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New Extended Clusters in Ternary Molybdenum Oxides*

R. E. McCARLEY, K.-H. LII, P. A. EDWARDS, AND L. F. BROUGH

Ames Laboratory, USDOE† and Department of Chemistry, Iowa State University, Ames, Iowa 50011

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Three new compounds representative of different structure types in the family of ternary metal oxides with extended metal–metal bonded arrays are discussed. $InMo_4O_6$ (isomorphous with $NaMo_4O_6$) contains infinite anion chains of condensed octahedral cluster units, $(Mo_4O_6^-)_\infty$, crosslinked to form channels where In^+ cations reside in sites of square pyramidal coordination to oxygen. The linear array of In atoms in the channels, with d(In–In) = 2.8628(4) Å, suggests some degree of In–In bonding, and these interactions may contribute to the metallic conductivity determined for this compound over the range 2–300 K. Infinite chains with Mo_2O_4 repeat units condensed as rhomboidal clusters fused on opposite edges are the outstanding structural feature of $NaMo_2O_4$. The compound also has a double-layer lattice MoO_2 with Na^+ ions fractionally occupying octahedral coordination sites between alternate layers. The compound $Ca_{5.45}Mo_{18}O_{32}$ contains three different kinds of cluster chains with Mo_1, Mo_2, and Mo_4 repeat units. Metal cluster electron counts on the three different repeat units, estimated from Mo–O bond strength–bond distance relations, are reflected in the formula $Ca_{5.45}(MoO_3^{2.26-})_2(Mo_2O_{3.5}^{0.22-})_4(Mo_4O_6^{2.65-})_2$.

Introduction

Until recently metal oxide phases with readily apparent extended arrays of metal–metal bonded units were relatively rare. The β-modification of ReO_2 (*1*), NbO (*2*), and the platinum bronze phases (*3*) which contain linear chains of weakly metal–metal bonded, square planar coordinated platinum atoms, were essentially the only structurally well-characterized examples. Since the dividing lines are rarely distinct one may also include in this category the early transition metal suboxides (*4*), where the bonding is surely dominated by metal–metal interactions similar to those in the pure elements. The dioxides with the undistorted rutile structure (*5*), viz. TaO_2, RuO_2, OsO_2, RhO_2, and IrO_2, though possessing metallic character, may be excluded from this category because their structures are dictated largely by the metal–oxygen bonding, and the metal–metal interactions at distances of >3.0 Å are much weaker. In the interesting case of $LiNbO_2$ (*6*) the conclusions about metal–metal bonding are uncertain. This structure is like that of $2H$–MoS_2 with Li intercalated into the van der Waals gap. The Nb–Nb distance of 2.90 Å within

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the hexagonal close-packed layers of Nb atoms are obviously short enough for a strong contribution from Nb–Nb bonding, but here it is not clear whether this is sufficient to dictate the structure.

The discovery of $NaMo_4O_6$ (*7*) greatly expanded our vision of new chemistry which might be possible in metal–metal bonded oxide systems. This structure, consisting of Mo_6O_{12}-type octahedral cluster units condensed by fusion on opposite edges to form infinite anion chains $[(Mo_2Mo_{4/2}O^{i}_{8/2}O^{i-a}_{2/2}O^{a-i}_{2/2})^{-}]_{\infty}$ was unprecedented among those known for oxide compounds. However, related structures were found somewhat earlier for Sc_5Cl_8 (*8*) and reduced halides of the lanthanide elements (*9*). We thus initiated a synthetic program to explore the structures that might exist in this new realm. Only new compounds with extended metal–metal bonded arrays (infinite chains) will be included in this discussion.

Synthesis

Among the compounds discussed here not all have been produced in single phase form. In general the composition of each new compound has been established through a combination of electron microprobe analysis and X-ray structure refinement of single crystals selected from reaction mixtures. Once the composition was established reactions were attempted for synthesis of the pure compound in polycrystalline form from stoichiometric mixtures of metal and metal oxide in pressed pellets. According to Guinier X-ray powder patterns single phase reaction products have been obtained in the following cases:

(i) $3Na_2MoO_4 + 8MoO_3 + 13Mo \rightarrow 6NaMo_4O_6$

(pressed pellet in sealed Mo tube, 1100°C, 5*d*)

(ii) $In + 2MoO_3 + 2Mo \rightarrow InMo_4O_6$

(pressed pellet in sealed fused silica tube, 895°C, 28*d*)

(iii) $9Sc_2O_3 + 30ZnO + 37MoO_3 + 59Mo \rightarrow 24Sc_{0.75}Zn_{1.25}Mo_4O_7$

(pressed pellet in sealed Mo tube, 1450°C, 7*d*)

(iv) $5.45CaMoO_4 + 3.40MoO_3 + 9.15Mo \rightarrow Ca_{5.45}Mo_{18}O_{32}$

(pressed pellet in sealed Mo tube, 1435°C, 3*d*).

In the case of $NaMo_2O_4$ pure single phase material has not yet been prepared. Single crystals, in the form of thin platelets, were selected from a reaction conducted under the following conditions.:

(v) $1.64Na_2MoO_4 + 2.3MoO_2 + Mo \rightarrow NaMo_2O_4$ + other products

(loose powder, sealed Ni tube, 900°C, 3*d*).

Structure Types

A complete listing of the structure types that have been elucidated in detail is given in Table I. All of these structures are characterized by infinite Mo–Mo bonded chains consisting of either Mo_4 or Mo_2 repeat units. The chains having Mo_4 repeat units may be considered as condensed octahedral cluster units sharing opposite edges, derived from the Mo_6O_{12} discrete cluster type by elimination of the two O atoms on the edges to be shared (*14*). Sharing of O atoms between repeat units leads to the connective formula $Mo_2Mo_{4/2}O_2O_{8/2}$. Crosslinking of these chains through Mo–O–Mo bridge bonding in different ways then provides the framework and coordination sites for the ternary metal cations in the various structure types, **I–IV.** The chains having Mo_2 repeat units conceptually are derived by condensation of rhomboidal clusters Mo_4O_{16} by sharing metal at-

TABLE I

STRUCTURE TYPES FOR COMPOUNDS HAVING INFINITE CHAIN STRUCTURES AMONG REDUCED MOLYBDENUM OXIDE PHASES

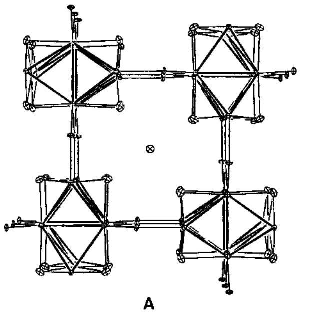
	Structure type	Crystal class	Lattice constants	Space group	Isomorphous members	Ref.
I	$NaMo_4O_6$	Tetragonal	$a = 9.570(3)$ $c = 2.8634(8)$	*P4/mbm*	MMo_4O_6 (M = K, Rb, In) $Sn_{0.9}Mo_4O_6$	*8* *11*
II	$Ba_5(Mo_4O_6)_8$	Orthorhombic	$a = 9.517(1)$ $b = 9.822(1)$ $c = 22.813(4)$	*Pbam*	$Sr_xMo_4O_6$?	*12*
III	$Sc_{0.75}Zn_{1.25}Mo_4O_7$	Orthorhombic	$a = 6.085(1)$ $b = 17.002(4)$ $c = 5.764(1)$	*Imam*	$M_xM'_{2-x}Mo_4O_7$[M, M' = $Ti_{0.5}Zn_{1.5}$, $Sc_{0.5}Fe_{1.5}$, $Fe(Fe_{0.9}Mo_{0.1})$, $Zn(Zn_{0.4}Al_{0.5}Mo_{0.1})$]	*13*
IV	$Mn_{0.7}Mo_4O_{5.5}$	Monoclinic	$a = 9.859(3)$ $b = 16.921(4)$ $c = 2.846(1)$ $\beta = 94.94(4)$	*P2₁/a*	None	*14*
V	$Na_{0.9}Mo_2O_4$	Monoclinic	$a = 12.448(9)$ $b = 2.893(3)$ $c = 4.934(3)$ $\beta = 104.02(7)$	*C2/m*	None	This work
VI	$Ca_{5.45}Mo_{18}O_{32}$	Monoclinic	$a = 24.234(7)$ $b = 2.8503(7)$ $c = 9.875(7)$ $\beta = 109.82(4)$	*C2/m*	None	This work

oms on opposite edges and O atoms between units, as indicated by the connective formula for **V**, $Na(Mo_{4/2}O_2O_{8/2}O_{6/3})$. In this case the metal chains are included between close-packed layers of O atoms, and the Na^+ ions are located in partially occupied, octahedral coordination sites between alternate layers.

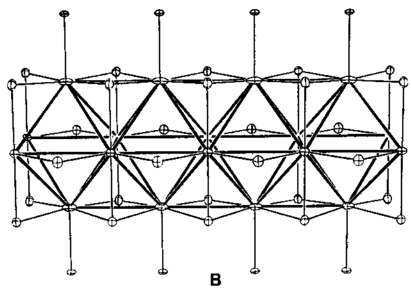
Structure type **VI** is the most complicated found so far, in that three types of infinite chains occur within the same structure. This is indicated in the formula $Ca_{5.45}(MoO_3)_2(Mo_2O_{7/2})_4(Mo_4O_6)_2$ which reflects the presence of chains containing fused rhomboidal units as in **V**, fused octahedral units as in **I–IV**, and single atom chains like those found in the M–M bonded dioxides having the distorted rutile structure, e.g., MoO_2 (*15*). Here there is unusual difficulty in assessing the apportionment of electrons for metal–metal bonding within the three kinds of repeat units. From the formula we may assume that a total of 10.9 electrons is transferred from Ca to the molybdenum oxide chains, but in what proportion are they distributed? This aspect has been examined and resolved within reasonable limits as discussed in a subsequent section.

Three of the compounds listed in Table I will be discussed in more detail. Each was chosen as a new compound representative of a very different structure type, as presenting unique problems in the interpretation of electron counting and bonding features, and as presenting interesting variants of important physical properties. We have thus chosen $InMo_4O_6$, type **I**, $NaMo_2O_4$, type **V**, and $Ca_{5.45}Mo_{18}O_{32}$, type **VI**, for this purpose.

$InMo_4O_6$. This compound is isomorphous with $NaMo_4O_6$. A view of the structure is shown in Fig. 1, which depicts the infinite Mo_4O_6 chains running parallel to the unique axis, and position of the In atoms in the channels created by crosslinking of the chains. Both analytical data and X-ray structure refinement show that the composition is very close to stoichiometric In Mo_4O_6. The In atoms are located in sites slightly displaced (0.28 Å) from the plane of four equidistant O atoms, d(In–O) =



A



B

FIG. 1. (A) A three-dimensional view down the c axis of $InMo_4O_6$. (B) The Mo_4O_6 cluster chain of In Mo_4O_6 as viewed perpendicular to the chain axis. Heavy lines are Mo–Mo bonds and thin lines are Mo–O bonds.

2.390(7) Å, each of which belongs to a separate Mo_4O_6 chain. This coordination geometry for In suggests that a sterically active lone pair of electrons projects radially away from the InO_4 pyramid, and that the cation is present as In^+. Confirmation of In(1+) comes from the In–O bond strength sum computed from the relation of Brown and Wu (*16*), $s(\text{In–O}) = [d(\text{In–O})/1.959]^{-7.0} = (2.390/1.959)^{-7.0} = 0.25$; $\Sigma s = \text{valence} = 4(0.25) = 1.00$. The latter is also consistent with a formal charge of -1.15 on the Mo_4O_6 units of the anion chains, computed in a similar way from the Mo–O bond strength–bond distance relation $s(\text{Mo–O}) = [d(\text{Mo–O})/1.882]^{-6.0}$ (*17*).

In this structure linear chains are formed from the In atoms, which are spaced only 2.8628(4) Å apart within the channels. W may then ask if In–In bonding is important in these chains. A comparison of this distance with In–In distances in the metal, 3.24 and 3.37 Å, suggests that In–In bonding may be important. However, In–In distances in compounds where metal–metal bonding is more certain, e.g., In_6S_7 (*18*), γ-InSe (*19*), and In_4Se_3 (*20*), average about 2.76 Å, and these usually contain In atoms in a higher formal oxidation state. We thus conclude that In–In bonding in $InMo_4O_6$ is likely to be weak, but may contribute in an important way to the electrical conductivity and other physical properties. Resistivity measurements parallel to the c-axis on a single crystal in the range 2–300 K clearly demonstrate that $InMo_4O_6$ is metallic, with $\rho(\text{parallel}) = 160 \times 10^{-6}$ ohm cm at 298 K.

The Mo–Mo bond distances within the $Mo_4O_6^-$ anion chains of $InMo_4O_6$ are quite similar to those in $NaMo_4O_6$ (*7*), as expected if the compounds are indeed isoelectronic. This is also confirmed by the Mo–O bond strength sums which indicate that the anion chains in $NaMo_4O_6$ and $InMo_4O_6$ bear the same charge.

$NaMo_2O_4$. Essential features of this structure are shown in Figs. 2 and 3. The layer arrangement shown in Fig. 2 is similar to that in the $CdCl_2$ or CdI_2 structures, in that the metal atoms are included in octahedral sites between close-packed oxide layers. Octahedral sites between every other layer are occupied fully by Mo atoms, and these sites in the alternate layers are approximately half-occupied by Na ions. Thus the Na ions can be viewed as intercalated within the van der Waals gap of the MoO_2 layer lattice. Within the MoO_2 layers the Mo atoms are shifted from the center of their octahedral sites toward neighboring Mo atoms such that the infinite chains of fused rhomboidal cluster units are formed parallel to the short b axis, as shown in Fig. 3. Each Mo atom thus is bonded to two Mo atoms parallel to the chain direction at 2.893(2) Å, and to two other Mo via the zigzag bonds at 2.535(2) Å. From the for-

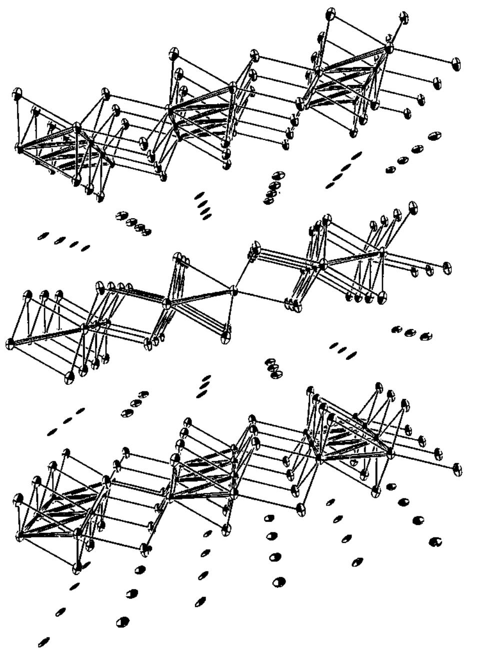


FIG. 2. The structure of $NaMo_2O_4$ as viewed down the b axis. Mo–Mo bonds are indicated by multiple lines, Mo–O bonds by single lines. Na atoms shown by unconnected ellipsoids.

mula $NaMo_2O_4$ we conclude that each Mo atom has 2.5 electrons (average) for participation in the metal–metal bonding. If the short bonds are considered as normal electron pair bonds, each Mo must contribute one electron to each of these bonds. The remaining 0.5 electron/Mo must then enter into the long bonds in the chain direction. Each long bond should then attain bond order 0.25, in rough agreement with the bond order, 0.34, calculated from d = 2.893 Å using the Pauling (*21*) relation $d(\text{obs.}) = d_1 - 0.6 \log n$, where d_1 is the single bond distance, 2.614 Å, computed from the distances in Mo metal, and n is the bond order. Equal spacing of the Mo atoms along the chain direction suggests that the bonding is delocalized and that the compound should exhibit high conductivity in the b direction. Interchain distances, d(Mo–Mo) = 3.200(2) Å, suggest that the interchain Mo–Mo interactions are very weak. Similarly, interlayer interactions should be even weaker, thus conductivity in both the a and c directions is expected to be quite small.

The structure of $NaMo_2O_4$ stands in sharp contrast to that of $Ba_{1.14}Mo_8O_{16}$ (*22*) and $K_2Mo_8O_{16}$ (*23*) where similar chains of Mo atoms are broken into discrete rhomboidal cluster units. The electron/Mo ratios, 2.28 for $Ba_{1.14}Mo_8O_{16}$ and 2.50 for $NaMo_2O_4$, are sufficiently close that the structural difference of discrete cluster units vs extended chains is not readily understood. In fact, the 2.50 e/Mo in $NaMo_2O_4$ should be ideal for forming the 10 e, completely bonded rhomboidal cluster unit like those found in the regular cluster units of $Ba_{1.14}Mo_8O_{16}$. Experiments are in progress to explore the possible oxidation–reduction chemistry of $NaMo_2O_4$ according to

$$NaMo_2O_4 = Na_{1-x}Mo_2O_4 + xNa^+ + xe^- \quad (1)$$

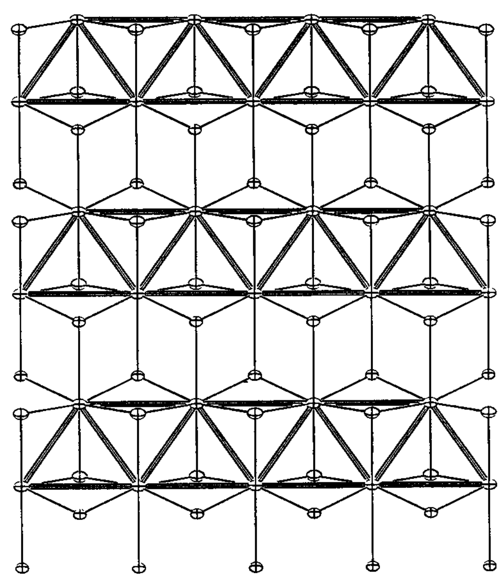


FIG. 3. The structure of the MoO_2 layers of $NaMo_2O_4$ as viewed perpendicular to the layer. Multiple lines represent Mo–Mo bonds, single lines Mo–O bonds.

$$NaMo_2O_4 + Na^+ + 1e^- = Na_{1+x}Mo_2O_4. \quad (2)$$

By such reactions it may be possible to vary the e/Mo ratio in the extended chains and thereby discern if the chain construction is altered significantly as a function of this quantity. It appears that the Na^+ occupation within the layers, which is only 50% in $NaMo_2O_4$, should be variable over the stoichiometric range $Na_{2-x}Mo_2O_4$, with $0 \leq x \leq 2$.

$Ca_{5.45}Mo_{18}O_{32}$. A view of this structure as projected down the short axis is shown in Fig. 4. Principal features include three kinds of extended chains interconnected by Mo–O–Mo bridge bonding to provide channels in which the Ca^{2+} ions are located. Stoichiometrically the extended chains occur as single-atom, two-atom, and four-atom repeat units in the ratios 2/4/2, respectively, as indicated by the anion formula units MoO_3^{n-}, $Mo_2O_{3.5}^{n-}$, and $Mo_4O_6^{n-}$, respectively. The single-atom chains are constructed like those of the metal atom chains extended along the c-axis of the rutile structure, but having the metal atoms drawn together in pairs to form alternately bonded and nonbonded distances (Mo5–Mo5) of 2.560(9) and 3.135(9) Å, respectively. Thus the metal atoms in these chains are bonded in the same fashion as those in the MoO_2 (*15*) distorted rutile structure.

In the chains containing the two-atom repeat units the metal–metal bonding is exactly like that found in the layered compound $NaMo_2O_4$. The intrachain Mo–Mo distances are 2.850(1) and 2.546(2) Å, respectively, for the bonds parallel to the chain direction (Mo3–Mo3), and the zigzag bonds between atoms on parallel edges of the fused rhomboids (Mo2–Mo3). These distances compare closely with the related distances in $NaMo_2O_4$ and indicate the anion chains must have comparable e/Mo ratios in the two compounds. This point is discussed further below.

The construction of the chains containing the four-atom repeat units is exactly like those found in $NaMo_4O_6$ (or $InMo_4O_6$), except that the average Mo–Mo intrachain bond distance is somewhat smaller, indicating perhaps a higher average cluster-electron count in the $Mo_4O_6^{n-}$ units of this compound.

For help in assessing the anion charge and metal cluster electron count on the separate chains in this complex structure we turn to the well-established empirical bond strength–bond distance relation for the

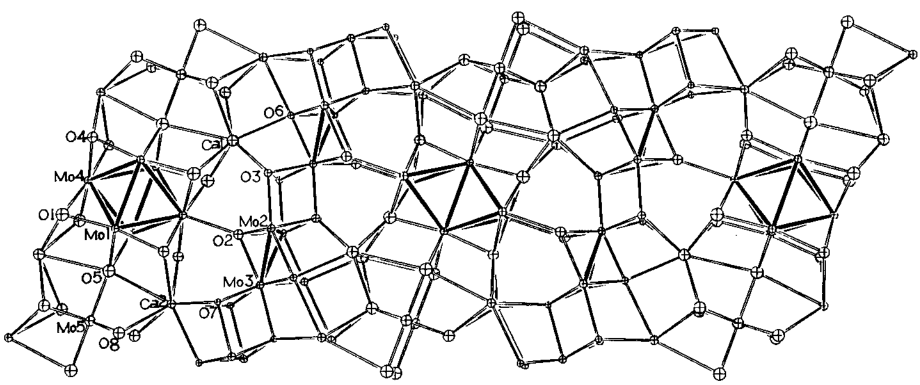


FIG. 4. The unit cell of $Ca_{5.45}Mo_{18}O_{32}$ as projected down the b axis. Positions of the various atoms in the unit cell are indicated. Mo1 and Mo4 belong to Mo_4O_6 units, Mo2 and Mo3 belong to $Mo_2O_{3.5}$ units, Mo5 to the single-atom chains.

TABLE II
VALENCE OF MOLYBDENUM AND NET ANION CHARGE FOR REPEAT UNITS OF CHAINS IN $Ca_{5.45}Mo_{18}O_{32}$

Repeat unit	Valence of Mo	Net anion charge ($q-$)
MoO_3	Mo5 3.74	2.26
$Mo_2O_{3.5}$	Mo2 3.42	0.22
	Mo3 3.36	
Mo_4O_6	Mo1 2.20	2.65
	Mo4 2.47	

Mo–O bonds (*16, 17*). The average oxidation state or valence of each Mo atom in the structure can be obtained by summing over the bond strength s for all of the Mo–O bonds attached to that atom, as given in

$$s = [d(\text{Mo–O})/1.882]^{-6.0} \quad (3)$$

$$\Sigma s(\text{Mo}_i) = \text{valence } (\text{Mo}_i). \quad (4)$$

Determination of the valence of each Mo then permits calculation of the net anion charge for each kind of repeat unit through the assumption that each O atom bears a formal charge of -2, as given in

$$q = \sum_i n_i v_i(\text{Mo}) - 2n(\text{O}), \quad (5)$$

where q is the formal anion charge, n_i is the number of Mo atoms of type i in the repeat unit, v_i is the valence of Mo of type i, and $N(0)$ is the number of oxygen atoms in the repeat unit. The results of these calculations for the three structural units of $Ca_{5.45}Mo_{18}O_{32}$ are given in Table II. In these computations an error of one standard deviation of the M–O bond distance results in an error of 0.01 to 0.02 in the M–O bond strength. Since positive and negative deviations are equally likely the average error in the quantity Σs should also be on the order of 0.02, but the maximum error should be ca. ± 0.1 valence unit.

If the results of these calculations are valid the sum of the anion charges per formula unit should be equal to the total cation charge from Ca^{2+}, i.e., $2(5.45) = 10.9$. We thus have for the formula $Ca_{5.45}(MoO_3^{m-})_2(Mo_2O_{3.5}^{n-})_4(Mo_4O_6^{p-})_2$ the equation

$$\begin{aligned}\Sigma q^- &= 2m + 4n + 2p \\ &= 2(2.26) + 4(0.22) \\ &\quad + 2(2.65) = 10.7. \quad (6)\end{aligned}$$

Within the expected maximum error of about ± 0.1 in the charge of each anion the agreement $\Sigma q^+ = 10.9$ and $\Sigma q^- = 10.7$ is extremely good.

A comparison of the metal cluster electron count for the three repeat units in $Ca_{5.45}Mo_{18}O_{32}$ with those of the same units in related compounds is instructive. From $MoO_3^{2.26-}$ we obtain 2.26 *e*/Mo for the Mo–Mo bonding in the single-atom chains, which compares favorably to 2.0 *e*/Mo for the bonding in MoO_2. That the *e*/Mo ratio is variable for structures with such single-atom chains is shown by the compound $LiMoO_2$ (*24*) where the observed Mo–Mo distance, 2.46 Å, is somewhat shorter than that in MoO_2, 2.52 Å (*15*). The charge of -0.22 on the $Mo_2O_{3.5}$ repeat unit gives a 5.22 *e*/Mo unit, nearly the same (probably within the margin of error) as the 5.00 *e*/Mo_2 unit in $NaMo_2O_4$. As noted above the nearly equal Mo–Mo bond distances within these units in the two compounds reflect this agreement in the bonding electron count. Finally, we may compare the metal cluster electron count for the Mo_4O_6 repeat units with those in other compounds containing these units. This comparison is given in Table III where it is seen that the anion charge and MCE count of $Ca_{5.45}Mo_{18}O_{32}$ are as high as those on any of the other compounds known to contain chains with the same type of repeat unit. The structure of $Ca_{5.45}Mo_{18}O_{32}$ is unique among these compounds in having the cation positions only partially occupied. Here the Ca positions are only 68.1% occupied, whereas the

TABLE III

VALENCE OF Mo ATOMS, ANION NET CHARGE, AND METAL CLUSTER ELECTRON COUNTS (MCE) FOR COMPOUNDS CONTAINING CHAINS WITH Mo_4O_6 REPEAT UNITS

Compound	Valence[a] Mo (waist)	Valence[a] Mo (apex)	Anion charge[a] (q^-)	MCE[b]
$NaMo_4O_6$	2.46	3.11	0.85	12.8
$InMo_4O_6$	2.46	2.96	1.15	13.2
$Sc_{0.75}Zn_{1.25}Mo_4O_7$	.2.04	2.73	2.46[c]	14.5
$Ti_{0.5}Zn_{1.5}Mo_4O_7$	2.08	2.76	2.33[c]	14.3
$Ca_{5.45}Mo_{18}O_{32}$	2.20	2.47	2.65	14.6

[a] See text for method of determination.
[b] Determined from formula with anion charge of $q-$.
[c] Anion charge based on Mo_4O_6 unit; charge will be two units greater for Mo_4O_7 units.

formula for complete occupation would be $Ca_8Mo_{18}O_{32}$. Why then does the compound choose the particular composition exhibited?

We find that a single crystal of $Ca_{5.45}Mo_{18}O_{32}$ is a semiconductor with a small band gap of 0.08 eV as determined from log ρ vs T^{-1} over the range 30 to 298 K. Evidently at this particular composition the conduction band is filled. If we assume that all of the metal–metal bonding states within the extended chains are filled at this point, we may thereby derive an estimate of the maximum number of electrons which can populate the individual chains. This then is the significance attached to the MCE counts determined for the cluster units in this particular structure. Notably the anion charge and MCE count for the Mo_4O_6 repeat unit is highest for the calcium compound and may well represent the maximum value attainable for this kind of chain. Further work will be necessary to see if additional cations can be added to this structure to test this hypothesis.

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