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Synthesis, structure and anti-fungal activity of dimeric Ag(I) complexes containing bis-imidazole ligands

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Abstract

Five Ag(I) complexes containing the ligands bis(imidazol-2-yl)methane (2-BIM) and its derivatives were prepared and $[Ag_2(2\text{-}BIM)_2](ClO_4)_2$ and $[Ag_2(2\text{-}BIM(Bz)OH)_2](ClO_4)_2 \cdot EtOH$ were characterised using X-ray crystallography. In each dimer the two Ag(I) ions are two-coordinate and there are small but definite argentophilic Ag–Ag (d^{10}–d^{10}) interactions. All of the complexes display anti-fungal activity when tested in vitro against the fungal pathogen *Candida albicans*.
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1. Introduction

In our efforts to develop new metal complexes that would greatly inhibit the growth of the human fungal pathogen *Candida albicans* [1–4] we have found that, to date, the most active drug tested in aqueous media is the Ag(I) complex $[Ag(phendio)_2]ClO_4$ (phendio = 1,10-phenanthroline-5,6-dione) [5]. As part of these ongoing studies into the synthesis and in vitro testing of new metal-based anti-fungal drugs we report here the preparation of five Ag(I) complexes containing bis(imidazole) ligands. Bis(imidazol-2-yl)methane (2-BIM) and its derivatives (Fig. 1), in which the two imidazole rings are linked via a single tetrahedral carbon atom, can be viewed as primitive models for multi-histidine coordination in biological systems. Such bis(imidazole) ligands have been shown to form stable six-membered chelate rings with a variety of transition metals [6–12], and the Pt(II) complex $[Pt(2\text{-}BIM(Me)OH)Cl_2]$ (2-BIM(Me)OH = bis(*N*-methylimidazol-2-yl)carbinol) [10] has been reported to exhibit notable antitumor activity.

2. Results and discussion

In the current study, $AgClO_4$ was reacted at room temperature with methanolic solutions of the five bis(imidazole) ligands shown in Fig. 1 to give the respective Ag(I) complex in moderate to good yield. The complexes were soluble in hot acetonitrile and DMSO and insoluble in water. The X-ray crystal structure of $[Ag_2(2\text{-}BIM)_2](ClO_4)_2$ (Fig. 2 and Table 1) showed the complex to be centrosymmetric, containing two $Ag(2\text{-}BIM)^+$ units. The two metal ions are two-coordinate and have identical atoms in the plane of the chelating ligand. Using its two imine N atoms each 2-BIM ligand bridges the pair of Ag(I) ions. All four N atoms (N1, N4A, N4, N1A) are coplanar and the two imidazole groups in each 2-BIM ligand have an interplanar angle of 75.52(8)°. The two Ag(I) ions are only weakly interacting, the distance separating them being 3.2612(4) Å. The binding of the two 2-BIM ligands is similar to that

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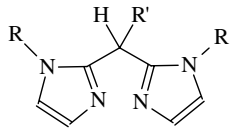

	R	R'
2-BIM	H	H
2-BIM(Bz)OH	$PhCH_2$	OH
2-BIM(Me)	Me	H
2-BIM(CN)	$NC(CH_2)_2$	H
2-BIM(ClBz)	Cl_2PhCH_2	H

Fig. 1. Ligand symbols and structures.

observed for the $Biim^{2-}$ ligand ($Biim^{2-}$ = 2,2′-biimidazolate) in the heteropolynuclear complex, $[\{Ru(pap)_2(Biim)\}_2Ag_2](ClO_4)_2 \cdot H_2O$ (pap = 2-(phenylazo)pyridine) [13]. The shorter Ag–Ag separation in the latter species is (2.8899 Å) is mainly a consequence of the smaller size of the $Biim^{2-}$ ligand compared to 2-BIM (no methylene bridge between the two imidazole rings in $Biim^{2-}$). The formula unit of $[Ag_2(2\text{-}BIM)_2](ClO_4)_2$ is completed by two lattice perchlorate, which are involved in hydrogen bonding to the hydrogen atoms of the imidazole nitrogen atoms (N2 and N3, and N2A and N3A, respectively). The lattice perchlorate anions show unsymmetric bridging interactions with Ag(I) ions of neighbouring cations ($AgOClO_3$ 2.965(2) and 3.264(2) Å). There are hydrogen bonding interactions along the *a* and *b* directions which link the units together in the lattice, forming sheets. However, there are no hydrogen bonds in the *c* direction, that is to say, between the sheets. There are some intermolecular π–π interactions involving the imidazole rings on adjacent dimer molecules and there is also evidence of some interdimer C–H···π interactions between neighbouring imidazole functions. A perspective view of the cell packing is shown in Fig. 3.

The X-ray crystal structure of $[Ag_2(2\text{-}BIM(Bz)OH)_2](ClO_4)_2 \cdot EtOH$ (Fig. 4 and Table 2) shows the asymmetric unit containing one $[Ag_2(2\text{-}BIM(Bz)OH)_2]^{2+}$ unit, two perchlorate anions and a solvate ethanol. The two Ag(I) ions are again bridged by the two ligands and each metal is approximately linearly coordinated to a pair of imine nitrogens. There are additional longer interactions with the perchlorate anions. The metal-metal distance of 3.018(4) Å is considerably shorter than in $[Ag_2(2\text{-}BIM)_2](ClO_4)_2$. Within the $[Ag_2(2\text{-}BIM(Bz)OH)_2](ClO_4)_2 \cdot EtOH$ complex molecule there appears to be some degree of intramolecular π–π interaction between the imidazole and phenyl rings of the opposing two 2-BIM(Bz)OH ligands in the dimer. Interestingly, the angles N(1A)–Ag(1)–Ag(2) and N(4B)–Ag(1)–Ag(2) are very different to one another (168.30(12)° and 68.35(8)°, respectively). One of the perchlorate anions in the complex is disordered and was modeled with two alternative sets of oxygen atom positions (50% occupancy each). The ethanol solvate is also disordered and was modeled as 50% occupancy of two alternative positions. Hydrogen atoms attached to carbon were inserted at calculated positions, whilst those attached to the 2-BIM(Bz)OH alcohol groups were located from difference maps and not further refined, those bonded to the disordered oxygen atom of the ethanol solvate were not located or included in the model. One view of the packing in the crystal is illustrated in Fig. 5.

Repeated attempts to grow crystals of $[Ag_2\{2\text{-}BIM(Me)\}_2](ClO_4)_2$, $[Ag_2\{2\text{-}BIM(CN)\}_2](ClO_4)_2$ and $[Ag_2\{2\text{-}BIM(BzCl)\}_2](ClO_4)_2$ suitable for X-ray structural anal-

Table 1
Selected bond lengths (Å) and angles (°) for $[Ag_2(2\text{-}BIM)_2](ClO_4)_2$

Bond lengths (Å)	
Ag(1)–N(4)#1	2.0953(17)
Ag(1)–N(1)	2.0957(17)
Ag(1)–Ag(1)#1	3.2612(4)
Ag(1)–O(11)#2	2.965(2)
Ag(1)–O(11)#3	3.264(2)
Bond angles (°)	
N(4)#1–Ag(1)–N(1)	167.80(7)
N(4)#1–Ag(1)–Ag(1)#1	91.08(5)
N(1)–Ag(1)–Ag(1)#1	99.94(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$; #2 $1+x, 1+y, z$; #3 $1-x, -y, 1-z$.

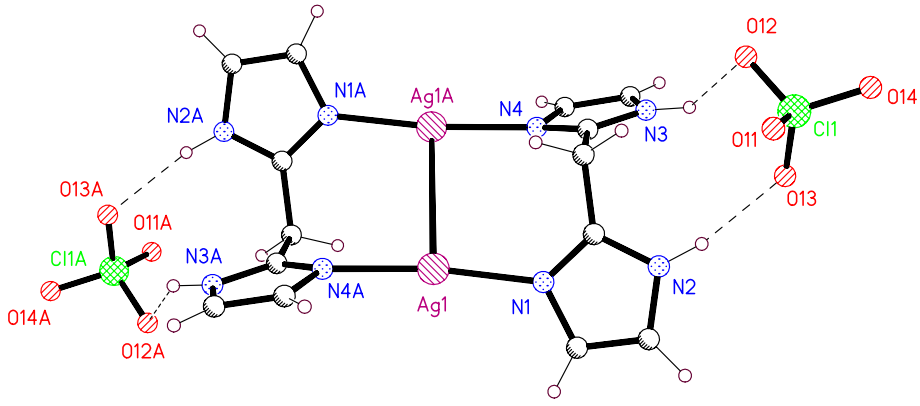

Fig. 2. X-ray crystal structure of $[Ag_2(2\text{-}BIM)_2](ClO_4)_2$.

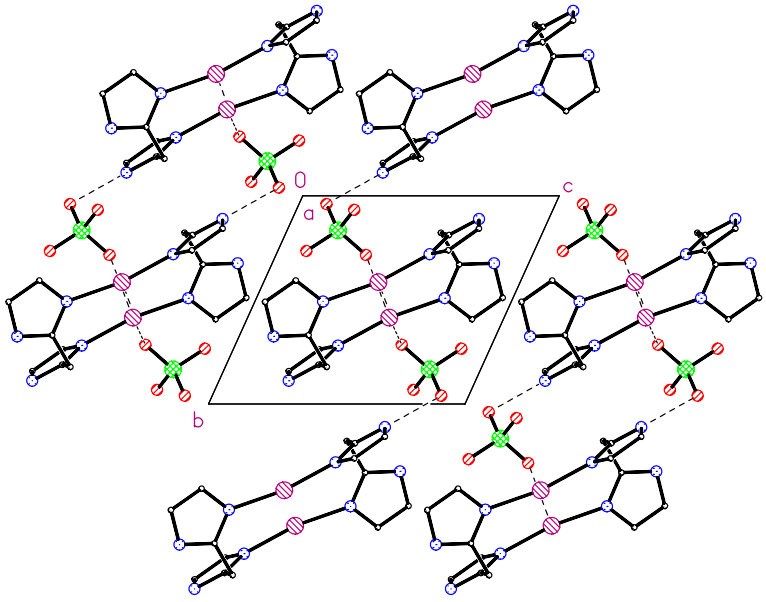

Fig. 3. Packing diagram for $[Ag_2(2\text{-}BIM)_2](ClO_4)_2$.

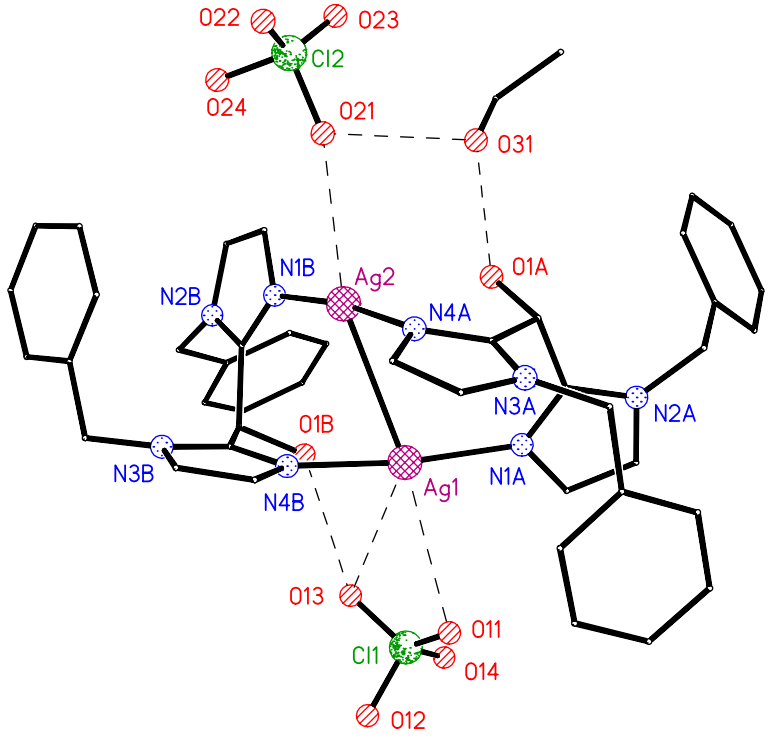

Fig. 4. X-ray crystal structure of $[Ag_2(2\text{-}BIM(Bz)OH)_2](ClO_4)_2 \cdot EtOH$.

ysis were unsuccessful. However, given the close similarities in the core structures of all five bis(imidazole) ligands the latter three silver complexes are thought to be essentially isostructural with $[Ag_2(2\text{-}BIM)_2]$ $(ClO_4)_2$ and $[Ag_2(2\text{-}BIM(Bz)OH)_2](ClO_4)_2 \cdot EtOH$ and are thus also formulated as dimers. For $[Ag_2\{2\text{-}BIM(CN)\}_2](ClO_4)_2$ there is also the possibility of the pendant cyano groups participating in the bonding to the metal since Ag(I) has a high affinity for organonitrile donors.

2.1. In vitro anti-Candida studies

All of the metal-free bis(imidazole) ligands and the Ag(I) complexes were screened for their ability to inhibit the growth of *C. albicans*. The minimum inhibitory concentration (MIC) is the concentration of drug (expressed as μg of complex per 1 cm^3 of aqueous growth medium solution) required to totally inhibit the growth of the fungal cells at 37 °C. As the complexes and the

Table 2
Selected bond lengths (Å) and angles (°) for $[Ag_2(2\text{-BIM(Bz)OH})_2](ClO_4)_2 \cdot EtOH$

Bond lengths (Å)	
Ag(1)–N(1A)	2.111(3)
Ag(1)–N(4B)	2.134(3)
Ag(1)–Ag(2)	3.0184(4)
Ag(1)–O(11)	3.211(6)
Ag(1)–O(13)	3.312(7)
Ag(2)–N(1B)	2.119(3)
Ag(2)–N(4A)	2.141(3)
Ag(2)–O(21)	3.012(7)
Ag(2)–O(21′)	3.234(14)
Bond angles (°)	
N(1A)–Ag(1)–N(4B)	168.30(12)
N(1A)–Ag(1)–Ag(2)	103.65(8)
N(4B)–Ag(1)–Ag(2)	68.35(8)
N(1A)–Ag(1)–O(11)	82.69(13)
N(4B)–Ag(1)–O(11)	105.55(13)
Ag(2)–Ag(1)–O(11)	173.58(10)
N(1A)–Ag(1)–O(13)	109.69(14)
N(4B)–Ag(1)–O(13)	81.74(14)
Ag(2)–Ag(1)–O(13)	133.53(10)
O(11)–Ag(1)–O(13)	41.35(13)
N(1B)–Ag(2)–N(4A)	172.79(12)
N(1B)–Ag(2)–O(21)	92.53(19)
N(4A)–Ag(2)–O(21)	93.9(2)
N(1B)–Ag(2)–Ag(1)	99.97(8)
N(4A)–Ag(2)–Ag(1)	74.23(8)
O(21)–Ag(2)–Ag(1)	164.88(17)
N(1B)–Ag(2)–O(21′)	76.8(2)
N(4A)–Ag(2)–O(21′)	109.3(2)
Ag(1)–Ag(2)–O(21′)	174.4(2)

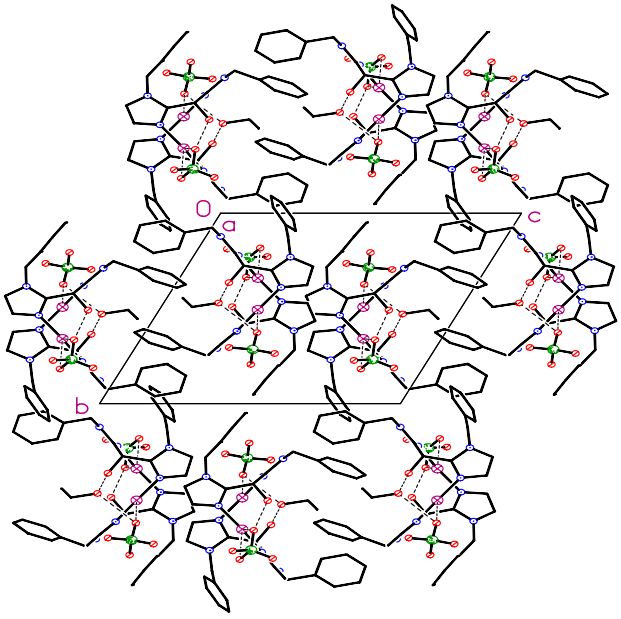

Fig. 5. Packing diagram for $[Ag_2(2\text{-BIM(Bz)OH})_2](ClO_4)_2 \cdot EtOH$.

ligands were essentially water insoluble the tests were carried out as suspensions of the complexes in the aqueous growth medium. In addition, because the complexes were soluble in DMSO a series of anti-fungal tests were also conducted using DMSO/water solutions of the complexes (see Section 3). In all cases, the activity of the complexes were compared to that of a control system in which the cells were grown in the absence of any added complex or free ligand (under these conditions the fungal cell replication was rapid). In addition, under the present biological test conditions an aqueous suspension of the anti-*Candida* prescription drug ketoconazole had an MIC value of ca. 2.5 $\mu g\,cm^{-3}$.

All of the metal-free ligands were found to be inactive against the fungal cells. As aqueous suspensions, the silver complexes were moderately active with MIC value ranges indicated in brackets: $[Ag_2(2\text{-BIM})_2](ClO_4)_2$ (10–20 $\mu g\,cm^{-3}$); $[Ag_2(2\text{-BIM(Bz)OH})_2](ClO_4)_2 \cdot EtOH$ (50–100 $\mu g\,cm^{-3}$); $[Ag_2\{2\text{-BIM(Me)}\}_2](ClO_4)_2$ (20–50 $\mu g\,cm^{-3}$); $[Ag_2\{2\text{-BIM(CN)}\}_2](ClO_4)_2$ (20–50 $\mu g\,cm^{-3}$). A considerable improvement in anti-fungal activity was observed upon administering the complexes as DMSO/water solutions as opposed to aqueous suspensions: $[Ag_2(2\text{-BIM})_2](ClO_4)_2$ (5–10 $\mu g\,cm^{-3}$); $[Ag_2(2\text{-BIM(Bz)-OH})_2](ClO_4)_2 \cdot EtOH$ (2.5–5 $\mu g\,cm^{-3}$); $[Ag_2\{2\text{-BIM(Me)}\}_2](ClO_4)_2$ (2.5–5 $\mu g\,cm^{-3}$); $[Ag_2\{2\text{-BIM(CN)}\}_2](ClO_4)_2$ (5–10 $\mu g\,cm^{-3}$); $[Ag_2\{2\text{-BIM(BzCl)}\}_2](ClO_4)_2$ (5–10 $\mu g\,cm^{-3}$). Besides greatly increasing the solubility of the complexes the DMSO is also thought to make the cells more permeable to the complexes so that they can enter the cells and exert their effects on the organism. In comparison, as an aqueous suspension $[Ag(phen\text{-}dio)_2]ClO_4$ has an MIC value of 0.3 $\mu g\,cm^{-3}$ [5].

3. Experimental

Chemicals were purchased from commercial sources and, unless specified, were used without further purification. Literature methods were used to prepare 2-BIM [14,15], 2-BIM(Me) [7,16] and 2-BIM(OH)Bz [17]. The preparation of the silver complexes was conducted in the absence of light and the samples were stored in the dark. Infrared spectra of solids (in a KBr matrix) were recorded in the region 4000–400 cm^{-1} on a Nicolet FT-IR Impact 400D infrared spectrometer and ^1H NMR spectra were run on a Bruker Avance 300 MHz instrument. Microanalytical data were provided by the Microanalytical Laboratory, National University of Ireland, Cork, Ireland.

3.1. 2-BIM(CN)

Acrylonitrile (3.6 g, 67 mmol) was added to a mixture of 2-BIM (5.0 g, 34 mmol), and triethylamine (6.8 g, 67 mmol) in acetonitrile (150 cm^3). The reaction mixture was refluxed with stirring for 5 h. The solvent was removed under reduced pressure giving a white solid, which was recrystallised from acetone. Yield: 4.7 g (55%). Mp 170 °C. *Anal.* Calc. C, 61.40; H, 5.50; N,

33.07. Found: C, 61.26; H, 5.47; N, 32.76%. ^{1}H NMR(DMSO-d_6): 7.17 (2H, d, $J = 1.3$ Hz), 6.8 (2H, d, $J = 1.3$ Hz), 4.3 (4H, t, $J = 6.7$ Hz), 4.2 (2H, s), 3.0 (4H, t, $J = 6.7$ Hz) ppm. ^{13}C NMR(DMSO-d_6): 143.6, 127.3, 120.8, 118.8, 25.4, 19.2 ppm. IR: 3125, 2932, 2264, 1485, 1447, 1383, 1287, 1166, 1134, 1089, 926, 722, 743, 705 cm^{-1}. Mass spec.: m/z: 254 (M^+, 4%), 200 (4), 173 (8), 161 (6), 148 (10), 134 (11), 120 (14), 107 (14), 94 (28), 82 (84), 66 (20), 54 (100).

3.2. 2-BIM(BzCl)

2,6-Dichlorobenzyl chloride (0.53 g, 2.7 mmol) was added to a stirred mixture of 2-BIM (0.2 g, 1.3 mmol) and sodium hydride (0.06 g, 2.5 mmol) in dry DMF (15 cm^3). The mixture was stirred overnight at room temperature and the solvent removed under reduced pressure. Water (20 cm^3) was added and the product extracted with dichloromethane, and the dichloromethane solution was then dried over magnesium sulphate. After filtration the solvent was removed under reduced pressure. The resulting brown oily residue was digested in cyclohexane and the white product precipitated upon cooling. Yield: 0.34 g (54%). Mp 93 °C. *Anal*. Calc. C, 54.10; H, 3.43; N, 12.02. Found: C, 54.09; H, 3.58; N, 11.73%. ^{1}H NMR ($CDCl_3$): 7.4 (2H, d, $J = 2$ Hz), 7.1 (2H, dd, $J = 8.3$ Hz), 6.9 (2H, d, $J = 1.3$ Hz), 6.7 (2H, d, $J = 1.3$ Hz), 6.5 (2H, d, $J = 8.3$ Hz), 5.2 (4H, s), 4.2 (2H, s). ^{13}C NMR ($CDCl_3$): 143, 134.5, 133.6, 132.7, 129.5, 129.1, 128.1, 127.5, 120.5, 47, 27 ppm. IR: 2945, 1593, 1485, 1447, 1389, 1274, 1121, 1057, 849, 733, 682 cm^{-1}. Mass spec.: m/z: 466 (M^+, 16%), 429 (4), 305 (26), 269 (8), 205 (8), 159 (100), 147 (8), 123 (16), 99 (6), 89 (16), 81 (38), 63 (10).

3.3. $[Ag_2(2\text{-}BIM)_2](ClO_4)_2$

Silver perchlorate (0.70 g, 3.37 mmol) was added to a stirred solution of 2-BIM (0.5 g, 3.37 mmol) in methanol (15 cm^3) and the mixture stirred for 1 h at room temperature. The precipitated white was filtered off, washed with methanol and air-dried. Yield: 1.00 g (83%). *Anal*. Calc. C, 23.64; H, 2.25; N, 15.76. Found: C, 23.58; H, 2.13; N, 15.78%. IR: 3344, 3151, 1293, 1095, 759, 624 cm^{-1}. ^{1}H NMR (ppm DMSO): 6.8 (8H, s), 4 (4H, s). The complex was soluble in hot acetonitrile and DMSO, and crystals suitable for X-ray analysis were obtained by recrystallising from acetonitrile.

3.4. $[Ag_2(2\text{-}BIM(Bz)OH)_2](ClO_4)_2 \cdot EtOH$

This white complex was prepared and recrystallised in a similar way to $[Ag_2(2\text{-BIM})_2](ClO_4)_2$ using silver perchlorate (0.06 g, 0.17 mmol) and 2-BIM(Bz)OH (0.1 g, 0.29 mmol). Yield: 0.11 g (68%). *Anal*. Calc. C, 43.87; H, 3.48; N, 9.70. Found: C, 44.21; H, 3.45; N, 9.69%. IR: 2485, 3138, 2971, 1497, 1459, 1287, 1102, 827, 717, 624 cm^{-1}. ^{1}H NMR (ppm DMSO): 5.2 (8H, dd), 6.4 (2H, d), 7.1 (8H, s), 7.35 (20H, m). The complex was soluble in hot acetonitrile, hot acetone and DMSO.

3.5. $[Ag_2\{2\text{-}BIM(Me)\}_2](ClO_4)_2$

To a solution of silver perchlorate (0.10 g, 0.48 mmol) in methanol (3 cm^3) was added a solution of 2-BIM(Me) (0.10 g, 0.56 mmol) in methanol (3 cm^3). A white precipitate formed immediately and the reaction mixture was stirred for 20 min at room temperature. The white product was filtered off, washed with methanol and then dried in air. Yield: 0.13 g (62%). *Anal*. Calc. C, 28.10; H, 3.13; N, 14.60. Found: C, 27.5; H, 3.00; N, 14.13%. IR: 3485, 3138, 2971, 1497, 1414, 1293, 1102, 772, 627 cm^{-1}. ^{1}H NMR (ppm DMSO): 3.5 (12H, s), 4.36 (4H, s), 6.8 (4H, s), 7.2 (4H, s). The complex was soluble in hot acetonitrile, hot acetone and DMSO.

3.6. $[Ag_2\{2\text{-}BIM(CN)\}_2](ClO_4)_2$

This white complex was prepared in a similar way to $[Ag_2\{2\text{-BIM(Me)}\}_2](ClO_4)_2$ using silver perchlorate (0.10 g, 0.48 mmol) and 2-BIM(CN) (0.20 g, 0.78 mmol). Yield: 0.32 g (89%). *Anal*. Calc. C, 33.81; H, 3.03; N, 18.20. Found: C, 33.46; H, 2.92; N, 18.20%. IR: 3511, 3138, 2984, 2264, 1497, 1427, 1287, 1102, 756, 627 cm^{-1}. ^{1}H NMR (ppm DMSO): 7.3 (4H, s), 6.8 (4H, s), 4.4 (4H, s), 4.2 (8H, t), 2.9 (8H, t). The complex was soluble in hot acetonitrile, hot acetone and DMSO.

3.7. $[Ag_2\{2\text{-}BIM(BzCl)\}_2](ClO_4)_2$

This white complex was prepared in a similar way to $[Ag_2\{2\text{-BIM(Me)}\}_2](ClO_4)_2$ using silver perchlorate (0.08 g, 0.38 mmol) in 3 ml methanol was added to 2-BIM(BzCl) (0.20 g, 0.43 mmol). Yield: 0.16 g (57%). *Anal*. Calc. C, 37.43; H, 2.37; N, 8.31. Found: C, 37.03; H, 2.41; N, 8.04%. IR: 3511, 3138, 1593, 1491, 1395, 1274, 1102, 836, 749, 628 cm^{-1}. ^{1}H NMR (ppm DMSO): 7.9 (4H, d), 7.56 (4H, dd), 7.5 (4H, d),7.25 (4H, d) 6.8 (4H, d), 5.5 (8H, s), 4.8 (4H, s). The complex was soluble in hot acetonitrile, hot acetone and DMSO.

3.8. Anti-Candida testing

Candida albicans ATCC 10231 was obtained from the American Type Culture Collection (Manasas, VA, USA). Cultures were grown on Sabouraud dextrose agar (SDA) plates at 37 °C and maintained at 4 °C for short-term storage. Minimum inhibitory concentrations (MICs) were determined as follows. RPMI-1640 broth medium was used for the anti-*Candida* susceptibility testing. RPMI (5.15 g) was dissolved in cold distilled water (425 cm^3) in a 1-l Duran bottle and the pH

adjusted to 4.0 using a few drops of HCl (ca. 2 M). The resulting solution was autoclaved and then allowed to cool to approximately 50 °C. Morpholinepropanesulfonic acid (MOPS) (17.3 g) and L-glutamate (0.15 g) were dissolved together with stirring in distilled water (50 cm^3) and the resulting solution filter sterilized. The MOPS and L-glutamate solution was added to the warm RPMI and the pH of the mixture adjusted to 7.0 using sterile NaOH (6 M). Prior to MIC testing, cells were grown on SDA at 37 °C for 24 h. Cell suspensions were prepared in sterile phosphate buffered saline (PBS, pH 7.2) and cells were counted microscopically following dilution with PBS. A microtitre plate was inoculated with cells at a density of 5×10^5 cells cm^{-3}. Test suspensions (in water) and solutions (in aqueous DMSO) of the silver complexes were each prepared as follows. *Suspensions in water*: the complex (0.02 g) was suspended in distilled water (10 cm^3) to yield a stock suspension of concentration 2000 $\mu g\,cm^{-3}$. Doubling dilutions of the stock suspension were made to yield a series of test suspensions ranging in complex concentration from 20 to 1.25 $\mu g\,cm^{-3}$. *Solutions in DMSO*: the complex (0.02 g) was dissolved in DMSO (10 cm^3) to yield a stock solution of concentration 2000 $\mu g\,cm^{-3}$. Doubling dilutions of the stock solution were made using distilled water to yield a series of test solutions ranging in complex concentration from 20 to 1.25 $\mu g\,cm^{-3}$. The DMSO concentration (% v/v) in the test solutions ranged from 1.0% to 0.06% (note that a 2% DMSO aqueous solution, without added complex, does not inhibit the growth of the microorganism whereas a 3% DMSO aqueous solution will arrest cell growth totally). For the aqueous test suspensions and the aqueous-DMSO test solutions the complex/cell mixtures were incubated at 37 °C for 24 h with continuous shaking and the assays were performed in triplicate. Plates were read using a Labsystems iEMS Reader MF (absorbance at $\lambda = 540$ nm) and data were statistically analysed.

3.9. X-ray crystallography

All of the data were collected at 150 K on a Bruker SMART 1000 diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using all the reflections. One of the prechlorate anions in $[Ag_2(2\text{-BIM(Bz)OH})_2](ClO_4)_2 \cdot EtOH$ is disordered and was modeled with two alternative sets of oxygen atom positions (50% occupancy each). The ethanol solvate is also disordered and was modeled as 50% occupancy of two alternative positions. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon were inserted at calculated positions. Hydrogen atoms bonded to nitrogen ($[Ag_2(2\text{-BIM})_2](ClO_4)_2$) or the ligand alcohol group ($[Ag_2(2\text{-BIM(Bz)OH})_2](ClO_4)_2 \cdot EtOH$) were located from difference maps and not further refined; those bonded to the disordered oxygen of the ethanol solvate in $[Ag_2(2\text{-BIM(Bz)OH})_2](ClO_4)_2 \cdot EtOH$ were not included in the model. All programmes used in the structure solution and refinement are included in the SHELXTL package [18] and data collection and refinement details are summarised in Table 3.

Table 3
X-ray crystallographic data. Crystal data and structure refinement for $[Ag_2(2\text{-BIM})_2](ClO_4)_2$ and $[Ag_2(2\text{-BIM(Bz)OH})_2](ClO_4)_2 \cdot EtOH$

Identification code	$[Ag_2(2\text{-BIM})_2](ClO_4)_2$	$[Ag_2(2\text{-BIM(Bz)OH})_2](ClO_4)_2 \cdot EtOH$
Empirical formula	$C_{14}H_{16}Ag_2Cl_2N_8O_8$	$C_{44}H_{46}Ag_2Cl_2N_8O_{11}$
Formula weight	710.99	1149.53
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.8149(10)	10.9636(7)
b (Å)	8.9902(11)	14.7743(9)
c (Å)	9.2559(11)	16.0180(10)
α (°)	108.046(2)	114.3870(10)
β (°)	98.283(2)	98.2900(10)
γ (°)	114.763(2)	95.8410(10)
Volume ($Å^3$)	532.47(11)	2300.6(2)
Z	1	2
F (0 0 0)	348	1164
Crystal size (mm)	$0.16 \times 0.25 \times 0.31$	$0.37 \times 0.25 \times 0.14$
θ range for data collection (°)	2.44–28.65	1.54–25.00
Reflections collected	4544	16522
Independent reflections [$R_{(int)}$]	2396 [0.0186]	8050 [0.0159]
Absorption correction	multiscan	multiscan
Maximum and minimum transmission	1.0000 and 0.8116	1.000000 and 0.912980
Data/restraints/parameters	2396/0/154	8050/98/667
R_1, wR_2 [$I > 2\sigma(I)$]	0.0198, 0.0526	0.0356, 0.0877
R_1, wR_2 (all data)	0.0204, 0.0530	0.0455, 0.0942

4. Supplementary data

X-ray supplementary data for $[Ag_2(2\text{-}BIM)_2](ClO_4)_2$ and $[Ag_2(2\text{-}BIM(Bz)OH)_2](ClO_4)_2 \cdot EtOH$ are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, England (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk), on request quoting the deposition numbers CCDC 219908 and CCDC 219909, respectively.

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