Cu(II) trflate reacts with 4,4′-bipyridyl in different solvents to yield the new 3D network [Cu(4,4′-bipy)2(CF3SO3)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 networks1 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 sladders, square grids, diamondoid networks and other interesting frames.

In our previous studies on the self-assembly of 4,4′-bipyridyl, has produced in the past years a variety of architectures, including single sladders, square grids, diamondoid networks and other interesting frames.

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 1.95 Å) and an interesting nanoporous behaviour.

The overall array contains nanoporous channels extending in the directions of the three crystallographic axes, the more open ones being those along the tetragonal axis (see Fig. 3). 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 η1-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 (D2d) networks. The topology of the net is peculiar: it is uniodinal, with short and long Schléflü symbols (4(8h) and 1.2b.7 Two [Cu(4,4′-bipy)2(CF3SO3)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

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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 CH₃Cl₂ 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 4₁ helices, 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.

When removed from the solution I slowly loses the guest solvent molecules (CH₃Cl₂ or THF), replaced in part by H₂O 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 I 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 I, treated with different solvents (tetrachloroethane, amyl acetate, 4-methyl-2-pentanone, 1-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 deformed pet with decrease of c and a modest increase of a. Since nitromethane shows an opposite distortion 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: C₇H₅Cl₂CuF₆N₄O₇S₂, M = 861.92, tetragonal, space group P4/m (no. 123); a = 28.484(8), c = 18.219(7) Å, U = 14782(8) Å³, T = 204 K, Z = 16, r(Mo-Kα) = 1.067 mm⁻¹, 39938 reflections measured, 3281 unique (Rint = 0.0775) used in all calculations. The final agreement index R1 was 0.0826 for 2634 independent significant [I > 3σ(I)] absorption corrected data (wR2) = 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 CH₃Cl₂ 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).


