



**COPPER(II) COMPLEXES OF HEPTANEDIOIC ACID
(hdaH₂) AND OCTANEDIOIC ACID (odaH₂): X-RAY
CRYSTAL STRUCTURES OF [Cu(η²-hda)(phen)₂] · 11.73H₂O
AND [Cu(η²-oda)(phen)₂] · 12H₂O (phen = 1,10-PHENANTHROLINE)**

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Abstract—The α,ω -dicarboxylic acids heptanedioic acid (hdaH₂) and octanedioic acid (odaH₂) reacted smoothly with [Cu₂(μ-O₂CCH₃)₄(H₂O)₂] in water giving the insoluble copper(II) complexes [Cu(hda)] (1) and [Cu(oda)] (2). Complexes 1 and 2 reacted further with 1,10-phenanthroline (phen) giving [Cu(η²-hda)(phen)₂] · xH₂O and [Cu(η²-oda)(phen)₂] · xH₂O (x ≈ 8), respectively. The X-ray crystal structures of [Cu(η²-hda)(phen)₂] · 11.73H₂O (3) and [Cu(η²-oda)(phen)₂] · 12H₂O (4) (i.e. x = 11.73 and 12, respectively) reveal that, for each complex, the copper(II) atom is at the centre of a distorted octahedron comprising four nitrogen atoms from two chelating phen ligands and two oxygen atoms from a single asymmetric chelating carboxylate function, with the remaining carboxylate group of the diacid uncoordinated.

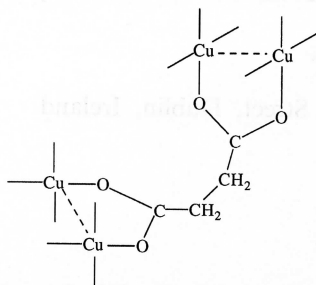
Carboxylates serve as an important class of ligands in inorganic and bioinorganic chemistry, and the versatility of the RCO₂⁻ ligand is attributed to the wide range of coordination modes that it can adopt. The coordination chemistry of monocarboxylic acids is well established and a large number of carboxylate complexes have been structurally characterized.¹ However, relatively few papers have appeared in the literature concerning the coordination chemistry of α,ω -dicarboxylic acids, HO₂C(CH₂)_nCO₂H, and only a small number of

these complexes have been structurally characterized.

In 1976, Mureinik² found that the dimolybdenum(II,II) complex [Mo₂(μ-O₂CCH₃)₄] reacted with a series of such dicarboxylic acids to give polymeric powders of general formula [Mo₂(μ-dicarboxylate)₂] · xH₂O. Asai *et al.*³ reported the syntheses and magnetic susceptibilities of a family of polymeric copper(II) complexes of formula [Cu(O₂C(CH₂)_nCO₂)] (n = 0–8), and found that, with the exception of the propanedioic acid complex (n = 1), all of the materials had effective magnetic moments in the range 1.20–1.45 B.M. per copper. These values were similar to those reported⁴ for hydrated copper(II) acetate (1.4 B.M. per cop-

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per) and considerably smaller than the theoretical spin-only value (1.73 B.M.). On the basis of the magnetic data, the authors concluded that the complexes ($n = 0, 2-8$) contained bridging bidentate carboxylate ligands which held two copper atoms in close proximity, in the same manner as has been observed in $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$.^{5,6} Verification of this came when O'Connor and Maslen⁷ determined the X-ray crystal structure of the butanedioic complex $[\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)]$, and showed it to consist of infinite chains of binuclear units, as shown below.



In 1989, Bianchi *et al.*⁸ reported the X-ray crystal structure of the tetraruthenium(I) pentanedioic acid complex $[\text{Ru}_4(\text{CO})_8(\text{O}_2\text{C}(\text{CH}_2)_3\text{CO}_2)_2(\text{PBu}_3)_4]$, which showed that each of the two dianionic diacid ligands were coordinated in a bridging bidentate fashion to separate diruthenium centres. More recently, we have prepared and structurally characterized the dimanganese(II,II) complex double salt $[\text{Mn}_2(\eta^1\eta^1\mu^2\text{-oda})(\text{phen})_4(\text{H}_2\text{O})_2][\text{Mn}_2(\eta^1\eta^1\mu^2\text{-oda})(\text{phen})_4(\eta^1\text{-oda})_2] \cdot 4\text{H}_2\text{O}$ (odaH₂ = octanedioic acid, phen = 1,10-phenanthroline).⁹ In this complex, both the dianion and the dication comprise two manganese centres bridged by a single oda^{2-} ligand which utilizes only one carboxylate oxygen from each end of the diacid. In the dianion, each manganese atom also has a unidentate oda^{2-} ligand, the other carboxylate moiety of the diacid remaining uncoordinated.

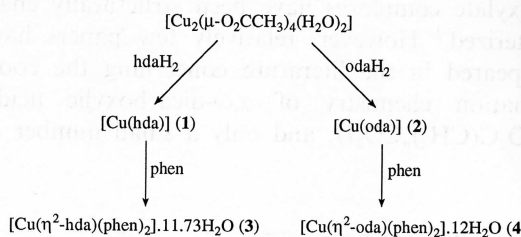
As part of our ongoing studies into the coordination chemistry of saturated aliphatic dicarboxylic acids, we have focused our attention on the isolation of copper(II) complexes of heptanedioic

acid (hdaH₂) and octanedioic acid (odaH₂). Here we report the synthesis, X-ray crystal structures, physical properties of $[\text{Cu}(\eta^2\text{-hda})(\text{phen})_2] \cdot 11.73\text{H}_2\text{O}$ (**3**) and $[\text{Cu}(\eta^2\text{-oda})(\text{phen})_2] \cdot 12\text{H}_2\text{O}$ (**4**).

RESULTS AND DISCUSSION

Synthetic routes to the copper(II) complexes shown in Scheme 1. The previously reported complexes $[\text{Cu}(\text{hda})]$ (**1**) and $[\text{Cu}(\text{oda})]$ (**2**) were prepared by a method similar to that used by Aspinall,³ involving the reaction of $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_4]$ with hdaH₂ and odaH₂ in refluxing water. The IR spectrum of **1** contains distinctive $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ bands at 1590 and 1415 cm^{-1} , respectively,¹⁰ giving a frequency difference (Δ) of 175 cm^{-1} . In the spectrum of **2** the corresponding bands appear at 1590 and 1430 cm^{-1} , respectively ($\Delta = 160 \text{ cm}^{-1}$). These values are very similar to those reported⁶ for $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_4]$ [$\nu_{\text{as}}(\text{OCO}) = 1603$, $\nu_{\text{s}}(\text{OCO}) = 1418$, $\Delta(\text{OCO}) = 185 \text{ cm}^{-1}$]. The observed room temperature magnetic moment of **1** (1.58 B.M.) was slightly higher than that reported previously (1.41 B.M.),³ while the moment obtained for **2** (1.43 B.M.) was very similar to the values quoted by two other researchers (1.44 and 1.45 B.M.).^{3,11} These magnetic moment values indicate that there is strong antiferromagnetic coupling between the metal centres in both complexes.^{1,3,4,11} The insolubility of **1** and **2** together with the magnetic and IR data for these complexes, suggests that they are most probably isostructural with the polymeric copper(II) complex of butanedioic acid.⁷

Although **1** and **2** were insoluble in water and in common organic solvents they did dissolve in ethanol containing dissolved 1,10-phenanthroline and complexes of approximate formulation $[\text{Cu}(\eta^2\text{-hda})(\text{phen})_2] \cdot 8\text{H}_2\text{O}$ and $[\text{Cu}(\eta^2\text{-oda})(\text{phen})_2] \cdot 8\text{H}_2\text{O}$, respectively, were subsequently isolated. When these octahydrates were recrystallized from water containing a few drops of ethanol, blue crystals of $[\text{Cu}(\eta^2\text{-hda})(\text{phen})_2] \cdot 11.73\text{H}_2\text{O}$ (**3**) and $[\text{Cu}(\eta^2\text{-oda})(\text{phen})_2] \cdot 12\text{H}_2\text{O}$ (**4**), respectively, deposited on standing.



Scheme 1

* The two complexes tended to lose water molecules of crystallization fairly rapidly upon standing in the laboratory atmosphere, ending up as powders. As a result of this progressive weight loss due to dehydration, it was impossible to obtain an accurate mass reading for the purpose of the microanalysis. Thus, the octahydrate formulations $[\text{Cu}(\eta^2\text{-hda})(\text{phen})_2] \cdot 8\text{H}_2\text{O}$ and $[\text{Cu}(\eta^2\text{-oda})(\text{phen})_2] \cdot 8\text{H}_2\text{O}$ are offered as approximations at the time of the microanalysis.

The X-ray crystal structures of **3** and **4** were determined, and due to the fact that both sets of crystals lose some of their water molecules of crystallization very rapidly (with consequent decomposition), the X-ray measurements were carried out using sealed capillaries. Views of **3** and **4** are shown in Fig. 1a and b, respectively, and the more impor-

tant bond distances and bond angles are listed in Table 1. In each complex only one of the carboxyl groups of the diacid dianion is bonded to copper. The $[\text{Cu}(\text{phen})_2]$ portions of both structures are very similar, with $\text{Cu}-\text{N}$ 1.994(5)–2.183(6) Å in **3** and 1.981(5)–2.168(6) Å in **4**, with the four bonds which have nitrogen *trans* to nitrogen

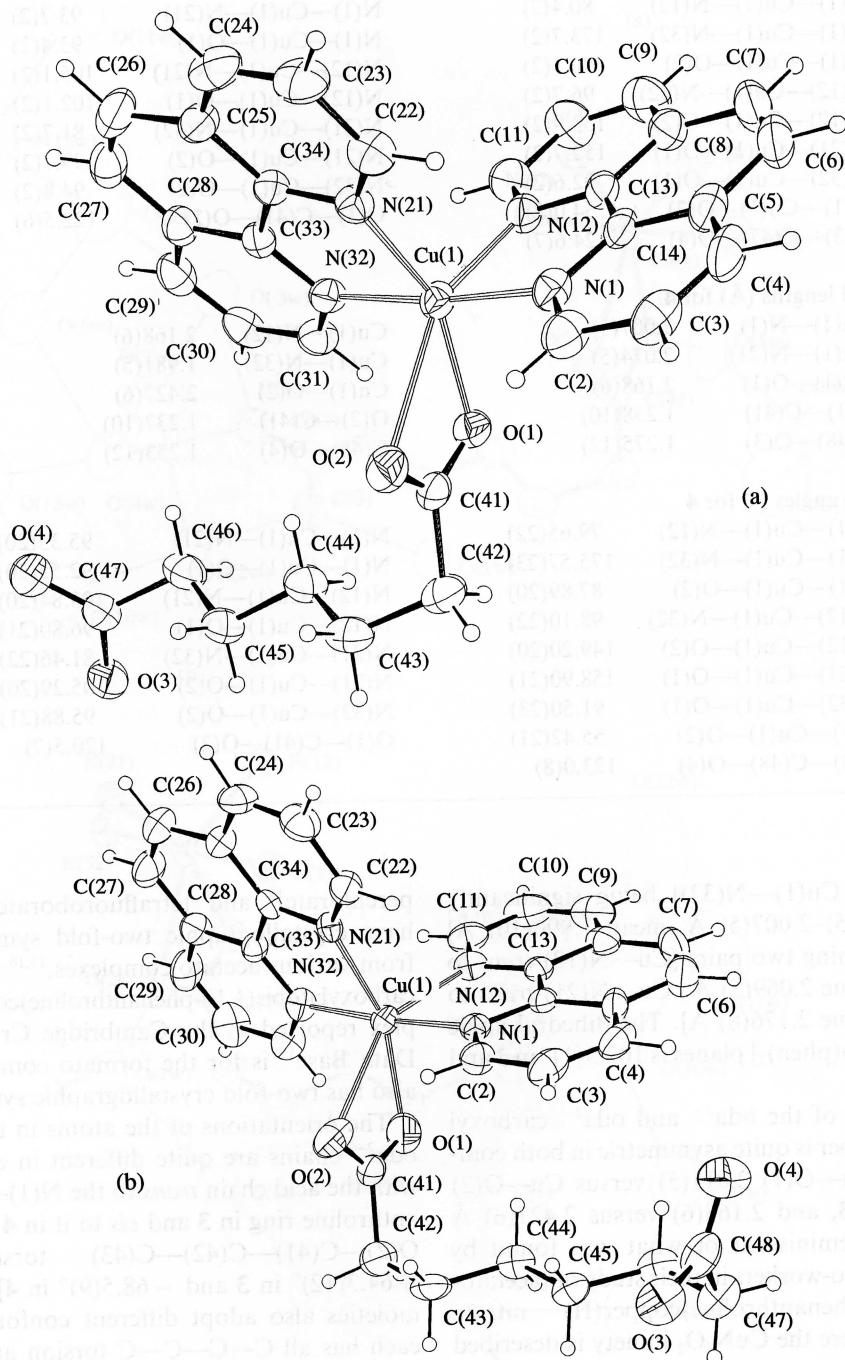


Fig. 1. ORTEP plots of: (a) $[\text{Cu}(\eta^2\text{-hda})(\text{phen})_2] \cdot 11.73\text{H}_2\text{O}$ (**3**) and (b) $[\text{Cu}(\eta^2\text{-oda})(\text{phen})_2] \cdot 12\text{H}_2\text{O}$ (**4**) with our numbering scheme. Ellipsoids are at the 30% level for non-hydrogen atoms, and hydrogens are shown as small spheres of arbitrary size. Water molecules are omitted for clarity.

Table 1. Selected molecular dimensions for **3** and **4**

Bond lengths (Å) for 3			
Cu(1)—N(1)	2.001(5)	Cu(1)—N(12)	2.183(6)
Cu(1)—N(21)	2.064(5)	Cu(1)—N(32)	1.994(5)
Cu(1)—O(1)	2.011(4)	Cu(1)—O(2)	2.679(5)
O(1)—C(41)	1.282(10)	O(2)—C(41)	1.239(9)
C(47)—O(3)	1.254(9)	C(47)—O(4)	1.237(10)
Bond angles (°) for 3			
N(1)—Cu(1)—N(12)	80.4(2)	N(1)—Cu(1)—N(21)	93.7(2)
N(1)—Cu(1)—N(32)	173.7(2)	N(1)—Cu(1)—O(1)	93.4(2)
N(1)—Cu(1)—O(2)	90.1(2)	N(12)—Cu(1)—N(21)	105.1(2)
N(12)—Cu(1)—N(32)	96.7(2)	N(12)—Cu(1)—O(1)	102.1(2)
N(12)—Cu(1)—O(2)	153.9(2)	N(21)—Cu(1)—N(32)	81.7(2)
N(21)—Cu(1)—O(1)	152.7(2)	N(21)—Cu(1)—O(2)	99.7(2)
N(32)—Cu(1)—O(1)	92.6(2)	N(32)—Cu(1)—O(2)	94.8(2)
O(1)—Cu(1)—O(2)	54.0(2)	O(1)—C(41)—O(2)	122.5(6)
O(3)—C(47)—O(4)	124.6(7)		
Bond lengths (Å) for 4			
Cu(1)—N(1)	2.007(5)	Cu(1)—N(12)	2.168(6)
Cu(1)—N(21)	2.074(5)	Cu(1)—N(32)	1.981(5)
Cu(1)—O(1)	2.168(6)	Cu(1)—O(2)	2.427(6)
O(1)—C(41)	1.238(10)	O(2)—C(41)	1.237(10)
C(48)—O(3)	1.275(12)	C(48)—O(4)	1.253(12)
Bond angles (°) for 4			
N(1)—Cu(1)—N(12)	79.65(22)	N(1)—Cu(1)—N(21)	95.33(20)
N(1)—Cu(1)—N(32)	175.57(23)	N(1)—Cu(1)—O(1)	92.55(20)
N(1)—Cu(1)—O(2)	87.89(20)	N(12)—Cu(1)—N(21)	103.84(20)
N(12)—Cu(1)—N(32)	98.10(22)	N(12)—Cu(1)—O(1)	96.80(21)
N(12)—Cu(1)—O(2)	149.20(20)	N(21)—Cu(1)—N(32)	81.46(22)
N(21)—Cu(1)—O(1)	158.90(21)	N(21)—Cu(1)—O(2)	105.29(20)
N(32)—Cu(1)—O(1)	91.50(23)	N(32)—Cu(1)—O(2)	95.88(21)
O(1)—Cu(1)—O(2)	55.42(21)	O(1)—C(41)—O(2)	120.5(7)
O(3)—C(48)—O(4)	123.0(8)		

[Cu(1)—N(1), Cu(1)—N(32)] being significantly shorter [1.981(5)—2.007(5) Å, mean 1.996(10) Å] than the remaining two pairs [Cu—N(12) *trans* to O(2), mean value 2.069(5) Å; Cu—N(21) *trans* to O(1), mean value 2.176(8) Å]. The dihedral angle between the [Cu(phen)₂] planes is 102.3(1)° in **3** and 104.3(1)° in **4**.

The bonding of the hda²⁻ and oda²⁻ carboxyl moieties to copper is quite asymmetric in both complexes, with Cu—O(1) 2.011(5) versus Cu—O(2) 2.679(5) Å in **3**, and 2.168(6) versus 2.427(6) Å in **4**. This is reminiscent of what was found by Hathaway and co-workers in their study of (acetato-*O,O'*)bis(1,10-phenanthroline)copper(II) nitrate dihydrate,¹² where the CuN₄O₂ moiety is described as basically five-coordinate with the second carboxylate oxygen occupying the sixth coordination position at a distance > 2.4 Å to give a (4+1+1*) type coordination.¹³ By contrast, the corresponding

perchlorate¹³ and tetrafluoroborate¹⁴ derivatives have crystallographic two-fold symmetry. Apart from various acetato complexes,^{15,16} the only other carboxylatobis(1,10-phenanthroline)copper(II) complex reported in the Cambridge Crystallographic Data Base¹⁷ is for the formato complex, and this also has two-fold crystallographic symmetry.¹⁸

The orientations of the atoms in the hda²⁻ and oda²⁻ chains are quite different in each complex, with the acid chain *trans* to the N(1)—C(14) phenanthroline ring in **3** and *cis* to it in **4** [compare the O(2)—C(41)—C(42)—C(43) torsion angles, +64.3(12)° in **3** and -68.5(9)° in **4**]. Both diacid moieties also adopt different conformations, but each has all C—C—C—C torsion angles close to *gauche* or fully-*trans* values. Other interatomic distances and angles in the phenanthroline and diacid ligands are as expected.

With these conformations, spaces between mol-

ecules are filled by water molecules which hydrogen bond to carboxyl oxygen atoms and to each other. The water molecules which are bonded to carboxyl oxygen atoms are more tightly held in the crystal lattice (smaller vibration parameters) than those that are only hydrogen bonded to other water mol-

ecules. In **3**, it soon became clear from peak heights in difference maps that not all the water molecules were present with full occupancy, and five of the 14 sites located were given occupancy parameters based on their peak heights and refined isotropically (Fig. 2a). Excluding partially occupied water mol-

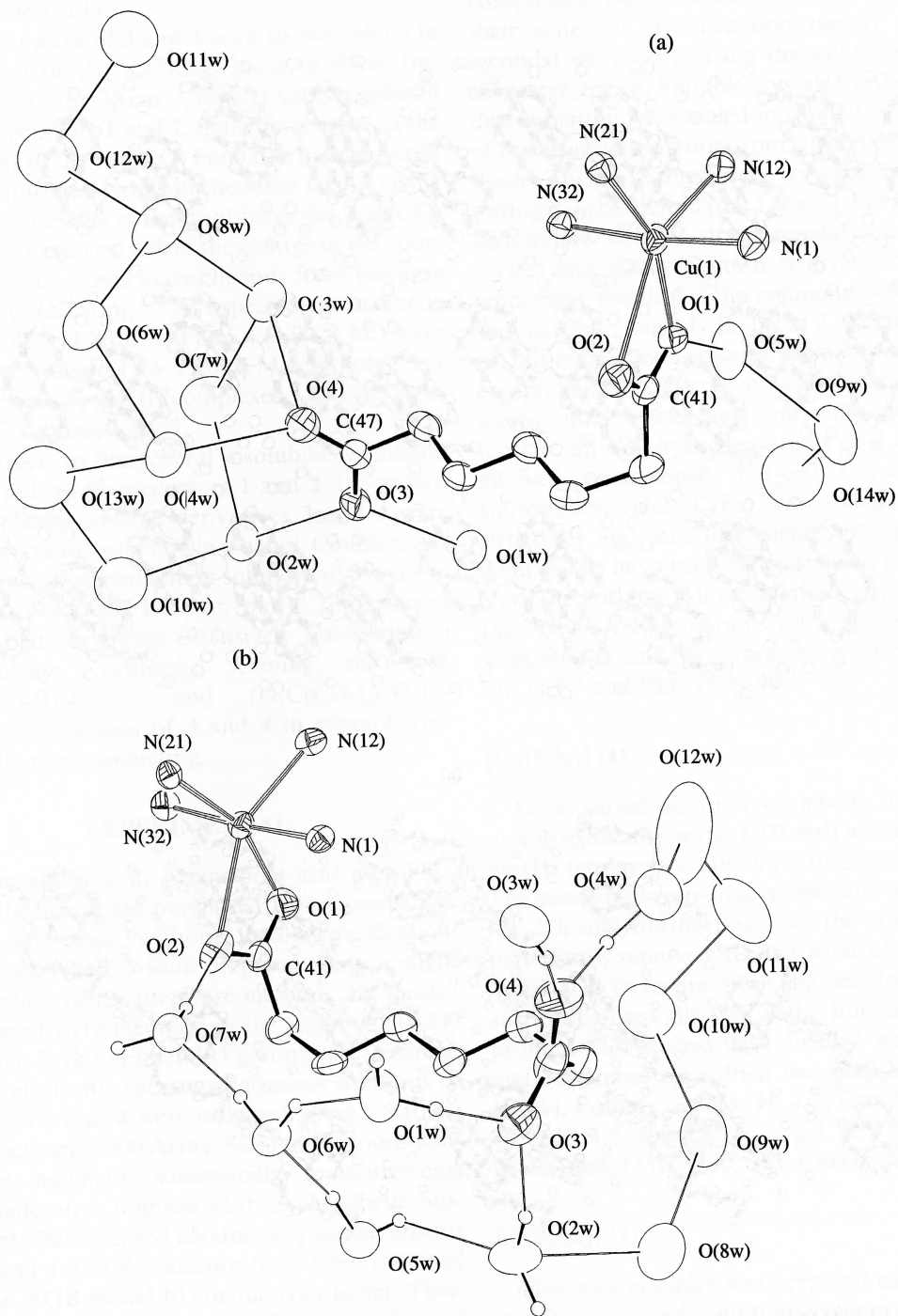


Fig. 2. ORTEP plots to show the water molecules in the asymmetric units of: (a) $[\text{Cu}(\eta^2\text{-hda})(\text{phen})_2] \cdot 11.73\text{H}_2\text{O}$ (**3**) and (b) $[\text{Cu}(\eta^2\text{-oda})(\text{phen})_2] \cdot 12\text{H}_2\text{O}$ (**4**). Ellipsoids are as in Fig. 1; for clarity, all phenanthroline carbon and hydrogen atoms and diacid hydrogen atoms are omitted.

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ecules, the shortest $O \cdots O$ potential hydrogen-bonded distances are in the range 2.680–2.952(2) Å. In **4**, 12 water molecules were found and 12 of the 24 hydrogen atoms were located unambiguously as shown in Fig. 2b. Here, the $O \cdots O$ hydrogen bond distances are in the range 2.578(12)–2.962(13) Å.

Figure 3a and b shows projections of nine (3×3)

unit cells for each structure along the shortest (*a*) axis direction, and from these diagrams it is easy to see why the hydrated crystals rapidly lose their waters of crystallization as there are clear “water-channels” in both structures. A thermogravimetric study of **3** and **4** conducted under N_2 showed that the two complexes exhibited very similar thermal behaviour. Both complexes showed the loss of

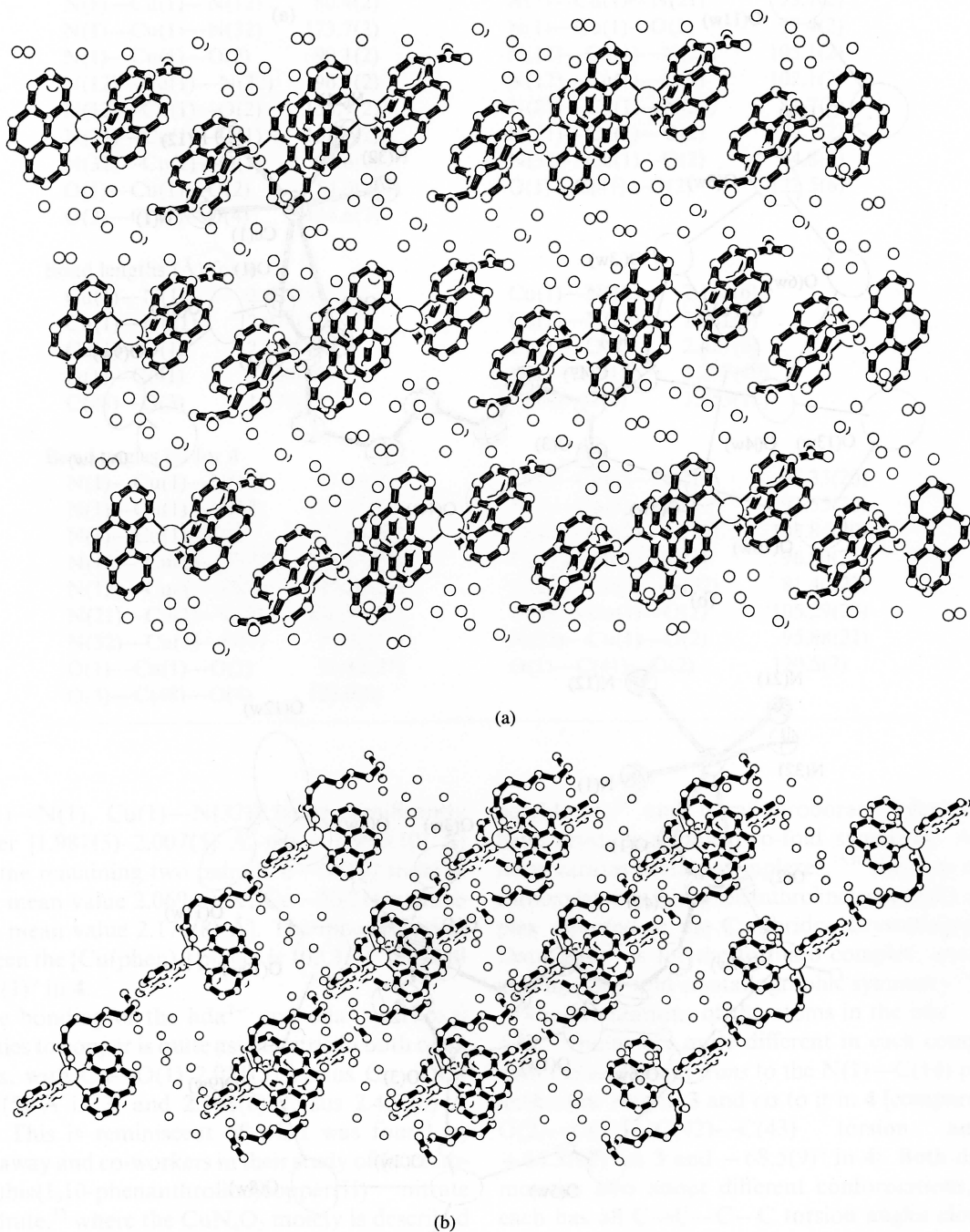


Fig. 3. PLUTON plots showing the open arrangement and water channels in the structures of: (a) $[Cu(\eta^2\text{-hda})(\text{phen})_2] \cdot 11.73\text{H}_2\text{O}$ (**3**) and (b) $[Cu(\eta^2\text{-oda})(\text{phen})_2] \cdot 12\text{H}_2\text{O}$ (**4**). The view is along the short *a*-axis in each case and shows the contents of nine (3×3) unit cells. Hydrogen atoms are omitted for clarity.

water molecules in a series of at least three thermal events (not perfectly resolved) over the temperature range *ca* 20–100°C. Decomposition of the remaining fragment $[\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{phen})_2]$ ($n = 5, 6$) was gradual up to *ca* 150°C, after which it accelerated markedly up to *ca* 240°C. There was no further weight loss up to the final temperature of 450°C and the residue which remained corresponded to Cu_2O .

The IR spectra of **3** and **4** both showed shifts in the position of the $\nu_{\text{as}}(\text{OCO})$ band to lower frequency (by 35 and 30 cm^{-1} , respectively) compared to their precursors **1** and **2**. Difficulties arose in the assignment of the $\nu_{\text{s}}(\text{OCO})$ band due to occurrence of phenanthroline bands in the same region of the spectrum. The shift in the position of the $\nu_{\text{as}}(\text{OCO})$ band does, however, reflect the change in the coordination mode of the diacid ligands from bridging bidentate to chelating.^{1,10} As expected, the magnetic moments of **3** (1.88 B.M.) and **4** (1.92 B.M.) were within the range (1.75–2.20 B.M.) reported for mononuclear copper(II) complexes, i.e. those lacking Cu–Cu interactions.¹⁹

In contrast to the general insolubility exhibited by their polymeric precursors **1** and **2**, the mononuclear phenanthroline derivatives **3** and **4** were highly soluble in water and in ethanol. Conductivity measurements carried out on solutions of **3** and **4** in water ($\Lambda_{\text{M}} = 102$ and $112 \text{ S cm}^2 \text{ mol}^{-1}$, respectively) showed that they were extensively dissociated in that solvent, probably forming the ions $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ and $(\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)^{2-}$ ($n = 5, 6$). Solutions of **3** and **4** in ethanol were essentially non-conducting.

EXPERIMENTAL

Heptanedioic acid, octanedioic acid and 1,10-phenanthroline were purchased from commercial sources and used without further purification. Complexes **1** and **2** were prepared using a slight modification of the literature method.³ IR spectra (KBr discs) were recorded in the region 4000–200 cm^{-1} on a Perkin–Elmer 783 grating spectrometer, and the electronic spectra of aqueous solutions of complexes **3** and **4** were obtained using a Milton Roy Spectronic 3000 Array. Solid-state, room-temperature magnetic susceptibility measurements were made on a Johnson Matthey Magnetic Susceptibility Balance, and conductivity measurements (26°C and 1.0 mM concentration) were obtained using an AGB model 10 conductivity meter. Thermogravimetric analyses (under N_2) were performed on a Stanton Redcroft TG 750/770 instrument which was coupled to a Houston Instrument Omniscrite (series D5000) recorder. Heating rate was

5°C min^{-1} . Elemental analyses were carried out by the Microanalytical Laboratory, University College Cork, Ireland.

Crystallography

Suitable plate-like blue crystals of **3** and **4** were obtained from aqueous solutions of the compounds. Both of these hydrated complexes lose their water of crystallization rapidly (in a few seconds) when taken from the solutions in which they were grown. Suitable crystals for the structure determination were sealed in capillaries with some of the saturated solution from which they were produced. There was some slight crystal decay (6–11%) during data collection (see Table 2), but not enough to interfere with the structure analyses. Details of crystal data, data collection, structure solution and refinement details for the compounds **3** and **4** are summarized concisely in Table 2. Refinement was by full-matrix least-squares calculations; with the exception of the partial occupancy water oxygen atoms in **3**, which were only allowed isotropic motion, all non-hydrogen atoms in **3** and **4** were allowed anisotropic motion. Crystallographic Information Files (CIFs) with full details of the structures and structure factor listings for both compounds have been deposited and are available from the authors. All calculations were made with the NRCVAX²⁰ programs on a Silicon Graphics work station, and the diagrams were prepared using ORTEP²¹ and PLUTON-94.²²

[Cu(hda)] (**1**)

To a stirred solution of hdaH_2 (0.20 g, 1.24 mmol) in distilled water (100 cm^3) was added dicopper(II) tetraacetate dihydrate (0.25 g, 0.63 mmol). The resulting green–blue suspension was refluxed for 2 h and during this time the condenser was periodically removed to allow some of the liberated acetic acid to escape from the reaction flask. The suspension was filtered whilst hot, and the blue product was washed with distilled water, ethanol and ether, and then dried *in vacuo*. Yield: 0.15 g (54%). Found: C, 38.5; H, 4.7; Cu, 29.7. Calc: C, 37.9; H, 4.5; Cu, 28.7%. $\mu = 1.58 \text{ B.M.}$ IR: 2940, 2860, 1590, 1415, 1340, 725, 670 cm^{-1} .

[Cu(oda)] (**2**)

This blue complex was prepared using the same stoichiometry and conditions as those employed for **1**. Yield: 0.22 g (74%). Found: C, 41.7; H, 5.7; Cu, 26.2. Calc: C, 40.8; H, 5.1; Cu, 26.9%. $\mu = 1.43 \text{ B.M.}$ IR: 2930, 2850, 1590, 1430, 1320, 730 cm^{-1} .

Table 2. Summary of crystal data, data collection, structure solution and refinement details

	3	4
Crystal data		
Empirical formula	C ₃₁ H _{49.46} CuN ₄ O _{15.73} C ₃₁ H ₂₆ CuN ₄ O ₄ ·11.73(H ₂ O)	C ₃₂ H ₅₂ CuN ₄ O ₁₆ C ₃₂ H ₂₈ CuN ₄ O ₄ ·12(H ₂ O)
Molar mass	793.43	812.32
Colour, habit	blue, plate	blue, plate
Crystal size (mm)	0.36 × 0.36 × 0.23	0.39 × 0.21 × 0.15
Crystal system	Triclinic	Triclinic
<i>a</i> (Å)	9.5835(5)	8.977(5)
<i>b</i> (Å)	12.5836(8)	15.276(3)
<i>c</i> (Å)	17.022(3)	16.539(2)
α (°)	80.799(8)	115.31(2)
β (°)	85.572(5)	92.07(2)
γ (°)	86.303(5)	104.54(3)
<i>V</i> (Å ³)	2017.5(4)	1957.8(12)
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>Z</i>	2	2
Molecular symmetry	none	none
<i>F</i> (000)	837	858
<i>D</i> _{calc} (g cm ⁻³)	1.306	1.378
μ (mm ⁻¹)	0.607	0.627
Data acquisition ^a		
Temp. (K)	293	293
Unit-cell reflections (θ range, °)	25 (9.5–13.7)	25 (8.0–12.0)
max. θ (°) for reflections	24.92	24.96
<i>hkl</i> range of reflections	–11 to 11; 0–14; –20 to 20	–10 to 10; 0–18; 19 to 19
Decay in three standard reflections	10.8	6.3
Reflections measured	7063	6894
Unique reflections	7063	6894
Reflections with <i>I</i> > 3 σ (<i>I</i>)	4308	3545
Absorption correction type	ψ -scans	ψ -scans
Min., max. abs. corr.	0.8826, 0.9985	0.8008, 0.8640
Structure solution and refinement ^b		
Refinement on	<i>F</i>	<i>F</i>
Solution method	Patterson heavy atom	Patterson heavy atom
C—H atom treatment	riding	riding
O—H atom treatment	not located	12H atoms ex diff. map
No. of variables in L.S.	462	478
<i>k</i> in $w = 1/(\sigma^2 F_0 + kF_0^2)$	0.008	0.008
<i>R</i> , <i>R</i> _w , <i>gof</i>	0.066, 0.094, 2.23	0.058, 0.070, 1.44
Density range in final Δ -map (e Å ⁻³)	–0.52, 0.66	–0.33, 0.42
Final shift/error ratio	0.006	0.003

^aData collection on an Enraf–Nonius CAD4 diffractometer with graphite monochromatized Mo-*K*_α radiation ($\lambda = 0.71069$ Å)

^bAll calculations were done on a Silicon Graphics 4D-35TG computer system with the NRCVAX system programs.

[Cu(η^2 -hda)(phen)₂] · 11.73H₂O (3)

Complex **1** (0.25 g, 1.13 mmol) and 1,10-phenanthroline (0.41 g, 2.27 mmol) were refluxed in ethanol (30 cm³) for 2 h. The resulting green solution was filtered whilst hot and on standing the blue product crystallized out. The following figures are based on the formulation [Cu(η^2 -hda)(phen)₂] · 8H₂O (see earlier footnote). Yield: 0.56 g (68%). Found: C, 50.7; H, 5.8; N, 7.7. Calc: C, 51.3; H, 5.8; N, 7.7%. $\mu = 1.88$ B.M. IR: 3370, 2940, 1555, 1515, 1425, 1395, 1335, 1305, 1285, 1225, 1145, 1105, 850, 720, 640, 420 cm⁻¹. $\lambda_{\text{max}} = 703$ nm, $\epsilon = 65$ dm³ mol⁻¹ cm⁻¹. The solid was recrystallized from water containing a few drops of ethanol and blue crystals of [Cu(η^2 -hda)(phen)₂] · 11.73H₂O (**3**) deposited on standing.

[Cu(η^2 -oda)(phen)₂] · 12H₂O (4)

This blue crystalline complex was prepared using the same stoichiometry and conditions as those employed for **3**. The following figures are based on the formulation [Cu(η^2 -oda)(phen)₂] · 8H₂O (see earlier footnote). Yield: 0.57 g (68%). Found: C, 51.3; H, 6.1; N, 8.3. Calc: C, 51.9; H, 5.9; N, 7.5%. $\mu = 1.92$ B.M. IR: 3370, 3040, 2920, 2860, 1560, 1515, 1420, 1340, 1290, 1240, 1195, 1150, 1105, 850, 720, 650, 425 cm⁻¹. $\lambda_{\text{max}} = 702$ nm, $\epsilon = 64$ dm³ mol⁻¹ cm⁻¹. The solid was recrystallized from water containing a few drops of ethanol and blue crystals of [Cu(η^2 -oda)(phen)₂] · 12H₂O (**4**) deposited on standing.

REFERENCES

1. R. C. Mehrotra and R. Bohra, *Metal Carboxylates*. Academic Press, New York (1983) and references therein.
2. R. J. Mureinik, *J. Inorg. Nucl. Chem. Lett.* 1976, **38**, 1275.
3. O. Asai, M. Kishita and M. Kubo, *J. Phys. Chem.* 1959, **63**, 96.
4. B. C. Guha, *Proc. R. Soc. Lond.* 1951, **A206**, 353; B. N. Figgis and R. L. Martin, *J. Chem. Soc.* 1956, 3837.
5. J. N. van Niekerk and F. R. L. Schoening, *Nature* 1953, **171**, 36.
6. J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.* 1953, **6**, 227.
7. B. H. O'Connor and E. N. Maslen, *Acta Cryst.* 1966, **20**, 824.
8. M. Bianchi, G. Menchi, P. Frediani, F. Piacenti, A. Scrivanti and U. Matteoli, *J. Molec. Catal.* 1989, **50**, 277.
9. M. T. Casey, M. McCann, M. Devereux, M. Curran, C. Cardin, M. Convery, V. Quillet and C. Harding, *J. Chem. Soc., Chem. Commun.* 1994, 2643.
10. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn, pp. 232–233. Wiley, New York (1978).
11. B. N. Figgis and D. J. Martin, *Inorg. Chem.* 1966, **1**, 100.
12. W. Fitzgerald, B. J. Hathaway and C. J. Simmons, *J. Chem. Soc., Dalton Trans.* 1985, 141.
13. B. J. Hathaway, *Struct. Bonding (Berlin)* 1973, **14**, 49.
14. C. J. Simmons, K. Seff, F. Clifford and B. J. Hathaway, *Acta Cryst.* 1983, **C39**, 1360.
15. C. J. Simmons, N. W. Alcock, K. Seff, W. Fitzgerald and B. J. Hathaway, *Acta Cryst.* 1985, **B41**, 42.
16. W. Fitzgerald and B. J. Hathaway, *Acta Cryst.* 1984, **C40**, 243.
17. F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rodgers and D. J. Watson, *Acta Cryst.* 1979, **B35**, 2331.
18. C. Escobar and O. Wittke, *Acta Cryst.* 1983, **C39**, 1643.
19. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn, p. 768. Wiley, New York (1988).
20. E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee and P. S. White, *J. Appl. Cryst.* 1989, **22**, 384.
21. C. K. Johnson, ORTEP—A Fortran Thermal Ellipsoid Plot Program. Technical Report ORNL-5138, Oak Ridge National Lab., U.S.A. (1976).
22. A. L. Spek, PLUTON Molecular Graphics Program. University of Utrecht, The Netherlands (1994).