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Binuclear and polymeric copper(II) dicarboxylate complexes: syntheses and crystal structures of $[Cu_2(pda)(Phen)_4](ClO_4)_2 \cdot 5H_2O \cdot C_2H_5OH$, $[Cu_2(oda)(Phen)_4](ClO_4)_2 \cdot 2.67H_2O \cdot C_2H_5OH$ and $\{[Cu_2(pda)_2(NH_3)_4(H_2O)_2] \cdot 4H_2O\}_n$ ($odaH_2$=octanedioic acid; $pdaH_2$=pentanedioic acid; Phen=1,10-phenanthroline)

Michael Devereux[a,*], Malachy McCann[b], James F. Cronin[a,b], George Ferguson[c], Vickie McKee[d]

[a]*Dublin Institute of Technology, Cathal Brugha Street, Dublin 1, Ireland*
[b]*Chemistry Department, St. Patrick's College, Maynooth, Co. Kildare, Ireland*
[c]*Department of Chemistry and Biochemistry, University of Guelph, Ontario, Canada NIG 2W1*
[d]*School of Chemistry, The Queen's University, Belfast BT9 5AG, UK*

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Abstract

Reaction of $[Cu(pda)(Phen)_2] \cdot 6H_2O$ and $[Cu(oda)(Phen)_2] \cdot 8H_2O$ {$pdaH_2$=pentanedioic acid; $odaH_2$=octanedioic acid; Phen=1,10-phenanthroline} with ethanolic solutions of sodium perchlorate gives the two binuclear copper(II) perchlorate salts $[Cu_2(pda)(Phen)_4](ClO_4)_2 \cdot 5H_2O \cdot C_2H_5OH$ (**1**) and $[Cu_2(oda)(Phen)_4](ClO_4)_2 \cdot 2.76H_2O \cdot C_2H_5OH$ (**2**), respectively. The X-ray crystal structures of **1** and **2** are quite similar with each comprising a discrete $[Cu_2(dicarboxylate)(Phen)_4]^{2+}$ dication, two uncoordinated perchlorate anions, an uncoordinated ethanol and several uncoordinated water molecules. The copper centres have N_4O ligation with each metal having approximately square pyramidal geometry. $\{[Cu(pda)]\}_n$ reacts with ammonium hydroxide to form the polymeric copper(II) amine species $\{[Cu_2(pda)_2(NH_3)_4(H_2O)_2] \cdot 4H_2O\}_n$ (**3**). The structure of **3**, as determined by X-ray crystallography, consists of polymeric chains in which the bridging pda^{2-} anions link two crystallographically similar copper atoms. The copper atoms are also ligated by two *transoidal* ammonia nitrogens and an oxygen atom from an apical water molecule, giving the metals an overall N_2O_3, slightly distorted, square pyramidal geometry. Spectroscopic and magnetic data for the three complexes are also reported.

Keywords: Copper(II) complexes; Dicarboxylate; Crystal structures

1. Introduction

Anomalies in copper metabolism in humans, whether caused by a deficiency of, or an inability to absorb, the metal can lead to the development of Menke's disease [1–3]. This disorder is characterised by severe neurologic, skeletal and developmental abnormalities [1]. Near normal growth rates and the survival of animal models for this disease has been achieved by the administration of copper(II) salts in the presence of decanedioic acid $\{HOOC(CH_2)_8COOH\}$ [4]. The nature of the copper complexes present in the system is not fully understood and, indeed, reports of this or similar complexes containing long-chained α,ω-dicarboxylic acid ligands are scarce [5,6].

As part of our recent studies into the coordination chemistry of dicarboxylic acids [7–22] we have been examining the reactions of copper(II) salts with several long-chained α,ω-dicarboxylic acids. $[Cu_2(\mu\text{-}CH_3COO)_4(H_2O)_2]$ is known to react smoothly [10] with $HOOC(CH_2)_5COOH$ (heptanedioic acid; $pdaH_2$) and $HOOC(CH_2)_6COOH$ (octanedioic acid; $odaH_2$) to give the polymeric copper(II) complexes $\{[Cu(hda)]\}_n$ and $\{[Cu(oda)]\}_n$, respectively. These complexes are believed to be similar to those described earlier by Asai et al. [5]. These somewhat insoluble complexes react with 1,10-phenanthroline (phen) to yield the highly soluble mononuclear species $[Cu(\eta^2\text{-}OOC(CH_2)_5COO)(phen)_2] \cdot 11,73H_2O$

*Corresponding author. Tel.: +353-1-402-4486; fax: +353-1-402-4499.

E-mail address: michael.devereux@dit.ie (M. Devereux)

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and $[Cu(\eta^2\text{-}OOC(CH_2)_6COO)(phen)_2]\cdot 12H_2O$. The X-ray crystal structures of the two phenanthroline complexes showed the copper centres ligated by the four nitrogen atoms of the two phenanthrolines and two oxygens from a single asymmetrically chelating carboxylate function of the dicarboxylate ligand, with the second carboxylate group of the diacid uncoordinated [10]. Reaction of copper(II) acetate with octanedioic acid and pyridine yielded the polymeric copper(II) complex $\{Cu_2(\eta^1\eta^1\mu_2\text{-oda})_2(py)_4(H_2O)\}_n$ [12]. The X-ray crystal structure of the latter complex showed it to consist of linear polymeric chains in which bridging oda^{2-} dianions link the metal centres. Each copper atom has N_2O_3 square-pyramidal coordination and is ligated by the nitrogen atoms of two *transoid* pyridines, an oxygen atom from an apical water molecule and a single carboxylate oxygen atom from each of the two *transoid* monodentate oda^{2-} ligands. Herein we report the facile syntheses, X-ray crystal structures and physical properties of the binuclear copper(II) complexes $[Cu_2(pda)(phen)_4](ClO_4)_2\cdot 5H_2O\cdot C_2H_5OH$ (**1**) and $[Cu_2(oda)(phen)_4](ClO_4)_2\cdot 2.76H_2O\cdot C_2H_5OH$ (**2**) and also the polymeric complex $\{Cu_2(pda)_2(NH_3)_4(H_2O)_2\}_n\cdot 4H_2O$ (**3**).

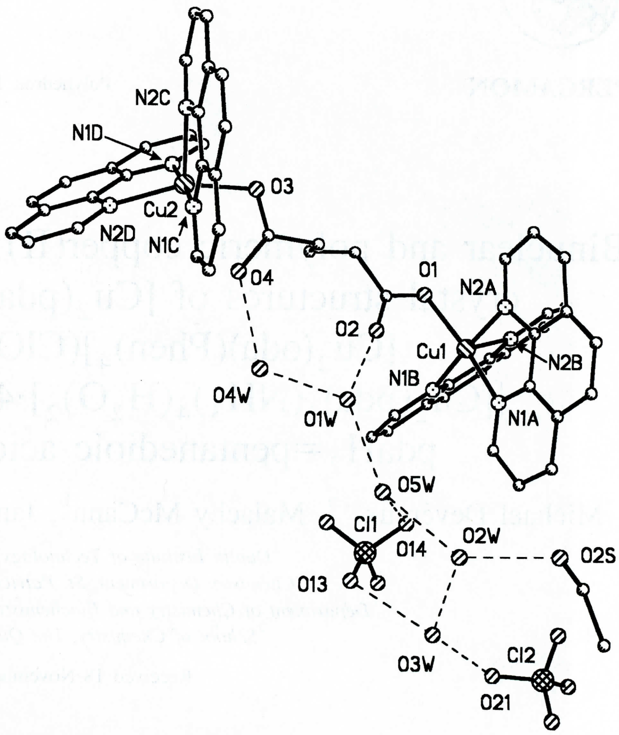
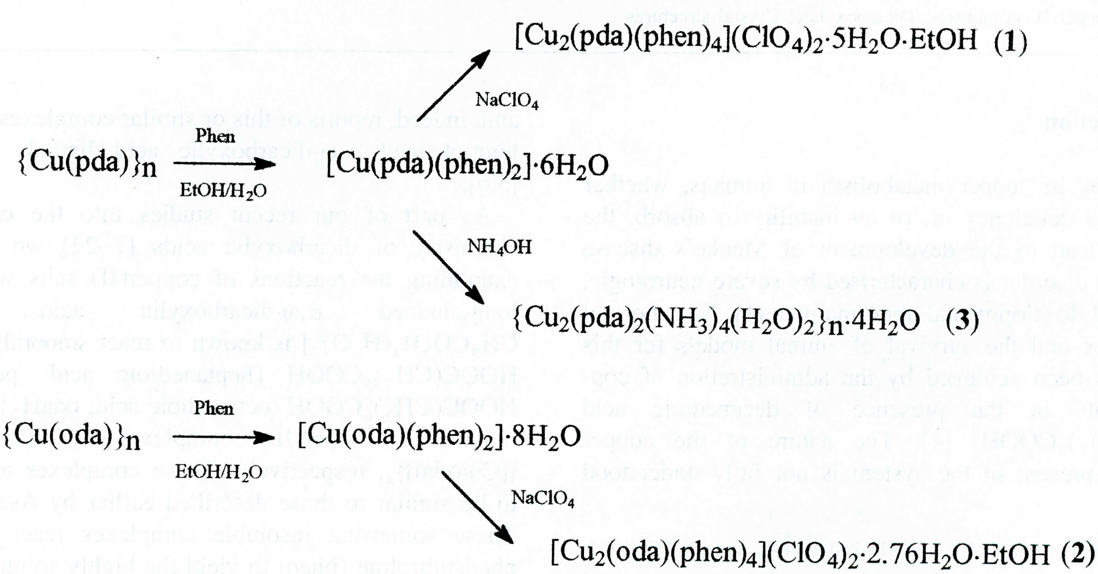


Fig. 1. Structure of $[Cu_2(pda)(phen)_4](ClO_4)_2\cdot 5H_2O\cdot C_2H_5OH$ (1).

2. Results and discussion

The mononuclear complexes $[Cu(pda)(phen)_2]\cdot 6H_2O$ [22] and $[Cu(\eta^2\text{-oda})(phen)_2]\cdot 12H_2O$ [10] were reacted with an excess of sodium perchlorate in ethanol to yield light blue solids which, upon recrystallisation from an ethanol:water (1:1) mixture, yielded dark blue crystals of the dicopper(II,II) perchlorate salts $[Cu_2(pda)(phen)_4](ClO_4)_2\cdot 5H_2O\cdot C_2H_5OH$ (**1**) and $[Cu_2(oda)(phen)_4](ClO_4)_2\cdot 2.67H_2O\cdot C_2H_5OH$ (**2**), respectively (Scheme 1).

The X-ray crystal structure of $[Cu_2(pda)(phen)_4](ClO_4)_2\cdot 5H_2O\cdot C_2H_5OH$ (**1**) is shown in Fig. 1 and selected bond lengths and angles for the complex are given in Table 1. Each copper(II) atom is coordinated to two phenanthroline molecules and to one oxygen atom from a dicarboxylate ion which bridges the two copper centres. Each carboxylate group of the di-



Scheme 1.

Table 1
Selected bond distances (Å) and angles (°) for $[Cu_2(pda)(phen)_4](ClO_4)_2\cdot 5H_2O\cdot C_2H_5OH$ (**1**)

Cu(1)–O(1)	1.958(6)	Cu(1)–N(1a)	2.030(7)
Cu(1)–N(1b)	2.004(7)	Cu(1)–N(2a)	2.003(8)
Cu(1)–N(2b)	2.202(7)	Cu(2)–O(3)	1.953(6)
Cu(2)–N(1d)	2.002(7)	Cu(2)–N(1c)	2.005(7)
Cu(2)–N(2d)	2.039(7)	Cu(2)–N(2c)	2.195(7)
O(1)–Cu(1)–N(2a)	90.3(3)	O(1)–Cu(1)–N(1b)	92.1(3)
N(2a)–Cu(1)–N(1b)	176.4(3)	O(1)–Cu(1)–N(1a)	158.8(3)
N(2a)–Cu(1)–N(1a)	81.4(3)	N(1b)–Cu(1)–N(1a)	97.3(3)
O(1)–Cu(1)–N(2b)	95.2(3)	N(2a)–Cu(1)–N(2b)	97.5(3)
N(1b)–Cu(1)–N(2b)	79.6(4)	N(1a)–Cu(1)–N(2b)	105.2(3)
O(3)–Cu(2)–N(1d)	89.1(3)	O(3)–Cu(2)–N(1c)	93.5(3)
N(1d)–Cu(2)–N(1c)	177.3(3)	O(3)–Cu(2)–N(2d)	155.3(3)
N(1d)–Cu(2)–N(2d)	81.7(3)	N(1c)–Cu(2)–N(2d)	95.7(3)
O(3)–Cu(2)–N(2c)	96.3(3)	N(1d)–Cu(2)–N(2c)	100.7(3)
N(1c)–Cu(2)–N(2c)	79.7(3)	N(1d)–Cu(2)–N(2c)	107.9(3)

carboxylate ligand is bound to each of the copper centres in a *syn* monodentate fashion. The geometry at the copper ions is approximately square–pyramidal, the apical ligand being one of the nitrogen donors {N(2b) and N(2c) for Cu(1) and Cu(2), respectively}. The planes of the phenanthroline ligands are inclined to each other at angles of 69.6(1)° and 66.0(1)° for Cu(1) and Cu(2), respectively. There is an extensive hydrogen–bonding network throughout the crystal involving all the water molecules, the ethanol solvate, the carbonyl oxygen atoms of the pentanedioate ligand, and to a lesser extent, the two perchlorate anions (Fig. 1 and Table 2). In addition, there are significant intermolecular π–π interactions between the phenanthroline ligands (Fig. 2).

The X-ray crystal structure of $[Cu_2(oda)(phen)_4](ClO_4)_2\cdot 2.67H_2O\cdot C_2H_5OH$ (**2**) is shown in Fig. 3 and selected bond lengths and angles for the complex are given in Table 3. The coordination at both copper(II) atoms in the complex dication is distorted tetragonal–pyramidal with three nitrogen atoms and one carboxyl oxygen atom forming the basal plane in each case, and the apical site occupied by the remaining phenanthroline nitrogen atom. The apical nitrogen to copper bonds {Cu(1)–N(42) and Cu(2)–N(82)} are approximately 0.20 Å longer than the other nitrogen to copper distances for each metal centre. The sixth site of what would be a distorted octahedral coordination at each copper(II) atom is occupied by the remaining carboxylate oxygen atoms [O(12) and O(82)], but the Cu···O distances (Cu(1)–O(12) 2.720(5) Å, Cu(2)–O(82) 2.915(5) Å) are too long to be considered as bonding. The central $(CH_2)_6$ chain of the dicarboxylate moiety linking the two copper(II) atoms is maximally extended {CH_2–CH_2–CH_2–CH_2 torsion angles are in the range 176.0(7) to 171.1(7)°} but the terminal carboxylate groups have a "gauche" conformation {torsion angles CH_2–CH_2–CH_2–CO_2 70.1(9) and 57.0(10)°}. The coordination conformation at each of the copper atoms in complex **2** is slightly different, and this is presumably attributable to crystal packing. The interplanar angles between the two phenanthroline planes at Cu(l) is 69.8(1)° while the corresponding angle at Cu(2) is 85.5(1)°. At the Cu(1) site oxygen O(11) is 0.50(1) Å below the plane of the three basal nitrogen atoms, with Cu(l) 0.03(1) Å and the remaining nitrogen atom N(42) 2.156(9) Å above the basal nitrogen plane. The corresponding displacements at the Cu(2) site for atoms O(81), Cu(2) and N(82) are −0.95(1), 0.081(4) and 2.073(8) Å, respectively. As was the case for **1** the $[Cu_2(diacid)(phen)_4]^{2+}$ dication of **2** is linked by O–H···O hydrogen bonds involving the water and ethanol molecules to yield an infinite hydrogen-bonded chain extending along the *a* direction. The perchlorate anions are also linked to this chain by O–H···O hydrogen bonds. π–π interactions between the phenanthroline groups are again evident in the structure.

The infra-red spectra of the perchlorate complexes **1** and **2** each contained prominent $\nu_{OCOasym}$ and ν_{OCOsym} stretching bands around 1586–1565 and 1309–1300 cm^{-1}, respectively. The relatively large values of Δ_{OCO} ($\nu_{OCOasym}-\nu_{OCOsym}$) calculated for the copper complexes (260 and 257 cm^{-1}, respectively) are as expected for a unidentate coordination mode of the carboxylate moieties [23].

Whereas the mononuclear precursors $[Cu(pda)(phen)_2]\cdot 6H_2O$ and $[Cu(oda)(phen)_2]\cdot 12H_2O$ were only soluble in ethanol and in water, the binuclear perchlorate salts were highly soluble in a range of solvents. Conductivity measurements carried out on solutions of **1** and **2** in DMF (Λ_M=117 and 122 S cm^2 mol^{-1}, respectively) and CH_3CN (Λ_M=236 and 278 S cm^2 mol^{-1}, respectively) showed that they dissociate extensively in these solvents. The relatively high values of the molar conductivity of the **1** and **2** would suggest that they do not form simple 1:1 electrolytes in either DMF or CH_3CN {i.e. the binuclear dication $[Cu_2(O_2C(CH_2)_nCO_2)(phen)_4]^{2+}$ and $2ClO_4^-$} but rather that they probably dissociate to give two mononuclear dications, two perchlorate anions and a dicarboxylate dianion as outlined below, with the equilibrium lying further to the right hand side:

$$[Cu_2(O_2C(CH_2)_nCO_2)(phen)_4](ClO_4)_2\cdot xH_2O\cdot C_2H_5OH \rightleftharpoons 2[Cu(L)_2(phen)_2]^{2+} + 2ClO_4^- + {}^-O_2C(CH_2)_nCO_2^- + xH_2O + C_2H_5OH$$

(L = DMF, CH_3CN)

Table 2
Selected hydrogen bond distances (Å) O–H···O for $[Cu_2(pda)(phen)_4](ClO_4)_2\cdot 5H_2O\cdot C_2H_5OH$ (**1**)

O(2)–O(1w)	2.711(0.010)	O(14a)–O(5w)	3.030(0.011)
O(4)–O(4w)	2.743(0.010)	O(2w)–O(3w)	2.768(0.011)
O(1w)–O(4w)	2.752(0.011)	O(13a)–O(3w)	2.919(0.010)
O(1w)–O(5w)	2.666(0.011)	O(21a)–O(3w)	2.940(0.011)
O(2w)–O(5w)	2.792(0.011)	O(2w)–O(2s)	2.730(0.010)

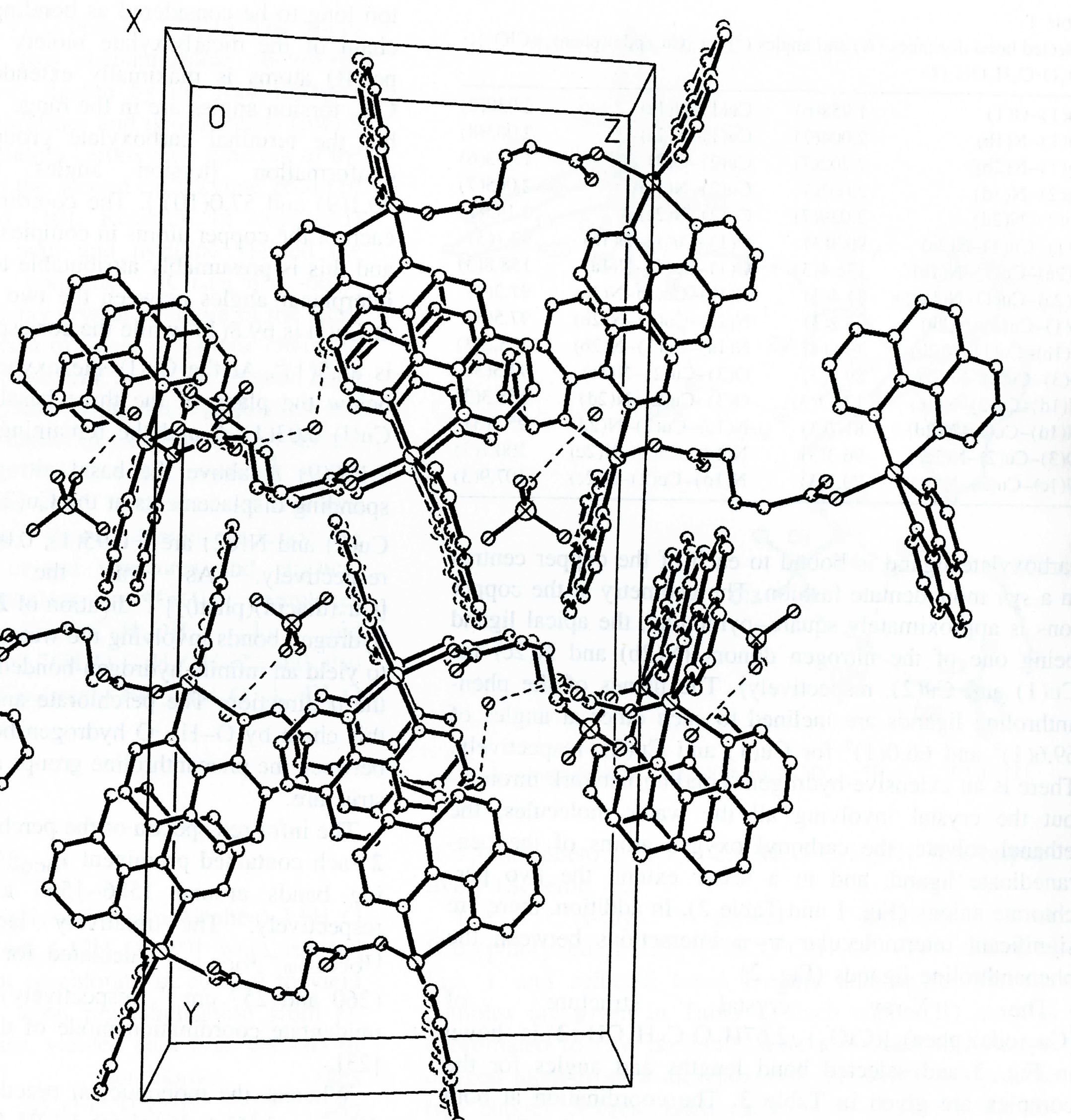


Fig. 2. A view down the x-axis of $[Cu_2(pda)(phen)_4](ClO_4)_2 \cdot 5H_2O \cdot C_2H_5OH$ (**1**).

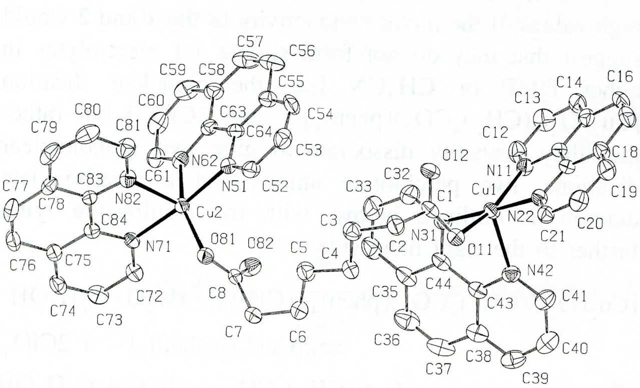


Fig. 3. Structure of the $[Cu_2(oda)(phen)_4]^{2+}$ dication of $[Cu_2(oda)(phen)_4](ClO_4)_2 \cdot 2.67H_2O \cdot C_2H_5OH$ (**2**).

The insoluble complex $\{Cu(pda)\}_n$ [22] reacted with NH_4OH to give the polymeric blue ammine adduct $\{[Cu_2(pda)_2(NH_3)_4(H_2O)_2] \cdot 4H_2O\}_n$ (**3**) in high yield. Crystals of (**3**) were grown from a dark blue ammonia/$\{Cu_2(pda)_2\}_n$/chloroform solution and the X-ray crystal structure of the complex was obtained (Fig. 4). The selected bond lengths and angles for the complex are given in Table 4. The coordination geometry around the copper atoms in **3** is essentially the same as that of the metal atoms in the octanedioic acid complex $\{Cu_2(oda)_2(py)_4(H_2O)\}_n$ [12]. Each copper(II) atom has a slightly distorted square-pyramidal geometry, with the apical site occupied by a water molecule and with pairs of *trans* nitrogen and oxygen atoms from the ammine and dicarboxylate groups, respectively. In the coordination sphere of each metal the Cu–O$_{carboxylate}$ bond lengths Cu(1)–O(11) and Cu(1)–O(51a) were essentially the same [1.983(2) and

Table 3
Selected bond lengths (Å) and angles (°) for $[Cu_2(oda)(phen)_4](ClO_4)_2 \cdot 2.67H_2O \cdot C_2H_5OH$ (**2**)

Cu(1)–O(11)	1.974(5)	Cu(2)–O(81)	1.970(5)
Cu(1)–N(11)	2.032(6)	Cu(2)–N(51)	1.997(6)
Cu(1)–N(22)	1.994(5)	Cu(2)–N(62)	2.062(6)
Cu(1)–N(31)	2.014(6)	Cu(2)–N(71)	2.000(5)
Cu(1)–N(42)	2.216(7)	Cu(2)–N(82)	2.201(6)
Cu(1)–O(12) contact distance	2.720(5)		
Cu(2)–O(82) contact distance	2.915(5)		
O(11)–Cu(1)–N(22)	91.8(2)	O(11)–Cu(1)–N(31)	89.0(2)
N(22)–Cu(1)–N(31)	177.8(3)	O(11)–Cu(1)–N(11)	162.5(2)
N(22)–Cu(1)–N(11)	81.6(2)	N(11)–Cu(1)–N(31)	97.2(2)
O(11)–Cu(1)–N(42)	93.8(2)	N(22)–Cu(1)–N(42)	103.1(2)
N(31)–Cu(1)–N(42)	78.8(3)	N(11)–Cu(1)–N(42)	103.4(2)
O(81)–Cu(2)–N(51)	92.6(2)	O(81)–Cu(2)–N(71)	92.6(2)
N(51)–Cu(2)–N(71)	174.2(2)	O(81)–Cu(2)–N(62)	155.3(2)
N(51)–Cu(2)–N(62)	81.7(2)	N(62)–Cu(2)–N(71)	94.6(2)
O(81)–Cu(2)–N(82)	108.1(2)	N(51)–Cu(2)–N(82)	96.8(2)
N(71)–Cu(2)–N(82)	79.0(2)	N(62)–Cu(2)–N(82)	96.4(2)

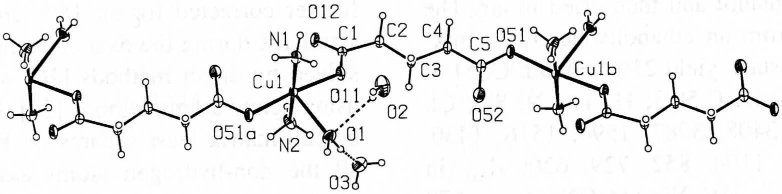


Fig. 4. Structure of $\{[Cu_2(pda)_2(NH_3)_4(H_2O)_2] \cdot 4H_2O\}_n$ (**3**) (Thermal ellipsoids are drawn at the 30% probability level).

1.980(2) Å]. The Cu(1)–N(1) and Cu(1)–N(2) bond lengths were also quite similar with values of 1.997(3) and 2.004(3) Å, respectively. The Cu–O(1) bond was the longest at 2.323(3) Å. The pentanedioate dianion is maximally extended (C–C–C–C torsion angles 178.9(3) and 178.5(4)°) and links the copper(II) atoms to form an infinite polymeric chain. In addition to the molecules coordinated to the copper centre there are two additional water molecules present in the asymmetric unit. These are linked by O–H···O and N–H···O hydrogen bonds to form a stable three-dimensional network within the crystal. All of the water hydrogen atoms and four of the six ammonia hydrogen atoms take part in hydrogen-bonding.

The infra-red spectrum of $\{[Cu_2(pda)_2(NH_3)_4(H_2O)_2] \cdot 4H_2O\}_n$ (**3**) showed $\nu_{OCOasym}$ and ν_{OCOsym} bands at 1572 and 1394 cm^{-1}, respectively. The Δ_{OCO} value of 173 cm^{-1} would seem to indicate that a bridging bidentate mode of coordination was being adopted by the carboxylate groups in this complex as opposed to the actual unidentate coordination mode revealed in the X-ray analysis. However, it has been recognised that strong intramolecular hydrogen-bonding between the uncoordinated carboxylate oxygen atom and a water molecule can equate the two C–O bonds and alter the absorption frequency of the $\nu_{OCOasym}$ and ν_{OCOsym} bands to give a lower than expected Δ_{OCO} value [24].

The electronic absorption spectra of complexes **1**, **2** (CH_3CN solutions) and **3** (nujol mull) each contained a single d–d absorption band in the region 678–689 nm. The complexes all had room temperature magnetic moments in the range expected for simple copper(II) species, i.e. those lacking Cu–Cu interactions [25].

Table 4
Selected bond distances (Å) and bond angles (°) for $\{[Cu_2(pda)_2(NH_3)_4(H_2O)_2] \cdot 4H_2O\}_n$ (**3**)

Cu(1)–O(11)	1.983(2)	Cu(1)–N(2)	2.004(3)
Cu(1)–O(51a)	1.980(2)	C(1)–O(11)	1.266(4)
Cu(1)–O(1)	2.323(3)	C(1)–O(12)	1.245(4)
Cu(1)–N(1)	1.997(3)		
N(1)–Cu(1)–N(2)	172.39(14)	N(2)–Cu(1)–O(51a)	91.44(12)
N(1)–Cu(1)–O(1)	95.66(14)	N(2)–Cu(1)–O(11)	88.62(12)
N(1)–Cu(1)–O(11)	88.76(12)	O(1)–Cu(1)–O(11)	83.24(10)
N(1)–Cu(1)–O(51a)	91.87(13)	O(1)–Cu(1)–O(51)	91.14(10)
N(2)–Cu(1)–O(1)	91.12(13)	Cu(1)–O(11)–C(1)	118.3(2)
O(11)–C(1)–O(12)	123.2(3)		

3. Experimental

Chemicals were purchased from commercial sources and used without further purification. IR spectra were recorded in the region 4000–400 cm^{-1} on a Nicolet-400 Impact spectrometer and UV–vis spectra were obtained using a Milton Roy Spectronic 3000 Array. Magnetic susceptibility measurements were made using a Johnson Matthey Magnetic Susceptibility balance. $[HgCo(SCN)_4]$ was used as a reference. Conductivity readings were obtained using an AGB Scientific Ltd model 10 conductivity meter. Satisfactory microanalytical data for the complexes were reported by the Microanalytical Laboratory, University College Cork, Ireland.

Safety Note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of the complexes should be prepared at any one time and they should be handled with care.

3.1. $[Cu_2(pda)(phen)_4](ClO_4)_2 \cdot 5H_2O \cdot C_2H_5OH$, **1**

$[Cu(pda)(phen)_2] \cdot 6H_2O$ (0.75 g, 1.13 mmol) was added to an ethonolic solution of sodium perchlorate (0.4 M, 50 cm^3) and the mixture was gently refluxed for 2 h. The precipitated light blue product was filtered off, washed with a small amount of ethanol and then dried in air. The solid was recrystallised from an ethanol:water (1:1) mixture to yield dark blue crystals, yield 21%. Found: C, 51.3; H, 4.0; N, 8.7; Cl, 5.9. Calc: C,50.3; H, 4.1; N, 8.5; Cl, 5.4%. IR ν/cm^{-1}(KBr): 3408, 3087, 1590, 1516, 1430, 1400, 1350, 1307, 1147, 1104, 852, 729, 630; Λ_M (in MeCN)=236 S cm^2 mol^{-1}; UV–Vis (MeCN) λ_{max}=678 nm, ϵ=279dm^3 mol^{-1} cm^{-1}; μ_{eff}=1.98 B.M. per copper. **1** was soluble in H_2O, EtOH, DMF, MeCN and Me_2CO.

3.2. $[Cu_2(oda)(phen)_4](ClO_4)_2 \cdot 2.76H_2O \cdot C_2H_5OH$, **2**

$[Cu(oda)(phen)_2] \cdot 8H_2O$ (0.75 g, 1.0 mmol) was added to an ethonolic solution of sodium perchlorate (0.4 M, 50 cm^3) and the mixture was gently refluxed for 1 h. The precipitated light blue product was filtered off whilst hot, washed with cold water and then dried in vacuo.. The solid was recrystallised from an ethanol:water (1:1) mixture to yield dark blue crystals, yield 24%. Found: C, 52.6; H, 4.2; N, 8.1; Cl, 4.7. Calc: C,52.8; H, 4.3; N, 8.5; Cl, 5.4%. IR ν/cm^{-1}(KBr): 3420, 2939, 1560, 1516, 1430, 1406, 1098, 849, 723, 658, 621; Λ_M (in MeCN)=278 S cm^2 mol^{-1}; UV–vis (in MeCN) λ_{max}=689 nm, ϵ=183dm^3 mol^{-1} cm^{-1}; μ_{eff}=1.91 B.M. per copper. Complex **2** was soluble in H_2O, EtOH, DMF, MeCN and Me_2CO.

3.3. $\{Cu_2(pda)_2(NH_3)_4(H_2O)_2\}_n \cdot 4H_2O$, **3**

$\{Cu(pda)\}_n$ (0.22g, 1.13 mmol) was dissolved in NH_4OH (S.G. 0.88, *ca.* 25 cm^3) and the resulting deep blue solution was stirred for 1 h and then filtered. Chloroform (10 cm^3) was added to the filtrate and on standing for 14 days deep blue crystals of the product formed in 76% yield. Found: C, 23.4; H, 5.8; N, 11.6. Calc: C, 21.3; H, 6.4; N, 9.9% (Discrepancies between found and calculated analytical figures are probably attributable to the fact that the complex rapidly loses water molecules of crystallization upon standing in the laboratory atmosphere). IR ν/cm^{-1}(KBr): 3442, 3328, 2676, 2927, 1629, 1578, 1436, 1400, 1356, 1239, 1061, 916, 756, 735, 680, 569; UV–vis (nujol) λ_{max}=689 nm; μ_{eff}=1.91 B.M. per copper. Complex **3** was insoluble in all common solvents.

3.4. X-ray crystallography

Data collection and refinement parameters are summarised in Table 5. The diffraction data were collected on either a Siemens P4 diffractometer (complex **1**) or an Enraf–Nonius CAD4 instrument (complexes **2** and **3**) using Mo K_α radiation (λ=0.71073 Å). Each data set was corrected for Lorentz and polarisation effects and empirical absorption corrections were applied. Data for **1** were further corrected for an 18% drop in the intensity of the standards during the data collection. The structure of **1** was solved by direct methods [26] while **2** and **3** were solved using heavy atom methods [27]. Each structure was refined by full-matrix least squares on F^2 using all the data, with all the non-hydrogen atoms assigned anisotropic atomic displacement parameters and hydrogen atoms bound to carbon inserted at calculated positions. Hydrogen atoms bound to water in complex **1** were not located and not included in the refinement. Complex **2** showed disorder of one of the perchlorate anions and the ethanol carbon atoms (modelled as disordered over two sites) along with partial occupancy of one of the three water molecules in the asymmetric unit. Attempts to model the perchlorate disorder were not successful and it was refined as a rigid tetrahedral group, consequently there are some residual electron density peaks (0.7–1.11 eÅ^{-3}) in this region. Complex **3** crystallises in a chiral space group and the analysis established unambiguously the absolute stereochemistry of the complex (Flack parameter 0.00(2)). The decision as to the exact chemical nature of the atoms labelled N(1) and N(2) was made after refinement of the occupancy parameters (with the atoms considered to be nitrogens) led to values not significantly different from unity, confirming this choice was the clear location (from difference maps) of the three hydrogen atoms on each nitrogen atom. The water hydrogen atoms were located and constrained to ride on the oxygen atoms to which they were bound. The programmes used in the final structure refinements are contained in the SHELXL-93 package [28].

Supplementary data

The supplementary data for the three structures are available from the CCDC, 12 Union Road, Cambridge

Table 5
Summary of crystal data, data collection, structure solution and refinement details

	Complex (**1**)	Complex (**2**)	Complex (**3**)
Complex	$[Cu_2(pda)(phen)_4](ClO_4)$ $\cdot 5H_2O \cdot C_2H_5OH$	$[Cu_2(oda)(phen)_4](ClO_4)$ $\cdot 2.67H_2O \cdot C_2H_5OH$	$\{[Cu_2(pda)(NH_3)(H_2O)_2]\}_n$ $\cdot 4H_2O$
Formula	$C_{55}H_{54}Cl_2Cu_2N_8O_{18}$	$C_{58}H_{57.34}Cl_2Cu_2N_8O_{15.67}$	$C_5H_{18}CuN_2O_7$
Description	Blue block	Blue block	Blue plate
Crystal size (mm)	1.0×0.40×0.20	0.39×0.32×0.26	0.44×0.35×0.08
Temperature (K)	123(2)	294(1)	294(1)
a (Å)	12.250(4)	10.412(1)	7.5234(7)
b (Å)	31.28(1)	27.878(3)	7.7774(7)
c (Å)	15.491(6)	19.963(3)	19.444(3)
β (°)	109.03(5)	95.59(1)	90
U (Å)	5656(4)	5767(1)	1137.7(2)
F(000)	2704	2715	588
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
Z	4	4	4
Density calc. (Mg/m^3)	1.542	1.52	1.645
μ (mm^{-1})	0.929	0.91	1.939
T_{max}, T_{min}	0.0.878, 0.800	0.800, 0.754	0.656, 0.395
θ range (°)	2–22.5	2–25	2–27
Index ranges	0≤h≥13	−12≤h≥12	0≤h≥9
	−1≤k≥33	0≤k≥33	0≤k≥9
	−16≤l≥15	0≤l≥23	0≤l≥24
Reflections collected	8097	10713	1450
Independent reflections	7358	10130	1450
R_{int}	0.051	0.015	–
Data/restraints/parameters	7343/0/767	10130/18/751	1450/6/157
GooF on F^2	1.079	0.93	1.037
R1, wR2 [$I>2\sigma(I)$]	0.0658, 0.1257	0.072, 0.1921	0.024, 0.061
R1, wR2 [all data]	0.1546, 0.1709	0.1552, 0.2274	0.0382, 0.0641

CB2 1EZ, UK, on request quoting the deposition numbers 110201, 111340 and 110010, respectively.

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