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Note

Hydrothermal synthesis and crystal structure of the trimolybdate, $(H_3NCH_2CH_2NH_3)Mo_3O_{10}$

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Abstract

The hydrothermal reaction of $Na_2MoO_4 \cdot 2H_2O$, MoO_3, $H_2NCH_2CH_2NH_2 \cdot 2HCl$ and H_2O in the mole ratio 6:6:10:300 at 160 °C under autogenous pressure yields colorless needles of $(H_3NCH_2CH_2NH_3)Mo_3O_{10}$ (**1**). The structure of **1** consists of distorted $\{MoO_6\}$ octahedra linked through face-, edge- and corner-sharing interactions into infinite chains. The ethylenediamminium cations occupy the channels between these chains. Crystal data: monoclinic space group $P2_1/n$, $a=8.083(2)$, $b=14.465(2)$, $c=8.919(2)$ Å, $\beta=98.19(1)°$, $V=1032.2(7)$ Å^3, $Z=4$, $D_{calc}=3.28$ g cm^{-3}; structure solution and refinement based on 2856 reflections converged at $R=0.0191$.

Introduction

Polymeric structures based on infinite chains of oxomolybdenum polyhedra are characteristic of the dimolybdate and trimolybdate systems, $\{[Mo_2O_7]^{2-}\}_\infty$ and $\{[Mo_3O_{10}]^{2-}\}_\infty$ [1–6]. While these structures share a common one-dimensional framework, the details of the polyhedral connectivity are clearly dependent on the templating effects of the cations. This feature is demonstrated by the structural variability associated with $(NH_4)_2Mo_3O_{10}$ [3], $K_2Mo_3O_{10}$ [6] and $(H_3NCH_2CH_2NH_3)Mo_3O_{10}$, whose preparation and structure are reported in this paper.

Experimental

Preparation of $(H_3NCH_2CH_2NH_3)Mo_3O_{10}$ (1)

A mixture of $Na_2MoO_4 \cdot 2H_2O$, MoO_3, ethylenediamine dihydrochloride and H_2O in the mole ratio 6:6:10:300 (5 ml volume) was placed in a Teflon-lined Parr acid digestion bomb and heated for 5 days at 160 °C and autogeneous pressure. After allowing the reaction mixture to cool for 6 h, colorless needles of **1** were collected, washed with water and air dried (yield: 1.2 g, 24%). The material is insoluble in all common organic solvents and in water. *Anal.* Calc. for $C_2H_{10}N_2O_{10}Mo_3$: C, 4.71; H, 1.96. Found: C, 4.65; H, 1.87%. IR (KBr pellet, 1000–400 cm^{-1} region): 965(m), 942(sh), 908(s), 891(vs), 862(vs), 823(m), 799(m), 739(s), 700(vs), 602(s), 554(s).

TABLE 1. Summary of crystal data and experimental conditions for the X-ray study of **1**

Composition	$C_2H_{10}N_2O_{10}Mo_3$
Space group	$P2_1/n$
a (Å)	8.083(2)
b (Å)	14.465(2)
c (Å)	8.919(2)
β (°)	98.19(1)
V (Å^3)	1032.2(7)
Z	4
D_{calc} (g cm^{-3})	3.28
T (K)	295
λ (Mo Kα) (Å)	0.71073
μ (cm^{-1})	36.3
No. observed reflections	2856 ($I_o \geq 3\sigma(I_o)$)
R	0.0191
R_w	0.0192
GOF	1.44

X-ray structure determination

X-ray data was collected on a Rigaku AFC5S four-circle diffractometer. Table 1 summarizes the crystal parameters and details of the structure solution and refinement. Non-hydrogen atoms were refined using anisotropic temperature factors. All hydrogen positions were located and refined isotropically. Atomic positional parameters and selected bond lengths and angles are presented in Tables 2 and 3, respectively.

Results and discussion

The hydrothermal reaction of $Na_2MoO_4 \cdot 2H_2O$, MoO_3, $H_2NCH_2CH_2NH_2 \cdot 2HCl$ and water yields colorless needles of $(H_3NCH_2CH_2NH_3)Mo_3O_{10}$ (**1**). As we and others have observed [7, 8], the identity of the cation is critical in the isolation of phases of a given composition and structure, a feature related to the role of the cations as templates for preparation of the solid.

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TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq}[a]
Mo(1)	1087(1)	9008(1)	5421(1)	10(1)
Mo(2)	4033(1)	10347(1)	3386(1)	10(1)
Mo(3)	7183(1)	9294(1)	2532(1)	12(1)
O(1)	131(3)	8656(2)	6923(3)	18(1)
O(2)	1317(3)	8000(2)	4456(3)	20(1)
O(3)	2221(3)	9712(2)	3441(2)	15(1)
O(4)	3447(3)	11310(2)	2332(3)	19(1)
O(5)	4938(3)	9617(2)	1814(2)	15(1)
O(6)	5612(3)	9197(2)	4639(2)	13(1)
O(7)	6819(3)	10724(2)	3483(2)	13(1)
O(8)	7204(3)	8107(2)	2452(3)	25(1)
O(9)	8071(3)	9640(2)	997(3)	23(1)
O(10)	9047(3)	9497(1)	4138(2)	13(1)
N(1)	6460(4)	11605(2)	514(3)	22(1)
N(2)	10337(4)	12191(3)	380(4)	27(1)
C(1)	7315(4)	12061(3)	−680(4)	21(1)
C(2)	9058(4)	11715(3)	−731(4)	24(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

To illustrate the point, under identical condition, the substitution of NaCl for $H_2NCH_2CH_2NH_2 \cdot 2HCl$ yields the dimolybdate species $Na_2Mo_2O_7$ [2].

The IR spectrum of **1** in the 1000–500 cm^{-1} range is quite complicated, an observation consistent with the presence of three structurally distinct molybdenum sites. The features in the 890–965 cm^{-1} range are ascribed to ν(Mo=O), while the bands in the 700–862 cm^{-1} region are most likely associated with ν(Mo–O–Mo) modes.

The fundamental structural motif of the anion of **1** may be described as a double chain of linked $\{MoO_6\}$ octahedra, as shown in Fig. 1. The metrical parameters associated with the three crystallographically independent molybdenum sites are unexceptional and exhibit the usual two short, two long, two intermediate Mo–O bond lengths [9].

As shown in Fig. 2, the $\{MoO_6\}$ polyhedra are linked in a complex pattern of edge-, corner- and face-sharing to produce the one-dimensional polymeric chains. Molybdenum sites Mo2 and Mo3 exhibit an uncommon face-sharing interaction, while the Mo1 octahedron is linked by edge-sharing to the Mo3 site and to an adjacent Mo1 site, and by corner-sharing to the Mo2 octahedra. As a consequence of this pattern of octahedral connectivities, the structure of **1** possesses terminal, doubly-bridging and triply-bridging oxo groups. Molybdenum centers Mo1 and Mo3 exhibit the common *cis*-dioxo arrangement of terminal oxo groups, while Mo2 has a single terminal oxo group.

The linkage of molybdenum octahedra in **1** is quite distinct from that previously reported for $(NH_4)_2Mo_3O_{10}$ [3] and $K_2Mo_3O_{10}$ [6]. As illustrated in Fig. 3, the

TABLE 3. Selected bond lengths (Å) and angles (°) for **1**

Mo1–O1	1.716(2)	O1...H10	1.95(1)
Mo1–O2	1.717(2)	O2...H5	2.09(1)
Mo1–O3	2.335(2)	O2...H9	2.39(1)
Mo1–O7	1.870(2)	O4...H9	2.41(1)
Mo1–O10	1.997(2)	O5...H7	1.96(1)
Mo1–O10a	2.203(2)	O6...H8	2.17(1)
Mo2–O3	1.736(2)	O7...H6	2.30(1)
Mo2–O4	1.709(2)	O8...H6	2.41(1)
Mo2–O5	1.977(2)		
Mo2–O6	2.289(2)		
Mo2–O6a	2.307(2)		
Mo2–O7	1.864(2)		
Mo3–O5	1.895(2)		
Mo3–O6	2.417(2)		
Mo3–O7	2.271(2)		
Mo3–O8	1.718(2)		
Mo3–O9	1.709(3)		
Mo3–O10	1.947(2)		
O1–Mo1–O2	103.4(1)	O4–Mo2–O5	98.4(1)
O1–Mo1–O3	171.2(1)	O4–Mo2–O6	162.2(1)
O1–Mo1–O7	97.4(1)	O4–Mo3–O7	91.2(1)
O1–Mo1–O10	97.2(1)	O4–Mo2–O6a	103.0(1)
O1–Mo1–O10a	96.5(1)	O5–Mo2–O6	73.8(1)
O2–Mo1–O3	84.8(1)	O5–Mo2–O7	72.2(1)
O2–Mo1–O7	106.4(1)	O5–Mo2–O6a	146.8(1)
O2–Mo1–O10	98.8(1)	O6–Mo2–O7	71.3(1)
O2–Mo1–O10a	159.2(1)	O6–Mo2–O6a	78.2(1)
O3–Mo1–O7	83.2(1)	O7–Mo2–O6a	82.1(1)
O3–Mo1–O10	78.1(1)	O5–Mo3–O6	72.1(1)
O3–Mo1–O10a	75.0(1)	O5–Mo3–O7	74.5(1)
O7–Mo1–O10	146.9(1)	O5–Mo3–O8	104.3(1)
O7–Mo1–O10a	76.6(1)	O5–Mo3–O9	98.5(1)
O10–Mo1–O10a	72.4(1)	O5–Mo3–O10	144.5(1)
O3–Mo2–O4	106.2(1)	O6–Mo3–O2	69.9(1)
O3–Mo2–O5	97.9(1)	O6–Mo3–O8	89.1(1)
O3–Mo2–O6	90.9(1)	O6–Mo3–O9	165.2(1)
O3–Mo2–O7	161.3(1)	O6–Mo3–O10	82.8(1)
O3–Mo2–O6a	100.2(1)	O7–Mo3–O8	158.2(1)
O7–Mo3–O10	73.5(1)	O7–Mo3–O9	97.1(1)
O8–Mo3–O9	104.6(1)	O9–Mo3–O10	100.1(1)
O8–Mo3–O10	99.8(1)		

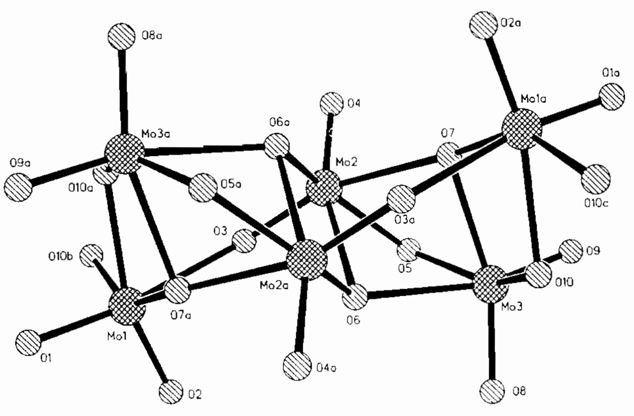

Fig. 1. A view of the structural motif of $\{[Mo_3O_{10}]^{2-}\}_\infty$ which consists of a double chain of linked $\{MoO_6\}$ octahedra. The atom labelling scheme is shown.

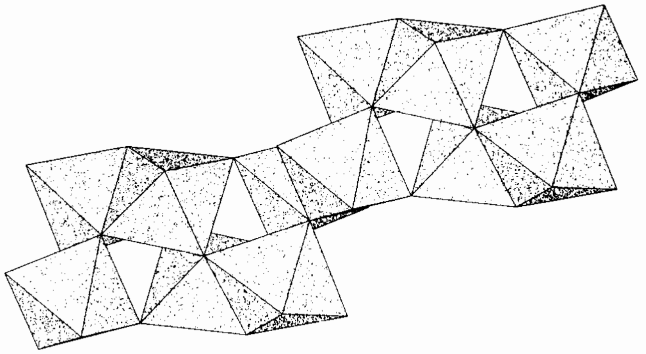

Fig. 2. A polyhedral representation of the structural core of $\{[Mo_3O_{10}]^{1-}\}_\infty$.

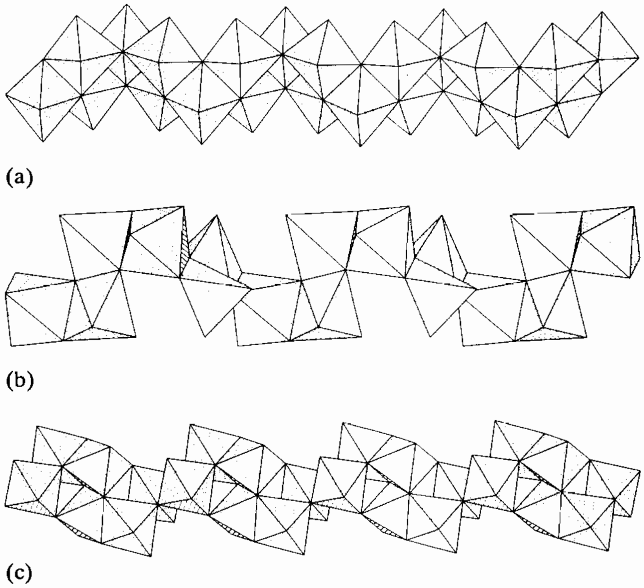

Fig. 3. A comparison of the distinct one-dimensional chains adopted by the anions of: (a) $K_2Mo_3O_{10}$, (b) $(NH_4)_2Mo_3O_{10}$, (c) $(H_3NCH_2CH_2NH_3)Mo_3O_{10}$.

structure of the anion of the former consists of double chains of exclusively edge-sharing octahedra, such that there are only terminal and triply-bridging oxo groups. In contrast, the latter contains edge-sharing $\{MoO_6\}$ octahedra and $\{MoO_5\}$ square pyramids.

There is no doubt that cations play a significant role in the isolation of the trimolybdate phases. There are number of significant contacts between the oxo groups of the $\{[Mo_3O_{10}]^{2-}\}_\infty$ chains and the hydrogen atoms associated with the nitrogen atoms of the ethylenediamminium cations. As illustrated in Fig. 4, the cations occupy channels formed by parallel stacking of three $\{[Mo_3O_{10}]^{2-}\}_\infty$ chains and exhibit strong hydrogen bonding to terminal and bridging oxo groups of the three chains.

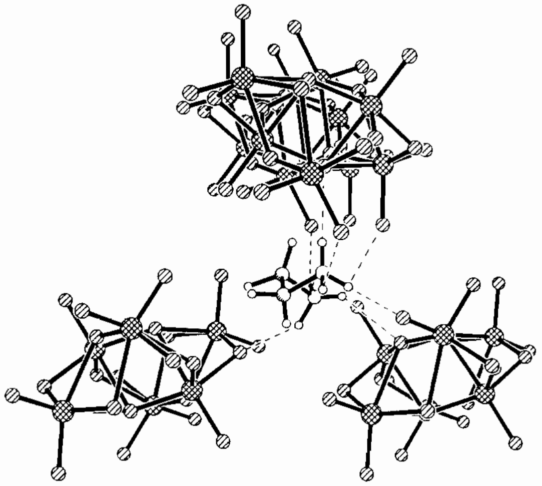

Fig. 4. A view of the environment of the $(H_3NCH_2CH_2NH_3)^{2+}$ cations.

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