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1-D Structures of assemblies containing oxamidato dicopper building blocks controlled by ditopic N-donor spacers

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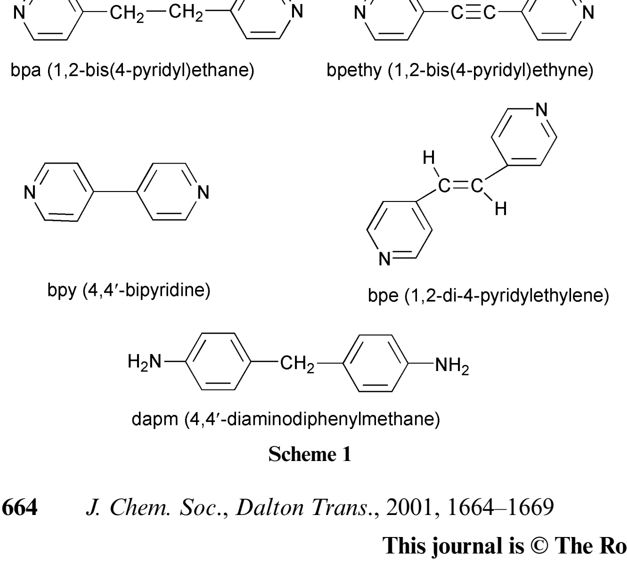
The assembly of the ditopic N-donor ligands bpy, bpe or dapm and the building block [Cu(*trans*-oxpy)Cu]$^{2+}$ (H_2oxpy = *N*,*N*′-bis(2-pyridylmethyl)oxamide) gave rise to three 1-D coordination polymers [Cu_2(*trans*-oxpy)(bpy)$(H_2O)_2]_n[NO_3]_{2n}\cdot nH_2O$ (bpy = 4,4′-bipyridine) **1**, [Cu_2(*trans*-oxpy)(bpe)$(H_2O)_2]_n[NO_3]_{2n}\cdot 3nH_2O$ (bpe = 1,2-di-4-pyridylethylene) **2** and [Cu_2(*trans*-oxpy)$(dapm)_2]_n[NO_3]_{2n}\cdot 6nH_2O$ (dapm = 4,4′-diaminodiphenylmethane) **3** and their structures were determined by single crystal X-ray crystallography. The copper atoms, which are located in distorted square-based pyramidal environments in all the complexes, are bridged alternately by oxpy and a ditopic spacer ligand to form infinite chains with fine structures varying with the flexibility of the ligand. Furthermore, there are interchain $\pi\cdots\pi$ interactions in **1** and **2** between the pyridyl rings of oxpy and the spacers. The dinuclear unit [Cu(*trans*-oxpy)Cu]$^{2+}$ displays an integrity in the assembly process. Variable temperature magnetic susceptibility measurements on **3** showed the presence of antiferromagnetic coupling interactions between the copper(II) ions bridged by oxpy. Thermal analyses indicated that dehydration occurred around 110 °C and these complexes are stable up to 230 °C.

Introduction

Many efforts have been devoted to the syntheses, structures and properties of supramolecular complexes for their potential application in material sciences.[1–10] Supramolecular chemistry as exemplified by the assembly with 4,4′-bipyridine (bpy) and its derivatives[11] is at the frontier of inorganometallic chemistry. The use of spacers containing two 4-pyridyl donor units has afforded very interesting structural motifs, such as double helices,[12] double sheets,[13] interpenetrated ladders[14] and brick-wall frameworks.[15] To our knowledge, most of these architectures were obtained by direct assembly of bpy and/or its derivatives with inorganic metal salts, while less attention was paid to their assembly with metal coordination complexes. The ligands bpethy (1,2-bis(4-pyridyl)ethyne),[16] bpa (1,2-bis-(4-pyridyl)ethane)[17] and bpy[18] (Scheme 1) were reported to be able to react directly with copper(II) salts to provide 3-D interpenetrated networks and 2-D rectangular grids. Previously, we have employed the *N*,*N*′-disubstituted oxamidato coordinated copper(II) complexes (Scheme 2), which proved to be excellent precursors for polymetallic systems,[19] to assemble with anionic spacers such as OH^-, N_3^-, and OCN^-, *etc.* giving rise to supramolecular architectures. Hereby we report the reactions of the copper(II) complex of H_2oxpy (*N*,*N*′-bis(2-pyridylmethyl)oxamide) with the neutral polyaromatic N-donor spacer bpy, bpe (1,2-di-4-pyridylethylene) or dapm (4,4′-diaminodiphenylmethane) (also see Scheme 1) in order to understand how the self-assembly process is controlled when some of the coordination sites of Cu^{II} are occupied by chelating ligands. The selection of the aforementioned ligands was based on the intention to investigate the influence of their conformational flexibility on the arrangement of the molecules in the crystal structures.



Scheme 1

Experimental

Syntheses

[Cu_2(*trans*-oxpy)(bpy)$(H_2O)_2]_n[NO_3]_{2n}\cdot nH_2O$ 1. An aqueous solution (15 cm^3) of $Cu(NO_3)_2\cdot 6H_2O$ (0.484 g, 2.0 mmol) was added to a stirred solution of H_2oxpy (0.139 g, 1.0 mmol) in water, followed by bpy (0.312 g, 2.0 mmol) in ethanol. The stirring was continued for 10–15 minutes and then the mixture was filtered. The filtrate was allowed to stand at ambient temperature for a week to yield black crystals. Yield: ≈45%. Calc. for $C_{24}H_{26}Cu_2N_8O_{11}$: C, 39.51; H, 3.59; N, 15.36. Found: C, 39.66; H, 3.48; N, 15.26%. IR(KBr pellets, cm^{-1}): 3409 (m), 3057 (w), 1665 (s), 1609 (s), 1560 (m), 1539 (w), 1482 (w), 1419 (m), 1384 (s), 1328 (s), 1278 (m), 1208 (w), 1159 (w), 1075 (w), 1053 (w), 1018 (w), 878 (w), 821 (w), 779 (m), 646 (w), 498 (w), 421 (w).

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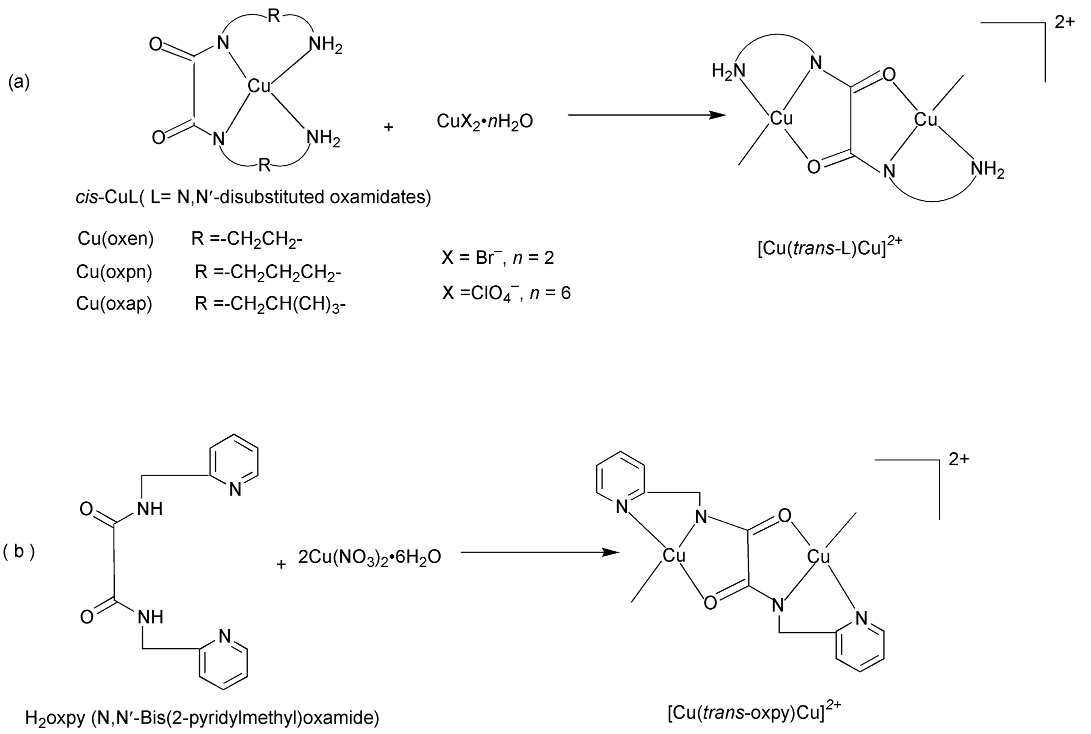

Scheme 2

[Cu_2(*trans*-oxpy)(bpe)$(H_2O)_2]_n[NO_3]_{2n}\cdot 3nH_2O$ 2. The synthetic procedure is similar to that of **1** except that bpy was replaced by bpe. Yield: ≈51%. Calc. for $C_{26}H_{32}Cu_2N_8O_{13}$: C, 39.45; H, 4.07; N, 14.15. Found: C, 39.67; H, 3.97; N, 14.02%. IR(KBr pellets, cm^{-1}): 3479 (w), 3395(w), 3043(w), 2924 (w), 1658 (s), 1609 (s), 1560 (m), 1482 (w), 1384 (s), 1314 (s), 1208 (w), 1159 (w), 1068 (w), 1025 (w), 990 (w), 878 (w), 835 (w), 772 (m), 716 (w), 554 (w), 498 (w), 414 (w).

[Cu_2(*trans*-oxpy)$(dapm)_2]_n[NO_3]_{2n}\cdot 6nH_2O$ 3. An aqueous solution (15 cm^3) of $Cu(NO_3)_2\cdot 6H_2O$ (0.484 g, 2.0 mmol) was first added to a stirred solution of H_2oxpy (0.139 g, 1.0 mmol) in water, the pH value adjusted to ≈5.0 by NaOH, then an ethanol solution (15 cm^3) of dapm (0.396 g, 2.0 mmol) added. The stirring was continued for several minutes to give green precipitates that were collected by filtration and washed with water and dried in a desiccator. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of an aqueous solution containing a mixture of H_2oxpy and $Cu(NO_3)_2\cdot 6H_2O$ and an ethanol solution of dapm in an H-tube. Yield: ≈65%. Calc. for $C_{40}H_{54}Cu_2N_{10}O_{14}$: C, 46.78; H, 5.26; N, 13.64. Found: C, 47.07; H, 4.84; N, 13.73%. IR(KBr pellets, cm^{-1}): 3444 (w), 3325 (w), 3268 (w), 1651 (s), 1616 (s), 1567 (m), 1510 (m), 1482 (w), 1384 (s), 1328 (s), 1257 (w), 1208 (w), 1180 (w), 1131 (m), 955 (w), 943 (w), 821 (w), 765 (w), 710 (w), 582 (w), 498 (w).

Physical measurements

IR spectra were recorded on a Nicolet FT-IR-170SX spectrophotometer in the 4000–400 cm^{-1} region. Variable-temperature magnetic susceptibilities in the temperature range 2–300 K were measured on a CF-1 extracting-sample magnometer at a magnetic field of 1.0 T with the powdered sample kept in capsules for weighing. Diamagnetic corrections were estimated from Pascal tables. TG analyses were carried out on the Perkin-Elmer TGA7 system. The temperature was raised from 30 to 500 °C at the rate of 10 °C min^{-1}.

X-Ray diffraction data collection and structure refinement

Single crystals with suitable dimensions were mounted on glass fibers and data collections were performed on a Bruker CCD Area Detector diffractometer by the φ and ω scan technique using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystallographic data are summarized in Table 1. For all complexes, the coordinates of the metal atoms were determined by direct methods, the remaining non-hydrogen atoms were located from successive Fourier difference syntheses. The structures were refined by full-matrix least-squares techniques with an anisotropic thermal parameters for all the non-hydrogen atoms. The occupancy O2w in **1** is 0.5. The atoms O3, O4 and O5 in **1** and C20, C21, O3, O4 and O5 in **2** are disordered, each located at two positions with an occupancy factor of 0.5. Most of the hydrogen atoms were located from the ΔF map and refined with overall isotropic thermal parameters, except H9a, H9b, H12, H16 and H26 of **2**, which were generated in idealized positions and fixed during the structural refinements. The calculations were performed on a COMPUCON PC/586 computer with the Bruker AXS SHELXTL/PC program package.[20] Selected atomic distances and bond angles are presented in Tables 2, 3 and 4 for **1**, **2** and **3**, respectively.

CCDC reference numbers 153691–153693.

See http://www.rsc.org/suppdata/dt/b0/b008807m/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis

As shown in Scheme 2(a), the copper(II) moieties *cis*-CuL with the oxamides(L) substituted by aliphatic amines reacted first with copper(II) salt to provide the dinuclear building block [Cu(*trans*-L)Cu]$^{2+}$ (L = oxen^{2-}, oxpn^{2-}, or oxap^{2-}), which then assembles with the second ligand (spacer) to give rise to polymeric compounds.[21] As for the ligand H_2oxpy containing the aromatic substituent pyridine (Scheme 2(b)), the dinuclear species [Cu(*trans*-oxpy)Cu]$^{2+}$ was obtained directly when H_2oxpy reacted with $Cu(NO_3)_2\cdot 6H_2O$ in the molar ratio 1 : 2. The building block was then linked by bpy, bpe or dapm to provide various coordination polymers.

Structure

[Cu_2(*trans*-oxpy)(bpy)$(H_2O)_2]_n[NO_3]_{2n}\cdot nH_2O$ 1. Complex **1** consists of polymeric one-dimensional chains formed from the

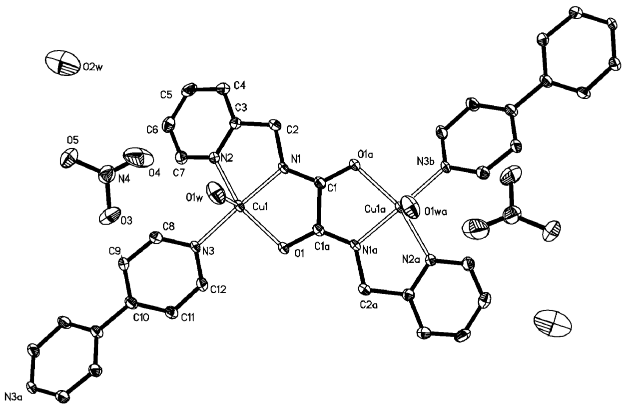

Fig. 1 Structure with atomic labeling of two asymmetric units of **1**; atoms are drawn with 30% probability ellipsoids (as in all the present cases).

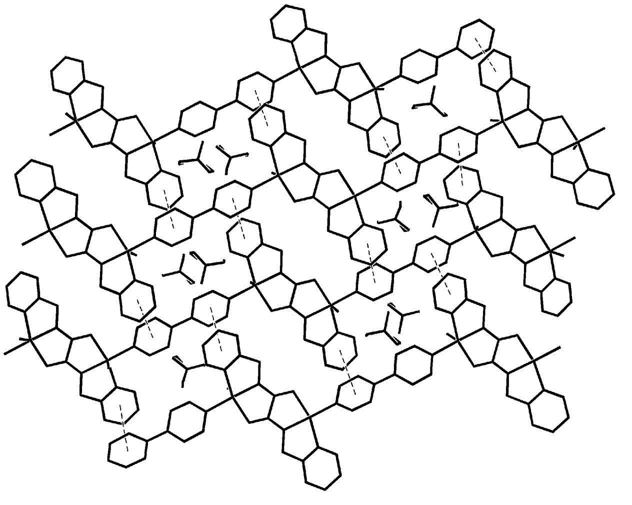

Fig. 2 Packing of $[Cu_2(\textit{trans}\text{-oxpy})(bpy)(H_2O)_2]_n[NO_3]_{2n}\cdot nH_2O$ **1** showing the interchain π · · · π interactions between py rings of bpy and oxpy.

Table 1 Crystallographic data for **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{24}H_{24}Cu_2N_8O_{11}$	$C_{26}H_{32}Cu_2N_8O_{13}$	$C_{20}H_{27}CuN_5O_7$
M	727.59	791.68	513.01
Space group	*C*2/*c*	$P2_1/n$	$P2_1/c$
a/Å	15.290(3)	17.5431(13)	9.6028(10)
b/Å	13.414(2)	8.8809(7)	15.4336(16)
c/Å	14.815(3)	21.5741(16)	15.7975(17)
β/°	115.298(4)	105.170(2)	104.869(2)
V/Å^3	2747.2(8)	3244.1(4)	2262.9(4)
μ/cm^{-1}	16.26	13.88	11.17
No. reflections used ($I \geq 2\sigma(I)$)	1966	5378	3274
No. parameters	271	532	407
T/°C	20(2)	20(2)	21(2)
R	0.0437	0.0487	0.0374
wR	0.0960	0.1406	0.0966

Details in common: monoclinic, $Z = 4$.

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

Cu1–N1	1.902(2)	Cu1–N3	1.968(3)
Cu1–O1	2.017(2)	Cu1–N2	2.041(3)
Cu1–O1w	2.329(3)	Cu1 · · · Cu1a	5.233
N1–Cu1–N3	177.17(12)	N1–Cu1–O1	83.37(10)
N3–Cu1–O1	94.77(10)	N1–Cu1–N2	80.82(11)
N3–Cu1–N2	100.24(11)	O1–Cu1–N2	155.50(11)
N1–Cu1–O1w	92.05(11)	N3–Cu1–O1w	90.35(11)
O1–Cu1–O1w	98.71(11)	N2–Cu1–O1w	100.44(12)

dinuclear units $[Cu(\textit{trans}\text{-oxpy})Cu]^{2+}$ linked together by bpy, and discrete nitrate anions and water molecules. Fig. 1 shows two asymmetric units in which the copper(II) ion is located in a square-based pyramidal environment with the basal plane composed of atoms O1, N1 and N2 from oxpy and N3 from bpy, while the axial position is occupied by a water molecule. The dihedral angle of the two pyridyl rings in bpy is 60.3°. As depicted in Fig. 2, the copper(II) atoms are alternately bridged by oxpy and bpy to give infinite zigzag chains in which interchain π · · · π interactions between the py rings of bpy and oxpy pull the chains together. The center to center distances of the py rings are in the range 3.65–3.92 Å, while the Cu · · · Cu distances through the oxpy and bpy bridges are 5.23 and 10.99 Å, respectively. The shortest interchain Cu · · · Cu distance is 7.57 Å, in between the two bridging distances within a chain. Hydrogen bonds (Fig. 2) are formed among both the ligated (H_2O1w) and free (H_2O2w) water molecules and the anions NO_3^- with distances 3.089 (O1wp · · · O4n) and 2.909 Å (O2wa · · · O5m).

$[Cu_2(\textit{trans}\text{-oxpy})(bpe)(H_2O)_2]_n[NO_3]_{2n}\cdot 3nH_2O$ 2. Complex **2** contains one-dimensional chains, formed from the dinuclear units $[Cu(\textit{trans}\text{-oxpy})Cu]^{2+}$ linked together by bpe, and discrete nitrate anions and water molecules. Shown in Fig. 3 are two asymmetric units of **2**. The copper atom is five-coordinate and adopts a square pyramidal geometry with the basal plane containing three atoms (N1, N2 and O1 for Cu1; N3, N4 and O2 for Cu2) from oxpy and one (N5 for Cu1 and N6a for Cu2) from bpe, while the axial position is again occupied by a water molecule (O2w for Cu1 and O1w for Cu2). The dihedral angle between the two pyridyl rings of bpe is only 11.7°, showing coplanarity. The copper(II) atoms are alternately bridged by oxpy and bpe to give an infinite zigzag chain with the Cu · · · Cu distances being 5.26 and 13.33 Å, respectively.

Fig. 4 shows that π · · · π interactions occur between the pyridyl rings of oxpy and between those of oxpy and bpe in neighboring chains. The shortest interchain Cu · · · Cu distance is 8.58 Å. The center to center distances of overlapping rings are in the range 3.60–3.70 Å. There are abundant hydrogen bonds between both coordinated and solvated water molecules and the nitrate anions. The distances are 2.804 (O1wc · · · O3wb), 2.766 (O6b · · · O3wb), 2.846 (O5wb · · · O7b), 2.915 (O5wb · · · O5a), 2.764 (O1wb · · · O4wa), 2.867 (O4wa · · · O3wa), 2.779 (O4wa · · · O5wa), 2.806 (O4b · · · O2we), 2.910 (O5b · · · O3wa) and 2.941 Å (O8 · · · O3w).

$[Cu_2(\textit{trans}\text{-oxpy})(dapm)_2]_n[NO_3]_{2n}\cdot 6nH_2O$ 3. Complex **3** is composed of one-dimensional cationic chains, which are formed by the dinuclear units $[Cu(\textit{trans}\text{-oxpy})Cu]^{2+}$ doubly linked by two dapm to give garland-like rings, and anions NO_3^- and water molecules. This is the only complex among the three that has double spacer bridges without water ligation. Fig. 5 shows four asymmetric units composing two of the garlands. The square pyramidal copper(II) center has the basal plane constructed by N4a, N3a and O1 from oxpy and N1 from dapm, while the axial position is occupied by N2b from the other dapm. The bond distance Cu1–N1 (basal 2.025 Å) is much shorter than that of Cu1–N2b (axial 2.339 Å). Atom O3ac of a nitrate ion weakly coordinates to Cu1j with the bond distance 2.872 Å. The dihedral angle of the two phenyl rings in a dapm is 97.1°. The Cu · · · Cu distances through oxpy and dapm bridges are 5.31 and 10.39 Å, respectively. Fig. 6 demonstrates the stacking of chains in **3** and the hydrogen bonding interactions between the water molecules and between H_2O and the anions with the distances 3.033 (O3aa · · · O1wa) and 2.845 (O3wd · · · O1wa), 2.943 (O3wd · · · O2we), and 2.976 Å (O3ac · · · O2we).

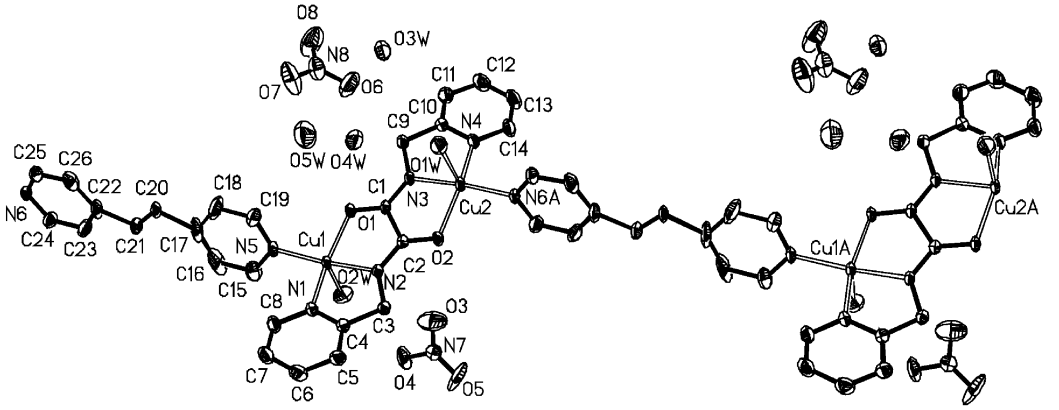

Fig. 3 Structure with atomic labeling of two asymmetric units of **2**.

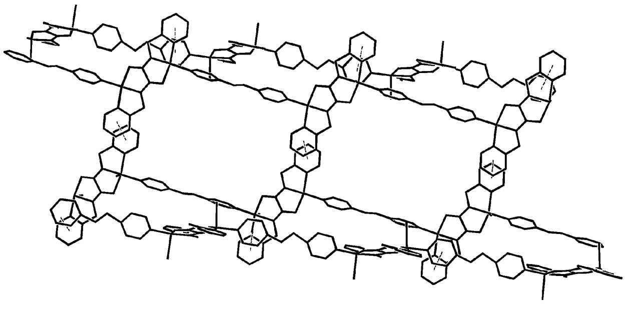

Fig. 4 Packing view of $[Cu_2(\textit{trans}\text{-oxpy})(bpe)(H_2O)_2]_n[NO_3]_{2n}\cdot3nH_2O$ **2** showing the π···π interactions between pyridyl rings of oxpy and between those of oxpy and bpe.

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

Cu1–N2	1.914(2)	Cu1–N5	1.969(3)
Cu1–O1	2.015(2)	Cu1–N1	2.029(3)
Cu1–O2W	2.345(3)	Cu2–N3	1.921(2)
Cu2–N6a	1.978(3)	Cu2–O2	2.023(2)
Cu2–N4	2.024(3)	Cu2–O1W	2.295(3)
Cu1···Cu2	5.257		
N1–Cu1–N5	171.72(12)	N2–Cu1–O1	83.15(9)
N5–Cu1–O1	94.59(10)	N2–Cu1–N1	81.01(10)
N5–Cu1–N1	98.75(11)	O1–Cu1–N1	157.23(10)
N2–Cu1–O2W	93.74(12)	N5–Cu1–O2W	94.42(13)
O1–Cu1–O2W	95.86(11)	N1–Cu1–O2W	101.39(12)
N3–Cu2–N6a	173.75(11)	N3–Cu2–O2	83.18(9)
N6a–Cu2–O2	93.72(10)	N3–Cu2–N4	80.67(11)
N6a–Cu2–N4	100.29(11)	O2–Cu2–N4	154.28(11)
N3–Cu2–O1W	89.87(12)	N6a–Cu2–O1W	96.04(12)
O2–Cu2–O1W	100.51(12)	N4–Cu2–O1W	99.33(12)

As described above, different from the structures constructed directly from copper(II) salts and bpy or its derivatives,[16–18] complexes **1**–**3** here are 1-D polymeric chains without interpenetration. This result may be attributed to the fact that three of the coordination sites of each copper(II) in the building block $[Cu(\textit{trans}\text{-oxpy})Cu]^{2+}$ have already been occupied by the oxpy, thus the spacer bpy, bpe or dapm can only bind to Cu^{II} through the unoccupied positions in restricted directions to provide low dimensional architectures. Complexes **1** and **2** contain zigzag chains with single bridges while **3** contains chains with double bridges. Noticeably, chains in **1** and **2** are associated with each other through the interchain π···π interactions.

The above result showed that the choice of spacer is crucial in the formation of polymeric structures. The rigid bpy and bpe link the building blocks with only a single bridge due to the restricted orientation of their donor groups, while the more flexible dapm with a methylene group in sp^3 hybridization can bend easily to accommodate two NH_2 in one macrocyclic double bridge ellipse with long axis (10.39 Å) and short one (9.32 Å).

Table 4 Selected bond lengths (Å) and angles (°) for **3**

Cu1–N3a	1.925(2)	Cu1–N1	2.025(2)
Cu1–N4a	2.045(2)	Cu1–O1	2.064(2)
Cu1–N2b	2.339(2)	Cu1···Cu1a	5.314
N3–Cu1a	1.925(2)		
N3a–Cu1–N1	163.04(6)	N3a–Cu1–N4a	81.00(6)
N1–Cu1–N4a	108.09(6)	N3a–Cu1–O1	82.21(6)
N1–Cu1–O1	87.40(6)	N4a–Cu1–O1	162.88(6)
N3a–Cu1–N2b	97.04(6)	N1–Cu1–N2b	95.75(7)
N4a–Cu1–N2b	98.38(6)	O1–Cu1–N2b	86.94(5)

There is one characteristic that needs to be pointed out: the moiety $[Cu(\textit{trans}\text{-oxpy})Cu]^{2+}$ in complexes **1**–**3** is rather rigid and a comparison of the relative atomic distances and bond angles (Tables 2–4) showed intramolecular synergism of the species; no significant variations in the structural parameters of the building block $[Cu(\textit{trans}\text{-oxpy})Cu]^{2+}$ among the three complexes. That is to say, the building block participates in the supramolecular self-assembly processes of **1**–**3** as a rigid entity.

Magnetic properties

The temperature dependence of the effective magnetic moment μ_{eff} per copper(II) atom of **3** is shown in Fig. 7. The fact that μ_{eff} reduces gradually with the decrease of temperature reveals an antiferromagnetic interaction. Obviously, the presence of different bridging paths may transmit different magnetic exchange interactions. Oxamidate is known to afford an effective exchange pathway to mediate a strong antiferromagnetic coupling interaction.[13,15] Since the Cu···Cu separation through the dapm bridge is so large (10.39 Å) that the magnetic orbitals of the two neighbouring copper(II) ions cannot overlap effectively, the exchange interaction transmitted by dapm could be negligible. Thus, the 1-D magnetic coupling system of **3** can be simplified as interacting dimers $[Cu(\textit{trans}\text{-oxpy})Cu]^{2+}$ with coupling constant J. On this basis it should be possible to interpret the data by means of a simple modified Bleaney–Bowers equation:[19e] $\chi_m = (2N\beta^2g^2/kT)[3 + \exp(-J/kT)]^{-1}(1 - p) + (N\beta^2g^2/2kT)p + N_\alpha$.

Least-squares fitting of the experimental data led to $J = -437.57$ cm^{-1}, $g = 2.09$, $p = 0.020$, and $R = 1.80 \times 10^{-3}$ with R defined as $\Sigma(\mu_{obsd} - \mu_{calcd})^2/\Sigma(\mu_{obsd})^2$, where ρ is the percentage of the paramagnetic impurities, N_α the temperature-independent paramagnetism (120×10^{-6} cm^3 mol^{-1}), and N, β and k have their usual meanings. The curve calculated with these parameters gave a reasonable fit to the experimental data as shown by the solid line in Fig. 7. The obtained J value is close to previously reported ones for other structurally characterized oxamidato-bridged copper(II) complexes,[19,21] which are in the

Table 5 The TGA data of **1**, **2** and **3**

Complex	Dehydration temperature range/°C	Wt. loss (%) measured	Wt. loss (%) calc.	Number of water molecules lost	Decomposition temp./°C
1	100–107	9.2	9.5	2	248
2	100–120	10.9	11.4	2	268
3	105–120	9.9	10.6	6	230

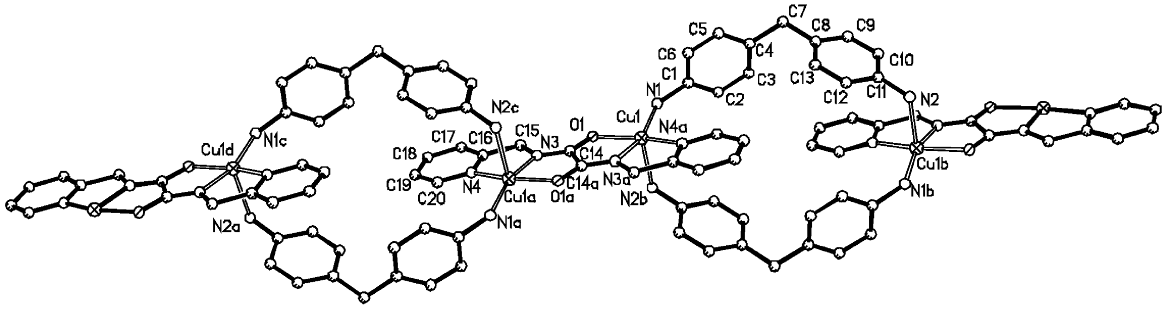

Fig. 5 Structure with atomic labeling of four asymmetric units of the chain in **3**. The anion and water molecules are omitted for clarity.

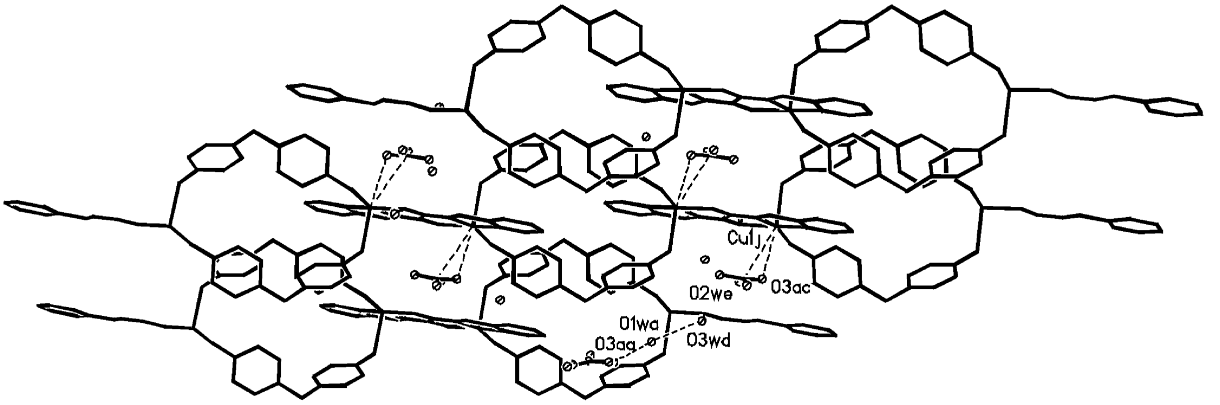

Fig. 6 Packing of the chains in $[Cu_2(oxpy)(dapm)_2]_n[NO_3]_{2n}\cdot 6nH_2O$ **3** showing the stacking and the hydrogen bonds with the water molecules and the oxygen atoms of the anions being labeled.

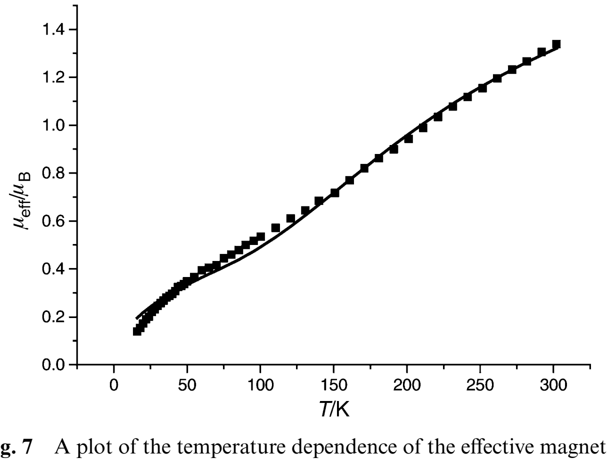

Fig. 7 A plot of the temperature dependence of the effective magnetic moment μ_{eff} for $[Cu_2(oxpy)(dapm)_2]_n[NO_3]_{2n}\cdot 6nH_2O$ **3**. (■) Experimental points; (—) calculated curve.

range −350 to 500 cm^{-1}. The change of the J value in different oxamidato-bridged complexes can be interpreted by a series of factors such as structural distortions.[22]

Thermal analyses

These complexes lost their solvated water molecules in the range 100–120 °C, but they are stable up to 230–268 °C. The TGA data listed in Table 5 indicated that the thermal behaviors of these complexes are similar to those for other previously reported oxamidato-bridged complexes.[21a]

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