

LETTER TO THE EDITOR

Hydrothermal Synthesis and Crystal Structure of Anhydrous Ethylenediamine Trimolybdate (C₂H₁₀N₂)[Mo₃O₁₀]

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EXPERIMENTAL

Synthesis

Crystals of (C₂H₁₀N₂)[Mo₃O₁₀] were synthesized hydrothermally from MoO₃ (Aldrich, 99.5%+), ZnCl₂ (Aldrich, 98%+), ethylenediamine (Aldrich, 99%+), and H₂O in the molar ratio 1:1:0.4:40. The reaction was performed (180°C, 24 h, autogeneous pressure) in a sealed hydrothermal bomb fitted with a 23-ml Teflon liner. The fitting rate was 20%. The pH decreased from 5 to 3 during the reaction. Fibrillar colorless crystals were obtained mixed with an unknown white powder whose diffraction pattern was subsequently indexed by the program DICVOL91 (6) in the monoclinic symmetry [$a = 15.800(3)$ Å, $b = 5.5884(6)$ Å, $c = 9.373(1)$ Å, and $\beta = 116.32(1)^\circ$] with satisfactory figures of merit [$M_{20} = 68$, $F_{20} = 111(0.0035, 51)$]. The mixture was washed with demineralized water and dried in air at room temperature. Fibrillar crystals were then extracted from the mixture. The yield was about 30%. The TGA measurements under oxygen flow show a weight loss of 15.33% occurring between 200 and 450°C. This result is in agreement with the theoretical value for the loss of the amine (%_{th} = 15.32). The resulting product is the orthorhombic molybdenum oxide MoO₃.

Structure Determination

A single crystal was mounted on a Siemens SMART system using a three-circle diffractometer equipped with a CCD bidimensional detector. A total of 9318 intensities were measured during 12 h; a summary of the data collection is given in Table 1. The data were corrected for Lorentz-polarization effects, and the SADABS program (7) was used for the absorption correction. The scattering factors and anomalous dispersion corrections were taken from the "International Tables for X-ray Crystallography" (8). The structure was solved in the $P2_1/n$ (No. 14) space group. All calculations were performed with the SHELXTL

Ethylenediamine trimolybdate, (C₂H₁₀N₂)[Mo₃O₁₀], has been hydrothermally synthesized (180°C, 24 h, autogeneous pressure). It crystallizes in the monoclinic system (space group $P2_1/n$) with $a = 8.0865(2)$ Å, $b = 14.4902(2)$ Å, $c = 8.9306(2)$ Å, $\beta = 98.170(1)^\circ$, and $Z = 4$. Its structure consists of hitherto unknown infinite chains running parallel to the a axis made up of distorted MoO₆ octahedra connected by corners, edges, and faces. Ethylenediamine cations are located between the chains and ensure the connectivity of the structure by hydrogen bonds.

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INTRODUCTION

Hydrothermal synthesis has been extensively used to prepare zeolitic materials and more especially metal phosphates. In this way, Meyer and Haushalter reported many reduced molybdenum phosphates with octahedral-tetrahedral frameworks (1). There is also much interest in molybdates and molybdenum oxides due to their catalytic activity and their capability of forming crystal structures which allow a rich intercalation chemistry. Whereas a large number of di-, tri-, and tetramolybdates have been isolated using secondary and tertiary amines (2–4), only a few molybdates of diamines have been investigated; with ethylenediamine only the structure of (C₂H₁₀N₂)[MoO₄] has been reported in the literature (5). It consists of isolated MoO₄ tetrahedra and ethylenediamine cations connected together by hydrogen bonds. Here we report the synthesis and the crystal structure of a new trimolybdate (VI) obtained from protonated ethylenediamine under hydrothermal conditions.

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TABLE 1
Conditions of Data Measurements and Structure Refinement
for (C₂H₁₀N₂) [Mo₃O₁₀]

Empirical formula	C ₂ H ₁₀ Mo ₃ N ₂ O ₁₀
Formula weight	509.94
Temperature	303(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 8.0865(2) Å, <i>α</i> = 90° <i>b</i> = 14.4902(4) Å, <i>β</i> = 98.170(1)° <i>c</i> = 8.9306(2) Å, <i>γ</i> = 90°
Volume, <i>Z</i>	1035.82(4) Å ³ , 4
Density (calculated)	3.270 g·cm ⁻³
Absorption coefficient	3.627 mm ⁻¹
<i>F</i> (000)	968
Crystal size	0.85 × 0.10 × 0.10 mm
Theta range for data collection	3.48 to 32.49°
Limiting indices	− 11 ≤ <i>h</i> ≤ 12, − 21 ≤ <i>k</i> ≤ 15, − 13 ≤ <i>l</i> ≤ 12
Reflections collected	9318
Independent reflections	3456 [<i>R</i> (int) = 0.0182]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3456/0/185
Goodness-of-fit on <i>F</i> ²	1.124
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0178, <i>wR</i> ₂ = 0.0444
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0193, <i>wR</i> ₂ = 0.0449
Extinction coefficient	0.0109(3)
Largest diff. peak and hole	0.713 and − 0.591 e ⁻ ·Å ⁻³

programs (9). Molybdenum atoms were first located using the direct methods analysis. Remaining atoms (including H atoms) were found by successive difference Fourier maps. The refinement with anisotropic thermal parameters for all atoms except H (which were refined with isotropic factors) gives *R*₁(*F*₀) = 0.018 and *wR*₂(*F*₀²) = 0.044 for 3456 reflections (*I* > 2σ(*I*)) and 185 parameters. The atomic coordinates are listed in Table 2. The anisotropic displacement parameters, the principal bond lengths and angles, and the most probable hydrogen bonds can be obtained from the authors upon request.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The structure of ethylenediamine trimolybdate can be described as a new type of chain [Mo₃O₁₀²⁻] running parallel to the *a* axis. It is made up of distorted MoO₆ octahedra connected by corners, edges, and faces (Fig. 1). Each octahedron has two short, two medium, and two long molybdenum–oxygen bonds with values respectively between 1.707(2) and 1.739(1) Å, 1.865(1) and 2.000(1) Å, 2.206(1) and 2.415(1) Å. The two short distances in the Mo(1)O₆ and Mo(3)O₆ polyhedra correspond to two terminal oxygen atoms in *cis* position as already observed in the structure of (C₆H₅NH₃)₂ [Mo₃O₁₀] · 4H₂O (10). For the Mo(2)O₆ octa-

TABLE 2
Atomic Coordinates (×10⁴) and Equivalent Isotropic
Displacement Parameters (Å²×10³) (C₂H₁₀N₂) [Mo₃O₁₀]

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Mo(1)	7183(1)	706(1)	7532(1)	12(1)
Mo(2)	4032(1)	− 347(1)	8386(1)	11(1)
Mo(3)	8913(1)	− 992(1)	9578(1)	11(1)
O(1)	6823(2)	− 723(1)	8483(2)	14(1)
O(2)	8072(2)	360(1)	6003(2)	24(1)
O(3)	7210(2)	1891(1)	7455(2)	25(1)
O(4)	9046(2)	503(1)	9142(2)	13(1)
O(5)	4939(2)	385(1)	6816(2)	15(1)
O(6)	5622(2)	801(1)	9640(2)	14(1)
O(7)	3448(2)	− 1310(1)	7335(2)	20(1)
O(8)	2217(2)	287(1)	8443(2)	16(1)
O(9)	9871(2)	− 1344(1)	8082(2)	20(1)
O(10)	8678(2)	− 2000(1)	10542(2)	21(1)
N(1)	3544(3)	− 1609(1)	4492(2)	23(1)
C(1)	2680(3)	− 2060(2)	5671(2)	22(1)
C(2)	943(3)	− 1715(2)	5730(3)	24(1)
N(2)	− 332(3)	− 2192(2)	4616(2)	28(1)
H(11)	4515(46)	1899(25)	4397(38)	34
H(12)	3750(44)	1071(26)	4765(39)	34
H(13)	3043(45)	1695(25)	3656(40)	34
H(21)	2676(40)	2703(22)	5544(34)	26
H(22)	3222(41)	1905(21)	6552(37)	26
H(31)	870(39)	1101(24)	5565(36)	29
H(32)	598(40)	1818(22)	6656(36)	29
H(41)	− 277(48)	2767(30)	4651(42)	42
H(42)	− 393(46)	2003(27)	3569(43)	42
H(43)	− 1283(49)	2068(26)	4825(41)	42

Note. *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

hedron, the two short distances also correspond to oxygen atoms in *cis* position but only one is terminal, the second linking Mo(2) and Mo(3). The chains could be described in terms of trimer units (see Fig. 1), where Mo(1)O₆ octahedron is connected to Mo(2)O₆ by a shared face and to Mo(3)O₆ by a shared edge. Mo(2)O₆ and Mo(3)O₆ polyhedra are also connected by a corner since O(1) belongs to the three molybdenum polyhedra. The Mo(2)O₆ octahedron shares an edge with an equivalent neighboring octahedron and a vertex with Mo(3)O₆ to form an hexamer unit [Mo₆O₂₀]⁴⁻. The hexamer units are connected together by sharing edges (Mo(3)O₆ octahedra) and corners (Mo(1)O₆ and Mo(3)O₆ polyhedra) to form infinite chains. Ethylenediamine cations are located between these chains and are connected to the oxygens of the molybdate units by hydrogen bonds (Fig. 2). Three types of [Mo₃O₁₀²⁻] infinite chains were already found in trimolybdate compounds. The first two consist of double chains and are only built up from edge-shared octahedra. They are either straight as in [(CH₃)₂NH₂]₄Mo₆O₂₀·2H₂O (11) or corrugated as observed in most cases (see for example the structures of the high

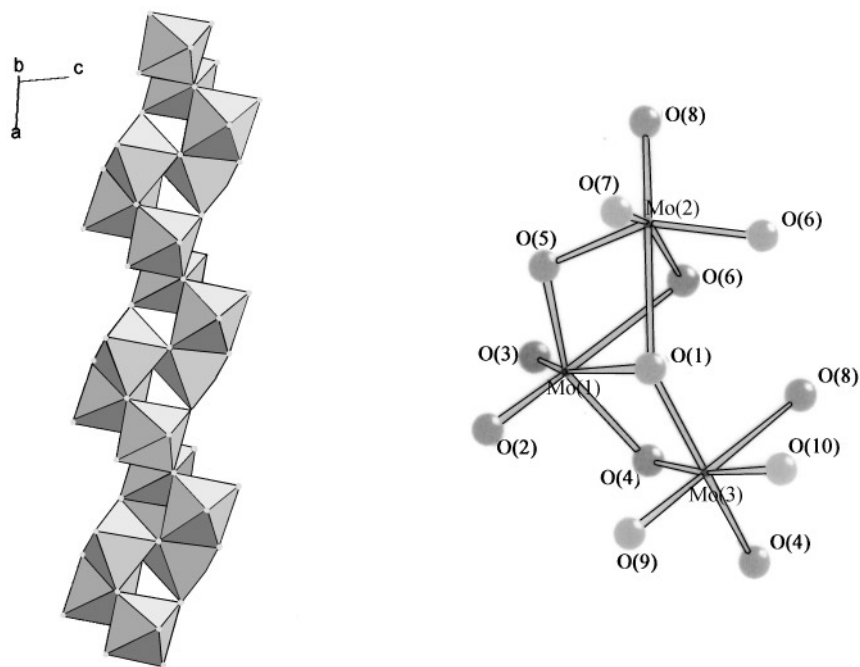


FIG. 1. View of a $[\text{Mo}_3\text{O}_{10}]$ chain. The insert represents a stick and ball model of the trimeric units.

pressure form of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}$ (12), $M_2^I\text{Mo}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ ($M^I = \text{NH}_4$, Rb, and Ag) (13–15), $\text{K}_2\text{Mo}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$ (16), and $(\text{C}_6\text{H}_5\text{NH}_3)_2\text{Mo}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$ (10)]. The third type is a

single chain, observed by Gatehouse and Leverett in the structure of $\text{K}_2\text{Mo}_3\text{O}_{10}$ (17), made up from edge-shared octahedral and square-pyramidal units.

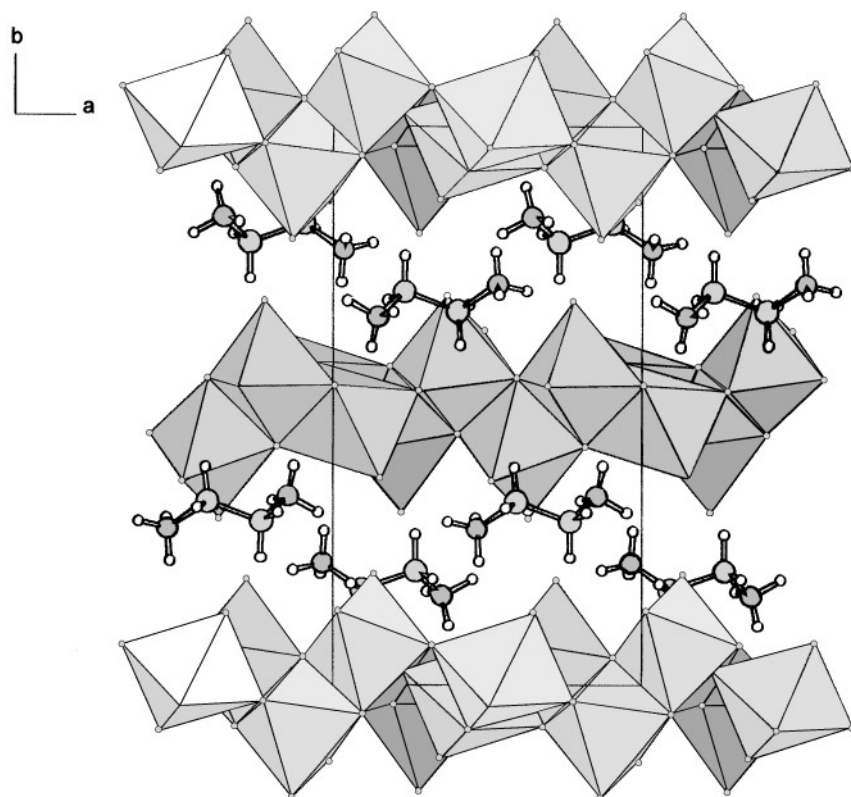


FIG. 2. Projection of the structure of $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Mo}_3\text{O}_{10}]$ along the c axis.

It is noteworthy that photochromic behavior was already observed in the solid state of some secondary and tertiary amine molybdates. A wide study was undertaken by Arnaud-Neu and Schwing-Weill on the photochemical properties of 65 amine molybdates of 14 different amines (2–4). A strong photochromic effect was observed for trimolybdates of secondary amines. It was proposed that the photochromic properties were induced by the nature of both the organic cation and the molybdc anion. The title compound also exhibits weak photochromism with a broad absorption band within the range 200–400 nm; its investigation is currently in progress.

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