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Hydrothermal synthesis and crystal structure of a new molybdenum oxide compound with manganese-*o*-phen subunit: $[Mn(o-phen)(H_2O)MoO_4] \cdot H_2O$ (*o*-phen = *o*-phenanthroline)

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Abstract

A new one-dimensional molybdenum oxide compound with manganese-*o*-phen subunit: $[Mn(o\text{-phen})(H_2O)MoO_4] \cdot H_2O$ (**1**) (*o*-phen = *o*-phenanthroline) was synthesized by thehydrothermal reaction of $Na_2MoO_4 \cdot 2H_2O$, $MnSO_4 \cdot H_2O$, oxalic acid, *o*-phenanthroline (*o*-phen) and water. Its structure was determined by elemental analyses, ESR spectrum, TG analysis, IR spectrum and single-crystal X-ray diffraction. Compound **1** crystallizes in triclinic system, space group *P*-1 with $a = 7.0401(2)$ Å, $b = 10.4498(2)$ Å, $c = 10.5720(2)$ Å, $\alpha = 73.26(7)^\circ$, $\beta = 83.34(8)^\circ$, $\gamma = 77.33(9)^\circ$, $V = 725.5089(0)$ Å^3, $Z = 2$, and $R_1 = 0.0322$ for 2337 observed reflections. Compound **1** exhibits one-dimensional chain structure. The chains are linked up via hydrogen bonding to 2D layers, which are further assembled through $\pi-\pi$ stacking interactions to a 3D supermolecular structure.

Keywords: Molybdenum oxide; Manganese; One-dimensional structure; Hydrogen bonding

1. Introduction

The significant contemporary interest in metal oxide-based inorganic–organic hybrid materials derives from their hierarchical structures and potential applications in certain fields, such as catalysis, sorption, electric conductivity, magnetism, and optical materials [1]. Therefore, the discovery of new materials and rational design of such solid oxides remains an important and very active subject. One useful strategy for the design of novel oxide materials exploits organic components as structure-directing subunits of a hybrid material. Examples of this general approach can be shown in the fields of supramolecular chemistry and crystal engineering [2]. The most extensively studied manifestations of such organic-inorganic composite materials are four primary classes, including zeolites [3], mesoporous oxides of the MCM-41 type [4], biomineralized materials, and microporous transition metal phosphates with entrained organic cations [5]. Subsequently, Zubieta and co-workers developed a potential fifth class of VOXI and MOXI families containing secondary metal–ligand complex subunits [6]. Representative examples of molybdenum oxides include $[Cu(o\text{-phen})_2Mo_4O_{13}]$ and $[Cu(o\text{-phen})MoO_4] \cdot H_2O$ [6], $[Cu(2,2'\text{-bpy})Mo_2O_7]$ [7], $[Ni(2,2'\text{-bpy})_2Mo_4O_{13}]$ [8], $[Ni(3,4'\text{-bipy})_2MoO_4] \cdot 3H_2O$ [9], and the family of one-dimensional iron molybdates $[FeCl(2,2'\text{-bpy})MoO_4]$, $[\{Fe(2,2'\text{-bpy})\}_2Mo_3O_{12}]$ and $[\{Fe(2,2'\text{-bpy})\}_2Mo_4O_{15}]$ [10]. In this type of molybdenum oxides, the secondary metal–ligand complex subunits are not only as charge-compensating and space-filling components but also as intimate structural components of bimetallic oxide.

The manganese coordination complexes have received much attention due to their application in catalysis, magnetism and photochemistry [11]. The recent success in the hydrothermal assembly of molybdenum oxides

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employing manganese–organonitrogen ligand complex subunits provides a powerful tool for synthesis of molybdenum oxides possessing unique structures and properties [12]. In view of this point, we have recently carried out an attempt to incorporate the complex manganese–organonitrogen ligand subunits into molybdenum oxides and successfully isolated a new compound, [Mn(*o*-phen)(H_2O)MoO_4]·H_2O (**1**). As far as we are aware, this type of molybdenum oxides incorporating manganese–organonitrogen ligand subunit have been less reported [12].

Table 1
Crystallographic parameters of compound **1**

Molecule formula	$C_{12}H_{12}MnMoN_2O_6$
Molecule weight	431.12
Crystal size	0.20 × 0.15 × 0.04 mm
Crystal color	Yellow
Crystal system	Triclinic
Space group	*P*-1
a (Å)	7.0401(2)
b (Å)	10.4498(2)
c (Å)	10.5720(2)
α (deg)	73.26(7)
β (deg)	83.34(8)
γ (deg)	77.33(9)
V (Å^3)	725.5089(0)
Z	2
D_C/(g cm^{-3})	1.973
F(000)	426
Goodness-of-fit on F^2	1.094
Absorption coefficient	1.764 mm^{-1}
Max. shift (Δ/σ) in final cycle	0.000
Largest diff. peak and hole (e Å^{-3})	0.770/−0.459
Data/restraints/parameters	2543/0/200
Final R indices [$I > 2\sigma(I)$][a]	
R indices (all data)	$R1 = 0.0322$, w$R_2 = 0.0803$
	$R_1 = 0.0361$, w$R_2 = 0.0833$

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\right]^{0.5}$.

2. Experimental

2.1. General procedures

All chemicals purchased were of reagent grade and used without purification. The hydrothermal reactions were performed in 20 mL Teflon-lined stainless-steel vessels under autogenous pressure with a filling capacity of approximately 60%. Water used in the reactions is distilled water. Elemental analyses (C, H and N) were performed on a Vario EL *III* CHNOS Elemental Analyzer. Mo and Mn were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range of 400–4000 cm^{-1} on an FTS-40 spectrophotometer using KBr pellets. TG analyses were carried out on a NETZSCH STA 449C instrument in flowing N_2 with a heating rate of 20°C min^{-1} in the temperature range of 30–600°C.

2.2. Preparation of [Mn(o-phen)(H_2O)MoO_4]·H_2O (1)

Compound **1** was isolated from the reaction of $Na_2MoO_4 \cdot 2H_2O$ (0.62 g, 2.56 mmol), $MnSO_4 \cdot H_2O$ (0.36 g, 2.13 mmol), oxalic acid (0.25 g, 1.98 mmol), *o*-phenanthroline (0.31 g, 1.72 mmol) and H_2O (12 mL) under autogenous pressure at 170°C for 4 days. After being cooled slowly to room temperature, the yellow crystals suitable for X-ray diffraction study were obtained. *Anal.* Calc. for **1**: C, 33.40; H, 2.78; N, 6.49; Mn, 12.73; Mo, 22.25 (%). Found: C, 33.31; H, 2.71; N, 6.57; Mn, 12.69; Mo, 22.11 (%). IR (KBr pellet, cm^{-1}): 3404 (s), 3061 (w), 1618 (s), 1591 (m), 1518 (s), 1427 (s), 1315 (m), 1146 (s), 1149 (m), 1101 (m), 924 (s), 897 (s), 860 (s), 810 (s), 725 (s), 638 (s).

2.3. X-ray crystallography

Crystals with dimensions 0.04 × 0.15 × 0.20 mm was selected for indexing and intensity data collections at 293 K on a CrystalClear CCD diffractometer with graphite monochromated Mo*K*α radiation ($\lambda = 0.71073$ Å) at room temperature, respectively. A total of 4457 independent reflections (2543 unique, $R_{int} = 0.0167$) were measured in the range of $3.26 < \theta < 25.03°$ ($-8 \leqslant h \leqslant 8$, $-10 \leqslant k \leqslant 12$, $-12 \leqslant l \leqslant 12$). The structure was solved by the direct method, a successive Fourier difference synthesis and refined by the full-matrix least-squares based on F^2 using the SHELXTL-97 program package. In all cases, all non-hydrogen atoms were refined anistropically. The crystallographic data of **1** are listed in Table 1. The final atomic coordinates, and selected bond lengths and angles are given in Tables 2 and 3.

3. Results and discussion

Compound **1** was originally separated in about 25% yield from the hydrothermal reaction of $Na_2MoO_4 \cdot 2H_2O$, $MnSO_4 \cdot H_2O$, oxalic acid, *o*-phenanthroline and water at 170°C for 4 days. We tried to increase the yield of **1** by changing the hydrothermal reaction conditions, such as stoichiometry, reaction temperature, pH value and so on, but only found some homogenized blue slurry or a large sum of black powders. However, when appropriate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was added into the reaction system, the crystals of **1** were obtained in the higher yield. This might be due to the fact that the isopolymolybdate can slowly release molybdenum sources and then contribute to the formation of large single crystals. On the other hand, we tried to synthesize the analogous compound of **1**

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **1**

Atom	x	y	z	U_{eq}
Mn(1)	2269(1)	1560(1)	3035(1)	18(1)
Mo(1)	7112(1)	1701(1)	4109(1)	17(1)
N(1)	2427(5)	3026(3)	971(3)	24(1)
N(2)	2592(5)	308(3)	1537(3)	21(1)
O(1)	1161(5)	3141(4)	4130(4)	44(1)
O(2)	5080(4)	1926(3)	3202(3)	30(1)
O(3)	6969(5)	3130(3)	4710(3)	34(1)
O(4)	7281(5)	218(3)	5415(3)	38(1)
O(5)	9190(4)	1604(3)	3025(3)	28(1)
O(6)	3332(5)	5065(4)	3791(4)	50(1)
C(1)	2488(7)	4348(5)	708(5)	34(1)
C(2)	2493(8)	5198(5)	−596(5)	41(1)
C(3)	2382(7)	4677(5)	−1629(5)	39(1)
C(4)	2338(6)	3279(5)	−1375(4)	29(1)
C(5)	2291(8)	2645(5)	−2407(4)	41(1)
C(6)	2327(8)	1289(5)	−2120(4)	40(1)
C(7)	2429(6)	455(5)	−782(4)	29(1)
C(8)	2541(7)	−970(5)	−442(5)	34(1)
C(9)	2663(7)	−1711(5)	862(5)	34(1)
C(10)	2678(6)	−1034(4)	1836(4)	28(1)
C(11)	2456(6)	1031(4)	259(4)	21(1)
C(12)	2382(6)	2492(4)	−49(4)	23(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (deg) for compound **1**

Mn(1)–O(4)$^{\#1}$	2.085(3)	Mn(1)–N(2)	2.291(3)
Mn(1)–O(2)	2.131(3)	Mo(1)–O(4)	1.746(3)
Mn(1)–O(5)$^{\#2}$	2.159(3)	Mo(1)–O(2)	1.750(3)
Mn(1)–O(1)	2.237(3)	Mo(1)–O(5)	1.755(3)
Mn(1)–N(1)	2.284(3)	Mo(1)–O(3)	1.764(3)
O(4)$^{\#1}$–Mn(1)–O(2)	91.36(12)	O(2)–Mn(1)–N(2)	107.59(12)
O(2)–Mn(1)–O(5)$^{\#2}$	166.81(12)	O(5)$^{\#2}$–Mn(1)–N(2)	84.54(11)
O(4)$^{\#1}$–Mn(1)–O(1)	101.53(14)	O(1)–Mn(1)–N(2)	162.23(13)
O(2)–Mn(1)–O(1)	85.15(12)	N(1)–Mn(1)–N(2)	72.56(12)
O(5)$^{\#2}$–Mn(1)–O(1)	81.91(12)	O(4)–Mo(1)–O(2)	110.82(15)
O(4)$^{\#1}$–Mn(1)–N(1)	160.74(13)	O(4)–Mo(1)–O(5)	110.27(15)
O(2)–Mn(1)–N(1)	84.88(12)	O(2)–Mo(1)–O(5)	107.69(13)
O(5)$^{\#2}$–Mn(1)–N(1)	94.17(12)	O(4)–Mo(1)–O(3)	110.40(15)
O(1)–Mn(1)–N(1)	96.97(13)	O(2)–Mo(1)–O(3)	109.96(15)
O(4)$^{\#1}$–Mn(1)–N(2)	90.74(12)	O(5)–Mo(1)–O(3)	107.61(14)

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

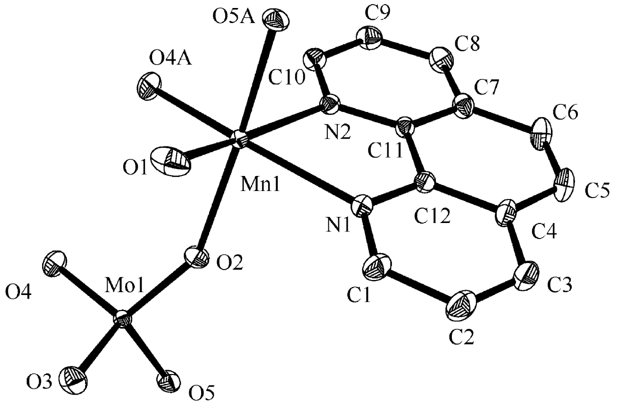

Fig. 1. Asymmetric unit of **1**, showing the atom-labeling scheme and 30% thermal ellipsoids.

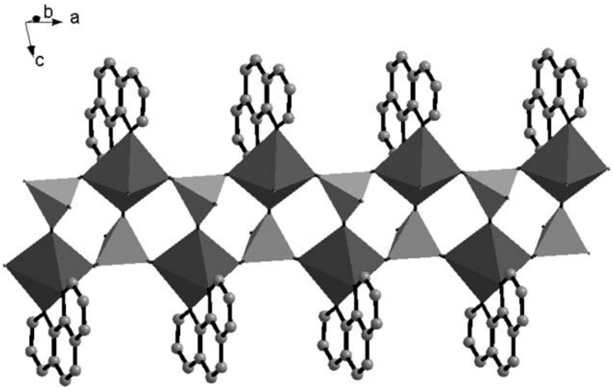

Fig. 2. The one-dimensional chain of **1**.

using 2,2′-bipy instead of *o*-phen as organic ligand under the similar basic conditions, but the attempt failed.

The crystal of **1** consists of one Mn(*o*-phen)(H_2O) complex subunit, one MoO_4 molybdenum oxide and one lattice water molecule. A locally expanded unit is shown in Fig. 1, showing the coordination environment of Mn and Mo atoms. The Mn atom is coordinated by four O atoms and two N atoms, of which the two N atoms are from one *o*-phen ligand, three O (O2, O4A, O5A) atoms are from three MoO_4 groups, and one O (O1) atom are from one water molecule. In the distorted octahedron $\{MnN_2O_4\}$, N1, N2, O1 and O4A atoms define the basal plane with the mean deviation of 0.2026 Å, while O2 and O5B atoms occupy the axial sites. The Mn–O distances are in the range of 2.085(3)–2.237(3) Å, and the Mn–N distances are 2.284(3), 2.291(3) Å, respectively. In MoO_4 group, there exist three O (O2, O4, O5) atoms taking part in coordination with average Mo–O distance of 1.750 Å. Thus, each Mo atom connects three adjacent Mn atoms via O2, O4 and O5 atoms, with corresponding Mo···Mn distances of 3.761, 3.827 and 3.661 Å, respectively.

As shown in Fig. 2, compound **1** consists of one-dimensional chains constructed from $\{MoO_4\}$ tetrahedra bridging $\{Mn(o\text{-phen})O_4\}$ subunits in a corner-sharing arrangement of polyhedra, with a cyclic $\{Mo_2Mn_2O_4\}$ core. Each MoO_4 group bridges three adjacent $\{MnN_2O_4\}$ octahedra and each $\{MnN_2O_4\}$ octahedron bridges three adjacent $\{MoO_4\}$ tetrahedra. The basal framework may also be described as a puckered one-dimensional ribbon constructed by edge-sharing (Mo–O–Mn) array of $\{Mo_2Mn_2O_4\}$ rings. In the

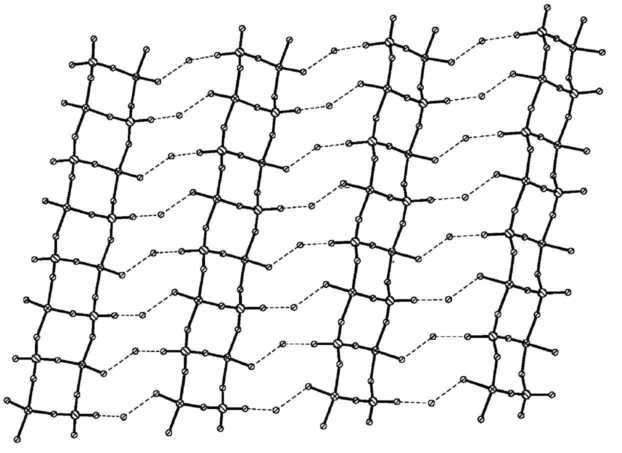

Fig. 3. The two-dimensional ladder-like network in the *ab* plane. All the H, N and C atoms are omitted for clearity.

direction of propagation of the {$Mo_2Mn_2O_4$} chain, two parallel *o*-phen rings, respectively, coordinate to two adjacent Mn atoms. The distance between the two *o*-phen rings is 7.04 Å. The overall structure can be depicted as $[Mn(o\text{-phen})(H_2O)]^{2+}$ clusters bridged by $\{MoO_4\}^{2-}$ subunits.

The basal framework of **1** is similar to those of the previously reported compounds [FeCl(2,2′-bpy)MoO_4] [10], [Cu(*o*-phen)MoO_4]·H_2O and [Zn(*o*-phen)MoO_4] [6], and [Fe(*o*-phen)MoO_4] [13]. In compound [FeCl(2,2′-bpy)MoO_4], the polyhedral motifs consist of {MoO_4} tetrahedra and {FeN_2O_3Cl} octahedra, while in the last three compounds, the polyhedral motifs display five-coordinate trigonal bipyramidal or square pyramidal substructures. The most interesting aspect of compound **1** is that there exist two kinds of strong hydrogen bonding between lattice water molecules and {$Mo_2Mn_2O_4$} chains. One is formed between lattice water molecule and coordinated water molecule with O···O distance of 2.704 Å, while another is formed between lattice water molecule and terminal O atom of {MoO_4} subunit with O···O distance of 2.753 Å. The lattice water molecules bridge adjacent {$Mo_2Mn_2O_4$} chains to a two-dimensional layer. Fig. 3 shows the ladder-like 2D network formed by {$Mo_2Mn_2O_4$} chains and lattice water molecules. It is worthwhile to discuss that between the two adjacent layers, each *o*-phen ring of one layer is partly inserted into the interspaces of the closest two *o*-phen rings of the other layer. All the *o*-phen rings are parallel to each other and cause $\pi-\pi$ stacking interactions with the inter-ring distance of about 3.52 Å. Thus, a 3D supermolecular architecture is formed through the $\pi-\pi$ stacking interactions (Fig. 4). As far as we are aware, though 3D supermolecular structures generated from 2D layers through hydrogen bonds are common phenomena in the chemistry of coordination polymers [14,15], such 3D supermolecular architectures constructed by 1D chains are still rare.

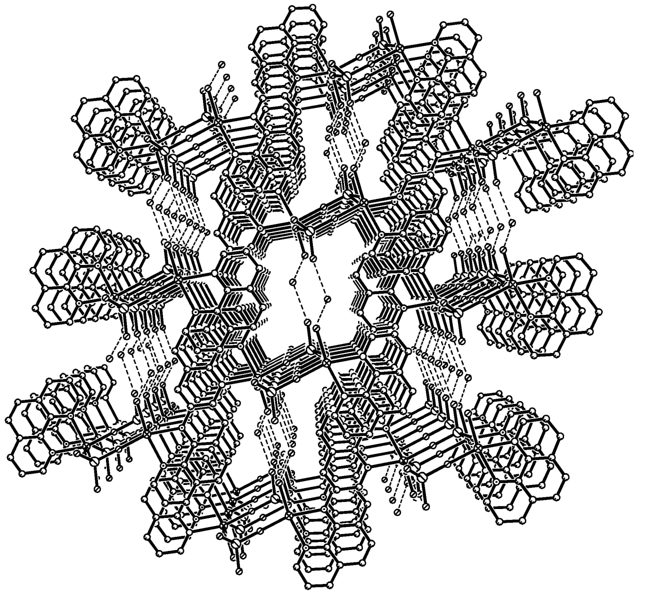

Fig. 4. View of the staking arrangement of **1** along the *a*-axis.

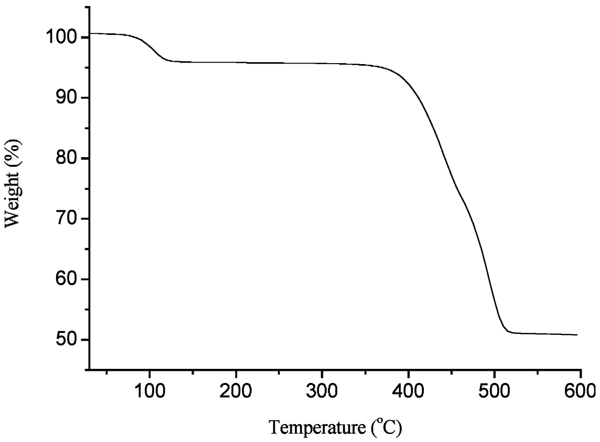

Fig. 5. TG curve of **1**.

The ESR spectrum of **1** has been performed at room temperature, giving a *g* value of ca. 2.0053 and a peak-to-peak line width of 473 G. This *g* value is characteristic of octahedrally coordinated Mn(II) ions [16]. The IR spectrum of **1** shows several strong bands at 924, 897, 860, 810, 725, 638 cm^{-1}, corresponding to the ν(Mo = O) or ν(Mo–O–Mo) vibrations. The banks in the range of 1618–1149 cm^{-1} regions are contributed to the characteristic peaks of *o*-phen ligand. The broad band at 3404 cm^{-1} should be attributed to O–H stretching vibration.

The TG curve of compound **1** exhibits two steps of weight loss (Fig. 5). The first weight loss occurs in the range of 75–120°C, corresponding to the removal of one free water molecule. The observed weight loss (4.07%) is consistent with the calculated value (4.17%). In the range of 120–350°C, the compound **1** keeps stable. The second weight loss is 44.41% from 350°C to 530°C, corresponding to the release of coordinated water and *o*-phen ligand (Calcd. 45.96%).

In conclusion, we have successfully synthesized one inorganic–organic hybrid molybdenum oxide compound incorporating manganese–organonitrogen ligand subunit. The 1D structure of **1** may be compared to those of [FeCl(2,2′-bpy)MoO_4] [10], [Cu(*o*-phen)MoO_4]·H_2O and [Zn(*o*-phen)MoO_4] [6], and [Fe(*o*-phen)MoO_4] [13], which exhibit a similar bimetallic oxide core. However, in compound **1**, a remarkable feature is that the 1D chains are linked up via hydrogen bonding to 2D layer structure, and the 2D layers are further assembled together through $\pi-\pi$ stacking interactions to a 3D supermolecular structure. The isolation of **1** further confirms the hydrothermal synthesis is a powerful method to obtain novel structural materials.

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-233047. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; mailto: deposit@ccdc.cam.ac.uk).

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