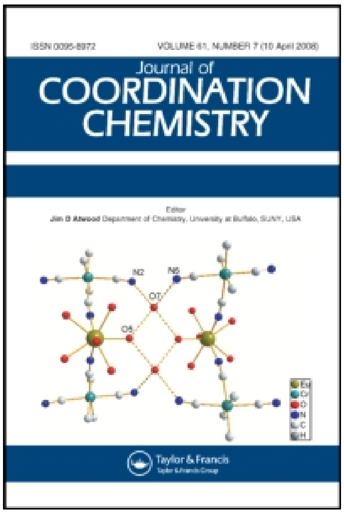

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Three pimelato-bridged Cu(II) phenanthroline complexes: $[Cu_2(phen)_2(H_2O)_2L_2] \cdot 4H_2O$, α- and β-$[Cu_2(phen)_2L_2] \cdot 4H_2O$, $H_2L = HOOC(CH_2)_5COOH$

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Reaction of $CuCl_2 \cdot 2H_2O$, 1,10-phenanthroline (phen) and pimelic acid with Na_2CO_3 in aqueous methanol afforded a mixture consisting of $[Cu_2(phen)_2(H_2O)_2(C_7H_{10}O_4)_2] \cdot 4H_2O$ (**1**), α-$[Cu_2(phen)_2(C_7H_{10}O_4)_2] \cdot 4H_2O$ (**2**) and β-$[Cu_2(phen)_2(C_7H_{10}O_4)_2] \cdot 4H_2O$ (**3**) at $pH = 5.8$. The structure of compound **1** has been reported earlier, and consists of hydrogen bonded H_2O molecules and dinuclear $[Cu_2(phen)_2(H_2O)_2(C_7H_{10}O_4)_2]$ molecules generated from pimelate anions, acting as bis(monodentates), bridging square pyramidal Cu ions. The structures of dimorphs **2** and **3** have been established using single-crystal X-ray diffraction methods. They are monoclinic and triclinic, respectively (**2**: $C2/c$, $a = 20.344(2)$, $b = 9.828(1)$, $c = 20.802(2)$ Å, $\beta = 116.10(7)^\circ$, $Z = 4$, $D_{calc} = 1.558\ g\,cm^{-3}$; **3**: $P\bar{1}$, $a = 10.124(2)$, $b = 10.658(2)$, $c = 10.847(2)$ Å, $\alpha = 111.36(3)$, $\beta = 116.27(3)$, $\gamma = 93.80(3)^\circ$, $Z = 1$, $D_{calc} = 1.529\ g\,cm^{-3}$). The structures of all three complexes are compared. Both **2** and **3** are composed of hydrogen bonded H_2O molecules and polymeric ${}^{1}_{\infty}[Cu_2(phen)_2(C_7H_{10}O_4)_2]$ chains, in which dimeric $Cu_2N_4O_4$ units with square pyramidal coordination geometry are bridged by pimelate anions. The dinuclear molecules in **1** and polymeric chains in **2** and **3** are assembled via π–π stacking and weak C–H···O hydrogen bonds into 2D layers, linked by hydrogen bonds.

Keywords: Coordination polymer; Copper; Pimelic acid; Phenanthroline; Crystal structure; Supramolecular assembly

1. Introduction

Recent years have witnessed rapidly growing interest in exploitation of di- and polycarboxylic acids for the design and construction of coordination polymers with various network topologies and properties that have potential application in the fields of molecular magnetism, electrical conductivity, photoluminescence, inclusion chemistry, molecular recognition and catalysis [1]. In contrast to rigid aromatic polycarboxylates, aliphatic α,ω-dicarboxylates, due to their conformational versatility,

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tend to bridge transition metal ions to form coordination polymers of low dimensionality [2–7]. Our interest in this field has focused on ternary mixed-ligand metal dicarboxylato complexes involving ancillary heteroaromatic N-donor ligands such as 1,10-phenanthroline (phen), 2,2-bipyridyl and 4,4-bipyridyl [8–10].

Coordination of dicarboxylates and such N-donor ligands to metal atoms generates a variety of supramolecular motifs and π–π stacking interactions between N-donor ligands have been found to be essential for supramolecular assemblies [11–22]. In this contribution, we compare three pimelato-bridged Cu(II) phenanthroline complexes $[Cu_2(phen)_2(H_2O)_2(C_7H_{10}O_4)_2]\cdot 4H_2O$ (**1**), α-$[Cu_2(phen)_2(C_7H_{10}O_4)_2]\cdot 4H_2O$ (**2**) and β-$[Cu_2(phen)_2(C_7H_{10}O_4)_2]\cdot 4H_2O$ (**3**) obtained from reaction of $CuCl_2\cdot 2H_2O$, phenanthroline and pimelic acid with Na_2CO_3 in aqueous methanol at pH = 5.8. It should be noted that the structure of **1** was reported earlier [23]. Basic structural units are dinulcear $[Cu_2(phen)_2(H_2O)_2(C_7H_{10}O_4)_2]$ molecules in **1** and polymeric ${}^{1}_{\infty}[Cu_2(phen)_2(C_7H_{10}O_4)_2]$ chains in the two polymorphs, **2** and **3**.

2. Experimental

2.1. *Syntheses*

All chemicals of reagent grade were commercially available and used without further purification. In a typical synthesis, 0.43 g (2.52 mmol) of $CuCl_2\cdot 2H_2O$, 0.50 g (2.52 mmol) of phenanthroline monohydrate and 0.40 g (2.52 mmol) of pimelic acid were successively added with stirring to 25 cm^3 of methanol plus 25 cm^3 of doubly distilled water. The mixture was stirred for another 30 min and filtered. To the green filtrate was added 2.0 cm^3 of aqueous 1.0 M Na_2CO_3 dropwise, leading to a blue solution (pH = 5.8), which was then kept at 50°C. Slow evaporation during several weeks produced a mixture of crystals of $[Cu_2(phen)_2(H_2O)_2(C_7H_{10}O_4)_2]\cdot 4H_2O$ (**1**), α-$[Cu_2(phen)_2(C_7H_{10}O_4)_2]\cdot 4H_2O$ (**2**) and β-$[Cu_2(phen)_2(C_7H_{10}O_4)_2]\cdot 4H_2O$ (**3**).

2.2. *X-ray crystallography*

Suitable single crystals of **2** and **3** were selected under a polarizing microscope and fixed with epoxy cement on glass fibres mounted on a Bruker P4 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) for cell determination and data collection. Lattice parameters were refined from the 2θ values (10–25°) of 25 carefully centred reflections and reflection intensities were collected at 293 K using the θ–2θ scan technique. Corrections for Lorentz polarization and absorption effects were performed on the basis of ψ-scans. The structures were solved by direct methods using SHELXS-97 [24]. Subsequent difference Fourier syntheses enabled all non-hydrogen atoms to be located. After several cycles of refinement, hydrogen atoms associated with C atoms were added in calculated positions and hydrogen atoms of H_2O molecules were derived from difference Fourier syntheses. Final full-matrix least-squares refinement using SHELXL-97 [25] converged smoothly with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. Crystal data, intensity collection and structure refinement details are summarized in table 1, and selected interatomic distances and bond angles are given in tables 2 and 3.

Table 1. Summary of crystal data, data collection, structure solution and refinement details for **1** **2** and **3**.

Compound	**2**	**3**
Empirical formula	$C_{38}H_{44}Cu_2N_4O_{12}$	$C_{38}H_{44}Cu_2N_4O_{12}$
Formula weight	875.85	875.85
Description	Blue block	Blue needle
Crystal size (mm)	0.47 × 0.24 × 0.22	0.56 × 0.20 × 0.11
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	20.344(2)	10.124(2)
b (Å)	9.828(1)	10.658(2)
c (Å)	20.802(2)	10.847(2)
α (°)		111.36(3)
β (°)	116.10(7)	115.27(3)
γ (°)		93.80(3)
Volume (Å^3)	3735.1(7)	950.9(3)
Z	4	1
D_{calc} (g cm^{-3})	1.558	1.529
$F(000)$	1816	454
μ (mm^{-1})	1.209	1.188
Refinement method	Full-matrix least-squares on F^2	
θ Range (°)	1.00–27.50	0.963–27.50
Reflections collected	5202	4923
Unique reflections (R_{int})	4297 (0.0446)	4204 (0.0179)
Data, restraints, parameters	3636, 0, 256	3707, 0, 256
Goodness-of-fit on F^2	1.143	1.120
R_1, wR_2 $[I \geq 2\sigma(I)]^{a}$	0.0367, 0.0972	0.0492, 0.1354
R_1, wR_2 (all data)^{a}	0.0471, 0.1020	0.0556, 0.1419
Extinction coefficients	0.0046(3)	0.032(4)
A, B values in w^{b}	0.0564, 1.0378	0.0866, 0.5370
$\rho_{\max}$, $\rho_{\min}$ (e Å^{-3})	0.591, −0.714	1.813, −1.340

$^{a}wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. $^{b}w = [\delta^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected interatomic distances (Å) and bond angles (°) for **2**.

Cu–O(1)	1.940(2)	O(1)/Cu/O(4)$^{\#1}$	90.63(6)	O(4)$^{\#1}$/Cu/N(1)	173.91(6)
Cu–O(4)$^{\#1}$	1.964(1)	O(1)/Cu/O(4)$^{\#2}$	88.69(6)	O(4)$^{\#1}$/Cu/N(2)	94.05(7)
Cu–O(4)$^{\#2}$	2.486(2)	O(1)/Cu/N(1)	94.31(7)	O(4)$^{\#2}$/Cu/N(1)	108.87(6)
Cu–N(1)	2.037(2)	O(1)/Cu/N(2)	174.86(7)	O(4)$^{\#2}$/Cu/N(2)	94.59(6)
Cu–N(2)	2.022(2)	O(4)$^{\#1}$/Cu/O(4)$^{\#2}$	74.76(6)	N(1)/Cu/N(2)	80.89(7)
Hydrogen bonding contacts					
D–H	d(D–H)	d(H ··· A)	∠(D–H ··· A)	d(D–H ··· A)	A
O(5)–H(5A)	0.85	1.96	157	2.771	O(2)$^{\#5}$
O(5)–H(5B)	0.86	1.86	171	2.714	O(3)$^{\#2}$
O(6)–H(6A)	0.84	2.03	165	2.848	O(5)$^{\#6}$
O(6)–H(6B)	0.86	2.03	171	2.877	O(1)
C(6)–H(6)	0.93	2.55	131	3.240	O(2)$^{\#7}$

Symmetry codes used are #1: $-x+1/2, -y+1/2, -z$; #2: $x, y+1, z$; #3: $-x+1/2, -y+3/2, -z$; #4: $x, y-1, z$; #5: $x-1/2, y+1/2, z$; #6: $-x+1/2, y-1/2, -z+1/2$; #7: $-x+1, -y+2, -z$.

3. Results and discussion

The structure of **1** [23] consists of dinuclear $[Cu_2(phen)_2(H_2O)_2(C_7H_{10}O_4)_2]$ complex molecules and lattice H_2O molecules, and is illustrated in figure 1 for purposes of comparison. The dinuclear complex, containing a 20-membered ring, is similar to the

Table 3. Selected interatomic distances (Å) and bond angles (°) for **3**.

Cu–O(1)	1.933(2)	O(1)/Cu/O(4)$^{\#1}$	90.3(1)	O(4)$^{\#1}$/Cu/N(1)	174.5(1)
Cu–O(4)$^{\#1}$	1.967(2)	O(1)/Cu/O(4)$^{\#2}$	90.3(1)	O(4)$^{\#1}$/Cu/N(2)	93.6(1)
Cu–O(4)$^{\#2}$	2.424(2)	O(1)/Cu/N(1)	95.2(1)	O(4)$^{\#2}$/Cu/N(1)	104.9(1)
Cu–N(1)	2.032(3)	O(1)/Cu/N(2)	175.0(1)	O(4)$^{\#2}$/Cu/N(2)	93.8(1)
Cu–N(2)	2.030(3)	O(4)$^{\#1}$/Cu/O(4)$^{\#2}$	75.9(1)	N(1)/Cu/N(2)	80.9(1)

Hydrogen bonding contacts

D–H	d(D–H)	d(H···A)	∠(D–H···A)	d(D–H···A)	A
O(5)–H(5A)	0.74	2.08	152	2.760	O(3)$^{\#1}$
O(5)–H(5B)	0.87	1.92	157	2.743	O(2)$^{\#5}$
O(6)–H(6A)	0.87	1.92	175	2.786	O(5)$^{\#6}$
O(6)–H(6B)	0.98	2.22	144	2.979	O(1)$^{\#3}$
C(3)–H(3)	0.93	2.32	144	3.116	O(6)$^{\#7}$
C(5)–H(5)	0.93	2.55	149	3.378	O(3)$^{\#8}$
C(6)–H(6)	0.93	2.41	139	3.169	O(2)$^{\#9}$
C(9)–H(9)	0.93	2.61	163	3.507	O(5)$^{\#10}$
C(10)–H(10)	0.93	2.46	145	3.265	O(6)

Symmetry codes used are #1: $-x+2, -y+1, -z+1$; #2: $x-1, y, z$; #3: $-x+1, -y+1, -z+1$; #4: $x+1, y, z$; #5: $-x+2, -y+1, -z+2$; #6: $-x+1, -y, -z+1$; #7: $x, y+1, z+1$; #8: $x-1, y, z+1$; #9: $-x+1, -y+1, -z+2$; #10: $-x+1, -y, -z+1$.

glutarato bridged complex [$Cu_2(phen)_2(H_2O)_2(C_5H_6O_4)_2$] [26], but different to the azelato analogue [$Cu_2(phen)_2(C_9H_{14}O_4)_2$] [27]. No intramolecular hydrogen bonds are evident in **1**. Equatorial Cu–N and Cu–O bond distances average to 2.026 Å and 1.954 Å, respectively, and the apical Cu–O bond is of 2.268 Å, which are comparable with others reported in the literature [28]. [$Cu_2(phen)_2(H_2O)_2(C_7H_{10}O_4)_2$] molecules lie on crystallographic 2*b* positions and terminal phenanthroline ligands engage in π–π stacking interactions with neighbouring molecules (mean interplanar distance 3.63 Å), leading to 1D ribbon-like chains extending in the [001] direction. The aqua ligands donate hydrogen atoms to the uncoordinated carboxylate O(3) atoms to form intrachain hydrogen bonds (table 2) and forming hydrogen bonds to lattice water molecules O(6). The latter function as weak C–H···O acceptors from an adjacent phenanthroline ligand and as O–H···O donors to two carboxylate oxygen of different chains. The extensive hydrogen bonding network obviously contributes to the stability of the crystal structure.

α-[$Cu_2(phen)_2(C_7H_{10}O_4)_2$] · $4H_2O$ (**2**) has a completely different structure based on 1D $^1_\infty$[$Cu_2(phen)_2(C_7H_{10}O_4)_2$] polymeric chains (figure 2). Cu ions are located in a square pyramidal environment defined by two N atoms of one phenanthroline ligand and three carboxylate O atoms of different pimelate anions. Two adjacent CuO_5 square pyramids are connected through two carboxylate O atoms (O(4) and its symmetry equivalent) into dimeric $Cu_2N_4O_4$ units with a rhombic four-membered Cu_2O_2 ring. Along the [010] direction, $Cu_2N_4O_4$ units are linked by pimelato ligands into 1D polymeric chains with 20-membered rings (figure 2). Cu···Cu separations in the rhombic Cu_2O_2 and 20-membered rings are 3.550 and 10.980 Å, respectively. Phenanthroline ligands are distributed on both sides of the chain so that pimelate anions are sandwiched between two antiparallel phenanthroline ligands with methylene hydrogen atoms pointing at the aromatic plane with mean C–H···π distance of 3.65 Å, suggesting intrachain C–H···π interactions [30]. Because of π–π stacking interactions between two adjacent phenanthroline ligands (mean interplanar phen-to-phen distance 3.45 Å), chains are assembled into 2D layers parallel to (001) as shown in figure 2.

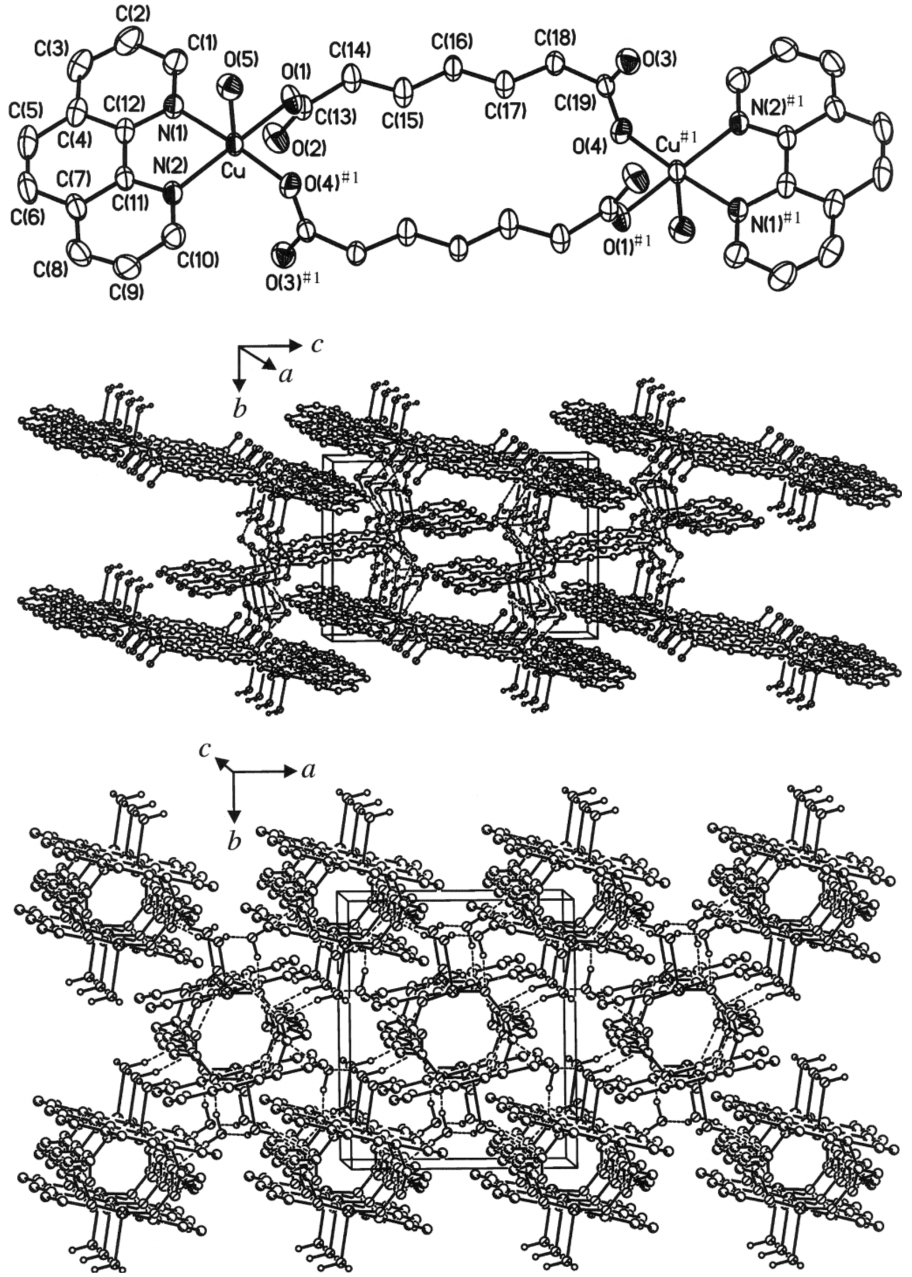

Figure 1. Top: ORTEP view of $[Cu_2(phen)_2(H_2O)_2(C_7H_{10}O_4)_2]$ in **1** together with the atom numbering scheme. Thermal ellipsoids are drawn at the 45% probability level; middle and bottom: the structure of **1** viewed along [100] and [001], respectively.

Phenanthroline donates a hydrogen atom to an uncoordinating carboxylate oxygen atom to form a weak C–H$\cdots$O hydrogen bond (table 2). The layers are stacked parallel to (001) in such a way that the π–π and C–H$\cdots\pi$ interactions propagate alternatively along [110] in one layer and along $[\bar{1}10]$ in the next. The two crystallographically

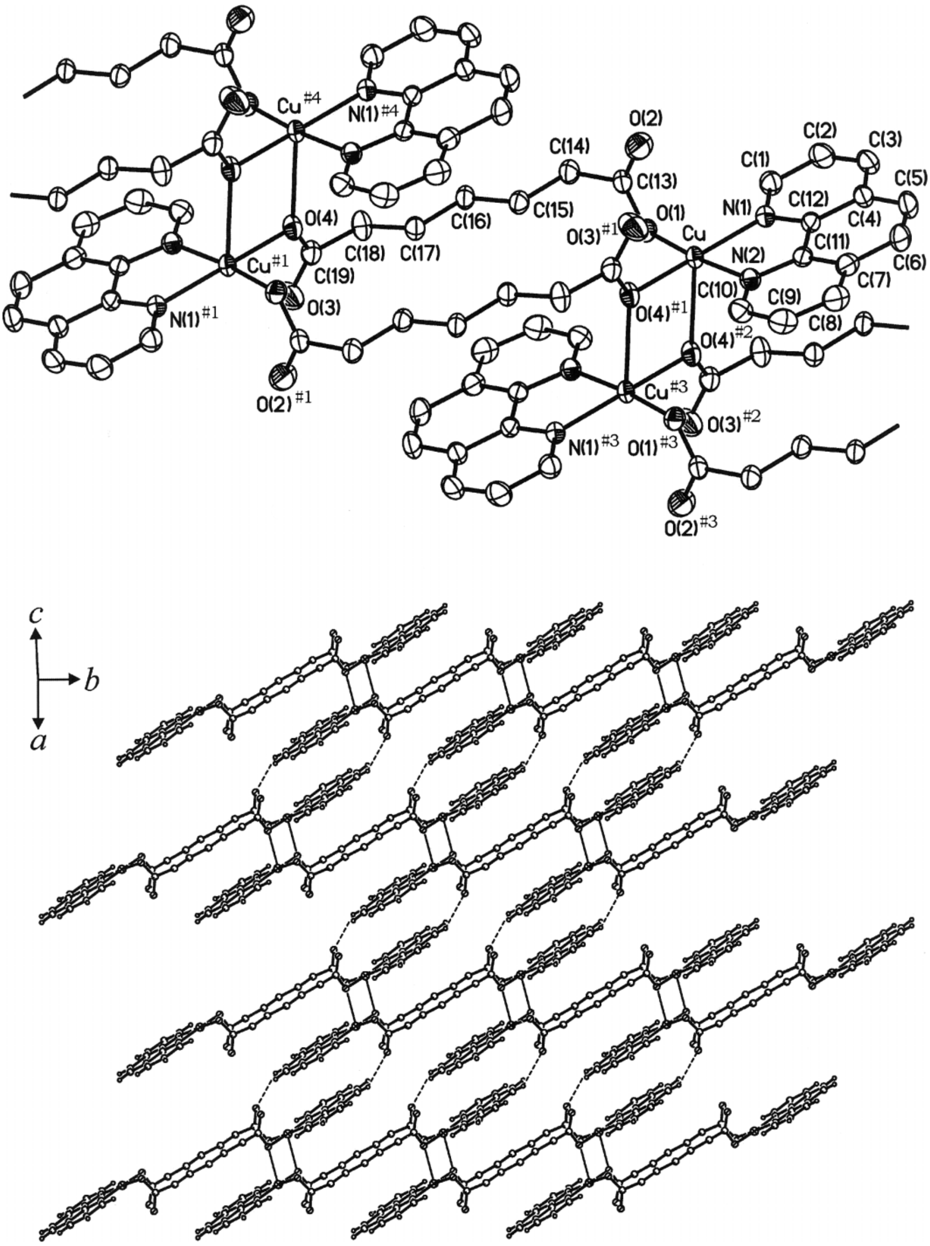

Figure 2. Top: ORTEP view of the ${}^{1}_{\infty}[Cu_2(phen)_2(C_7H_{10}O_4)_2]$ chain in **2** together with the atom numbering scheme. Thermal ellipsoids are drawn at the 45% probability level; bottom: polymeric chains assembled into 2D layers via π–π stacking interactions and C–H···O hydrogen bonds.

distinct lattice water molecules are located between the layers. One is hydrogen bonded to two uncoordinated carboxylate oxygen atoms of different chains and the other forms hydrogen bonds to a coordinating carboxylate oxygen and the other lattice water (table 2).

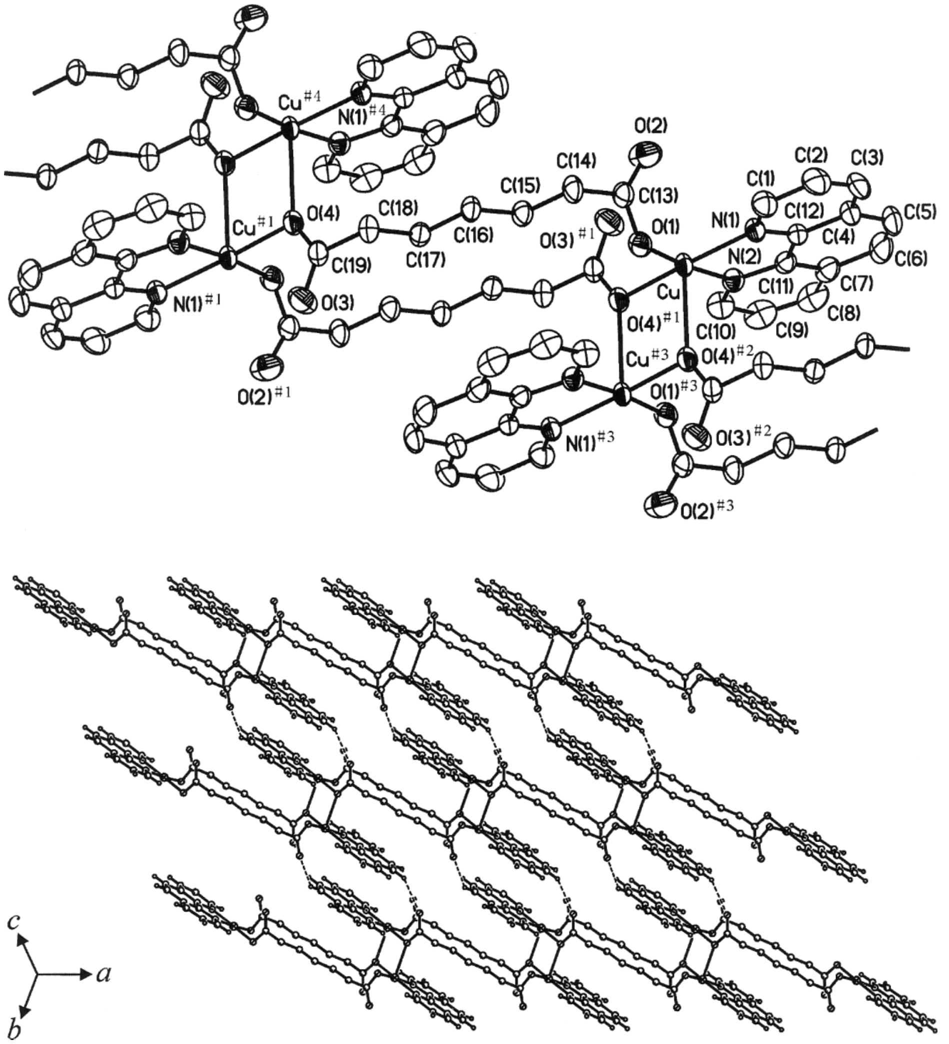

Figure 3. Top: ORTEP view of the $^{1}_{\infty}[Cu_2(phen)_2(C_7H_{10}O_4)_2]$ chain in **3** together with the atom numbering scheme. Thermal ellipsoids are drawn at the 45% probability level; bottom: polymeric chains assembled into 2D layers via π–π stacking interactions and C–H$\cdots$O hydrogen bonds.

The complex β-$[Cu_2(phen)_2(C_7H_{10}O_4)_2]\cdot 4H_2O$ (**3**) also contains ID $^{1}_{\infty}[Cu_2(phen)_2(C_7H_{10}O_4)_2]$ chains (figure 3). The Cu ions in **2** and **3** display nearly identical coordination geometries, but a significant difference lieshin the axial Cu–O bond distances (tables 2 and 3). The latter has a shorter axial Cu–O bond distance (2.424 Å) than the former (2.486 Å). Cu$\cdots$Cu separations within the rhombic Cu_2O_2 and 20-membered rings are 3.474 Å and 11.057 Å, respectively. The polymeric chains display weak intrachain C–H$\cdots\pi$ interactions between pimelato methylene groups and phenanthroline ligands (mean C–H$\cdots\pi$ distance: 3.69 Å) [30] and the phenanthroline ligands are engaged in interchain π–π stacking (mean interplanar phen-to-phen distance: 3.49 Å). As shown in figure 3, the polymeric chains extending along [100] are assembled

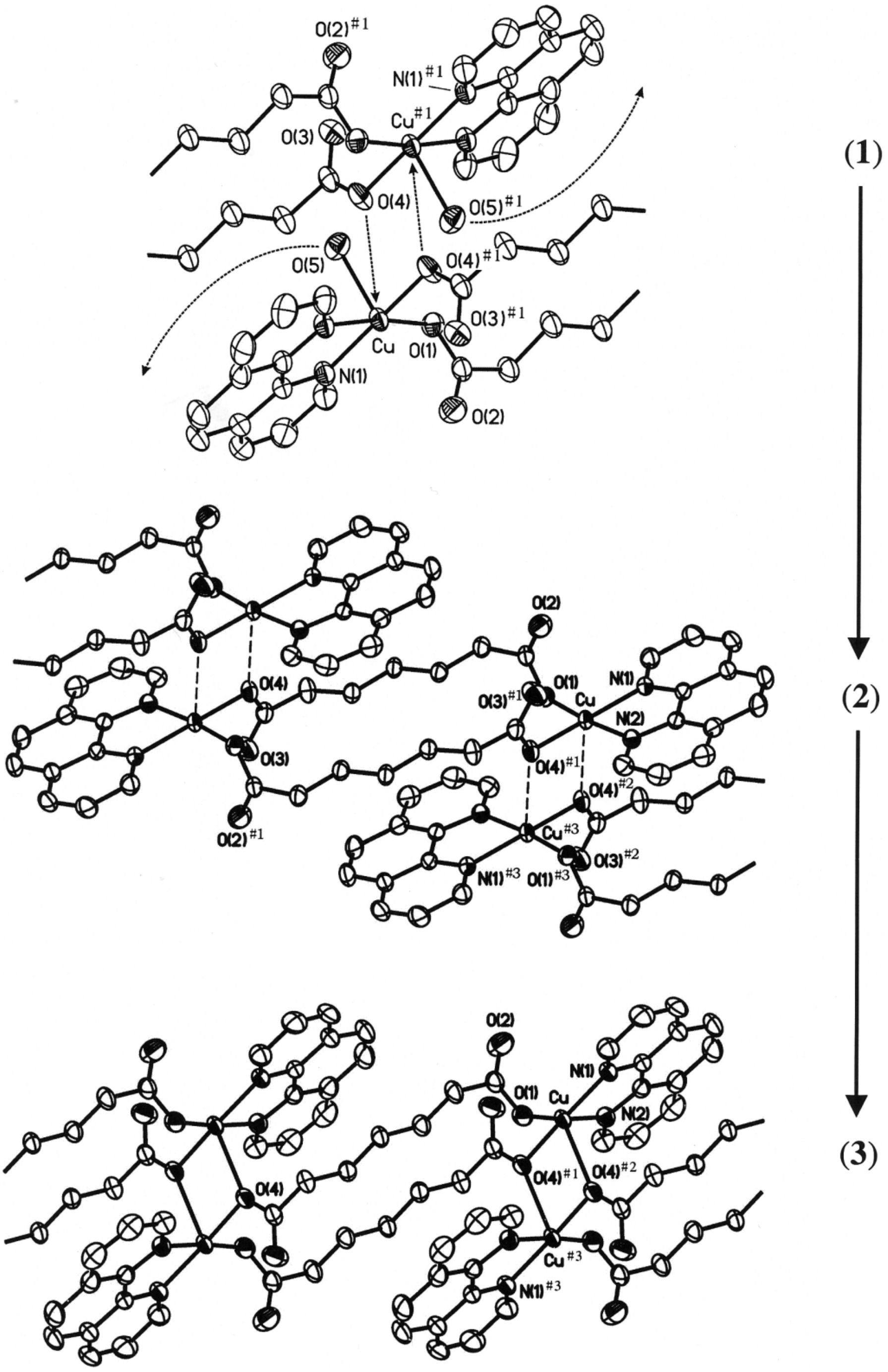

Figure 4. Assembly of polymeric chains in **2** and **3** from the dinuclear complex in **1**.

Table 4. Selected interatomic distances (Å) and bond angles (°) for pimelate anions in **1** [23], **2** and **3**.

Bonds	**1**	**2**	**3**	Angles	**1**	**2**	**3**
C(13)–O(1)	1.274(2)	1.286(3)	1.278(4)	O(1)/C(13)/O(2)	122.4(2)	123.5(2)	123.6(3)
C(13)–O(2)	1.235(2)	1.221(3)	1.211(4)	O(1)/C(13)/C(14)	116.5(2)	115.2(2)	115.0(3)
C(13)–C(14)	1.513(2)	1.516(3)	1.516(4)	O(1)/C(13)/C(14)	121.1(2)	121.2(2)	121.4(3)
C(14)–C(15)	1.519(2)	1.514(3)	1.513(4)	C(13)/C(14)/C(15)	112.3(1)	110.2(2)	111.0(3)
C(15)–C(16)	1.519(2)	1.522(3)	1.510(4)	C(14)/C(15)/C(16)	113.0(1)	113.1(2)	113.2(3)
C(16)–C(17)	1.521(2)	1.521(3)	1.518(4)	C(15)/C(16)/C(17)	112.6(1)	112.9(2)	113.9(3)
C(17)–C(18)	1.525(2)	1.513(3)	1.526(4)	C(16)/C(17)/C(18)	112.5(1)	113.1(2)	112.4(3)
C(18)–C(19)	1.519(2)	1.511(3)	1.508(4)	C(17)/C(18)/C(19)	110.1(1)	112.7(2)	111.9(3)
C(19)–O(3)	1.245(2)	1.222(3)	1.234(4)	C(18)/C(19)/O(3)	120.5(2)	121.8(2)	121.0(3)
C(19)–O(4)	1.267(2)	1.283(3)	1.281(4)	C(18)/C(19)/O(4)	115.5(2)	115.4(2)	116.7(3)
				O(3)/C(19)/O(4)	124.0(2)	122.7(2)	122.3(3)

into 2D layers parallel to (010), stabilized by weak C–H···O hydrogen bonds between the phenanthroline C–H groups (C(5) and C(6)) and uncoordinating carboxylate oxygen atoms, as well as by O–H···O hydrogen bonds between the O(5) water molecule and uncoordinated carboxylate oxygen atoms of neighbouring chains. The other water molecule (O(6)) forms hydrogen bonds to the former water oxygen atom and a coordinated carboxylate oxygen atom. Both lattice water oxygen atoms engage in weak C–H···O hydrogen bonds with phenanthroline ligands to hold the 2D layers together.

The dimeric $Cu_2N_4O_4$ units in **2** and **3** exhibit close similarities to those in $[Cu_2(phen)_2(C_8H_{12}O_4)_2] \cdot 3H_2O$ [31] and $[Cu_2(phen)_2(C_{10}H_{16}O_4)_2] \cdot 6H_2O$ [10], where the copper dimers are interlinked by suberate $(C_8H_{12}O_4)^{2-}$ and sebacate $(C_{10}H_{16}O_4)^{2-}$ anions, respectively, into 2D networks. The polymeric chains in **2** and **3** could be derived from the dinuclear $[Cu_2(phen)_2(H_2O)_2(C_7H_{10}O_4)_2]$ complex molecules. As illustrated in figure 4, dinuclear molecules approach one another and two coordinating carboxylate oxygen atoms (O(4) atoms) bond to Cu, to replace the aqua ligands. The polymeric chain in **2** could be viewed as an intermediate between the dinuclear complex in **1** and the polymeric chain in **3**. The pimelate anions in the title complexes assume an more or less identical configurations with normal bonding values [32, 33]. All carbon atoms of pimelate anions are coplanar and terminal carboxylate groups are twisted away from the carbon plane. Dicarboxylate anions in **1** function as bis(monodentate) bridging ligands whereas they interlink three metal atoms in **2** and **3**, with carboxylate groups bonded to one and two Cu atoms, respectively. As expected, C–O bond distances to the coordinated oxygen atoms are significantly longer than those that are uncoordinated (table 4).

Supplementary data

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 136949 ($C_{12}H_{20}Mn_2N_4O_{10}$ **1**), CCDC 259508 (α-$C_{12}H_{20}Cu_2N_4O_{10}$ **2**) and CCDC 259509 (β-$C_{12}H_{20}Cu_2N_4O_{10}$ **3**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or email: deposit@ccdc.cam.ac.uk).

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