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A three-dimensional nanoporous flexible network of 'square-planar' copper(II) centres with an unusual topology†

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Cu(II) triflate reacts with 4,4′-bipyridyl in different solvents to yield the new 3D network $[Cu(4,4'\text{-bipy})_2(CF_3SO_3)_2]$, based on pseudo-square planar nodes and consisting of crossing layers of large rhombic meshes (22 × 22 Å) fused together into an overall (two-fold interpenetrated) array, with a topology unprecedented within coordination frames and an interesting nanoporous behaviour.

Coordination networks[1] are of great current interest not only because of their potential applications as zeolite-like materials,[2] for molecular selection, ion exchange and catalysis, but also for their intriguing architectures, new topologies and intertwining phenomena. Many of these frameworks have been obtained using bis(4-pyridyl) ligands of different length as spacers, the most simple of which, 4,4′-bipyridyl, has produced in the past years a variety of architectures, including single ladders, square grids, diamondoid networks and other interesting frames.

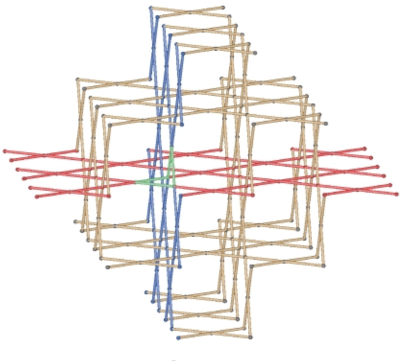
In our previous studies on the self-assembly of 4,4′-bipy with Cu(II) triflate in ethanol we have observed that part of the metal was reduced to copper(I), giving crystals of the four-fold interpenetrated diamondoid species $[Cu(4,4'\text{-bipy})_2]CF_3SO_3$,[3] but we were then unable to isolate a Cu(II) derivative. We have now reinvestigated the same reaction on varying the solvent system. The interest for such building elements is mainly due to the possibility of obtaining new 4-connected frames, considering that Cu(II) with bis(4-pyridyl) spacers in molar ratio 1 : 2 can give extended motifs containing pseudo-square planar metal centres, with four equatorial pyridyl groups and two weakly coordinated anions in axial direction. The presence of such 'square planar' units can generate, besides to the more usual 2D square grids, also 3D networks with interesting topologies, less common within coordination polymers, like those of the cubic NbO (6^48^2), the tetragonal $CdSO_4$ (6^58) or the 'dense net' (7^59) suggested by O'Keeffe and Hyde.[4] Examples of copper(II) networks with the second[5] and the third[6] of these topologies have been, indeed, reported, containing bis(4-pyridyl) ligands of different nature, but none of the NbO type. Moreover, Batten and Robson, in their review on interpenetrating nets,[1b] describe another 3D topology exclusively based on square planar centres, characterized in the (two-fold interpenetrated) hydrogen-bonded framework of a benzene solvated diol[7] (whose ideal net is shown in Scheme 1). We have now succeeded in preparing a novel 3D network of this type, namely $[Cu(4,4'\text{-bipy})_2(CF_3SO_3)_2]$, which, out of the four above mentioned topologies, adopts the last one, unprecedented within coordination polymers and surprisingly shared by two such different chemical systems. We describe here this (two-fold interpenetrated) open network displaying, like other Cu(II)/4,4′-bipy systems,[2c,8] an interesting nanoporous behaviour.

The reactions were carried out at room temperature by mixing under stirring Cu(II) triflate in aqueous solution and 4,4′-bipy dissolved in different solvents (THF, tetrachloroethane, nitromethane) with a metal : ligand molar ratio of 1 : 2. A polycrystalline blue precipitate of $[Cu(4,4'\text{-bipy})_2(CF_3SO_3)_2]\cdot x\text{Solv}$ (**1**), is obtained in high yields within few minutes. Single dark blue crystals form within 24 h upon layering a solution of the ligand in THF on a water solution of the metal salt in the same molar ratio. However, crystals of much better quality for a structural study can be obtained in a month at the interface of a water solution of the salt layered over a solution of 4,4′-bipy in CH_2Cl_2. These crystals, investigated by X-ray analysis,‡ correspond to $[Cu(4,4'\text{-bipy})_2(CF_3SO_3)_2].2CH_2Cl_2.H_2O$ (**1a**). The XRPD patterns of the polycrystalline samples, as well as of the crushed crystals obtained from both the above methods, are all very similar, revealing the presence of a common structural motif.

The crystal structure of **1a** contains a fascinating 3D polymeric architecture consisting of two identical interwoven nets of the topological type illustrated in Scheme 1. All the metals are equivalent and play the role of square-planar nodes in the network. The Cu(II) coordination is Jahn–Teller distorted octahedral, with four equatorial pyridyl groups (Cu–N 2.01–2.02 Å) and two axial η^1-triflates (Cu–O 2.48 Å). A single net is characterized by the presence of layers of large rhombic units, with edges as long as *ca.* 22.1 Å, and a ratio (long diagonal/short diagonal) of 1.187 (see Fig. 1, top). The peculiarity of the network is that two sets of crossing layers (dihedral angle of 114.8 *vs.* 90° in the ideal net of Scheme 1) are fused together by sharing the metal atoms at the midpoints of the rhombic edges (Fig. 1, bottom). Short four-membered rings are thus formed, with edges of 11.06 Å, that are highly folded (D_{2d}) squares. The network is potentially flexible in that it can be sligthly stretched or compressed in the direction of the ***c*** axis (see later). The topology of the net is peculiar: it is uninodal, with short and long Schläfli symbols (4^28^4) and ($4.4.8_4.8_4.8_8.8_8$).§

Two $[Cu(4,4'\text{-bipy})_2(CF_3SO_3)_2]$ frames interpenetrate as illustrated in Fig. 2, in the same way as in the hydrogen-bonded system rationalized by Batten and Robson.[1b,7]

The overall array contains nanoporous channels extending in the directions of the three crystallographic axes, the more open ones being those along the tetragonal ***c*** axis (see Fig. 3). The



Scheme 1

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† Electronic supplementary information (ESI) available: XRPD spectra. See http://www.rsc.org/suppdata/cc/b2/b202588d/

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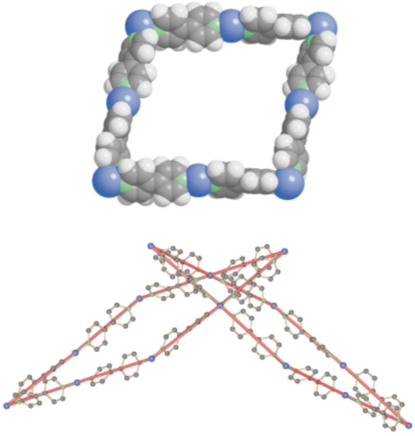

Fig. 1 Views of a large rhombic unit (top) and of two fused rhombi of a single net in **1a** (bottom).

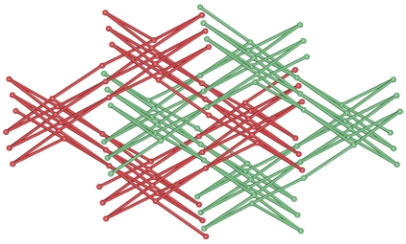

Fig. 2 Schematic view of the interpenetration in **1a**.

network topology plays a fundamental role in that it produces two distinct types of the latter channels, both of square section (*ca.* 10 × 10 Å), with a chessboard disposition. The triflate anions are coordinated to the Cu(II) atoms in such a way that they occupy only one class of these channels, that also contain solvated water molecules ('hydrophilic' channels). The solvated CH_2Cl_2 molecules, on the other hand, occupy the second class of channels ('hydrophobic' channels). The two types of channels exhibit completely different structures of the walls: the 'hydrophobic' ones are limited by two-fold entangled 4_1 helixes, while the 'hydrophilic' ones are simply formed by the stacking of the folded squares, alternately belonging to the two different interpenetrated nets (see Fig. 3). Moreover, the computed free voids in the 'helical' channels are 23% of the cell volume, *vs.* 9.5% in the other ones.

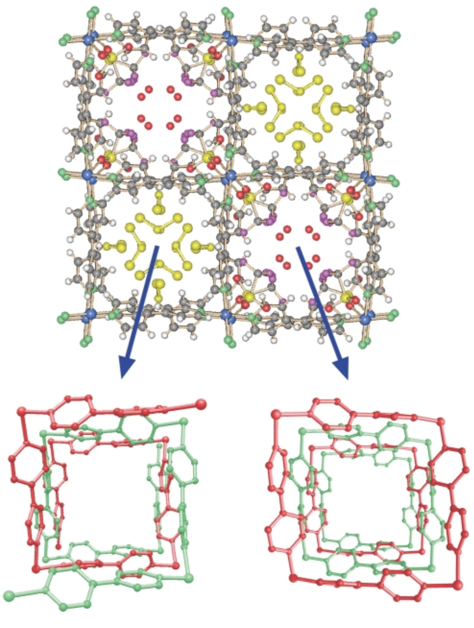

Fig. 3 A view of the channels down ***c*** in compound **1a**; the two distinct types of structural motifs are also illustrated.

When removed from the solution **1** slowly loses the guest solvent molecules (CH_2Cl_2 or THF), replaced in part by H_2O molecules from the air. The network is resistant to the loss of solvent. The TG analyses show that the guest solvents are eliminated from the network on rising the temperature from room temperature up to *ca.* 120 °C, while decomposition of the frame begins only above *ca.*270 °C. The XRPD spectra recorded after heating samples of **1** at 200 °C for 30 min show that the structure of the network is maintained. Experiments have been carried out to test the nanoporous behaviour: polycrystalline samples of **1**, treated with different solvents (tetrachloroethane, amyl acetate, 4-methyl-2-pentanone, *n*-decane, nitromethane) have been monitored by XRPD, to follow the depletion process. Changes in the patterns with time, showing anisotropic displacements of the diffraction peaks, have been observed. The more significant results have been obtained with amyl acetate. A Rietveld analysis of the profiles gave the modifications of the cell parameters during the solvent elimination (see ESI): the flexible frame, initially stretched along ***c***, relaxes to the depleted form with decrease of ***c*** and a modest increase of ***a***. Since nitromethane shows an opposite distorsion behaviour, it seems reasonable to ascribe the difference to the uneven population of preferred crystal sites (inside the helical channels or in the interchannel regions), though the details of the inclusion process remain unexplained. Further studies are in progress to clarify these points by testing a variety of new guest molecules.

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Notes and references

‡ *Crystal data* for compound **1a**: $C_{24}H_{22}Cl_4CuF_6N_4O_7S_2$, M = 861.92, tetragonal, space group $I4_1/acd$ (no. 142), a = 28.484(8), c = 18.219(7) Å, U = 14782(8) Å^3, T = 204 K, Z = 16, μ(Mo-Kα) = 1.067 mm^{-1}, 39938 reflections measured, 3281 unique (R_{int} = 0.0775) used in all calculations. The final agreement index $R1$ was 0.0826 for 2634 independent significant [$I > 3\sigma(I)$] absorption corrected data [$wR(F^2)$ = 0.255 for all data]. Anisotropic thermal factor were assigned to all the non-hydrogen atoms. A double model was used for the triflate anion and one of the CH_2Cl_2 molecules. CCDC reference number 181898. See http://www.rsc.org/suppdata/cc/b2/b202588d/ for crystallographic data in CIF or other electronic format.

§ This net has been classified by O'Keeffe, as Net #97 (personal communication). Ermer has suggested a relationship to the diamond topology, by considering as nodes the folded square units (O. Ermer and L. Lindenberg, *Helv. Chim. Acta*, 1988, **71**, 1084).

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