ChemComm

A coordination polymer based on twofold interpenetrating three-dimensional four-connected nets of 4^26^38 topology, [CuSCN(bpa)] [bpa = 1,2-bis(4-pyridyl)ethane]†

Quan-Ming Wang, Guo-Cong Guo and Thomas C. W. Mak*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New territories, Hong Kong SAR, P.R. China. E-mail: tcwmak@cuhk.edu.hk

Received (in Cambridge, UK) 24th June 1999, Accepted 17th August 1999

The novel coordination polymer [CuSCN(bpa)] [bpa = 1,2-bis(4-pyridyl)ethane] consists of two interpenetrating three-dimensional four-connected frameworks of rare 4^26^38 topology, each being constructed from the cross-linkage of infinite zigzag $[(CuSCN)_2]_\infty$ chains by bpa ligands.

The construction of coordination networks with different topological characteristics has received significant recent attention.[1] One of the rational synthetic strategies is to bind symmetrically different metal centers with bi- or multi-dentate ligands. A variety of infinitely extended frameworks, in particular those involving interpenetration,[2] have been designed on the basis of the unifying concept of a net, as elaborated by Wells over two decades ago.[3] The majority of interpenetrating 3D four-connected nets are constructed of tetrahedral or square-planar nodes. From the topological point of view, these four-connected nets can be classified as (i) diamond-related nets of 6^6 topology (all tetrahedral centers); (ii) quartz-like nets of 6^48^2-b topology or NbO-like nets of 6^48^2-a topology (all square-planar centers) and (iii) PtS-like 4^28^4 nets (equal numbers of square-planar and tetrahedral centers).[2,4] Additionally, two new types of four-connected nets of 6^58 and 7^59 topologies have been recently reported in the compounds $[Cu(bpa)_2(NO_3)_2]_n$[5] [bpa = 1,2-bis(4-pyridyl)ethane] and $[\{Cu(bpethy)_2(H_2O)_2\}$-$\{Cu(bpethy)_2(NO_3)(H_2O)\}_2](NO_3)_4\cdot$bpethy$\cdot 1.33H_2O$[6] [bpethy = 1,2-bis(4-pyridyl)ethyne], respectively. Furthermore, two structures of 4^26^38-a type ($SrAl_2$-like) have been found in [Cu(AcTCNE)]$\cdot Me_2CO$[7] (AcTCNE = 1,1,2,2-tetracyanopentan-4-on-1-ide) and $[Ag(sebn)_2](PF_6)$[8] (sebn = 1,10-decanedinitrile) by Carlucci *et al.*

By combining flexible organic ligands with an uncharged inorganic motif containing a bifunctional polyatomic anion of suitable length, such as CuSCN or CuN_3, we hope to generate porous 3D coordination networks that may display varying degrees of interpenetration. Interestingly, our attempt to incorporate the bpa ligand into CuSCN resulted in a non-diamond 3D coordination polymer [CuSCN(bpa)] **1**, despite the fact that most Cu(I) coordination polymers exhibit diamond structures as this d^{10} ion naturally fulfills the role of a tetrahedral node.[9] To our knowledge, the doubly interpenetrating frameworks of unusual 4^26^38 topology in the present coordination polymer is unprecedented.

The hydrothermal reaction of CuSCN and bpa in molar ratio 1:1 at 180 °C leads to the formation of red air-stable compound **1**.‡ Single crystal X-ray analysis§ has revealed that **1** contains two interpenetating 3D nets, each individual framework being constructed from the building unit shown in Fig. 1. The Cu(1) and Cu(2) atoms are each located in a severely distorted tetrahedral environment, being coordinated by two N atoms of different bpa ligands, one thiocyanato S atom and one N atom of another thiocyanate ligand, with bond angles in the range 102.9(2)–118.9(2) and 97.6(2)–117.1(1)° at Cu(1) and Cu(2), respectively.

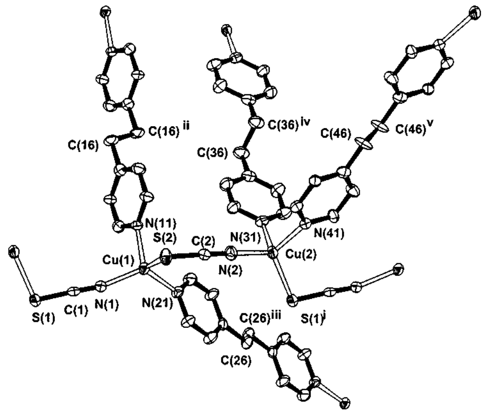

Fig. 1 The local coordination environments of Cu(I) ions in **1**; atoms are shown as 30% thermal ellipsoids. All four independent bpa ligands are located at inversion centers. Selected bond distances (Å) and angles (°): Cu(1)–N(1) 1.949(5), Cu(1)–N(21) 2.044(4), Cu(1)–N(11) 2.128(4), Cu(1)–S(2) 2.330(2), Cu(2)–N(2) 1.964(5), Cu(2)–N(41) 2.088(4), Cu(2)–N(31) 2.117(4), Cu(2)–S(1)^i 2.296(2); N(1)–Cu(1)–N(21) 118.9(2), N(1)–Cu(1)–N(11) 102.9(2), N(21)–Cu(1)–N(11) 104.8(2), N(1)–Cu(1)–S(2) 112.2(1), N(21)–Cu(1)–S(2) 108.7(1), N(11)–Cu(1)–S(2) 108.5(1), N(2)–Cu(2)–N(41) 111.1(2), N(2)–Cu(2)–N(31) 100.6(2), N(41)–Cu(2)–N(31) 97.6(2), N(2)–Cu(2)–S(1)^i, 117.1(1), N(41)–Cu(2)–S(1)^i 114.7(1), N(31)–Cu(2)–S(1)^i 113.2(1). Symmetry codes: i $x + 1, y, z$; ii $-x - 1, -y + 1, -z + 1$; iii $-x, -y, -z + 1$; iv $-x, -y + 1, -z + 1$; v $-x + 1, -y + 1, -z + 2$.

As shown in Fig. 2, the independent SCN^- ligands bridge Cu(1) and Cu(2) alternately to form a zigzag $[(CuSCN)_2]_\infty$ chain running parallel to the *a* direction, with bond angles Cu(1)–S(2)–C(2) 99.7(2)°, Cu(1)–N(1)–C(1) 168.1(4)° and Cu(2)–S(1)^i–C(1)^i 102.4(2)°, Cu(2)–N(2)–C(2) 167.1(4)°. Such chains are inter-connected through two bpa ligands (N21 and

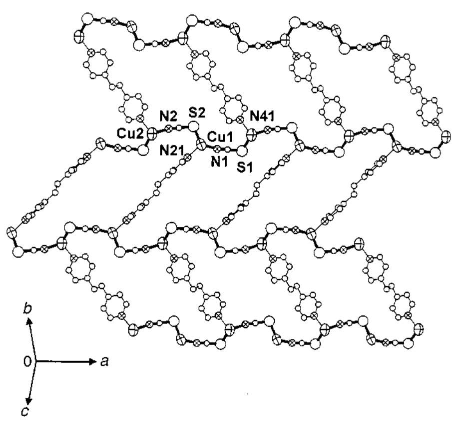

Fig. 2 A two-dimensional brick-like 6^3 network viewed along the [011] direction. Filled bonds represent $[(CuSCN)_2]_\infty$ zigzag chains running parallel to the *a* axis. The pyridyl planes of bpa N(21) and bpa N(41) make a dihedral angle of 112.7°.

---

† Dedicated to the memory of Dr James C. N. Ma (1927–1999).

N41) that bridge copper centers to generate a 2D brick-like network, which is similar to the brick-wall patterns previously reported in two-dimensional coordination compounds.[10] The pyridyl planes of bpa N21 and bpa N41 make a dihedral angle of 112.7°. Neighboring networks are further linked by the remaining bpa ligands (N11 and N31) to form a 3D framework. The dihedral angle between the pyridyl planes of bpa N11 and bpa N31 is 99.2°.

The 2D networks of 6^3 topology are stacked in an ABAB… sequence, and the mode of their linkage to build up a 3D framework is illustrated schematically in Fig. 3. It can be seen that there are three kinds of shortest circuits around every four-connected node: two 4-gons, three 6-gons and one 8-gon. Each of the resulting channels, which lie horizontally in Fig. 3, has a 10-vertex ring at its boundary. In contrast, the 6^3 nets in the $SrAl_2$-type network stack directly on top of one another so that an 8-vertex ring constitutes the boundary of each channel.[7,8]

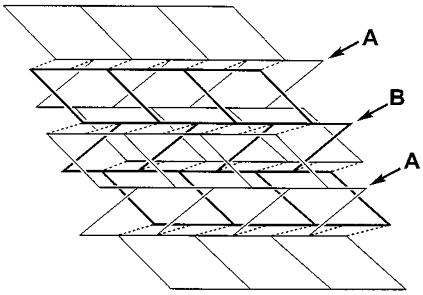

Fig. 3 Schematic representation showing the topology of a 4^26^38 3D network. The copper(I) ions are located at the nodes. Horizontal lines represent SCN^- ligands, inclined lines indicate bpa N(21) and N(41) ligands, and dashed lines indicate the bpa N(11) and N(31) ligands that form bridges between the 2D brick-like networks of 6^3 topology. A perspective view of a stack of three 2D networks is shown: the middle layer B (thick lines) is sandwiched between two type A layers (thin lines), and two adjacent layers are related by the translation vector (***a*** + ***c***).

Two 3D frameworks interpenetrate to form the crystal structure of **1**. The overall structure can alternatively be regarded as two identical 2D brick networks that interpenetrate in an inclined way, with the bridging bpa ligands (N11 and N31) occupying the voids.

The thiocyaniate ligands function as linking rods to bridge copper(I) centers to make the coordination framework of **1** a neutral one, in contrast to many common examples that are charged.[11] Several neutral Cu(I) coordination polymers have been synthesized by solution methods, for example [Cu(4,4′-bpy)Cl][12] and $[Cu_2(SCN)_2(pyz)]$ (pyz = pyrazine).[13] However, their structures are very different from **1**, as [Cu(4,4′-bpy)Cl] is built of two-fold interpenetrating 2D networks and $[Cu_2(SCN)_2(pyz)]$ has a non-interpenetrating structure. The formation of 3D frameworks depends on not only the coordination geometry at the metal centers but also the nature of the anions and the bridging ligands. In the case of **1**, the presence of four independent, centrosymmetric bpa ligands is responsible for generating the unusual framework structure.

In contrast to the extensively studied rigid ligand 4,4′-bipyridine, the flexible ligand bpa has recently attracted the interest of chemists.[5,14] The less exploited bpa ligand can adopt *gauche* and *anti* conformations, and this conformational freedom can even engender supramolecular isomerism in coordination polymers.[15] Since all four independent bpa ligands in **1** occupy $\bar{1}$ sites and exhibit the *anti* conformation, it is conceivable that other isomers may be generated in a Cu(I) system containing all *gauche* or mixed *gauche/anti* bpa ligands. Further investigation of neutral metal complexes of bpa is in progress.

This work is supported by Hong Kong Research Grants Council Earmarked Grant CUHK 4179/97P and Direct Grant A/C 2060129 of The Chinese University of Hong Kong.

Notes and references

‡ *Synthesis*: CuSCN (61 mg, 0.5 mmol), bpa (92 mg, 0.5 mmol) and 2 mL distilled water were placed in a thick-walled Pyrex tube of *ca.* 6 mL capacity, and then the mixture was frozen in liquid nitrogen. The tube was subsequently flame-sealed under vacuum and kept in a furnace at 180 °C for 24 h, and then cooled to 60 °C at 6 °C h^{-1}. From the brown powdery bulk residue, red block-like crystals of [CuSCN(bpa)] **1** were isolated in *ca.* 10% yield and washed with water. IR (KBr pellet)/cm^{-1}: 2102.9s, 2091.4s, 1605.0s, 1418.0s, 1007.6m, 825.7s, 820.7s, 761.1m, 548.1m, 535.0m. The IR spectrum of the brown powder is similar to that of **1**, except that a single peak at 2103.9 cm^{-1} appears at the position of the doublet in the spectrum of **1**. This suggests that the brown powder is a different product containing a simpler SCN^- bridging mode. Both red crystals of **1** and the brown powder are insoluble in water, MeCN and DMF.

§ *Crystal data*: [CuSCN(bpa)] **1**, $C_{13}H_{12}CuN_3S$, M = 305.86, monoclinic, space group $P2_1/c$ (no. 14), a = 10.782(2), b = 17.348(2), c = 14.084(2) Å, β = 97.405(3)°, V = 2612.4(6) Å^3, Z = 8, D_c = 1.555 Mg m^{-3}, $F(000)$ = 1248, μ(Mo-Kα) = 1.815 mm^{-1}. 11977 reflections measured, 5941 unique (R_{int} = 0.0886), final $R1$ = 0.0417, $wR2$ = 0.0759 for 2215 independent reflections [$I > 2\sigma(I)$]. Data collection was performed at 293 K on a Bruker SMART 1000 CCD diffractometer using frames of oscillation range 0.3°, with $2 < \theta < 27.5°$. CCDC 182/1379. See http://www.rsc.org/suppdata/cc/1999/1849/ for crystallographic files in .cif format.

1 R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Liu, in *Supramolecular Architecture*, ed. T. Bein, American Chemical Society, Washington DC, ch. 19, 1992; M. Munakata, L. P. Wu and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, 1999, **46**, 173; A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.* 1999, **183**, 117.

2 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.

3 A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley, New York, 1977; A. F. Wells, *Further Studies of Three-Dimensional Nets*, ACA Monograph No. 8, American Crystallographic Association, 1979.

4 B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, *Nature* (*London*), 1994, **369**, 727.

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

6 L. Carlucci, G. Ciani, P. Macchi and D. M. Proserpio, *Chem. Commun.*, 1998, 1837.

7 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1088.

8 L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpio and S. Rizzato, *Chem. Eur. J.* 1999, **5**, 237.

9 See, *e.g.* B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546; L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1994, 1325; M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa and M. Maekawa, *J. Am. Chem. Soc.*, 1996, **118**, 3117; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1994, 2755; A. J. Blake, N. R. Champness, S. S. M. Chung, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 1005; S. Lopez, M. Kahraman, M. Harmata and S. W. Keller, *Inorg. Chem.*, 1997, **36**, 6138.

10 M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 7287; L. Carlucci, G. Ciani and D. M. Proserpio, *New J. Chem.*, 1998, 1319.

11 See, *e.g.* B. F. Abrahams, S. R. Batten, M. J. Grannas, H. Hamit, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed.*, 1999, **38**, 1475; A. J. Blake, N. R. Champness, A. N. Khlobystov, D. A. Lemenovskii, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 2027; O. M. Yaghi, H. Li and M. O'Keeffe, *Mater. Res. Soc. Symp. Proc.*, 1997, **453**, 127.

12 O. M. Yaghi and G. Li, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 207.

13 A. J. Blake, N. R. Champness, M. Crew, L. R. Hanton, S. Parsons and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1998, 1533; A. J. Blake, N. R. Brooks, N. R. Champness, L. R. Hanton, P. Hubberstey and M. Schröder, *Pure Appl. Chem.*, 1998, **70**, 2351.

14 M. Fujita, Y. J. Kwon, M. Miyazawa and K. Ogura, *J. Chem. Soc., Chem. Commun.*, 1994, 1977; C. S. Hong and Y. Do, *Inorg. Chem.*, 1998, **37**, 4470; D. Rochon, M. Andruh and R. Melanson, *Can. J. Chem.*, 1998, **76**, 1564; C. V. K. Sharma and R. D. Rogers, *Chem. Commun.*, 1999, 83; M. L. Hernández, M. G. Barandika, M. K. Urtiaga, R. Cortés, L. Lezama, M. I. Arriortua and T. Rojo, *J. Chem. Soc., Dalton Trans.*, 1999, 1401.

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

Communication 9/05085J