

The three-dimensional coordination network in poly[di- μ_3 -cyanido- μ_5 -[5-(pyridin-4-yl)tetrazolato]-tricopper(I)]

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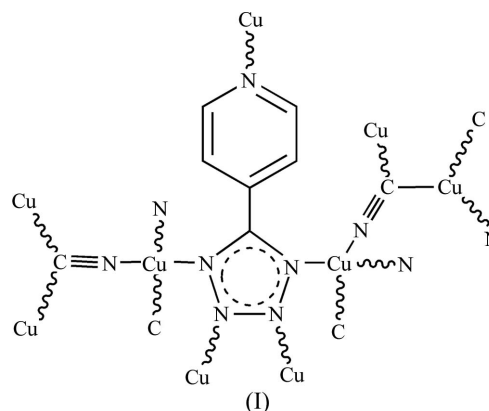
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In the title three-dimensional tetrazolate-based coordination polymer, poly[bis(μ_3 -cyanido- $\kappa^3 N:C:C$)[μ_5 -5-(pyridin-4-yl)-tetrazolato- $\kappa^5 N:N':N'':N''':N''''$]tricopper(I)], $[\text{Cu}_3(\text{C}_6\text{H}_4\text{N}_5)(\text{CN})_2]_n$, there are two types of coordinated Cu^{I} atoms. One type exhibits a tetrahedral environment and the other, residing on a twofold axis, adopts a trigonal coordination environment. The closest $\text{Cu} \cdots \text{Cu}$ distance is only 2.531 (2) Å, involving a bridging cyanide C atom. All four tetrazolate and the pyridine N atom of the 4-(pyridin-4-yl)-1*H*-tetrazolate anion are coordinated to these Cu^{I} atoms and exhibit a μ_5 -bridging mode. The three-dimensional coordination network can be topologically simplified as a rarely observed (3,3,4,5)-connected network with the Schläfli symbol $(4.6.8^4)_2.(4^2.6.8^7).(6.8^2)_3$.

Comment

The unique coordination abilities of 5-substituted 1*H*-tetrazoles such as 5-(2-, 3- or 4-pyridyl)-1*H*-tetrazole (abbreviated as 2-Hptz, 3-Hptz or 4-Hptz, respectively) to transition metal ions have been used extensively in the construction of functional coordination complexes [metal-organic frameworks (MOFs), fluorescent and ferroelectric materials *etc.* (Xiong *et al.*, 2002; Jiang *et al.*, 2004; Ye *et al.*, 2005; Li *et al.*, 2009; Ouellette & Zubieta 2009; Song *et al.*, 2010)]. By controlling the reaction conditions, such as the temperature, the pH of the medium or the solvent used, the tetrazole group can be coordinated to metal centres in μ_1 -, μ_2 -, μ_3 - or μ_4 -modes (Wang *et al.*, 2005; Yang *et al.*, 2009). However, μ_4 -bridging coordination complexes are apparently less common than the other three, which may be due to the spatial hindrance of the tetrazole group. A search for 5-substituted tetrazolate metal-organic complexes in the Cambridge Structural Database (CSD, Version 5.33, plus February 2012 update; Allen, 2002) yielded 1183 hits, of which there were only 24 complexes

where the tetrazolate anions adopt a μ_4 -bridging mode (*ca* 2.0% of all the complexes). With the aim of preparing novel μ_4 -bridge-based tetrazolate metal-organic complexes where the tetrazole group can be generated from an *in situ* reaction (Yang *et al.*, 2009), we have used 4-cyanopyridine, NaN_3 and CuCN as the raw materials under hydrothermal conditions to give the title novel metal coordination polymer, (I), and report its crystal structure here.



Complex (I) crystallizes in the monoclinic $C2/c$ space group, with the asymmetric unit consisting of one and a half Cu^{I} cations, half a 4-ptz anion and a whole CN^- anion, with atoms Cu2, N3, C3 and C4 residing on a twofold rotation axis (Fig. 1). The pyridyl group in the 4-ptz anion is moderately twisted away from the tetrazole group, with a dihedral angle of 45.0 (1)° between their respective planes. For the central Cu atoms, the Cu1 coordination environment is a distorted tetrahedron, with $\text{Cu}-\text{N}/\text{C}$ bond lengths in the range 1.977 (3)–2.090 (2) Å. As far as atom Cu2 is concerned, although a very long inter-atomic contact of 2.870 (3) Å exists between Cu2 and N4($x - \frac{1}{2}, -y + \frac{5}{2}, z - \frac{1}{2}$), its coordination environment can be best described as planar-trigonal, with the metal atom residing completely in the plane, and with bond

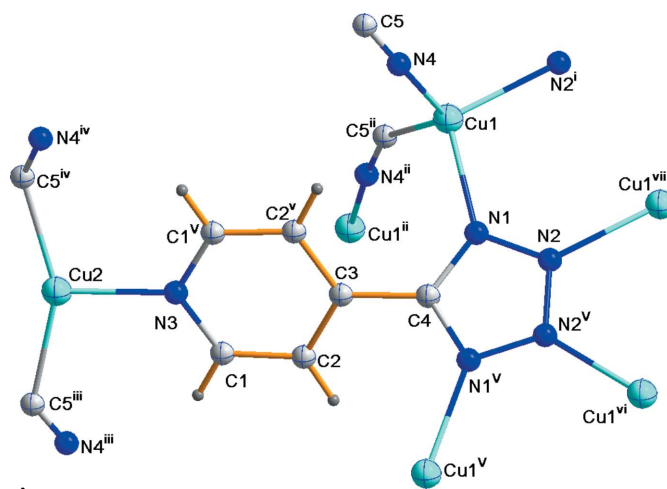


Figure 1
The coordination environments of the Cu^{I} ions and the 4-ptz ligand of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$; (ii) $x, -y + 2, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, y + \frac{1}{2}, z - 1$; (iv) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x + 1, y, -z + \frac{1}{2}$; (vi) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (vii) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$.]

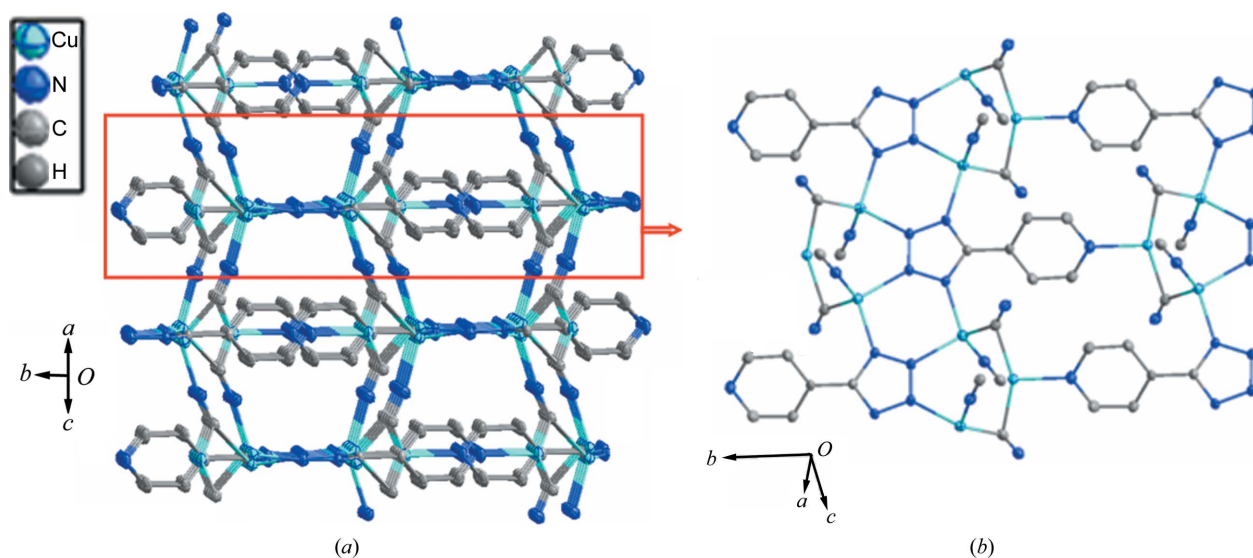


Figure 2

(a) Part of the crystal structure of (I), showing the formation of the three-dimensional coordination network linked by CN^- anions coordinated to Cu^{I} centres in adjacent $(10\bar{1})$ layers. (b) Part of the crystal structure of (I), showing the two-dimensional layer parallel to the $(10\bar{1})$ plane formed by the coordination of the five N atoms of the 4-ptz anion and the C atoms of the CN^- anions.

lengths of 2.018 (3) and 2.068 (3) Å for $\text{Cu2}-\text{N3}$ and $\text{Cu2}-\text{C5}(x - \frac{1}{2}, y + \frac{1}{2}, z - 1)$, respectively (Table 1). It is worth mentioning that all five N atoms in the 4-ptz anion are coordinated to Cu^{I} centres, with the four tetrazole N atoms coordinated only to Cu1 and the pyridyl N atom bonded only to Cu2 . The CN^- anion is coordinated *via* atom N4 to Cu1 at one end and, at the other end, *via* atom C5 to $\text{Cu1}(x, -y + 2, z + \frac{1}{2})$ and $\text{Cu2}(x + \frac{1}{2}, y - \frac{1}{2}, z + 1)$ simultaneously, with a $\text{Cu}\cdots\text{Cu}$ distance for this pair of Cu^{I} ions of only 2.5306 (6) Å, which is comparable with some analogues (Qin *et al.*, 2011; Zhou *et al.*, 2009).

In the crystal packing of (I), a three-dimensional coordination network is formed (Fig. 2a). The network can be analysed in terms of three aspects. Firstly, *via* the coordination of only a 4-ptz anion to Cu1 and Cu2 , these two types of ionic components are linked into a one-dimensional chain running parallel to the $[101]$ direction (Fig. 2b). Secondly, *via* the μ_2 coordination of cyano atom C5 to adjacent $[101]$ chains, a two-dimensional layer structure runs parallel to the $(10\bar{1})$ plane, in which the Cu^{I} cations are arrayed alternately, separated by 4-ptz anions (Fig. 2b). Thirdly, adjacent $(10\bar{1})$ layers are joined together through the coordination of up and down cyano atoms N4 of the $(10\bar{1})$ plane to the Cu1 centres, forming a three-dimensional network.

To better understand this network from a topological view, the Cu1 , Cu2 , CN^- and 4-ptz ions can be regarded as 4-, 3-, 3- and 5-connected nodes. Thus, the whole network can be simplified as a (3,3,4,5)-connected topological network with the Schläfli symbol $(4.6.8^4)_2.(4^2.6.8^7).(6.8^2)_3$ (Fig. 3). This is a new kind of topological network, according to analysis by *TOPOS* (Blatov, 2006). In comparison, Wang *et al.* (2009) have recently conducted an experiment using almost identical reactants to this work, only with CuCN replaced by CuBr . However, they obtained a completely different three-dimen-

sional metal-organic polymer with a generally observed (3,4)-connected topological network. From this, we conclude that subtle alteration of the reaction conditions in a hydrothermal reaction may lead to entirely different products.

The spectroscopic characteristics of (I) were also investigated. The absorption band around 3437 cm^{-1} in its IR absorption spectrum can be assigned to the stretching vibration of the aromatic C-H bonds, and the band at 2062 cm^{-1} to the classical stretching vibration of the $\text{C}\equiv\text{N}$ bond of the CN^- anion. In its solid luminescent spectrum upon excitation at 346 nm, (I) shows two emission peaks at 363 and 435 nm.

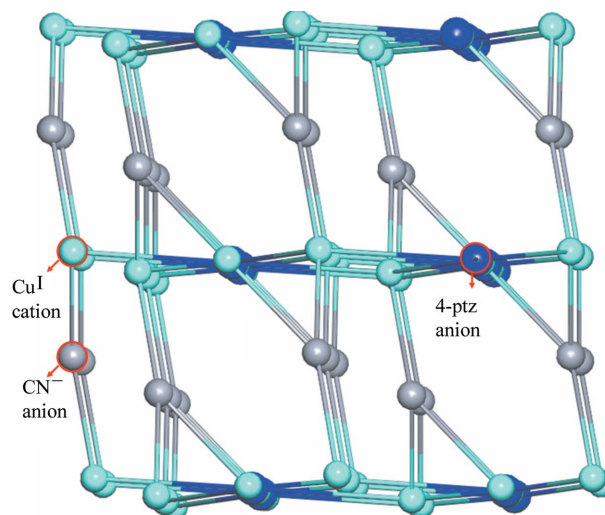


Figure 3

The simplified (3,3,4,5)-connected topological network when Cu2 , a CN^- anion, Cu1 and a 4-ptz anion are regarded as 3-, 3-, 4- and 5-connected nodes, respectively. (In the electronic version of the paper, the cyan, grey and blue spheres represent the Cu^{I} cation, CN^- anion and 4-ptz anion, respectively.)

The former can be attributed to ligand-to-metal charge transfer (LMCT) and the latter should be largely attributed to intra-ligand π - π^* fluorescent emission (Huang *et al.*, 2006).

Experimental

All reagents and solvents were used as obtained without further purification. Equivalent molar amounts of 4-cyanopyridine (0.052 g, 0.5 mmol), NaN_3 (0.033 g, 0.5 mmol) and CuCN (1.5 mmol, 0.13 g) were mixed in water (15 ml). The mixture was stirred for 10 min at ambient temperature and then heated in a 23 ml capacity Teflon-lined reaction vessel at 433 K for 3 d. After slow cooling to room temperature at a rate of 5 K h^{-1} , the product was collected manually, washed with water and air-dried to give colourless block-shaped crystals of (I) (yield 0.03 g).

Crystal data

$[\text{Cu}_3(\text{C}_6\text{H}_4\text{N}_5)(\text{CN})_2]$	$V = 1007.5$ (3) \AA^3
$M_r = 388.80$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 12.4823$ (19) \AA	$\mu = 6.26$ mm^{-1}
$b = 11.8834$ (18) \AA	$T = 298$ K
$c = 8.7986$ (13) \AA	$0.13 \times 0.12 \times 0.11$ mm
$\beta = 129.467$ (2) $^\circ$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3717 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008)	1245 independent reflections
$T_{\min} = 0.497$, $T_{\max} = 0.573$	1135 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	84 parameters
$wR(F^2) = 0.066$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.69$ e \AA^{-3}
1245 reflections	$\Delta\rho_{\text{min}} = -0.46$ e \AA^{-3}

C-bound H atoms were positioned geometrically, with C—H = 0.93 \AA , and treated as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2002); cell refinement: SMART; data reduction: SAINT (Bruker, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2008); software used to prepare material for publication: XCIF (Sheldrick, 2008).

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—N1	2.071 (2)	Cu1—C5 ⁱⁱ	1.977 (3)
Cu1—N2 ⁱ	2.090 (2)	Cu2—N3	2.018 (3)
Cu1—N4	2.003 (2)	Cu2—C5 ⁱⁱⁱ	2.068 (2)
C5 ⁱⁱ —Cu1—N1	103.80 (10)	N4—Cu1—N1	105.57 (10)
C5 ⁱⁱ —Cu1—N2 ⁱ	115.05 (10)	N4—Cu1—N2 ⁱ	105.85 (9)
C5 ⁱⁱ —Cu1—N4	120.41 (10)	N3—Cu2—C5 ⁱⁱⁱ	103.88 (8)
N1—Cu1—N2 ⁱ	104.64 (8)	C5 ⁱⁱⁱ —Cu2—C5 ^{iv}	152.25 (15)

Symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$; (ii) $x, -y + 2, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, y + \frac{1}{2}, z - 1$; (iv) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3248). Services for accessing these data are described at the back of the journal.

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