

Zigzag Octahedral Cluster Chains in BaMo₆O₁₀

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A novel ternary molybdenum oxide, BaMo₆O₁₀, was discovered and its crystal structure was determined from single-crystal X-ray diffraction data. BaMo₆O₁₀ crystallizes in the orthorhombic space group *Pnma* with $a = 10.154(2)$, $b = 8.641(2)$, $c = 9.184(2)$ Å, $V = 805.7(3)$ Å³, $Z = 4$, $R = 0.0438$, $R_w = 0.0401$ for 652 independent reflections with $I > 3.0 \sigma(I)$. The structure contains infinite zigzag molybdenum oxide chains built up from M_6X_{12} -type clusters, crosslinked to form channels where Ba²⁺ cations reside. Bond distance analysis results indicate that BaMo₆O₁₀ is perfectly bonded with all valence electrons of the Mo atoms in either Mo-Mo or Mo-O bonding states. © 1988 Academic Press, Inc.

Introduction

There has been remarkable progress in the cluster chemistry of molybdenum oxides since the discovery of the milestone compound NaMo₄O₆ (1) about a decade ago. These reduced ternary oxides of molybdenum cover the range from discrete metal clusters (2), oligomers (3), and unidirectional condensed metal cluster chains (1, 4-6), to condensed metal cluster chains running in two orthogonal directions (7).

Compounds with the composition A_xMo₄O₆ (A = monovalent or divalent metal cations) are composed of infinite metal cluster chains based on *trans*-edge-sharing M_6X_{12} -type clusters. The counter

cations occupy sites in channels formed by four metal cluster chains crosslinked by metal-oxygen bonds. The sodium ion in NaMo₄O₆, which crystallizes in a tetragonal space group, fully occupies the site at (0,0, $\frac{1}{2}$). In Ba_{0.62}Mo₄O₆ (5) and Pb_{0.77}Mo₄O₆ (6), the channels can only be partially filled and the divalent cations are three-dimensionally ordered in the lattice. The structure of Ba_{0.62}Mo₄O₆ is a low-symmetry (orthorhombic) version of that of NaMo₄O₆ probably due to the electrostatic repulsion between the large divalent barium ions. Therefore, one expects a drastic structural modification of the NaMo₄O₆-type structure if the available sites in the channel are fully occupied by Ba²⁺. We report here the

TABLE I
POSITIONAL AND EQUIVALENT ISOTROPIC THERMAL
PARAMETERS^a FOR BaMo₆O₁₀

Atom	x	y	z	U_{eq} ($\text{\AA}^2 \times 10^3$)
Ba	0.3971(2)	0.25	0.4959(2)	7(1)
Mo1	0.0346(2)	0.25	0.3827(2)	6(1)
Mo2	0.9592(2)	0.0844(2)	0.6170(2)	4(1)
Mo3	0.7222(2)	0.25	0.6275(3)	4(1)
Mo4	0.7862(2)	0.0950(2)	0.3865(2)	4(1)
O1	0.9492(12)	0.0880(13)	0.2565(15)	7(3)
O2	0.6991(13)	-0.0828(14)	0.2542(15)	11(3)
O3	0.2060(18)	0.25	0.2484(22)	6(4)
O4	0.1426(12)	0.0920(14)	0.5040(16)	8(3)
O5	0.0433(18)	0.25	0.7445(22)	7(4)
O6	0.6319(11)	0.0909(13)	0.5091(16)	6(3)

^a Equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

synthesis and crystal structure of the compound BaMo₆O₁₀ which contains zigzag metal oxide chains built up from M_6X_{12} -type clusters.

Experimental

The discovery of BaMo₆O₁₀ was quite unintentional. During the investigation of molybdenum phosphates, a large number of new structures containing molybdenum in oxidation states less than +6 were discovered (see, e.g., (8)). Among these phosphates a few compounds contain silicon in the framework (Mo₃P₅SiO₁₉; (9a); MoP₃SiO₁₁; (9b)). The silicon contents were from the fused silica tubes as reaction containers. Attempts were planned for the preparation of early transition metal silicates. A reaction mixture containing BaMoO₄, MoO₃, and Mo (mole ratio 1 : 1 : 1) was sealed in a fused silica tube and the reaction conducted at 1200°C for several days. Upon opening the devitrified and shrunk silica tube, some black, chunky crystals were found in the bulk product. The structural determination of one of these chunks indicated that the composition was BaMo₆O₁₀. A black chunk having the dimensions 0.12 × 0.08 × 0.06 mm was selected for indexing and intensity data collection. The compound crystallizes

in the orthorhombic space group $Pnma$ (No. 62) with one Ba, two Mo, and two O at 4c special positions, and two Mo and four O at general positions. The multiplicity of the Ba atom was allowed to refine but did not deviate significantly from full occupancy. Crystal data for BaMo₆O₁₀: space group $Pnma$, $a = 10.154(2)$, $b = 8.641(2)$, $c = 9.184(2)$ Å, $V = 805.7(3)$ Å³, $Z = 4$, $D_c = 7.20$ g/cm³. A total of 762 reflections were obtained of which 652 had $I > 3.0 \sigma(I)$ (86% observed) giving a data : parameter ratio of 10.9 : 1 and $R = 0.0438$, $R_w = 0.0401$, and $GOF = 3.64$. For MoK α radiation, $\mu = 136.67$ cm⁻¹ and an empirical absorption correction was applied. The Ba and Mo atoms were refined anisotropically and the O atoms were refined isotropically. Final positional and thermal parameters are collected in Table I. Selected bond distances are given Table II.

Description and Discussion of the Structure

A view of the structure is shown in Fig. 1, which depicts the infinite Mo₆O₁₀ chains

TABLE II
SELECTED INTERATOMIC DISTANCES (Å)
FOR BaMo₆O₁₀

Ba-O1	2.76(1) (2×)	Mo1-O1	2.01(1) (2×)
Ba-O2	2.89(1) (2×)	Mo1-O3	2.14(1)
Ba-O3	2.99(2)	Mo1-O4	2.08(1) (2×)
Ba-O4	2.92(1) (2×)	Mo2-O1	2.11(1)
Ba-O5	2.81(1)	Mo2-O2	2.04(1)
Ba-O6	2.76(1) (2×)	Mo2-O4	2.13(1) (2×)
Ba-O6	2.96(1) (2×)	Mo2-O5	2.04(1)
Mo1-Mo2	2.695(3) (2×)	Mo3-O2	2.02(1) (2×)
Mo1-Mo2	2.890(3) (2×)	Mo3-O5	2.16(1)
Mo1-Mo4	2.856(3) (2×)	Mo3-O6	1.98(1) (2×)
Mo2-Mo2	2.730(3)	Mo4-O1	2.04(1)
Mo2-Mo2	2.861(3)	Mo4-O2	2.15(1)
Mo2-Mo3	2.802(3)	Mo4-O3	2.00(1)
Mo2-Mo4	2.753(2)	Mo4-O4	2.04(1)
Mo2-Mo4	3.015(3)	Mo4-O6	1.93(1)
Mo3-Mo4	2.668(3) (2×)		
Mo4-Mo4	2.679(3)		

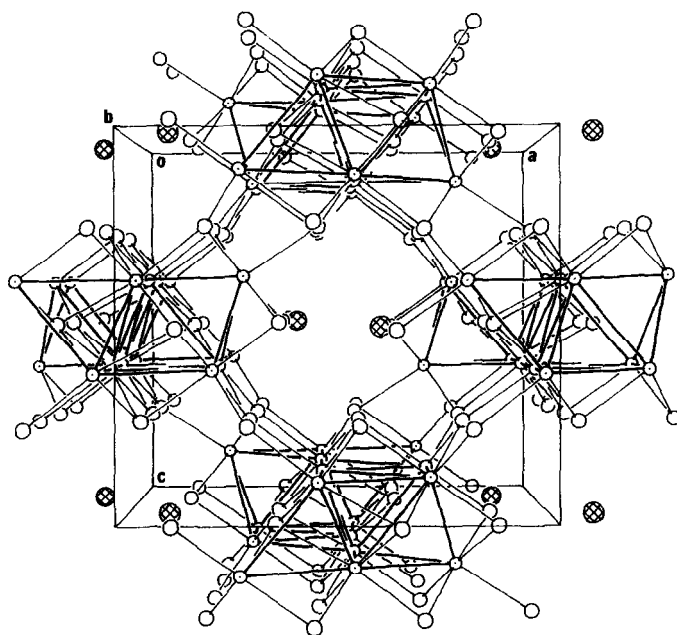


FIG. 1. A three-dimensional view down the b axis of $\text{BaMo}_6\text{O}_{10}$. The Ba, Mo, and O atoms are represented by large cross-hatched circles, small dotted circles, and medium open circles, respectively. Heavy lines are Mo-Mo bond and thin lines are Mo-O bonds.

running parallel to the b -axis. Four infinite chains are interlinked through Mo-O-Mo bonds to form channels where the Ba^{2+} ions are located. A segment of one of the chains

is provided in Fig. 2, which reveals that the chain consists of M_6X_{12} -type clusters linked on opposite edges in a zigzag way. The molybdenum atoms are found to have different

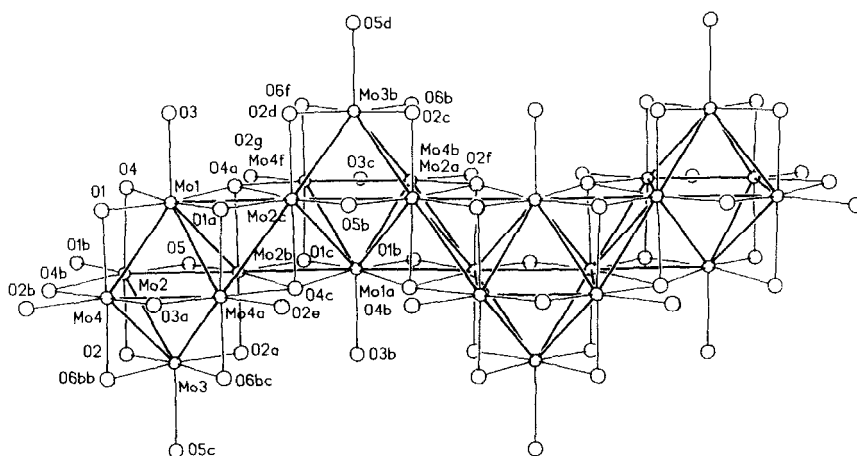


FIG. 2. A section of a zigzag octahedral cluster chain of $\text{BaMo}_6\text{O}_{10}$ as viewed perpendicular to the chain axis.

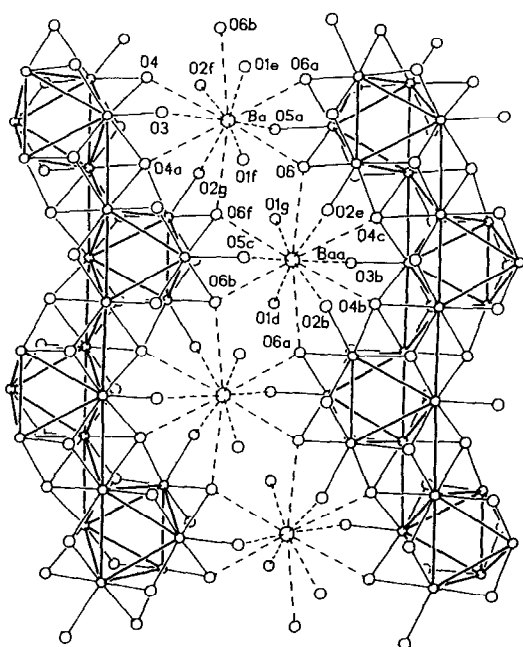


FIG. 3. The coordination environment of the Ba^{2+} ion in $BaMo_6O_{10}$. The Ba, Mo, and O atoms are represented by large, small, and medium open circles, respectively.

coordination numbers: Mo1 (5 O + 6 Mo), Mo2 (5 O + 7 Mo), Mo3 (5 O + 4 Mo), and Mo4 (5 O + 5 Mo). For each cluster unit there are 12 intracluster bonds and 5 intercluster bonds, with distances ranging from 2.668 to 3.015 Å. The apex Mo atoms (Mo1, Mo3) lie in mirror planes perpendicular to the *b*-axis at $y = \frac{1}{4}$. The Mo–Mo bond distances within a cluster unit, Mo1–Mo4 (2.856), Mo1–Mo2 (2.695), Mo2–Mo2 (2.861), Mo4–Mo4 (2.679), Mo2–Mo4 (2.753), Mo2–Mo3 (2.802), and Mo3–Mo4 (2.668 Å), result in an average distance of 2.759 Å, which is only 0.032 Å longer than the distance between nearest neighbors in bcc molybdenum metal. There are three different intercluster Mo–Mo bond lengths of 2.890 Å (mo1–Mo2), 2.727 Å (Mo2–Mo2), and 3.015 Å (Mo2–Mo4). All Mo atoms are each bonded to five O atoms. The Mo–O bond distances range from 1.930 to 2.163 Å,

with the shortest of these involving the oxygen atom bridging only one octahedron edge. The oxygen atoms O2, O3, and O5 lie above octahedra edges but coordinate neighboring cluster chains in corner positions (O^{i-a} or O^{a-i}). Oxygen 1 and 4 are each shared between cluster units within the chains (O^{i-i}). Oxygen 6 bridges only one octahedron edge (O^i). Therefore, both intra- and intercluster sharing of atoms can be described in the connectivity formula $Ba^{2+}[Mo_6(O^{i_2}O^{i-i}_{4/2}O^{i-a}_{6/2})O^{a-i}_{6/2}]^{2-}$. Of special note is the peculiar geometry around O4 which is bonded to four Mo atoms within the chains. Figure 3 shows the coordination environment of the Ba^{2+} ion in $BaMo_6O_{10}$. The Ba^{2+} ion is surrounded by 12 oxygen atoms at distances of 2.757 to 2.986 Å. The Ba–O distances are a little shorter than the calculated Ba–O distance (2.99 Å) based on Ba^{2+} (1.61 Å, CN = 12) and O^{2-} (1.38 Å, CN = 4) (10) and accordingly the Ba^{2+} ion is tightly bonded to the oxygen atoms and does not exhibit large thermal parameters.

The average valence of Mo in $BaMo_6O_{10}$ is +3. An assessment of the valence of the individual Mo atoms using the bond-length bond-strength formula (11) for the Mo–O bond [$s = (d_{Mo-O}/1.882)^{-6.0}$] yields the following results: Mo1, +2.94; Mo2, +2.66; Mo3, +3.22; Mo4, +3.24. The summation of the assessed valences over the Mo atoms of the cluster repeat unit is equal to 17.96, which is in excellent agreement with the value of 18 based on the stoichiometry. The bond orders for the Mo–Mo bonds can be calculated by using the Pauling bond order (PBO) equation $d_n = d_1 - 0.6 \log n$ (12), where d_n and d_1 are the bond distances for bonds of order *n* and 1, respectively, and *n* is the bond order. The sum of the number of electrons devoted to Mo–O bonding and the number of electrons devoted to Mo–Mo bonding should be equal to the periodic group number if all valence electrons of the metal atom are involved in bonding. A

calculation using the bond-length bond-strength formula and the PBO equation ($d_1(\text{Mo-Mo}) = 2.614 \text{ \AA}$) for the Mo atoms in $\text{BaMo}_6\text{O}_{10}$ gives: Mo1, 5.89; Mo2, 6.06; Mo3, 5.82; Mo4, 6.01. The sum over individual Mo-Mo bonds of the cluster repeat unit using the PBO equation yields 8.97. The metal-centered electron (MCE) available for metal-metal bonding is 17.94 ($= 2 \times 8.97$). The number of antibonding electrons is one-half of the difference between the MCE derived from PBO sums and the MCE derived from the formula of the compound (13). Thus, within the limits of error $\text{BaMo}_6\text{O}_{10}$ has no electrons in antibonding states. These results indicate that $\text{BaMo}_6\text{O}_{10}$ is perfectly bonded with all valence electrons of the Mo atoms in either Mo-Mo or Mo-O bonding states.

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