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Poly[triaquaocta-μ-cyano-dicopper(II)molybdate(IV) monohydrate]

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Key indicators

Single-crystal X-ray study
T = 90 K
Mean σ(N–C) = 0.004 Å
H-atom completeness 1%
R factor = 0.037
wR factor = 0.099
Data-to-parameter ratio = 17.2

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

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The structure of the title compound, $Cu_2[Mo(CN)_8]\cdot 4H_2O$, contains Mo^{IV} ions in a distorted square-antiprismatic geometry (site symmetry 1) linked through CN ligands to four Jahn–Teller-distorted octahedral Cu^{II} ions (site symmetry 2) and four trigonal–bipyramidal Cu^{II} ions (site symmetry 1).

Comment

Over the past few years, cyano-bridged metal assemblies have been widely studied as functionalized molecular magnets, due to their flexible design and simple synthesis. Hexacyano-bridged magnets are known to exhibit high critical temperatures (Ferlay *et al.*, 1995; Hatlevik *et al.*, 1999; Holmes & Girolami, 1999; Ohkoshi *et al.*, 2000) and interesting functionalities (Sato *et al.*, 1996; Miller, 2000; Verdaguer *et al.*, 2002; Ohkoshi *et al.*, 2004). Recently, octacyano-bridged magnets have received attention, due to their variety of crystal structures and coordination geometries. It is known that octacyanometallates $[M(CN)_8]^{n-}$ (M = Mo or W; n = 3, 4) can adopt three different configurations, *viz.* square antiprism (D_{4h}), dodecahedron (D_{2d}) and bicapped trigonal prism (C_{2v}), depending on the surrounding chemical environment (Leipoldt *et al.*, 1994). Single crystals of Cu^{II}–Mo^{IV} analogues containing organic ligands (Rombaut *et al.*, 2001; Li *et al.*, 2002; Larionova *et al.*, 2003; Podgajny *et al.*, 2003; Herrera *et al.*, 2004; Atanasov *et al.*, 2006), NH_3 ligands (Meske & Bobel, 1999; Hozumi *et al.*, 2006; Zhan *et al.*, 2006; Wang *et al.*, 2006) and alkali ions such as Cs^+ (Hozumi *et al.*, 2005; Withers *et al.*,

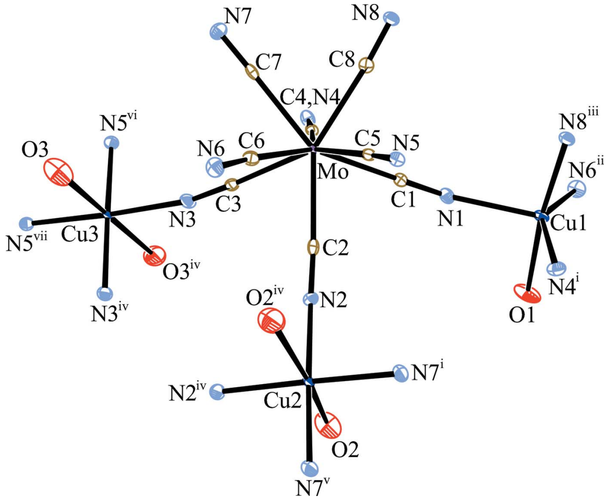

Figure 1
A structural diagram of (I), showing the coordination environments around the Cu^{II} and Mo^{IV} ions. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $x, -y, z - \frac{1}{2}$; (iii) $-x + 1, -y, -z + 1$; (iv) $-x, y, -z + \frac{3}{2}$; (v) $x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (vii) $x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.]

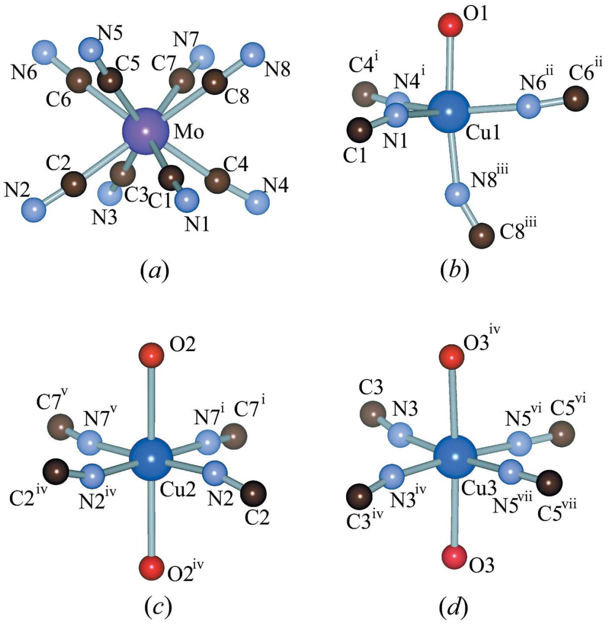

Figure 2
The coordination environments around (*a*) Mo, (*b*) Cu1, (*c*) Cu2 and (*d*) Cu3 in the structure of (I). H atoms have been omitted. [Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, z$; (ii) $x, -y, z-\frac{1}{2}$; (iii) $-x+1, -y, -z+1$; (iv) $-x, y, -z+\frac{3}{2}$; (v) $x-\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (vi) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (vii) $x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$]

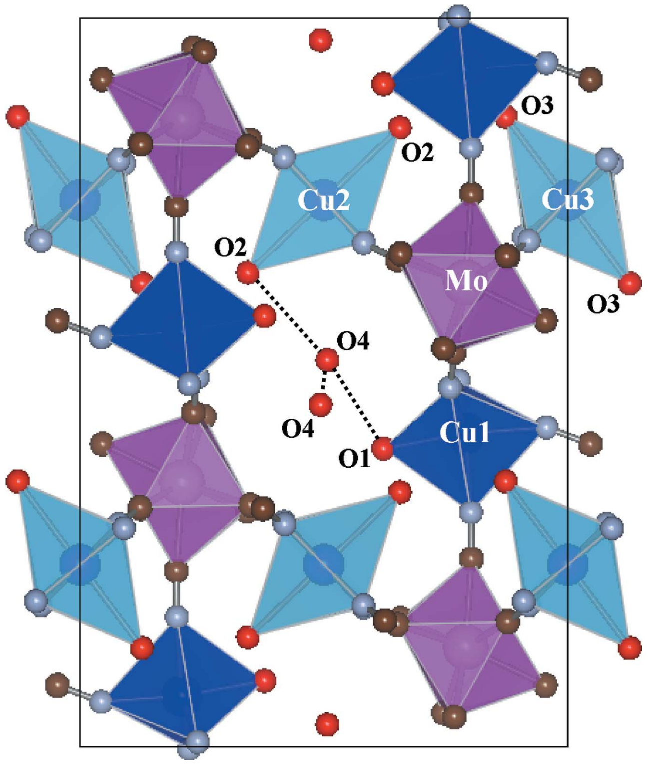

Figure 3
The unit-cell packing of (I) viewed down the *b* axis. Bronze, grey and red spheres represent C, N and O atoms, respectively. The dotted lines show the proposed hydrogen bonds around atom O4 of a water molecule.

2005) have been reported. Bimetallic Cu^{II}–Mo^{IV} assemblies are known to be photo-sensitive materials, such as microcrystalline $Cu^{II}_2[Mo^{IV}(CN)_8]\cdot 8H_2O$ (Ohkoshi *et al.*, 2006) and $[Mo^{IV}(CN)_2(CN-Cu^{II}L)_6](ClO_4)_8$ [L = tris(2-aminoethyl)amine; Herrera *et al.*, 2004]. In the present work, we describe the title novel bimetallic complex, $Cu^{II}_2[Mo^{IV}(CN)_8]\cdot 4H_2O$, (I).

Fig. 1 shows the coordination environments around the Cu^{II} and Mo^{IV} ions of (I). The MoC_8 geometry is a distorted square antiprism and the Mo—C bond distances range from 2.139 (3) to 2.165 (3) Å (Fig. 2*a*). Eight CN ligands link Mo to four Cu1, two Cu2 and two Cu3 ions. Cu1 is coordinated by four cyano N atoms and one O atom (Fig. 2*b*) in a trigonal–bipyramidal environment. On the other hand, Cu2 and Cu3 are coordinated by four cyano N atoms and two O atoms (Fig. 2*c* and *d*) with Jahn–Teller-distorted octahedral geometries. There is also an O atom of a water molecule (O4) in the unit cell which is presumably hydrogen bonded to atoms O1, O2 and O4($-x, -y, -z+1$) with O$\cdots$O distances of 2.755 (4), 2.875 (4) and 2.839 (4) Å, respectively (Fig. 3). Mo links to Cu through cyanide bridges to form a three-dimensional structure containing zeolitic water molecules. The Cu coordination is different from that in $Cu_2[Mo(CN)_8]\cdot 8H_2O$, which has been shown by EXAFS to correspond to a regular octahedral geometry (Ohkoshi *et al.*, 2006).

Measurement of the magnetic susceptibility *versus* temperature suggests that the magnetic interaction between the Cu^{II} ions through the diamagnetic $-NC-Mo^{IV}-CN-$ bridges is a weak antiferromagnetic coupling in (I).

Experimental

Single crystals of (I) were prepared in the dark by the slow diffusion of aqueous solutions of $Cu^{II}Cl_2\cdot 2H_2O$ (15.0 mg, 0.088 mmol) and $K_4[Mo^{IV}(CN)_8]\cdot 2H_2O$ (21.8 mg, 0.044 mmol). The resulting solution was kept for 4 to 5 months at 313 K and purple cubic crystals were obtained. Elemental analyses showed that the formula is $Cu^{II}_2[Mo^{IV}(CN)_8]\cdot 4H_2O$. Calculated: C 19.1, H 1.6, N 22.3, Cu 25.3, Mo 19.1%; found: C 18.8, H 1.6, N 22.6, Cu 25.3, Mo 19.1%. The CN stretching frequency was observed at 2162 cm^{-1} in the IR spectrum. In the UV–VIS diffuse reflectance spectrum, a broad absorption band was observed with a maximum at 550 nm; this was assigned to the intervalence transfer (IT) band between $Mo^{IV}-CN-Cu^{II}$ and $Mo^{V}-CN-Cu^{I}$.

Crystal data

$Cu_2[Mo(CN)_8]\cdot 4H_2O$
$M_r = 503.23$
Orthorhombic, *Pbcn*
$a = 11.868$ (3) Å
$b = 14.931$ (3) Å
$c = 17.741$ (4) Å
$V = 3143.7$ (13) Å^3
$Z = 8$
$D_x = 2.126$ Mg m^{-3}
$D_m = 2.14(9)$ Mg m^{-3}
D_m measured by flotation in toluene and tetrabromoethane
Mo $K\alpha$ radiation
$\mu = 3.50$ mm^{-1}
$T = 90$ (1) K
Cube, purple
$0.10 \times 0.10 \times 0.10$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.559$, $T_{max} = 0.705$
28148 measured reflections
3605 independent reflections
2906 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.5°$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.099$
$S = 1.01$
3605 reflections
209 parameters
H-atom parameters not refined
$w = 1/[0.0008F_o^2 + \sigma(F_o^2)]/(4F_o^2)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 3.41$ e Å^{-3}
$\Delta\rho_{min} = -0.73$ e Å^{-3}

The H atoms of the water molecules cound not be located. The highest residual electron-density peak is located at a distance of 0.98 Å from the Mo^{IV} ion.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *VICS* (Izumi & Dilanian, 2005); software used to prepare material for publication: *CrystalStructure*.

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