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A novel three-dimensional inorganic framework: hydrothermal synthesis and crystal structure of $CuMo_3O_{10} \cdot H_2O$

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Abstract

A novel three-dimensional inorganic bimetallic compound $Cu[Mo_3O_{10}] \cdot H_2O$ **1** has been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Compound **1** crystallizes in the orthorhombic system, space group *Pnma*, $a = 8.6085(17)$ Å, $b = 7.5822(15)$ Å, $c = 13.690(3)$ Å, $V = 893.6(3)$ Å^3, $Z = 4$, $\lambda(\text{Mo}K\alpha) = 0.71073$ Å ($R(F) = 0.0357$ for 1101 reflections). The structure of compound **1** is based on $[\{Mo_3O_{10}\}^{2-}]_\infty$ isopolyoxomolybdate chains bonded together with CuO_4 tetrahedra into a three-dimensional inorganic open framework. Three types of Mo–Cu layers and one-dimensional tunnels are observed in the title compound.

Keywords: Crystal structure; Bimetallic open framework; Isopolyoxomolybdate chains; Hydrothermal synthesis

1. Introduction

The significant contemporary interest in polyoxometalates (POMS) [1] reflects their fascinating properties and great potential application in catalysis, material science, medicine, analytical chemistry, nanotechnology, chemical sensing, magnetochemistry, photochemistry and electrochromism [2]. The rational design and synthesis of one-, two- and three-dimensional (1-D, 2-D and 3-D) polyoxometalate materials, which are constructed from novel building blocks with desired features, is still one of the major challenges.

Several successful strategies have been developed to design the materials built on POMS. One of the effective strategies is to introduce organic-amine ligand as structure-directing agent to form organic–inorganic hybrid material. These hybrid materials can be divided into four subclasses: (I) V–O–*L* system [3]; (II) V–O–*M*–*L* system [4]; (III) Mo–O–*L* system [5]; and (IV) Mo–O–*M*–*L* system [6] (*L*: ligand; *M*: the first row transition metals). The other strategy is to connect POMS ions with metal cations (without the incorporation of additional conventional ligands) via covalent bonds [7]. For example, the 1-D chainlike trimetal heteropolyanion based on pseudo-Keggin fragments has been synthesized and reported by our group [8]; mixed-metal frameworks based on polyoxovanadate clusters and Fe, Co, Zn ions are also successful examples [9]. Furthermore, a new higher dimensional polyoxoanions-based architecture, $[Gd(H_2O)_3]_3[GdMo_{12}O_{40}] \cdot 3H_2O$ [10], which consists of Silverton-type anions linked by gadolinium(III) cations into a 3-D framework, has been recently reported.

However, the compound which is built on 1-D isopolyoxomolybdate chains linked by secondary metals (without the incorporation of additional conventional ligands) into 3-D open frameworks has not been described to date. To our knowledge, only five examples of compounds, 1-D $Rb_2Mo_3O_{10}$, $RbNaMo_3O_{10}$, [13c] $Na(NH_4)Mo_3O_{10}$ [13a], $(NH_4)_2[Mo_3O_{10}]$ [13b], and three-dimensional $[Cu_2(pyrd)Mo_3O_{10}]$ [6d], constructed from 1-D isopolyoxomolybdate chains (see Fig. 2b) have been synthesized and structurally characterized by single-crystal X-ray diffraction. In this paper, we report the hydrothermal synthesis, crystal structure of a novel 3-D neutral framework, $CuMo_3O_{10} \cdot H_2O$. The most remarkable structure feature of **1** is that the isopolymolybdate chains $[\{Mo_3O_{10}\}^{2-}]_\infty$ are linked by CuO_4 tetrahedra to form 3-D architecture.

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2. Experimental

2.1. General procedures

All chemicals were commercially purchased and used without further purification. Mo and Cu were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centauri FT/IR spectrophotometer using KBr pellets. XPS analysis was performed on a VG ESCALAB MK II with an Mg$K\alpha$ (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during analysis. TG analysis was performed on Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10°C min^{-1}.

2.2. Hydrothermal synthesis

A solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (1.0 g, 0.81 mmol), $CuSO_4 \cdot 5H_2O$ (0.448 g, 1.79 mmol) and H_2O (10 g, 555.6 mmol) was adjusted to pH = 4 with 2 M HCl under continuous stirring and sealed in a 18 mL Teflon-lined autoclave, then heated to 170°C for 56 h. After cooling to room temperature at 10°C h^{-1}, the black block crystals were collected in 38% yield (based on Mo) by filtration and air-dried. Elemental analyses found: Cu, 11.92%; Mo, 54.23%; Calc for $CuMo_3O_{10} \cdot H_2O$ **1**: Cu, 12%; Mo, 54.37%.

2.3. X-ray crystallography

The structure of compound **1** was determined by the single-crystal X-ray diffraction. A black single crystal with dimensions of $0.772 \times 0.186 \times 0.129$ mm^3 was glued on a glass fiber. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with the oscillation scans mode in the range of $1.71 < \theta < 27.48°$. The structure was solved by direct methods using the program SHELXS-97 [11] and refined by full-matrix least-squares methods on F^2 using the SHELXL-97 [12] program package. All of the non-hydrogen atoms were refined anisotropically. Positions of the hydrogen atoms attached to oxygen were not located accurately. Crystal data are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Atomic coordinates, bond lengths and angles, and anisotropic displacement parameters are deposited in supplementary information. Further details of the crystal details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; mailto:crysdata@fiz.karlsruhe.de) on quoting the depository number CSD 391230.

Table 1
Crystal data and Structure refinement parameters for $CuMo_3O_{10} \cdot H_2O$

Empirical formula	$CuMo_3O_{10} \cdot H_2O$
Formula weight	529.37
Crystal system	Orthorhombic
Space group	*Pnma*
a (Å)	8.6085(17)
b (Å)	7.5822(15)
c (Å)	13.690(3)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	893.6(3)
Z	4
Calculated density (mg/m^3)	3.920
F(000)	972.0
μ (mm^{-1})	6.507
Reflections collected/unique	1932/1101 [$R_{\text{int}} = 0.0158$]
Goodness-of-fit on F^2	0.865
Final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0357$, $wR_2{}^b = 0.0985$
R indices (all data)	$R_1{}^a = 0.0375$, $wR_2{}^b = 0.1013$

[a] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o{}^2)^2]\}^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (deg) for $CuMo_3O_{10} \cdot H_2O$

Cu(1)–O(4)#4	1.907(4)	O(4)#4–Cu(1)–O(3)#5	96.40(12)
Cu(1)–O(3)#6	2.190(4)	O(4)#4–Cu(1)–O(3)#6	96.40(12)
Cu(1)–O(3)#5	2.190(4)	O(2)–Cu(1)–O(3)#6	97.02(11)
Cu–O(2)	1.879(4)	O(2)–Cu(1)–O(3)#5	97.02(11)
Mo(1)–O(2)	1.729(4)	O(3)#5–Cu(1)–O(3)#6	98.2(2)
Mo(1)–O(5)	1.924(2)	O(2)–Cu(1)–O(4)#4	159.43(19)
Mo(1)–O(6)	2.211(4)	O(5)–Mo(1)–O(6)	74.81(9)
Mo(1)–O(7)#2	2.210(5)	O(2)–Mo(1)–O(5)	101.36(10)
Mo(1)–O(5)#3	1.924(2)	O(2)–Mo(1)–O(5)#3	101.36(10)
Mo(1)–O(4)	1.747(4)	O(5)#3–Mo(1)–O(6)	74.81(9)
Mo(2)–O(1)	1.703(3)	O(4)–Mo(1)–O(5)	102.44(10)
Mo(2)–O(6)	1.9539(11)	O(4)–Mo(1)–O(5)#3	102.44(10)
Mo(2)–O(5)	2.281(3)	O(2)–Mo(1)–O(4)	104.6(2)
Mo(2)–O(5)#2	2.196(3)	O(4)–Mo(1)–O(6)	90.63(18)
Mo(2)–O(3)	1.725(4)	O(2)–Mo(1)–O(7)#2	87.01(16)
Mo(2)–O(7)	1.9610(11)	O(5)–Mo(1)–O(7)#2	74.74(9)
O(6)–Mo(1)–O(7)#2	77.77(14)	O(5)#3–Mo(1)–O(7)#2	74.74(9)
O(1)–Mo(2)–O(3)	105.06(14)	O(1)–Mo(2)–O(6)	96.44(15)
O(1)–Mo(2)–O(7)	101.19(15)	O(1)–Mo(2)–O(5)#2	94.55(14)
O(3)–Mo(2)–O(6)	98.28(17)	O(3)–Mo(2)–O(5)	89.15(12)
O(3)–Mo(2)–O(7)	93.4(2)	O(5)#2–Mo(2)–O(5)	72.95(12)
O(7)–Mo(2)–O(5)#2	74.35(14)	O(6)–Mo(2)–O(5)#2	87.50(13)
O(6)–Mo(2)–O(5)	72.62(12)	O(7)–Mo(2)–O(5)	86.19(12)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y-3/2, z$; #2, $-x-2, -y-2, -z-2$; #3, $x, -y-5/2, z$; #4, $x+1/2, y, -z-3/2$; #5, $-x-5/2, y-1/2, z+1/2$; #6, $-x-5/2, -y-2, z+1/2$.

3. Result and discussion

The single-crystal X-ray diffraction reveals that the compound **1** is constructed from 1-D $[\{Mo_3O_{10}\}^{2-}]_\infty$ chains and CuO_4 tetrahedra, which are linked into a 3-D bimetallic oxide framework. There are one crystallographically unique Cu center and two Mo centers in

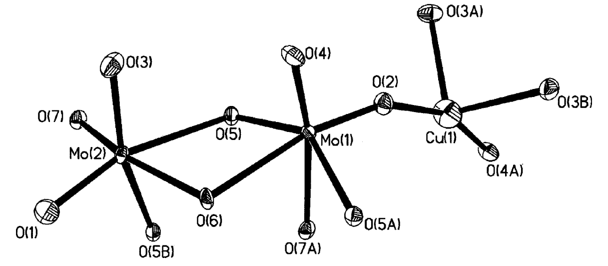

Fig. 1. ORTEP drawing of **1**, showing the local coordination environment of Mo and Cu with thermal ellipsoids at 50% probability.

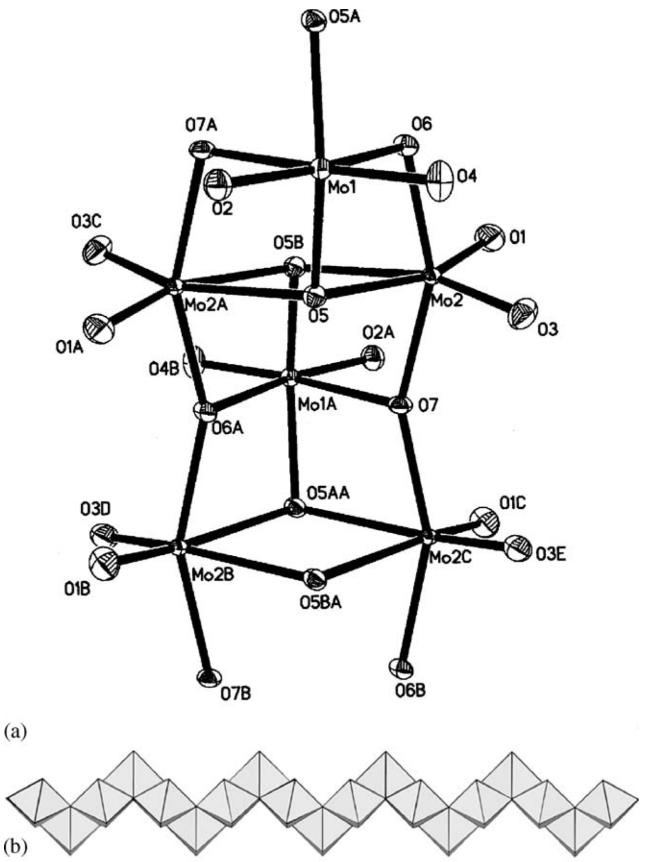

Fig. 2. (a) Ball and stick representation of the Mo_6 structural moiety of $\{[Mo_3O_{10}]^{2-}\}_\infty$ chain. (b) A simplified polyhedral view of the infinite 1-D chain of **1**.

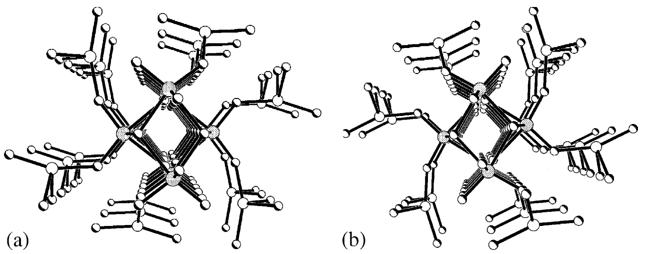

Fig. 3. A view of the structure of two types of Mo–Cu chains, along the *b*-axis.

the asymmetrical unit, as shown in Fig. 1. The Cu site exhibits a distorted tetrahedral coordination geometry with four O donors (O(4A), O(3A), O(3B), O(2)). The Mo(1) and Mo(2) site both adopt a strongly distorted octahedral environment coordinated by six O donors [the Mo(1) is coordinated by O(7A), O(6), O(5), O(5A), O(4), O(2) and Mo(2) is coordinated by O(7), O(6), O(5), O(5B), O(3), O(1)].

The two Mo(2) octahedra and one Mo(1) octahedron share two edges to form $[Mo_3O_{10}]^{2-}$ moiety. Each $[Mo_3O_{10}]^{2-}$ moiety is then joined up with another $[Mo_3O_{10}]^{2-}$ moiety by sharing two edges of an Mo(1) octahedron to constitute a Mo_6 unit as shown in Fig. 2a (four Mo(2) and two Mo(1)). Translational repetition of the Mo_6 units though sharing edges results in an infinite 1-D Mo–O chain (see Fig. 2b), structurally analogous to that observed in the one-dimensional $Na(NH_4)Mo_3O_{10}$, $(NH_4)_2$ $[Mo_3O_{10}]$ and three-dimensional $[Cu_2(pyrd)Mo_3O_{10}]$.

The 1-D $[\{Mo_3O_{10}\}^{2-}]_\infty$ chains are connected by CuO_4 tetrahedra into a 3-D bimetallic oxide framework. Each Cu site is coordinated with two oxo groups of two adjacent Mo(2) sites of one chain and links two adjacent chains together by bonding to two oxo groups from two Mo(1) sites, while each Mo(1) site bridges two Cu sites and each Mo(2) bridges one Cu site to form Mo–Cu chains. Viewed along the *b*-axis, the arrangement of Mo–Cu chains exhibit two opposite directions, which are represented by A and B, respectively (see Fig. 3). It is noteworthy that the 1-D $[\{Mo_3O_{10}\}^{2-}]_\infty$ chains are linked by CuO_4 tetrahedra to form three types of Mo–Cu layers: L(1) (A···A···A, along *a*-axis), L(2)(B···B···B, along *a*-axis) and L(3) (A···B···A···B, along the diagonal line of *ac* plane), as shown in Fig. 4. All of them are constructed from $[\{Mo_3O_{10}\}^{2-}]_\infty$ chains bridged by double CuO_4 tetrahedra which differ from the Mo–Cu layer structure in $[Cu_2(pyrd)Mo_3O_{10}]$ where $[\{Mo_3O_{10}\}^{2-}]_\infty$ chains are linked by single CuO_3N tetrahedron to form Mo–Cu layer structure. In the L(1), Mo–Cu layer is composed of $[\{Mo_3O_{10}\}^{2-}]_\infty$ chains linked by double bridges of Mo(1)–Cu–Mo(2) similar to that in the L(2). Different from L(1) and L(2), $[\{Mo_3O_{10}\}^{2-}]_\infty$ chains in the L(3) are linked by double bridges of Mo(1)–Cu–Mo(2) and Mo(1)–Cu–Mo(1) to form Cu–Mo layer structure. Finally, L(1) and L(2) are linked through oxo bridges along *c*-axis with L(1)···L(2)···L(1)···L(2) sequence to form 3-D bimetallic structure. The 3-D structure may also be described as L(3) are linked by oxo bridges along diagonal line of ac plane with L(3)···L(3)···L(3) sequence (see Fig. 5).

Viewed along the *a*-axis, the infinite plane layer of L1 and L2 are stacked into a 3-D crystal structure, resulting in the formation of 1-D tunnels along *a*-axis. The tunnels is surrounded by two CuO_4 tetrahedra and two Mo_7 subunits and occupied by water molecules. Therefore, the porous of compound **1** may have potential application in the catalysis and adsorption.

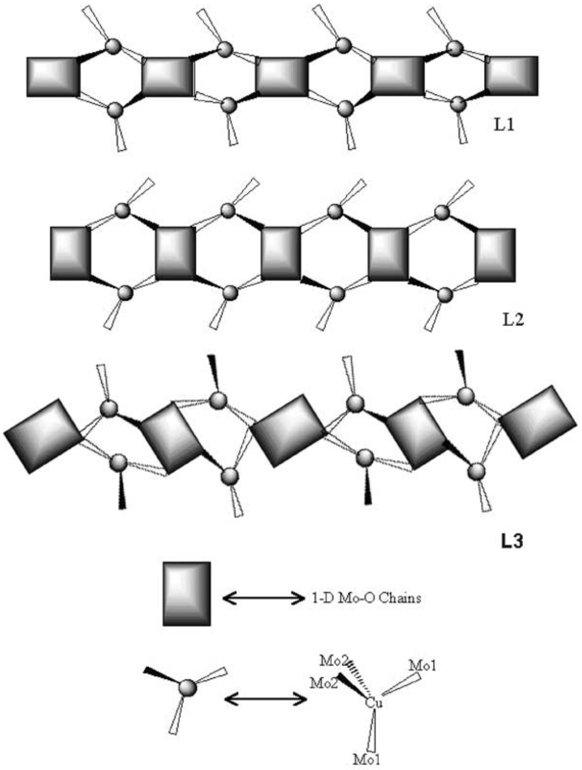

Fig. 4. Schematic illustration of the structure of three types of Cu–Mo layers, viewed along the *b*-axis.

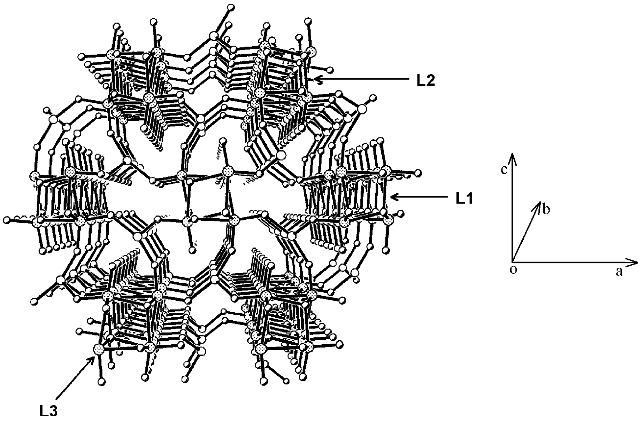

Fig. 5. The packing arrangement of compound **1** along *b*-axis, all crystalline water molecules are omitted for clarity.

Thermogravimetric analysis proves that **1** possesses high thermal stability. In the TG curve of **1**, there exists only one weight loss stage. From 20°C to 327°C, compound **1** is stable. In the temperature 327–465°C, the weight loss is 3.26%, corresponding to the release of lattice water molecules. The whole weight loss (3.26%) is in good agreement with the calculated value (3.40%).

In the IR spectra of **1**, vibration model for $v(\mathrm{Mo=O})$, $v(\mathrm{Mo{-}O{-}Mo})$, $v(\mathrm{Mo{-}O{-}Cu})$ and $v(\mathrm{Cu{-}O})$ are observed at 931, 852, 671 and 563 $\mathrm{cm^{-1}}$, respectively. The band at 3457 and 1419 $\mathrm{cm^{-1}}$ is ascribed to water molecules, stretching vibration and bending vibration of O–H, respectively. The XPS measurement of the compound **1** in the energy region of $\mathrm{Mo}3d_{3/2}$ and $\mathrm{Mo}3d_{5/2}$ gives two peaks (the higher is at 232.1 eV), attributed to Mo^{6+} [14], in the energy region of $\mathrm{Cu}2p_{1/2}$ and $\mathrm{Cu}2p_{3/2}$ also gives two peaks (the higher is at 932.8 eV), attributed to Cu^{2+}, in accordance with the valence sum calculations [15] for Mo^{6+} and Cu^{2+}. All these results further confirm the structure analysis.

In conclusion, a new inorganic 3-D bimetallic compound $\mathrm{Cu[Mo_3O_{10}]\cdot H_2O}$ **1** has been obtained by hydrothermal technique in the present work. X-ray crystallography shows that **1** is constructed from 1-D $[\{\mathrm{Mo_3O_{10}}\}^{2-}]_\infty$ chains linked by $\mathrm{CuO_4}$ tetrahedra via covalent bonds into 3-D skeleton. Viewed along the *b*-axis, three types of Mo–Cu layers are formed in the compound **1**. It was speculated that the tetrahedral coordination mode adopted by transition metal is important condition for linking isopolyoxomolybdate chains to a high-dimensional structure. Since copper atoms in **1** can be replaced by other transition metal, a series of similar 3-D bimetallic compound may be synthesized.

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