An unprecedented triply interpenetrated chiral network of ‘square-planar’ metal centres from the self-assembly of copper(II) nitrate and 1,2-bis(4-pyridyl)ethyne

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Copper(II) nitrate reacts with 1,2-bis(4-pyridyl)ethyne (bpethy) in ethanol to yield mixtures containing, beside to a one-dimensional ladder-like polymer, a networked [Cu(bpethy)₂] species, with a triply interpenetrated chiral frame based on pseudo-square planar metal centres, showing a topology theoretically predicted but never observed before, and containing uncoordinated ligands as guest molecules.

The crystal engineering of networked coordination polymers, of potential utility as zeolite-like materials, has produced in recent times novel interesting assemblies by using suitable bidentate spacer ligands. Among these an important class is represented by ligands containing two 4-pyridyl donor units interconnected by chains or groups of different types, which can afford varied lengths, linear or non-linear geometries, and conformationally rigid or non-rigid molecular skeletons. With the most simple of these ligands, i.e. 4,4′-bipyridyl, a variety of architectures have been obtained in the past years. The use of longer bis(4-pyridyl) spacers has afforded very interesting structural motifs, as double helices, double sheets, interpenetrated ladders and brick-wall frames, and interpenetrated diamondoid nets and other noteworthy species. We have studied the self-assembly process of one of these ligands, the rigid linear 1,2-bis(4-pyridyl)ethyne (bpethy), with copper(II) nitrate.

The choice of such building elements was performed with the aim to gain some control of the networking process, since the nitrate anions, due to their donor ability, are known to give rise either to T-shaped metal centres (metal to ligand molar ratio 1 : 1.5) or to pseudo-square planar metal centres (metal to ligand molar ratio 1 : 2). Moreover, in the latter case an array of single sheets of squares, commonly observed with 4,4′-bipyridyl, seemed to us rather unlikely, taking into account the increased length of bpethy (ca. 9.8 vs. 7.1 Å).

Looking, therefore, for a 3D network of square planar centres as the target, besides the prototypical frame of NbO (topology 6₄⁶⁻), we have found only two other examples, suggested by O’Keeffe, and referred to as the tetragonal CdSO₄ (B) and the so-called ‘dense’ net (C). In a very recent communication a product from the self-assembly of copper(II) nitrate and 1,2-bis(4-pyridyl)ethane has been described, containing a (twofold interpenetrated) 3D net based on pseudo-square planar copper centres, which has been erroneously ascribed to the NbO topological type (A) but, indeed, belongs to the CdSO₄ one (B). We report here the first example of a (triply interpenetrated) coordination network of the third topological type (C). Again a theoretically anticipated topology, of unlike existence within simple inorganic compounds, can be accomplished in the area of coordination polymers. The reactions of Cu(NO₃)₂·3H₂O with bpethy afford mixtures of products. On layering over an ethanolic solution of the salt an ethanolic solution of the ligand (molar ratio 1 : 2) the formation of small elongated blue crystals is observed after few days. The product, investigated by single crystal X-ray analysis, corresponds to [Cu(bpethy)(NO₃)₂]·0.5EtOH. On allowing the solution to concentrate almost to dryness by evaporation, the reaction further proceeds, giving flat hexagonal blue crystals of a second species, also characterized by X-ray analysis, together with other minor unidentified products. Compound 1 consists of one-dimensional linear chains of Cu⁺⁺ ions linked by bpethy ligands, which run in parallel pairs joined by bridging nitrate anions, in a ladder-like fashion. The metal ions exhibit Jahn–Teller distorted octahedral coordinations (2 N atoms of bpethy, 2 O atoms of a chelating nitrate, and 2 O atoms of two asymmetric μ-η¹-anions, see Fig. 1, top). The ladders propagate in two different directions (rotated by 39.6°) as shown in Fig. 1, bottom. Compound 2 is a more complex and interesting species, formulated as [[Cu(bpethy)₂(H₂O)]₂[Cu(bpethy)₂(NO₃)₂](H₂)₂]·[NO₃]₂·bpethy·1.33H₂O. It contains a fascinating tridimensional polymeric architecture consisting of three interwoven nets, each belonging to the topological type C of Scheme 1. A single net (Fig. 2) presents linear Cu–bpethy–Cu–bpethy–chains both parallel and perpendicular to the trigonal crystallographic c axis, joined at the square-planar metal centres (Cu–Cu contacts all ca. 13.6 Å). The chains perpendicular to

Fig. 1 A view of one mesh of the ladder in 1 (top) and a schematic view of the packing of the ladders (bottom)

Chem. Commun., 1998 1837
Indeed, the three nets are not identical because of the difference in the one-dimensional helical coordination polymer \([\text{Ag}(\text{pytz})](\text{NO}_3)_2\) for A, 1488 for B, 2078 for C and 980 for diamond). This net can be slightly distorted in such a manner to tolerate the presence of tetrahedral centres substituting the square planar centres. This is the case for CdSO₄ itself as well as for the coordination polymer [Ag(hexamethylenetetramine)][NO₃]₂; O. M. Yaghi, H. Li and M. O’Keeffe, Mater. Res. Soc. Symp. Proc., 1997, 453, 127.

Crystal data: \([\text{Cu}(\text{bpeh}))(\text{NO}_3)_2\]·0.5EtOH, monoclinic, space group C2/c (no. 15), \(a = 25.540(4), b = 9.186(3), c = 15.482(12) \AA, \beta = 117.08(4)^\circ\), \(V = 3234(3) \AA^3\), \(Z = 8\), \(D_c = 1.605\ \text{Mg\ m}^{-3}\), final \(R\) value 0.0933 for 1039 independent absorption corrected (\(\psi\)-scan) reflections \(I > 2 \sigma(I)\).

\([\text{Cu}(\text{bpeh}))(\text{H}_2\text{O})]_2([\text{Cu}(\text{bpeh}))(\text{NO}_3)(\text{H}_2\text{O})]_2[\text{NO}_3]_2\text{bpeh}-1.33\text{H}_2\text{O}, \) trigonal, space group \(P_3_1(\text{no. 152})\), \(a = 13.652(1), c = 40.648(2) \AA, V = 6560.9(8) \AA^3, Z = 3, D_c = 1.450 \text{Mg m}^{-3}\), final \(R\) value 0.0789 for 3952 independent absorption corrected (SADABS) reflections \(I > 2 \sigma(I)\).

The data collections were performed by the \(\psi\)-scan method, Mo-K\(\alpha\) radiation \((\lambda = 0.7107 \text{ Å}), at 293 K on an Enraf-Nonius CAD-4 diffractometer for I and at 243 K on a SMART-CCD area-detector diffractometer for II, within the limits \(3 < \theta < 25^\circ\) (I) and \(1 < \theta < 26^\circ\) (II). The structures were solved by direct methods (SIR97)\(^\dagger\) and refined by full-matrix least squares (SHELX97).\(^\dagger\)\(^\ddagger\) Anisotropic thermal factors were assigned in 1 to Cu and the NO\(_3\)-atoms and in 2 to all the non-hydrogen atoms except for a disordered nitrate and a solvated water molecule. The assignment of the absolute structure for 2 was confirmed by the statistics and the refinement of the absolute structure parameter as implemented in SHELX97, to a value of 0.074(1).\(^\ddagger\) All the diagrams were obtained using the SCHAKAL97 program.\(^\ddagger\) CCDC 182/953.

The topological density has been defined\(^\dagger\)\(^\ddagger\) as the cumulative sum of the numbers of topological neighbours for the first ten coordination shells (1186 for A, 1488 for B, 2078 for C and 980 for diamond).

Notes and References
\(^\dagger\) This net can be slightly distorted in such a manner to tolerate the presence of tetrahedral centres substituting the square planar centres.
\(^\ddagger\) Crystal data: [Cu(bpy)](NO₃)₂·0.5EtOH, monoclinic, space group C2/c (no. 15), \(a = 25.540(4), b = 9.186(3), c = 15.482(12) \AA, \beta = 117.08(4)^\circ\), \(V = 3234(3) \AA^3\), \(Z = 8\), \(D_c = 1.605\ \text{Mg\ m}^{-3}\), final \(R\) value 0.0933 for 1039 independent absorption corrected (\(\psi\)-scan) reflections \(I > 2 \sigma(I)\).

\(^\ddagger\) A schematic view of the three interpenetrated nets C in compound 2.

\(^\ddagger\) In the one-dimensional helical coordination polymer [Ag(pytz)](NO₃)₂ [pytz = 3,6-di(4-pyridyl)-1,2,4,5-tetrazine]\(^\ddagger\) the nitrate ions show weak interactions with the metal ions (Ag···O 2.79 Å). We have rationalized that, by assuming these contacts also as bonds, the overall topology is of type C, three-fold interpenetrated; however, given the long Ag···O distances, a one-dimensional chain description is perhaps more appropriate.

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