described here shows that such centers are certainly capable of existence should the molybdenum atoms in molybdoenzymes be closely associated. It may also be noted that $[Mo_2O(S_2CNEt_2)_6]^+$ is formed from, and is oxidized to, two mononuclear metal centers, thus showing similarity to Wentworth's proposed formation and oxidation of dinuclear enzyme centers.[2]

Acknowledgment. We are indebted to Dr. G. B. Robertson and G. M. McLaughlin for access to the diffractometer and ANUCRYS program library and for helpful discussions.

Registry No. 1, 88253-60-5; 2, 88293-52-1; 3, 88293-53-2; 4, 88293-54-3; $[Mo_2O(S_2CNMe_2)_6]BF_4$, 88253-62-7; $[Mo_2O(S_2CNMe_2)_6]ClO_4$, 88293-55-4; $[MoO(S_2CNEt_2)_3]BF_4$, 70788-19-1; $MoCl(S_2CNEt_2)_3$, 84493-50-5; triphenylphosphine, 603-35-0.

Supplementary Material Available: Tables containing thermal parameters of non-hydrogen atoms, calculated hydrogen atom parameters, additional bond lengths, bond angles, and interatomic distances, least-squares planes and related dihedral angles, geometrical parameters for the tetrafluoroborate ion, and parameters for reduction of compound 1 (7 pages). Ordering information is given on any current masthead page.

Contribution from the Chemical Crystallography Laboratory, Oxford University, Oxford OXI 3PD, England,
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Preparation and Crystal Structure of $La_3Mo_4SiO_{14}$, an Unusual Cluster Compound of Molybdenum

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Black needles of $La_3Mo_4SiO_{14}$ (average Mo oxidation state: 3.75) were prepared by electrolytic reduction at 1100 °C of a melt containing Na_2MoO_4, MoO_3, and La_2O_3. The silicon was abstracted from the porcelain crucible. The compound crystallizes in orthorhombic space group *Pnma* with $a = 17.684$ (4) Å, $b = 5.643$ (1) Å, $c = 11.037$ (2) Å, $V = 1101.4$ (5) Å^3, and $Z = 4$. Diffraction data (Mo Kα radiation, $2\theta(\max) = 60°$) were collected on a Syntex $P2_1$ automated diffractometer, and the structure was refined by blocked-cascade full-matrix least-squares methods to $R_F = 4.2\%$ and $R_{wF} = 4.5\%$ with use of 1755 independent reflections. The structure contains triangular Mo_3O_{13} units with Mo–Mo distances of 2.550 (1) and 2.562 (1) Å and edge-sharing MoO_6 octahedra with Mo–Mo distances alternately 2.551 (1) and 3.13 (1) Å along the chain direction. The Si is tetrahedrally coordinated (mean Si–O distance: 1.64 Å), and the three crystallographically distinct La atoms have coordination numbers of 8, 9, and 10, the stereochemistry in each case being based upon trigonal-prismatic coordination.

Introduction

Examples of mixed-metal oxides in which molybdenum adopts a formal oxidation state of 4 or less are comparatively few. Among the more interesting mixed Mo(IV) oxides are $M_2Mo_3O_8$ (M = Mg, Mn, Fe, Co, Ni, Zn, Cd),[2] which contain the Mo_3O_{13} unit. This unit has a triangle of molybdenum atoms joined by Mo–Mo bonds. Other Mo(IV) oxides are known, but structural information is more limited. Among compounds in which Mo is yet further reduced, Reau et al.[3] have reported the preparation of $Na_2Mo_3O_6$ with an average Mo oxidation state 3.33, but this compound has been prepared only as a polycrystalline material and its crystal structure is not known. Recently, Torardi and McCarley have reported the preparation and structure of, for example, $LiZn_2Mo_3O_8$,[4] $NaMo_4O_6$,[5] and $Ba_{0.62}Mo_4O_6$[6] with average oxidation states for Mo of 3.67, 2.75, and 2.69, respectively. The lithium compound contains a Mo_3O_{13} cluster while the sodium and barium compounds contain octahedral units, Mo_6O_8.

In the belief that these cluster compounds are not isolated examples but are representative of a large family of oxides containing molybdenum in low formal oxidation states, we are undertaking a program aimed at preparing such materials by both solid-state and electrolytic reactions. The latter method has been particularly useful for the preparation of tungsten and molybdenum oxide bronzes[7] and appeared particularly appropriate for our endeavors. Here we report the preparation and crystal structure of $La_3Mo_4SiO_{14}$, a compound with an average Mo oxidation state of 3.75, which contains two distinct structural elements of molybdenum.

Experimental Section

Synthesis and Analysis. All chemicals used in these syntheses were of reagent grade or better. MoO_3 was ignited at 475 °C before use, while La_2O_3 and Nd_2O_3 were treated similarly at 1000 °C. Single crystals of the title compound were prepared by the electrolysis of a melt formed at 1100 ± 10 °C from a mixture of sodium molybdate, molybdenum(VI) oxide, and lanthanum oxide. The reactants were weighed to the nearest 0.01 g and mixed carefully before heating. Typical charges weighed from 25 to 35 g. Smooth platinum-foil electrodes with a nominal surface area of 2 cm^2 were used, and the charge was contained in a Coors porcelain crucible. Although the title compound forms over the range of molar ratios of Na_2MoO_4:MoO_3:La_2O_3 = (3.50–3.00):(3.50–3.00):1.00, reactions at the extremes produce multiphase products and the optimum ratios appear to be about 3.10:3.10:1.00. After the operating temperature was reached, the melt was allowed to equilibrate for 1 h before electrolysis began. Typically, a constant current of 200 mA was passed for 30–40 min. The electrolysis was carried out without a protective atmosphere and was terminated by removing the electrodes from the melt and allowing them to cool to room temperature. The black needles, which grow from the cathode in clusters, were separated from the solidified matrix by washing alternately with hot 5% potassium carbonate solution and hot 2 M hydrochloric acid. Washings were continued until all of the molybdate matrix was removed and the acid washings no longer turned blue, indicating that all the soluble reduced products had been removed. The yield of purified product was small,

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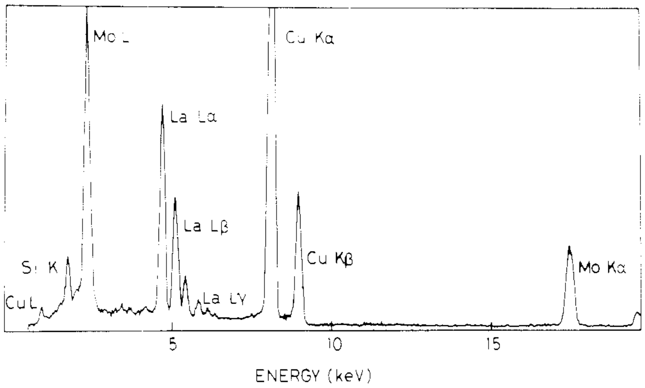

Figure 1. X-ray emission spectrum taken from a microcrystal of $La_3Mo_4SiO_{14}$ (operating voltage 100 kV). The Cu lines arise from the copper mesh used to hold the sample.

Table I. Atomic Positional (Fractional Coordinates) Parameters with Estimated Standard Deviations in Parentheses for $La_3Mo_4SiO_{14}$

atom	x	y	z
La(1)	0.33632 (3)	0.25000	0.12964 (4)
La(2)	0.34551 (3)	0.25000	0.49514 (4)
La(3)	0.53406 (3)	0.25000	0.70272 (5)
Si	0.06570 (14)	0.25000	0.1034 (2)
Mo(1)	0.33799 (3)	0.02297 (10)	0.82016 (4)
Mo(2)	0.21587 (4)	0.25000	0.86093 (5)
Mo(3)	0.50758 (6)	0.2242 (10)	0.00700 (7)
O(1)	−0.0205 (5)	0.25000	0.0529 (7)
O(2)	0.12628 (0)	0.25000	0.99144 (0)
O(3)	0.0820 (3)	0.0010 (9)	0.1766 (4)
O(11)	0.2880 (4)	0.75000	0.7413 (5)
O(12)	−0.2211 (4)	0.25000	0.7938 (6)
O(21)	0.1502 (3)	−0.0002 (10)	0.8020 (4)
O(22)	−0.2696 (3)	0.5098 (8)	0.0340 (4)
O(31)	−0.0996 (4)	0.75000	0.6006 (6)
O(32)	0.0448 (3)	0.0019 (10)	0.6141 (5)
O(33)	0.0926 (4)	0.75000	0.4084 (6)

Table II. Selected Interatomic Distances in Angstroms for $La_3Mo_4SiO_{14}$ with Estimated Standard Deviations in Parentheses

La(1)-O(11B)	2.521 (6)	La(1)-O(22D)	2.548 (4)
La(1)-O(21B)	2.380 (5)	La(1)-O(32C)	2.543 (5)
La(1)-O(21D)	2.380 (5)	La(1)-O(32D)	2.543 (5)
La(1)-O(22A)	2.548 (4)	La(1)-O(33A)	2.747 (6)
La(2)-O(1A)	2.429 (7)	La(2)-O(12A)	2.610 (6)
La(2)-O(2)	2.866 (4)	La(2)-O(21B)	2.557 (4)
La(2)-O(2A)	2.866 (4)	La(2)-O(21D)	2.557 (4)
La(2)-O(3A)	2.768 (4)	La(2)-O(22C)	2.529 (4)
La(2)-O(3C)	2.768 (4)	La(2)-O(22F)	2.529 (4)
La(3)-O(1)	2.981 (5)	La(3)-O(21E)	2.493 (5)
La(3)-O(2B)	2.693 (1)	La(3)-O(32A)	2.467 (5)
La(3)-O(3A)	2.510 (5)	La(3)-O(32E)	2.467 (5)
La(3)-O(3C)	2.510 (5)	La(3)-O(33)	3.185 (5)
La(3)-O(21A)	2.493 (5)		
Mo(1)-Mo(1E)	2.562 (1)	Mo(1)-O(12A)	2.078 (5)
Mo(1)-Mo(1F)	3.081 (1)	Mo(1)-O(22E)	2.015 (4)
Mo(1)-Mo(2)	2.551 (1)	Mo(1)-O(31A)	2.087 (4)
Mo(1)-O(3C)	2.129 (4)	Mo(1)-O(33B)	2.024 (5)
Mo(1)-O(11A)	1.978 (4)		
Mo(2)-O(2)	2.141 (1)	Mo(2)-O(21C)	1.940 (5)
Mo(2)-O(12A)	2.039 (6)	Mo(2)-O(22B)	2.021 (4)
Mo(2)-O(21)	1.940 (5)	Mo(2)-O(22E)	2.021 (4)
Mo(3)-Mo(3A)	3.128 (11)	Mo(3)-O(32C)	2.171 (7)
Mo(3)-Mo(3B)	2.549 (11)	Mo(3)-O(32D)	1.970 (6)
Mo(3)-O(31A)	1.933 (7)	Mo(3)-O(32F)	1.947 (6)
Mo(3)-O(32B)	2.147 (6)	Mo(3)-O(33A)	2.084 (6)
Si-O(1)	1.623 (8)	Si-O(3)	1.646 (5)
Si-O(2A)	1.636 (2)	Si-O(3B)	1.646 (5)

approximately 0.1–0.2 g for a 30-min run in a porcelain crucible.

A semiquantitative emission spectrographic analysis of the needles showed the presence of 0.3–3% by weight of silicon and 0.2–0.9% aluminum. Except for La and Mo, no other elements were observed in concentration above 0.05%. The product was also examined in a JEOL 100CX TEMSCAN analytical electron microscope. X-ray emission spectra taken from individual microcrystallites[8] confirmed that Si and possibly Al are present not as a separate phase but within the needles (Figure 1). A calibration constant for the ratio method[9] was determined with use of standard samples of La–Mo(VI) oxides, and the La:Mo ratio of the needles was found to be 0.745. Atomic absorption spectroscopy indicated a Si:Al ratio of approximately 5. Further, the average oxidation number of molybdenum, as determined by a standard cerimetric method, was found to be 3.82. These results are consistent with the formulation $La_3Mo_4SiO_{14}$ (or approximately $La_3Mo_4Si_{0.8}Al_{0.2}O_{14}$ if the Al content is included), and this is confirmed by the X-ray structure determination.

The synthesis procedure outlined above has also been used to prepare $Nd_3Mo_4SiO_{14}$, whose X-ray diffraction pattern indicates that it is isomorphous with the lanthanum compound. No reliable chemical analysis of this compound has been made, but its unit cell parameters, as determined by Weissenberg photography on a crystal prepared in a porcelain crucible are $a = 17.44 \pm 0.05$ Å, $b = 10.86 \pm 0.02$ Å, $c = 5.64 \pm 0.01$ Å, and $Z = 4$.

Structure Determination. Crystal data: $La_3Mo_4SiO_{14}$, $M_r = 1052.6$, orthorhombic, $a = 17.684$ (4) Å, $b = 5.643$ (1) Å, $c = 11.037$ (2) Å, space group *Pnma*, $V = 1101.4$ (5) Å^3, $F(000) = 1859$, Mo Kα X radiation (graphite monochromator), $\lambda = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 152.1$ cm^{-1}, D_{exptl}(pycnometer) $= 6.40 \pm 0.08$ g/cm^3, $D_{\text{calcd}} = 6.39$ g/cm^3 ($Z = 4$).

Experimental Details. The crystal selected for data collection was of dimensions ca. 0.09 × 0.04 × 0.40 mm, bounded by the faces ⟨010⟩, ⟨100⟩, ⟨001⟩. Diffracted intensities were collected at 295 K for 2.9° $< 2\theta <$ 60° on a Syntex P2_1 four-circle automated diffractometer, by methods described elsewhere.[10] Of the 1857 intensities collected, 1922 were unique, but only 1755 with $I > 4\sigma(I)$ were used in the final cycles of refinement, where $\sigma(I)$ is the estimated standard deviation of the observed intensities based on counting statistics alone. All data were corrected for Lorentz, polarization, X-ray absorption, and extinction effects. The structure was solved by a combination of Patterson and direct-methods techniques. The remaining oxygen atoms were located from successive electron density difference syntheses. The structure was refined by blocked-cascade full-matrix refinement[11] with anisotropic thermal parameters for all atoms. The refinement converged at R_F (R_{wF}) = 0.042 (0.045) for 1755 data, with use of a weighting scheme of the form $w = [\sigma^2(F_o) + 0.00012(F_o)^2]^{-1}$, which gave a satisfactory analysis, where $\sigma(F_o)$ is the error in $|F_o|$ based on counting statistics alone. The final electron density synthesis showed only random fluctuations around the heavy-metal atoms, and none of the more isolated small peaks could be refined as additional oxygen atoms. Scattering factors were taken from ref 12.

The $U(22)$ thermal parameter of Mo(3) was large (5 × $U(11)$ or $U(33)$) in *Pnma* refinement in which Mo(3) was placed on the mirror plane. In the final stages, a displacement of this atom from the mirror plane was allowed, yielding a model that could be interpreted in terms of alternately long and short Mo–Mo distances along the *b* axis, but without long-range order. Such an arrangement could be accommodated without disorder in space group *Pn*2_1*a*, but attempts to refine the structure in this space groups were unsuccessful, probably because the positions of all the other atoms are well described by the higher symmetry space group. Table I lists the atomic parameters with their estimated standard deviations and anisotropic thermal parameters. Selected interatomic distances are given in Table II.

Results and Discussion

The silicon that is found in the title compound clearly comes from the porcelain crucible used for the electrolysis. When

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Table III. Selected Bond Angles in Degrees for $La_3Mo_4SiO_{14}$

Mo(1E)-Mo(2)-Mo(1)	60.3 (0)
Mo(2)-Mo(1E)-Mo(1)	59.8 (0)
Mo(1E)-Mo(1)-Mo(2)	59.8 (0)
Mo(3B)-Mo(3)-Mo(3A)	168.1 (5)
O(22E)-Mo(1)-O(11A)	93.1 (2)
O(22E)-Mo(1)-O(31A)	87.4 (2)
O(22E)-Mo(1)-O(3C)	172.5 (2)
O(22E)-Mo(1)-O(33B)	90.2 (2)
O(22E)-Mo(1)-O(12A)	101.8 (2)
O(11A)-Mo(1)-O(31A)	81.1 (2)
O(11A)-Mo(1)-O(3C)	85.4 (2)
O(11A)-Mo(1)-O(33B)	167.4 (2)
O(11A)-Mo(1)-O(12A)	89.4 (2)
O(31A)-Mo(1)-O(3C)	85.0 (2)
O(31A)-Mo(1)-O(33B)	86.8 (2)
O(31A)-Mo(1)-O(12A)	167.1 (2)
O(3C)-Mo(1)-O(33B)	89.7 (2)
O(3C)-Mo(1)-O(12A)	98.4 (2)
O(33B)-Mo(1)-O(12A)	101.5 (3)
O(2)-Mo(2)-O(21)	77.4 (1)
O(2)-Mo(2)-O(22E)	87.8 (1)
O(2)-Mo(2)-O(12A)	165.4 (2)
O(2)-Mo(2)-O(22B)	87.8 (1)
O(2)-Mo(2)-O(21C)	77.5 (1)
O(21)-Mo(2)-O(22E)	89.2 (2)
O(21)-Mo(2)-O(12A)	92.7 (2)
O(21)-Mo(2)-O(22B)	164.1 (2)
O(21)-Mo(2)-O(21C)	93.2 (3)
O(22E)-Mo(2)-O(12A)	102.9 (2)
O(22E)-Mo(2)-O(12A)	84.2 (1)
O(22E)-Mo(2)-O(21C)	164.1 (2)
O(12A)-Mo(2)-O(22B)	102.9 (2)
O(12A)-Mo(2)-O(21C)	92.7 (2)
O(22B)-Mo(2)-O(21C)	80.4 (2)
O(31A)-Mo(3)-O(32B)	91.2 (3)
O(31A)-Mo(3)-O(32C)	90.8 (3)
O(31A)-Mo(3)-O(33A)	171.6 (6)
O(31A)-Mo(3)-O(32D)	97.1 (2)
O(31A)-Mo(3)-O(32F)	97.5 (3)
O(32B)-Mo(3)-O(32C)	87.1 (3)
O(32B)-Mo(3)-O(33A)	83.4 (3)
O(32B)-Mo(3)-O(32D)	169.6 (3)
O(32B)-Mo(3)-O(32F)	86.2 (3)
O(32C)-Mo(3)-O(33A)	82.6 (3)
O(32C)-Mo(3)-O(32D)	80.9 (3)
O(32C)-Mo(3)-O(32F)	169.4 (3)
O(33A)-Mo(3)-O(32D)	87.6 (3)
O(33A)-Mo(3)-O(32F)	88.5 (3)
O(32D)-Mo(3)-O(32F)	98.8 (3)
O(1)-Si(1)-O(3)	109.5 (3)
O(1)-Si(1)-O(2A)	110.4 (3)
O(1)-Si(1)-O(3B)	109.5 (3)
O(3)-Si(1)-O(2A)	104.8 (2)
O(3)-Si(1)-O(3B)	117.2 (4)
O(2A)-Si(1)-O(3B)	104.8 (2)

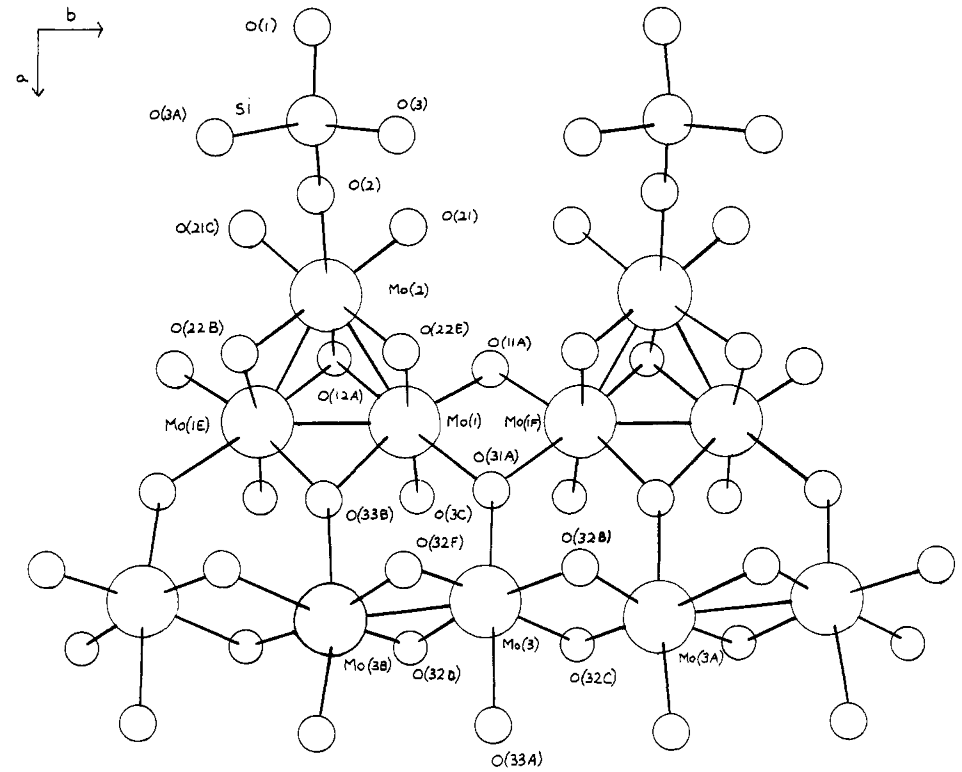

Figure 2. The Mo–O and Si–O units in $La_3Mo_4SiO_{14}$.

a new McDanel, high-density-alumina crucible is used instead of porcelain, the initial product is a mass of small hexagonal plates with a composition close to $LaMo_2O_5$.[13] Older used crucibles yield what appears to be the aluminum analogue of the title compound, i.e. $La_3Mo_4AlO_{14}$.

$La_3Mo_4SiO_{14}$ has a complex structure containing two different structural elements of molybdenum (Figure 2). Two Mo(1) atoms and one Mo(2) atom form a triangle with Mo–Mo distances of 2.550 (1) and 2.562 (1) Å; each molybdenum is approximately octahedrally coordinated by oxygen, giving the unit an overall stoichiometry of Mo_3O_{13}. This unit has previously been found in oxides of general formulas $ABMo_3O_8$[2,14] $AB_2Mo_3O_8$[4] and in molecular species such as $[Mo_3O_4(C_2O_4)_3(H_2O)_2]^{2-}$[15] and $[Mo_3OCl_3(O_2CCH_3)_3(H_2O)_3]^{2+}$.[16] The other Mo atom, Mo(3), is accommodated in infinite chain of edge-sharing octahedra. The displacement of Mo(3) from the mirror plane, although apparently lacking long-range order in the *Pnma* description, suggests that the Mo atoms are paired along the chain, as in MoO_2; the Mo–Mo

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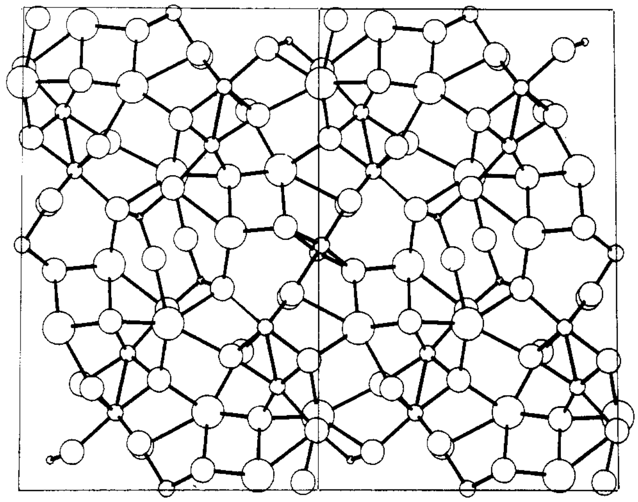

Figure 3. Relationship of the metal and silicon atom arrangement with respect to the oxygen network as viewed down the *b* axis. Spheres of descending size denote La, O, Mo, and Si, respectively.

distances are alternately 2.55 (1) and 3.13 Å, compared with 2.511 (1) and 3.112 (1) Å in MoO_2.

The silicon atom is tetrahedrally coordinated by oxygen with Si–O distances of about 1.64 Å. Bond lengths found typically in feldspar minerals are[17,18] Si–O = 1.60–1.61 Å and Al–O = 1.74–1.75 Å, so that value found here is consistent with a small partial occupancy of this site by Al.

The coordination of each of the three lanthanum atoms is irregular but is based in each case on a trigonal-prismatic arrangement of oxygen atoms. For La(1), two of the large faces are capped, and for La(2), two large faces and the two small faces are capped. La(3) is somewhat more distorted, with one oxygen atom above one of the large faces, and two above another. Thus the coordination numbers of the lanthanums are 8, 10, and 9 for La(1), La(2), and La(3), respectively.

A particularly interesting aspect of this compound is the distribution of electrons among the molybdenum atoms. If we assign the usual oxidation states to La, Si, and O, we are left with nine electrons per asymmetric unit for Mo. Cotton,[19] using an approximate molecular orbital treatment, showed that an Mo_3O_{13} cluster can accommodate up to eight d electrons. The six-electron cluster should be the most stable since the orbitals involved are all strongly bonding while the seventh and eighth electrons will enter an orbital that will be slightly bonding or antibonding. The most plausible distributions in $La_3Mo_4SiO_{14}$ are as follows: seven electrons for Mo_3O_{13} and two per Mo in the chain or eight electrons for Mo_3O_{13} and one per Mo in the chain. Both seven- and eight-electron examples in molybdenum oxides are known, but the observed distances in this compound are between those in $LiZn_2Mo_3O_8$ (Mo–Mo = 2.578 Å, seven electrons) and $Zn_3Mo_3O_8$ (Mo–Mo = 2.580 Å, eight electrons) on the one hand[5] and that in $Zn_2Mo_3O_8$ (2.524 Å, six electrons) on the other.[2] MoO_2, which was cited previously as an example of a compound with very similar chains, contains two electrons per metal atoms. On the other hand, $CrMoO_4$, which has been shown by ESCA studies[20] to contain pentavalent molybdenum, has magnetic properties that are consistent with a strong Mo–Mo interaction.[21] Although the structure of this compound i not known that certainty,[22] it appears to be isomorphous with $CrWO_4$, which has been shown[23] to contain slightly puckered chains of W with alternating long and short W–W distances of 2.616 and 3.162 Å, respectively. Thus, the structure of $La_3Mo_4SiO_{14}$ appears compatible with either of these distributions.

Obviously the electron count has to be modified if we allow for the presence of Al on the Si site. The existence of $La_3Mo_4AlO_{14}$ might appear to be more consistent with the first model, where one would find the more stable trigonal cluster containing only six electrons. If this is so, then the Mo–Mo distances within the cluster would be expected to be very close to those found in $Zn_2Mo_3O_8$ (i.e. close to 2.52 Å).

It is also worth noting that the Mo_3O_{13} triangles are close to each other and to the infinite chain. Thus, two of the MoO_6 octahedra within each triangle share a common edge with adjacent triangles, and the same octahedra share common corners with MoO_6 octahedra in the infinite chain (Figure 2). One could reasonably argue that the chain–cluster combination represents a single unit and that the electrons must be allocated to it as a whole. It should also be noted that these chain–cluster units, which run parallel to the *b* axis, are separated from similar units by about 5.5 Å, which leads one to expect that the electronic properties of these compounds should be highly anisotropic. In an effort to answer these questions, a detailed structural study of the aluminum compound has been initiated along with an examination of the electrical properties of these materials.

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Registry No. $La_3Mo_4SiO_{14}$, 88685-52-3; Na_2MoO_4, 7631-95-0; MoO_3, 1313-27-5; La_2O_3, 1312-81-8; Mo, 7439-98-7.

Supplementary Material Available: Listings of thermal parameters, observed and calculated structure factors, bond distances, and bond angles (20 pages). Ordering information is given on any current masthead page.

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