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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
H-atom completeness 76%
Disorder in solvent or counterion
R factor = 0.032
wR factor = 0.085
Data-to-parameter ratio = 12.3

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

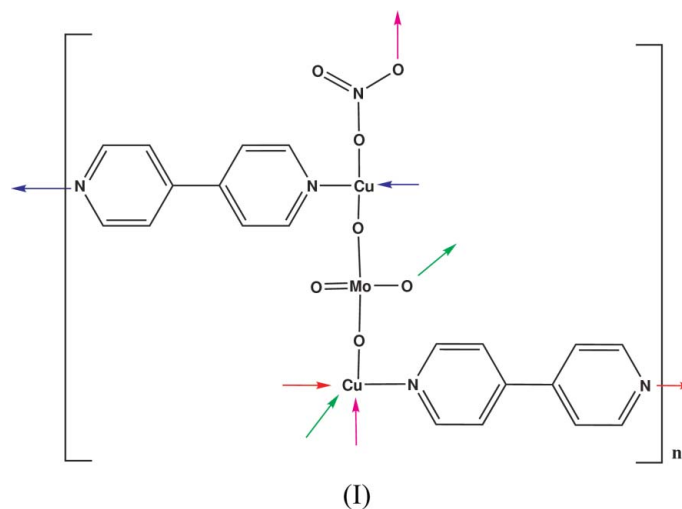
Poly[[tris(μ_2 -4,4'-bipyridyl- $\kappa^2\text{N}:\text{N}'$)bis(μ_2 -nitrate- $\kappa^2\text{O},\text{O}'$)hexa- μ_2 -oxo-dioxodimolybdenumtricopper(II)] tetrahydrate]: a polymeric hybrid framework containing Cu^{2+} , 4,4'-bipyridine, $[\text{MoO}_4]^{2-}$ and NO_3^- building units

The hydrothermally prepared title compound, $\{[\text{Cu}_3\text{Mo}_2(\text{NO}_3)_2\text{O}_8(\text{C}_{10}\text{H}_8\text{N}_2)_3]\cdot 4\text{H}_2\text{O}\}_n$, is a hybrid organic/inorganic polymer containing a 16-atom ring built up from molybdate anions, nitrate ions and copper cations. This inorganic network is crosslinked by infinite linear 4,4'-bpy-bridged copper chains (4,4'-bpy is 4,4'-bipyridine) to form channels along the *c* axis containing the disordered non-coordinated water molecules.

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Comment

A number of molybdenum oxide-containing hybrid organic/inorganic polymers have been shown to adopt specific architectures and show novel properties (Hagrman & Zubieta, 2000; Rarig & Zubieta, 2001; Duan *et al.*, 2003; Kirsch *et al.*, 2005). 4,4'-Bipyridine (4,4'-bpy) has been used extensively as the organic ligand in the preparations of hybrid polymers to achieve various open framework structures due to its strong coordination ability and its own size and shape (Lu, Wu, Zhuang & Huang, 2002; Lu, Wu, Lu *et al.*, 2002; Hagrman *et al.*, 1998; Finn *et al.*, 2002; Rarig *et al.*, 2002). We report here the synthesis, by a hydrothermal reaction, and structure of a new Mo/O/Cu/4,4'-bpy organic/inorganic hybrid polymer, (I).



The crystal structure reveals that the polymeric network of (I) is built up from Cu^{II} , NO_3^- , $[\text{MoO}_4]^{2-}$ and 4,4'-bipyridine units (Table 1). There are two kinds of copper cations in (I). Atom Cu2 (site symmetry $\bar{1}$) is coordinated by two O atoms from two NO_3^- anions and two O atoms from two $[\text{MoO}_4]^{2-}$ anions. The distorted octahedral coordination is completed by two N atoms from two 4,4'-bpy molecules, such that an infinite Cu/bpy chain exists along *c*. In this chain, the two pyridine rings of 4,4'-bpy are coplanar and parallel to (010). The other

kind of copper ion, Cu1, is five-coordinated by two O atoms from two $[\text{MoO}_4]^{2-}$ anions, one O atom from an NO_3^- anion and two N atoms from two 4,4'-bpy molecules, thereby forming a second infinite chain parallel to the first. In this chain, the two pyridine rings of 4,4'-bpy twist by about 30° .

As shown in Fig. 1, the most interesting feature of (I) is the 16-membered inorganic ring formed by four Cu^{II} ions, two NO_3^- anions and two $[\text{MoO}_4]^{2-}$ anions. The two kinds of infinite chains link the 16-membered rings to form channels along the crystallographic c axis, containing the highly disordered/mobile water molecules.

Experimental

The tetra-*n*-butylammonium salt of $[\text{P}_2\text{Mo}_{18}\text{O}_{61}]_4^-$ was prepared following the procedure of Himeno *et al.* (1990). A mixture of $[\text{N}(\text{C}_4\text{H}_9)_4]_4\text{P}_2\text{Mo}_{18}\text{O}_{61}$ (0.10 g, 0.027 mmol), 4,4'-bpy (0.156 g, 1 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.242 g, 1 mmol) was dissolved in water (15 ml) with stirring at room temperature. The pH was adjusted to 3 by addition of 1 M HNO_3 . The solution was heated to 433 K for 50 h and then cooled to 373 K at a rate of 3 K h^{-1} . The solution was kept at 373 K for 32 h and then cooled to room temperature at the same rate. Blue block-shaped crystals of (I) were collected by filtration and air-dried (yield 30%).

Crystal data

$[\text{Cu}_3\text{Mo}_2(\text{NO}_3)_2\text{O}_8(\text{C}_{10}\text{H}_8\text{N}_2)_3] \cdot 4\text{H}_2\text{O}$	$Z = 1$
$M_r = 1175.14$	$D_x = 2.064 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.6189 (18) \text{ \AA}$	Cell parameters from 5192 reflections
$b = 10.639 (2) \text{ \AA}$	$\theta = 2.4\text{--}28.3^\circ$
$c = 10.986 (2) \text{ \AA}$	$\mu = 2.36 \text{ mm}^{-1}$
$\alpha = 79.523 (3)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 64.995 (3)^\circ$	Block, blue
$\gamma = 70.574 (3)^\circ$	$0.16 \times 0.14 \times 0.12 \text{ mm}$
$V = 959.8 (3) \text{ \AA}^3$	

Data collection

Bruker SMART APEX CCD diffractometer	3703 independent reflections
φ and ω scans	3482 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$R_{\text{int}} = 0.017$
$T_{\text{min}} = 0.704$, $T_{\text{max}} = 0.765$	$\theta_{\text{max}} = 26.0^\circ$
7441 measured reflections	$h = -11 \rightarrow 11$
	$k = -13 \rightarrow 13$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 2.0607P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	$(\Delta/\sigma)_{\text{max}} = 0.004$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
3703 reflections	$\Delta\rho_{\text{min}} = -0.80 \text{ e \AA}^{-3}$
301 parameters	
H-atom parameters constrained	

Table 1

Selected bond distances (\AA).

Mo1—O5	1.720 (3)	Cu1—O6 ⁱ	2.267 (3)
Mo1—O6	1.722 (3)	Cu2—O2 ⁱⁱ	2.529 (3)
Mo1—O7	1.748 (2)	Cu2—O7	1.925 (2)
Mo1—O4	1.764 (2)	Cu2—N4	1.984 (3)
Cu1—O4	1.917 (2)	C3—C4	1.475 (5)
Cu1—O3	1.918 (2)	C13—C13 ⁱⁱⁱ	1.477 (6)
Cu1—N3	2.050 (3)		

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

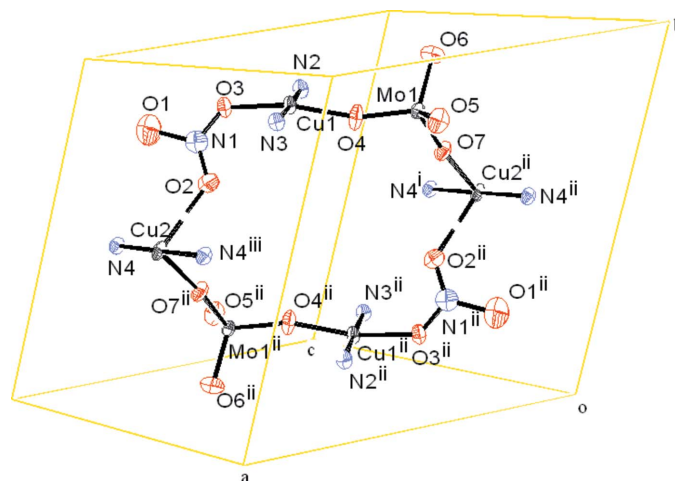


Figure 1

A view of the 16-membered ring of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms and water molecules have been omitted for clarity. [Symmetry codes: (i) $1 - x, y, z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $x, y, 1 - z$.]

All aromatic H atoms were constrained to an ideal geometry with C—H distances of 0.93 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Various short O(water)···O(framework) contacts in the range $2.7\text{--}2.8 \text{ \AA}$ suggest that O—H···O hydrogen bonds may be present, but water molecule H atoms were not located in the present study.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

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