

Some Reduced Ternary and Quaternary Oxides of Molybdenum. A Family of Compounds with Strong Metal-Metal Bonds

Several new, reduced ternary and quaternary oxides of molybdenum are reported, each containing molybdenum in an average oxidation state < 4.0 . All are prepared by reactions between a molybdate salt; metal oxide, if needed; and MoO_2 sealed in Mo tubes held at 1100°C for ca. 7 days. Refinement of the substructure of the new compound $\text{Ba}_{0.62}\text{Mo}_4\text{O}_6$ was based on an orthorhombic cell, with $a = 9.509(2)$, $b = 9.825(2)$, $c = 2.853(1)$ Å, $Z = 2$ in space group $Pbam$; weak supercell reflections indicate the true structure has $c = 8(2.853)$ Å. The chief structural feature is closely related to that of NaMo_4O_6 (C. C. Torardi, R. E. McCarley, *J. Amer. Chem. Soc.* **101**, 3963 (1979)), which consists of infinite chains of Mo_6 octahedral clusters fused on opposite edges, bridged on the outer edges by O atoms and crosslinked by Mo-O-Mo bonding to create four-sided tunnels in which the Ba^{2+} ions are located. The structure of $\text{Ba}_{1.13}\text{Mo}_8\text{O}_{16}$ is triclinic, $a = 7.311(1)$, $b = 7.453(1)$, $c = 5.726(1)$ Å, $\alpha = 101.49(2)$, $\beta = 99.60(2)$, $\gamma = 89.31(2)^\circ$, $Z = 1$, space group $P\bar{1}$. It is a low-symmetry, metal-metal bonded variant of the hollandite structure, in which two different infinite chains, built up from $\text{Mo}_4\text{O}_8^{2-}$ and $\text{Mo}_4\text{O}_8^{26-}$ cluster units, respectively, are interlinked via Mo-O-Mo bridge bonding to create again four-sided tunnels in which the Ba^{2+} ions reside. Other compounds prepared and characterized by analyses and X-ray powder diffraction data are $\text{Pb}_x\text{Mo}_4\text{O}_6$ ($x \sim 0.6$), $\text{LiZn}_2\text{Mo}_3\text{O}_8$, CaMo_5O_8 , $\text{K}_2\text{Mo}_{12}\text{O}_{19}$, and $\text{Na}_2\text{Mo}_{12}\text{O}_{19}$.

We recently reported on the synthesis and structure of the new ternary molybdenum oxide NaMo_4O_6 (1) which consists of infinite chains derived from octahedral metal clusters fused on opposite (parallel) edges. Oxygen atoms bridge the outwardly exposed edges of the octahedral units and bind one chain to another through Mo-O-Mo bridges as indicated in the connectivity $\text{Na}^+ [(\text{Mo}_2\text{Mo}_{4/2}\text{O}_{2/2}\text{O}_{8/2})\text{O}_{2/2}]^-$. In the tetragonal crystals ($a = 9.559(3)$, $c = 2.860(1)$ Å) the infinite chains run parallel to the c axis and are interlinked in such a way that channels accommodating the Na^+ ions are provided. Within the Mo_4O_6 repeat unit of each chain there are 13 Mo-Mo bonds of average bond order 0.5 and average bond length 2.801 Å. This structure has many interesting features but the strong metal-metal bonding clearly dominates in determining the architecture of the chains. In the course of further research, several new compounds have been prepared whose

composition, structure, and properties signal the existence of a large family of ternary and quaternary molybdenum oxides dominated by strong metal-metal bonding. We give here a preliminary report of the structures of the new barium molybdates $\text{Ba}_{0.62}\text{Mo}_4\text{O}_6$ and $\text{Ba}_{1.13}\text{Mo}_8\text{O}_{16}$ (2), and of the preparation of $\text{LiZn}_2\text{Mo}_3\text{O}_8$, $\text{Pb}_x\text{Mo}_4\text{O}_6$, CaMo_5O_8 , $\text{K}_2\text{Mo}_{12}\text{O}_{19}$, and $\text{Na}_2\text{Mo}_{12}\text{O}_{19}$. Complete reports of the structures and properties of these compounds will appear in subsequent papers.

Metallic gray needles of $\text{Ba}_{0.62}\text{Mo}_4\text{O}_6$ were grown from a powdered reaction mixture consisting of BaMoO_4 , MoO_2 , and Mo in 1:4:3 mole ratio, pressed into a pellet, sealed in a molybdenum tube, and held at 1100°C for 7 days. A small needle selected from the product proved to be orthorhombic: $a = 9.509(2)$, $b = 9.825(2)$, $c = 2.853(1)$ Å, $Z = 2$, space group $Pbam$. The structure was determined from 265 independent reflections and refined with anisotropic

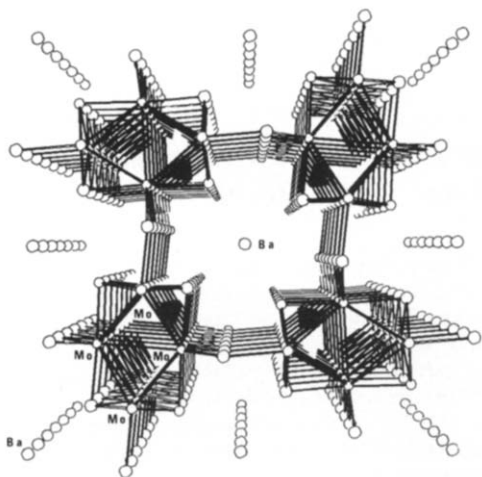


FIG. 1. A three-dimensional view down the c axis of $\text{Ba}_{0.62}\text{Mo}_4\text{O}_6$. Heavy filled lines represent Mo-Mo bonds and unfilled lines represent Mo-O bonds. Positions of Ba and Mo atoms are indicated.

temperature factors for all atoms to convergence at $R = 0.057$ and $R_w = 0.095$. A three-dimensional presentation of the structure as viewed down the c axis is shown in Fig. 1. The principal features of this structure are exactly like those of NaMo_4O_6 except the unit cell is distorted from tetragonal to orthorhombic symmetry, in part a result of a slight rotation of each Mo_4O_6 chain about its own axis parallel to the c axis¹. Within the infinite chains shown in Fig. 2, the Mo-Mo bond distances remain quite comparable to those in NaMo_4O_6 , viz 2.853(1), 2.794(2), 2.785(2), and 2.780(4) Å in $\text{Ba}_{0.62}\text{Mo}_4\text{O}_6$ vs 2.860(1), 2.778(2), and 2.751(3) Å in NaMo_4O_6 . The Mo-O bond distances in the two compounds also are comparable, 2.048 Å (av) in $\text{Ba}_{0.62}\text{Mo}_4\text{O}_6$ vs 2.038 Å (av) in NaMo_4O_6 . Not unexpectedly, the most significant difference in the two structures is centered in the positions occupied by the large cations. In NaMo_4O_6

¹ The rotation of each chain is in a direction opposite to that of each of its neighbors, thus the O-O distances between atoms in neighboring chains are reduced in one direction and increased in the other direction within the a - b plane.

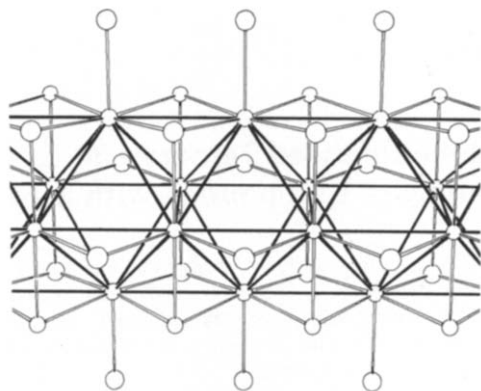


FIG. 2. The cluster chain of $\text{Ba}_{0.62}\text{Mo}_4\text{O}_6$ as viewed perpendicular to the chain axis. The repeat distance along the chain is 2.853(1) Å. Heavy lines are Mo-Mo bonds and unfilled lines are Mo-O bonds.

the Na^+ ions fully occupy positions of tetragonal symmetry within the channels, such that each Na^+ is coordinated to eight O atoms at 2.740(8) Å. The structure of $\text{Ba}_{0.62}\text{Mo}_4\text{O}_6$ has been refined with Ba in the twofold special positions $2b$ ($0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and the fourfold special positions $4e$ ($0, 0, \pm 0.350; \frac{1}{2}, \frac{1}{2}, \pm 0.350$) having total occupancy per unit cell of 0.25 and 1.00, respectively. Oscillation photographs about the c

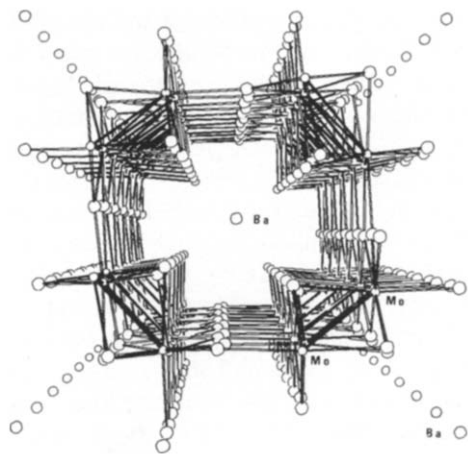


FIG. 3. A three-dimensional view down the c axis of $\text{Ba}_{1.13}\text{Mo}_8\text{O}_{16}$. Heavy filled lines are Mo-Mo bonds and unfilled lines are Mo-O bonds. Positions of Ba and Mo atoms are indicated.

axis show the presence of very weak superlattice reflections indicating that the true unit-cell dimension along the c axis is $8(2.853)$ Å. Refinement of the structure with Ba in the indicated positions was based on a model which assumed that the cations are ordered within a given channel, such that Ba atoms occupy five of the eight possible cation sites along that channel in the supercell. Based on these considerations, the stoichiometric formula is indicated to be $Ba_5Mo_{32}O_{48}$. The cause of the reduction in symmetry from tetragonal for $NaMo_4O_6$ to orthorhombic for $Ba_{0.62}Mo_4O_6$ is not obvious. If the effect is electronically driven then it results from only an additional 0.24 electrons per Mo_4O_6 unit.

A three-dimensional view down the c axis of $Ba_{1.13}Mo_8O_{16}$ is given in Fig. 3.² In this view there is a remarkable resemblance between this structure and that of $NaMo_4O_6$ or $Ba_{0.62}Mo_4O_6$. In each case the metal-cluster chains are knit together to form tunnels in which the M^+ or M^{2+} cations are located. However in $Ba_{1.13}Mo_8O_{16}$ the infinite chains are composed of Mo_4O_8 repeat units as shown in Fig. 4. The interlinking of the cluster units within and between chains via Mo–O–Mo bonding can be represented in the connectivity formula $Mo_4O_2O_{8/2}O_{6/3}$, thus if the clusters occurred as isolated molecular units they would be of the type M_4X_{16} . Molecular species, sans metal–metal bonding, which have the same structural arrangement are $Ti_4(OR)_{16}$, where R = methyl (3) and

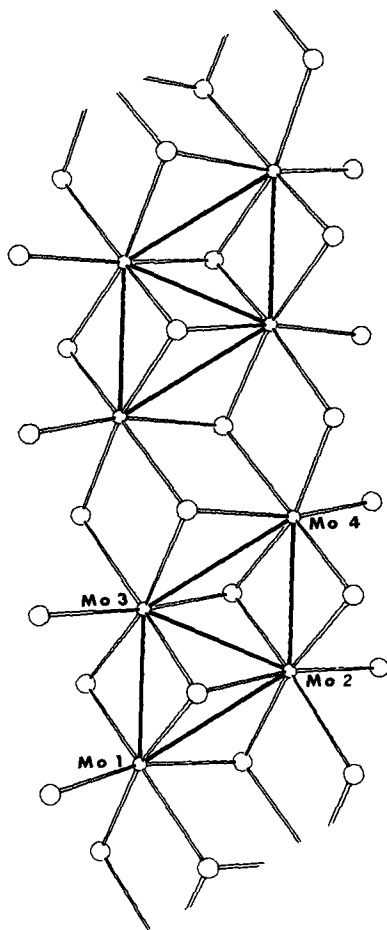


FIG. 4. A section of one chain containing the $Mo_4O_2O_{8/2}O_{6/3}$ cluster units in $Ba_{1.13}Mo_8O_{16}$. Heavy filled lines are Mo–Mo bonds and unfilled lines are Mo–O bonds.

² A columnar crystal of $Ba_{1.13}Mo_8O_{16}$ was selected from a multiphase product obtained from a mixture of $BaMoO_4$ and MoO_2 in mole ratio 2:5 held at $1100^\circ C$ for 7 days in a sealed Mo tube. The crystal proved to be triclinic, $a = 7.311(1)$, $b = 7.453(1)$, $c = 5.726(1)$ Å, $\alpha = 101.49(2)$, $\beta = 99.60(2)$, $\gamma = 89.31(2)^\circ$, $Z = 1$, space group $P\bar{1}$. The structure was refined to $R = 0.036$, $R_w = 0.049$ using 1024 reflections with $I \geq 3\sigma_I$. The Ba content of the unit cell was established through refinement of the occupation number for Ba in three different sites.

ethyl (4), and $W_4O_{16}^{8-}$ as found in the salts $Ag_8W_4O_{16}$ (5) and $Ag_{26}I_{18}W_4O_{16}$ (6). $Ba_{1.13}Mo_8O_{16}$ is the first ternary molybdenum oxide found to adopt a modified hollandite structure (7), where the structure is reduced in symmetry through strong metal–metal bonding to form the tetranuclear cluster units.

A very interesting feature of the structure is that there are two different types of infinite chains. One chain is composed of regular cluster units as shown in Fig. 4,

where the five Mo–Mo bonds in the edge-shared bitriangle (rhombus) are nearly equal. The other chain consists of similar cluster units which have two long and three short Mo–Mo bonds, i.e., two long and two short outer edges of the rhombus. A comparison of bond distances between Mo atoms in the two cluster units is given in Table I.

Within the clusters of regular geometry the Mo–Mo bonding is understood as resulting from 10 electrons in bonding σ orbitals directed along the five bonded edges. This indicates that the Mo atoms on the shared edge of the triangles furnish three electrons each and are in the net oxidation state 3+, whereas the Mo atoms on the outer apices furnish two electrons each and are in the 4+ net oxidation state. Each regular cluster unit then must assume anionic charge $\text{Mo}_4\text{O}_8^{2-}$. From the Mo–Mo distances in the distorted cluster units it appears that the three short bonds are of order 1.0 and the two elongated bonds are approximately of order 0.5. Thus a total of ca. eight electrons is involved in the Mo–Mo bonding, and the net oxidation states are ca. 3.5+ for the atoms on the shared edge and 4.5+ for the atoms on the outer apexes. In both the regular and distorted cluster units, the shortest Mo–O distances are those about the outer apical atoms, which supports their assessment of a higher

net oxidation state. In view of these considerations the compound may be formulated as the mixed-valence species $\text{Ba}_1^{2+}\text{Mo}_4\text{O}_8^{2-}$ ($\text{Mo}_4\text{O}_8^{0,26-}$).

In retrospect, the observed distortion of the "electron-deficient" cluster is understandable in terms of removal of two electrons from the Mo–Mo bonding orbitals. If these electrons were removed from the central bond of the rhombus the cluster should relax into a square or rectangle, but the Mo–O–Mo bridge bonding constrains the cluster such that this is not a favorable rearrangement. Similarly, removing just one of the outer bonds of the rhombus would localize the disturbance on just two of the metal atoms; any stability due to delocalized bonding among the four metal atoms would be lost, and there would be a larger spread of net oxidation states among the four metal atoms, viz., 5+, 4+ (two times) and 3+. Thus elongation of two outer, parallel edges of the rhombus permits retention of the cluster geometry and preserves delocalized bonding within the cluster unit.

Other compounds having clusters of the same rhomboidal geometry are ReSe_2 (8), ReS_2 (9), and $M^1\text{Nb}_4X_{11}$ (10), where $M^1 = \text{Rb}$ or Cs , and $X = \text{Cl}$ or Br . In the latter there are 10 electrons for Nb–Nb bonding in the rhombus, just as in the regular $\text{Mo}_4\text{O}_8^{2-}$ units. It appears that 2 of the 12 electrons per Re_4Se_8 cluster unit in ReSe_2 are utilized to form Re–Re bonds between adjacent cluster units, linking the units into infinite, one-dimensional chains; the remaining 10 electrons thus form the bonding set for the five Re–Re bonds within the individual rhomboidal units. However the structures of both $M^1\text{Nb}_4X_{11}$ and the rhenium dichalcogenides are derived from a close-packed, double-layer arrangement which contrasts with the tunnel structure observed for $\text{Ba}_{1,13}\text{Mo}_8\text{O}_{16}$.

Other compounds which have been obtained from reactions in sealed Mo tubes at

TABLE I
BOND DISTANCES IN THE TWO CLUSTER TYPES
FOUND IN $\text{Ba}_{1,13}\text{Mo}_8\text{O}_{16}$

Bonded atoms	Bond distance (Å)	
	Regular cluster	Distorted cluster
Mo1–Mo2	2.616(1)	2.847(1)
Mo3–Mo4	2.616(1)	2.847(1)
Mo1–Mo3	2.578(1)	2.546(1)
Mo2–Mo4	2.578(1)	2.546(1)
Mo2–Mo3	2.578(2)	2.560(1)

1100°C are $\text{LiZn}_2\text{Mo}_3\text{O}_8$, $\text{Pb}_x\text{Mo}_4\text{O}_6$, $\text{K}_2\text{Mo}_{12}\text{O}_{19}$, $\text{Na}_2\text{Mo}_{12}\text{O}_{19}$, and CaMo_5O_8 . The structure³ of $\text{LiZn}_2\text{Mo}_3\text{O}_8$ is closely related to that of $\text{Zn}_2\text{Mo}_3\text{O}_8$ (11), which contains trinuclear cluster units $\text{Mo}_3\text{O}_8 = \text{Mo}_3\text{O}_4\text{O}_{6/2}\text{O}_{3/3}$ (M_3X_{13} type). In $\text{Zn}_2\text{Mo}_3\text{O}_8$ the trinuclear clusters have a total of six electrons for Mo–Mo bonding at the observed distance of 2.524(2) Å on each edge of the triangle. In $\text{LiZn}_2\text{Mo}_3\text{O}_8$ the same cluster units persist, but with seven electrons involved in the Mo–Mo bonding. The Mo–Mo distance, 2.578(1) Å, on each edge of the triangle indicates the extra electron resides in an orbital antibonding with respect to the Mo–Mo interactions.

While the exact composition of $\text{Pb}_x\text{Mo}_4\text{O}_6$ has not been established because of difficulties in obtaining single-phase preparations, it has been established to be isomorphous with $\text{Ba}_{0.62}\text{Mo}_4\text{O}_6$ through X-ray powder diffraction data. We thus expect its composition to approximate $\text{Pb}_{0.6}\text{Mo}_4\text{O}_6$. The compounds formulated as CaMo_5O_8 , $\text{K}_2\text{Mo}_{12}\text{O}_{19}$, and $\text{Na}_2\text{Mo}_{12}\text{O}_{19}$ have been secured as single-phase preparations. The composition of the first two compounds was established via chemical analyses for the metallic elements and with oxidation state determinations for molybdenum.⁴ From X-ray powder diffraction data the latter compound appears to be isomorphous with $\text{K}_2\text{Mo}_{12}\text{O}_{19}$, and both appear to exhibit metallic conductivity from rough two-probe resistance measure-

ments. Although large crystals of each of these compounds have been obtained, none suitable for single-crystal structure determination have been found. Work on the structure and properties of these compounds is continuing.

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³ Crystals of $\text{LiZn}_2\text{Mo}_3\text{O}_8$ have been determined to be *R*-centered hexagonal, $a = 5.812(1)$, $c = 30.013(8)$ Å, space group $R\bar{3}m$, $Z = 6$. The structure has been solved and refined to $R = 0.043$ and $R_w = 0.056$ from single-crystal data.

⁴ For determination of the oxidation state of molybdenum, samples were dissolved in standardized ceric sulfate–3 *M* H_2SO_4 solution. After complete oxidation of all molybdenum to Mo(VI) the excess Ce(IV) was titrated with standard Fe(II) solution.