

Non-hydrothermal Synthesis of a Complex $\{[\text{Zn}(\text{phen})_2]_2(\gamma\text{-Mo}_8\text{O}_{26})\}$ Constructed from $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$ Anions

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An octamolybdate-supported complex, $\{[\text{Zn}(\text{phen})_2]_2(\gamma\text{-Mo}_8\text{O}_{26})\}$ (phen = 1,10-phenanthroline) (**1**), has been obtained and characterized by IR spectroscopy, TGA analysis and single crystal X-ray diffraction. Crystal data: $\text{C}_{48}\text{H}_{40}\text{O}_{26}\text{N}_8\text{Mo}_8\text{Zn}_2$, monoclinic, $P2_1/n$, $a = 12.986(5)$, $b = 16.704(5)$, $c = 13.996(5)$ Å, $\beta = 106.551(5)^\circ$, $V = 2910.2(18)$ Å³, $Z = 2$. The structure of compound **1** consists of a γ -octamolybdate cluster covalently attached to two $[\text{Zn}(\text{phen})_2]^{2+}$ complexes. The complexes are tightly packed via C–H \cdots O contacts between phen and $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$ anions.

Key words: Non-hydrothermal Synthesis, Inorganic–Organic Hybrid, Octamolybdate

Introduction

Recently, inorganic-organic hybrid materials have attracted extensive interest owing to their enormous variety of intriguing structural topologies and their fascinating properties as well as great potential for applications in many fields, such as catalysis, medicine, sorption, electron conductivity, magnetism, and photochemistry [1–4]. Of the various polyoxometalate structures, the most interesting one is the octamolybdate family with a variety of structural isomers including α -, β -, and γ -octamolybdates *etc.* [5]. Up to now, α - and β -octamolybdates have been extensively studied; however, compounds containing γ -octamolybdate are still rather rare. Known examples for such complexes with $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$ anion structures include $[\text{Cu}(\text{im})_2]_4[\gamma\text{-Mo}_8\text{O}_{26}]$ [6], $(\text{Himi})_4[(\text{nic-O})_2(\text{Mo}_8\text{O}_{26})]$ [7], $[\text{H-amp}]_4[\text{Mo}_8\text{O}_{26}(\text{DMF})] \cdot 2\text{H}_2\text{O}$ [8], $[\{\text{Cu}(\text{pyrd})\}_4(\gamma\text{-H}_4\text{Mo}_8\text{O}_{26})]$ [9], $[\text{Me}_3\text{N}(\text{CH}_2)_6\text{NMe}_3]_2[\text{Mo}_8\text{O}_{26}] \cdot 2\text{H}_2\text{O}$ [10], and $[\text{Cu}(\text{en})_2]_2[\text{Mo}_8\text{O}_{26}]$ [11]. To the best of our knowledge, all of the reported γ -octamolybdate supported transition metal complexes, with a nitrogen-containing organic ligand, were synthesized hydrothermally. In this context, we obtained a new supramolecular framework using an aqueous synthetic method, and report here its structure. In the title compound **1**,

the $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$ anion links two $[\text{Zn}(\text{phen})_2]^{2+}$ complexes to form a neutral unit. The complexes are tightly packed by C–H \cdots O contacts between phen molecules and $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$ anions.

Results and Discussion

Synthesis

$(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}]$ [12] is one of the basic heteropolyacids which can be easily broken down [13]. During decomposition, a self-assembly process can happen. In the view of this idea, we used this compound as raw material. Consequently, compound **1** was synthesized from $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}]$ in water with the pH value adjusted to about 4.5 with CH_3COOH . Dropwise addition of ZnCl_2 and phen $\cdot\text{H}_2\text{O}$ in DMF to the $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}]$ solution resulted in an insoluble solid which could be dissolved in acetonitrile.

Structure description

Single crystals suitable for X-ray diffraction were grown from acetonitrile. The structure determination has shown that the fundamental building unit of compound **1** includes a $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$ anion and two $[\text{Zn}(\text{phen})_2]^{2+}$ complex cations (Fig. 1). The $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$ unit consists of six edge-sharing MoO_6 octahedra and two five-coordinate MoO_5 trigonal bipyra-

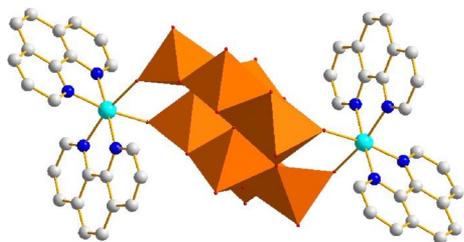


Fig. 1. Representation of the molecular structure unit of $\{[\text{Zn}(\text{phen})_2]_2(\gamma\text{-Mo}_8\text{O}_{26})\}$ (all H atoms are omitted for clarity).

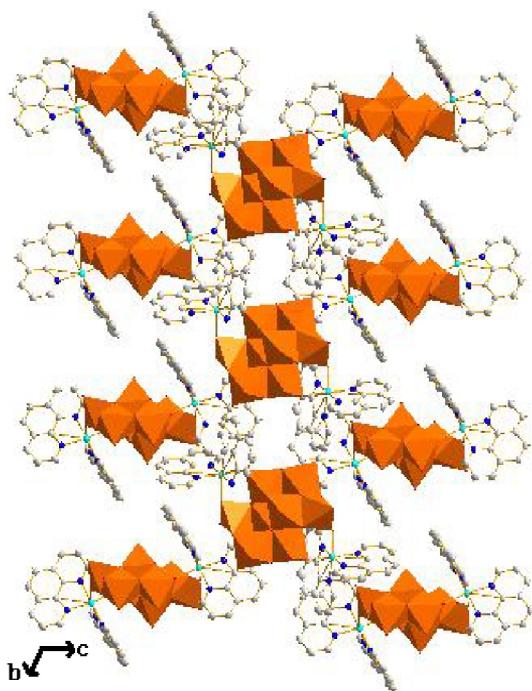


Fig. 2. The extended structure viewed along the crystallographic *a* axis (without H atoms).

mids. The oxygen atoms within the $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$ cluster can be divided into four sets according to their bonding features, namely, terminal oxygen atoms with Mo–O distances of 1.690(7)–1.737(7) Å, doubly bridging oxygen atoms with Mo–O distances of 1.741(6)–2.341(9) Å, triply bridging oxygen atoms with Mo–O distances of 1.909(2)–2.247(4) Å, and quadruply bridging oxygen atoms with Mo–O distances of 1.921(4)–2.548(4) Å. All Mo–O bond lengths are within the expected ranges. Bond sum calculations show that the oxidation state of all the Mo atoms is in the range of 5.96–6.03, which agrees with the expected value of 6 for Mo atoms in the $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$ anions [14].

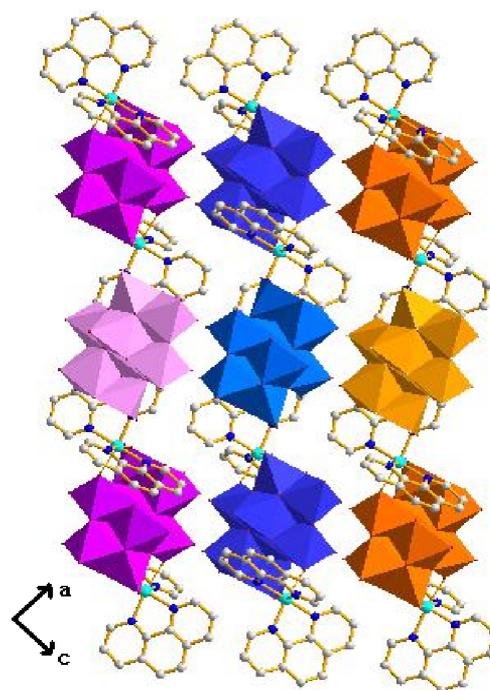


Fig. 3. The extended structure viewed along the *b* axis. Light and dark complexes are in different layers, and phen molecules in the light complexes are omitted for clarity.

The Zn(II) center exhibits a distorted octahedral coordination geometry defined by four N atoms from two phen ligands and two bridging O atoms from one $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$ anion. The apical positions of each octahedron are occupied by a nitrogen atom from a phen molecule and a bridging O atom from the $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$ anion; the equatorial plane of each octahedron is defined by three N atoms from two phen molecules and an O atom from the $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$ anion. The Zn center is approximately located on this equatorial plane. The Zn–O bond lengths are in the range 2.089(3)–2.090(3) Å.

Along the crystallographic *a* axis, each $\{[\text{Zn}(\text{phen})_2]_2(\gamma\text{-Mo}_8\text{O}_{26})\}$ cluster is connected with four adjacent clusters by C–H \cdots O hydrogen bonds, like C(10)–H(10) \cdots O(8) (2.669 Å), C(24)–H(24) \cdots O(5) (2.766 Å), C(25)–H(25) \cdots O(5) (2.892 Å), resulting in a 2D sheet structure (Fig. 2). Along the *b* axis, hydrogen bonds are also found between the 2D sheet structures, such as C(8)–H(8) \cdots O(9) (2.615 Å), and C(3)–H(3) \cdots O(3) (2.483 Å). The hydrogen bonds link the $\{[\text{Zn}(\text{phen})_2]_2(\gamma\text{-Mo}_8\text{O}_{26})\}$ units into a tightly packed structure (Fig. 3). The detailed distances of the C–H \cdots O contacts are summarized in Table 3.

Table 1. Details of data collection and structure refinement for compound **1**.

Formula	$\text{C}_{48}\text{H}_{32}\text{Mo}_8\text{N}_8\text{O}_{26}\text{Zn}_2$
M_r	2035.12
Crystal size, mm ³	$0.28 \times 0.24 \times 0.22$
Crystal system	monoclinic
Space group	$P2_1/n$
a , Å	12.986
b , Å	16.704
c , Å	13.996
β , deg	106.55(5)
V , Å ³	2910.2
Z	2
D_{calcd} , g cm ⁻³	2.32
$\mu(\text{MoK}\alpha)$, mm ⁻¹	0.737
$F(000)$, e	1960
hkl range	$-16 \leq h \leq 16$; $-21 \leq k \leq 21$; $-18 \leq l \leq 18$
θ range, deg	3.04–27.44
Refl. collect./unique/ R_{int}	27341/6607/0.0748
Data/ref. parameters	6607/410
$R1/wR2$ [$I \geq 2\sigma(I)$]	0.0295/0.0658
$R1/wR2^a$ (all data)	0.0413/0.0679
GoF^b (F^2)	0.910
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	0.791/–1.318

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (0.0096P)^2]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$;
^b $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

IR spectrum of compound **1**

The IR spectrum was recorded in KBr in the 4500–450 cm⁻¹ region and exhibits complex patterns of bands at 955, 880 and 796 cm⁻¹ ascribed to $\nu(\text{Mo}-\text{O})$. A series of bands in the region 1380–1690 cm⁻¹ are characteristic of the phen ligands. These results are in accordance with structural findings.

Thermal analysis

The thermal behavior of compound **1** was studied from 25 to 600 °C. The TG curve exhibits one step of weight loss (36.11%) in the temperature range 320–520.5 °C, corresponding to the loss of the phen groups, in agreement with the calculated value (35.4%).

In summary, a new compound, $\{[\text{Zn}(\text{phen})_2]_2(\gamma\text{-Mo}_8\text{O}_{26})\}$ (**1**) has been synthesized under non-hydrothermal conditions. Endeavors are being devoted to the synthesis of other organic-inorganic hybrid solids containing different transition metal complexes.

Experimental Section

General methods and materials

$(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}]$ was synthesized according to refs. [12, 13]. Other reagents were purchased commercially

Table 2. Selected bond lengths (Å) and angles (deg) for $\{[\text{Zn}(\text{phen})_2]_2(\gamma\text{-Mo}_8\text{O}_{26})\}$.

Zn(1)–N(1)	2.066(4)	Mo(2)–O(12)	1.909(2)
Zn(1)–N(2)	2.073(3)	Mo(2)–O(4)	1.921(2)
Zn(1)–N(3)	2.064(3)	Mo(2)–O(13)	2.202(3)
Zn(1)–N(4)	2.060(4)	Mo(2)–O(4) ^{#1}	2.516(2)
Zn(1)–O(1)	2.089(3)	Mo(3)–O(9)	1.691(3)
Zn(1)–O(2)	2.090(3)	Mo(3)–O(8)	1.693(3)
Mo(1)–O(1)	1.746(3)	Mo(3)–O(7)	1.955(3)
Mo(1)–O(3)	1.694(3)	Mo(3)–O(10)	2.017(3)
Mo(1)–O(4)	2.163(3)	Mo(3)–O(12)	2.166(2)
Mo(1)–O(6) ^{#1}	2.342(3)	Mo(4)–O(11)	1.697(3)
Mo(1)–O(7) ^{#1}	1.871(3)	Mo(4)–O(2)	1.738(3)
Mo(1)–O(13)	2.028(2)	Mo(4)–O(10)	1.835(3)
Mo(2)–O(5)	1.693(2)	Mo(4)–O(13)	1.912(2)
Mo(2)–O(6)	1.742(3)	Mo(4)–O(12)	2.247(3)
N(1)–Zn(1)–N(2)	80.43(1)	O(2)–Zn(1)–O(1)	88.76(1)
N(4)–Zn(1)–N(3)	80.64(1)	Mo(1)–O(1)–Zn(1)	147.69(1)
N(4)–Zn(1)–N(1)	177.21(1)	Mo(4)–O(13)–Mo(1)	142.24(1)
N(3)–Zn(1)–N(1)	98.50(1)	Mo(4)–O(13)–Mo(2)	107.46(1)
N(4)–Zn(1)–N(2)	97.03(1)	Mo(1)–O(13)–Mo(2)	103.63(1)
N(3)–Zn(1)–N(2)	97.33(1)	Mo(2)–O(12)–Mo(3)	125.02(2)
N(4)–Zn(1)–O(2)	91.41(1)	Mo(2)–O(12)–Mo(4)	105.80(1)
N(3)–Zn(1)–O(2)	89.03(1)	Mo(3)–O(12)–Mo(4)	94.82(9)
N(1)–Zn(1)–O(2)	91.22(1)	Mo(4)–O(2)–Zn(1)	149.41(2)
N(2)–Zn(1)–O(2)	170.14(2)	Mo(2)–O(6)–Mo(1) ^{#1}	115.51(1)
N(4)–Zn(1)–O(1)	89.97(1)	Mo(1) ^{#1} –O(7)–Mo(3)	117.52(1)
N(3)–Zn(1)–O(1)	170.29(1)	N(2)–Zn(1)–O(1)	86.17(1)
N(1)–Zn(1)–O(1)	91.00(1)		

Table 3. Selected distances of C–H...O contacts (Å) for $\{[\text{Zn}(\text{phen})_2]_2(\gamma\text{-Mo}_8\text{O}_{26})\}$.

C(10)–H(10)...O(8)	2.669	C(24)–H(24)...O(5)	2.766
C(25)–H(25)...O(5)	2.892	C(8)–H(8)...O(9)	2.615
C(3)–H(3)...O(3)	2.483		

and used without further purification. Deionized water was used for the synthesis. The infrared spectrum was recorded on a Nicolet 170SX FT-IR spectrophotometer with a KBr pellet in the 4000–400 cm⁻¹ region. TG analysis was performed on a Netzsch STA 449C microanalyzer in an atmosphere of nitrogen with a heating rate of 10 °C min⁻¹ from 25 to 600 °C.

Synthesis

0.168 g (0.1 mmol) of $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}]$ was dissolved in deionized water (10 mL). The solution was heated to 80 °C with stirring, and simultaneously, the pH value of this solution was carefully adjusted to about 4.5 with a dilute CH_3COOH solution (1 M). After 15 min, ZnCl_2 (0.136 g, 1 mmol) and phen·H₂O (0.02 g, 0.1 mmol) were dissolved in DMF (10 mL), and the resulting solution was added dropwise to the $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}]$ -containing solution with stirring. The mixture was heated and stirred for 1 h at 80 °C. After it had cooled to r.t., the insoluble solid was separated by

filtration and dissolved in acetonitrile (20 mL). The filtrate was allowed to evaporate slowly. After one week, yellow block crystals suitable for X-ray diffraction were isolated. $\text{C}_{48}\text{H}_{40}\text{O}_{26}\text{N}_8\text{Mo}_8\text{Zn}_2$; calcd. Zn 6.37, Mo 37.61, C 28.21, H 1.96, N 5.48; found Zn 6.71, Mo 38.02, C 27.89, H 1.79, N 5.31.

Crystal structure determination

Single crystal X-ray diffraction data for compound **1** were collected on a Bruker Apex CCD diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. An absorption correction was applied using a multi-scan technique. The structure was solved by Direct Methods (SHELXS-97 [15]) and refined by full-matrix least-squares on F^2 (SHELXL-97) [16]. All the non-hydrogen atoms were

refined anisotropically. The hydrogen atoms on the carbon atoms of the phen molecules were located in a Fourier map and refined as riding on their C atoms.

Additional details of data collection and structure refinement are listed in Table 1, and selected bond lengths and angles are listed in Table 2.

CCDC 688398 contains the supplementary crystallographic data for compound **1**, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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