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# A novel class of interpenetrated 3-D network of a dimeric cupric-tetracarboxylate unit†

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**The hydrothermal reaction of Cu(II), fumaric acid and 4,4′-bipyridine (bpy) in equimolar amounts at 160 °C resulted in a new type of two-fold interpenetrating 3-D coordination network composed of tetracarboxylate dicopper(II) units bridged by bipyridine spacers.**

The design of metallo-organic based polymers with original architectures which could offer great potential for chemical and structural diversity is one of the major current challenges in inorganic chemistry.[1] These polymeric networks include systems mimicking zeolites or possessing magnetic properties.[1,2] A large number of metallo-organic based 3-D networks, a few of them consisting of interlocked structures, have been reported in the literature.[3] The use of dicarboxylate spacers *e.g.* terephthalate, malonate, oxalate *etc.* is a continuous challenge for chemists attempting to construct such polymeric compounds.[3–6] However, systems with a fumarate bridge are not so common due to their poor solubility in common organic solvents.[1,2] For entropic reasons, synthesis at higher temperature can promote the formation of a polymer framework of higher dimensionality through the loss of ancillary ligands.[7] Our exploration of the hydrothermal chemistry of the Cu-fumarate system has resulted in the discovery of a novel class of metal–organic based interpenetrated 3-D system obtained by a one-pot synthesis from three components *i.e.* Cu(II), 4,4′-bipyridine and fumaric acid. To the best of our knowledge, this is the first interlocked 3-D network composed of dicopper(II) units bridged by two different organic spacers.

In a typical synthesis, the reaction of Cu(NO$_3$)$_2$, fumaric acid and 4,4′-bipyridine in H$_2$O–MeOH (1 : 1) medium at 160 °C results in green single crystals.‡ The single crystal X-ray structural determination§ evidences a two-fold interpenetrating 3-D coordination network[6] built-up of dicopper(II)-tetracarboxylate units linked by difunctional bpy ligands (Fig. 1).

The structure was successfully solved using the space group *C*2/*m*, where the organic ligands present two conformations, each at half occupancy, and metal ions located on a mirror plane. All the crystals examined were twinned and each of the two lattices exhibit a symmetry consistent with space group $P2_1/a$, a non-isomorphic subgroup of the centered *C* cell, if the mirror plane (twin operator) is omitted.

In the dinuclear core (Fig. 2) the copper ions, bridged by four carboxylate anions, display a slightly distorted octahedral geometry with equatorial Cu–O bond lengths that disclose comparable values in a range from 1.950(19) to 1.994(10) Å.

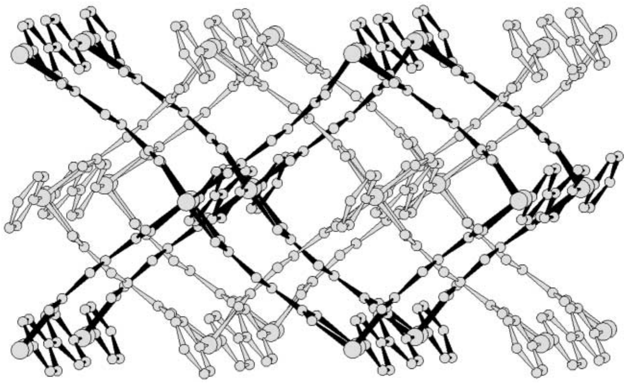

**Fig. 1** Perspective view of the crystal packing showing the two interpenetrated 3-D nets (untwinned framework, see text).

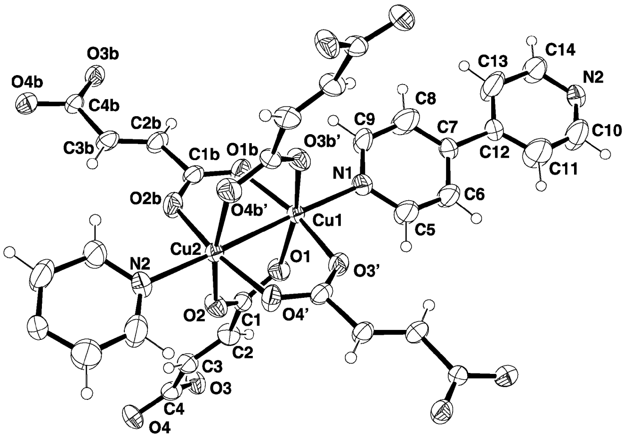

**Fig. 2** ORTEP[13] drawing (40% thermal ellipsoids) of the dinuclear copper(II) unit with atom numbering scheme. Selected bond lengths (Å) and angles (°): Cu(1)–Cu(2) 2.675(1), Cu(1)–O(1) 1.950(19), Cu(1)–O(1b) 1.966(19), Cu(1)–O(3′) 1.970(14), Cu(1)–O(3b′) 1.977(14), Cu(2)–O(2) 1.987(8), Cu(2)–O(2b) 1.960(9), Cu(2)–O(4′) 1.994(10), Cu(2)–O(4b′) 1.959(10), Cu(1)–N(1) 2.140(5), Cu(2)–N(2) 2.137(5); N(1)–Cu(1)–Cu(2) 174.6(2), N(2)–Cu(2)–Cu(1) 174.5(2), O(1b)–Cu(1)–O(3′) 166.1(7), O(1)–Cu(1)–O(3b′) 166.8(7), O(4b′)–Cu(2)–O(2) 166.5(4), O(2b)–Cu(2)–O(4′) 168.5(4).

The hexacoordination about each metal is completed by the bpy nitrogen [Cu(1)–N(1) = 2.140(5), Cu(2)–N(2) = 2.137(5) Å] and by the other ion at 2.675(1) Å. The latter value is comparable to Cu–Cu distances detected in discrete molecules containing a dimeric copper(II) unit,[7,8] although some differences are

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† Electronic supplementary information (ESI) available: a fit of the magnetic data for the Cu(II) dimer to the Bleaney–Bowers equation. See http://www.rsc.org/suppdata/dt/b1/b110015g/

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apparent and seem to be caused not only by electronic properties of the axial ligands, but also by the different conformation of bpy and by crystal packing. The metals are displaced by about 0.22 Å from the mean $O_4$ basal plane towards the axial N donor. The coplanar C(7) ··· N(1)–Cu(1)–Cu(2)–N(2) ··· C(12) fragment deviates appreciably from linearity and the N–Cu–Cu angles are about 174.3°. The bpy connector binds two metals at 11.378 Å, while the distance between copper ions spaced by the fumarate anion is 8.744 Å. The latter value and the length of the *c* axis represent the edges of the square parallelopipeds affording the two-fold 3-D interpenetrated structure with copper dimers at the nodes (Fig. 1), leading to an inter-net Cu ··· Cu separation of 6.253 Å. A water molecule, inserted in the void space of the framework, is weakly H-bonded to carboxylate oxygens. The present coordination net has the same topology as that found in $Mn[N(CN)_2]_2(pyz)$ (pyz = pyrazine)[9] and in [M(tp)(bpy)] (tp = terephthalate and M = Co, Cd, Zn).[10]

Variable temperature magnetic behaviour of the complex was investigated using a SQUID magnetometer in the temperature range 300–15 K within an applied magnetic field of 50 kOe (the susceptibility data were corrected for diamagnetism and TIP). The susceptibility curve (Fig. 3) shows a round maximum at 270 K indicating a very strong antiferromagnetic coupling is involved [the inset shows the temperature dependent of the $\chi_M T$ product per two copper(II) ions]. It is well known that the carboxylato bridge in a *syn–syn* conformation is able to mediate very strong antiferromagnetic interactions in copper(II) complexes. First we have analyzed its magnetic data through a simple Bleaney–Bowers expression [eqn. (1)] derived from the isotropic spin Hamiltonian of eqn. (2) with local spin $S = 1/2$.

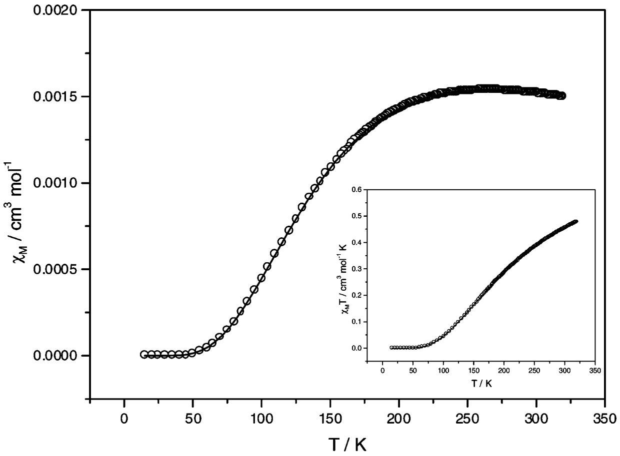

**Fig. 3** The temperature dependence of molar susceptibility for the title complex, the solid line shows the best fit obtained (see text). Inset: plot of $\chi_M T$ *versus* $T$ data.

$$\chi = 2Ng^2\beta^2(1 - \rho)/kT[3 + \exp(-J/kT)] + Ng^2\beta^2\rho/2kT \quad (1)$$

$$H = -JS_1S_2 \quad (2)$$

The best-fit parameters are $J = -295.7$ cm$^{-1}$, $g = 2.01$, $\rho = 0.008$ and an agreement factor $R = 2.3 \times 10^{-5}$. However the fitting can be improved, with a better resultant $R$ factor, by introducing the interdimer interaction through the fumarate pathway ($J'$) with the parameters $J = -294.8$ cm$^{-1}$, $J' = -3.2$ cm$^{-1}$, $R = 2.1 \times 10^{-6}$ (Fig. 3).[11] The large antiferromagnetic coupling observed in this compound is in agreement with those observed in the large family of tetra-μ-carboxylato-*O*,*O*′-dicopper(II) complexes, where the most common $J$ value observed is about −300 cm$^{-1}$.[12]

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## Notes and references

‡ In a typical synthesis 1 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ was heated with 1 mmol of fumaric acid and 1 mmol of 4,4′-bipyridine in 15 cm$^3$ of 50 : 50 water–methanol at 160 °C for 20 h in a Teflon-lined steel vessel. Overnight cooling of the resulting solution in the vessel yielded a microcrystalline green solid along with suitable single crystals for an X-ray structure determination. Anal. calc.: C, 41.50; H, 2.49; N, 5.38. Found: C, 41.85; H, 2.38; N, 5.40%. IR: $\nu(COO^-)$, 1362, 1571 cm$^{-1}$.

§ Crystal data: $C_{18}H_{13}Cu_2N_2O_{8.5}$, $M = 520.38$, $T = 293(2)$ K, monoclinic, space group *C*2/*m*, $a = 13.074(4)$, $b = 11.614(3)$, $c = 14.033(4)$ Å, $\beta = 104.99(2)°$ $V = 2058.3(10)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.679$ g cm$^{-3}$, $\mu$(Mo-Kα) = 2.116 mm$^{-1}$, $F(000) = 1044$. $\theta$ range for data collection 3.23 to 28.28°, limiting indices: $h = -17/17$, $k = -15/15$, $l = -17/18$. Final $R = 0.0559$, $wR2 = 0.1403$, $S = 1.093$ for 258 parameters and 5028 reflections, 2616 unique [$R$(int) = 0.0476], 2075 of which with $I > 2\sigma(I)$, max positive and negative peaks in $\Delta F$ map 0.883 and −0.611 e Å$^{-3}$. CCDC reference number 173525. See http://www.rsc.org/suppdata/dt/b1/b110015g/ for crystallographic data in CIF or other electronic format.

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