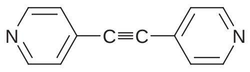
An unprecedented triply interpenetrated chiral network of 'square-planar' metal centres from the self-assembly of copper(II) nitrate and 1,2-bis(4-pyridyl)ethyne

Lucia Carlucci, Gianfranco Ciani,* Piero Macchi and Davide M. Proserpio

Dipartimento di Chimica Strutturale e Stereochimica Inorganica and Centro CNR, Via G. Venezian 21, 20133 Milano, Italy. E-mail: davide@csmtbo.mi.cnr.it

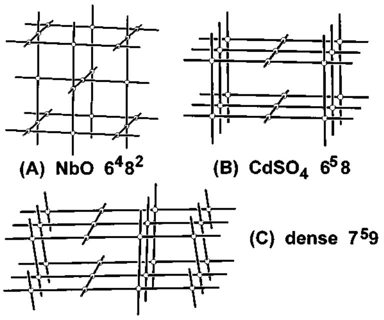
Copper(II) nitrate reacts with 1,2-bis(4-pyridyl)ethyne (bpethy) in ethanol to yield mixtures containing, beside to a one-dimensional ladder-like polymer, a networked [Cu(bpethy)$_2$] species, with a triply interpenetrated chiral frame based on pseudo-square planar metal centres, showing a topology theoretically 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 variated 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.[1] The use of longer bis(4-pyridyl) spacers has afforded very interesting structural motifs, as double helices,[2] double sheets,[3] interpenetrated ladders[4,5] and brick-wall frames,[4] interpenetrated diamondoid nets[6] and other noteworthy species.[7,8] 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.



bpethy

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)[1a,4] or to pseudo-square planar metal centres (metal to ligand molar ratio 1 : 2).[1b] Moreover, in the latter case an array of single sheets of squares, commonly observed with 4,4′-bipyridyl,[1b,9] 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 6^48^2, A in Scheme 1) we have found only two other examples, suggested by O'Keeffe,[10] and referred to as the tetragonal CdSO$_4$ (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,[11] 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 CdSO$_4$ 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(NO$_3$)$_2$·3H$_2$O 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)(NO$_3$)$_2$]·0.5EtOH **1**. On allowing the solution to concentrate almost to dryness by evaporation, the reaction further proceeds, giving flat hexagonal blue crystals of a second species **2**, also characterized by X-ray analysis,‡ together with other minor unidentified products. Compound **1** consists of one-dimensional linear chains of Cu^{II} 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-η^1-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)$_2$(H$_2$O)$_2$}{Cu(bpethy)$_2$(NO$_3$)(H$_2$)}$_2$][NO$_3$]$_4$·bpethy·1.33H$_2$O. 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



Scheme 1

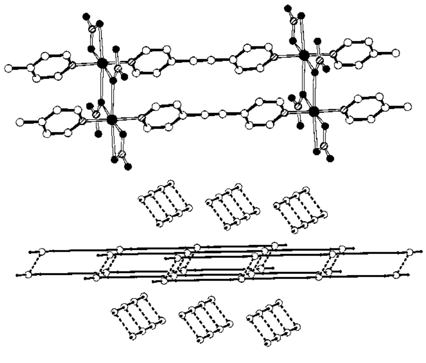


Fig. 1 A view of one mesh of the ladder in **1** (top) and a schematic view of the packing of the ladders (bottom)

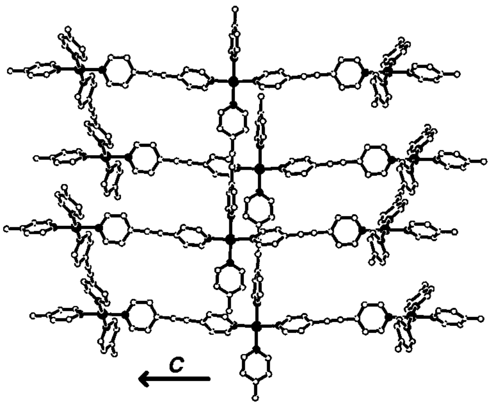


Fig. 2 A view of part of a single dense net C in compound **2**

the ***c*** axis are rotated by 120° about this axis on passing to each successive layer, in a 3_1 helical disposition, thus resulting in a chiral network. The topology of this network exhibits some peculiar features among the known four-connected nets:[10] (i) it is unique in not containing circuits shorter than heptagons; (ii) it has the highest 'topological density'§ (and is thus termed 'dense'); (iii) each metal node is ideally surrounded by eight equidistant neighbours but directly connected only to four of these. The voids present in a single net are too large to be left filled only by the counter ions. Thus three $[Cu(bpethy)_2]$ nets of the same topology interpenetrate as illustrated in Fig. 3.¶ Indeed, the three nets are not identical because of the difference in the coordination of the Cu^{II} ions: the octahedral metal environments show in all cases four equatorial N-bonded pyridyl groups, but the axial (loosely bonded) ligands are two water molecules in one of the three nets (net I, black), and a water molecule and a η^1-nitrate anion in the other two (nets II and III, white and dotted). In spite of the threefold interpenetration there are still voids that contain, besides free nitrate anions, disordered water molecules and uncoordinated bpethy ligands (Fig. 3). These molecules, moreover, form hydrogen bonds involving the two nitrogen atoms and two water molecules coordinated to the copper ions of nets II and III (N···O 2.82 Å), giving rise to hydrogen bond bridges Cu–(H_2O)–bpethy–(H_2O)–Cu, of length 17.59 Å. Taking into accout these interactions nets II and III together can be described as an unique tridimensional five-connected array, interpenetrated by the four-connected net I. Interpenetration phenomena involving different types of nets are quite rare; we have found only one previous example, *i.e.* the interpenetration of two different diamondoid networks in K_2PdSe_{10}.[12] Though the preference of compound **2** for the C type topology, rather than A or B, remains unexplained, the unusual features observed (new topology, interpenetration of different motifs, network chirality, guest molecules anchored to the frame) make this species an interesting solid state rarity, as well as a notewhorty reference structure for the engineering of frames based on square-planar metal centres.

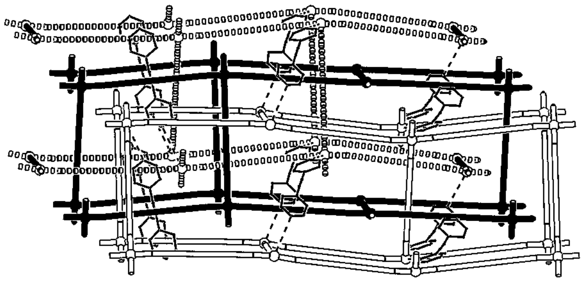


Fig. 3 A schematic view of the three interpenetrated nets C in **2**. Net I (black) is crystallographically independent, while nets II and III (white and dotted) are related by twofold axes. The solvated ligand molecules are also shown with their hydrogen bonds (dashed lines).

Notes and References

† This net can be sligthly distorted in such a manner to tolerate the presence of tetrahedral centres substituting the square planar centres. This is the case for $CdSO_4$ itself as well as for the coordination polymer $[Ag_2$(hexamethylenetetramine)]$[NO_3]_2$; O. M. Yaghi, H. Li and M. O'Keeffe, *Mater. Res. Soc. Symp. Proc.*, 1997, **453**, 127.

‡ *Crystal data*: **1** $[Cu(bpethy)(NO_3)_2]\cdot 0.5EtOH$, monoclinic, space group $C2/c$ (no. 15), a = 25.540(8), b = 9.186(3), c = 15.482(12) Å, β = 117.08(4)°, V = 3234(3) Å^3, Z = 8, Dc = 1.605 Mg m^{-3}, final R value 0.0933 for 1039 independent absorption corrected (ψ-scan) reflections [$I > 2\sigma(I)$].

2: $[\{Cu(bpethy)_2(H_2O)_2\}\{Cu(bpethy)_2(NO_3)(H_2O)\}_2](NO_3)_4\cdot bpethy\cdot 1.33H_2O$, trigonal, space group $P3_121$ (no. 152), $a = b$ = 13.652(1), c = 40.648(2) Å, V = 6560.9(8) Å^3, Z = 3, D_c = 1.450 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 ω-scan method, Mo-Kα radiation (λ = 0.710 73 Å), at 293 K on an Enraf-Nonius CAD-4 diffractometer for **1** and at 243 K on a SMART-CCD area-detector diffractometer for **2**, within the limits $3 < \theta < 25°$ (**1**) and $1 < \theta < 26°$ (**2**). The structures were solved by direct methods (SIR97)[13] and refined by full-matrix least squares (SHELX97).[14] 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 SHELX-97, to a value of 0.07(4).[15] All the diagrams were obtained using the SCHAKAL97 program.[16] CCDC 182/953.

§ The topological density has been defined[10] 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).

¶ In the one-dimensional helical coordination polymer $[Ag(pytz)](NO_3)$ [pytz = 3,6-di(4-pyridyl)-1,2,4,5-tetrazine][8] 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.

1 (*a*) P. Losier and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2779; (*b*) M. Fujita, Y. J. Kwon, S. Washizu, and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (*c*) R. W. Gable, B. F. Hoskins, and R. Robson, *J. Chem. Soc., Chem Commun.*, 1990, 1677; (*d*) L. R. MacGillivray, S. Subramanian, and M. J. Zaworotko, *J. Chem. Soc., Chem Commun.*, 1994, 1325; (*e*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Chem Commun.*, 1994, 2755; (*f*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401.

2 L. Carlucci, G. Ciani, D. W, v. Gudenberg and D. M. Proserpio, *Inorg. Chem.*, 1997, **36**, 3812.

3 T. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972.

4 M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 7287.

5 A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovskii, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 2027.

6 A. J. Blake, N. R. Champness, S. S. M. Chung, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 1005.

7 D. Whang and K. Kim, *J. Am.Chem. Soc.*, 1997, **119**, 451.

8 M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, and M. Schröder, *Angew.Chem., Int.Ed. Engl.*, 1997, **36**, 2327.

9 J. Lu, T. Paliwala, S. C. Lim, C. Yu, T. Niu and A. J. Jacobson, *Inorg. Chem.*, 1997, **36**, 923.

10 M. O'Keeffe, *Z. Kristallogr.*, 1991, **196**, 21; M. O'Keeffe and B. G. Hyde, *Crystal structures I: patterns and symmetry*, Mineralogical Society of America, Washington, D.C., 1996; see also M. O'Keeffe, *Nature*, 1998, **392**, 879.

11 K. N. Power, T. L. Hennigar and M. J. Zaworotko, *Chem. Commun.*, 1998, 595.

12 K.-W. Kim and M. G. Kanatzidis, *J Am. Chem. Soc.*, 1992, **114**, 4878.

13 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

14 G. M. Sheldrick SHELX-97, University of Göttingen, Germany, 1997.

15 H. D. Flack, *Acta Crystallogr. Sect. A*, 1983, **A39**, 876.

16 E. Keller, SCHAKAL97, University of Freiburg, Germany, 1997.

Received in Cambridge, UK, 15th May 1998; 8/03662D