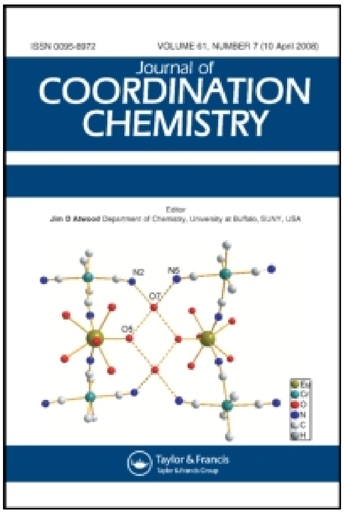

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Hydrothermal synthesis and crystal structure of a 1-D compound constructed from molybdovanadate clusters $[V_2Mo_6O_{26}]^{6-}$ and copper complexes

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A 1-D organic–inorganic hybrid compound, $\{Cu(en)_2\}[V_2Mo_6O_{26}\{Cu(en)_2\}_2] \cdot 4H_2O$ [en = ethylenediamine] (**1**), was hydrothermally synthesized and characterized by IR, UV spectroscopy, TG/DTA analyses, and single crystal X-ray diffraction. The X-ray crystallography analysis reveals an infinitely extended 1-D chain constructed from a molybdovanadate cluster $[V_2Mo_6O_{26}]^{6-}$ as a building unit, two copper(II) complex fragments, $\{Cu(en)_2\}^{2+}$, as attached groups and a copper(II) fragment, $\{Cu(en)_2\}^{2+}$, as a bridging group. Each chain links to adjacent chains through weaker secondary Cu–O interactions forming an interesting 3-D supramolecular architecture.

Keywords: Molybdovanadate cluster; Hydrothermal synthesis; Crystal structure

1. Introduction

Heteropolymolybdates have fascinating structures and redox-active molybdenum, with potential applications in catalysis, ion exchange, and molecular sieves [1–4]. An interesting area of heteropolymolybdate chemistry is the small but growing family of mixed molybdenum-vanadate with a variety of structural features and unusual physicochemical properties [5–8]. Mixed molybdenum-vanadates covalently linked by transition metal complexes have rapidly advanced organic–inorganic hybrid materials, with many examples of mixed molybdenum-vanadates supported transition metal complexes, including 0-D $[Cu(en)_2(H_2O)]_4[Cu(en)_2]_{3.5}[PMo_8^{VI}V_6^{VI}O_{42}Cu(en)\,(1,10'\text{-phen})]_3 \cdot 14H_2O$ [9], 1-D chain $[Cu_5^{I}(2,4'\text{-bipy})_6(OH)][PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2] \cdot 1.5H_2O$ [10], 2-D layer structure $[en]_{0.5}[Cu(en)_2]_2[Cu(en)_2Mo_6^{VI}Mo_2^{V}V_8^{IV}O_{40}(Mo^{IV}O_4)] \cdot 0.5H_2O$ [11], and 3-D framework $H_3\{V^{V}Mo_8^{VI}V_6^{VI}O_{42}[Cu(en)_2]_4\}$ $[MoO_4]_2 \cdot 14H_2O$ [12]. However, in contrast to the rich information on Keggin type and capped Keggin type mixed molybdenum-vanadates, the molybdovanadate cluster $[V_2Mo_6O_{26}]^{6-}$ remains

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undeveloped; reports on $[V_2Mo_6O_{26}]^{6-}$ have been concentrated on several discrete structures [13–15], and no organic–inorganic hybrid constructed from $[V_2Mo_6O_{26}]^{6-}$ with transition metal complexes has been reported. Herein, we report the hydrothermal synthesis and structural characterization of a new molybdovanadate-based organic–inorganic compound $\{Cu(en)_2\}[V_2Mo_6O_{26}\{Cu(en)_2\}_2] \cdot 4H_2O$ (**1**), in which $[V_2Mo_6O_{26}]^{6-}$ clusters are supported by $\{Cu(en)_2\}^{2+}$ groups and adjacent molybdovanadate clusters are interconnected through $\{Cu(en)_2\}^{2+}$ bridging groups into an infinitely extended chain.

2. Experimental

2.1. *Materials and physical measurements*

All reagents were obtained from commercial sources and used without purification. C, H, and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. An IR spectrum was recorded on a Nicolet 170 FT-IR spectrometer using KBr pellets from 4000 to 400 cm^{-1}. UV spectra were obtained on a U-4100 spectrometer (distilled water as solvent) in the range of 400–190 nm. The TG/DTA analysis were performed on a Perkin-Elmer 7 thermal analysis instrument in flowing N_2 with a heating rate of 10°C min^{-1} from 25 to 750°C.

2.2. *Preparation of compound 1*

A mixture of $Na_2MoO_4 \cdot 2H_2O$ (1.48 g, 6.12 mmol), $Cu(OAc)_2 \cdot 2H_2O$ (0.80 g, 3.68 mmol), V_2O_5 (0.60 g, 3.30 mmol), en (0.3 mL, 4.48 mmol), KOH (0.20 g, 3.56 mmol), and water (20 mL) was stirred for 30 min in air (the initial pH was adjusted to 7.20 by 2 M KOH) and then sealed in a Teflon-lined stainless steel autoclave and heated at 180°C for 7 days. After cooling the autoclave to room temperature over 48 h, the mixture gives a large amount of purple block-shaped crystals. The crystals were filtered, washed with water, and dried at ambient temperature to give **1** in 62% yield based on molybdenum. Elemental analysis Calcd (%) for $C_{12}H_{56}N_{12}Cu_3Mo_6O_{30}V_2$ (1716.80): C, 8.40; H, 3.29; N, 9.79. Found (%): C, 8.45; H, 3.38; N, 9.72.

2.3. *X-ray crystallography of compound 1*

A crystal of **1** (dimensions $0.20 \times 0.15 \times 0.12\ mm^3$) was carefully selected under an optical microscope and glued at the tip of a thin glass fiber with cyanoacrylate adhesive. Intensity data were collected on a Bruker APEX-II CCD detector with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL-97 software [16, 17]. The organic hydrogens were generated geometrically. A summary of crystal data and structure refinement for **1** is provided in table 1. Selected bond lengths and angles of **1** are listed in table 2.

Table 1. Crystallographic data and structure refinement for **1**.

Empirical formula	$C_{12}H_{56}N_{12}Cu_3Mo_6O_{30}V_2$
Molecular weight	1716.80
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell deminseions (Å, °)	
a	13.3421(8)
b	19.6752(12)
c	9.8734(6)
β	95.838(1)
V (Å^3)	2578.4(3)
Z	2
d_{Calcd} (g cm^{-1})	2.201
Absorption coefficient (mm^{-1})	3.050
T (K)	296(2)
Wavelength (Å)	0.71073
$R[I > 2\sigma(I)]^{a}$	0.0305
Rw (all data)^{b}	0.0814

$^{a}R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^{b}Rw = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Mo(1)–O(2)	1.707(2)	Mo(1)–O(1)	1.720(2)
Mo(1)–O(9)	1.917(2)	Mo(1)–O(8)	1.932(2)
Mo(1)–O(11)	2.261(2)	Mo(1)–O(12)^{a}	2.333(2)
Mo(2)–O(4)	1.713(3)	Mo(2)–O(3)	1.716(3)
Mo(2)–O(8)	1.911(2)	Mo(2)–O(7)^{a}	1.915(2)
Mo(2)–O(10)^{a}	2.318(2)	Mo(2)–O(11)	2.342(2)
Mo(3)–O(5)	1.714(3)	Mo(3)–O(6)	1.717(3)
Mo(3)–O(7)	1.910(2)	Mo(3)–O(9)	1.931(2)
Mo(3)–O(12)^{a}	2.270(2)	Mo(3)–O(10)	2.310(2)
Cu(2)–N(3)	2.007(3)	Cu(2)–N(6)	2.007(3)
Cu(2)–N(4)	2.009(3)	Cu(2)–N(5)	2.010(3)
Cu(2)–O(13)	2.4448(2)	Cu(1)–N(2)	2.006(4)
Cu(1)–O(6)	2.417(3)	Cu(1)–N(1)	2.020(4)
V(1)–O(10)	1.743(2)	V(1)–O(13)	1.652(2)
V(1)–O(11)	1.762(2)	V(1)–O(12)	1.746(2)
O(11)–Mo(1)–O(12)^{a}	75.60(8)	O(2)–Mo(1)–O(1)	104.20(12)
O(9)–Mo(1)–O(8)	151.15(10)	O(10)^{a}–Mo(2)–O(11)	75.27(8)
O(4)–Mo(2)–O(3)	104.38(14)	O(8)–Mo(2)–O(7)^{a}	150.00(10)
O(12)^{a}–Mo(3)–O(10)	75.49(8)	O(5)–Mo(3)–O(6)	103.80(13)
O(7)–Mo(3)–O(9)	151.69(10)	N(4)–Cu(2)–N(5)	97.20(14)
N(3)–Cu(2)–N(6)	93.63(14)	N(2)–Cu(1)–O(6)	85.15(13)
N(2)–Cu(1)–N(1)^{b}	96.17(19)	O(12)–V(1)–O(11)	111.58(11)
O(13)–V(1)–O(10)	108.84(12)	V(1)–O(10)–Mo(3)	128.32(12)
Mo(3)–O(6)–Cu(1)	129.16(15)		

$^{a}-x+1, -y, -z+1$; $^{b}x, y, z+1$.

3. Results and discussion

3.1. *Crystal structures of compound 1*

Single crystal X-ray diffraction analysis reveals that **1** consists of a hexamolybdodivanadate cluster $[V_2Mo_6O_{26}]^{6-}$, two attached $\{Cu(en)_2\}^{2+}$, a bridging $\{Cu(en)_2\}^{2+}$, and four crystallization water molecules (figure 1). The structure of the molybdovanadate

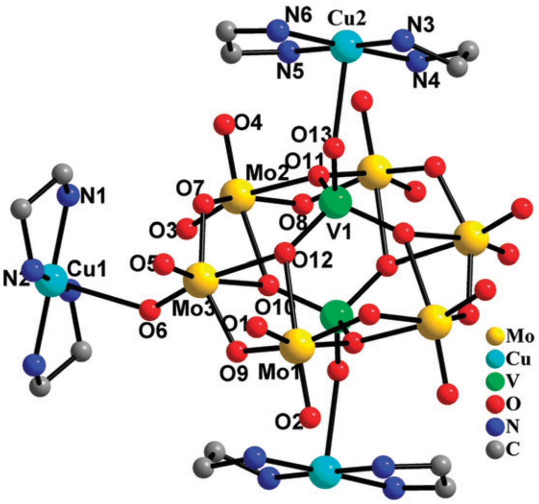

Figure 1. View of the molecule structure of **1** (H atoms and water molecules omitted for clarity).

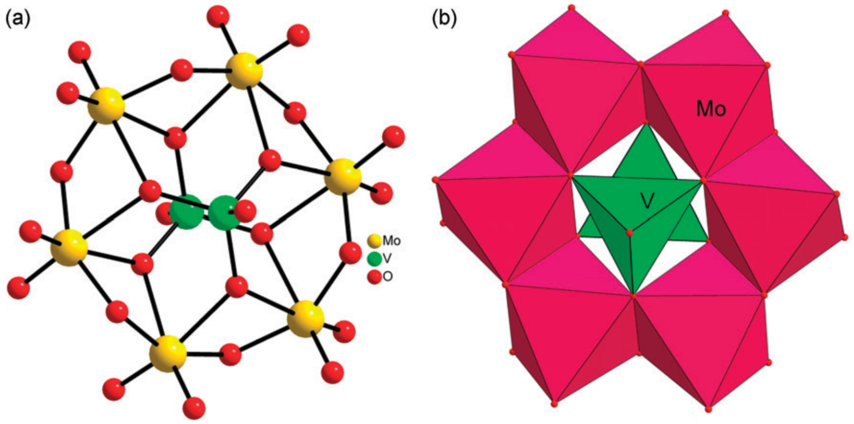

Figure 2. Ball-and-stick (a) and polyhedral (b) representation of $[V_2Mo_6O_{26}]^{6-}$.

cluster $[V_2Mo_6O_{26}]^{6-}$ is similar to $[\alpha\text{-}Mo_8O_{26}]^{4-}$, which is closed to a D_{3d} point symmetry [18, 19], that is, two $\{VO_4\}$ units cap opposite faces of a $\{Mo_6O_6\}$ ring constructed from six $\{MoO_6\}$ octahedra linked in edge-sharing mode. Each capped $\{VO_4\}$ tetrahedron links to three terminal oxo-groups within the $\{Mo_6O_6\}$ ring. In turn, each of these oxo-groups adopts the μ_3 bridging mode, linking two molybdenums and the vanadium (figure 2). Three kinds of oxygens exist in $[V_2Mo_6O_{26}]^{6-}$, terminal oxygen O_t, doubly bridging oxygen $O(\mu_2)$, and triply bridging oxygen $O(\mu_3)$. Thus, the Mo–O bond lengths can be grouped into three sets: $Mo\text{–}O_t = 1.707(2)\text{–}1.720(2)$ Å, $Mo\text{–}O(\mu_2) = 1.910(2)\text{–}1.932(2)$ Å, and $Mo\text{–}O(\mu_3) = 2.261(2)\text{–}2.342(2)$ Å. The V–O bond lengths fall into two classes: $V\text{–}O_t = 1.652(2)$ Å and $V\text{–}O(\mu_3) = 1.743(2)\text{–}1.762(2)$ Å. Each $[V_2Mo_6O_{26}]^{6-}$ is covalently bonded to two $\{Cu(en)_2\}^{2+}$ groups through the terminal oxygens of two opposite capping $\{VO_4\}$ tetrahedra, and adjacent

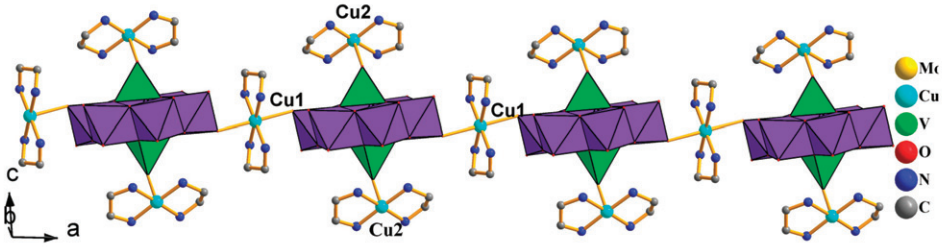

Figure 3. View of the 1-D chain of **1** (H atoms and water molecules omitted for clarity).

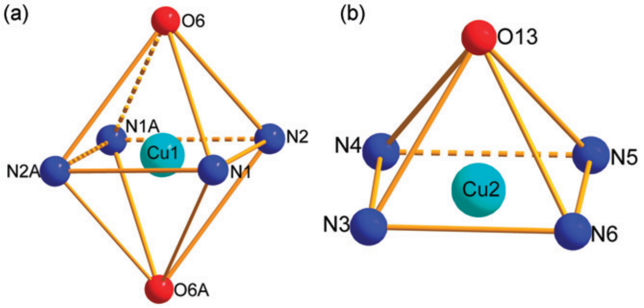

Figure 4. The coordination geometric frameworks of Cu1 and Cu2.

molybdovanadate clusters are then linked through a $\{Cu(en)_2\}^{2+}$ via corner-sharing interactions of the two terminal oxygens of two non-adjacent $\{MoO_6\}$ octahedra, forming a 1-D coordination chain parallel to the *a*-axis (figure 3). The space between the chains is filled with water molecules.

The coppers in **1** display two different coordination environments (shown in figure 4). Cu1 in the bridging group $\{Cu(en)_2\}^{2+}$ covalently bonds to two terminal oxygens from two $\{MoO_6\}$ octahedra, in "4 + 2" $\{CuN_4O_2\}$ distorted octahedral geometry, defined by two oxygens bridging two $\{MoO_6\}$ octahedra from two different cluster anions, and four nitrogens of two en ligands with bond lengths Cu1–O $(MoO_6) = 2.417(3)$ Å and Cu1–N = 2.006(4)–2.020(4) Å. Cu2 in the attached group adopts "4 + 1" $\{CuN_4O\}$ distorted square pyramidal geometry with the basal plane defined by four nitrogen donors from two en molecules and one terminal oxygen donor from $\{VO_4\}$ belonging to $[V_2Mo_6O_{26}]^{6-}$; the Cu2–N distances are in the range of 2.007(3)–2.010(3) Å and the Cu(2)–O (VO_4) distance is 2.445 Å. Thus, both the octahedral and square pyramidal coordination spheres of Cu^{2+} centers are Jahn–Teller distorted.

Adjacent chains link in an interesting 3-D supramolecular architecture through weaker secondary Cu–O interactions (figure 5), the Cu2–O2 distance between the attached group and the terminal oxygen atom of $\{VO_4\}$ from the adjacent chains is 2.790 Å. The structure of **1** exhibits extensive hydrogen-bonding interactions among water molecules, en groups, and polyoxoanions with $N–H \cdots O$ distances of 2.924 to 3.362 Å. The extensive hydrogen-bonding interactions play an important role in stabilization of the 3-D supramolecular architecture. Compound **1** is the first example of $[V_2Mo_6O_{26}]^{6-}$ supported and bridged by copper coordination cations.

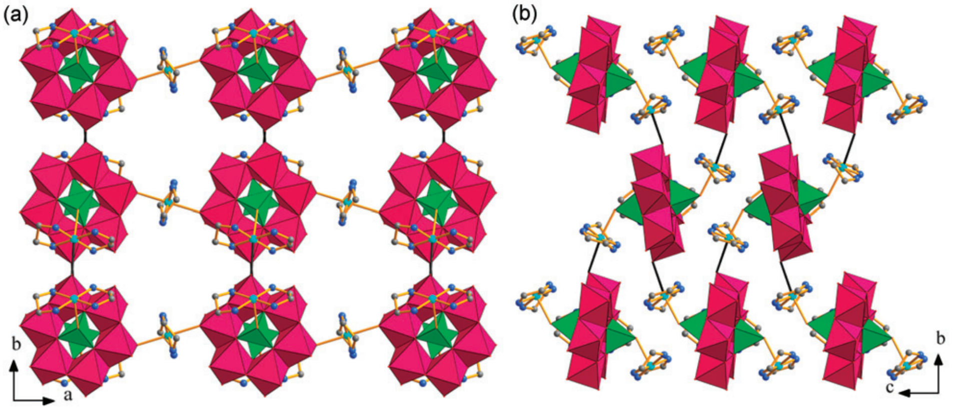

Figure 5. Polyhedral representation of the 3-D supramolecular architecture of **1** (the weaker secondary Cu–O interaction is represented by the dark dotted lines) along the *c*-axis (a) and along the *a*-axis (b) (H atoms and water molecules omitted for clarity). Color code: MoO_6, red; VO_4, green.

3.2. *IR and UV spectra*

The IR spectrum of **1** exhibits strong absorptions at 1045, 931, 876, 757, 702, and 630 cm^{-1}, attributed to ν(M=O) or ν(M–O–M) (M = Mo or V) [12, 20]. A series of bands at 1104, 1171, 1277, 1319, 1455, 1588, 2886, 2940, 3128, and 3243 cm^{-1} are attributed to the en groups [12]. The peak at 3437 cm^{-1} is assigned to water.

The UV absorption spectrum of **1** (Supplementary material) between 190 and 400 nm exhibits one band at 205 nm, characteristic of polyoxomolybdate charge-transition absorption of $O_t \rightarrow Mo$ [21, 22].

3.3. *Thermal properties*

The thermal behavior of **1**, investigated under N_2 flow from 25 to 750°C, exhibits three steps of weight loss (Supplementary material). The first weight loss is 3.75% in the range of 25–212°C, corresponding to release of water molecules of crystallization (Calcd 3.94%). The second weight loss is 21.22% from 212 to 514°C, assigned to the loss of en. The last weight loss is 15.53% in the range of 514–698°C; we are not sure about the reason for the weight loss, but probably due to the sublimation of some MoO_3 molecules. Two endothermal peaks are observed at 74°C and 235°C in the DTA curve, which are related to the heat-absorbing loss of crystal water and en molecules, and two endothermal peaks are observed at 593°C and 672°C in the same DTA curve, from sublimation of MoO_3 and decomposition of the skeleton structure of molybdovanadate anion.

Supplementary material

Crystallographic data for the structural analysis reported in this article have been deposited with the Cambridge Crystallographic Data Centre with the deposited CCDC No. 694603. Copies of this information may be obtained free of charge from

The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

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