

Extended network *via* hydrogen bond linkages of zig-zag co-ordination chains [$\{\text{Cu}_2(\textit{trans}\text{-oxen})(\mu\text{-OH})(\mu\text{-H}_2\text{O})\}_n\}^{n+}$ or $[\text{Cu}_2(\textit{trans}\text{-oxen})(\mu\text{-OCN})_2]_n$ [$\text{H}_2\text{oxen} = N,N'$ -bis(2-aminoethyl)-oxamide]

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The *trans*-oxamidato-bridged polymeric complexes $[\text{Cu}_2(\textit{trans}\text{-oxen})(\mu\text{-OH})(\mu\text{-H}_2\text{O})]_n\text{Br}_n \cdot 2n\text{H}_2\text{O}$ **1** and $[\text{Cu}_2(\textit{trans}\text{-oxen})(\mu\text{-OCN})_2]_n \cdot n\text{H}_2\text{O}$ **2** [$\text{H}_2\text{oxen} = N,N'$ -bis(2-aminoethyl)oxamide] with zig-zag co-ordination chains were synthesized and characterized by single-crystal X-ray diffraction methods. The cationic chains [$\{\text{Cu}_2(\textit{trans}\text{-oxen})(\mu\text{-OH})(\mu\text{-H}_2\text{O})\}_n\}^{n+}$ in **1** bridged alternately by *trans*-oxamidate, $\mu\text{-OH}$ and $\mu\text{-H}_2\text{O}$ arranged in three directions intersect with one another to yield an extended network *via* the interchain hydrogen bonds formed by metal-co-ordinated OH^- and H_2O and the solvate water molecules with the linkages $\text{Cu}\text{-OH} \cdots \text{OH}\text{-Cu}$ and $\text{Cu}\text{-H}_2\text{O} \cdots \text{H}_2\text{O} \cdots \text{H}_2\text{O}\text{-Cu}$. The neutral chains $[\text{Cu}_2(\textit{trans}\text{-oxen})(\mu\text{-OCN})_2]_n$ in **2** bridged alternately by *trans*-oxamidate and double cyanate bridges in an asymmetric N-bonded end-on mode are joined together by bridging H_2O molecules *via* the hydrogen bond linkage $\text{Cu}(\textit{oxen}) \cdots \text{H}_2\text{O} \cdots (\textit{oxen})\text{Cu}$ to produce the extended network structure. The magnetic calculations showed the presence of antiferromagnetic couplings between the copper(II) ions through both the *trans*-oxamidate and $\mu\text{-OH}$ or cyanate bridges.

One of the most active research topics of current chemistry and molecular material science is the crystal engineering of low- and three-dimensional metal co-ordination molecules and supramolecules¹ aimed at creating systems to perform optical, electronic and magnetic functions,² as well as intercalation systems³⁻⁵ for ion- or molecule-exchange and catalytic properties.⁶ The strategies used for the architecture of functional systems depend on the nature of the interactions responsible for creating networks. One of the best strategies to fabricate 2-D and 3-D systems is to utilize the hydrogen bonding of the co-ordinated ligands in addition to their co-ordination capability. A useful way to realize the strategy is to interlink the 1-D co-ordination molecules *via* the hydrogen interactions between the chains, though networks assembled by this way have not yet attracted great attention.⁷⁻¹⁰

N,N'-Disubstituted oxamides are well known to be versatile ligands which can chelate as well as bridge metal ions to build polynuclear and low-dimensional molecules.¹¹ One of the most outstanding characteristics of these ligands is the transformation of *cis-trans* conformation, which makes it practical to design tunable molecular materials with extended structures and desired properties. On one hand, the bidentate chelating character of the mononuclear metal compounds of *cis*-oxamidates makes them good precursors to build bi-,¹² tri-¹³ and even penta-nuclear¹⁴ homo- and hetero-metallic molecular entities. On the other hand, the bis-terdentate character of *trans*-oxamidates favours the formation of *trans*-oxamidato-bridged binuclear units with unsaturated co-ordinated sites, which may act as the building blocks to be further linked by a second bridging group to construct extended systems.^{15,16} When these remaining co-ordinated sites are occupied simply by terminal ligands, the products isolated are simply binuclear dimers.¹⁷ Fortunately, it is found that these building blocks can easily be linked by bridging ligands such as azide,^{15a,c,16b}

cyanate,^{15b} cyanide,^{16e} pyrimidine,^{16a,d} 4,4'-bipyridine^{16a} and carboxylate^{15d,e,16c,f} to construct 1-D chain or 2-D sheet-like co-ordination polymers. Moreover, the strong H-bonding character of these ligands containing N and O donors makes it useful for the design of 3-D supramolecular structures *via* H-bond linkages of the *trans*-oxamidato-bridged 1-D chains or 2-D sheets.

In a systematic work aimed at the architecture of polymeric metal complexes of *N,N'*-disubstituted derivatives and the investigation of its host-guest chemistry, two *trans*-oxamidato-bridged polymeric complexes $[\text{Cu}_2(\textit{trans}\text{-oxen})(\mu\text{-OH})(\mu\text{-H}_2\text{O})]_n\text{Br}_n \cdot 2n\text{H}_2\text{O}$ **1** and $[\text{Cu}_2(\textit{trans}\text{-oxen})(\mu\text{-OCN})_2]_n \cdot n\text{H}_2\text{O}$ **2** [$\text{H}_2\text{oxen} = N,N'$ -bis(2-aminoethyl)oxamide] were obtained with the co-ordination zig-zag chains interacting with one another *via* hydrogen bonds to produce extended network structures.

Experimental

Preparations

The ligand H_2oxen and its mononuclear compound $\text{Cu}(\textit{oxen}) \cdot 2\text{H}_2\text{O}$ were prepared by literature methods.¹⁸

$[\text{Cu}_2(\textit{trans}\text{-oxen})(\mu\text{-OH})(\mu\text{-H}_2\text{O})]_n\text{Br}_n \cdot 2n\text{H}_2\text{O}$ 1. An aqueous solution (5 cm³) of CuBr_2 (0.22 g, 1.0 mmol) was added to an aqueous solution of $\text{Cu}(\textit{oxen}) \cdot 2\text{H}_2\text{O}$ ¹¹ (0.27 g, 1.0 mmol) in water (30 cm³) with a colour change from violet-red to blue. An aqueous solution (10 cm³) of Na_2CO_3 (0.11 g, 1.0 mmol) or $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (0.38 g, 1.0 mmol) was then added dropwise with stirring at room temperature. After stirring for 10 min more, the solution was filtered and the filtrate was allowed to stand at room temperature for several days. Well shaped dark blue single crystals were obtained by slow evaporation. Yield: 48% (Found: C, 15.8; H, 4.1; N, 12.4. Calc. for $\text{C}_6\text{H}_{19}\text{BrCu}_2\text{N}_4\text{O}_6$: C, 16.0; H, 4.3; N, 12.4%). IR (KBr pellet)/cm⁻¹: 3416s (br), 3310s, 3240m, 3158m, 2980w, 2938m, 2860w, 1658s, 1595m, 1447m, 1349m, 1324s, 1032m, 547s, 449m.

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Table 1 Crystal data, data collection and refinement parameters for compounds **1** and **2**

	1	2
Formula	C ₆ H ₁₉ BrCu ₂ N ₄ O ₆	C ₈ H ₁₄ Cu ₂ N ₆ O ₅
<i>M</i>	450.24	401.33
Colour and habit	Dark blue prism	Black green prism
Crystal size/mm	0.60 × 0.60 × 0.44	0.52 × 0.40 × 0.28
System	Rhombohedral	Monoclinic
Space group	R $\bar{3}c$	C2/c
<i>a</i> /Å	14.873(2)	12.8780(10)
<i>b</i> /Å	14.873(2)	6.8970(10)
<i>c</i> /Å	34.872(7)	16.1170(10)
β /°		107.670(10)
<i>U</i> /Å ³	6680(2)	1364.0(2)
<i>T</i> /K	290(2)	290(2)
<i>Z</i>	18	4
<i>D</i> _c /g cm ⁻³	2.015	1.954
μ (Mo-K α)/cm ⁻¹	55.82	31.50
<i>F</i> (000)	4032	808
2 θ range/°	3.94 to 50	5.3 to 58
<i>h</i> , <i>k</i> , <i>l</i> Ranges	0–17, –17 to 1, 0–41	–17, 0–9, –21 to 20
Independent reflections	1323	1813
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	965	1484
<i>R</i> ^a	0.0349	0.0234
<i>R</i> ' ^b	0.0820	0.0582
No. of variables	93	125
<i>S</i>	0.909	1.018
Residual extrema/e Å ⁻³	+0.681 to –0.399	+0.449 to –0.342
(Δ / σ) _{max}	0.008	0.001
<i>R</i> _{int}	0.0307	0.0107

^a $R = \sum ||F_o| - |F_c||/|F_o|$. ^b $R' = [\sum w(|F_o|^2 - |F_c|^2)]/[\sum w(F_o)^2]^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (0.0504P)^2]$ for **1**, $w = 1/[\sigma^2(F_o)^2 + (0.0387P)^2]$ for **2** where $P = [\max(F_o^2) + 2F_c^2]/3$.

[Cu₂(*trans*-oxen)(μ -OCN)₂]_{*n*}·*n*H₂O **2.** To an aqueous solution (40 cm³) of Cu(oxen)·2H₂O (0.27 g, 1.0 mmol) was added an aqueous solution (10 cm³) of CuBr₂ (0.22 g, 1.0 mmol) with stirring. An aqueous solution (10 cm³) of KOCN (0.16 g, 2.0 mmol) was then added dropwise to the above blue solution to yield a green precipitate. After stirring for a while, the solution was filtered and allowed to stand at room temperature for several days to give black-green crystals. Yield: 42% (Found: C, 23.7; H, 3.6; N, 21.0. Calc. for C₈H₁₄Cu₂N₆O₅: C, 23.9; H, 3.5; N, 20.9%). IR (KBr pellet)/cm⁻¹: 3543w, 3479m, 3325s, 3261m, 3170w, 2959w, 2896w, 2853w, 2214s, 1651s, 1602m, 1440w, 1349m, 1314m, 1039m, 674w, 625w, 527w, 463w. Well shaped single crystals suitable for X-ray diffraction were obtained by the slow-diffusion method using an H-tube. The starting materials were an aqueous solution of KOCN in one arm and Cu(oxen)·2H₂O and CuBr₂ in an equimolar ratio in the other arm of the H-shaped tube.

Crystal structure determinations

Single crystals with suitable dimensions were mounted on glass fibers and data collection were performed on a Siemens P4 diffractometer by ω -scan techniques using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Intensity data were collected in the 2 θ range 4–50 and 5.3–58° for **1** and **2**, respectively. The crystal data, data collection and refinement parameters are summarized in Table 1.

The coordinates of the metal atoms were determined by direct methods and the remaining non-hydrogen atoms were located from successive Fourier-difference syntheses. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all the non-hydrogen atoms. For compound **1**, the hydrogen atoms were located from the ΔF map [H(40a)] and an analysis of the geometry, and were included with a common thermal parameter; exceptions being those of O(2) and O(3) which remained undetermined. The

Table 2 Selected atomic distances (Å) and bond angles (°) for compound **1**

Cu–O(2)	1.894(2)	Cu–N(1)	1.903(4)
Cu–N(2)	2.011(4)	Cu–O(1a)	2.028(3)
Cu–O(4)	2.639(2)	Cu···Cu(a)	5.235(2)
Cu···Cu(b)	3.119(3)	O(2)···O(2b)	2.722(2)
O(4)···O(3)	2.862(2)		
O(2)–Cu–N(1)	177.38(13)	O(2)–Cu–N(2)	98.97(12)
N(1)–Cu–N(2)	83.3(2)	O(2)–Cu–O(1a)	94.26(8)
N(1)–Cu–O(1a)	83.63(14)	N(2)–Cu–O(1a)	165.58(2)
O(4)–Cu–N(2)	85.36(5)	O(4)–Cu–O(2)	88.22(8)
O(4)–Cu–O(1a)	89.87(6)	O(4)–Cu–N(1)	93.28(12)
Cu–O(2)–Cu(b)	110.9(2)	Cu–O(4)–Cu(b)	72.5(2)
O(4)–H(4oc)···O(3)	150.2(2)	O(4)–H(4oa)···O(3b)	150.2(2)

Table 3 Selected atomic distances (Å) and bond angles (°) for compound **2**

Cu–N(1)	1.912(2)	Cu–N(3)	1.916(2)
Cu–N(2)	2.018(2)	Cu–O(1)	2.0363(13)
Cu–N(3b)	2.604(2)	Cu···Cu(a)	5.260(2)
Cu···Cu(b)	3.246(3)	O(3w)···O(1)	2.892(2)
O(3w)···N(2)	3.060(2)		
N(1)–Cu–N(3)	175.79(7)	N(1)–Cu–N(2)	82.86(7)
N(3)–Cu–N(2)	98.71(7)	N(1)–Cu–O(1)	82.86(6)
N(3)–Cu–O(1)	95.30(6)	N(2)–Cu–O(1)	165.32(6)
N(1)–Cu–N(3b)	92.54(6)	N(2)–Cu–N(3b)	94.35(6)
N(3)–Cu–N(3b)	92.05(7)	O(1)–Cu–N(3b)	89.55(6)
Cu–N(3)–Cu(b)	90.53(5)	C(2)–N(1)–Cu	117.37(11)
C(1a)–N(1)–Cu	116.48(12)	O(3w)–H(3w)···O(1)	154.0(2)

O(2) and O(4) atoms lie on a C₂ axis, and Br(1) and Br(2) on C₃ and I₃ axes, respectively. For compound **2**, all the H atoms were located from Fourier-difference syntheses and refined with a common thermal parameter. Although the thermal factor for O(2) is considerably higher than that of any other non-hydrogen atoms, the normal *U*_{eq} values for N(3) and C(4) support the presence of N-bonded cyanate and exclude the possibility of a mobile cyanate anion. All calculations were performed on an IBM PC/486 computer with the Siemens SHELXTL-P4/PC program package.¹⁹ The selected atomic distances and bond angles are presented in Tables 2 and 3 for **1** and **2**, respectively.

CCDC reference number 186/877.

See <http://www.rsc.org/suppdata/dt/1998/1133/> for crystallographic files in .cif format.

Physical measurements

The IR spectra were obtained using a Perkin-Elmer 577 spectrophotometer as KBr pellets. Variable-temperature magnetic susceptibilities in the temperature range 4–300 K were measured on a model CF-1 superconducting extracting sample magnetometer at a magnetic field of 5.0 T for **1** and on a SQUID magnetometer in 1.0 T magnetic field for **2** with the powdered samples kept in capsules for weighing. The temperature was raised gradually from 4.2 to 300 K. Data were recorded at an applied field gradient $H(dH/dX)$ of 1.4×10^{-1} T × T/cm. An interval of 30 s was kept between data collections and each measurement took 10 s.

Results and Discussion

The structure of compound **1** contains $\{[\text{Cu}_2(\textit{trans}\text{-oxen})(\mu\text{-OH})(\mu\text{-H}_2\text{O})]_n\}^{n+}$ cations, Br[–] anions and solvated water molecules. The cation exhibits a zig-zag chain structure with bridging ligands oxen^{2–}, HO[–] and H₂O, where the binuclear copper units Cu(oxen)Cu of *trans*-oxamidate are linked by $\mu\text{-OH}^-$ and $\mu\text{-OH}_2$ bridges which are symmetrically located in the equatorial and axial sites, respectively, as shown in Fig. 1.

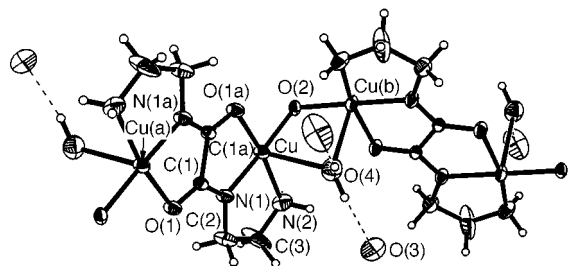


Fig. 1 A perspective view of four symmetry-related asymmetric units with the atom numbering scheme showing cationic zig-zag chain structure in compound **1**

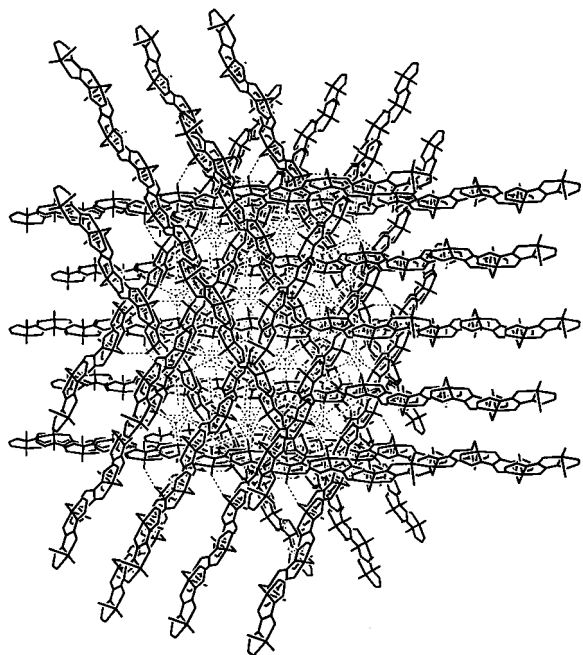


Fig. 2 A View of the extended network down the *c* axis of compound **1**, showing the H-bond interactions of the zig-zag chains extended in three different directions

The bond Cu–O(2) [1.894(2) Å] is much shorter than Cu–O(4) [2.639(2) Å], and the bridging angle Cu–O(2)–Cu(b) (110.9°) is much larger than Cu–O(4)–Cu(b) (72.5°). An inversion centre occurs at the middle of the C(1)–C(1a) amide bond and a *C*₂ axis is located on the line linking atoms O(2) and O(4). The oxamidate in a *trans*-conformation behaves as a bis-terdentate bridging ligand bonding to two copper atoms to form four five-membered chelating rings. The sp² hybridization of the deprotonated amide nitrogen atom [N(1)] together with the fact that the bond C(1)–N(1) [1.289(6) Å] is much shorter than N(1)–C(2) [1.436(6) Å] reveals the former to have a considerable extent of double-bond character.

The copper atom is in a distorted square-based pyramidal environment with the equatorial plane consisting of N₂O₂ from *trans*-oxamidate and the μ-OH, and the apical site occupied by O of μ-OH₂. The mean co-ordination planes of Cu and Cu(b) with a dihedral angle of 68.2° form a dihedral angle of 92.4° with the mean plane defined by the bridging pathway CuO(2)Cu(b)O(4). The intrachain copper···copper separations through *trans*-oxen and oxo bridges are 5.235 and 3.119 Å, respectively, while the shortest interchain distance is 4.592 Å. The co-ordinated water [H₂O(4)] associates with the lattice waters [H₂O(3) and H₂O(3b)] *via* hydrogen bonds with distances O(4)···O(3) [O(3b)] of 2.862 Å. The zig-zag chains extending in three different directions which are symmetry-related to one another *via* a *C*₃ axis intersect one another, affording an interwoven network with a reversibly oriented equilateral triangular arrangement, thus forming hexagonal cavities in which the Br[−] anions are located. The μ-OH groups

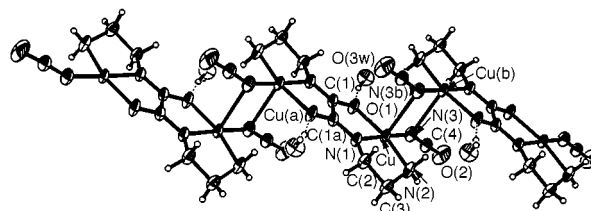


Fig. 3 A perspective view of four symmetry-related asymmetric units with the atom numbering scheme showing the neutral zig-zag chain structure of compound **2**

in the three chains form interchain H bonds to one another with an O···O distance of 2.722 Å to build an extended network as shown in Fig. 2. Moreover, the chains also interact with one another *via* the weak hydrogen bonds between the amine N and amide O atoms with a distance of 3.006 Å.

The structure of compound **2** consists of neutral polymeric molecules [Cu₂(*trans*-oxen)(μ-OCN)₂]_n and solvated H₂O molecules and exhibits a zig-zag chain structure derived from the linkages of *trans*-oxamidato-bridged dimeric units Cu(*trans*-oxen)Cu *via* both equatorial and axial bridging modes of the double cyanate groups as shown in Fig. 3. The *trans*-oxamidate behaves as a bis-terdentate ligand chelating as well as bridging the copper ions, whereas cyanate behaves as a N-bonded bridging group in a severely asymmetric end-on mode with the Cu–N bond [2.604(2) Å] in an axial site much longer than that in an equatorial one [1.916(2) Å].^{15b} The bridging angle Cu–N(3)–Cu(b) is 90.5°. The cyanate group is quasi-linear with an N(3)–C(4)–O(2) angle of 176.3(3)° while the linkage C(4)–N(3)–Cu is bent with an angle of 151.8(2)°. The zig-zag chain is centrosymmetric with the inversion centers at the middle of the amide C(1)–C(1a) and N(3)–N(3b) [or Cu···Cu(b)] bonds, respectively.

The copper centre is in an elongated square-based pyramidal environment with N₃O donors from oxamidate and cyanate in the equatorial plane and the axial site occupied by the N atom from another cyanate group bound equatorially to the Cu(b) center. Each deprotonated *trans*-oxamidate joins with two copper centers to yield four five-membered rings with the bond Cu–N_{amide} [1.912(2) Å] much shorter than Cu–N_{amine} [2.018(2) Å]. The mean co-ordination plane CuO(1)N(1)N(2)N(3) forms a dihedral angle of 89.6° with the least-squares plane defined by the bridging atoms Cu, N(3), Cu(b) and N(3b). The solvated H₂O molecules with atom O_{water} on the *C*₂ axes associate with the amide O and amine N atoms *via* a series of hydrogen bonds between the co-ordination chain and H₂O molecules with O_{amide}···H₂O and H₂O···H₂N_{amine} distances of 2.892 and 3.060 Å, respectively. Thus, the neighbouring co-ordination chains are joined with one another *via* the H₂O-bridged interchain H-bonded linkage O_{amide}···H₂O···O_{amide}, to produce an extended network as illustrated in Fig. 4. Moreover, a direct interchain H-bonded interaction also occurs between the cyanate O and amine N atoms of oxamidate with a distance of 2.983 Å similar to that (2.976 Å) found in the complex [Cu₂(apox)(NCO)₂] [H₂apox = *N,N'*-bis(3-aminopropyl)-oxamide].^{15b} However, the packing and linkages of the chains in the two complexes have significant differences. The chains are linked *via* H-bonded H₂O bridges as well as by direct H-bond interactions in compound **2**, whereas only the direct interchain H-bond interactions join the [Cu₂(apox)(NCO)₂] chains. The copper···copper distances through the bridging *trans*-oxamidate groups and OCN[−] are 5.260 and 3.246 Å, respectively, while the shortest interchain distance is 4.140 Å.

The temperature dependences of the effective magnetic moment μ_{eff} per copper(II) atom of complexes **1** and **2** are shown in Fig. 5. The fact that μ_{eff} reduces gradually with the decrease of the temperature reveals an antiferromagnetic interaction. Obviously, the presence of different bridging paths may induce different magnetic exchange interactions. Oxamidate is

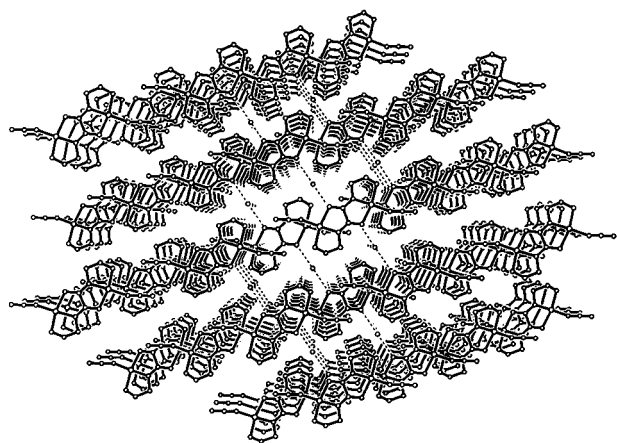


Fig. 4 A view of the extended network down the *b* axis of compound **2**, showing the H-bonded linkages between the zig-zag chains *via* the H₂O molecules

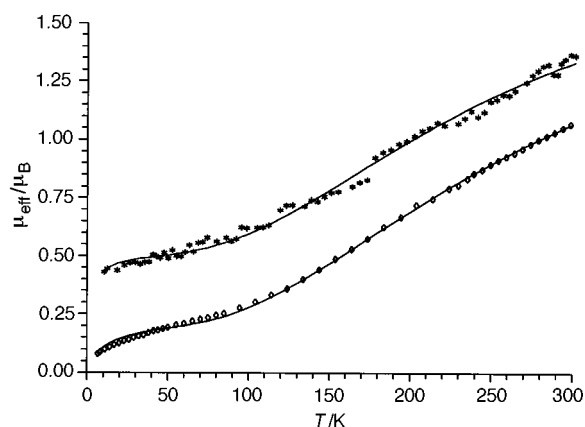


Fig. 5 Plots of the temperature dependences of the effective magnetic moments μ_{eff} for compounds **1** (*) and **2** (\diamond). The solid lines represent the best calculated curve; $\mu_B \approx 9.27 \times 10^{-24} \text{ J T}^{-1}$

known to afford an effective exchange pathway to mediate a strong antiferromagnetic coupling interaction.^{13–16} For compound **1**, the exchange transmitted *via* the μ -OH bridge is also antiferromagnetic due to the fact that the bridging angle Cu–(μ -OH)–Cu (110.9°) is much larger than 97°, the critical angle for the exchange interaction of a μ -OH bridge.²⁰ As for the bridging pathway Cu–(μ -OH)₂–Cu, the magnetic interaction is negligible because of the unfavourable axial co-ordination. For compound **2**, it is known that N-bonded cyanate in an end-on fashion usually transmits antiferromagnetic exchange between copper(II) ions.²¹ On these grounds, the magnetic system of the two complexes can be described as alternating chains with antiferromagnetic coupling for both oxamidate and μ -OH or cyanate bridges, which can be interpreted using the empirical expression proposed by Hatfield²² for alternating chains with

$$H = -\sum_{i=1}^{n/2} (S_{2i}S_{2i-1} + a_{2i}S_{2i+1}),$$

taking into account the inter-chain interaction in a molecular model. This model resulted in an excellent fit to the magnetic data and the best fitting parameters are $J_1 = -381.2 \text{ cm}^{-1}$, $J_2 = -91.3 \text{ cm}^{-1}$, $\theta = -4.4 \text{ K}$ and $g = 2.27$ for **1** and $J_1 = -464.4 \text{ cm}^{-1}$, $J_2 = -20.1 \text{ cm}^{-1}$, $\theta = -30.4 \text{ K}$ for **2**, where J_1 and J_2 denote the coupling constants of the oxamidate and μ -OH or cyanate bridges, respectively, and θ is the coupling interaction between chains *via* H bonds.

The hydrogen-bonding interaction involved here is relevant to the construction of higher dimensional metal co-ordinating polymers. Although it is difficult to control the crystal engineering involving hydrogen bonding linkages, the supramolecular pathway is still a good strategy to realize the self-assembly of inorganic materials with zeolite-like cavities or channels.

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