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The 3,4-connected layered hybrid oxide poly[tetrakis(μ-2,4′-bipyridine-κ^2N:N')-(μ_4-β-octamolybdato-κ^4O:O':O'':O''')-tetracopper(**I**)]

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Key indicators

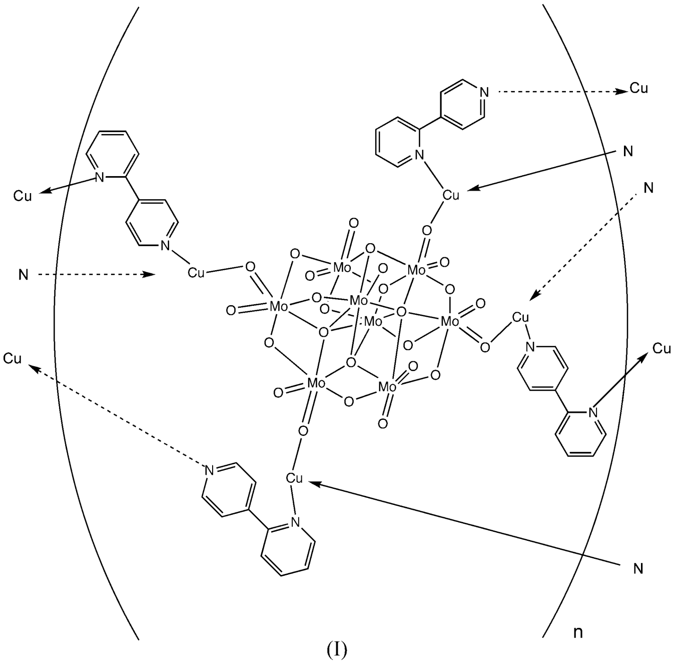
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
R factor = 0.023
wR factor = 0.059
Data-to-parameter ratio = 15.3

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

The title compound, $[Cu_4(\beta\text{-}Mo_8O_{26})(C_{10}H_8N_2)_4]_n$, is a two-dimensional 3,4-connected network coordination polymer containing two crystallographically distinct T-coordinated Cu^I atoms, each of which is bound to two N atoms from two bridging 2,4′-bipyridine ligands and a terminal O atom belonging to a centrosymmetric β-octamolybdate anion. Rippled cationic $[Cu(2,4'\text{-bpy})]_n^{n+}$ chain motifs are linked into ‘brick-wall’ two-dimensional layers by *exo*-tetradentate β-octamolybdate anions. The layers stack *via* C—H···O interactions to form a three-dimensional structure.

Comment

Mixed-metal inorganic–organic hybrid oxides have attracted significant attention, due to their extremely diverse structural chemistry and intriguing porous (Khan *et al.*, 2004) and magnetic properties (Rarig *et al.*, 2002). The most common organodiimine ligands employed in the construction of these materials are the rigid rod tether 4,4′-bipyridine (Jin *et al.*, 2006) and its chelating analogue 2,2′-bipyridine (Finn *et al.*, 2002). By comparison, other isomers of bipyridine have been under-utilized (Liu *et al.*, 2006). Here, we report the synthesis and crystal structure of the title copper(I) molybdate, (I), incorporating 2,4′-bipyridine (2,4′-bpy).



(I)

Compound (I) possesses an asymmetric unit consisting of two independent Cu^I atoms, two 2,4′-bpy ligands and one-half

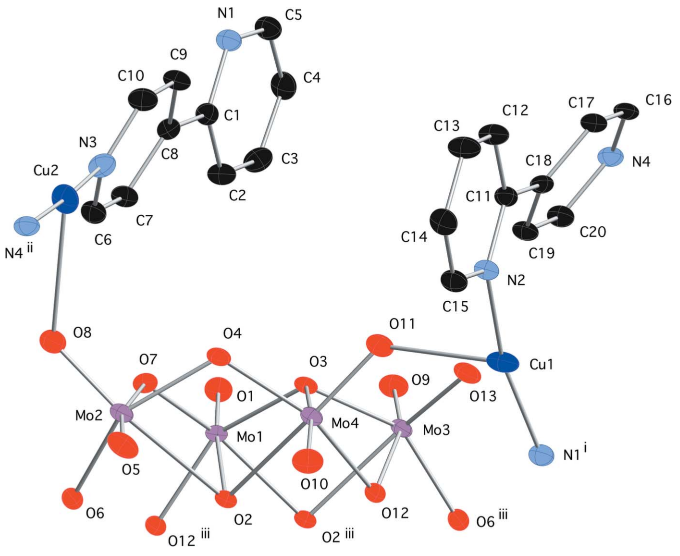


Figure 1
The asymmetric unit of (I), with symmetry-equivalent N and O atoms to complete the coordination environments about Cu and Mo, showing 50% probability ellipsoids and the atom-numbering scheme. The symmetry codes are as in Table 1. H atoms have been omitted.

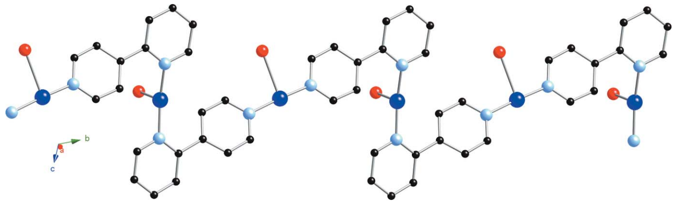


Figure 2
A single $[Cu(2,4'\text{-bpy})]_n$ chain motif in (I). Only O atoms bound to Cu are shown. Cu atoms are dark blue, N atoms light blue, O atoms red and C atoms black.

of a β-octamolybdate anion. A complete $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion, where all Mo atoms exhibit distorted octahedral coordination with corner- and edge-sharing of O atoms, is generated by operation of the inversion centre within the centrosymmetric triclinic unit cell (Fig. 1). Thus (I) is best formulated as $\{[Cu(2,4'\text{-bpy})]_4(\beta\text{-}Mo_8O_{26})\}_n$.

Each Cu^I atom manifests a three-coordinate T-shaped geometry, with two N donors from two distinct 2,4′-bpy ligands oriented in a *trans* disposition, and with a terminal O atom from a β-octamolybdate anion completing the coordination. Cu1 is observed to bind to the 2-position N atoms of the 2,4′-bpy ligands, while Cu2 is ligated by the 4′-position N-atom termini. Selected bond lengths and angles for (I) are given in Table 1.

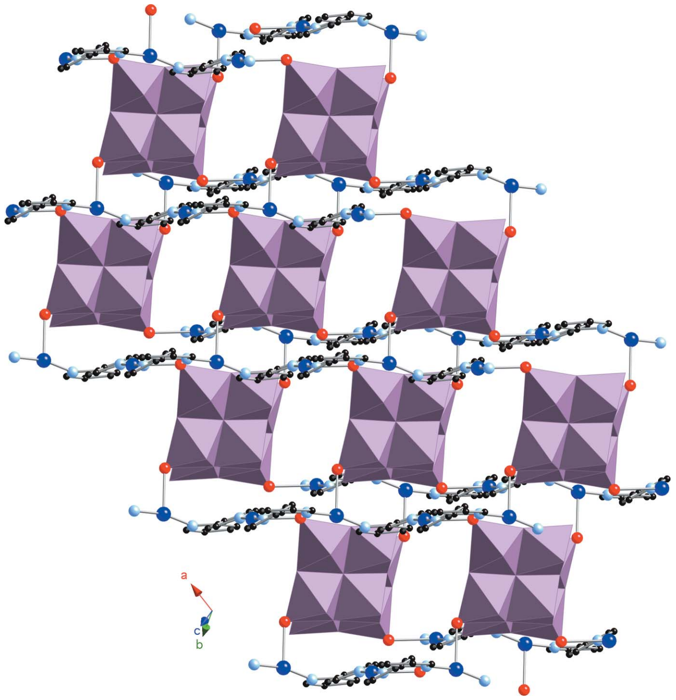


Figure 3
A single 3,4-connected layer of (I), which runs parallel to the *ab* crystal plane. The β-octamolybdate anions are shown in polyhedral representations for clarity.

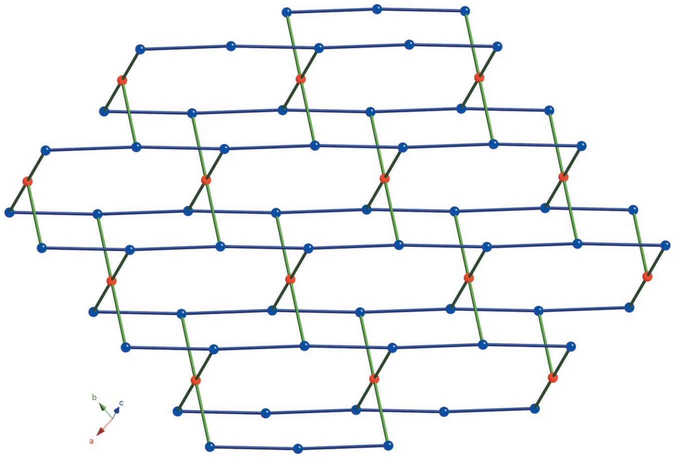


Figure 4
A framework perspective of the two-dimensional $(6^28)(6^28^4)$ topology structure of (I). Cu atoms are shown as dark blue and the β-octamolybdate centroids, located on crystallographic inversion centres, are depicted in red.

Adjacent Cu atoms are linked through bridging 2,4′-bpy ligands into rippled one-dimensional $[Cu(2,4'\text{-bpy})]_n^{n+}$ chain motifs (Fig. 2), where juxtaposed T-shaped Cu coordination planes are tilted by ~81° and ~83°, as defined by the O—Cu$\cdots$Cu—O dihedral angles. The intrachain Cu$\cdots$Cu contact distances are alternately 6.803 (1) and 6.952 (1) Å. The chains are subsequently covalently linked through *exo*-tetradentate $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions to form two-dimensional layered motifs parallel to the *ab* crystal plane (Fig. 3). The through-anion Cu$\cdots$Cu contact distances between neighbouring $[Cu(2,4'\text{-bpy})]_n^{n+}$ chains are 8.085 (1), 10.159 (1), 11.968 (2) and 13.926 (2) Å.

With each Cu atom considered as a 3-connected T-shaped node and each polymolybdate anion treated as a 4-connected square-planar node, compound (I) displays a 3,4-connected 'brick wall' layered structure with $(6^28)(6^28^4)$ topology (Fig. 4). The $\{[Cu(2,4'\text{-bpy})]_4(\beta\text{-}Mo_8O_{26})\}_n$ layers then pack together along the crystallographic *c* direction (Fig. 5) *via* C—H$\cdots$O supramolecular interactions (Table 2), to generate the three-dimensional structure of (I).

Experimental

All chemicals were obtained commercially. A mixture of copper(II) sulfate pentahydrate (69 mg, 0.28 mmol), molybdenum(VI) oxide (40 mg, 0.28 mmol), 2,4′-bipyridine (87 mg, 0.56 mmol) and water (10.0 g, 555 mmol) was placed in a 23 ml Teflon-lined Parr acid digestion bomb, which was then heated under autogenous pressure at 453 K for 48 h. Orange blocks of the title compound were obtained after manual separation from a fine brown precipitate *via* repeated washing with water and decantation. The crystals were then washed with acetone and air-dried.

Crystal data

$[Cu_4Mo_8O_{26}(C_{10}H_8N_2)_4]$
$M_r = 2062.46$
Triclinic, $P\overline{1}$
$a = 10.631$ (2) Å
$b = 10.948$ (2) Å
$c = 12.701$ (3) Å
$\alpha = 99.427$ (3)°
$\beta = 114.082$ (3)°
$\gamma = 100.871$ (3)°
$V = 1276.7$ (5) Å^3
$Z = 1$
$D_x = 2.682$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 3.62$ mm^{-1}
$T = 173$ (2) K
Block, orange
0.40 × 0.20 × 0.16 mm

Data collection

Bruker SMART 1K diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.412$, $T_{max} = 0.560$
15119 measured reflections
5945 independent reflections
5371 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.059$
$S = 1.09$
5945 reflections
389 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 2.0526P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.61$ e Å^{-3}
$\Delta\rho_{min} = -0.86$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.00123 (13)

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.913 (2)	Mo2—O4	1.939 (2)
Cu1—N1^{i}	1.916 (2)	Mo2—O7	2.256 (2)
Cu1—O11	2.408 (2)	Mo2—O2	2.504 (2)
Cu2—N3	1.895 (3)	Mo3—O13	1.697 (2)
Cu2—N4^{ii}	1.897 (3)	Mo3—O9	1.700 (2)
Cu2—O8	2.564 (2)	Mo3—O6^{iii}	1.898 (2)
Mo1—O1	1.697 (2)	Mo3—O3	1.986 (2)
Mo1—O7	1.747 (2)	Mo3—O2^{iii}	2.310 (2)
Mo1—O12^{iii}	1.930 (2)	Mo3—O12	2.450 (2)
Mo1—O3	1.940 (2)	Mo4—O10	1.697 (2)
Mo1—O2^{iii}	2.149 (2)	Mo4—O11	1.715 (2)
Mo1—O2	2.416 (2)	Mo4—O4	1.901 (2)
Mo2—O5	1.703 (2)	Mo4—O12	1.981 (2)
Mo2—O8	1.710 (2)	Mo4—O2	2.288 (2)
Mo2—O6	1.903 (2)	Mo4—O3	2.365 (2)
N2—Cu1—N1^{i}	166.67 (11)	N3—Cu2—N4^{ii}	176.59 (11)
N2—Cu1—O11	91.17 (9)	N3—Cu2—O8	94.60 (9)
N1^{i}—Cu1—O11	102.16 (9)	N4^{ii}—Cu2—O8	88.62 (9)

Symmetry codes: (i) $x+1, y, z$; (ii) $x, y+1, z$; (iii) $-x+2, -y+1, -z+2$.

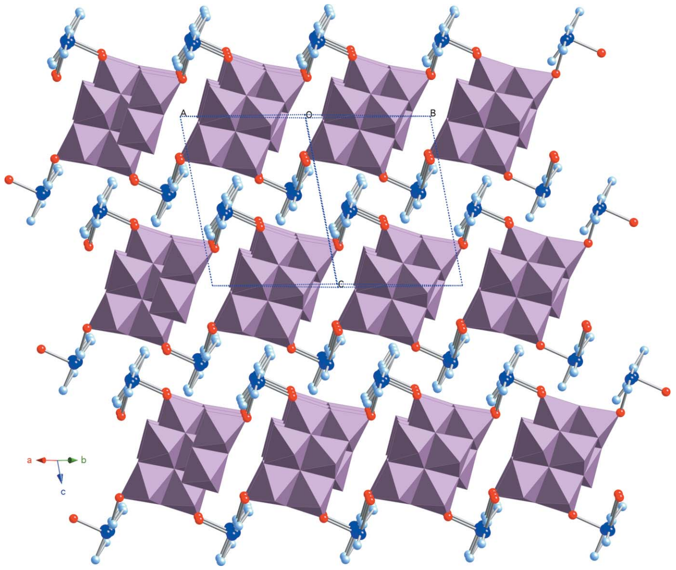


Figure 5
A partial packing diagram for (I), depicting the stacking of neighbouring layers along the crystallographic *c* direction. C atoms have been omitted for clarity.

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O5^{iv}	0.93	2.46	3.07	124
C7—H7···O1^{v}	0.93	2.47	3.03	119
C10—H10···O4^{vi}	0.93	2.42	3.25	148
C12—H12···O9^{vii}	0.93	2.55	3.46	168
C14—H14···O10^{viii}	0.93	2.47	3.12	127
C16—H16···O3^{vii}	0.93	2.45	3.02	120

Symmetry codes: (iv) $x-1, y-1, z$; (v) $-x+1, -y+1, -z+2$; (vi) $-x+1, -y+1, -z+1$; (vii) $-x+1, -y, -z+1$; (viii) $-x+2, -y+1, -z+1$.

All H atoms were placed in calculated positions, with C—H = 0.93 Å, and refined in riding mode, with $U_{iso} = 1.2U_{eq}$(C). The largest Fourier map difference peak was located 0.83 Å from atom H14.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalMaker* (Palmer, 2005); software used to prepare material for publication: *SHELXL97*.

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