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Supramolecular architectures from the self-assembly of *trans*-oxamidato-bridged dicopper(II) building blocks and phenyldicarboxylates

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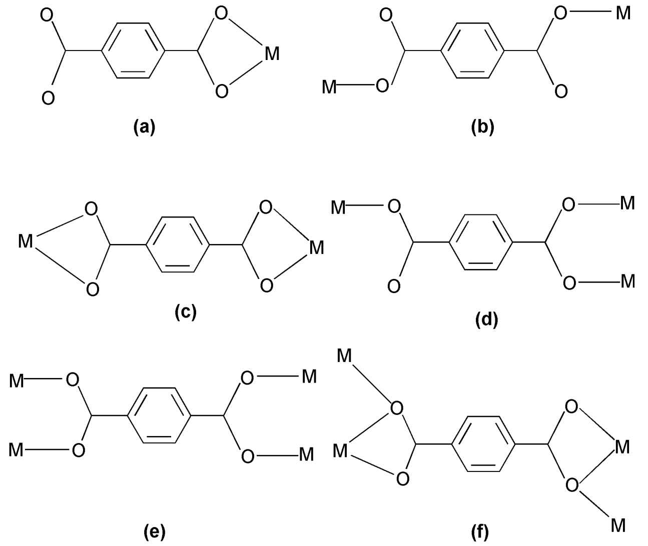
Compounds [Cu$_2$(*trans*-oxen)(tp)]$_n$·2nH$_2$O (**1**·2nH$_2$O), [{Cu$_2$(*trans*-oxpn)(H$_2$O)$_2$}{Cu$_2$(*trans*-oxpn)}(isophth)$_2$]$_n$·7nH$_2$O (**2**·7nH$_2$O) and [Cu$_2$(*trans*-oxen)(phth)]$_n$·2nH$_2$O (**3**·2nH$_2$O) [H$_2$oxen = *N*,*N*′-bis(2-aminoethyl)oxamide, H$_2$oxpn = *N*,*N*′-bis(3-aminopropyl)oxamide, tp = terephthalate, isophth = isophthalate and phth = phthalate] were obtained from the self-organization of *trans*-oxamidato-bridged dicopper(II) building blocks [Cu$_2$(*trans*-L)]$^{2+}$ (L = oxen or oxpn) and phenyldicarboxylate spacers with differently oriented carboxyl groups and their crystal structures determined. All the compounds consist of solvated water molecules and 2-D polymeric coordination networks containing rectangular, H-shaped mosaics and distorted rectangular grids for **1**, **2**, and **3**, respectively. In addition, variegated hydrogen bonds involving solvated water molecules link the 2-D nets into 3-D frameworks. New bridging modes were discovered for the three isomeric phenyldicarboxylates. Magnetic calculations on **2**·7nH$_2$O showed that the planar oxamidato bridge transmits antiferromagnetic interactions between the Cu(II) ions.

Introduction

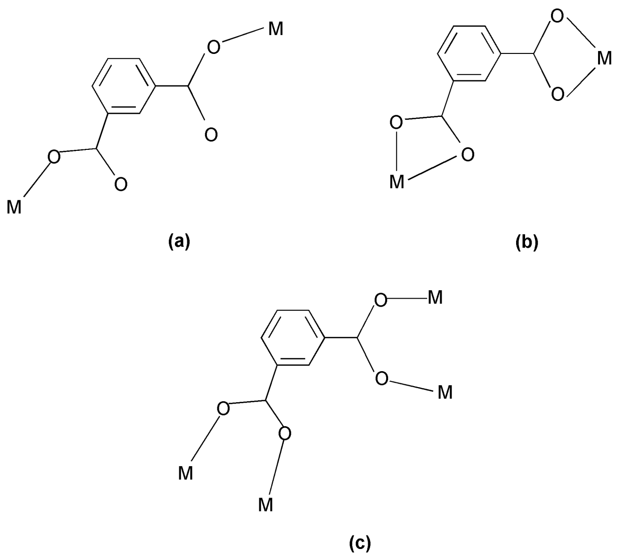
Great attention has been paid in recent years to supramolecular chemistry reflecting the intense contemporary interest in the rational design of functional materials with extended architectures.[1–15] Phenyldicarboxylates with variously oriented carboxyl groups have been utilized to build coordination networks for two separate reasons. On the one hand, they can furnish the directional conformation of structures *via* coordination interactions with versatile bonding modes as well as *via* non-covalent bonding interactions such as hydrogen bonding and/or π–π overlapping interactions;[16–23] on the other hand, these phenyldicarboxylates can provide different superexchange pathways transmitting magnetic interactions between paramagnetic metal centers owing to the diversity of their bonding modes.[24–46]

The reported coordination modes of the carboxyl groups in these dicarboxylates are summarized in Schemes 1–3,[16–23,28–33] of which those for phth (phthalate) are the most abundant. It can be seen that these dicarboxylates can bind to one to four metal ions and afford the so-called short bridges along one of the carboxyl groups as well as the long bridges with both carboxyl groups involved.[49] Though magnetic interactions transmitted through phenyldicarboxylate bridges are usually weak,[25,26,48,49] the magnitude and nature of the coupling interactions can be influenced by a series of factors such as the separation of the metal centers,[45,47,51] bridging modes,[43,48,49] degree of coplanarity between the coordination basal planes and the ligand, and the dihedral angles among the carboxylato planes and the phenyl ring.[47–53]

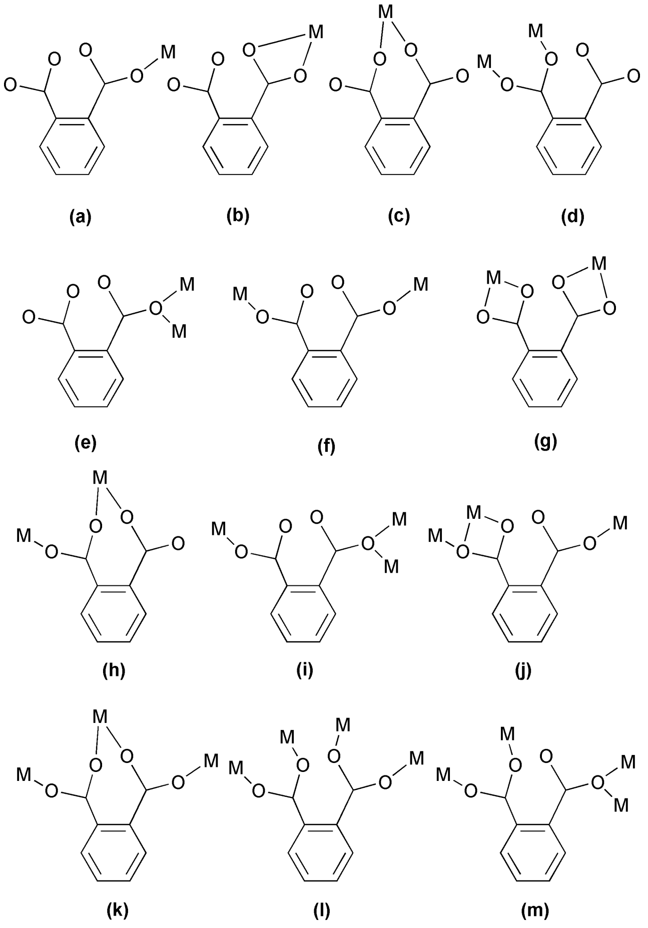
Magnetic systems with tp (terephthalate) as bridges between paramagnetic metal centers have been extensively studied,[47–51] whereas those with isophth (isophthalate)[25,52] and phth[53,54] are less widely reported. In fact, compounds of phenyldicarboxylates are mostly dinuclear and oligonuclear,[41–43,47,48,52,53,55] while those with polymeric structures and transition metal varieties are still relatively limited, especially for isophth. To achieve a strategy combining both covalent and non-covalent interactions and to explore the influence of the orientation of the two carboxyl groups in these dicarboxylates on the supramolecular architectures, we report here the syntheses and crystal structures of three compounds [Cu$_2$(*trans*-oxen)(tp)]$_n$·2nH$_2$O



Scheme 1



Scheme 2



Scheme 3

($\mathbf{1}\cdot 2n\mathrm{H_2O}$), [{$\mathrm{Cu_2}$(*trans*-oxpn)$\mathrm{(H_2O)_2}$}{$\mathrm{Cu_2}$(*trans*-oxpn)}-(isophth)$_2$]$_n$·$7n\mathrm{H_2O}$ ($\mathbf{2}\cdot 7n\mathrm{H_2O}$), [$\mathrm{Cu_2}$(*trans*-oxen)(phth)]$_n$·$2n\mathrm{H_2O}$ ($\mathbf{3}\cdot 2n\mathrm{H_2O}$) [$\mathrm{H_2}$oxen = *N*,*N*′-bis(2-aminoethyl)oxamide, $\mathrm{H_2}$oxpn = *N*,*N*′-bis(3-aminopropyl)oxamide] containing 2-D networks constructed by *trans*-oxamidato-bridged building blocks [$\mathrm{Cu_2}$(trans-L)]$^{2+}$ (L = oxen or oxpn) and phenyldicarboxylates.

Results and discussion

Synthesis

According to the synthetic routes shown in Scheme 4, the reaction of *cis*-CuL (L = oxen or oxpn) with equimolar amounts of $\mathrm{Cu(ClO_4)_2\cdot 6H_2O}$ provides the dimeric units [$\mathrm{Cu_2}$(*trans*-L)]$^{2+}$.[56,57] These building blocks are then connected by the spacer phenyldicarboxylates with differently oriented carboxyl groups to form the resulting polymers. As the result, three compounds with extended 2-D polymeric networks containing differently shaped grids are obtained. The addition of phenyldicarboxylates to the mixture of *cis*-CuL and equimolar $\mathrm{Cu^{2+}}$ usually leads to dark blue precipitates immediately. Thus, well-shaped single crystals were grown by slow diffusion of the reagents in an H-tube ($\mathbf{1}\cdot 2n\mathrm{H_2O}$), recrystallization of the precipitate in hot water ($\mathbf{2}\cdot 7n\mathrm{H_2O}$) or slow solvent evaporation of the filtrate after filtration ($\mathbf{3}\cdot 2n\mathrm{H_2O}$).

The compounds exhibit characteristic strong and broad vibration bands of ν_a(COO) and ν_s(COO). The Δ value, which represents the separation of ν_a(COO) and ν_s(COO), reflects the coordination modes of the carboxyl groups.[58] Compound **1** shows the bands ν_a(COO) (1568 $\mathrm{cm^{-1}}$) and ν_s(COO) (1359 $\mathrm{cm^{-1}}$) with Δ of *ca.* 209 $\mathrm{cm^{-1}}$, which is much larger than that (Δ = 170 $\mathrm{cm^{-1}}$) for $\mathrm{K_2tp}$[43] and consistent with the unidentate (mono-atomic bridge) coordination mode (Scheme 5(a)) in tp. The band ν_s(COO) in **2** splits (1356 and 1321 $\mathrm{cm^{-1}}$) and two Δ values (204 and 239 $\mathrm{cm^{-1}}$) are observed, suggesting the existence of both bi- and uni-dentate ligations of isophth (Scheme 5(b)), which is in accord with the result of X-ray analysis.[52] Compared with the Δ value (160 $\mathrm{cm^{-1}}$) for $\mathrm{Na_2phth}$,[59] the value in **3** is 232 $\mathrm{cm^{-1}}$, indicating the occurrence of a mono-atomic bridging mode for phth (Scheme 5(c)).[60]

The dehydration of the compounds **1**–**3** occurs in the range 80–150 °C, while the polymeric moieties are stable up to 250–277 °C. TGA data listed in Table 1 indicate that the thermal behaviors of the three compounds are similar to that of other oxamidato-bridged compounds previously reported.[56]

Structures

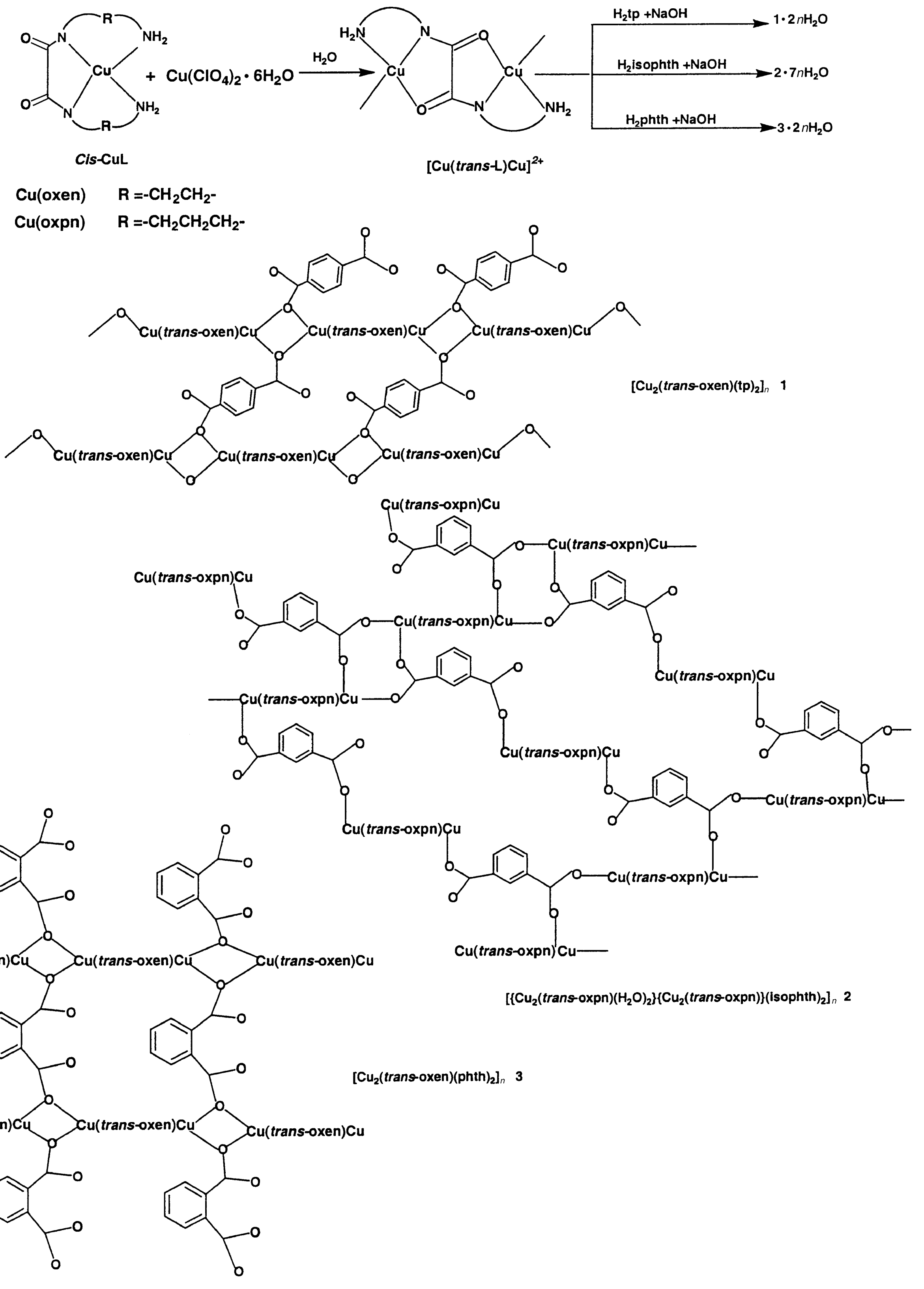
As illustrated in Figs. 1, 3 and 5 the copper(II) ions in the compounds are similarly in the square-pyramidal geometry of $\mathrm{O_3N_2}$. The base plane in **1** or **3** is composed of three atoms $\mathrm{N_2O}$ from oxen and one oxygen atom from tp or phth while the axial position is occupied by an oxygen atom of another spacer. The basal planes for the Cu(II) ions in **2** are defined by three atoms $\mathrm{N_2O}$ from oxpn and one oxygen atom from isophth for Cu(1) and Cu(2), but from $\mathrm{H_2O}$ for Cu(3) and Cu(4), and the axial positions are all occupied by an oxygen atom of another spacer. The oxamidato ligands oxen and oxpn adopt the *trans*-conformation to chelate and bridge two copper(II) ions forming the dicopper building block [$\mathrm{Cu_2}$(*trans*-L)]$^{2+}$ (L = oxen or oxpn) in the bis-terdentate fashion, which are further connected by the spacer dicarboxylates and afford more complicated structures *via* coordination interactions. Further particulars of the compounds are discussed individually below.

$\mathbf{1\cdot 2}n\mathbf{H_2O}$. Four asymmetric units are shown in Fig. 1 with selected bond lengths and angles in Table 2. Each of the two carboxyl groups in tp offers a mono-atomic bridge by using one oxygen atom as the asymmetric μ-O bridge bound to copper(II) ions equatorially (Cu1–O2 1.947(2) Å) and axially (Cu1a–O2 2.401(2) Å). Thus, each tp connects four binuclear motifs [$\mathrm{Cu_2}$(*trans*-oxen)]$^{2+}$ to form the extended 2-D network with rectangular grids as depicted in Fig. 2. Each grid contains two dicopper motifs and two tp ligands as the four edges with dimensions *ca.* 9.7 × 4.9 Å. The Cu · · · Cu separation through oxen, tp and μ-O bridges are 5.275, 9.672, and 3.354 Å, respectively. The water molecules between the 2-D nets form hydrogen bonds with the uncoordinating carboxyl oxygen atoms of tp and the amino groups of oxen to pull nets together and build up the 3-D framework.

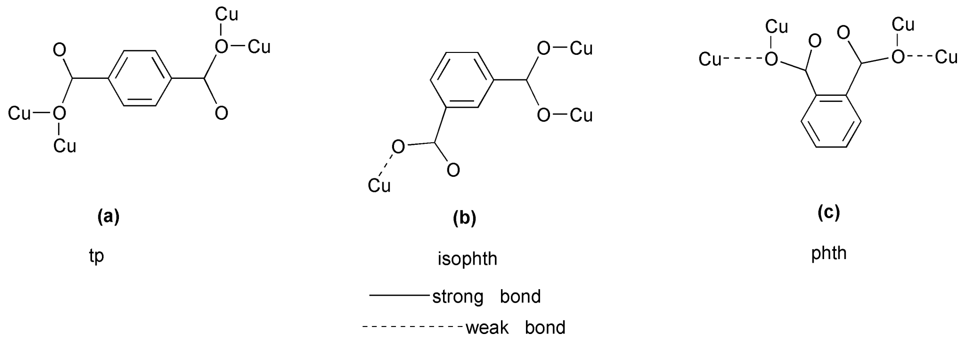
$\mathbf{2\cdot 7}n\mathbf{H_2O}$. One asymmetric unit is illustrated in Fig. 3 with selected bond lengths and angles in Table 3. One of the two carboxyl groups in isophth provide a tri-atomic η^2-bridge using

Table 1 TGA data

Compound	Dehydration temperature range/°C	Measured weight loss (%)	Calculated weight loss (%)	No. of water molecules lost	Decomposition temperature/°C
1·2nH$_2$O	101–160	7.5	7.2	2	≈268
2·7nH$_2$O	80–130	14.8	14.2	9	≈277
3·2nH$_2$O	110–150	7.3	7.2	2	≈250



Scheme 4



Scheme 5

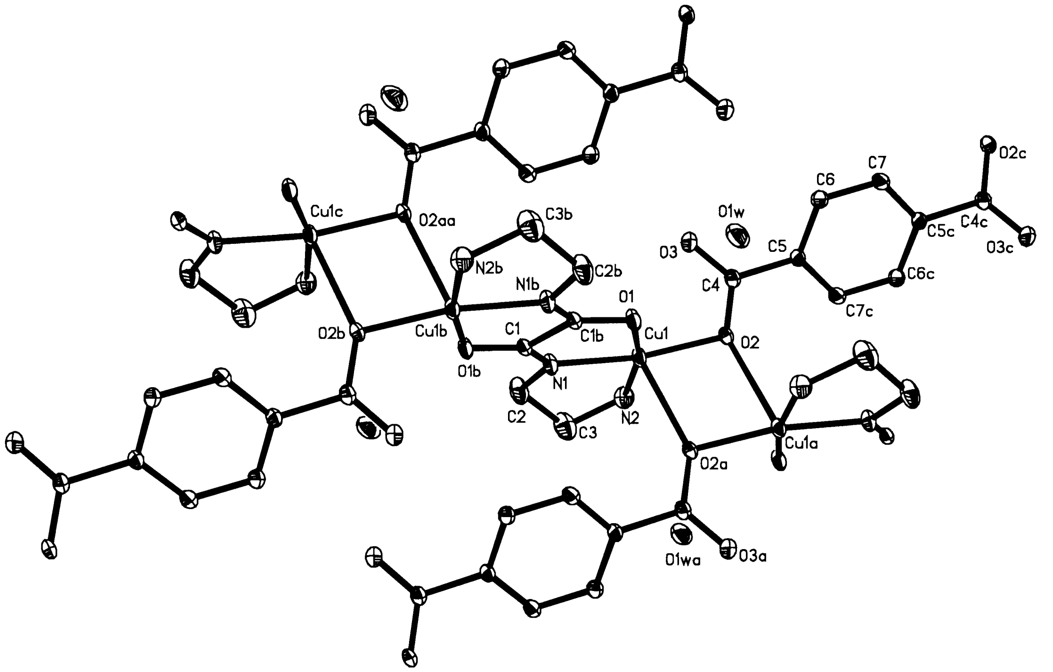


Fig. 1 ORTEP[65] view of the asymmetric units in **1**·$2n\mathrm{H_2O}$ with atomic numbering scheme. Thermal ellipsoids are drawn with 30% probability.

Table 2 Selected bond distances (Å) and angles (°) for **1**·$2n\mathrm{H_2O}$

Cu1–N1	1.917(2)	Cu1–O2	1.947(2)
Cu1–N2	2.008(2)	Cu1–O1	2.029(2)
Cu1–O2a	2.401(2)	Cu1 ··· Cu1b	5.275
N1–Cu1–O2	170.36(8)	N1–Cu1–N2	83.65(9)
O2–Cu1–N2	97.42(8)	N1–Cu1–O1	82.83(7)
O2–Cu1–O1	96.47(7)	N2–Cu1–O1	166.08(8)
N1–Cu1–O2a	110.02(7)	O2–Cu1–O2a	79.57(6)
N2–Cu1–O2a	91.41(8)	O1–Cu1–O2a	90.09(7)

Symmetry code: (a) $-x + 1, -y, -z$; (b) $-x, -y, -z$.

two oxygen atoms to coordinate the copper ions in $[\mathrm{Cu_2}(\textit{trans}\text{-oxpn})]^{2+}$ equatorially (O1 and O6a) (Cu1–O1, 1.990(4); Cu2–O6a, 1.998(4) Å) and axially (O5 and O2a), while the other only acts as a monodentate η^2-group bonding axially to the copper(II) in $[\mathrm{Cu_2}(\textit{trans}\text{-oxpn})(\mathrm{H_2O})_2]^{2+}$. The axial coordination interactions for the first carboxyl group (Cu1–O5, 2.346(5); Cu2–O2a, 2.323(5) Å) are stronger than the second one (Cu4–O8, 2.476; Cu3–O3a, 2.506 Å). Therefore, each isophth combines two $[\mathrm{Cu_2}(\textit{trans}\text{-oxpn})]^{2+}$ and one $[\mathrm{Cu_2}(\textit{trans}\text{-oxpn})(\mathrm{H_2O})_2]^{2+}$ to form the 2-D network with H-shaped mosaics as shown in Fig. 4. The Cu ··· Cu separations through oxpn, tri-atomic and isophth bridges are 5.272, 4.754, and 7.020 Å, respectively. Abundant hydrogen bonds among the solvated, the coordinated water molecules, and the uncoordinated carboxyl oxygen atoms cross-link the 2-D nets into a 3-D framework.

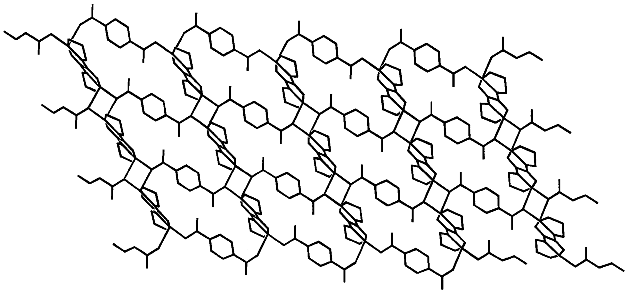


Fig. 2 A view of the 2-D extended network of **1** with the 2 + 2 rectangular grids.

3·2nH₂O. Two asymmetric units are shown in Fig. 5 with selected bond lengths and angles in Table 4. The coordination mode of the spacer phth is similar to that of tp in **1**·$2n\mathrm{H_2O}$. Each carboxyl group supplies one oxygen atom as the μ-O bridge bonding to the copper(II) ions equatorially and axially, and forms the mono-atomic bridge between the building blocks. The bond lengths in the basal planes are 1.953(3) (Cu1–O4) and 1.940(3) Å (Cu2–O6a). Those in the axial positions are 2.465 (Cu1–O6b) and 2.460 Å (Cu2–O4b), which are weaker than their counterparts in **1**·$2n\mathrm{H_2O}$. Therefore, each phth connects four dinuclear motifs $[\mathrm{Cu_2}(\textit{trans}\text{-oxen})]^{2+}$ to build up an extended network as depicted in Fig. 6, which exhibits the distorted rectangular grid consisting of two $[\mathrm{Cu_2}(\textit{trans}\text{-oxen})]^{2+}$ and two phth with dimensions of *ca.* 7.5 × 7.9 Å. The Cu ··· Cu

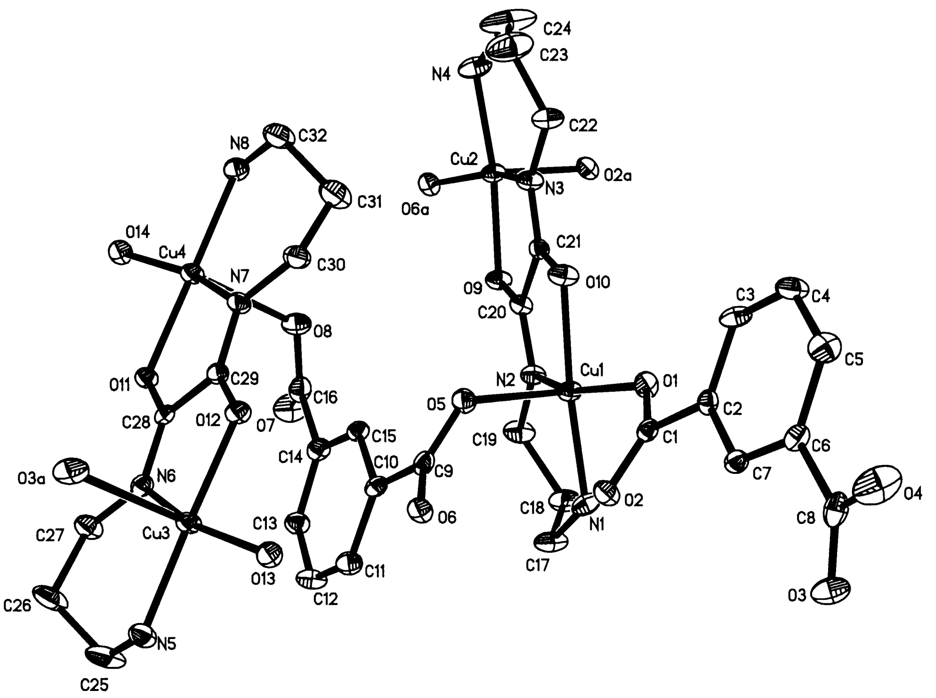


Fig. 3 ORTEP view of the asymmetric units in $\mathbf{2}\cdot7n\mathrm{H_2O}$ with atomic numbering scheme. Thermal ellipsoids are drawn with 30% probability.

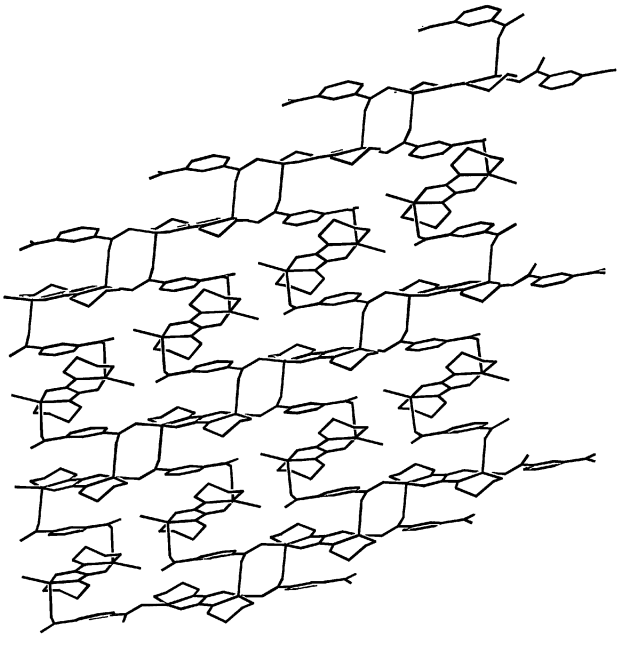


Fig. 4 A view of the 2-D extended network of **2** with the 4 + 4 H–shaped mosaics.

Table 3 Selected bond distances (Å) and angles (°) for $\mathbf{2}\cdot7n\mathrm{H_2O}$

Cu1–N2	1.968(5)	Cu1–N1	1.985(6)
Cu1–O10	1.987(4)	Cu1–O1	1.990(4)
Cu1–O5	2.346(5)	Cu2–N3	1.973(5)
Cu2–N4	1.978(6)	Cu2–O9	1.985(4)
Cu2–O6a	1.998(4)	Cu2–O2a	2.323(5)
Cu3–N6	1.935(6)	Cu3–O13	1.966(4)
Cu3–O12	1.975(5)	Cu3–N5	1.984(6)
Cu3–O3a	2.506	Cu4–O8	2.476
Cu4–N7	1.942(5)	Cu4–O14	1.971(4)
Cu4–O11	1.984(4)	Cu4–N8	2.001(6)
Cu1 ··· Cu2	5.270	Cu3 ··· Cu4	5.212
N2–Cu1–N1	95.1(2)	N2–Cu1–O10	83.4(2)
N1–Cu1–O10	174.0(3)	N2–Cu1–O1	156.8(2)
N1–Cu1–O1	92.4(2)	O10–Cu1–O1	86.9(2)
N2–Cu1–O5	110.6(2)	N1–Cu1–O5	96.6(2)
O10–Cu1–O5	89.3(2)	O1–Cu1–O5	90.3(2)
N3–Cu2–N4	94.6(2)	N3–Cu2–O9	83.2(2)
N4–Cu2–O9	171.3(3)	N3–Cu2–O6a	158.2(2)
N4–Cu2–O6a	91.9(2)	O9–Cu2–O6a	87.3(2)
N3–Cu2–O2a	109.2(2)	N4–Cu2–O2a	97.6(2)
O9–Cu2–O2a	91.0(2)	O6a–Cu2–O2a	90.4(2)
N6–Cu3–O13	163.3(2)	N6–Cu3–O12	84.3(2)
O13–Cu3–O12	86.6(2)	N6–Cu3–N5	97.0(2)
O13–Cu3–N5	91.9(2)	O12–Cu3–N5	178.1(2)
N7–Cu4–O14	163.1(2)	N7–Cu4–O11	84.6(2)
O14–Cu4–O11	86.2(2)	N7–Cu4–N8	96.5(2)
O14–Cu4–N8	92.5(2)	O11–Cu4–N8	178.8(2)

Symmetry codes: (a) $x + 1, y, z$.

distances through oxen, phth and μ-O bridges are 5.282, 7.486, and 3.438 Å, respectively. The water molecules between the 2-D nets form hydrogen bonds with the uncoordinating carboxyl oxygen atoms and the amino groups and the nets are linked up to produce the 3-D framework.

The coordination modes of the phenyldicarboxylates in **1**, **2** and **3** are shown in Scheme 5, which are novel and different from those reported in the literature, as illustrated in Schemes 1–3 for tp, isophth and phth, respectively. Among the coordination modes of tp shown in Scheme 1, (b) appears with high frequency. The spacer tp in **1** adopts the unique bis(mono-atomic) bridging mode combining four Cu(II) ions through two asymmetric μ-O bridges (Scheme 5(a)). Three bonding modes for isophth have been reported (Scheme 2), where it was shown to attach two or four metal ions. In contrast, the two carboxyl groups of isophth in **2** behave as a tri-atomic bridge and a unidentate group separately, connecting three copper(II) ions with one weak bond, shown as a dotted line in Scheme 5(b). The bonding mode (d) of phth in Scheme 3 is the most common one. However, the mode with each of the two carboxyl groups of phth in **3** using one oxygen atom as the mono-atomic μ-O bridge (Scheme 5(c)) is new. In the previously reported complex $[\mathrm{Cu_2}(\textit{trans}\text{-oxpn})(\text{phth})]_n\cdot2n\mathrm{H_2O}$,[56] phth adopted mode (i) in Scheme 3 with one of the carboxyl groups ligating in a unidentate equatorial mode, whereas the other acts as an asymmetric μ-O bridge coordinating to Cu(II) equatorially and axially. It can be seen that during the processes of assembly with the dicopper building blocks $[\mathrm{Cu_2}(\textit{trans}\text{-L})]^{2+}$ (L = oxpn or oxen), the spacers tp, isophth and phth prefer to bind to more than

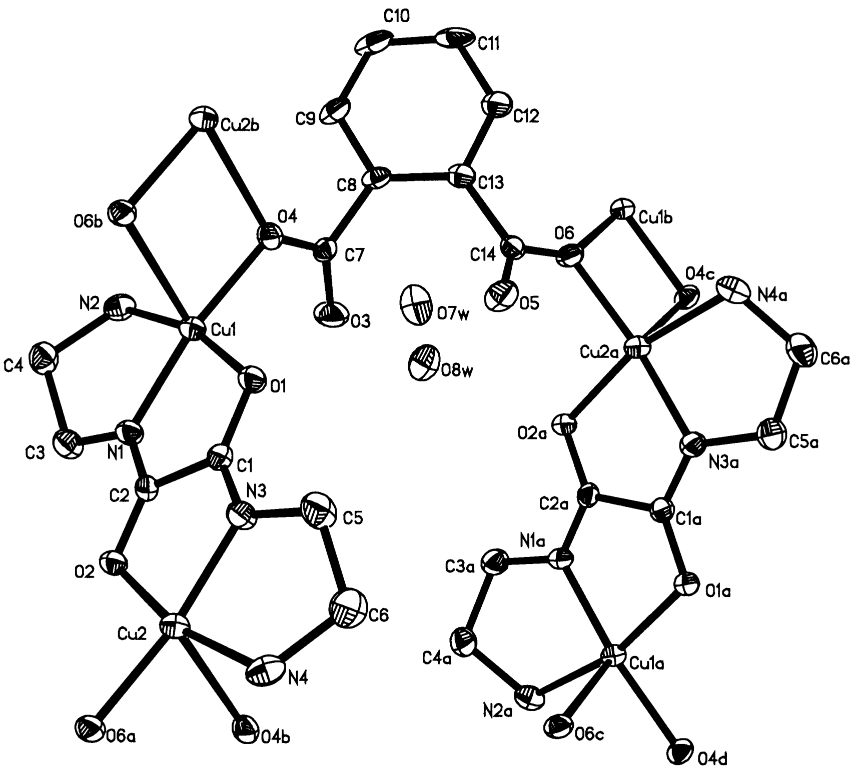


Fig. 5 ORTEP view of the asymmetric units in **3**·2nH$_2$O with atomic numbering scheme. Thermal ellipsoids are drawn with 30% probability.

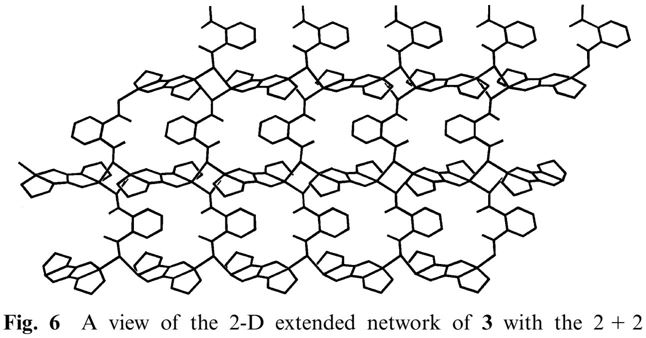


Fig. 6 A view of the 2-D extended network of **3** with the 2 + 2 distorted rectangular grids.

two copper(II) ions. Consequently, 2-D polymeric coordination networks are constructed.

Magnetic properties

The temperature dependence of the effective magnetic moment per molecule of **2**·7nH$_2$O in the form of μ_{eff} *vs.* T is shown by the data points in Fig. 7. The fact that μ_{eff} decreases gradually with decreasing temperature reveals an antiferromagnetic interaction in this compound. Oxamidate is known to afford an effective exchange pathway to mediate a strong antiferromagnetic coupling interaction.[61] In **2**·7nH$_2$O, the molecule is composed of building blocks [Cu(*trans*-oxpn)Cu]$^{2+}$ and spacers isophth with the separations of Cu···Cu 5.272, 4.754, and 7.020 Å through oxpn, η^2-isophth, and η^1-isophth, respectively. However, the two neighboring copper(II) ions between two building blocks through the spacers are coordinated equatorially and axially by the carboxyl groups, thus overlap of the magnetic orbitals for coupling interactions is disfavored. So, the magnetic exchange transmitted by isophth should be far smaller than that by the oxpn bridge. Therefore, the 2-D magnetic coupling system of **2**·7nH$_2$O can be simplified as interacting dimeric units [Cu(*trans*-oxpn)Cu]$^{2+}$ with coupling constant J, while that through isophth creates an inter-dimeric molecular field (θ). On this basis, it should be possible to interpret the data by means of a modified Bleaney–Bowers equation[62] with an intermolecular interaction.

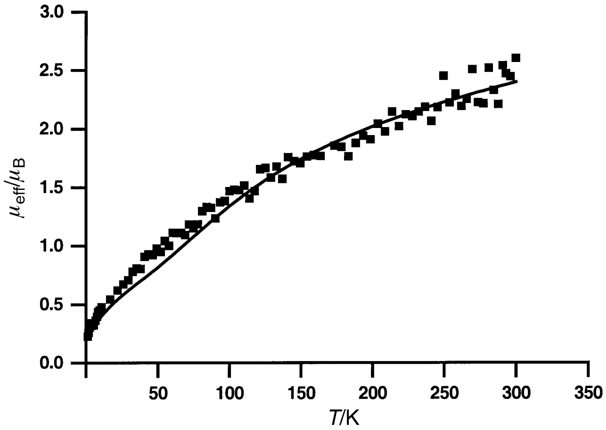


Fig. 7 Plot of the temperature dependence of the effective magnetic moments (μ_{eff}) for **2**·7nH$_2$O. (■) Experimental points; (—) Calculated curve.

$$\chi_m = \frac{2N\beta^2g^2}{k(T-\theta)}\left[3+\exp\left(-\frac{J}{kT}\right)\right]^{-1}(1-\rho)+\frac{N\beta^2g^2}{2k(T-\theta)}\rho+2N_\alpha \qquad (1)$$

$$\mu_{eff}(\mathrm{Cu}) = 2.828\sqrt{\chi_m T/2} \qquad (2)$$

Least-squares fitting of the experimental data led to $J = -310.00$ cm^{-1}, $g = 2.10$, $\theta = -3.00$ K, and $\rho = 0.01$, where ρ is the percentage of the paramagnetic impurities, N_α is the temperature-independent paramagnetism. The parameters N, β and k have their usual meanings. The curve calculation with these parameters gave a reasonably satisfactory fit to the experimental data as shown by the solid line in Fig. 7. The negative θ reveals that the total contribution for isophth bridges and hydrogen bonds is antiferromagnetic.

Table 4 Selected bond distances (Å) and angles (°) for $\mathbf{3}\cdot 2n\mathrm{H_2O}$

Cu1–N1	1.925(3)	Cu1–O4	1.953(3)
Cu1–N2	2.009(4)	Cu1–O1	2.039(3)
Cu1–O6b^{i}	2.465	Cu2–O4b^{iii}	2.460
Cu2–N3	1.921(3)	Cu2–O6a^{ii}	1.940(3)
Cu2–N4	2.008(4)	Cu2–O2	2.018(3)
Cu1 ··· Cu2	5.282		
N1–Cu1–O4	170.34(13)	N1–Cu1–N2	82.7(2)
O4–Cu1–N2	98.3(2)	N1–Cu1–O1	82.51(13)
O4–Cu1–O1	96.53(12)	N2–Cu1–O1	165.18(14)
N3–Cu2–O6a^{ii}	169.50(14)	N3–Cu2–N4	83.8(2)
O6a–Cu2–N4	98.30(14)	N3–Cu2–O2	83.06(13)
O6a–Cu2–O2	95.53(12)	N4–Cu2–O2	165.88(13)

Symmetry codes: $^{i}x + 1/2, 1-y, z$ $^{ii}x-1/2, -y, z$ $^{iii}x, y-1, z$.

Similarly, the carboxyl oxygen atoms in $\mathbf{1}\cdot 2n\mathrm{H_2O}$ and $\mathbf{3}\cdot 2n\mathrm{H_2O}$ also coordinate to the copper(II) equatorially and axially, and the magnetic environments of the Cu(II) ions are similar to those in **2**, therefore the magnetic study for these two compounds was not carried out.

Conclusions

It is noteworthy that using phenyldicarboxylate dianions with differently oriented carboxyl groups as spacers, networks with variously shaped grids can be constructed due to the versatile coordination modes of the carboxylate groups. The spacer tp has been used as a semi-rigid linear bidentate connector bound to square planar or octahedral metal centers to build networks with square or rectangular grids.[19] Herein the dicopper units are linearly arranged and connected by tp to give the 2 + 2 rectangular grids in **1**. When isophth and phth are used as spacers, 4 + 4 H-shaped mosaics and 2 + 2 distorted rectangular grids are obtained in **2** and **3**, respectively. This can be interpreted by the different relative orientation of the two carboxyl groups. In fact, the polymeric networks of **1** and **3** are identical in terms of structural topology. The two carboxylates in tp are linear whereas in isophth and phth they are angular, which affects the structural patterns. That is to say, grids in **1** look rectangular while in **3** they appear distorted rectangular. Compound $\mathbf{2}\cdot 7n\mathrm{H_2O}$ represents a polymeric coordination network with a fascinating structural feature. The examples reported here illustrate the fact that the orientations of the coordination groups and the coordination modes of the spacer can dominate the shapes of grids in the nets. The findings on these compounds should enrich the crystal engineering strategy of coordination networks. Since the coordination mode of the carboxyl group is versatile, it can be expected that more new structures could be constructed by employing the aromatic multi-carboxylates as spacers.

Experimental

Materials

All chemicals, unless otherwise indicated, were purchased commercially and used as received. Cu(oxen)·$2\mathrm{H_2O}$ and Cu(oxpn) were synthesized according to the methods reported in the literature.[63]

CAUTION! Though no problems were encountered in this work, perchlorate salts containing organic ligands are potentially explosive. They should be prepared in small quantities and handled with care.

Syntheses

$\mathbf{1\cdot 2}\boldsymbol{n}\mathbf{H_2O}$**.** To an aqueous solution (40 cm^3) of Cu(oxen)·$2\mathrm{H_2O}$ (0.272 g, 1.00 mmol) was added an aqueous solution (5 cm^3) of $\mathrm{Cu(ClO_4)_2\cdot 6H_2O}$ (0.371 g, 1.00 mmol) with stirring at room temperature. The color of the solution changed from violet-red to blue immediately. After several minutes, an aqueous solution (10 cm^3) of terephthalic acid (0.166 g, 1.00 mmol) and NaOH (0.080 g, 2.00 mmol) was added and dark blue precipitates appeared at once, which were collected and dried in a desiccator. Single crystals suitable for X-ray analysis were grown by slow diffusion of two individual solutions in the H-tube (one contained equimolar Cu(oxen)·$2\mathrm{H_2O}$ and $\mathrm{Cu(ClO_4)_2\cdot 6H_2O}$, the other $\mathrm{H_2}$tp acid neutralized by NaOH). (Found: C, 33.41; H, 4.06; N, 11.25. Calc. for $\mathrm{C_{14}H_{20}N_4O_8Cu_2}$: C, 33.67; H, 4.04; N, 11.22%).

$\mathbf{2\cdot 7}\boldsymbol{n}\mathbf{H_2O}$**.** This compound was obtained as a blue precipitate by the same procedures as for $\mathbf{1}\cdot 2n\mathrm{H_2O}$ except that Cu(oxen)·$2\mathrm{H_2O}$ and $\mathrm{H_2}$tp were replaced by Cu(oxpn) and $\mathrm{H_2}$isophth, respectively. Single crystals were obtained by recrystallization of the blue precipitate in hot aqueous solution. (Found: C, 33.11; H, 4.94; N, 9.83. Calc. for $\mathrm{C_{32}H_{58}Cu_4N_8O_{21}}$: C, 33.57; H, 5.11; N, 9.79%).

$\mathbf{3\cdot 2}\boldsymbol{n}\mathbf{H_2O}$**.** This compound was obtained by the same procedure as for $\mathbf{1}\cdot 2n\mathrm{H_2O}$ except that $\mathrm{H_2}$tp was replaced by $\mathrm{H_2}$phth. Single crystals were obtained directly from solvent evaporation of the filtrate which was allowed to stand at room temperature for several days to give blue black crystals. (Found: C, 33.40; H, 4.25; N, 11.28. Calc. for $\mathrm{C_{14}H_{20}N_4O_8Cu_2}$: C, 33.67; H, 4.04; N, 11.22%).

Physical measurements

IR spectra were recorded on a Nicolet FT-IR-170SX spectrophotometer in the region 4000–400 cm^{-1}. TG analyses were carried out on a Perkin-Elmer TGA7 system under a nitrogen atmosphere. The temperature was raised from 30 to 500 °C at a rate of 10 °C min^{-1}. Variable-temperature magnetic susceptibilities in the temperature range 2–300 K were measured on a CF-1 extracting-sample magnetometer at a magnetic field of 5.0 T with the powdered samples kept in capsules for weighing. Diamagnetic corrections were estimated from Pascal tables.

Crystallography

Intensity data for $\mathbf{1}\cdot 2n\mathrm{H_2O}$ and $\mathbf{3}\cdot 2n\mathrm{H_2O}$ were recorded on a Bruker CCD Area Detector Diffractometer using Mo-Kα radiation (λ = 0.71073 Å) in ϕ and ω scan modes while those for $\mathbf{2}\cdot 7n\mathrm{H_2O}$ were recorded on a Siemens P4 diffractometer in the ω scan mode. For all compounds, direct methods and Fourier techniques were used to solve the crystal structures. The structures were refined by full-matrix least-squares techniques with anisotropic thermal parameters for all the non-hydrogen atoms. Hydrogen atoms of $\mathbf{2}\cdot 7n\mathrm{H_2O}$ were generated in idealized positions while those of $\mathbf{1}\cdot 2n\mathrm{H_2O}$ and $\mathbf{3}\cdot 2n\mathrm{H_2O}$ were located from the ΔF map and refined with overall isotropic thermal parameters. The calculations for $\mathbf{2}\cdot 7n\mathrm{H_2O}$ were performed with the Siemens SHELXTL PC, while those for $\mathbf{1}\cdot 2n\mathrm{H_2O}$ and $\mathbf{3}\cdot 2n\mathrm{H_2O}$ with the Bruker SHELXTL NT V 5.1.[64] The crystallographic data are summarized in Table 5. The selected atomic distances and bond angles are presented in Tables 2–4.

CCDC reference numbers 164202–164204.

See http://www.rsc.org/suppdata/dt/b1/b102570h/ for crystallographic data in CIF or other electronic format.

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Table 5 Crystallographic data

	$\mathbf{1}\cdot 2n\mathrm{H_2O}$	$\mathbf{2}\cdot 7n\mathrm{H_2O}$	$\mathbf{3}\cdot 2n\mathrm{H_2O}$
Formula	$C_{14}H_{20}N_4Cu_2O_8$	$C_{32}H_{58}N_8Cu_4O_{21}$	$C_{14}H_{20}N_4Cu_2O_8$
M	499.42	1145.02	499.42
Space group	$P2_1/c$	$P2_1$	$Pca2_1$
Crystal system	Monoclinic	Monoclinic	Orthorhombic
a/Å	7.7373(10)	9.3800(10)	15.951(2)
b/Å	14.014(2)	20.613(2)	7.8879(8)
c/Å	9.1101(12)	12.0930(10)	14.826(2)
β/°	110.472(2)	104.270(10)	
V/Å^3	925.4(2)	2266.0(4)	1865.5(3)
Z	2	2	4
D_c/g m^{-3}	1.792	1.678	1.778
μ(Mo-Kα)/cm^{-1}	23.50	19.38	23.31
Measured reflections	5991	5294	11849
Unique reflections	2113 ($R_{\mathrm{int}} = 0.0290$)	4815 ($R_{\mathrm{int}} = 0.0283$)	4246 ($R_{\mathrm{int}} = 0.0478$)
Observed reflections ($I > 2\sigma(I)$)	1832	3712	3455
R	0.0321	0.0352	0.0361
wR	0.0917	0.0841	0.0782

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