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A three component fully interlocked 3-D network: crystal structure and magnetic properties†

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A one-pot reaction of three different components [Cu(II), fumarate dianion and piperazine] leads to the self assembly of a magnetic molecular fully interlocked 3D structure with (4,4) nets formed by equal 2D sheets.

One of the challenges in modern inorganic chemistry is the design of molecular extended systems possessing original architectures and predictable physical properties. Such novel molecular assemblies include networks mimicking zeolites or possessing magnetic metallic ions.[1,2] One of the intriguing assemblages encountered is that consisting of interlocked structures like catenanes where interlacing rings may be achieved by a rational synthetic approach.[3] A few systems with interpenetrated two-dimensional networks are known and during the last decade three examples of molecular systems containing paramagnetic ions with fully interlocked structures have been reported.[4,5]

We report, here, a new molecular magnetic system with a fully interlocked three-dimensional structure of general formula [Cu(fum)(ppz)(H_2O)$_2$] (fum = fumarate dianion and ppz = piperazine) obtained from a one-pot synthesis of three different components *i.e.* Cu(II), piperazine and fumarate, using an unusual crystallization process. To the best of our knowledge, this is the first molecular interlocked system where the 2D sheets are assembled from two different types of organic bridges.

Reaction of $CuCl_2$, Na_2fum, and piperazine in H_2O–MeOH results in the formation of a sky blue insoluble solid. Deep blue single crystals were obtained by slow evaporation of an ammoniacal solution of the solid,‡ and the structure was determined by single crystal X-ray diffraction.§ As shown in Figs. 1 and 2, the present compound is a 3D polymeric, interpenetrating network consisting of equivalent 2D sheets, of composition [Cu(fum)(ppz)(H_2O)$_2$]$_n$ with a (4,4) topology, where copper ions provide the 4-connecting nodes bridging through ppz and fum ligands. In the structure Cu^{II} ions, ppz and fum ligands are situated at crystallographic centres of symmetry. The sides of the parallelogram forming the grid are provided by the ppz molecules in the direction of the crystallographic *c* axis (6.947 Å), the others are part of zigzag Cu–fum chains running parallel to the diagonal of plane *ab* (length of 8.960 Å). The coordinating dicarboxylate oxygen atoms are those in *anti* position with respect to the adjacent H atom of the ligand. The metals within a sheet are all coplanar in an essentially square planar environment, since two water molecules at pseudo-axial positions are at 3.058(6) Å, too far apart to attest an octahedral geometry around copper. The (4,4) nets are inclined interpenetrated to form an interlocked 3D structure. This is the highest dimensionality found for fum bridged Cu^{II} complexes since all previous such complexes are dimeric or 1D chains.[2] Along the line of intersection of any particular pair of interpenetrating sheets each Cu(fum)$_2$(ppz)$_2$ window encircles a Cu–fumarate–Cu entity of the other sheet, in such a way to allow the formation of weak hydrogen bonds [3.035(4) Å] between unligated oxygen O(2) and ppz nitrogen

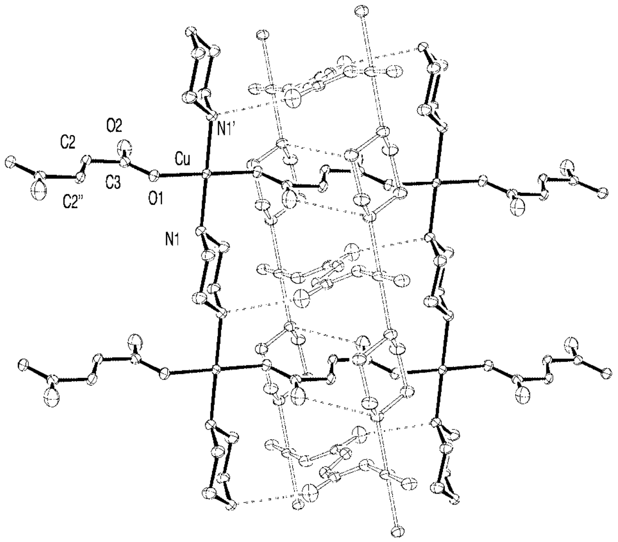

Fig. 1 Perspective view of two interpenetrated sheets (represented by open and filled bonds) showing the N(1)–H···O(2) hydrogen bonds (dashed lines). Selected bond lengths (Å), angles and torsion angles (°): Cu–O(1) 1.968(2), Cu–N(1) 2.047(3); O(1)–Cu-O(1′) 180.00(1), O(1)–Cu–N(1′) 93.05(9), O(1)–Cu–N(1) 86.95(9), N(1′)–Cu–N(1) 180.00(2), C(2)–C(3)–O(1)–Cu, −172.2(2), C(2″)–C(2)–C(3)–O(1) −8.3(5)°.

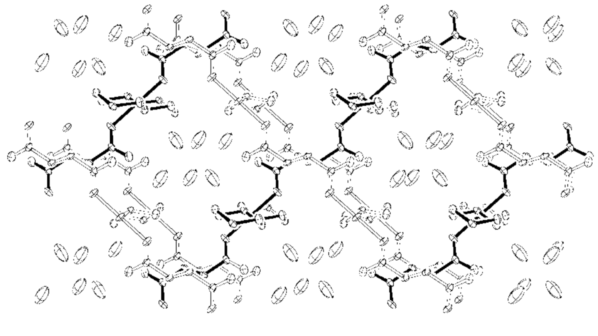

Fig. 2 View of the crystal structure of [Cu(fum)(ppz)(H_2O)$_2$]$_n$ down the crystallographic *c* axis, showing the channels hosting the water molecules.

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† Electronic supplementary information (ESI) available: magnetic results and further crystallographic details (atomic coordinates, bond distances and angles and hydrogen bonds). See http://www.rsc.org/suppdata/cc/b1/b102072m/

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N(1). The dicarboxylate bridging ligands lie at a repeat distance of half the crystallographic axis *c*, suggesting π contacts among these groups (the closest C–C separation is 3.492 Å). When viewed along the *c* axis the structure is seen to contain 168 Å^3 channels filled with water of crystallization (Fig. 2). The crystallographically independent water molecule, located at 2.761(5) Å from O(2), is rather disordered and is weakly hydrogen bonded also to two close symmetry related units [2.95(1) and 3.02(1) Å]. This crystal structure which displays an inclined interpenetration of two (4,4) nets is unique and unprecedented. To the best of our knowledge, only one structure with this type of interpenetration has been reported to date where the sheets are different, formed by a 2D layer and 1D chains, the latter connected through H-bonds.[6] Thermogravimetric analysis reveals a weight loss at 155 °C corresponding to the loss of two water molecules per formula unit [calc. 12.0; obs. 11.8%].

The magnetic behaviour of the complex was investigated using a SQUID magnetometer in the temperature region 280–3 K within an applied magnetic field of 50 kOe. The $\chi_M = f(T)$ plot (Fig. 3) is consistent with the presence of an antiferromagnetic interactions between the Cu^{II} ions within the compound. It has already been reported that through-bond coupling leads to important magnetic interaction in Cu^{II}–piperazine–Cu^{II} entities while the interaction through fumarate is very small since through-bond coupling is negligible.[7] The susceptibility data were thus fitted by the theoretical law for an antiferromagnetic $S = 1/2$ regular infinite chain. The least square fit leads to the following parameters: $J = -15.3$ cm^{-1}, $g = 2.04$, $\rho = 0.011$, TIP $= 60 \times 10^{-6}$ and an agreement factor $R = 2.4 \times 10^{-4}$. The quality of the fit may be improved by introducing an intermolecular interaction parameter *zj* that takes into account the interaction between the magnetic chains in the framework of the molecular field approximation.[8] The inset of Fig. 3 shows that a better fit of the maximum can then be obtained with the following parameters: $J = -14.7$ cm^{-1}, $g = 2.04$, $\rho = 0.013$, $zj = -4.2$ cm^{-1}, TIP $= 60 \times 10^{-6}$ and an agreement factor of 6.5×10^{-6}. Since each piperazine bridged chain is surrounded by two other chains within the 2D layers, *z* is equal to 2 (we have neglected the interaction through H-bonds) which leads to an exchange coupling parameter of -2 cm^{-1} between the Cu^{II} ions through fumarate. DFT calculations is underway in order to rationalize in a more quantitative way the amplitude of the magnetic interaction between the two different bridges.

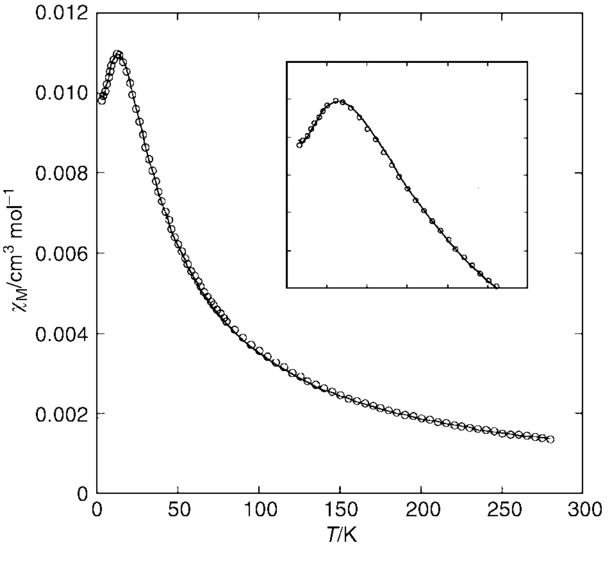

Fig. 3 Molar magnetic susceptibility *vs.* temperature plot for [Cu(fum)ppz)(H$_2$O)$_2$]$_n$. Solid lines shows the best fit obtained considering the interchain magnetic interaction in addition to intrachain interaction.

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Notes and references

‡ A 5 mL aqueous solution of CuCl$_2$·2H$_2$O (1 mmol, 0.1705 g) was mixed with an aqueous solution (10 mL) containing Na$_2$fum (1 mmol, 0.1600 g) and piperazine (1 mmol, 0.0860 g). A sky blue solid, insoluble in common organic solvents separated out immediately. It was filtered off, washed with water and dissolved in a minimum amount of ammonia (14 M). Suitable blue single crystals for X-ray diffraction were obtained by slow evaporation of the ammoniacal solution of the solid in a refrigerator.

§ *Crystal data*: C$_8$H$_{16}$CuN$_2$O$_6$, $M = 299.77$, monoclinic, space group $C2/c$, $a = 12.785(8)$, $b = 12.556(8)$, $c = 6.947(5)$ Å, $\beta = 99.69(1)$°, $U = 1099.3(12)$ Å^3, $F(000) = 620$, $Z = 4$, $D_c = 1.811$ g cm^{-3}, μ(Mo-Kα) = 2.007 mm^{-1}. Intensity data collected on an Enraf-Nonius CAD-4 single crystal diffractometer employing the ω–2θ scan method; absorption correction was applied. The structure was refined using a full matrix refinement procedure (SHELXL97), with anisotropic thermal parameters assigned to all non-hydrogen atoms. All hydrogen atoms were observed in the difference map; those of fumarate and piperazine molecules were constrained at geometrical estimates, while coordinates of hydrogen atoms of water molecule were refined. At convergence $R1 = 0.0428$, $wR2 = 0.1081$ for 1292 unique reflections and 86 parameters, [3358 reflections collected, $R_{int} = 0.0701$, 1216 with $I > 2\sigma(I)$].

CCDC reference number 160683. See http://www.rsc.org/suppdata/cc/b1/b102072m/ for crystallographic data in CIF or other electronic format.

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