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PAPER

Varying structural motifs in oxyanions (NO_3^- , CO_3^{2-}) and phenoxyacetate (PhOAc^-) bridged coordination polymers derived from alkoxy-bridged dicopper building blocks with $\{\text{Cu}_2\text{O}_2\}$ core†

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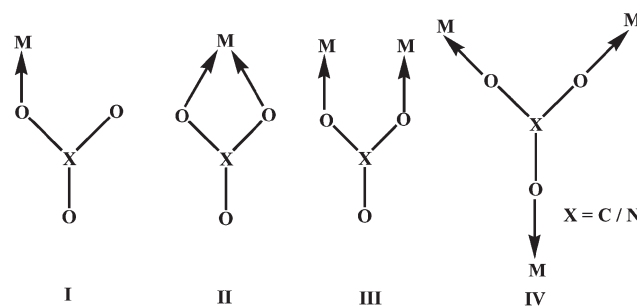
The oxyanions (NO_3^- , CO_3^{2-}) and phenoxyacetate (PhOAc^-) bridged three 1D-coordination polymeric chains, $\{[\text{Cu}_2(\mu\text{-hep})_2(\mu\text{-NO}_3)]_2\}_n$ (**1**), $\{[\text{Cu}_2(\mu\text{-hep})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}(\mu\text{-CO}_3)\}_n$ (**3**) and $\{[\text{Cu}_2(\mu\text{-hep})_2(\mu\text{-PhOAc}^-)]_2\}_n$ (**2**) (hep-H = 2-(2-hydroxyethyl)pyridine) have been synthesized. In **1–3** the alkoxide bridged dicopper building units, $[\text{Cu}(\mu\text{-hep})]_2$ with Cu_2O_2 core, are linked *via* the respective anions. Detailed structural analysis reveals that in **1** or **2**, two units of NO_3^- (**1**) or PhOAc^- (**2**), respectively, bind with the four copper ions in two adjacent alkoxide bridged dimeric units in *head-to-head* and *tail-to-tail* fashion and the same binding mode continues along the polymeric chain. This in effect yields a 12-membered metallacyclic ring in between two dimeric core units. However, in **3** only one CO_3^{2-} group bridges the two copper centres associated with the two neighbouring alkoxide bridged dimeric units in *head-to-tail* mode which in turn forms a *zig-zag* polymeric chain. Two coordinated and two lattice water molecules from two adjacent polymeric layers in the structure of **3** form water tetramers. Furthermore, the interaction of water tetramer with the uncoordinated $\text{C}=\text{O}$ group of the bridging CO_3^{2-} develops an additional *zig-zag* chain which is being trapped between the two outer *zig-zag* coordination polymeric chains in **3**. The polymeric chains in **1–3** further develop a 2D-network pattern *via* an extensive non-covalent hydrogen bonding as well as $\text{C-H}\cdots\pi$ and $\pi\cdots\pi$ interactions.

Introduction

A convenient practice for fabrication of metal complex derived coordination polymeric materials is to use suitable bridging ligands or spacers such as pyrazine,¹ bis(4-pyridyl) derivatives: 4,4'-bipyridyl,² bis-(4-pyridyl)ethylene,³ bis(4-pyridyl)ethane,⁴ *trans*-4,4'-azo-pyridine⁵ and carboxylate groups.⁶ Previous investigations have also established that the oxyanions, such as sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), vanadate (VO_4^{3-}) and molybdate (MoO_4^{2-}), can effectively interconnect the primary building units in coordination polymeric chains.⁷

Oxyanions such as nitrate (NO_3^-) and carbonate (CO_3^{2-}) are known to be versatile in nature. At the discrete molecular level they can function either as charge compensating counter anions⁸ in metal complexes, or can bind to the metal ion as simple monodentate (**I**)/bidentate (**II**) ligands¹⁰ or can hold two (**III**) or

three metal ions (**IV**).¹¹ On the other hand, phenoxyacetate (PhOAc^-) can only bind with one or two metal ions as shown in **I** and **III**.^{9e,f,11g,h}



The use of NO_3^- ,¹² PhOAc^- ,¹³ CO_3^{2-} ,^{2–14} as bridging units in the construction of extended networks based on copper complexes is also attractive because of the built in flexibility of such anions and this indeed leads to unique molecular frameworks which are established to be useful as novel materials for catalytic¹⁵ and magnetic applications.¹⁶

The present work originates from our interest in designing newer classes of coordination polymeric frameworks of copper by using selective anions: NO_3^- , PhOAc^- or CO_3^{2-} , as effective inter-connectors between the rather rare alkoxy-bridged dicopper

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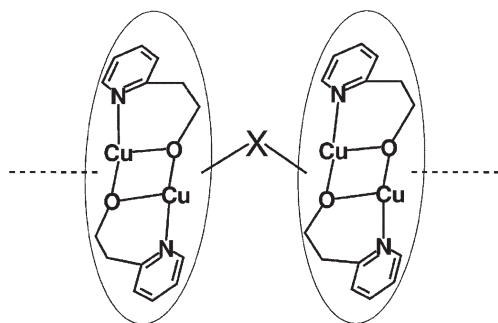
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based building units $[\text{Cu}(\mu\text{-hep}^-)]_2$ (**A**) (hep-H = 2-(2-hydroxyethyl)pyridine).¹⁷ This approach has led to the formation of varying coordination polymeric motifs in **1**, **2** and **3**, where the bridging anions link to the same dimeric building blocks, **A**, in different fashions along the polymeric chain.



$\text{X} = \text{NO}_3^-$ (**1**), PhOAc^- (**2**) and CO_3^{2-} (**3**)

A

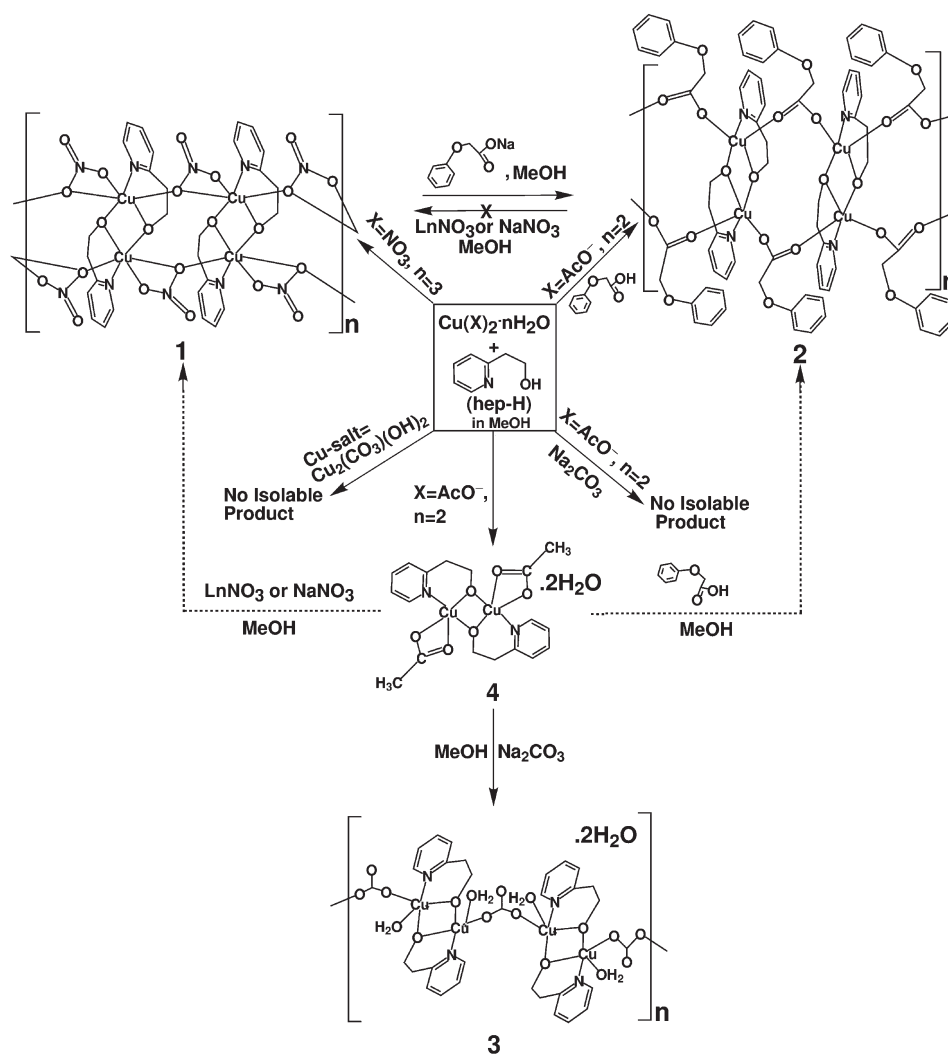
It should be noted that to the best of our knowledge no report is available so far on the PhOAc^- and CO_3^{2-} bridged Cu_2O_2

building block derived coordination polymeric chains, for example in **A**. Only two examples, $[\text{Cu}_4(\text{L})(\text{OMe})_3(\text{NO}_3)_2(\text{H}_2\text{O})]_n$ ($\text{L} = [1,3\text{-bis}(3\text{-oxo-3-phenylpropionyl)-2-hydroxy-5-methylbenzene}]$)¹⁸ and $[\text{Cu}(\text{ap})\text{NO}_3]_2$ ($\text{ap} = 3\text{-amino-1-propanol}$)¹⁹ are available in the literature where the Cu_2O_2 building units are bridged by the NO_3^- group yielding the coordination polymeric chain.

Results and discussion

Synthesis and characterisation

The nitrate (NO_3^-) bridged coordination polymer (**1**) has been synthesized by the reactions of 2-(2-hydroxyethyl)pyridine (hep-H) with a methanolic solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ at 298 K (Scheme 1). The phenoxyacetate ($\text{Ph-O-CH}_2\text{COO}^- = \text{PhOAc}^-$) bridged polymeric **2** has been synthesized from a methanolic solution of a mixture of copper acetate dihydrate, hep-H and phenoxyacetic acid at 298 K by the replacement of the acetate group attached to the precursor copper complex by the bulkier phenoxyacetate group (Scheme 1). However, the similar reaction of copper acetate dihydrate with the hep-H ligand in MeOH at 298 K but in the absence of phenoxyacetic acid was reported to result in a discrete dimeric complex $[(\text{AcO}-)\text{Cu}(\mu\text{-hep}^-)]_2$ ($\text{AcO}^- = \text{acetate}$) (**4**)



Scheme 1

Table 1 Selected crystallographic parameters of **1–3**

	1	2	3
Empirical formula	C ₇ H ₈ N ₂ O ₄ Cu	C ₁₅ H ₁₅ NO ₄ Cu	C ₁₅ H ₂₄ N ₂ O ₉ Cu ₂
Formula weight	247.69	336.82	503.44
Crystal symmetry	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	13.5980(5)	4.794(5)	18.0701(7)
<i>b</i> /Å	4.7885(2)	24.697(5)	6.6051(3)
<i>c</i> /Å	14.5449(8)	11.500(5)	15.6456(7)
<i>α</i> /°	90	90	90
<i>β</i> /°	112.389(5)	93.631(5)	104.807(4)
<i>γ</i> /°	90	90	90
<i>V</i> /Å ³	875.69(7)	1358.8(16)	1805.37(13)
<i>Z</i>	4	4	4
<i>μ</i> /mm ⁻¹	2.482	1.622	2.410
<i>D</i> /g cm ⁻³	1.879	1.646	1.852
<i>F</i> (000)	500	692	1032
<i>θ</i> range/°	3.03 to 24.98	3.30 to 25.00	3.08 to 25.00
Reflections collected/unique	5299/1539 [<i>R</i> (int) = 0.0160]	4222/4222 [<i>R</i> (int) = 0.0000]	7817/1595 [<i>R</i> (int) = 0.0478]
Data/restraints/parameters	1539/0/127	4222/0/196	1595/0/144
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0199, 0.0529	0.0450, 0.1118	0.0412, 0.0913
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0226, 0.0539	0.0601, 0.1192	0.0546, 0.0972
GOF	1.090	1.098	0.985
largest diff. peak and hole/e Å ⁻³	0.319 and -0.265	0.425 and -0.711	2.615 and -0.462

(Scheme 1) instead of a polymeric material as in **2**. Thus, a drastic change in molecular framework, dimeric form in **4** to polymeric form in **2**, is observed on simple switching from the lighter acetate group to the bulkier phenoxyacetate (PhOAc⁻) group. In **1** and **2**, hep⁻ bridged parent dimeric copper units [Cu(μ-hep)]₂ are interconnected by the respective anions along the polymeric chain in *head-to-head* and *tail-to-tail* modes (Scheme 1). The hep⁻ derived dimeric building unit in **1** or **2** is stabilised by the central Cu₂O₂ core as in the discrete dimeric structure of **4**. In contrast, the reaction of commercially available copper carbonate hydroxide (Cu₂(CO₃)·2OH) and hep-H ligand or copper acetate dihydrate, hep-H ligand and sodium carbonate failed to yield any isolable product. Therefore, an alternative synthetic route was explored to synthesize the corresponding carbonate bridged polymeric species. Since in **1** and **2** the dimeric [Cu(μ-hep)]₂ units are essentially interconnected by anions (Scheme 1), therefore the recently reported hep⁻-bridged dimeric complex, [(OAc)Cu(μ-hep)₂Cu(OAc)]·2H₂O (**4**), was reacted with Na₂CO₃ in methanol at 298 K. This indeed resulted in the desired carbonate bridged coordination polymeric complex **3** where the same dimeric building units, [Cu(μ-hep)]₂, are linked through the CO₃²⁻ groups. Though in **1** or **2** the adjacent two dimeric copper units, [Cu(μ-hep)]₂, are connected by two units of NO₃⁻ or PhOAc⁻ in *head-to-head* and *tail-to-tail* modes, in **3** only one CO₃²⁻ group bridges between the neighbouring dimeric building blocks in *head-to-tail* fashion (Scheme 1). Moreover, unlike **1** and **2**, in **3** one water molecule is bonded to each copper ion in the dimeric unit and there are two lattice water molecules (see later). However, the reaction of **4** with the Ln(NO₃)₃ or NaNO₃ and phenoxyacetic acid results in NO₃⁻ and PhOAc⁻ bridged polymeric frameworks as in **1** and **2**, respectively, instead of the framework analogous to **3** (Scheme 1).

In addition, **1** can readily be transformed to **2** in the presence of the sodium salt of phenoxyacetate, however, the reverse process, **2** → **1** in the presence of Ln(NO₃)₃ or NaNO₃ surprisingly failed to occur altogether. On the other hand the interconversion of **3** → **1** or **2** by using Ln(NO₃)₃/NaNO₃ or the

sodium salt of phenoxyacetate, respectively, and the reverse process of the synthesis of **3** from **1** or **2** by using Na₂CO₃, failed.

The detailed structural characterisations of **1–3** reveal that the complexes exhibit 1D-coordination polymeric features but with different modes of connectivity along the extended polymeric frameworks based on the bridging anions (see later).

The complexes exhibit satisfactory microanalytical data. The IR spectra of the complexes show characteristic vibrations. The presence of lattice and coordinated water molecules in **3** has been evidenced by strong IR bands near 3400 cm⁻¹ (see Experimental section).

Structural aspects

The coordination polymeric structures of **1–3** have been established by their single crystal X-ray structures. Selective crystallographic parameters and bond distances/angles are listed in Table 1 and Table 2, respectively.

{[Cu₂(μ-hep)₂(μ-NO₃)₂]_n (**1**). The nitrate (NO₃⁻) bridged coordination polymeric complex {[Cu₂(μ-hep)₂(μ-NO₃)₂]_n (**1**)

Table 2 Selected bond lengths (Å) and angles (°) for **1–3**

Bond length (Å)/Bond angle (°)	1	2	3
Cu1–Cu1#1	2.9650(5)	3.0057(15)	3.060(6)
Cu1–O1	1.9166(14)	1.940(3)	1.918(3)
Cu1–O1#	1.9283(13)	1.930(3)	1.941(3)
Cu1–O2	2.0123(14)	1.988(3)	1.954(3)
Cu1–O3/O111 ^a	2.3953(14)	2.349(3)	2.449(1)
Cu1–N1	1.9771(17)	1.997(3)	2.020(3)
Cu(1)–O(1)–Cu(1)#1	100.91(6)	101.88(13)	104.94(12)
O(1)–Cu(1)–O(1)#1	79.09(6)	78.12(13)	75.06(12)
O(1)–Cu(1)–N(1)	91.91(6)	90.45(13)	93.01(12)
O(1)#1–Cu(1)–N(1)	170.79(6)	168.11(12)	167.23(13)
O(3)–C(8)–O(2)	—	124.7(4)	—
O–X–O	117.63(16)	—	116.3(5)

^a Cu–O111 in the case of **3**.

crystallises in the monoclinic $P2_1/n$ space group with a crystallographically imposed inversion centre. The asymmetric unit consists of one Cu ion, bonded with the nitrogen and alkoxide donors of the bridging hep⁻. The other two vacant sites around the Cu ion are occupied by one monodentate and one bridging oxygen atoms of adjacent two NO₃⁻ groups. The monomeric copper centre in the asymmetric unit forms a dimer *via* the bridging alkoxide groups of hep⁻ ligands. The infinite 1D chain of **1** (Fig. 1a) is formed *via* the linkage of the alkoxide bridged (hep⁻) dimeric building units by the nitrate function where the two oxygen atoms of NO₃⁻ participate in the chain forming process leaving the non-coordinated third oxygen for the further H-bonding networking (Fig. 1c). In **1** the adjacent dicopper based $\{[\text{Cu}(\mu\text{-hep}^-)]_2\}$ two building units are connected by two NO₃⁻ groups in *head-to-head* and *tail-to-tail* modes. The two oxygen atoms of the bridging NO₃⁻ group bind differently with the Cu ions in the neighbouring dicopper based building units $\{[\text{Cu}(\mu\text{-hep}^-)]_2\}$: while one oxygen atom of the NO₃⁻ bridges between the two copper centres of the adjacent two dimers, the other oxygen donor specifically binds with the single copper centre as shown in **Form B** and the same pattern repeats along

the chain of **1** (Fig. 1a). It may be noted that the NO₃⁻ group is generally known to connect the neighbouring copper centres in either discrete polynuclear or polymeric complexes as shown in **Form C** where two oxygen donors of NO₃⁻ link with two copper centres independently.²⁰ Though the alternate binding mode of NO₃⁻ *i.e.* **Form B** as appears in **1**, has been reported earlier in a few discrete copper complexes,²¹ only one polymeric copper system, *catena*-((μ₂-nitrate)-(μ₂-tetrakis(pyrazolyl)borate)-aqua-(nitrate-*O,O*)-(nitrate-*O*)-dicopper(II)) with NO₃⁻ group in **Form B** bridging mode is known so far.²²

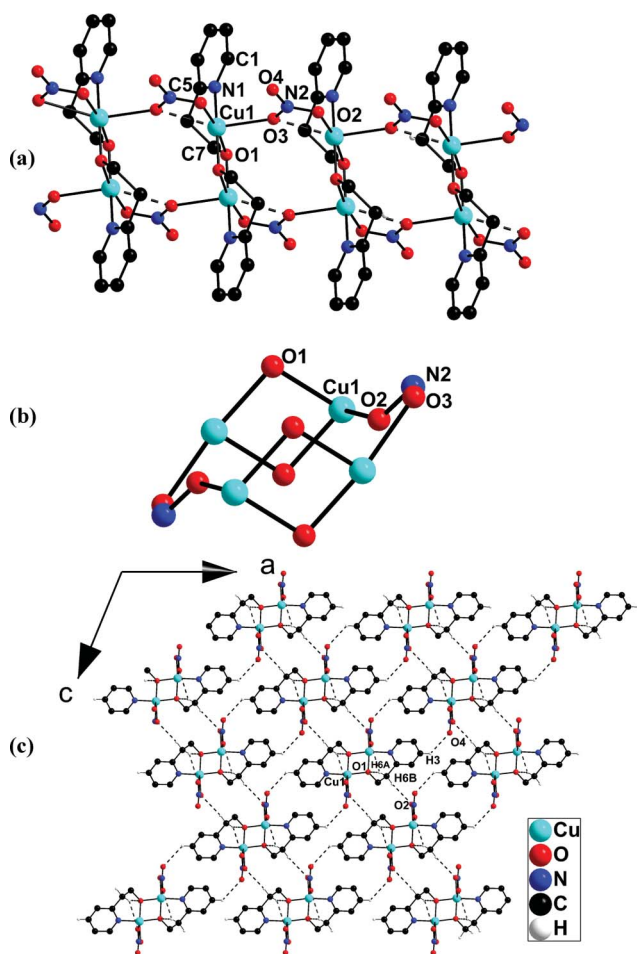
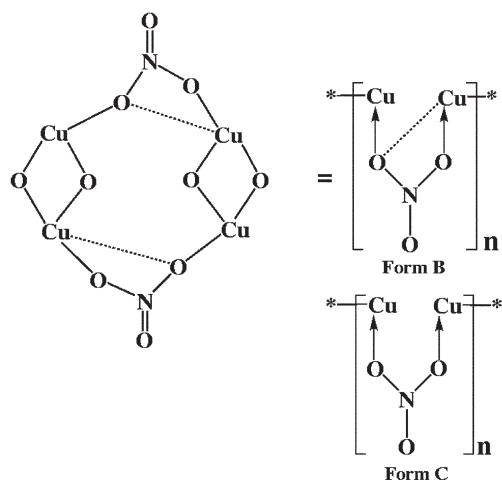


Fig. 1 (a) Perspective view of the 1D-coordination polymeric chain in **1**. (b) The formation of a 12-membered metallacyclic ring in between the nitrate bridged neighbouring dimeric building units which appears like a chair with two handles. (c) Packing diagram of the hydrogen bonded 2D-network in **1** along the *b*-axis.



The Cu(1)⋯Cu(1A)# distance and the Cu(1)–O(1)–Cu(1A)# angle of the central Cu₂O₂ core in the dimeric building unit $\{[\text{Cu}(\mu\text{-hep}^-)]_2\}$ in **1** are 2.9650(5) Å and 100.91(6)°, respectively. The other distances associated with the copper-hep⁻ unit in the dimeric building block *i.e.* Cu–N and Cu–O(bridging hep⁻) distances are 1.9771(17) and 1.9166(14)/1.9283(13) Å, respectively, which match fairly well with the earlier reported hep⁻-derived discrete dimeric complex $\{[\text{Cu}(\mu\text{-hep}^-)(\text{OAc}^-)]_2\}$ (**4**).^{17b}

Each Cu(II) ion along the chain is in distorted octahedral arrangement with CuNO₅ configuration, where the basal plane is composed of one nitrogen and two bridging oxygen donors from the bidentate hep⁻ ligands and one monodentate oxygen atom of the NO₃⁻ group and the axial positions are occupied by the two bridging oxygen atoms from two NO₃⁻ groups. The Cu–O axial distances along the polymeric chain in **1** are alternately long and short, 2.616(12) and 2.3953(14) Å, respectively. The Cu–O distances involving the NO₃⁻ group, Cu–O (bridging) and Cu–O (monodentate) are 2.3953(14)/2.616(12) and 2.0123(14) Å, respectively.

If the longer Cu–O(3) (NO₃⁻) distance of 2.616(12) Å in **1** is ignored then a 12-membered ring which apparently looks like a chair with two arms can be considered to form between the nitrate bridged neighbouring dimeric building units (Fig. 1b).

The packing diagram of the 1D polymeric chain of **1** exhibits intramolecular and intermolecular C–H⋯O hydrogen bonds (Fig. 1c, Table 3). The intramolecular C–H⋯O hydrogen bonding involves an α-CH₂ group of the hep⁻ ligand and the alkoxy bridged oxygen atom O1 associated with the dimeric building unit and the same continues along the polymeric chain. The intermolecular C–H⋯O hydrogen bond reveals that each layer is connected to two adjacent layers *via* two different types of hydrogen bonds involving: (i) non-coordinated oxygen atom

Table 3 Hydrogen bonding parameters (Å, °) for **1–3**^a

D–H···A	H···A	D···A	D–H···A
1			
C3–H3···O4#1	2.675(2)	3.341(3)	127.60(5)
2			
C3–H3···O4#1	2.525(3)	3.342(5)	144.10(3)
3			
O111–H444···O222#1	2.342(1)	2.869(5)	122.42(12)
O222–H111···O2#1	2.003(1)	2.771(4)	166.44(21)
O222–H111···O111#1	2.784(6)	2.869(5)	88.19(80)
O111–H333···O222#2	1.928(3)	2.774(5)	169.62(40)
O222–H222···O3#3	1.789(3)	2.749(5)	166.60(87)

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

O(4) of the bridging NO₃[−] and the hydrogen atom H(3) of the coordinated pyridine ring of hep[−] ligand and (ii) α-CH₂ hydrogen atom and monodentate oxygen atom of the bridging NO₃[−] group leading to the formation of a hydrogen bonded 2D network. The distance between the two adjacent layers in the 2D network is 9.26 Å.

{[Cu₂(μ-hep)₂(μ-PhOAc[−])₂]_n} (2). The phenoxyacetate bridged polymeric complex {[Cu₂(μ-hep)₂(μ-PhOAc[−])₂]_n} (**2**) crystallises in the monoclinic *P*2₁/*n* space group with a crystallographically imposed inversion centre. The asymmetric unit consists of one Cu, which is bonded with the nitrogen donor and the bridging alkoxide group of the hep[−] ligand. The other two vacant sites of the Cu ion are occupied by the two monodentate phenoxyacetate groups (PhOAc[−]). The Cu ions in the basic dimeric unit are further connected with the copper ions of the neighbouring dimeric units on either side through the pendant oxygen donors of the two phenoxyacetate functions which yields a 1D coordination polymeric chain of **2** (Fig. 2a). Along the polymeric chain the building dimeric units are connected in *head-to-head* and *tail-to-tail* fashion via the mediation of the bridging PhOAc[−] as in **1**.

Unlike the bridging NO₃[−] group in **1**, the bridging PhOAc[−] function in **3** binds with the two Cu ions associated with the adjacent dimeric blocks exclusively as a monodentate ligand, **Form C**. However, the **Form B** bridging mode of PhOAc[−] has been reported in one hexameric copper complex, hexakis((μ₂-phenoxyacetato-*O,O',O''*)-(μ₂-phenoxyacetato-*O,O'*)-copper(II)).²³ Each Cu^{II} ion in **2** is therefore exhibiting the penta-coordinated CuO₄N configuration with square pyramidal geometry, where the basal plane is composed of one nitrogen and two bridging oxygen donors from the bidentate hep[−] ligands and one monodentate oxygen atom of the PhOAc[−] group and the axial position is occupied by the one bridging oxygen atom of another PhOAc[−] group. The separation between the two copper atoms in the central basic dimeric unit Cu(1)···Cu(1A)# of 3.005(2) Å and the Cu(1)–O(1)–Cu(1A) angle of 101.88(3)° are within the range reported for the analogous compounds containing a Cu₂O₂ core.^{14a,17}

The PhOAc[−] linked two adjacent basic hep[−] bridged dimeric units form a 12-membered metallacyclic ring which resembles a chair with two arms (Fig. 2b).

The back and leg-rest fragments in the chair form of the 12-membered metallacyclic part in **1** and **2** show slightly different angular arrangements (Fig. 1b and 2b). The torsion angle in **1**,

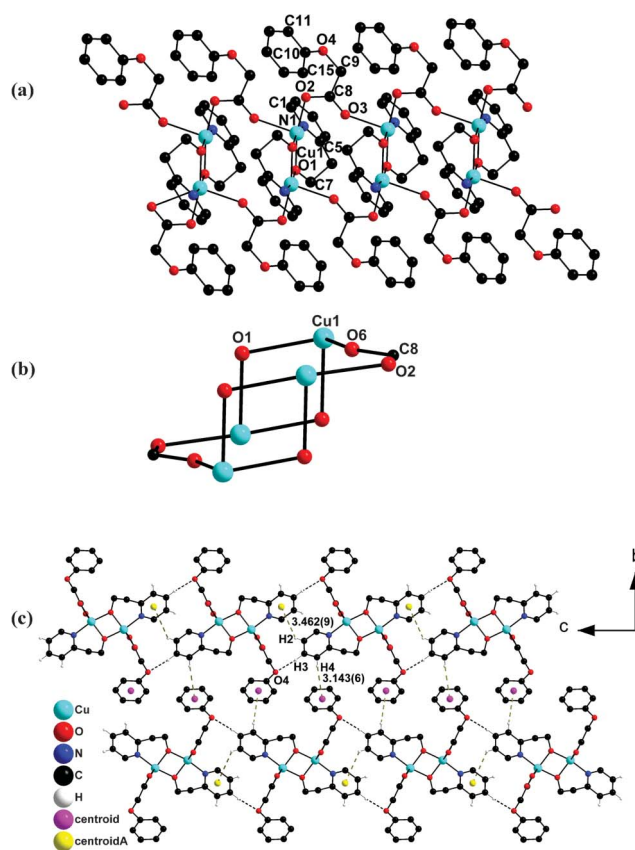


Fig. 2 (a) Perspective view of the 1D-coordination polymeric chain in **2**. (b) The formation of a 12-membered metallacyclic ring between the phenoxyacetate bridged neighbouring dimeric building units which appears like a chair with two handles. (c) Packing diagram showing the formation of a 2D network in **2** along the *a*-axis.

consisting of Cu1 O3 N2 O2, of 164° is in semi-bent conformation whereas that in **2** is almost in linear form: Cu1 O3 C8 O2 of 175°.

It should be stated that the formation of such a large ring (12-membered, Fig. 1b and 2b) due to the *head-to-head* and *tail-to-tail* binding modes of the bridging NO₃[−] or PhOAc[−] group with the adjacent dicopper building units in **1** or **2** has not been reported earlier in other NO₃[−] or PhOAc[−] bridged polymeric copper complexes.

The packing diagram of **2** reveals the existence of intermolecular strong hydrogen bonding between the adjacent layers of the polymeric unit of **2** involving C(3)–H(3) of the pyridine ring of the coordinated hep[−] in one layer and the oxygen atom (O4) of the bridging phenoxyacetate group in the next layer with H(3)···(O4) = 2.525 Å and C(3)–H(3)···(O4) = 144.10° (Fig. 2c, Table 3). Unlike **1**, the packing diagram of **2** shows C(2)–H(2)···π supramolecular interaction between pyridine rings of hep[−] ligands in two adjacent layers with edge to face orientation of *d* = 3.462(9) Å, *A* = 104.97(4)° and C(4)–H(4)···π interaction between the pyridine ring of hep[−] ligand in one layer and the benzene ring of the phenoxyacetate group in the adjacent layer with an edge to face orientation of *d* = 3.143(6) Å, *A* = 166.24(4)°. These indeed result in a 2D network (Fig. 2c) and the distance between the adjacent layers in the 2D network is 8.608 Å.

$\{[\text{Cu}_2(\mu\text{-hep})_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}(\mu\text{-CO}_3)\}_n$ (**3**). Unlike the nitrate (**1**) or phenoxyacetate bridged (**2**) coordination polymeric species, in the 1D-polymeric chain of $\{[\text{Cu}_2(\mu\text{-hep})_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}(\mu\text{-CO}_3)\}_n$ (**3**) only one CO_3^{2-} group is found to bridge between the neighbouring two parent dimeric core units, $\{\text{Cu}_2(\mu\text{-hep})_2\}$ in *head-to-tail* fashion (Fig. 3a). During the transformation of dimeric $[(\text{AcO}^-)\text{Cu}(\mu\text{-hep}^-)]_2$ ($\text{AcO}^- = \text{acetate}$) (**4**) to polymeric $\{[\text{Cu}_2(\mu\text{-hep})_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}(\mu\text{-CO}_3)\}_n$ (**3**) the bidentate acetate group attached to each Cu ion in **4** gets substituted by one water molecule and one monodentate CO_3^{2-} group keeping the parent Cu_2O_2 core of **4** unaltered. Moreover, the two water molecules and two CO_3^{2-} groups attached to two Cu centres in the building dimeric unit in **3** are mutually in *trans* orientation leading to a *zig-zag* pattern of the polymeric chain (Fig. 3a).

3 crystallises in the monoclinic $C2/c$ space group with a crystallographically imposed inversion centre (Tables 1 and 2). Each dimeric unit in the carbonate bridged polymeric **3** *i.e.* $\{[\text{Cu}_2(\mu\text{-hep})_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}(\mu\text{-CO}_3)\}_n$ consists of two coordinated water molecules *trans* to each other, and also two lattice water molecules. Each Cu(II) ion in the dimeric unit is in a penta-coordinated (CuO_4N) environment with the equatorial plane occupied by two μ -alkoxide oxygen atoms, one pyridine nitrogen of the bidentate hep^- ligand and one oxygen donor of the bridging carbonate group. The axial position is occupied by the water molecule resulting in a distorted square pyramidal geometry with the built-in Jahn–Teller distortion (Table 2).

As in **1** and **2** the dimeric core structure $\{[\text{Cu}(\mu\text{-hep}^-)]_2\}$ in the polymeric array in **3** is essentially stabilised by the presence of a central four-membered planar Cu_2O_2 ring with $\text{Cu}\cdots\text{Cu}$ distance of 3.060(6) Å. The carbonate group in **3** bridges between the two copper centres, each in adjacent dimeric building units, $\{\text{Cu}_2(\mu\text{-hep}^-)_2(\text{H}_2\text{O})_2\}$ in *head-to-tail* mode through the two oxygen atoms of the carbonate groups leaving the third oxygen

atom free as in **Form A** which however involves strong hydrogen bonding interactions with the lattice water molecules (see later).

The packing diagram of polymeric complex **3** reveals the presence of inter-molecular $\text{O}\cdots\text{H}\cdots\text{O}$ and $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds as well $\text{C}\cdots\text{H}\cdots\pi$ interactions. The hydrogen atoms associated with the two lattice water molecules and two coordinating water molecules from two adjacent layers of the *zig-zag* coordination polymer of **3** yield a water tetramer (uudd) along the *b*-axis (Fig. 3b, Table 3). The water tetramer along with the associated two hydrogen atoms in turn forms a six-membered chair like conformation. The water tetramers are further linked with the coordinated and uncoordinated 'O' atoms of the bridging CO_3^{2-} groups in two adjacent layers which eventually forms a six-membered ring (Fig. 3b).

Remarkably, the two lattice water molecules (O222), alternate coordinated water molecules (O111) and uncoordinated 'O' atoms (O3) of the bridging CO_3^{2-} group collectively generate an additional 1D *zig-zag* chain which is being trapped within the two outer *zig-zag* coordination polymeric chains of **3** (Fig. 4a,b).

Moreover, along the *a*-axis each of those layers (stated above) is further extended through $\text{C}\cdots\text{H}\cdots\text{O}$ and $\text{C}\cdots\text{H}\cdots\pi$ interactions involving the hydrogen atom H2 of the pyridine ring of hep^- from one layer to the coordinated water molecule in another layer ($\text{C}\cdots\text{H}_2\cdots\text{O111}$) and the same hydrogen atom (H2) is also simultaneously involved in the $\text{C}\cdots\text{H}\cdots\pi$ interaction leading to the formation of a 2D network (Fig. 4c).

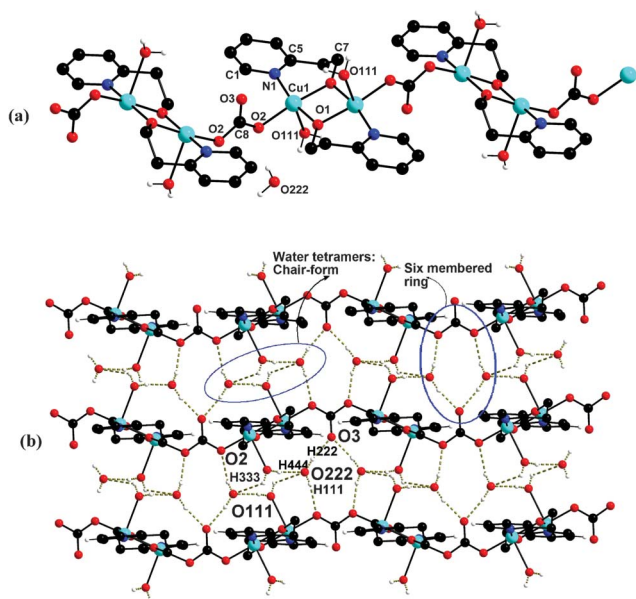


Fig. 3 (a) Perspective view of the 1D-coordination polymeric chain in **3**. (b) The formation of hydrogen bonded water tetramers and six-membered rings.

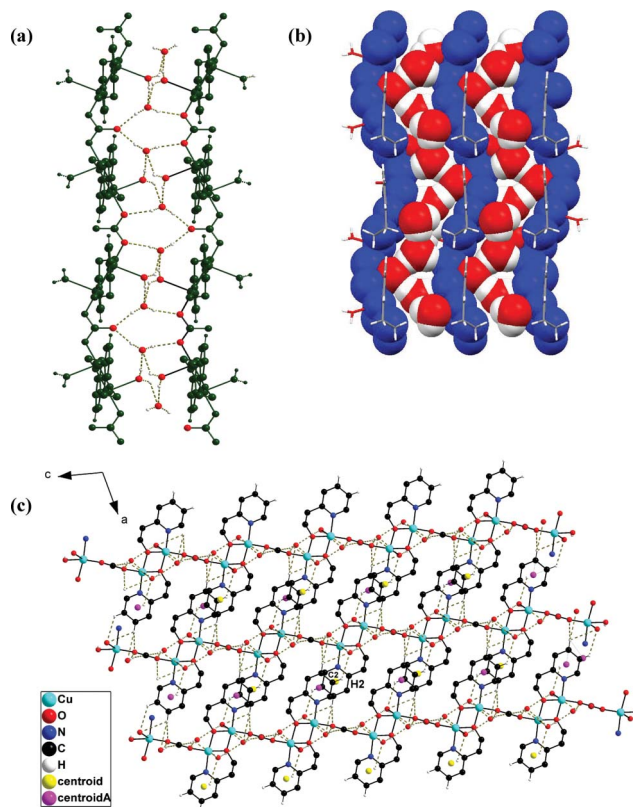


Fig. 4 (a) The hydrogen bonded *zig-zag* chain of oxygen atoms of water tetramers and uncoordinated CO_3^{2-} groups (red) in between two *zig-zag* chains of the outer coordination polymers (green). (b) Space filling model of (a). (c) Packing diagram shows the formation of a 2D network in **3** along the *b*-axis.

Thermal analysis

The DTA (differential thermal analysis) of compound **3** exhibits three absorption peaks at 61 °C, 316 °C, and 453 °C. The first weight loss of 3.8% (calcd: 3.57%) in TGA (thermogravimetric analysis) takes place between 35 and 48 °C corresponding to the loss of one lattice water molecule per formula unit, $\{[\text{Cu}_2(\mu\text{-hep})_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}(\mu\text{-CO}_3)\}_n$. The second weight loss of 17.13% (calcd: 17.46%) in the range of 48 to 82 °C accounts for the loss of two CO_2 per formula unit and the weight loss of 53.40% (calcd: 52.49%) from 82 to 650 °C corresponds to the loss of one coordinated water molecule and two hep⁻. Further weight loss at higher temperature matches with the total decomposition.

Comparative structural motifs in 1–3

The following striking structural similarities and differences have been recognised in **1–3**. (i) Oxyanions (NO_3^- , CO_3^{2-}) and phenoxyacetate (PhOAc^-) bridged **1–3** exhibit 1D-coordination polymeric features where the dicopper based building blocks, $\{[\text{Cu}(\mu\text{-hep}^-)]_2\}$, stabilise *via* the presence of a central Cu_2O_2 core. (ii) **1–3** also form 2D-extended networks through a wide variety of non-covalent interactions. (iii) Two NO_3^- or PhOAc^- groups in **1** or **2** bridge between the dicopper based two adjacent building units ($[\text{Cu}(\mu\text{-hep}^-)]_2$) in *head-to-head* and *tail-to-tail* modes leading to the formation of a new 12-membered chair-like structure. (iv) In **1** each NO_3^- function bridges the two copper centres associated with the two adjacent building units as in **Form B**, whereas in **2** the PhOAc^- group bridges between the two adjacent Cu ions as in **Form C**. (v) Unlike **1** and **2**, in **3** only one CO_3^{2-} group bridges between the two copper centres in two adjacent building units in *head-to-tail* form which indeed prevents the formation of any large internal ring like in **1** or **2**. However, the *head-to-tail* connecting mode of the CO_3^{2-} group extends the *zig-zag* pattern of **3**. (vi) The coordinated and lattice water molecules and the non-coordinated oxygen of CO_3^{2-} in **3** collectively form an additional *zig-zag* layer between the two outer *zig-zag* layers of the coordination polymers. (vii) The non-bonded Cu \cdots Cu, O \cdots O distances and Cu–O–Cu angles in **1**, **2** and **3** of 2.97 Å, 2.45 Å, 100.91°; 3.01 Å, 2.44 Å, 101.88° and 3.06 Å, 2.35 Å, 104.94°, respectively, are close to the reported polymeric^{14a} or discrete²⁴ copper complexes.

Magnetic properties of 1–3

The polymeric complexes **1–3** encompassing building units with a central Cu_2O_2 core exhibit similar magnetic properties in the temperature range of 300–100 K. The solid state magnetic moments of 1.25, 1.42 and 1.27 B.M. at 300 K for **1**, **2** and **3**, respectively, sharply decrease to close to zero at around 100 K (Fig. S1, ESI†) which implies that the Cu(II) centres in the complexes are antiferromagnetically coupled.²⁵ The magnetic simulation using the julX program²⁶ extends the J/cm^{-1} values of –240, –260 and –275 for **1**, **2** and **3**, respectively.

1–3 exhibit axial EPR spectra with $g_{\parallel} > g_{\perp}$ (Fig. S1, inset† and Table 4), consistent with the tetragonally elongated square pyramidal geometry around the copper(II) ion.²⁷ The $\langle g \rangle$ value in the range of 2.102–2.198 matches fairly well with that obtained from the magnetic simulation of 2.10.

Table 4 EPR data of **1–3** (polycrystalline state) at 298 K

Complex	g_{\parallel}	g_{\perp}	$\langle g \rangle^a$	A_{\parallel}
1	2.284	2.014	2.198	140
2	2.221	1.989	2.146	136
3	2.15	2.001	2.102	132

^a $\langle g \rangle = [(g_{\parallel}^2 + g_{\perp}^2 + g_{\perp}^2)/3]^{1/2}$.

Conclusion

The present article demonstrates the design of oxyanions (NO_3^- , CO_3^{2-}) and phenoxyacetate (PhOAc^-) bridged varying structural motifs in polymeric copper complexes (**1–3**) based on alkoxide derived dicopper building units $[\text{Cu}(\mu\text{-hep})_2]$ with a central Cu_2O_2 core (Hhep = 2-(2-hydroxyethyl)pyridine). The simultaneous *head-to-head* and *tail-to-tail* binding modes of NO_3^- or PhOAc^- groups with the adjacent Cu_2O_2 units in **1** or **2**, respectively, result in unprecedented twelve-membered metal-lacyclic rings. On the other hand, *head-to-tail* cross-linking of the CO_3^{2-} group with the adjacent Cu_2O_2 units in **3** develops a unique *zig-zag* coordination polymeric chain *via* a self-assembly process and two such adjacent chains in turn extend the support to hold the new *zig-zag* chain of water tetramers inside the outer layers *via* extensive hydrogen bonding.

Experimental

Materials and physical measurements

The commercially available starting materials, dihydrated copper acetate, trihydrate copper nitrate, 2-(2-hydroxyethyl)pyridine (hep-H), phenoxyacetic acid (Ph–O–CH₂–COOH), sodium carbonate and reagent grade methanol were used as received. Elemental analyses were carried out with a Perkin-Elmer 240C elemental analyser. FT-IR spectra of complexes as KBr pellets and DTA/TGA experiments were done on a Nicolet spectrophotometer and Perkin Elmer instrument, respectively. The complex $[\text{Cu}(\mu_2\text{-hep})(\text{OAc})_2]\cdot 2\text{H}_2\text{O}$ (**4**) was prepared by following the reported methods.¹⁷ The magnetic measurements were performed in a commercial PPMS magnetometer (Quantum Design, 6000 Lusk Boulevard, San Diego, CA) equipped with a superconducting 14 T magnet. The program julX written by E. Bill was used for the simulation and analysis of magnetic susceptibility data.²⁶ The EPR measurements were made with a Varian model 109C E-line X-band spectrometer fitted with a quartz Dewar for 77 K. Thermogravimetric analyses for complexes **1–3** were measured under a flow of nitrogen gas from room temperature to 850 °C at a heating rate of 10 °C min⁻¹.

Synthesis of 1–3

$\{[\text{Cu}_2(\mu\text{-hep})_2(\mu\text{-NO}_3)]_2\}_n$ (**1**). A solution of hep-H (123 mg, 1 mmol) in methanol (25 cm³) was added to a solution of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (242 mg, 1 mmol) in methanol (25 cm³) and the resultant solution was stirred for 6 h at room temperature. The solution was then passed through filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was allowed to stand at room temperature for crystallisation. On slow evaporation dark blue single crystals of **1** were obtained after a week. M.P.: 245–247 °C. Yield: 185 mg (76%).

Anal. Calcd for $C_{14}H_{16}Cu_2N_4O_8$ ($M_r = 495.38$): C, 34.01; H, 3.26; N, 11.34. Found: C, 34.00; H, 3.21; N, 11.27. IR (KBr, cm^{-1}): 2949(w), 2921(w), 29029(w), 2850(m), 1641(w), 1609(s), 1571(m), 1485(vs), 1440(s), 1380(vs), 1219(w), 1112(m), 1081(s), 1056(m), 876(m), 840(w), 769(s), 598(m).

$\{[Cu_2(\mu\text{-hep})_2(\mu\text{-PhOAc}^-)]_2\}_n$ (2**).** A solution of hep-H (123 mg, 1 mmol) in methanol (25 cm^3) was added to a solution of $Cu(OC(=O)CH_3)_2 \cdot 2H_2O$ (199 mg, 1 mmol) in methanol (25 cm^3). Phenoxyacetic acid ($Ph-O-CH_2-COOH$, 152 mg, 1 mmol) was added to the above reaction mixture and the resultant solution was stirred for 6 h at room temperature. The solution was then passed through filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was allowed to stand at room temperature for crystallisation. Dark blue single crystals of **2** were obtained within 3 days by slow evaporation of the solvent. M.P.: 249–251 °C. Yield: 290 mg (82%). Anal. Calcd for $C_{15}H_{15}CuNO_4$ ($M_r = 336.82$): C, 53.57; H, 4.50; N, 4.17. Found: C, 53.60; H, 4.64; N, 4.27. IR (KBr, cm^{-1}): 3066(w), 3030(vw), 2943(w), 2893(w), 2816(m), 1573(vs), 1491(vs), 1386(vs), 1301(s), 1257(s), 1217(vs), 1144(s), 972(w), 913(m), 867(m), 773(s), 750(s), 726(s), 680(s), 604(s), 563(w), 505(w).

$\{[Cu_2(\mu\text{-hep})_2(H_2O)_2] \cdot 2H_2O(\mu\text{-CO}_3)\}_n$ (3**).** A solution of $[Cu(\mu_2\text{-hep})(OAc)]_2 \cdot 2H_2O$ (**4**) (280 mg, 0.5 mmol) in methanol (25 cm^3) was added to an aqueous solution of Na_2CO_3 (60 mg, 0.6 mmol) and the resultant solution was stirred for 4 h at room temperature. The precipitate thus formed was then washed with excess methanol and the filtrate was allowed to stand at room temperature for crystallisation. On slow evaporation light green single crystals of **3** were obtained within two weeks. M.P.: 259–261 °C. Yield: 173 mg (62%). Anal. Calcd for $C_{15}H_{24}N_2O_9Cu_2$ ($M_r = 503.44$): C, 35.86; H, 4.82; N, 5.58. Found: C, 35.60; H, 4.64; N, 5.60. IR (KBr, cm^{-1}): 3466(br), 3070(w), 2948(w), 2899(s), 2857(vs), 1609(vs), 1568(s), 1459(vs), 1384(m), 1384(m), 1357(w), 1275(vs), 1153(s), 1094(m), 1024(s), 974(w), 879(m), 768(m), 726(s), 616(vs), 579(s), 508(w).

Alternative method for the synthesis of **1 and **2**.** A methanolic solution of $La(NO_3)_3 \cdot 6H_2O$ (217 mg, 0.5 mmol) or $Ce(NO_3)_3 \cdot 6H_2O$ (217 mg, 0.5 mmol) or $Na(NO_3)$ (85 mg, 0.5 mmol) was added to a solution of preformed $[Cu(\mu_2\text{-hep})(OAc)]_2 \cdot 2H_2O$ (**5**) (280 mg, 0.5 mmol) in methanol (25 cm^3) and the resultant solution was stirred for 3 h at room temperature. The solution was then passed through filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was allowed to stand at room temperature for crystallization. Dark blue single crystals of **1** were obtained within 5 days by slow evaporation of the solvent. M.P.: 247–249 °C. Yield: 185 mg (76%). Anal. Calcd for $C_{14}H_{16}Cu_2N_4O_8$ ($M_r = 495.38$): C, 34.01; H, 3.26; N, 11.34. Found: C, 34.06; H, 3.32; N, 11.37.

Similarly, **2** was prepared by the reaction of methanolic solution of phenoxyacetic acid ($Ph-O-CH_2-COOH$, 75 mg, 0.5 mmol) and preformed $[Cu(\mu_2\text{-hep})(OAc)]_2 \cdot 2H_2O$ (**4**) (280 mg, 0.5 mmol) in methanol (25 cm^3) under magnetic stirring for 4 h at room temperature. The reaction mixture was filtered using Whatman filter paper, 70 mm, and the filtrate was allowed to stand at room temperature for crystallisation. Dark blue single

crystals of **2** were obtained within a week by slow evaporation of the solvent. M.P.: 250–252 °C. Yield: 290 mg (82%). Anal. Calcd for $C_{15}H_{15}CuNO_4$ ($M_r = 336.82$): C, 53.57; H, 4.50; N, 4.17. Found: C, 53.62; H, 4.61; N, 4.23.

2 can also be prepared from **1** via the reaction sodium salt of phenoxyacetic acid ($Ph-O-CH_2-COONa$, 75 mg, 0.5 mmol) in methanol (25 cm^3) with a methanolic solution of **1** (250 mg, 0.5 mmol) under magnetic stirring for 6 h at 298 K. The reaction mixture was filtered using Whatman filter paper, 70 mm, filter paper and the filtrate was allowed to stand at room temperature for crystallisation. Dark blue single crystals of **2** were obtained within a 10 days by slow evaporation of the solvent. M.P.: 250–252 °C. Yield: 290 mg (82%). Anal. Calcd for $C_{15}H_{15}CuNO_4$ ($M_r = 336.82$): C, 53.57; H, 4.50; N, 4.17. Found: C, 53.51; H, 4.54; N, 4.13.

Crystal structure determination

Single crystal X-ray structural studies of **1**, **2** and **3** were performed on a CCD Oxford Diffraction XCALIBUR-S diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 150(2) K using graphite-monochromated Mo-K α radiation ($\lambda_\alpha = 0.71073\text{ \AA}$). The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least squares with SHELXL-97, refining on F^2 .²⁸ **2** appears to be a non-merohedral twin, and the problem was tackled using Rotax, which is a program found in WinGX, by using BASF values of 0.23869 0.15492 0.18016 0.03584 0.08242.

The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The water molecules (both coordinated and lattice) in **3** were generated by Fourier maps. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally $1.2 \times U_{eq}$ of their parent atoms. All the H-bonding interactions, mean plane analyses, and molecular drawings were obtained using the program Diamond (version 3.1d). The crystal and refinement data are summarized in Table 1, and selected bond distances and bond angles are shown in Tables 2 and 3.

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References

- (a) T. D. Keene, H. R. Ogilvie, M. B. Hursthouse and D. J. Price, *Eur. J. Inorg. Chem.*, 2004, 1007; (b) J-H. Yu, J. Lu, X. Zhang, L. Ye, Q. Hou and J-Q. Xu, *Inorg. Chem. Commun.*, 2006, **9**, 415; (c) J-H. Yu, L. Ye, M-H. Bi, Q. Hou, X. Zhang and J-Q. Xu, *Inorg. Chim. Acta*, 2007, **360**, 1987; (d) D-T. Nguyen, E. Chew, Q. Zhang, A. Choi and X. Bu, *Inorg. Chem.*, 2006, **45**, 10722; (e) C. Ma, W. Wang, X. Zhang, C. Chen, Q. Liu, H. Zhu, D. Liao and L. Li, *Eur. J. Inorg. Chem.*, 2004, 3522; (f) L. Brammer, M. D. Burgard, C. S. Rodger, J. K. Swearingen and N. P. Rath, *Chem. Commun.*, 2001, 2468; (g) S. Takamizawa, E. Nakata, T. Akatsuka, C. Kachi-Terajima and R. Miyake, *J. Am. Chem. Soc.*, 2008, **130**, 17882; (h) J-X. Yuan, M. L. Hu, Y. Q. Cheng, L. C. Chen and S. W. Ng, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2002, **58**, m270.

- 2 (a) C. Hu and U. Englert, *Angew. Chem., Int. Ed.*, 2006, **45**, 3457; (b) S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka and M. Yamashita, *J. Am. Chem. Soc.*, 2002, **124**, 2568; (c) T. Gadzikwa, B. S. Zeng, J. T. Hupp and S. T. Nguyen, *Chem. Commun.*, 2008, 3672; (d) J. W. Johnson, A. J. Jacobson, S. M. Rich and J. F. Brody, *J. Am. Chem. Soc.*, 1981, **103**, 5246; (e) R. Fu, S. Hu and X. Wu, *Inorg. Chem.*, 2007, **46**, 9630; (f) D. Tanaka, K. Nakagawa, M. Higuchi, S. Horike, Y. Kubota, T. C. Kobayashi, M. Takata and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2008, **47**, 3914; (g) G. J. Halder and C. J. Kepert, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **61**, m113; (h) S. Mukhopadhyay, P. B. Chatterjee, D. Mandal, G. Mostafa, A. Caneschi, J. van Slageren, T. J. R. Weakley and M. Chaudhury, *Inorg. Chem.*, 2004, **43**, 3413; (i) K. Biradha, K. V. Domasevich, B. Moulton, C. Seward and M. J. Zaworotko, *Chem. Commun.*, 1999, 1327; (j) J. T. Sampanthar and J. J. Vittal, *J. Chem. Soc., Dalton Trans.*, 1999, 1993; (k) S. Shimomura, S. Horike, R. Matsuda and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**, 10990.
- 3 (a) X. Li, R. Cao, D. Sun, W. Bi, Y. Wang, X. Li and M. Hong, *Cryst. Growth Des.*, 2004, **4**, 775; (b) M. Schweiger, S. R. Seidel, A. M. Arif and P. J. Stang, *Inorg. Chem.*, 2002, **41**, 2556; (c) S. W. Lee, H. J. Kim, Y. K. Lee, K. Park, J.-H. Son and Y.-U. Kwon, *Inorg. Chim. Acta*, 2003, **353**, 151; (d) C. S. Lai and E. R. T. Tiekink, *CrystEngComm*, 2004, **6**, 593; (e) G. S. Papaefstathiou, I. G. Georgiev, T. Friscic and L. R. MacGillivray, *Chem. Commun.*, 2005, 3974; (f) E.-Y. Choi, K. Park, C.-M. Yang, H. Kim, J.-H. Son, S. W. Lee, Y. H. Lee, D. Min and Y.-U. Kwon, *Chem.-Eur. J.*, 2004, **10**, 5535; (g) B. Chen, S. Ma, F. Zapata, F. R. Fronczek, E. B. Lobkovsky and H.-C. Zhou, *Inorg. Chem.*, 2007, **46**, 1233; (h) T. K. Maji, K. Uemura, H. C. Chang, R. Matsuda and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 326.
- 4 (a) A. K. Ghosh, D. Ghoshal, E. Zangrando, J. Ribas and N. R. Chaudhuri, *Dalton Trans.*, 2006, 1554; (b) S. Konar, E. Zangrando, M. G. B. Drew, T. Mallah, J. Ribas and N. R. Chaudhuri, *Inorg. Chem.*, 2003, **42**, 5966; (c) J.-C. Dai, X.-T. Wu, S.-M. Hu, Z.-Y. Fu, J.-J. Zhang, W.-X. Du, H.-H. Zhang and R.-Q. Sun, *Eur. J. Inorg. Chem.*, 2004, 2096; (d) Q.-X. Jia, Y.-Q. Wang, Q. Yue, Q.-L. Wang and E.-Q. Gao, *Chem. Commun.*, 2008, 4894; (e) L.-F. Ma, L.-Y. Wang, Y.-Y. Wang, S. R. Batten and J.-G. Wang, *Inorg. Chem.*, 2009, **48**, 915; (f) G. J. Halder, K. W. Chapman, S. M. Neville, B. Moubarak, K. S. Murray, J. F. Letard and C. J. Kepert, *J. Am. Chem. Soc.*, 2008, **130**, 17552; (g) B. Rather and M. J. Zaworotko, *Chem. Commun.*, 2003, 830.
- 5 (a) B. Li, L. Zhu, S. Wang, J. Lang and Y. Zhang, *J. Coord. Chem.*, 2003, **56**, 933; (b) M. Kondo, M. Shimamura, S. Noro, T. Yoshitomi, S. Minakoshi and S. Kitagawa, *Chem. Lett.*, 1999, 285; (c) S. Noro, M. Kondo, T. Ishii, S. Kitagawa and H. Matsuzaka, *J. Chem. Soc., Dalton Trans.*, 1999, 1569; (d) G. J. Halder, C. J. Kepert, B. Moubarak, K. S. Murray and J. D. Cashion, *Science*, 2002, **298**, 1762; (e) J. P. Barrio, J. N. Rebilly, B. Carter, D. Bradshaw, J. Bacsa, A. Y. Ganin, H. Park, A. Trewin, R. Vaidhyanathan, A. I. Cooper, J. E. Warren and M. J. Rosseinsky, *Chem.-Eur. J.*, 2008, **14**, 4521; (f) B. Li, B. Z. Xu, Z. Huang and Q. Wu, *J. Coord. Chem.*, 2002, **55**, 1183; (g) S. Noro, S. Kitagawa, T. Nakamura and T. Wada, *Inorg. Chem.*, 2005, **44**, 3960; (h) S. Noro, R. Kitaura, S. Kitagawa, T. Akutagawa and T. Nakamura, *Inorg. Chem.*, 2006, **45**, 8990.
- 6 (a) E. Colacio, M. Ghazi, R. Kivekäs and J. M. Moreno, *Inorg. Chem.*, 2000, **39**, 2882; (b) S. J. Rettig, R. C. Thompson, J. Trotter and S. Xia, *Inorg. Chem.*, 1999, **38**, 1360; (c) V. Tangoulis, G. Psomas, C. Dendrinou-Samara, C. P. Raptopoulou, A. Terzis and D. P. Kessissoglou, *Inorg. Chem.*, 1996, **35**, 7655; (d) A. D. Burrows, C. G. Frost, M. F. Mahon and C. Richardson, *Angew. Chem., Int. Ed.*, 2008, **47**, 8482.
- 7 (a) D. Hagrman, R. P. Hammond, R. Haushalter and J. Zubieta, *Chem. Mater.*, 1998, **10**, 2091; (b) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *CrystEngComm*, 2003, **5**, 190; (c) D. Hagrman, R. C. Haushalter and J. Zubieta, *Chem. Mater.*, 1998, **10**, 361; (d) R. C. Finn and J. Zubieta, *J. Chem. Soc., Dalton Trans.*, 2002, 856; (e) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *J. Chem. Soc., Dalton Trans.*, 2000, 3821; (f) K. Abu-Shandi, C. Janiak and B. Kersting, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2001, **57**, 1261; (g) Z. Shi, S. Feng, S. Gao, L. Zhang, G. Yang and J. Hua, *Angew. Chem., Int. Ed.*, 2000, **39**, 2325.
- 8 (a) I. Viera, M. H. Torre, O. E. Piro, E. E. Castellano and E. J. Baran, *J. Inorg. Biochem.*, 2005, **99**, 1250; (b) Y. Zhang, L. K. Thompson, J. N. Bridson and M. Bubenik, *Inorg. Chem.*, 1995, **34**, 5870; (c) H. M. J. Hendriks, P. J. M. W. L. Birker, J. van Rijn, G. C. Verschoor and J. Reedijk, *J. Am. Chem. Soc.*, 1982, **104**, 3607; (d) L. K. Thompson, A. W. Hanson and B. S. Ramaswamy, *Inorg. Chem.*, 1984, **23**, 2459; (e) T. Gajda, Y. Dupre, I. Torok, J. Harmer, A. Schweiger, J. Sander, D. Kuppert and K. Hegetschweiler, *Inorg. Chem.*, 2001, **40**, 4918; (f) J.-P. Lang, H. Kawaguchi and K. Tatsumi, *J. Organomet. Chem.*, 1998, **569**, 109; (g) L. Coghi, M. Lanfranchi, G. Pelizzi and P. Tarasconi, *Transition Met. Chem.*, 1978, **3**, 69; (h) G. Mezei, P. Baran and R. G. Raptis, *Angew. Chem., Int. Ed.*, 2004, **43**, 574; (i) R. Custelcean, P. Remy and P. V. Bonnesen, *Angew. Chem., Int. Ed.*, 2008, **47**, 1866.
- 9 (a) L. Latos-Grazynski, J. Lisowski, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, 1987, **109**, 4428; (b) P. de Hoog, P. Gamez, M. Luken, O. Roubeau, B. Krebs and J. Reedijk, *Inorg. Chim. Acta*, 2004, **357**, 213; (c) G. De Munno and G. Denti, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1984, **40**, 616; (d) F. A. Mautner and M. A. S. Goher, *Polyhedron*, 1993, **12**, 2823; (e) C. H. L. Kennard, G. Smith, E. J. O'Reilly and K. E. Brown, *Inorg. Chim. Acta*, 1981, **52**, 55; (f) G. Smith, E. J. O'Reilly and C. H. L. Kennard, *Cryst. Struct. Commun.*, 1981, **10**, 1397; (g) G. Smith, E. J. O'Reilly, C. H. L. Kennard and T. C. W. Mak, *Inorg. Chim. Acta*, 1982, **65**, L219.
- 10 (a) I. A. Koval, M. Huisman, A. F. Stassen, P. Gamez, M. Lutz, A. L. Spek and J. Reedijk, *Eur. J. Inorg. Chem.*, 2004, 591; (b) T. D. Keene, M. B. Hursthouse and D. J. Price, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2004, **60**, m381; (c) P. C. Healy, C. H. L. Kennard, G. Smith and A. H. White, *Cryst. Struct. Commun.*, 1981, **10**, 883; (d) M.-S. Wang, G.-C. Guo, L.-Z. Cai, G.-W. Zhou and J.-S. Huang, *Jiegou Huaxue (Chin. J. Struct. Chem.)*, 2003, **22**, 427.
- 11 (a) M. Fondo, A. M. Garcia-Deibe, N. Ocampo, J. Sanmartin and M. R. Bermejo, *Dalton Trans.*, 2004, 2135; (b) B. F. Abrahams, M. G. Haywood and R. Robson, *Chem. Commun.*, 2004, 938; (c) S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa and M. Munakata, *Inorg. Chem.*, 1995, **34**, 1455; (d) Y. Zhang, L. K. Thompson, J. N. Bridson and M. Bubenik, *Inorg. Chem.*, 1995, **34**, 5870; (e) Y.-B. Dong, T. Sun, J.-P. Ma, X.-X. Zhao and R.-Q. Huang, *Inorg. Chem.*, 2006, **45**, 10613; (f) M.-L. Tong, M. Monfort, J. M. C. Juan, X.-M. Chen, X.-H. Bu, M. Ohba and S. Kitagawa, *Chem. Commun.*, 2005, 233; (g) K. L. V. Mann, J. C. Jeffery, J. A. McCleverty and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1998, 3029; (h) C. H. L. Kennard, E. J. O'Reilly and G. Smith, *Polyhedron*, 1984, **3**, 689; (i) G. Psomas, C. P. Raptopoulou, L. Iordanidis, C. Dendrinou-Samara, V. Tangoulis and D. P. Kessissoglou, *Inorg. Chem.*, 2000, **39**, 3042.
- 12 F. B. Hulsbergen, R. W. M. ten Hoedt, G. C. Verschoor, J. Reedijk and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1983, 539.
- 13 G. Smith, E. J. O'Reilly, C. H. L. Kennard and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 243.
- 14 (a) R. P. Doyle, M. Julve, F. Lloret, M. Nieuwenhuyzen and P. E. Kruger, *Dalton Trans.*, 2006, 2081; (b) S. Youngme, N. Wannarit, T. Remsungnen, N. Chaichit, G. A. van Albada and J. Reedijk, *Inorg. Chem. Commun.*, 2008, **11**, 179; (c) J. Sertucha, A. Luque, O. Castillo, P. Román, F. Lloret and M. Julve, *Inorg. Chem. Commun.*, 1999, **2**, 14; (d) J. Y. Lu, A. L. Reynolds and K. A. Rannels, *CrystEngComm*, 2001, **3**, 144; (e) J. P. Naskar, M. G. B. Drew, A. Hulme, D. A. Tocher and D. Datta, *CrystEngComm*, 2005, **7**, 67.
- 15 (a) A. Clearfield, *Prog. Inorg. Chem.*, 1998, **47**, 371; (b) A. Hu, H. L. Ngo and W. Lin, *Angew. Chem., Int. Ed.*, 2003, **42**, 6000.
- 16 (a) O. Kahn, *Molecular Magnetism*, VCH Publishers Inc., New York, 1993; (b) J. S. Miller and M. Drillon, *Magnetism: Molecules to Materials*, Wiley-VCH, Weinheim, 2001; (c) C. J. O'Connor, *Research Frontiers in Magnetochemistry*, World Scientific, Singapore, 1993.
- 17 (a) M. M. Shaikh, A. K. Srivastava, P. Mathur and G. K. Lahiri, *Inorg. Chem.*, 2009, **48**, 4652; (b) M. M. Shaikh, A. K. Srivastava, P. Mathur and G. K. Lahiri, *Dalton Trans.*, 2010, **39**, 1447.
- 18 G. Aromi, J. Ribas, P. Gamez, O. Roubeau, H. Kooijman, A. L. Spek, S. Teat, E. MacLean, H. Stoeckli-Evans and J. Reedijk, *Chem.-Eur. J.*, 2004, **10**, 6476.
- 19 T. Lindgren, R. Sillanpää, K. Rissanen, L. K. Thompson, C. J. O'Connor, G. A. van Albada and J. Reedijk, *Inorg. Chim. Acta*, 1990, **171**, 95.
- 20 (a) B. Duffin, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1968, **24**, 396; (b) B. Duffin and S. C. Wallwork, *Acta Crystallogr.*,

- 1966, **20**, 210; (c) Xiang-Jian Kong, Yan-Ping Ren, La-Sheng Long, Rong-Bin Huang and Lan-Sun Zhang, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **61**, m2346; (d) R. Allmann, M. Krestl, C. Bolos, G. Manoussakis and G. S. Nikolov, *Inorg. Chim. Acta*, 1990, **175**, 255.
- 21 (a) K. Sakai, Y. Yamada, T. Tsubomura, M. Yabuki and M. Yamaguchi, *Inorg. Chem.*, 1996, **35**, 542; (b) M. Jagoda, S. Warzeska, H. Pritzkow, H. Wadepohl, P. Imhof, J. C. Smith and R. Kramer, *J. Am. Chem. Soc.*, 2005, **127**, 15061; (c) J. B. Fontecha, S. Goetz and V. McKee, *Angew. Chem., Int. Ed.*, 2002, **41**, 4553.
- 22 A. M. Thomas, A. Mukherjee, M. K. Saha, M. Nethaji and A. R. Chakravarty, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 2004, **43**, 1626.
- 23 J. R. Carruthers, K. Prout and F. J. C. Rossotti, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1975, **31**, 2044.
- 24 V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 2107.
- 25 J. W. Hall, W. E. Marsh, R. R. Weller and W. E. Hatfield, *Inorg. Chem.*, 1981, **20**, 1033.
- 26 http://ewww.mpi-muelheim.mpg.de/bac/logins/bill/julX_en.php.
- 27 A. Banerjee, S. Sarkar, D. Chopra, E. Colacio and K. K. Rajak, *Inorg. Chem.*, 2008, **47**, 4023.
- 28 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A64**, 112. Program for Crystal Structure Solution and Refinement, University of Goettingen, Germany, 1997.