(7) | 95(9) | 88(8) | -60(8) | 52(7) | -32(7) |
| C(8) | 32(5) | 73(7) | 50(6) | -35(6) | 24(5) | -4(5) |
| C(9) | 35(5) | 86(8) | 30(5) | -18(5) | 7(4) | 14(5) |
| C(10) | 36(5) | 49(6) | 26(5) | 4(4) | 10(4) | 15(4) |
| C(11) | 51(6) | 83(8) | 38(6) | 11(6) | 17(5) | 29(6) |
| C(12) | 62(7) | 76(8) | 59(7) | 40(6) | 34(6) | 27(6) |
| C(13) | 62(7) | 49(6) | 66(7) | 17(5) | 36(6) | 19(5) |
| C(14) | 43(5) | 33(5) | 29(4) | 8(4) | 17(4) | 9(4) |
| C(15) | 39(5) | 34(5) | 22(4) | -5(4) | 13(4) | 12(4) |
| O(3) | 49(3) | 23(3) | 31(3) | 10(2) | 27(3) | 5(3) |
| O(4) | 39(3) | 35(3) | 19(3) | 4(2) | 18(2) | -3(3) |
| C(16) | 50(5) | 20(4) | 21(4) | -2(3) | 24(4) | -6(4) |
| C(17) | 39(5) | 19(4) | 21(4) | 11(3) | 21(4) | 8(4) |
| C(18) | 38(5) | 24(4) | 32(5) | 4(3) | 23(4) | 8(4) |
| C(19) | 41(5) | 36(5) | 22(4) | 2(4) | 22(4) | -2(4) |
| C(20) | 41(5) | 41(5) | 24(4) | -8(4) | 13(4) | -3(4) |
| C(21) | 41(5) | 41(5) | 43(6) | -10(4) | 15(4) | -8(4) |
| C(22) | 39(5) | 37(5) | 39(5) | 4(4) | 24(4) | -7(4) |
| C(23) | 37(5) | 25(4) | 25(4) | 7(3) | 20(4) | 1(4) |
| C(24) | 44(5) | 27(4) | 22(4) | 11(3) | 22(4) | 3(4) |
| C(25) | 29(4) | 19(4) | 17(4) | 5(3) | 16(3) | 5(3) |
| C(26) | 46(5) | 26(4) | 28(5) | 18(4) | 26(4) | 14(4) |

| | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|
| C(27) | 60(6) | 20(4) | 19(4) | 6(3) | 21(4) | 12(4) |
| C(28) | 55(5) | 19(4) | 25(4) | -6(3) | 19(4) | 3(4) |
| C(29) | 48(5) | 21(4) | 23(4) | 0(3) | 24(4) | 1(4) |
| C(30) | 37(5) | 20(4) | 19(4) | -1(3) | 20(4) | 8(3) |
| N(1) | 34(4) | 32(4) | 31(4) | 0(3) | 15(3) | 2(3) |

Table 47. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$.

| | x | y | z | U(eq) |
|-------|------|-------|-------|-------|
| H(4) | 1545 | -181 | -1268 | 61 |
| H(5) | 773 | -2122 | -1923 | 90 |
| H(6) | -130 | -2149 | -3455 | 105 |
| H(7) | -280 | -290 | -4323 | 87 |
| H(9) | 167 | 2055 | -4514 | 62 |
| H(11) | 665 | 4340 | -4746 | 69 |
| H(12) | 1394 | 6279 | -4161 | 75 |
| H(13) | 2236 | 6429 | -2599 | 67 |
| H(14) | 2315 | 4630 | -1651 | 41 |
| H(19) | 2965 | -2360 | -1 | 36 |
| H(20) | 1960 | -4019 | -570 | 43 |
| H(21) | 1665 | -5577 | 378 | 51 |
| H(22) | 2310 | -5358 | 1920 | 43 |
| H(24) | 3275 | -4077 | 3255 | 34 |
| H(26) | 4218 | -2841 | 4577 | 36 |
| H(27) | 5341 | -1364 | 5235 | 38 |
| H(28) | 5913 | -143 | 4305 | 39 |
| H(29) | 5328 | -372 | 2765 | 33 |
| H(1A) | 3211 | 1955 | 2608 | 48 |
| H(1B) | 3997 | 2463 | 2499 | 48 |
| H(1C) | 3820 | 983 | 2463 | 48 |

Table 48. Hydrogen bonds for $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | $\angle(\text{DHA})$ |
|---------------------|--------|----------|----------|----------------------|
| N(1)-H(1A)...O(1)#2 | 0.91 | 2.42 | 3.222(8) | 146.5 |
| N(1)-H(1B)...O(4)#3 | 0.91 | 2.32 | 3.103(7) | 143.4 |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y, -z$ #2 $x, -y+1/2, z+1/2$ #3 $-x+1, y+1/2, -z+1/2$

UV-Vis and Fluorescence Spectral Data

Table 49. Complex and ligand UV-Vis maxima.

| Complex | Absorbance max (nm) | Ligand 1 max (nm) | Ligand 2 max (nm) |
|---|---------------------|-------------------|-------------------|
| $[\text{Ag}_2(9\text{-aca})_2]_n$ | 373 | 366 (7) | N/A |
| $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$ | 373 | 366 (7) | 280 (1) |
| $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$ | 373 | 366 (7) | no maximum |
| $[\text{Ag}(2\text{-Ph-imid})]$ | 273 | 262(6) | N/A |
| $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$ | 373 | 366 (7) | 271 (5) |
| $[\text{Ag}(4,5\text{-dicyanoimid})]$ | 264 | 256 (4) | N/A |
| $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ | 366 | 366 (7) | 283 (2) |
| $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ | 372 | 366 (7) | N/A |

Table 50. Complex and ligand 1 fluorescence data (^a excited at 366 nm, ^b excited at 283 nm).

| Complex | Emission max (nm) | Emission intensity (AU) | Ligand 1 Emission max (nm) | Ligand 1 Emission intensity (AU) |
|---|--------------------------------------|-------------------------|----------------------------|----------------------------------|
| $[\text{Ag}_2(9\text{-aca})_2]_n$ | 448 | 61 | 451 (7) | 942 (7) |
| $[\text{Ag}(\text{imidH})_{2.3}(\text{CH}_3\text{CN})_{0.7}](9\text{-aca})$ | 448 | 175 | 450 (7) | 968 (7) |
| $[\text{Ag}(\text{apim})](9\text{-aca})\cdot\text{H}_2\text{O}$ | 440 | 53 | 450 (7) | 968 (7) |
| $[\text{Ag}(2\text{-Ph-imid})]$ | 342 | 44 | 340 (6) | 167 (6) |
| $[\text{Ag}(4\text{-Ph-imidH})_2(9\text{-aca})]$ | 448 | 108 | 450 (7) | 968 (7) |
| $[\text{Ag}(4,5\text{-dicyanoimid})]$ | 347 | 1 | 299 (4) | 0.5 (4) |
| $[\text{Ag}_2(2\text{-Mebenz-imidH})_4](9\text{-aca})_2$ | 451 ^a 299 ^b | 318 333 | 451 (7) | 461 (7) |
| $[\text{Ag}_4(9\text{-aca})_4(\text{NH}_3)_2]$ | 446 | 15 | 451 (7) | 939 (7) |

Table 51. Complex and ligand 2 fluorescence data (^a excited at 366 nm, ^b excited at 283 nm).

| Complex | Emission max (nm) | Emission intensity (AU) | Ligand 2 Emission max (nm) | Ligand 2 Emission intensity (AU) |
|---|--------------------------------------|-------------------------|----------------------------|----------------------------------|
| [Ag ₂ (9-aca) ₂] _n | 448 | 61 | N/A | N/A |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | 448 | 175 | 561 (1) | 15 (1) |
| [Ag(apim)](9-aca)·H ₂ O | 440 | 53 | 0 (4) | 0 (4) |
| [Ag(2-Ph-imid)] | 342 | 44 | N/A | N/A |
| [Ag(4-Ph-imidH) ₂](9-aca)] | 448 | 108 | 290 (5) | 2 (5) |
| [Ag(4,5-dicyanoimid)] | 347 | 1 | N/A | N/A |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ | 451 ^a 299 ^b | 318 333 | 299 (2) | 554 (2) |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] | 446 | 15 | N/A | N/A |

In vivo Data

Table 52. Survival of *G. mellonella* larvae after prophylactic treatment with silver(I) compounds and infection with a lethal dose of *C. albicans*.

| Drug Concentration (#poor solubility) | % Survival after 24 h. | % Survival after 48 h | % Survival after 72 h |
|--|------------------------------|-----------------------------|-----------------------------|
| Control (1×10^8 cells cm^{-3}) | 70 | 30 | 10 |
| Ketoconazole# | | | |
| 100 $\mu\text{g cm}^{-3}$ | 95 | 80 | 75 |
| 10 $\mu\text{g cm}^{-3}$ | 80 | 55 | 50 |
| 5 $\mu\text{g cm}^{-3}$ | 85 | 60 | 50 |
| AgNO ₃ | | | |
| 100 $\mu\text{g cm}^{-3}$ | 100 | 95 | 80 |
| 10 $\mu\text{g cm}^{-3}$ | 90 | 85 | 70 |
| 0.625 $\mu\text{g cm}^{-3}$ | 80 | 70 | 55 |
| AgClO ₄ | | | |
| 100 $\mu\text{g cm}^{-3}$ | 80 | 70 | 55 |
| 10 $\mu\text{g cm}^{-3}$ | 70 | 50 | 40 |
| 0.625 $\mu\text{g cm}^{-3}$ | 40 | 25 | 20 |
| [Ag ₂ (9-aca) ₂] _n | | | |
| 100 $\mu\text{g cm}^{-3}$ | 90 | 70 | 60 |
| 10 $\mu\text{g cm}^{-3}$ | 95 | 60 | 55 |
| 1.250 $\mu\text{g cm}^{-3}$ | 95 | 60 | 50 |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | | | |
| 100 $\mu\text{g cm}^{-3}$ | 80 | 60 | 50 |
| 10 $\mu\text{g cm}^{-3}$ | 80 | 45 | 35 |
| 1.560 $\mu\text{g cm}^{-3}$ | 70 | 45 | 25 |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | | | |
| 100 $\mu\text{g cm}^{-3}$ | 75 | 45 | 30 |
| 10 $\mu\text{g cm}^{-3}$ | 60 | 40 | 30 |
| 0.390 $\mu\text{g cm}^{-3}$ | 50 | 20 | 10 |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | | | |
| 100 $\mu\text{g cm}^{-3}$ | 80 | 70 | 65 |
| 10 $\mu\text{g cm}^{-3}$ | 60 | 50 | 35 |
| 2.5 $\mu\text{g cm}^{-3}$ | 65 | 25 | 15 |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | | | |
| 100 $\mu\text{g cm}^{-3}$ | 85 | 70 | 50 |
| 10 $\mu\text{g cm}^{-3}$ | 90 | 45 | 30 |
| 1.560 $\mu\text{g cm}^{-3}$ | 90 | 55 | 35 |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | | | |
| 100 $\mu\text{g cm}^{-3}$ | 100 | 40 | 20 |
| 10 $\mu\text{g cm}^{-3}$ | 90 | 50 | 30 |
| 2 $\mu\text{g cm}^{-3}$ | 100 | 50 | 35 |

| Drug Concentration (#poor solubility) | % Survival after 24 h. | % Survival after 48 h | % Survival after 72 h |
|--|------------------------|-----------------------|-----------------------|
| [Ag(2-Me-imidH) ₂ (9-aca)] | | | |
| 100 µg cm ⁻³ | 65 | 30 | 30 |
| 10 µg cm ⁻³ | 60 | 15 | 10 |
| 1.560 µg cm ⁻³ | 50 | 10 | 10 |
| [Ag(1-Bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | | | |
| 100 µg cm ⁻³ | 100 | 60 | 60 |
| 10 µg cm ⁻³ | 90 | 60 | 60 |
| 1.560 µg cm ⁻³ | 65 | 50 | 15 |
| [Ag ₂ (1-Bu-imid) ₂ (9-aca) ₂] | | | |
| 100 µg cm ⁻³ | 80 | 80 | 70 |
| 10 µg cm ⁻³ | 70 | 40 | 30 |
| 1.560 µg cm ⁻³ | 60 | 30 | 15 |
| [Ag(apim)](9-aca)·H ₂ O | | | |
| 100 µg cm ⁻³ | 100 | 80 | 70 |
| 10 µg cm ⁻³ | 70 | 40 | 40 |
| 0.400 µg cm ⁻³ | 40 | 40 | 20 |
| [Ag(2-Ph-imid)] [#] | | | |
| 100 µg cm ⁻³ | 100 | 80 | 70 |
| 10 µg cm ⁻³ | 95 | 65 | 45 |
| 3.125 µg cm ⁻³ | 90 | 60 | 35 |
| [Ag(4-Ph-imidH) ₂ (9-aca)] | | | |
| 100 µg cm ⁻³ | 100 | 60 | 45 |
| 10 µg cm ⁻³ | 75 | 50 | 40 |
| 3.125 µg cm ⁻³ | 50 | 30 | 20 |
| [Ag(4,5-dicyanoimid)] [#] | | | |
| 100 µg cm ⁻³ | 90 | 70 | 60 |
| 10 µg cm ⁻³ | 95 | 70 | 50 |
| 0.780 µg cm ⁻³ | 75 | 50 | 35 |
| [Ag(Benz-imid)] [#] | | | |
| 100 µg cm ⁻³ | 85 | 70 | 60 |
| 10 µg cm ⁻³ | 80 | 70 | 50 |
| 3.125 µg cm ⁻³ | 70 | 50 | 35 |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ | | | |
| 100 µg cm ⁻³ | 90 | 60 | 40 |
| 10 µg cm ⁻³ | 90 | 60 | 25 |
| 3.125 µg cm ⁻³ | 75 | 50 | 30 |
| [Ag(2-Mebenz-imid)] [#] | | | |
| 100 µg cm ⁻³ | 80 | 50 | 40 |
| 10 µg cm ⁻³ | 70 | 40 | 40 |
| 6.250 µg cm ⁻³ | 75 | 50 | 30 |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] | | | |
| 100 µg cm ⁻³ | 100 | 90 | 90 |
| 10 µg cm ⁻³ | 100 | 80 | 70 |
| 0.390 µg cm ⁻³ | 85 | 75 | 65 |

Table 53. Survival of *G. mellonella* larvae after infection with a lethal dose of *C. albicans* and treatment with silver(I) compounds.

| Drug Concentration (#poor solubility) | % Survival after 24 h. | % Survival after 48 h | % Survival after 72 h |
|--|------------------------------|-----------------------------|-----------------------------|
| Control (1×10^8 cells cm^{-3}) | 70 | 30 | 10 |
| Ketoconazole# | | | |
| 100 $\mu\text{g cm}^{-3}$ | 100 | 95 | 75 |
| 10 $\mu\text{g cm}^{-3}$ | 90 | 45 | 30 |
| 5 $\mu\text{g cm}^{-3}$ | 70 | 45 | 20 |
| AgNO ₃ | | | |
| 100 $\mu\text{g cm}^{-3}$ | 95 | 85 | 75 |
| 10 $\mu\text{g cm}^{-3}$ | 95 | 80 | 55 |
| 0.625 $\mu\text{g cm}^{-3}$ | 90 | 70 | 60 |
| AgClO ₄ | | | |
| 100 $\mu\text{g cm}^{-3}$ | 70 | 50 | 40 |
| 10 $\mu\text{g cm}^{-3}$ | 75 | 50 | 25 |
| 0.625 $\mu\text{g cm}^{-3}$ | 30 | 15 | 10 |
| [Ag ₂ (9-aca) ₂] _n | | | |
| 100 $\mu\text{g cm}^{-3}$ | 90 | 65 | 50 |
| 10 $\mu\text{g cm}^{-3}$ | 100 | 50 | 45 |
| 1.25 $\mu\text{g cm}^{-3}$ | 100 | 40 | 35 |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | | | |
| 100 $\mu\text{g cm}^{-3}$ | 90 | 60 | 30 |
| 10 $\mu\text{g cm}^{-3}$ | 95 | 35 | 30 |
| 1.560 $\mu\text{g cm}^{-3}$ | 80 | 40 | 35 |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | | | |
| 100 $\mu\text{g cm}^{-3}$ | 65 | 40 | 30 |
| 10 $\mu\text{g cm}^{-3}$ | 60 | 40 | 25 |
| 0.390 $\mu\text{g cm}^{-3}$ | 50 | 25 | 10 |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | | | |
| 100 $\mu\text{g cm}^{-3}$ | 80 | 40 | 25 |
| 10 $\mu\text{g cm}^{-3}$ | 80 | 30 | 10 |
| 2.5 $\mu\text{g cm}^{-3}$ | 80 | 25 | 10 |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | | | |
| 100 $\mu\text{g cm}^{-3}$ | 100 | 60 | 60 |
| 10 $\mu\text{g cm}^{-3}$ | 90 | 40 | 30 |
| 1.560 $\mu\text{g cm}^{-3}$ | 85 | 35 | 30 |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | | | |
| 100 $\mu\text{g cm}^{-3}$ | 90 | 60 | 45 |
| 10 $\mu\text{g cm}^{-3}$ | 95 | 40 | 30 |
| 2 $\mu\text{g cm}^{-3}$ | 90 | 30 | 30 |
| [Ag(2-Me-imidH) ₂ (9-aca)] | | | |
| 100 $\mu\text{g cm}^{-3}$ | 90 | 75 | 70 |
| 10 $\mu\text{g cm}^{-3}$ | 90 | 70 | 65 |
| 1.560 $\mu\text{g cm}^{-3}$ | 80 | 55 | 30 |

| Drug Concentration (#poor solubility) | % Survival after 24 h. | % Survival after 48 h | % Survival after 72 h |
|---|------------------------|-----------------------|-----------------------|
| [Ag(1-Bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] 100 µg cm ⁻³ | 80 | 45 | 35 |
| 10 µg cm ⁻³ | 70 | 40 | 40 |
| 1.560 µg cm ⁻³ | 70 | 40 | 25 |
| [Ag ₂ (1-Bu-imid) ₂ (9-aca) ₂] 100 µg cm ⁻³ | 90 | 80 | 65 |
| 10 µg cm ⁻³ | 70 | 50 | 35 |
| 1.560 µg cm ⁻³ | 40 | 20 | 20 |
| [Ag(apim)](9-aca)·H ₂ O 100 µg cm ⁻³ | 100 | 90 | 70 |
| 10 µg cm ⁻³ | 80 | 50 | 40 |
| 0.400 µg cm ⁻³ | 70 | 30 | 20 |
| [Ag(2-Ph-imid)]# 100 µg cm ⁻³ | 100 | 70 | 60 |
| 10 µg cm ⁻³ | 95 | 45 | 30 |
| 3.125 µg cm ⁻³ | 100 | 40 | 20 |
| [Ag(4-Ph-imidH) ₂ (9-aca)] 100 µg cm ⁻³ | 80 | 40 | 20 |
| 10 µg cm ⁻³ | 60 | 30 | 20 |
| 3.125 µg cm ⁻³ | 50 | 30 | 10 |
| [Ag(4,5-dicyanoimid)]# 100 µg cm ⁻³ | 85 | 60 | 60 |
| 10 µg cm ⁻³ | 90 | 60 | 40 |
| 0.780 µg cm ⁻³ | 70 | 55 | 30 |
| [Ag(Benz-imid)]# 100 µg cm ⁻³ | 75 | 60 | 50 |
| 10 µg cm ⁻³ | 80 | 55 | 40 |
| 3.125 µg cm ⁻³ | 60 | 50 | 30 |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ 100 µg cm ⁻³ | 90 | 50 | 10 |
| 10 µg cm ⁻³ | 80 | 30 | 10 |
| 3.125 µg cm ⁻³ | 80 | 40 | 10 |
| [Ag(2-Mebenz-imid)]# 100 µg cm ⁻³ | 60 | 50 | 50 |
| 10 µg cm ⁻³ | 60 | 60 | 50 |
| 0.625 µg cm ⁻³ | 60 | 40 | 40 |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] 100 µg cm ⁻³ | 85 | 65 | 60 |
| 10 µg cm ⁻³ | 80 | 50 | 40 |
| 0.390 µg cm ⁻³ | 60 | 45 | 30 |

Table 54. Significance of prophylactic treatment (categories and p values).

| Drug Concentration (#poor solubility) | Significant after 24 h. (p value) | Significant after 48 h (p value) | Significant after 72 h (p value) |
|--|-----------------------------------|----------------------------------|----------------------------------|
| Ketoconazole [#] | | | |
| 100 µg cm ⁻³ | No (0.2758) | Yes* (0.0285) | Yes** (0.0076) |
| 10 µg cm ⁻³ | No (0.6147) | No (0.3736) | No (0.0571) |
| 5 µg cm ⁻³ | No (0.6147) | No (0.1888) | No (0.0571) |
| AgNO ₃ | | | |
| 100 µg cm ⁻³ | No (0.9671) | Yes** (0.0076) | Yes** (0.0022) |
| 10 µg cm ⁻³ | No (0.2758) | Yes* (0.0285) | Yes** (0.0076) |
| 0.625 µg cm ⁻³ | No (0.6147) | No (0.0812) | No (0.0571) |
| AgClO ₄ | | | |
| 100 µg cm ⁻³ | No (0.6147) | No (0.0812) | No (0.0571) |
| 10 µg cm ⁻³ | No (1.000) | No (0.3736) | No (0.1311) |
| 0.625 µg cm ⁻³ | No (0.1888) | No (0.6147) | No (0.5416) |
| [Ag ₂ (9-aca) ₂] _n | | | |
| 100 µg cm ⁻³ | No (0.2758) | No (0.0812) | Yes* (0.0223) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.1888) | No (0.0571) |
| 1.250 µg cm ⁻³ | No (0.2758) | No (0.1888) | No (0.0571) |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | | | |
| 100 µg cm ⁻³ | No (0.6174) | No (0.1888) | No (0.0571) |
| 10 µg cm ⁻³ | No (0.6147) | No (0.6477) | No (0.2758) |
| 1.560 µg cm ⁻³ | No (1.000) | No (0.6477) | No (0.5416) |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | | | |
| 100 µg cm ⁻³ | No (1.000) | No (0.6477) | No (0.2758) |
| 10 µg cm ⁻³ | No (0.6477) | No (0.6477) | No (0.2758) |
| 0.390 µg cm ⁻³ | No (0.3736) | No (0.6147) | No (1.000) |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | | | |
| 100 µg cm ⁻³ | No (0.6147) | No (0.0812) | Yes* (0.0223) |
| 10 µg cm ⁻³ | No (0.6477) | No (0.3736) | No (0.2758) |
| 2.5 µg cm ⁻³ | No (0.6477) | No (0.6147) | No (1.000) |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | | | |
| 100 µg cm ⁻³ | No (0.6147) | No (0.0812) | No (0.0571) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.6477) | No (0.2758) |
| 1.560 µg cm ⁻³ | No (0.2758) | No (0.3736) | No (0.2758) |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | | | |
| 100 µg cm ⁻³ | No (0.0671) | No (0.6477) | No (0.5416) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.3736) | No (0.2758) |
| 2 µg cm ⁻³ | No (0.0671) | No (0.3736) | No (0.2758) |
| [Ag(2-Me-imidH) ₂ (9-aca)] | | | |
| 100 µg cm ⁻³ | No (0.6477) | No (1.000) | No (0.2758) |
| 10 µg cm ⁻³ | No (0.6477) | No (0.2758) | No (1.000) |
| 1.560 µg cm ⁻³ | No (0.3736) | No (0.2758) | No (1.000) |

| Drug Concentration (#poor solubility) | Significant after 24 h. (p value) | Significant after 48 h (p value) | Significant after 72 h (p value) |
|--|---|--|--|
| [Ag(1-bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] 100 µg cm ⁻³ 10 µg cm ⁻³ 1.560 µg cm ⁻³ | No (0.0671) No (0.2758) No (0.6477) | No (0.1888) No (0.1888) No (0.3736) | Yes* (0.0223) Yes* (0.0223) No (1.000) |
| [Ag ₂ (1-bu-imid) ₂ (9-aca) ₂] 100 µg cm ⁻³ 10 µg cm ⁻³ 1.560 µg cm ⁻³ | No (0.6147) No (1.000) No (0.6477) | Yes* (0.0285) No (0.6477) No (0.3736) | Yes** (0.0076) No (0.2758) No (1.000) |
| [Ag(apim)](9-aca)·H ₂ O 100 µg cm ⁻³ 10 µg cm ⁻³ 0.400 µg cm ⁻³ | No (0.0671) No (1.000) No (0.1888) | Yes* (0.0285) No (0.6477) No (0.6477) | Yes** (0.0076) No (0.1311) No (0.5416) |
| [Ag(2-Ph-imid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.0671) No (0.2758) No (0.2758) | Yes* (0.0285) No (0.1888) No (0.1888) | Yes** (0.0076) No (0.1311) No (0.2758) |
| [Ag(4-Ph-imidH) ₂ (9-aca)] 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.0671) No (1.000) No (0.3736) | No (0.1888) No (0.3736) No (1.000) | No (0.1311) No (0.1311) No (0.5416) |
| [Ag(4,5-dicyanoimid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 0.780 µg cm ⁻³ | No (0.2758) No (0.2758) No (1.000) | No (0.0812) No (0.0812) No (0.3736) | Yes* (0.0223) No (0.0571) No (0.2758) |
| [Ag(Benz-imid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.6147) No (0.6147) No (1.000) | No (0.0812) No (0.0812) No (0.3736) | Yes* (0.0223) No (0.0571) No (0.2758) |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.2758) No (0.2758) No (1.000) | No (0.1888) No (0.1888) No (0.3736) | No (0.1311) No (0.5416) No (0.2758) |
| [Ag(2-Mebenz-imid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 6.250 µg cm ⁻³ | No (0.6147) No (1.000) No (1.000) | No (0.3736) No (0.6477) No (0.3736) | No (0.1311) No (0.1311) No (0.2758) |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] 100 µg cm ⁻³ 10 µg cm ⁻³ 0.390 µg cm ⁻³ | No (0.0671) No (0.0671) No (0.6147) | Yes** (0.0076) Yes* (0.0285) No (0.0812) | Yes*** (0.0005) Yes** (0.0076) Yes* (0.0223) |

Table 55. Significance of treatment of infection (categories and p values).

| Drug Concentration (#poor solubility) | Significant after 24 h (p value) | Significant after 48 h (p value) | Significant after 72 h (p value) |
|--|----------------------------------|----------------------------------|----------------------------------|
| Ketoconazole [#] | | | |
| 100 µg cm ⁻³ | No (0.0671) | Yes** (0.0076) | Yes** (0.0076) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.6477) | No (0.2758) |
| 5 µg cm ⁻³ | No (1.000) | No (0.6477) | No (0.5416) |
| AgNO ₃ | | | |
| 100 µg cm ⁻³ | No (0.2758) | Yes * (0.0285) | Yes** (0.0076) |
| 10 µg cm ⁻³ | No (0.2758) | Yes* (0.0285) | No (0.0571) |
| 0.625 µg cm ⁻³ | No (0.2758) | No (0.0812) | Yes* (0.0223) |
| AgClO ₄ | | | |
| 100 µg cm ⁻³ | No (1.000) | No (0.3736) | No (0.1311) |
| 10 µg cm ⁻³ | No (1.000) | No (0.3736) | No (0.5416) |
| 0.625 µg cm ⁻³ | No (0.0812) | No (0.2758) | No (1.000) |
| [Ag ₂ (9-aca) ₂] _n | | | |
| 100 µg cm ⁻³ | No (0.2758) | No (0.1888) | No (0.0571) |
| 10 µg cm ⁻³ | No (0.0671) | No (0.3736) | No (0.1311) |
| 1.250 µg cm ⁻³ | No (0.0671) | No (0.6477) | No (0.2758) |
| [Ag ₂ (9-aca) ₂ (DMSO) ₂] _n | | | |
| 100 µg cm ⁻³ | No (0.2758) | No (0.1888) | No (0.2758) |
| 10 µg cm ⁻³ | No (0.2758) | No (1.000) | No (0.2758) |
| 1.560 µg cm ⁻³ | No (0.6147) | No (0.6477) | No (0.2758) |
| [Ag(imidH) _{2.3} (CH ₃ CN) _{0.7}](9-aca) | | | |
| 100 µg cm ⁻³ | No (0.6477) | No (0.6477) | No (0.2758) |
| 10 µg cm ⁻³ | No (0.6477) | No (0.6477) | No (0.5416) |
| 0.390 µg cm ⁻³ | No (0.3736) | No (0.6147) | No (1.000) |
| [Ag ₆ (imidH) ₄ (9-aca) ₆ (MeOH) ₂] | | | |
| 100 µg cm ⁻³ | No (0.6147) | No (0.6477) | No (0.5416) |
| 10 µg cm ⁻³ | No (0.6147) | No (1.000) | No (1.000) |
| 2.5 µg cm ⁻³ | No (0.6147) | No (0.6147) | No (1.000) |
| [Ag(1-Me-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] | | | |
| 100 µg cm ⁻³ | No (0.0671) | No (0.1888) | Yes* (0.0223) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.6477) | No (0.2758) |
| 1.560 µg cm ⁻³ | No (0.6147) | No (1.000) | No (0.2758) |
| [Ag ₂ (1-Me-imid) ₂ (9-aca) ₂] | | | |
| 100 µg cm ⁻³ | No (0.2758) | No (0.1888) | No (0.1311) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.6477) | No (0.2758) |
| 2 µg cm ⁻³ | No (0.2758) | No (1.000) | No (0.2758) |
| [Ag(2-Me-imidH) ₂ (9-aca)] | | | |
| 100 µg cm ⁻³ | No (0.2758) | No (0.0812) | Yes** (0.0076) |
| 10 µg cm ⁻³ | No (0.2758) | No (0.0812) | Yes* (0.0223) |
| 1.560 µg cm ⁻³ | No (0.6147) | No (0.3736) | No (0.2758) |

| Drug Concentration (#poor solubility) | Significant after 24 h (p value) | Significant after 48 h (p value) | Significant after 72 h (p value) |
|--|---|---|--|
| [Ag(1-bu-imid) ₂] ₂ [Ag ₄ (9-aca) ₆] 100 µg cm ⁻³ 10 µg cm ⁻³ 1.560 µg cm ⁻³ | No (0.6147) No (1.000) No (1.000) | No (0.6477) No (0.6477) No (0.6477) | No (0.2758) No (0.1311) No (0.5416) |
| [Ag ₂ (1-bu-imid) ₂ (9-aca) ₂] 100 µg cm ⁻³ 10 µg cm ⁻³ 1.560 µg cm ⁻³ | No (0.2758) No (1.000) No (0.1888) | Yes* (0.0285) No (0.3736) No (0.6147) | Yes* (0.0223) No (0.2758) No (0.5416) |
| [Ag(apim)](9-aca)·H ₂ O 100 µg cm ⁻³ 10 µg cm ⁻³ 0.400 µg cm ⁻³ | No (0.0671) No (0.6147) No (1.000) | Yes** (0.0076) No (0.3736) No (1.000) | Yes** (0.0076) No (0.1311) No (0.5416) |
| [Ag(2-Ph-imid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.0671) No (0.2758) No (0.0671) | No (0.0812) No (0.6477) No (0.6477) | Yes* (0.0223) No (0.2758) No (0.5416) |
| [Ag(4-Ph-imidH) ₂ (9-aca)] 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.6147) No (0.6477) No (0.3736) | No (0.6477) No (1.000) No (1.000) | No (0.5416) No (0.5416) No (1.000) |
| [Ag(4,5-dicyanoimid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 0.780 µg cm ⁻³ | No (0.6147) No (0.2758) No (1.000) | No (0.1888) No (0.1888) No (0.3736) | Yes* (0.0223) No (0.1311) No (0.2758) |
| [Ag(Benz-imid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (1.000) No (0.6147) No (0.6477) | No (0.1888) No (0.3736) No (0.3736) | No (0.0571) No (0.1311) No (0.2758) |
| [Ag ₂ (2-Mebenz-imidH) ₄](9-aca) ₂ 100 µg cm ⁻³ 10 µg cm ⁻³ 3.125 µg cm ⁻³ | No (0.2758) No (0.6147) No (0.6147) | No (0.3736) No (1.000) No (0.6477) | No (1.000) No (1.000) No (1.000) |
| [Ag(2-Mebenz-imid)]# 100 µg cm ⁻³ 10 µg cm ⁻³ 6.250 µg cm ⁻³ | No (0.6477) No (0.6477) No (0.6477) | No (0.3736) No (0.1888) No (0.6477) | No (0.0571) No (0.0571) No (0.1311) |
| [Ag ₄ (9-aca) ₄ (NH ₃) ₂] 100 µg cm ⁻³ 10 µg cm ⁻³ 0.390 µg cm ⁻³ | No (0.6147) No (0.6147) No (0.6477) | No (0.1888) No (0.3736) No (0.6477) | Yes* (0.0223) No (0.1311) No (0.2758) |