



Sebacato-bridged Cu(II) phen complexes:
syntheses and crystal structures of ${}^2_{\infty}[\text{Cu}_2(\text{phen})_2\text{L}_{4/2}](\text{H}_2\text{O})_6$ and
 $[(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2](\text{HL})_2(\text{H}_2\text{L})(\text{H}_2\text{O})_4$
(H_2L = sebacic acid; phen = 1,10-phenanthroline)

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Abstract

Reactions of freshly-prepared $\text{Cu}(\text{OH})_2$ with sebacic acid (H_2L) and 1,10-phenanthroline (phen) in $\text{EtOH}/\text{H}_2\text{O}$ (1:1 v/v) and $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (1:1 v/v) at pH 6.4 afforded two novel sebacato-bridged Cu(II) phen complexes ${}^2_{\infty}[\text{Cu}_2(\text{phen})_2\text{L}_{4/2}](\text{H}_2\text{O})_6$ (**1**) and $[(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2](\text{HL})_2(\text{H}_2\text{L})(\text{H}_2\text{O})_4$ (**2**), respectively. Complex **1** consists of $2\text{D } {}^2_{\infty}[\text{Cu}_2(\text{phen})_2\text{L}_{4/2}]$ layers and lattice H_2O molecules. The Cu atoms are each square-pyramidally coordinated by two N atoms of one phen ligand and three O atoms of different sebacato ligands. Two adjacent square pyramids are edge-shared to form $[\text{Cu}_2\text{N}_4\text{O}_4]$ dimers, which are interlinked by sebacato ligands to $2\text{D } {}^2_{\infty}[\text{Cu}_2(\text{phen})_2\text{L}_{4/2}]$ layers with rhombus-like 52-membered rings. The resulting layers are assembled by interlayer π - π stacking interactions and hydrogen bonding interactions. Complex **2** comprises divalent $[(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2]$ complex cations, hydrogensebacate anions, sebacic acid molecules and lattice H_2O molecules. In the divalent complex cations, the Cu atoms are each octahedrally coordinated by four N atoms of two phen ligands and two O atoms of one bis-chelating sebacato ligand. The complex cations are assembled via π - π stacking interactions into positively charged 2D network. The hydrogensebacate anions, sebacic acid molecules and H_2O molecules build negatively charged 2D hydrogen-bonded networks. Both positively and negatively charged 2D networks are interwoven with each other to generate a novel supramolecular architecture. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Copper; Self-assembly; Supramolecules; X-ray structures

1. Introduction

Currently, rational design and syntheses of polymeric metal-organic coordination networks with specific topologies have been a most active research topic, since incorporation of active groups into coordination polymers offer an excellent opportunity for the construction of promising advanced materials with nonlinear optical effect, magnetic properties, host-guest chemistry, catalysis and electrical conductivity [1–8]. Molecular self-assembly of transition metal ions with organic ligands has proven to be a highly efficient strategy in the

construction of coordination polymers [9,10]. To this goal, rigid bridging ligands such as 4,4'-bipyridine, pyrazine, 4-pyridinecarboxaldehyde, benzene-1,3,5-tricarboxylate, 1,2,4,5-benzenetetracarboxylate have been extensively used [11–18]. Previous investigations carried by other groups or by us have shown that the flexible α,ω -dicarboxylato ligands ($\text{OOC}-(\text{CH}_2)_n-\text{COO}$, $n = 1-8$) could bridge transition metal ions in different coordinating fashions to form 1D, 2D and 3D coordination polymers [8,19–23]. Efforts have also been dedicated to the supramolecular assembly of transition metals with the flexible α,ω -dicarboxylato and hetero-aromatic N-donor ligands and, as a result, a variety of mixed ligand complexes have been obtained [24–38]. Structure determinations indicate that the α,ω -dicarboxylate anions tend to coordinate metal atoms to form low

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dimensional complexes such as discrete complex ions, complex molecules and catena polymeric chains. Mixed ligand complexes with 2D networks are very rare. Additionally, most work was restricted to the low members of the saturated α,ω -dicarboxylate anions and only a few studies have been carried out using sebacate anions ($\text{OOC}-(\text{CH}_2)_8-\text{COO}$) as ligands [39]. Recently, McCann et al. have found that Cu(II) and Mn(II) α,ω -dicarboxylate complexes possess antimicrobial and anti-Candida activity [40,41]. In this paper, we report two sebacato-bridged Cu(II) complexes ${}^2_{\infty}[\text{Cu}_2(\text{phen})_2\text{L}_{4/2}](\text{H}_2\text{O})_6$ (**1**) and $[(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2](\text{HL})_2(\text{H}_2\text{L})(\text{H}_2\text{O})_4$ (**2**). Within complex **1**, the $[\text{Cu}_2(\text{phen})_2]$ subunits are interlinked by sebacato ligands into 2D grid-like open networks. The principal building blocks in complex **2** are the dinuclear $[(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2]^{2+}$ complex cations resulting from two $[\text{Cu}(\text{phen})_2]$ moieties bischelated by sebacato ligands. In both complexes, significant π - π stacking interactions play important roles in supramolecular assembly.

2. Results and discussion

2.1. Syntheses

Our earlier investigation indicated that reactions of equimolar CuCl_2 , 1,10-phenanthroline, sebacic acid ($\text{H}_2\text{L} = \text{HOOC}-(\text{CH}_2)_8-\text{COOH}$) with Na_2CO_3 in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ produced $[\text{Cu}(\text{phen})\text{L}]\cdot 3\text{H}_2\text{O}$ [42] and $[\text{Cu}_2(\text{phen})_2(\text{H}_2\text{O})_2(\text{OH})_2](\text{HCO}_3)_2\cdot 6\text{H}_2\text{O}$ [43] at pH = 6.4 and 10.2, respectively. However, reactions of phenanthroline, sebacic acid and $\text{Cu}(\text{OH})_2$, which was freshly precipitated by addition of NaOH to an aqueous solution of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, yielded ${}^2_{\infty}[\text{Cu}_2(\text{phen})_2\text{L}_{4/2}](\text{H}_2\text{O})_6$ (**1**) and $[(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2](\text{HL})_2(\text{H}_2\text{L})(\text{H}_2\text{O})_4$ (**2**) at pH = 6.4 in $\text{EtOH}/\text{H}_2\text{O}$ (1:1 v/v) and $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (1:1 v/v), respectively. This finding implies that a neutral solution is obviously favorable for the sebacate anions to coordinate to Cu atoms. Additionally, self-assembly of Cu(II) ions with phen and sebacic acid is solvent dependent and the products rely on the Cu(II) sources used even though the same solvent mixture was employed.

2.2. Structure of ${}^2_{\infty}[\text{Cu}_2(\text{phen})_2\text{L}_{4/2}](\text{H}_2\text{O})_6$ (**1**)

The basic building subunits in **1** are the centrosymmetric $[\text{Cu}_2\text{N}_4\text{O}_4]$ dimers resulting from edge-sharing of two $[\text{CuN}_2\text{O}_3]$ square pyramids via two μ_2 carboxylate O atoms at the canted edges (Fig. 1). As usual, the basal Cu–O bond distances of 1.944 and 1.963 Å are slightly shorter than the Cu–N bond distances of 2.020 and 2.035 Å, and the axial Cu–O bond distance is 2.407 Å (Table 2). The Cu atom is displaced by 0.049(1) Å from

the best plane defined by O(1), N(1), N(2) and O(3)^a towards the apical O(3)^b atom. The Cu···Cu distance within the dimer is 3.419(1) Å. The $[\text{Cu}_2\text{N}_4\text{O}_4]$ dimers are interlinked by the bridging sebacato ligands into 2D ${}^2_{\infty}[\text{Cu}_2(\text{phen})_2\text{L}_{4/2}]$ open layers with rhombus-like 52-membered rings and the chelating phen ligands disposed on both sides (Fig. 1). Such grid-like networks extend infinitely parallel to (101) and are arranged so that adjacent phen planes from different layers face antiparallel to each other with the interplanar phen-to-phen distance of 3.51 Å, suggesting substantial π - π stacking interactions [44–49]. The chelating phen ligands of the 2D layers exhibit nearly perfect coplanarity.

Each carboxylate group of the bridging sebacato ligand offers one O atom, respectively, to coordinate one Cu atom and to bridge two Cu atoms. As expected, the C–O bond length to the bidentate carboxylate O atom is 1.282 Å, slightly longer than that (1.273 Å) to the monodentate carboxylate O atom, and the C–O bond lengths to the non-coordinating carboxylate O atoms are averaged at 1.239 Å.

Out of the three crystallographically distinct H_2O molecules intercalated between 2D ${}^2_{\infty}[\text{Cu}_2(\text{phen})_2\text{L}_{4/2}]$ layers, one donates two hydrogen atoms to two non-coordinating carboxyl O atoms of different sebacato ligands belonging to the same layer, while the remaining two participate in hydrogen bonds both to the non-coordinating carboxyl O atom and to the third water O atom ($d(\text{O}\cdots\text{O}) = 2.785\text{--}2.852$ Å, $\angle(\text{O}\text{--}\text{H}\cdots\text{O}) = 144^\circ\text{--}177^\circ$).

2.3. Structure of $[(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2](\text{HL})_2(\text{H}_2\text{L})(\text{H}_2\text{O})_4$ (**2**)

The crystal structure is composed of the centrosymmetric dinuclear $[(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2]^{2+}$ complex cations, twisted hydrogenesebacate anions, linear sebacic acid molecules and lattice H_2O molecules.

The dinuclear complex cations are generated from two $[\text{Cu}(\text{phen})_2]$ moieties bischelated by one 'Z' shaped sebacato ligand (Fig. 2). The Cu atoms are each octahedrally surrounded by four N atoms from two phen ligands and two O atoms from one carboxyl group of the bridging sebacato ligand to complete '4+1+1' coordination geometry with one pyridyl N atom and one carboxyl O atom at the apical positions. The basal Cu–O(3) bond length is 1.976 Å and the basal Cu–N bond distances fall in the range 2.014–2.044 Å. The axial Cu–N(4) and Cu–O(4) bond lengths are 2.241 and 2.692 Å, respectively. Two phen planes and the carboxyl plane around the Cu atom stand nearly perpendicularly to one another.

Within the crystal structure, the divalent complex cations are arranged so that the symmetry related phen ligands of the adjacent complex cations face antiparallel

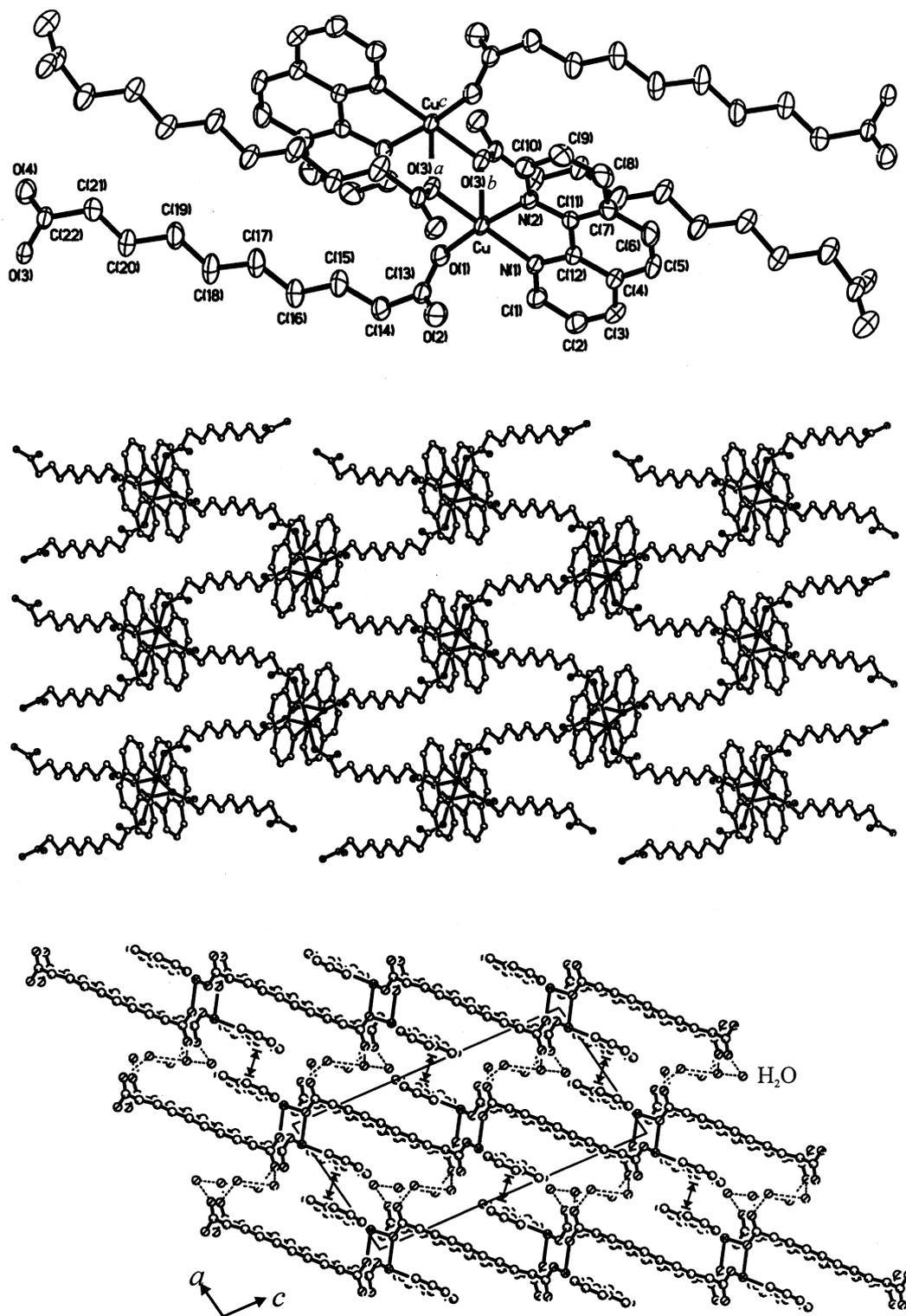


Fig. 1. (Top) ORTEP view of a selected subunit of the $2D_{\infty} [Cu_2(phen)_2L_{4/2}]$ layer with displacement ellipsoids (45% probability) and atomic labeling, (middle) a section of the $2D_{\infty} [Cu_2(phen)_2L_{4/2}]$ layer, and (bottom) supramolecular assembly of $2D_{\infty} [Cu_2(phen)_2L_{4/2}]$ layers with H_2O molecules in tunnels parallel to $[010]$ in **1**; the π - π stacking interactions and hydrogen bondings are indicated by double arrows and dashed lines, respectively.

to each other and the mean phen-to-phen distance of 3.43 \AA indicates strong intercationic π - π stacking interactions [44–49]. Through such interactions, the

complex cations are assembled into positively charged open networks extending infinitely parallel to (100) (Fig. 3).

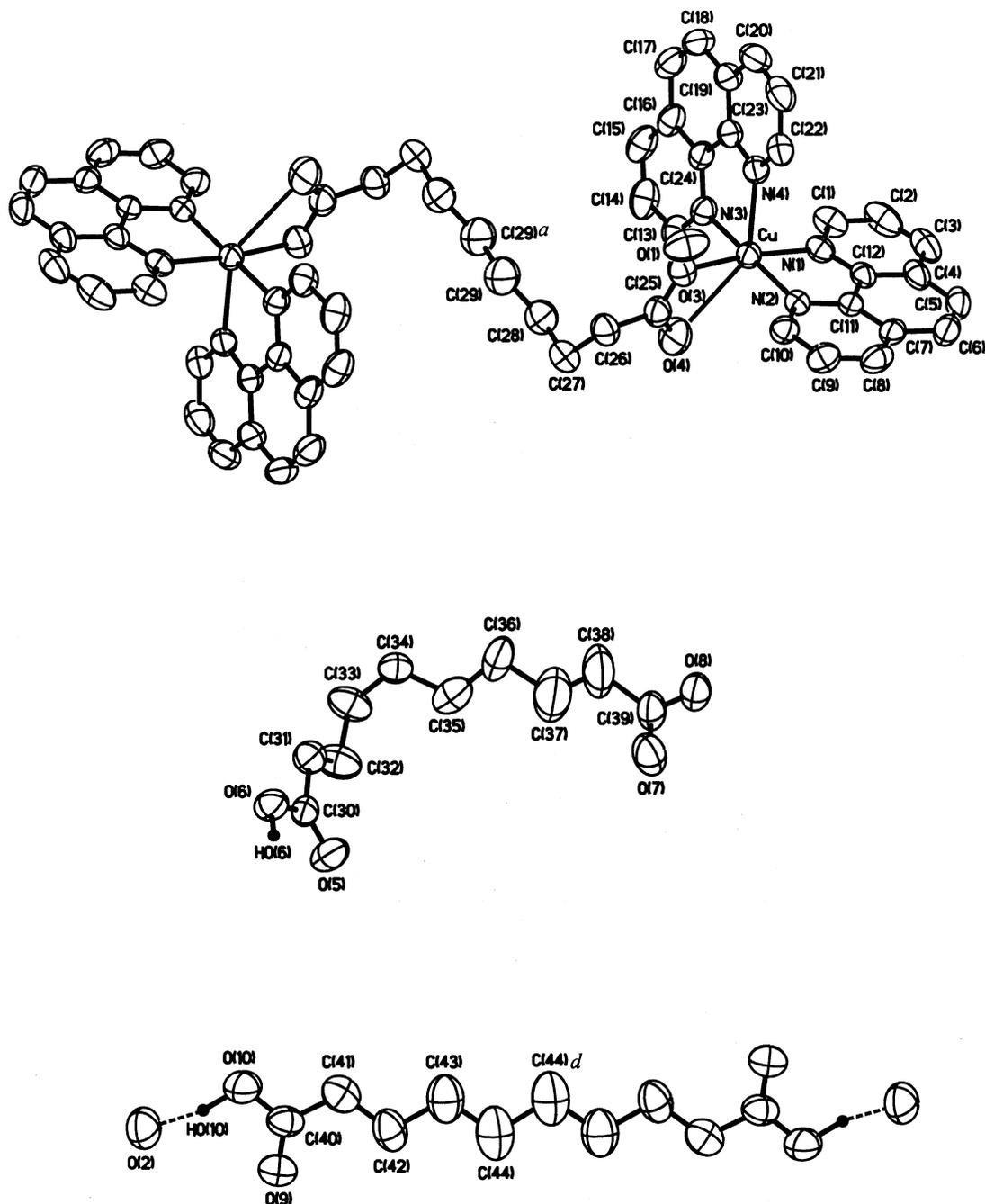


Fig. 2. ORTEP view of (top) divalent $[(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2]^{2+}$ complex cation, (middle) hydrogensebacate anion and (bottom) sebacic acid molecule in **2** with displacement ellipsoids (45% probability) and atomic labeling.

Along the $[100]$ direction, the twisted hydrogensebacate anions are linked into 1D zigzag chains via strong head-to-tail hydrogen bonds ($d(\text{O}(6)\cdots\text{O}(8)^b) = 2.562 \text{ \AA}$, $\angle(\text{O}(6)\text{--H}\cdots\text{O}(8)^b) = 166^\circ$, $b: x+1, y, z$). Additionally, the carboxylate group of the hydrogensebacate anion, via two carboxylate O atoms, is hydrogen bonded to two crystallographically distinct H_2O molecules (Table 2), of which one accepts hydroxyl hydrogen atom from the linear sebacic molecule to form a strong hydrogen bond with $d(\text{O}(10)\cdots\text{O}(2)) = 2.531 \text{ \AA}$ and \angle

$(\text{O}(10)\text{--H}\cdots\text{O}(2)) = 167^\circ$. Moreover, the H_2O molecules are hydrogen bonded to each other. Such extensive hydrogen bonds assemble the twisted hydrogensebacate anions, linear sebacic molecules and water molecules to form negatively charged open bilayers parallel to (001) . The resulting bilayers are held together by the interweaving of the positively-charged open networks (Fig. 4). Furthermore, the carboxylate O(3) strongly coordinated to Cu atom forms hydrogen bond to one water molecule, which is found important for the interdigita-

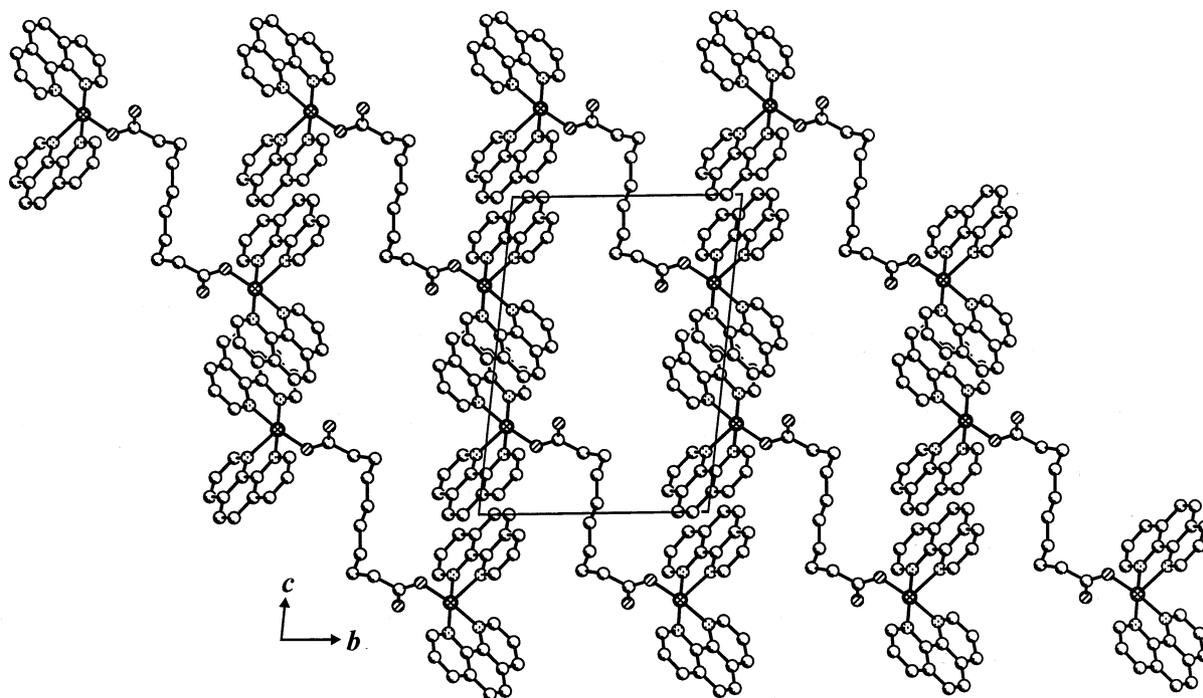


Fig. 3. Supramolecular assembly of the divalent $[(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2]^{2+}$ complex cations via π - π stacking interactions into 2D positively charged network in **2**.

tion of the negatively charged bilayers and the positively charged networks.

For the present 'Z' shaped twisted sebacato ligands, the C–O bond length to the coordinating O(3) atom is 1.272 Å, significantly longer than that to

the O(4) atom (1.224 Å), and the bite O(3)–C(25)–O(4) bond angle is 122.7(4)°. As far as the hydrogen-sebacate anions and sebacic acid molecules are concerned, all the C–C and C–O bond lengths are of normal values.

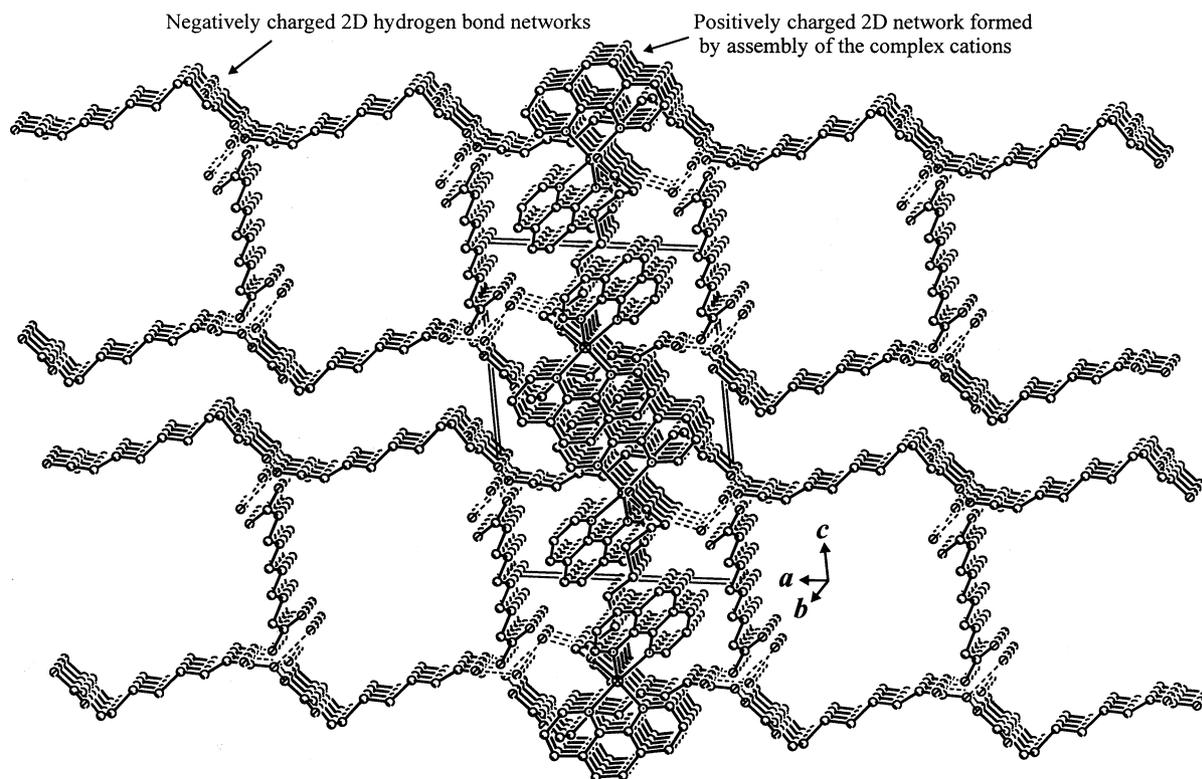


Fig. 4. Negatively charged 2D hydrogen bonded networks with the complex cations in **2**.

Comparison of the title complexes **1** and **2** with the previously-reported $[\text{Cu}(\text{phen})\text{L}]\cdot 3\text{H}_2\text{O}$ indicates that the sebacate anion is an interesting flexible ligand bridging Cu atoms in three modes, that is, (i) the 'L' shaped twisted sebacato ligands in $[\text{Cu}(\text{phen})\text{L}]\cdot 3\text{H}_2\text{O}$ bis-monodentately link Cu atoms into 1D chains which are assembled via π - π stacking interactions into supra-molecular bi-chains [42], (ii) the nearly linear sebacato ligands in **1** tridentately interlink Cu atoms into 2D open networks and (iii) the 'Z' shaped twisted sebacato ligand bis-chelate two Cu atoms to form dinuclear complex cations in **2**.

3. Experimental

All chemicals of p.a. grade were commercially available and used without further purification. The C, H and N microanalyses were performed with a Heraeus Rapid—CHNO elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Protege 460 spectrometer.

3.1. Preparation of $[\text{Cu}_2(\text{phen})_2\text{L}_{4/2}](\text{H}_2\text{O})_6$ (**1**)

Addition of 6.0 ml (1 M) NaOH to a stirred aqueous solution of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.43 g, 2.50 mmol) in 5.0 ml H_2O yielded a blue precipitate, which was separated, washed with distilled water several times until free from detectable Cl^- ions and finally added to a stirred solution of sebacic acid (0.51 g, 2.50 mmol) in 50 ml $\text{EtOH}/\text{H}_2\text{O}$ (1:1 v/v). To the resulting suspension was added phenanthroline monohydrate (0.50 g, 2.50 mmol). The mixture was further stirred for approximately 30 min and the insoluble solid was filtered off. The filtrate (pH = 6.4) was allowed to stand at room temperature. Slow evaporation for several days afforded a small amount of dark blue crystals. *Anal. Calc.* for $\text{C}_{44}\text{H}_{60}\text{Cu}_2\text{N}_4\text{O}_{14}$: C, 53.06; H, 6.07; N, 5.62. Found: C, 53.39; H, 5.98; N, 5.36%.

3.2. Preparation of $[(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2](\text{HL})_2(\text{H}_2\text{L})(\text{H}_2\text{O})_4$ (**2**)

An analogous procedure was employed except that 50 ml $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (1:1 v/v) was used instead of $\text{EtOH}/\text{H}_2\text{O}$. Blue crystals were formed in a blue filtrate (pH 6.4) by slow evaporation for several days. Yield: approximately 65%. *Anal. Calc.* for $\text{C}_{44}\text{H}_{60}\text{Cu}_2\text{N}_4\text{O}_{14}$: C, 61.26; H, 6.31; N, 6.50. Found: C, 60.83; H, 6.12; N, 6.89%. IR (cm^{-1}): 3410vs (br), 2929s, 2853s, 1570vs, 1515vs, 1426vs, 1302m, 1226m, 1146m, 1105m, 953vs, 724vs, 647m.

3.3. Crystal structure determination

The reflection intensities for complexes **1** and **2** were collected at 293 K on a Bruker P4 diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using the θ - 2θ scan technique. SHELXS-97 [50] and SHELXL-97 [51] programs were used for structure determination and refinements. The structures were solved by direct methods and refined with full-matrix least-squares techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms associated with carbon atoms were generated geometrically, while the aqua and hydroxyl hydrogen atoms were located from the difference Fourier syntheses. Details of crystal data, collection and refinement of the two

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

	1	2
Empirical formula	$\text{C}_{44}\text{H}_{60}\text{Cu}_2\text{N}_4\text{O}_{14}$	$\text{C}_{88}\text{H}_{108}\text{Cu}_2\text{N}_8\text{O}_{20}$
Formula weight	498.02	1724.90
Description	blue block	blue block
Crystal size (mm)	$0.47 \times 0.22 \times 0.18$	$0.36 \times 0.22 \times 0.22$
Temperature (K)	293(2)	293(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions		
<i>a</i> (\AA)	11.095(2)	11.746(1)
<i>b</i> (\AA)	10.199(1)	12.259(1)
<i>c</i> (\AA)	21.221(4)	16.338(2)
α ($^\circ$)		80.03(1)
β ($^\circ$)	101.26(1)	79.18(1)
γ ($^\circ$)		69.16(1)
Volume (\AA^3)	2355.1(7)	2145.0(4)
<i>Z</i>	2	1
D_{calc} (g cm^{-3})	1.405	1.335
$F(000)$	1044	910
Absorption coefficient (mm^{-1})	0.971	0.571
Absorption correction	empirical	empirical
Maximum and minimum transmission	0.499, 0.478	0.806, 0.755
θ Range ($^\circ$)	0.95–27.50	1.00–27.50
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Reflections collected	6926	11290
Independent reflections (R_{int})	5419 (0.0415)	9842 (0.0372)
Data/restraints/parameters	3755/0/316	5645/0/537
Goodness of fit on F^2	1.085	1.029
R_1, wR_2 [$I \geq 2\sigma(I)$] ^a	0.0506, 0.1229	0.0697, 0.1595
R_1, wR_2 (all data) ^a	0.0833, 0.1443	0.1340, 0.1950
<i>A, B</i> values in weighting scheme ^b	0.0778, 0.0000	0.0960, 0.4437
Extinction coefficient	0.010(1)	0.008(1)
Largest difference peak and hole (e \AA^{-3})	0.868, -0.706	0.693, -0.408

^a $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

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

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

${}^2_{\infty}[\text{Cu}_2(\text{phen})_2\text{L}_{4/2}](\text{H}_2\text{O})_6$ (1) ^a					
<i>Bond lengths</i>					
Cu–O(1)	1.944(2)	Cu–N(1)	2.020(2)	Cu–O(3) ^b	2.407(2)
Cu–O(3) ^a	1.963(2)	Cu–N(2)	2.035(2)		
<i>Bond angles</i>					
O(1)–Cu–O(3) ^a	90.5(1)	O(3) ^a –Cu–N(1)	174.7(1)	N(1)–Cu–O(3) ^b	106.3(1)
O(1)–Cu–N(1)	93.3(1)	O(3) ^a –Cu–N(2)	94.8(1)	N(2)–Cu–O(3) ^b	95.1(1)
O(1)–Cu–N(2)	174.3(1)	O(3) ^a –Cu–O(3) ^b	77.5(1)	Cu–O(3a)–Cu ^c	102.5(1)
O(1)–Cu–O(3) ^b	88.2(1)	N(1)–Cu–N(2)	81.3(1)		
$(\text{phen})_2\text{Cu}(\mu\text{-L})\text{Cu}(\text{phen})_2(\text{HL})_2(\text{H}_2\text{L})(\text{H}_2\text{O})_4$ (2) ^b					
<i>Bond lengths</i>					
Cu–O(3)	1.976(3)	Cu–N(2)	2.014(3)	Cu–N(4)	2.241(3)
Cu–N(1)	2.044(3)	Cu–N(3)	2.035(3)	Cu–O(4)	2.692(4)
<i>Bond angles</i>					
O(3)–Cu–N(1)	173.2(1)	N(1)–Cu–N(2)	81.4(1)	N(2)–Cu–N(3)	174.0(1)
O(3)–Cu–N(2)	93.3(1)	N(1)–Cu–N(3)	94.0(1)	N(2)–Cu–N(4)	105.2(1)
O(3)–Cu–N(3)	91.0(1)	N(1)–Cu–N(4)	93.7(1)	N(2)–Cu–O(4)	93.3(1)
O(3)–Cu–N(4)	91.8(1)	N(1)–Cu–O(4)	122.4(1)	N(3)–Cu–N(4)	78.9(1)
O(3)–Cu–O(4)	53.3(1)	N(1)–Cu–O(4)	141.8(1)	N(3)–Cu–O(4)	85.8(1)
<i>Hydrogen bonding contacts</i>					
D–H···A	D–H	H···A	D···A	D–H···A	
O(1)–H(AO1)···O(8) ^b	0.661	2.222	2.879	173	
O(1)–H(BO1)···O(3)	0.965	1.886	2.822	163	
O(2)–H(AO2)···O(1) ^c	0.866	2.040	2.851	155	
O(2)–H(BO2)···O(7)	0.767	1.933	2.664	159	
O(6)–H(O6)···O(8) ^b	0.875	1.703	2.562	166	
O(10)–H(O10)···O(2)	1.083	1.465	2.531	167	

^a Symmetry codes: (a) $-x-1/2, y+1/2, -z+1/2$; (b) $x+1/2, -y+3/2, z-1/2$; (c) $-x, 2-y, -z$.

^b Symmetry codes: (a) $-x+1, -y+1, -z+2$; (b) $x+1, y, z$; (c) $x-1, y, z$; (d) $-x, -y+3, -z+2$.

complexes are summarized in Table 1, while selected interatomic distances and bond angles are listed in Table 2.

4. Supplementary data

Supplementary data for the two structures are available upon request quoting the deposition numbers CCDC 169477 and CCDC 169478 for **1** and **2**, respectively, from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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