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A three-dimensional Cu^{II}–W^{IV} bimetallic porous assembly containing a zigzag ladder structure

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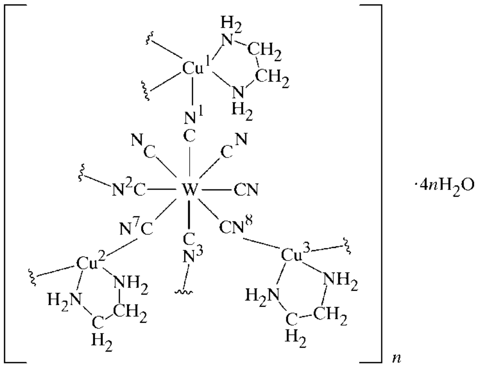
The asymmetric unit of the three-dimensional Cu^{II}–W^{IV} polymeric assembly $\{[Cu(en)_2][Cu(en)][W(CN)_8]\cdot 4H_2O\}_n$ (en is ethylenediamine, $C_2H_8N_2$) or $\{[Cu_2W(CN)_8(C_2H_8N_2)_3]\cdot 4H_2O\}_n$, which can be named as polymeric bis(ethylenediamine)copper(II) (ethylenediamine)copper(II) octacyanotungstate(IV) tetrahydrate or penta-μ-cyano-tricyanotris(ethylenediamine)dicopper(II)tungsten(IV) tetrahydrate, consists of two half $[Cu(en)_2]^{2+}$ cations (Cu^{2+} on inversion centres), a $[Cu(en)]^{2+}$ cation and a $[W(CN)_8]^{4-}$ ion, together with four water molecules. The latter Cu^{II} site is coordinated by five N atoms from an en ligand and by three cyanides in a distorted square-pyramidal geometry. The Cu^{II} atoms of the two $[Cu(en)_2]^{2+}$ cations reside in an elongated octahedral coordination environment, and one of them is localized at a centre of inversion. The W atom is coordinated by eight cyano groups in an irregular square antiprism. Five of these act as bridging units connecting the W and the three Cu atoms, to form an infinite three-dimensional porous network containing a zigzag ladder structure.

Comment

Recently, there has been a growing interest in the design and construction of engineered supramolecular frameworks with specific topologies, utilizing molecular precursors containing the cyano group, which is used for its distinct advantage in connecting transition metal ions (Berseth *et al.*, 2000; Ohba *et al.*, 1999; Sokol *et al.*, 2001; Sra *et al.*, 2000; Zhang *et al.*, 2000). These cyano-containing synthons are mainly cyanometallate anions, which show various geometries, *e.g.* linear, as in $[Ag(CN)_2]^-$, trigonal, as in $[Cu(CN)_3]^{2-}$, tetrahedral, as in $[Cd(CN)_4]^{2-}$, square planar, as in $[Ni(CN)_4]^{2-}$, and octahedral, as in $[Fe(CN)_6]^{3-}$ (Yuan *et al.*, 2000). This geometric diversity of the cyanometallates makes it possible for chemists to construct desired structures in an effective manner.

Currently, hexacyanometallate ions, $[M(CN)_6]^{n-}$ (M is Fe, Cr, Mn, *etc.*), acting as good building blocks, have been successfully employed to obtain bimetallic assemblies with one-dimensional (1D) chain, 1D rope-ladder, two-dimensional (2D) honeycomb, 2D square and three-dimensional (3D) cubane network structures (Ohba *et al.*, 1999). Octacyanometallates, $[M(CN)_8]^{n-}$ (M is Mo or W), as one of these potential connecting moieties, may show various geometrical structures, *e.g.* square antiprism, dodecahedron, or bicapped trigonal prism (Zhong *et al.*, 2000). These flexible species may be used as versatile synthons to construct a variety of supramolecular architectures or networks with novel topological structures. However, structurally characterized complexes based on $[M(CN)_8]^{4-}$ are still very rare (Sieklucka *et al.*, 2000). Here, we present the structure of a novel 3D Cu^{II}–W^{IV} porous coordination polymer, $\{[Cu(en)_2][Cu(en)][W(CN)_8]\}_n\cdot 4nH_2O$, (I) (en is ethylenediamine).



(I)

The asymmetric unit of (I) consists of a $[W(CN)_8]^{4-}$ ion, a $[Cu(en)]^{2+}$ ion, two half $[Cu(en)_2]^{2+}$ ions and four water molecules. The W atom is coordinated by eight CN groups in an irregular square antiprism, with W—C distances ranging from 2.156 (5) to 2.172 (5) Å (Fig. 1). Atoms Cu2 and Cu3 are located at the special equivalent positions $(0,0,\frac{1}{2})$ and (0,0,0), respectively, and both are in an elongated octahedral coordination environment, in which four N atoms from two en ligands occupy the equatorial positions, with $Cu—N_{eq}$ bond distances in the range 2.011 (6)–2.024 (4) Å.

The axial sites are occupied by two N atoms from the bridging cyanide groups on different $[W(CN)_8]^{4-}$ anions. Owing to Jahn–Teller effects, the two $Cu—N_{cyano}$ distances are much longer than those of the equatorial positions, with Cu2—N7 = 2.644 (5) Å and Cu3—N8 = 2.500 (4) Å.

The Cu1 sphere can be described as a distorted square-pyramidal geometry, with N1 as the axial atom and $N2^{i}$, $N3^{ii}$, N9 and N10 as the equatorial coordinated atoms, where atoms $N2^{i}$ and $N3^{ii}$ are from the cyanides of another two adjacent $[W(CN)_8]$ moieties [symmetry codes: (i) $-1-x$, $-1-y$, $1-z$; (ii) $x-1$, y, z]. Consequently, for each $[W(CN)_8]$ unit, there are five cyano groups acting as bridging units and another three as terminal groups.

Through the bridging cyano groups (C1≡N1, C2≡N2 and C3≡N3), atoms W1 and Cu1 are linked to form a 1D infinite zigzag ladder structure along the *a* axis (Fig. 1*b*). The ladder is made up of two different collateral $Cu_2W_2(CN)_4$ 12-atom

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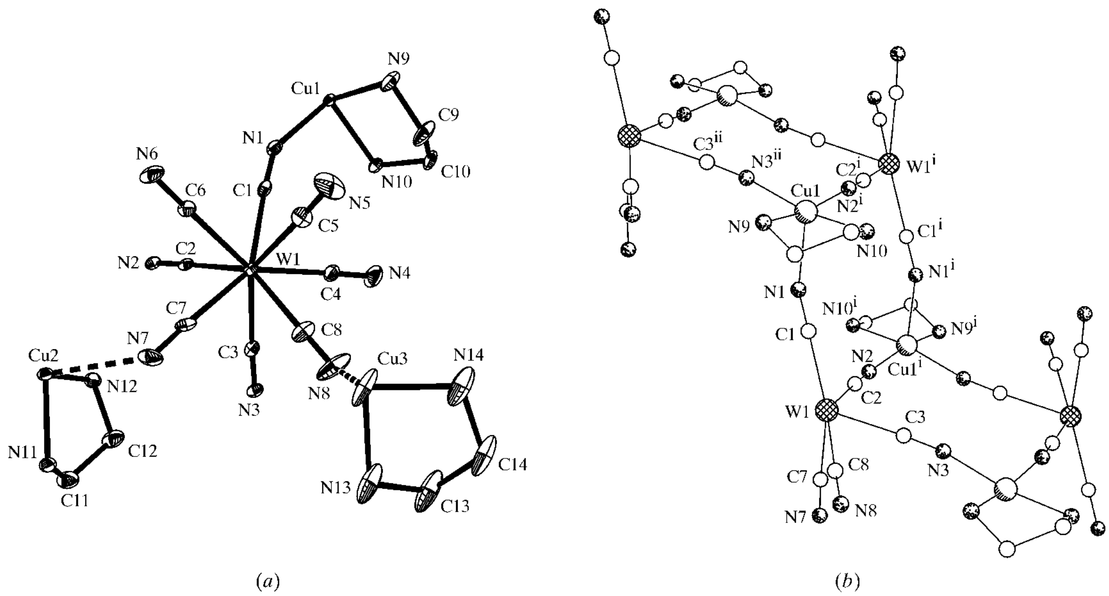

Figure 1
The molecular structure of (I). (*a*) A drawing of the asymmetric unit, with displacement ellipsoids at the 25% probability level. (*b*) A perspective view of the zigzag ladder portion. H atoms and non-bridging cyano groups have been omitted for clarity [symmetry codes: (i) $-1 - x, -1 - y, 1 - z$; (ii) $x - 1, y, z$].

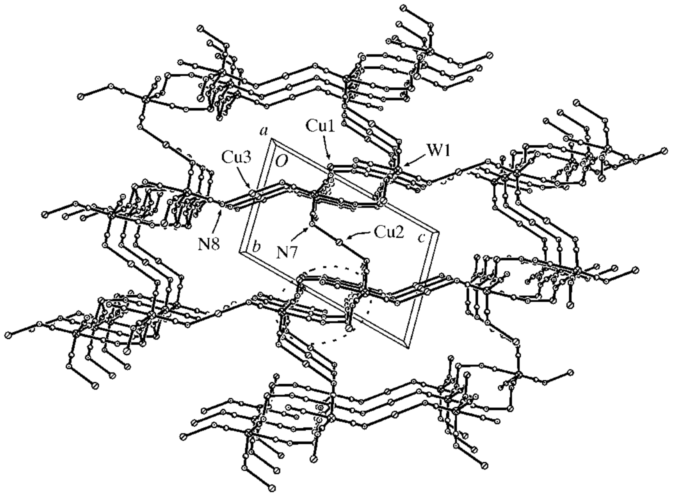

Figure 2
A perspective view of (I) projected onto the *bc* plane, showing the three-dimensional porous structure. The dashed curve encircles the position of the zigzag ladder along the *a* axis. The en ligands, water molecules and non-bridged cyano groups have been omitted for clarity.

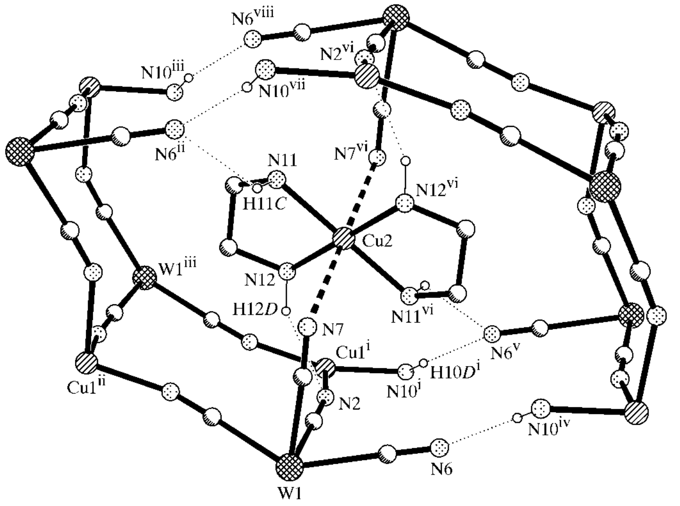

Figure 3
A perspective view of a cavity which encapsulates a $[Cu2(en)_2]^{2+}$ cation. Atoms unrelated to this box have been omitted for clarity. [Symmetry codes: (i) $-x - 1, -y - 1, -z + 1$; (ii) $x + 1, y, z$; (iii) $-x, -y - 1, -z + 1$; (iv) $x, y + 1, z$; (v) $-x - 1, -y, -z + 1$; (vi) $-x, -y, -z + 1$; (vii) $x + 1, y + 1, z$; (viii) $-x, -y, -z + 1$.]

macrocyclic units $[(Cu1-N1\equiv C1-W1-C2\equiv N2-)_2$ and $(Cu1-N3\equiv C3-W1-C2\equiv N2-)_2]$, with a dihedral angle of 120.6° based on the two Cu_2W_2 planes. Along the *b* axis, the zigzag ladders are connected together by $W1-C7\equiv N7-Cu2$ linkages to form 2D sheets. Meanwhile, another kind of linkage, of the form $W1-C8\equiv N8-Cu3$, connects the 2D sheets to construct a 3D porous network structure, as depicted in Fig. 2.

It is worth noting that the displacement ellipsoids of the atoms of the Cu2 cation system are smaller than those of the Cu3 cation system. This may be interpreted from the unique coordination environment about the Cu2 system. Between every two adjacent zigzag ladders, boxes are formed by two pairs of the above mentioned collateral $Cu_2W_2(CN)_4$ 12-atom macrocyclic units joined by four $N11^{i}-H11C^{i}\cdots N6^{v}$ hydrogen bonds (see Fig. 3 for symmetry codes). In each cavity, a $[Cu(en)_2]^{2+}$ cation system (Cu2) is encapsulated, as shown in Fig. 3. The four N atoms (N11, N12, $N11^{vi}$, $N12^{vi}$; see Fig. 3 for symmetry code) of two en ligands are fixed by four $N_{en}-H\cdots N_{cyano}$ hydrogen bonds (Fig. 3, Table 2), and the two $C7\equiv N7$ groups act like pincers to clamp the Cu2 atom, through two weak Cu1—N7 interactions. Thus, the Cu2 cation system is stabilized steadily in the void.

Experimental

An aqueous solution (20 ml) of $Cu(ClO_4)_2 \cdot 6H_2O$ (74.1 mg, 0.20 mmol), ethylenediamine (0.001 ml, 0.40 mmol) and $K_4[W(CN)_8] \cdot 2H_2O$ (58.4 mg, 0.10 mmol) was stirred at 313 K for 30 min. The resulting solution was left for several days at room temperature in the absence of light, and dark-blue crystals of (I) were obtained in *ca* 70% yield.

Crystal data

$[Cu_2W(CN)_8(C_2H_8N_2)_3] \cdot 4H_2O$
$M_r = 771.48$
Triclinic, $P\overline{1}$
$a = 9.0072$ (7) Å
$b = 9.7391$ (6) Å
$c = 15.5818$ (11) Å
$\alpha = 75.407$ (3)°
$\beta = 85.574$ (3)°
$\gamma = 81.367$ (4)°
$V = 1306.68$ (16) Å^3
$Z = 2$
$D_x = 1.961$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8762 reflections
$\theta = 2.6$–27.5°
$\mu = 6.06$ mm^{-1}
$T = 150$ (2) K
Platelet, dark blue
0.25 × 0.20 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.250$, $T_{max} = 0.548$
7452 measured reflections
4533 independent reflections
4194 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 25°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.061$
$S = 1.01$
4533 reflections
359 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2 + 5.1937P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -1.48$ e Å^{-3}

H atoms on C and N atoms were treated as riding atoms, with geometric restraints (C—H = 0.99 Å and N—H = 0.92 Å) and with $U_{iso}(H) = 1.2U_{eq}(C,N)$. The water molecules were disordered over two sets of sites. Only a few partial H atoms of the water molecules could be found from the difference maps, so the water H atoms were not included in the refinement.

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.222 (4)	Cu2—N11	2.024 (4)
Cu1—N2^i	1.992 (4)	Cu2—N12	2.019 (4)
Cu1—N3^{ii}	1.990 (4)	Cu3—N8	2.500 (4)
Cu1—N9	2.014 (4)	Cu3—N13	2.011 (6)
Cu1—N10	2.022 (4)	Cu3—N14	2.012 (6)
Cu2—N7	2.644 (5)		
N2^i—Cu1—N1	95.89 (15)	C3—N3—Cu1^{iii}	158.8 (4)
C1—N1—Cu1	150.1 (3)	C7—N7—Cu2	122.0 (4)
C2—N2—Cu1^i	163.9 (3)	C8—N8—Cu3	133.9 (4)

Symmetry codes: (i) $-1-x, -1-y, 1-z$; (ii) $x-1, y, z$; (iii) $1+x, y, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N10—H10D···N6^i	0.92	2.12	2.978 (6)	155
N11—H11C···N6^{ii}	0.92	2.39	3.054 (6)	129
N12—H12D···N2	0.92	2.50	3.279 (5)	142
N13—H13C···N5^{iii}	0.92	2.38	3.252 (8)	158

Symmetry codes: (i) $x, y-1, z$; (ii) $1+x, y, z$; (iii) $-x, -y, -z$.

Data collection: *TEXSAN* (Molecular Structure Corporation, 2000); cell refinement: *TEXSAN*; data reduction: *TEXSAN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1099). Services for accessing these data are described at the back of the journal.

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