Acta Crystallographica Section E
**Structure Reports**
**Online**
ISSN 1600-5368

# $[Cu^I_4Cu^{II}(CN)_6(DMF)_4]_n$ (DMF is *N*,*N*′-dimethylformamide): redetermination and topological analysis of a mixed-valence copper–cyanide coordination polymer with a unique six-connected self-penetrating network

**Xiao-Jun Zhao,[a] Stuart R. Batten[b] and Miao Du[a]***

[a]College of Chemistry and Life Science, Tianjin Normal University, Tianjin 300074, People's Republic of China, and [b]School of Chemistry, Monash University 3800, Australia

Correspondence e-mail:
dumiao@public.tpt.tj.cn

Received 30 July 2004
Accepted 4 August 2004
Online 13 August 2004

**Key indicators**

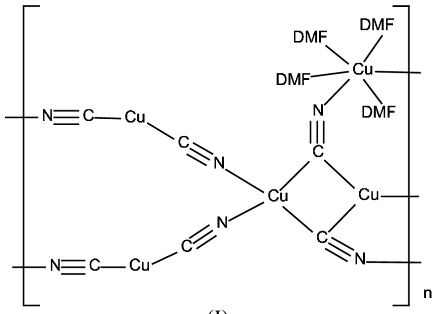
Single-crystal X-ray study
*T* = 293 K
Mean σ(N–C) = 0.008 Å
*R* factor = 0.048
*wR* factor = 0.092
Data-to-parameter ratio = 17.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title coordination polymer, poly[[tetrakis(*N*,*N*′-dimethylformamide)pentacopper(I,II)]-tetra-$\mu_2$-cyano-di-$\mu_3$-cyano], $[Cu_5(CN)_6(C_3H_7NO)_4]_n$, whose structure [Peng & Liaw (1986). *Inorg. Chim. Acta*, **113**, L11–L12] has been redetermined using CCD data, contains four crystallographically independent copper centres, including three $Cu^I$ ions with tetrahedral or linear geometries and one $Cu^{II}$ ion in an octahedral environment. These copper centres are connected by bidentate and tridentate cyanide bridges to form a unique self-penetrating network with $4^4 6^{10} 8$ topology, which has been analyzed in detail. Three of the Cu atoms have site symmetries of $\overline{1}$, 2 and 2.

## Comment

There is currently intense interest in metal–organic coordination polymers as new materials for applications such as gas storage, molecule-based magnets and non-linear optical devices (Yaghi *et al.*, 2003). One of the most important aspects in this field is the analysis of network topology (Batten & Robson, 1998). While some network topologies are extremely common [*e.g.* one-dimensional chains, two-dimensional (4,4) or (6,3) sheets and three-dimensional diamondoid or α-Po nets], there are an infinite number of possible network topologies, and the careful analysis of unusual networks is of inherent interest to the understanding of framework assembly. The crystal structure of the title polymer, (I), which was obtained as a by-product, has been reported previously (Peng & Liaw, 1986) with lattice parameters *a* = 14.034 (4) Å, *b* = 12.591 (3) Å, *c* = 16.403 (3) Å and β = 91.99 (2)°. Because of the limitations of the knowledge of coordination polymer and crystal engineering at that time, the network topology of this structure was not discussed. We report here the redetermination of (I) (Fig. 1) using CCD data and the detailed analysis of the unusual self-penetrating network topology.



(I)

The structure of (I) consists of four crystallographically distinct Cu atoms [including three $Cu^I$ (tetrahedral Cu1, linear

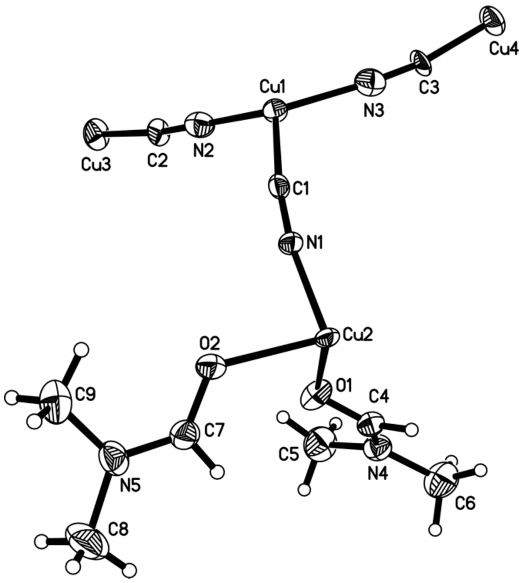


**Figure 1**
Asymmetric unit of (I), showing 35% probability displacement ellipsoids (H atoms are shown as spheres of arbitrary size).

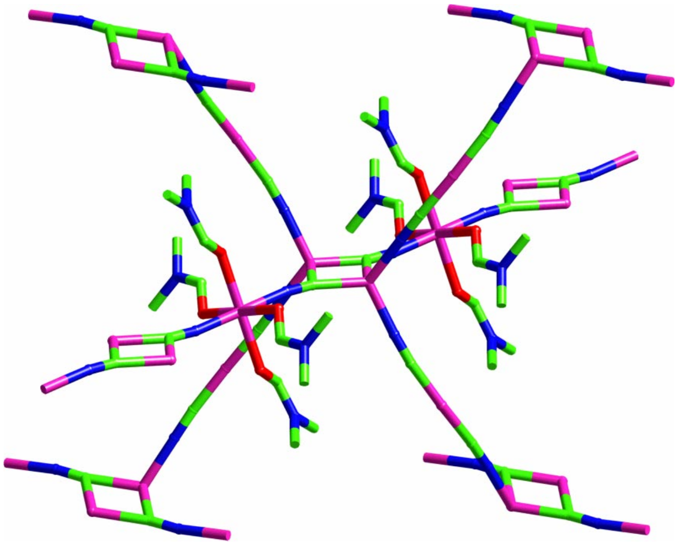


**Figure 2**
Local structure in (I) (H atoms have been omitted for clarity) in stick representation. Cu atoms: purple stick ends; C: green stick ends; N: blue stick ends; O: red stick ends.

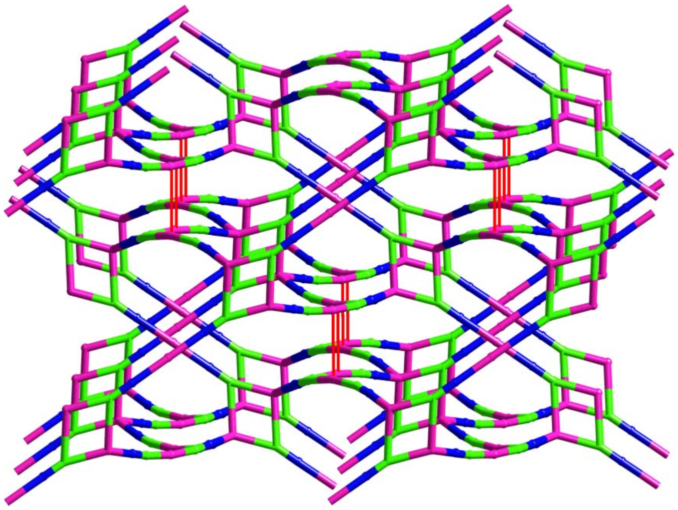


**Figure 3**
Extended network in (I) (DMF molecules have been omitted for clarity). Colour key as in Fig. 2; additionally, the red lines represent Cu···Cu interactions (intradimer interactions are not shown).

Cu3 and Cu4) and one Cu$^{II}$ (octahedral Cu2) atoms] connected by bidentate and tridentate bridging cyanide ligands into a three-dimensional network (Figs. 2 and 3). Considerations of charge balance and coordination geometry led to the assignment of Cu1, Cu3 and Cu4 as being in oxidation state I, and Cu2 as being in oxidation state II. The cyanide constituent atoms were assigned as C or N on the basis of Cu—C/N bond lengths and comparative refinements with alternative assignments.

The basic building block of this framework is a $(\mathrm{Cu1})_2$ dimer in which two tetrahedral Cu1 atoms are bridged by two bidentate cyanide C atoms [Cu1—Cu1$^{i}$ = 2.5619 (13) Å, Cu1—C1 = 1.972 (5) Å and Cu1—C1$^{i}$ = 2.330 (5) Å; symmetry code as in Table 1]. These cyanide ligands are also part of a linear $\mathrm{CN(Cu2)(DMF)_4NC}$ bridge, which connects adjacent $(\mathrm{Cu1})_2$ dimers. The Cu2 atom shows the distinctive Cu$^{II}$ Jahn–Teller distortion [Cu2—N1 = 1.936 (4) Å, Cu2—O2 = 2.084 (3) Å and Cu1—O1 = 2.321 (4) Å]. The dimers are further connected by four linear $\mathrm{Cu(CN)_2}$ bridges [two containing Cu3 and two containing Cu4; Cu3—C2 = 1.811 (5) Å, Cu4—C3 = 1.814 (5) Å, Cu1—N2 = 1.985 (5) Å and Cu1—N3 = 1.993 (5) Å]. Thus each dimer is connected to six other dimers (Fig. 2) and, consequently, the structure can be represented as a six-connecting network, with the nodes representing the $(\mathrm{Cu1})_2$ dimers (Fig. 3). The network topology is unusual in two respects. Firstly, the most common topology for six-connecting networks is that of $\alpha$–Po (Schäfli symbol $4^{12}6^{3}$); the network described here [Schäfli symbol $4^{4}6^{10}8$; see Carlucci *et al.* (2003)] is clearly different. Secondly, the network is self-penetrating. A self-penetrating network is one in which some of the 'shortest' circuits (which are not all the same size) are penetrated by rods of the same network in a rotaxane-like fashion (Batten & Robson, 1999). Such a motif is highlighted in Fig. 4, where the blue shortest circuit is penetrated by a rod (red) of the same net. This rod contains the bulky $\mathrm{Cu_2(DMF)_4}$ moiety. A number of other self-penetrating networks have been reported recently (see http://web.chem.monash.edu.au/Department/Staff/Batten/Intptn.htm for a full list of self-penetrating networks), including the structure of $\mathrm{Cd(CN)_2(pyrazine)}$, which has the same network topology as the title compound (Abrahams *et al.*, 1994), but with the important difference that a single Cd node is equivalent to the $(\mathrm{Cu1})_2$ dimers described here.

The reasons behind this unusual network topology are hard to define, although one factor may be the requirements of the polymer to accommodate the bulky $\mathrm{Cu_2(DMF)_4}$ moiety (note the higher proportion of 6- and 8-membered shortest circuits in the Schäfli symbol as stated above in comparison to $\alpha$-Po). In addition, there are weak Cu···Cu interactions [Cu3···Cu4$^{iii}$ = 3.0085 (19) Å] between $\mathrm{Cu(CN)_2}$ rods in this

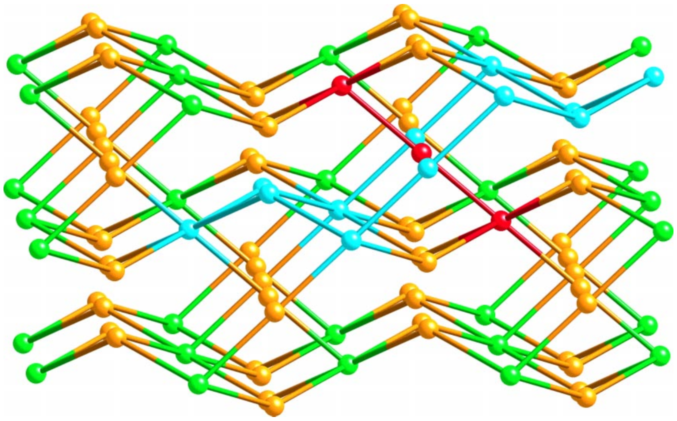


**Figure 4**
Schematic diagram of the network topology in (I). Green nodes represent the centres of the dimers, while the orange spheres show other Cu atoms and represent the kinked $Cu(CN)_2$ and linear $Cu(DMF)_4(NC)_2$ links between the dimers. A shortest circuit [blue, referring to the $(Cu1)_2$ dimeric nodes] and the rod passing through it (red) are highlighted to illustrate the self-penetration.

structure – these are shown as thin red lines in Fig. 3. Examination of the structure with *PLATON* (Spek, 2003) shows that there are no solvent-accessible voids in the crystal structure of (I).

## Experimental

The hydrothermal reaction of $Cu(OAc)_2 \cdot H_2O$ with isonicotinic acid, 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole, dimethylformamide (DMF) and water in a 3:2:2:10:800 molar ratio at 433 K for 96 h produced a small amount of yellow crystals of (I) in *ca* 10% yield. The cyanide ion in the final product is formed by the acid-catalyzed decomposition of isonicotinic acid under hydrothermal condition (Kang *et al.*, 2004). IR (KBr pellet, $cm^{-1}$): 2934 (*m*, C—H), 2123 (*vs*, C≡N), 1650 (*vs*, C=O). Analysis calculated for $C_{18}H_{28}Cu_5N_{10}O_4$: C 28.21, H 3.68, N 18.27%; found: C 28.04, H 3.89, N 18.17%.

### *Crystal data*

$[Cu_5(CN)_6(C_3H_7NO)_4]$
$M_r = 766.25$
Monoclinic, $C2/c$
$a = 14.054\ (4)$ Å
$b = 12.597\ (4)$ Å
$c = 16.424\ (5)$ Å
$\beta = 92.008\ (6)^\circ$
$V = 2905.9\ (15)$ Å$^3$
$Z = 4$

$D_x = 1.752$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 718 reflections
$\theta = 2.5$–$23.9^\circ$
$\mu = 3.64$ mm$^{-1}$
$T = 293\ (2)$ K
Prism, yellow
0.32 × 0.20 × 0.16 mm

### *Data collection*

Bruker SMART CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.389$, $T_{max} = 0.594$
8240 measured reflections

2971 independent reflections
1795 reflections with $I > 2\sigma(I)$
$R_{int} = 0.071$
$\theta_{max} = 26.4^\circ$
$h = -15 \rightarrow 17$
$k = -13 \rightarrow 15$
$l = -20 \rightarrow 13$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.092$
$S = 0.97$
2971 reflections
174 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.66$ e Å$^{-3}$
$\Delta\rho_{min} = -0.45$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu1—C1 | 1.972 (5) | Cu2—N1 | 1.936 (4) |
| Cu1—N2 | 1.985 (5) | Cu2—O2 | 2.084 (3) |
| Cu1—N3 | 1.993 (5) | Cu2—O1 | 2.321 (4) |
| Cu1—C1$^{i}$ | 2.330 (5) | Cu3—C2 | 1.811 (5) |
| Cu1—Cu1$^{i}$ | 2.5619 (13) | Cu3—Cu4$^{iii}$ | 3.0085 (19) |
| Cu2—N1$^{ii}$ | 1.936 (4) | Cu4—C3 | 1.814 (5) |
| | | | |
| C1—Cu1—N2 | 115.11 (18) | N1$^{ii}$—Cu2—O1 | 89.68 (15) |
| C1—Cu1—N3 | 114.22 (18) | N1—Cu2—O1 | 90.32 (15) |
| N2—Cu1—N3 | 116.47 (18) | O2$^{ii}$—Cu2—O1 | 88.13 (15) |
| C1—Cu1—C1$^{i}$ | 107.44 (17) | O2—Cu2—O1 | 91.87 (15) |
| N2—Cu1—C1$^{i}$ | 101.11 (17) | N1$^{ii}$—Cu2—O1$^{ii}$ | 90.32 (15) |
| N3—Cu1—C1$^{i}$ | 99.75 (17) | C2—Cu3—C2$^{iv}$ | 173.8 (3) |
| N1$^{ii}$—Cu2—O2$^{ii}$ | 89.34 (15) | C3—Cu4—C3$^{v}$ | 169.1 (4) |
| N1—Cu2—O2$^{ii}$ | 90.66 (15) | Cu1—C1—Cu1$^{i}$ | 72.56 (17) |
| N1—Cu2—O2 | 89.34 (15) | | |

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

All H atoms were visible in difference maps; however, they were finally placed in calculated positions (C—H = 0.93 and 0.96 Å) and included in the final refinement in the riding-model approximation, with $U_{iso}$(H) value of $1.2U_{eq}$(C) for aldehyde H atoms and $1.5U_{eq}$(C) for methyl H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXL*97.

This work was supported financially by the Starting Fund of Tianjin Normal University and the Natural Science Foundation of Tianjin (043604011). SRB acknowledges financial support from the Australian Research Council.

## References

Abrahams, B. F., Hardie, M. J., Hoskins, B. F., Robson, R. & Sutherland, E. E. (1994). *J. Chem. Soc. Chem. Commun.* pp. 1049–1050.

Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.

Batten, S. R. & Robson, R. (1999). *Molecular Catenanes, Rotaxanes and Knots, A Journey Through the World of Molecular Topology*, edited by J.-P. Sauvage & C. Dietrich-Buchecker, pp. 77–105. Weinheim: Wiley-VCH.

Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Version 2.1c. Crystal Impact GbR, Bonn, Germany.

Bruker (1998). *SMART*, *SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Carlucci, L., Ciani, G. & Proserpio, D. M. (2003). *Coord. Chem. Rev.* **246**, 247–289.

Kang, Y., Yao, Y.-G., Qin, Y.-Y., Zhang, J., Chen, Y.-B., Li, Z.-J., Wen, Y.-H., Cheng J.-K. & Hu, R.-F. (2004). *Chem. Commun.* pp. 1046–1047.

Peng, S. M. & Liaw, D. S. (1986). *Inorg. Chim. Acta*, **113**, L11—L12.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Yaghi, O. M., O'Keeffe, M., Ockwig, N. W., Chae, H. K., Eddaoudi, M. & Kim. J. (2003). *Nature* (*London*), **423**, 705–714.