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# Halide and Chalcogenide Clusters of the Early Transition Metals

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# Halide and chalcogenide clusters of the early transition metals

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In the last decade remarkable progress has been made in the cluster chemistry of the early transition elements. Earlier work on the metal halide cluster compounds of Nb, Ta, Mo, W and Re served to establish the promise and potential in this area. Now cluster chemistry has been extended to halides of Sc, Y, the lanthanides, Zr and Hf, as well as to oxides, sulphides and selenides of Nb, Ta, Mo and Re. After a brief survey of significant developments in these areas, attention is focused on results from recent work on Mo and W cluster compounds. The discussion includes syntheses, structures and properties of some novel halide clusters, but major emphasis is devoted to new ternary and quaternary molybdenum oxides prepared at high temperatures. Among these solid-state materials are found discrete cluster arrays ($LiZn_2Mo_3O_8$, $Zn_3Mo_3O_8$, and $Ba_{1.14}Mo_8O_{16}$) and structures with extended metal–metal bonding ($NaMo_4O_6$, $Ba_5(Mo_4O_6)_8$, $Sc_{0.75}Zn_{1.25}Mo_4O_7$ and $Ti_{0.5}Zn_{1.5}Mo_4O_7$).

## INTRODUCTION

In recent years there has been an explosive growth in our knowledge of metal–metal bonded compounds of the early transition metals, extending even into the lanthanides. This growth has come as a result of the experimental realization that reactions leading to reduction and formation of compounds with these elements in reduced oxidation states must be performed in special non-contaminating containers, often at high temperatures, and often for an extended time, e.g. weeks or months (Corbett 1981 *a*). Since reduced compounds of these elements generally react with silica at high temperature, the use of inert, sealed metal containers is dictated. In many reactions the metallic element of the compound to be formed is used as the reducing agent, e.g. as between the metal and its normal halide. The desired reaction may lack suitable gaseous or liquid phases for rapid material transport between reactants, or the surface of the metal may become blocked by the formation of an adherent film. If such conditions pertain, the desired reaction can be retarded to such a degree that thermodynamically favoured products are missed by the experimenter, and the premature conclusion reached that new reduced phases are not formed in the system. Such problems have indeed delayed progress in the development of metal cluster chemistry for particularly the lanthanide, Group III and Group IV transition elements (Corbett 1980). To some extent these problems also have plagued the realization of extensive cluster chemistry in metal chalcogenide systems of the Group V and Group VI elements. Much of the recent work reported here for molybdenum oxide compounds is illustrative of this point.

## MILESTONE COMPOUNDS (STRUCTURES)

A collection of important compounds whose discovery and structure elucidation marked turning points in the further development of cluster chemistry for the early transition elements in Groups III, IV and V is given in table 1. It is remarkable that essentially all of the cluster chemistry for the lanthanide, Group III and Group IV elements has been developed within the last 10 years. From the number of compounds already known it is apparent that this area will continue to grow and mature. Because excellent discussions of the recent results in this area have been published, the systems will not be elaborated further (Corbett 1980, 1981; Simon 1981).

TABLE 1. MILESTONE CLUSTER COMPOUNDS OF THE EARLY TRANSITION METALS AND SUBSEQUENT DISCOVERIES

| periodic group | compound | cluster type | subsequent discoveries |
|---|---|---|---|
| III[a] | $Sc_7Cl_{12}$ | $M_6X_{12}$ | $La_7I_{12}$, $Ce_7I_{12}$, $Pr_7I_{12}$, $Gd_7I_{12}$, $Er_7I_{12}$, $Lu_7I_{12}$ |
| | $Gd_2Cl_3$ | $[M_4X_6]_\infty$ | $Y_2Cl_3$, $Y_2Br_3$, $Gd_2Br_3$, $Tb_2Cl_3$, $Tb_2Br_3$, $Er_2Cl_3$, $Tm_2Cl_3$ |
| | $Sc_5Cl_8$ | $[MX_2 \cdot M_4X_6]_\infty$ | $Gd_5Br_8$, $Tb_5Br_8$ |
| | $Sc_7Cl_{10}$ | $[MX_2 \cdot M_6X_8]_\infty$ | $Er_7I_{10}$ |
| | $Er_4I_5$ | $[M_4X_5]_\infty$ | — |
| | ScCl | XMMX layers | YCl, YBr, LaCl, LaBr, CeCl, CeBr, PrCl, PrBr, NdBr, GdCl, GdBr, TbCl, TbBr, DyBr, HoCl, HoBr, ErBr |
| IV[a] | $Zr_6Cl_{15}$ | $M_6X_{12}$ | $Zr_6Cl_{12}$, $Zr_6Br_{12}$, $Zr_6I_{12}$, $Zr_6Cl_{12} \cdot M_2ZrCl_6$ (M = Na, K, Cs) |
| | $ZrI_2$ | zig-zag chain | |
| | ZrCl | XMMX layers | ZrBr, HfCl, $ZrClH_{0.5}$, $ZrClH_{1.0}$, $ZrBrH_{0.5}$, $ZrBrH_{1.0}$ |
| V | $Nb_3Cl_8$[b] | $M_3X_{13}$ | $Nb_3Br_8$[c], $Nb_3I_8$[c] |
| | $CsNb_4Cl_{11}$[d] | $M_4X_{16}$ | $CsNb_4Br_{11}$ |
| | $Nb_6Cl_{14} \cdot nH_2O$[e] | $M_6X_{12}$ | $Nb_6Cl_{14}$[f], $Nb_6F_{15}$[g], $Ta_6Cl_{15}$[h], $Ta_6Br_{15}$[h], $Ta_6I_{14}$[i], $Mg_3Nb_6O_{11}$[j] |
| | $NbI_{11}$[k] | $M_6X_8$ | $HNb_6I_{11}$, $CsNb_6I_{11}$, $CsHNb_6I_{11}$ |

*References:* [a], Corbett (1980, 1981), Simon (1981) and references therein; [b], Schafer & von Schnering (1964); [c], Simon & von Schnering (1966); [d], Broll *et al.* (1969); [e], Harned (1913); [f], Simon *et al.* (1965); [g], Schäfer *et al.* (1965); [h], Bauer & von Schnering (1968); [i], Bauer *et al.* (1965); [j], Marinder (1977); [k], Imoto & Simon (1982) and references therein.

For the transition elements of Group VI, new clusters and compounds with extended metal–metal bonding have been discovered at a startling pace in the last 10 years. Excluding the interesting variety of metal–metal bonded dimers, before 1970 the only discrete cluster compounds known were the trinuclear $M_3X_{13}$ type first elucidated in the compound $Zn_2Mo_3O_8$ (McCarroll *et al.* 1957) and derivatives based upon the $M_6X_8^{4+}$ metal halide units (Cotton & Wilkinson 1980). Subsequently, many new cluster types have been found with both halide and chalcogenide bridging ligands, and the number of metal atoms ranging from three to twelve in the discrete units. Still more recent work has demonstrated the stability of structures with infinite chains of metal–metal bonded repeat units consisting of metal octahedra sharing edges or faces. Such compounds offer characteristics of both the elemental metals from which they are formed and the more conventional isolated cluster species. The most recent progress in these areas with emphasis on work conducted in this laboratory is summarized below according to cluster size (nuclearity).

One further note should be added here. Because space does not permit coverage of all recent work, some important compound types will not be included in this discussion. Most notable among these are the exciting and intensively studied ternary molybdenum sulphide and selenide compounds $M_xMo_6S_8$, $M_xMo_6Se_8 \cdot Mo_9Se_{11}$, $M_xMo_6S_8 \cdot Mo_{12}S_{14}$ and $MMo_3S_3$, often referred to as the 'Chevrel phases' (Chevrel *et al.* 1971). Several excellent discussions and reviews of these compounds have been published recently and the interested inquirer should consult these references (Yvon 1979; Fischer 1978; Corbett 1981; Burdett 1982).

## TRINUCLEAR CLUSTERS

### $M_3X_{13}$ *cluster type*

The earliest discovery of trinuclear cluster compounds was made in 1957 by McCarrol *et al.* (1957) during their examination of phases formed in the ternary molybdenum oxide system MO–$MoO_2$. This work established a series of compounds $M_2^{II}Mo_3O_8$ with $M^{II}$ = Mg, Mn, Fe, Co, Ni, Zn or Cd, all isomorphous with the structure determined for $Zn_2Mo_3O_8$ (Ansell & Katz 1966). The structure of the triangular cluster unit shown in figure 1 consists of three $MoO_6$ octahedra sharing common edges such that each cluster unit is bound to 13 O atoms, hence the formulation as $Mo_3O_{13}$($M_3X_{13}$) cluster type. Oxygen atoms are shared between cluster units in the hexagonal lattice as indicated in the connective formula $Zn_2Mo_3O_4O_{\frac{6}{2}}O_{\frac{3}{3}}$. Strong metal–metal bonding is indicated by diamagnetism and the short Mo–Mo distance, 2.524 (2) Å,† for the equivalent edges of the cluster units in $Zn_2Mo_3O_8$. Because each $Mo^{IV}$ atom may contribute two electrons to the Mo–Mo cluster bonding, a total of six metal cluster electrons (m.c.es) are available to form three bonds, and thus each edge of the triangle may be considered as a Mo–Mo single bond. A subsequent m.o. treatment of the bonding by Cotton (1964) confirmed this assessment. In $C_{3v}$ symmetry the nine d-orbitals ($t_{2g}$ type) not used in σ-bonding to O atoms were used to construct the m.o. level ordering $1a_1^2 + 1e^4$ (bonding), $2a_1$ (essentially non-bonding) and $2e + 3e + a_2$ (antibonding). I shall return to the question of the bonding or antibonding character of the $2a_1$ orbital later.

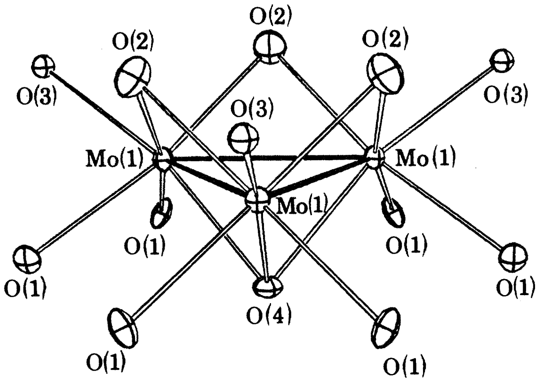

FIGURE 1. The structure of clusters of the type $M_3X_{13}$. The atom labelling scheme is that used in discussion of the bonding in $Zn_2Mo_3O_8$, $LiZn_2Mo_3O_8$ and $Zn_3Mo_3O_8$.

Since the initial discovery of this class of compounds, many new derivatives having the same cluster type have been characterized. These include a second solid-state series $LiM^{III}Mo_3O_8$, with $M^{III}$ = Sc, Y (Donohue & Katz 1964) and lanthanides from Sm to Lu (Kerner-Czescleba & Tourne 1976), and many molecular complexes. Notable among the latter are $W_3O_4F_9^{5-}$, the first tritungsten cluster (Mattes & Menneman 1977); $W_3(CCH_2CMe_3)O_3Cr_3(O_2CCMe_3)_{12}$ (Katovic & McCarley), the first unit of this kind with a face-bridging alkylidyne ligand;

$$Mo_3OCl_3(O_2CMe)_3(H_2O)_3^{2+}$$

(Bino *et al.* 1979), the first such cluster with eight m.c.es; and the recent identification (Murmann & Shelton 1980) of $Mo_3O_4(H_2O)_9^{4+}$ as the red aquo-ion of $Mo^{IV}$ previously identified as a dimer (Ardon & Pernick 1973; Cramer *et al.* 1979). In each of these cases the M–M bond distances fall

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† 1 Å = $10^{-10}$ m = $10^{-1}$ nm.

within the narrow range 2.51–2.61 Å. The Mo–Mo distance of 2.550(2) Å for the species with 8 m.c.es is especially interesting because it indicates that the addition of two electrons to the $2a_1$ m.o. has very little effect on the Mo–Mo bonding. However, the $Mo_3OCl_3(O_2CMe)_3(H_2O)_3^{2+}$ unit has three edge-bridging Cl atoms instead of the O atoms typical of other species, and their effect on Mo–Mo bond distances must also be considered.

TABLE 2. SOME IMPORTANT BOND DISTANCES (ÅNGSTRÖMS) IN $Zn_2M_3O_8$, $LiZn_2Mo_3O_8$ AND $Zn_3Mo_3O_8$

| bond† | $Zn_2Mo_3O_8$‡ | $LiZn_2Mo_3O_8$ | $Zn_3Mo_3O_8$ |
|---|---|---|---|
| Mo(1)–Mo(1) | 2.524 (2) | 2.578 (1) | 2.580 (2) |
| Mo(1)–O(1) | 2.058 (10) | 2.063 (6) | 2.100 (9) |
| Mo (1)–O(2) | 1.928 (20) | 2.003 (8) | 2.056 (13) |
| Mo(1)–O(3) | 2.128 (30) | 2.138 (5) | 2.160 (8) |
| Mo(1)–O(4) | 2.002 (30) | 2.079 (7) | 2.054 (11) |
| Mo(1)–O(av.) | 2.017 | 2.058 | 2.088 |

† Refer to figure 1 for numbering scheme.
‡ Data from Ansell & Katz (1966).

The question of the role of the $2a_1$ m.o. in $Mo_3O_{13}$ cluster units has been examined recently in this laboratory (Torardi & McCarley 1982). The object of the study was to prepare and determine structural parameters for compounds related to $Zn_2Mo_3O_8$, with appropriate substitution of $Zn^{2+}$ so that reduced cluster units containing seven and eight m.c.es could be secured. Three new compounds of this type were successfully prepared at high temperatures, namely $ScZnMo_3O_8$ and $LiZn_2Mo_3O_8$, each with seven m.c.es, and $Zn_3Mo_3O_8$, with eight m.c.es, by the following reactions:

$$3Sc_2O_3 + 6ZnO + 11MoO_3 + 7Mo \xrightarrow[\text{Mo tube}]{1100\ ^{\circ}\text{C}} 6ScZnMo_3O_8; \qquad (1)$$

$$Li_2MoO_4 + 4ZnO + 4MoO_2 + Mo \xrightarrow[\text{Mo tube}]{1100\ ^{\circ}\text{C}} 2LiZn_2Mo_3O_8; \qquad (2)$$

$$6ZnO + 5MoO_2 + Mo \xrightarrow[\text{Mo tube}]{1100\ ^{\circ}\text{C}} 2Zn_3Mo_3O_8. \qquad (3)$$

Single crystals resulting from (2) and (3) proved to be isomorphous and to have structures related to that of $Zn_2Mo_3O_8$, differing from the latter in the hexagonal layer stacking sequence and repeat distance. Although single crystals of $ScZnMo_3O_8$ were not obtained, X-ray powder patterns showed conclusively that this compound is isomorphous with $Zn_2Mo_3O_8$, and thus also constitutes one of the desired derivatives with seven m.c.es.

Structural parameters for $Zn_2Mo_3O_8$, $LiZn_2Mo_3O_8$ and $Zn_3Mo_3O_8$ are compared in table 2. It is seen that the principal effects of adding the seventh and eighth m.c.e. are a lengthening of the Mo–Mo bonds and a simultaneous elongation of the Mo–O bonds to the edge-bridging O atoms. Other changes in bond distances are not statistically significant within standard deviations. The observed changes with increasing m.c.e. count suggest that the seventh and eighth electrons enter a molecular orbital that is antibonding with respect to both the Mo–Mo and edge-bridging M–O interactions. Indeed, such an orbital can be formed by mixing of the one $t_{2g}$-type d-orbital on each metal atom not used in the M–M σ-bonding with the pπ, formally non-bonding orbitals, on the three edge-bridging O atoms. The interactions between these three d-orbitals and three oxygen pπ orbitals lead to a filled bonding set $a_1 + e$, localized mainly on the edge-bridging

O atoms, and an antibonding set $a_1^* + e^*$. In $Zn_2Mo_3O_8$, the $a_1^*$ m.o. constitutes the l.u.m.o. and corresponds to the previously mentioned $2a_1$ level; in $LiZn_2Mo_3O_8$ and $Zn_3Mo_3O_8$ this orbital then becomes the h.o.m.o. and is occupied by one and two electrons, respectively. The magnetic properties of the latter compounds are in agreement with this scheme, indicating the filling of an orbital singlet level with the addition of one or two electrons to the $(Mo_3O_4O_{\frac{6}{2}}O_{\frac{3}{3}})^{4-}$ cluster anion. Very recent results from both electrochemical and chemical studies of the aquo ion $Mo_3O_4(H_2O)_9^{4+}$ show that chemically reversible two or three-electron reduction of the trimer can be affected, accompanied by protonation of the reduced species (Richens & Sykes 1982). The nature of the aqueous three-electron reduction product remains to be elucidated, but it seems quite likely that the two-electron reduced species is closely related, structurally and electronically, to the cluster anions of $LiZn_2Mo_3O_8$ and $Zn_3Mo_3O_8$.

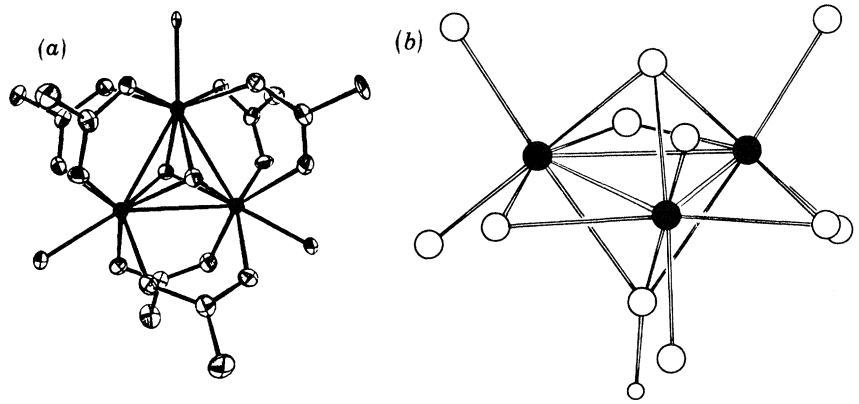

FIGURE 2. Structural representation of clusters with bicapped triangular configuration. (*a*) Clusters of the $M_3X_{17}$ type; (*b*) clusters of the $M_3X_{11}$ type. Metal positions are indicated by filled circles.

### *Bicapped* $M_3X_{17}$ *and* $M_3X_{11}$ *cluster types*

Two additional structural types have recently been discovered for trinuclear clusters of molybdenum and tungsten. These consist of the $M_3X_{17}$ type, exemplified by

$W_3O_2(O_2CMe)_6(H_2O)_3^{2+}$ (Bino *et al.* 1978),

$Mo_3O(CMe)(O_2CMe)_6(H_2O)_3^{+}$ (Bino *et al.* 1981 *a*)

and $Mo_3(CMe)_2(O_2CMe)_6(H_2O)_3^{n+}$ (Bino *et al.* 1981 *b*),

with the triangle of metal atoms capped on either side by triply bridging O atoms, one O atom and one $CCH_3$, or only $CCH_3$ ligands, respectively. A second bicapped arrangement, of the type $M_3X_{11}$, has been found in the compound $MoO(ONe)_{10}$, where Ne represents the neopentyl radical (Chisholm *et al.* 1981). Skeletal structural arrangements in these two new cluster types are shown in figure 2.

In the $M_3X_{17}$ cluster type two triply bridging ligands cap the face of the triangle on either side, six carboxylate ligands bridge the three edges from above and below, and three terminal aquo ligands bond in the plane of the triangle, one to each metal atom. As a result of this arrangement each metal atom is coordinated to six ligand atoms in roughly trigonal prismatic geometry with the seventh ligand bonded perpendicular to the exposed square face. Counting the metal bonds, each metal thus attains a coordination number of nine. Accordingly, the metal–metal bond distances in these derivates are longer than in the $M_3X_{13}$ cluster type, even in those cases where both types have the same m.c.e. count and formal M–M bond order. An interesting facet of the chemistry of the $M_3X_{17}$ clusters is that either one or two bridging $\mu_3$-alkylidyne ligands may be incorporated into the cluster in place of the $\mu_3$-O atoms. The clusters with two $\mu_3$-alkylidyne ligands have been isolated in oxidized form with four or five m.c.es and average M–M bond order of $\frac{4}{6}$ or $\frac{5}{6}$, respectively. These characteristics are reflected in the M–M bond distances, which fall in the range 2.885–2.892 Å for the oxidized derivatives. A Fenske–Hall m.o. treatment of the dioxo-capped clusters of this type has recently appeared (Bursten *et al.* 1982). It was concluded that the interaction of the two capping O atoms destabilized the M–M bonding somewhat through a depopulation of the bonding $a_1$ m.o. constructed from the Mo $4dz^2$ atomic orbitals directed towards the centre of the cluster.

The second type of bicapped cluster was obtained as the result of addition of $MoO(ONe)_4$ across the metal–metal bond of the dimer $Mo_2(ONe)_6$:

$$MoO(ONe)_4 + Mo_2(ONe)_6 \longrightarrow Mo_3O(ONe)_{10}. \qquad (4)$$

Chisholm *et al.* (1981) proposed that the addition represents the potential of a generalized method,

$$M{\equiv}M + M{\equiv}X \longrightarrow M_3X, \qquad (5)$$

for the synthesis of triangulo complexes. In $Mo_3O(ONe)_{10}$ the molybdenyl O atom becomes one of the capping ligands and a neopentoxo ligand the second. The overall arrangement represents an alternative way of achieving an octahedral coordination sphere for each metal atom, as opposed to the arrangement in $M_3X_{13}$ clusters. Thus it is not surprising that the average Mo–Mo distance of 2.529(9) Å found in $MoO(ONe)_{10}$, with six m.c.es, is closely comparable with those found in $Mo_3O_{13}$ clusters with six m.c.es. We may expect that other examples of the $M_3X_{11}$ cluster type will soon be found as investigations in this area continue.

## TETRANUCLEAR CLUSTERS

One of the most remarkable developments in cluster chemistry has been the sudden proliferation of tetranuclear cluster units of different geometries, all occurring in compounds of Mo or W. Up to 1975 the literature provided no reports of structurally characterized $Mo_4$ or $W_4$ clusters. Subsequently the synthesis and structure of five different cluster types have been described. These are each discussed below.

### *Tetrahedral clusters*

The solid-state compounds $GaMo_4S_8$ (Vandenberg & Brown 1975) and $Mo_4S_4Br_4$ (Perrin *et al.* 1975), formed at high temperature in reactions between the elements, each contain tetrahedral cluster units. Each structure is derived from the basic spinel structure, $A_2B_4X_8$, with $Mo^{III}$ occupying octahedral (B) sites in the cubic close-packed anion lattice and $Ga^{III}$ or vacancies in the tetrahedral (A) sites. The cluster units are formed by the mutual displacement of four adjacent Mo atoms from the centre of their sites towards one another to form the metal–metal bonded tetrahedron. The four faces of the tetrahedron are capped by S atoms to form a ‘cubane’ $Mo_4S_4$ unit. Each Mo is also bound to three terminal ligands, either S or Br, which are shared

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with other cluster units as indicated in the formulas $\mathrm{GaMo_4S_4S_{\frac{12}{3}}}$ and $\mathrm{Mo_4S_4Br_{\frac{12}{3}}}$. The Ga compound is electron-deficient in the sense that there are only 11 m.c.es to form the six bonds ($d(\mathrm{Mo{-}Mo}) = 2.823$ Å) of the tetrahedron, but the tetrahedral cluster in $\mathrm{Mo_4S_4Br_4}$ is bonded with the full complement of 12 m.c.es ($d(\mathrm{Mo{-}Mo}) = 2.798$ Å). Although it seems quite reasonable that molecular clusters of this type might be prepared, e.g. $\mathrm{Mo_4S_4Br_4L_8}$, none so far have been reported.

### *Square planar and butterfly clusters*

These cluster types are grouped together because they have the common feature that they may be considered as fragments of the well known octahedral cluster units $\mathrm{Mo_6X_8^{4+}}$. Removal of two Mo atoms from *trans* positions of the octahedron leads to the fragment $\mathrm{Mo_4X_8}$ with a square arrangement of metal atoms and the eight ligands still disposed at the corners of a cube, as shown in figure 3. Chisholm *et al.* (1982) have recently prepared the $\mathrm{Mo^{III}}$ compound $\mathrm{Mo_4(OPr^i)_8Cl_4}$, where the $\mathrm{Mo_4(OPr^i)_8^{4+}}$ cluster core has the arrangement indicated above. In this case the 12 m.c.es must all reside in bonding orbitals as evidenced by the short Mo–Mo distance, 2.378(2) Å. This bond distance is even shorter than that expected for an average bond order of 1.5 required by 12 electrons in the square. It thus appears that the square fragment leads to unusually stable metal–metal bonding.

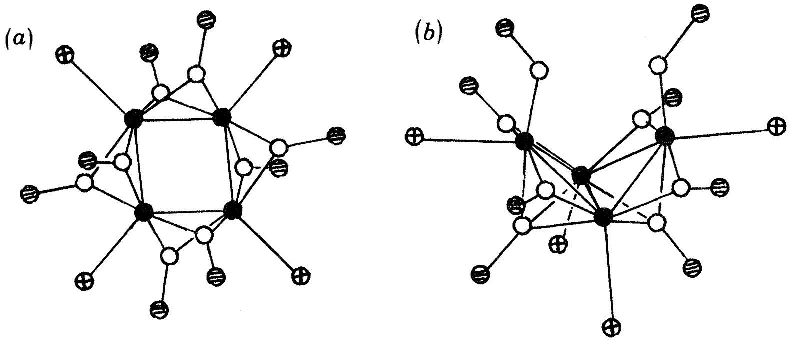

FIGURE 3. The structure of tetranuclear clusters. (*a*) The square cluster of $\mathrm{Mo_4(OPr^i)_8Cl_4}$; (*b*) the butterfly structure of $\mathrm{Mo_4(OPr^i)_8Br_4}$. Metal positions are indicated by filled circles, oxygen positions by open circles, carbon positions by shaded circles and halogen positions by crossed circles.

An important feature of the preparative route to $\mathrm{Mo_4(OPr^i)_8Cl_4}$ is its formation by addition of triply bonded dimers:

$$2\mathrm{Mo_2(OPr^i)_6} + 4\mathrm{CH_3COCl} \longrightarrow \mathrm{Mo_4(OPr^i)_8Cl_4} + 4\mathrm{CH_3COOPr^i}. \tag{6}$$

Relatively few reactions of this type are known leading to oligomerization of multiply metal–metal bonded species. The first reactions of this type are found with quadruply bonded dimers, leading to rectangular cluster species discussed in the next section.

In the related preparation of $\mathrm{Mo_4(OPr^i)_8Br_4}$ (Chisholm *et al.* 1982),

$$2\mathrm{Mo_2(OPr^i)_6} + 4\mathrm{CH_3COBr} \longrightarrow \mathrm{Mo_4(OPr^i)_8Br_4} + 4\mathrm{CH_3COOPr^i}, \tag{7}$$

which might be expected to provide the bromide analogue of the square cluster arrangement, instead leads to the butterfly cluster shown in figure 3. This butterfly or opened-tetrahedron arrangement also may be viewed as a fragment of the $\mathrm{Mo_6X_8}$ octahedral cluster with two metal

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atoms removed from *cis* positions. The eight $OPr^i$ ligands remain disposed roughly at the corners of a cube, although among these, two become triply bridging, four doubly bridging, and two terminal ligand types – each giving a distinct set of resonances in the $^1H$ n.m.r. spectrum. The Mo–Mo distance, 3.287 Å, corresponding to the elongated edge of the opened tetrahedron, is essentially a non-bonded distance. The five short Mo–Mo distances, 2.50 Å (averaged), again indicate very strong metal–metal bonding, a reflexion of 12 m.c.es for five bonds and an average Mo–Mo bond order of 1.20. Since the halogen atoms in these $Mo_4(OPr^i)_8X_4$ clusters are bound in terminal positions they should not play an important role in determining the geometric difference between the square and butterfly arrangements. Although the reason for this difference must be left to further investigations, we may conjecture that the kinetic pathways in (6) and (7) are different. If this is so, then the most stable cluster arrangement cannot yet be identified for these compounds.

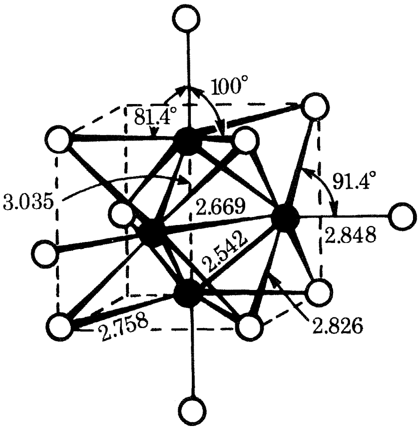

FIGURE 4. Structure of the butterfly cluster anion found in $(Bu_4N)_2Mo_4I_{11}$. Representation of the structure of $Mo_4I_7$ core of $Mo_4I_{11}^{2-}$ as a fragment of the $Mo_6I_8^{4+}$ cluster unit.

The first example of a butterfly four-atom fragment of the $Mo_6X_8$ octahedral clusters was found in the compound $(Bu_4N)_2Mo_4I_{11}$ (Stensvad *et al.* 1978). In this case one of the eight ligands at the corners of the cube is lost. The seven remaining ligands assume the positions shown in figure 4, and are divided into two triply bridging and five doubly bridging modes. Each metal bears one terminal ligand to complete the coordination sphere. A clear distinction of the three Mo–I bonding modes is found in the I $3d_{\frac{5}{2},\frac{3}{2}}$ X-ray photoelectron spectrum, which can be deconvoluted to provide three bands in the intensity ratio 2:5:4 expected for binding energies in the order $I^{tb} > I^{db} > I^{t}$. The $Mo_4I_{11}^{2-}$ cluster presents a greater problem for the interpretation of bonding because 15 m.c.es may participate, and also because the opened edge of the tetrahedron, $d$(Mo–Mo) = 3.035 Å, is not clearly a non-bonded distance. A rough m.o. analysis of bonding has led to the conclusion that 12 electrons reside in bonding m.o.'s and the three additional electrons occupy essentially non-bonding orbitals localized on the Mo atoms at the ends of the long bond. This analysis of the bonding is consistent with the structures of both $Mo_4(OPr^i)_8Br_4$ and $Mo_4I_{11}^{2-}$ which have comparable Mo–Mo bond distances for the five short bonds in the butterfly units. Addition of three non-bonding electrons in $Mo_4I_{11}^{2-}$ hardly disturbs the structure. On this basis a series of compounds having this structure type might be expected with m.c.e. counts ranging between 12 and 16.

### *Rectangular clusters*

These clusters were first discovered (McGinnis *et al.* 1978) as the result of addition of the 'activated' quadruply bonded dimers, $Mo_2Cl_4(PPh_3)_2(MeOH)_2$, with ligand elimination as follows:

$$2Mo_2Cl_4(PPh_3)_2(MeOH)_2 \xrightarrow[25\,°C]{C_6H_6} Mo_4Cl_8(PPh_3)_4 + 4MeOH; \qquad (8)$$

$$2Mo_2Cl_4(PPh_3)_2(MeOH)_2 \xrightarrow[HCl,\ 60\,°C]{CH_3OH-C_{10}H_{12}} Mo_4Cl_8(MeOH)_4 + 4PPh_3. \qquad (9)$$

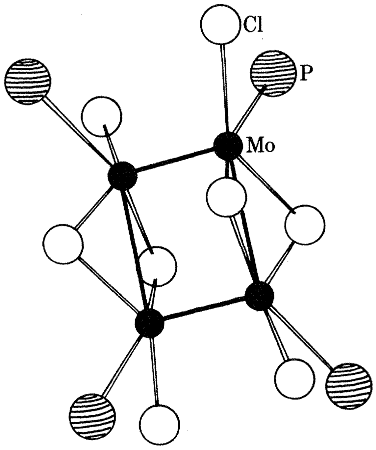

FIGURE 5. The structure of the rectangular cluster unit of $Mo_4Cl_8(PEt_3)_4$. For clarity the ethyl groups of the $PEt_3$ ligands have been omitted.

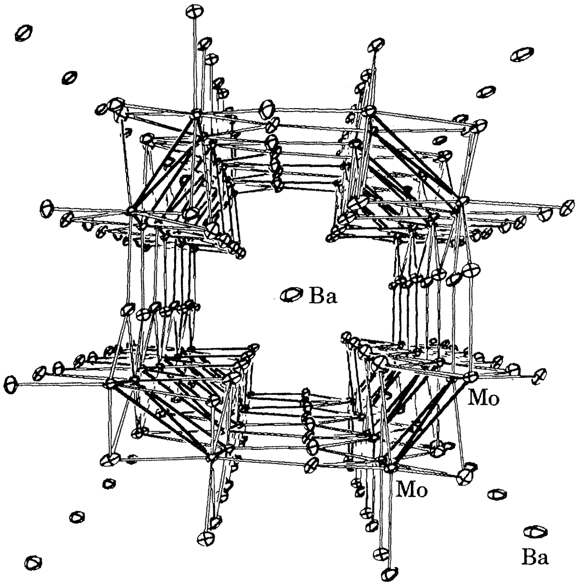

FIGURE 6. A three-dimensional view of the structure of $Ba_{1.14}Mo_8O_{16}$ as seen down the *c*-axis with the eye directly in line with the central stack of Ba atoms.

Subsequent replacement of $PPh_3$ or MeOH with $PEt_3$ or $PBu^{n}_{3}$ led to crystalline derivatives whose structure showed the presence of rectangular clusters with the basic framework shown in figure 5. Bond distances within the $Mo_4$ rectangle of $Mo_4Cl_8(PEt_3)_4$, 2.211(3) and 2.901(2) Å, indicate that the short and long distances correspond to Mo–Mo triple bonds and single bonds, respectively. Schematically the addition can be represented as

$$\begin{array}{c} \mathrm{M}\equiv\mathrm{M} \\ + \\ \mathrm{M}\equiv\mathrm{M} \end{array} \longrightarrow \begin{array}{ccc} \mathrm{M} & \equiv & \mathrm{M} \\ | & & | \\ \mathrm{M} & \equiv & \mathrm{M} \end{array} . \qquad (10$$

Studies of the electronic spectral changes that take place on going from dimers to the rectangular clusters indicate that the δ-bonding components of the quadruple bonds in the dimers are recast to form the σ-bonds corresponding to the long edges of the rectangle (Ryan & McCarley 1982). This interesting bond arrangement is unprecedented in chemistry; its analogue among organic compounds, cyclobutadiyne, is unlikely to be stable because of bond angle strain.

Subsequent synthetic and structural work has shown that the formation of the rectangular clusters can be efficiently achieved by a variety of approaches, and for tungsten as well as molybdenum (McCarley *et al.* 1981):

$$2K_4Mo_2Cl_8 + 4PEt_3 \xrightarrow[\text{reflux}]{CH_3OH} Mo_4Cl_8(PEt_3)_4 + 8KCl; \qquad (11)$$

$$2Mo_2(O_2CMe)_4 + 4AlCl_3 + 4PEt_3 \xrightarrow[25\ ^\circ C]{THF} Mo_4Cl_8(PEt_3)_4 + 4AlCl(O_2CMe)_2; \qquad (12)$$

$$2Mo_2Cl_4(PBu^{n}_{3})_4 + 2Mo(CO)_6 \xrightarrow[\text{reflux}]{C_6H_5Cl} Mo_4Cl_8(PBu^{n}_{3})_4 + 2Mo(CO)_4(PBu^{n}_{3})_2 + 4CO; \qquad (13)$$

$$2W_2Cl_6(THF)_2(PBu^{n}_{3})_2 + 4Na(Hg) \xrightarrow{THF} W_4Cl_8(PBu^{n}_{3})_4 + 4NaCl + 4THF. \qquad (14)$$

By using the approach represented in (12) it is possible to form the interesting mixed-metal cluster $Mo_2W_2Cl_8(PMe_3)_4$, via

$$2MoW(O_2CCMe_3)_4 + 4PMe_3 + 8AlCl_3 \xrightarrow[\text{reflux}]{THF} Mo_2W_2Cl_8(PMe_3)_4 + 8AlCl_2(O_2CCMe_3) \qquad (15)$$

(Carlin & McCarley). A structural determination of this compound indeed shows the presence of the rectangular cluster, but because of disordering of the metal positions, the particular isomer formed could not be identified. From the mode of formation, starting with the pure heteronuclear dimer $MoW(O_2CCMe_3)_4$, the expected product should consist of one of the following isomers,

$$\begin{array}{ccc} \mathrm{Mo} & \equiv & \mathrm{W} \\ | & & | \\ \mathrm{Mo} & \equiv & \mathrm{W} \end{array} \quad \text{or} \quad \begin{array}{ccc} \mathrm{Mo} & \equiv & \mathrm{W} \\ | & & | \\ \mathrm{W} & \equiv & \mathrm{Mo} \end{array} ,$$

or a mixture of them. It is hoped that a study of the $^{31}P$ n.m.r. spectra, currently in progress, will permit a definitive answer to this problem.

### *Rhomboidal clusters*

As a result of recent work in this laboratory on reduced ternary oxides of molybdenum, a new family of strongly metal–metal bonded compounds has been discovered (McCarley *et al.* 1981; Torardi & McCarley 1981). One member of this family is the interesting and puzzling compound $Ba_{1.14}Mo_8O_{16}$, prepared at 1100 °C via

$$1.14BaMoO_4 + 5.72MoO_2 + 1.14Mo \longrightarrow Ba_{1.14}Mo_8O_{16}. \qquad (16)$$

The structure of this compound proved to be a low-symmetry variant (triclinic, P$\bar{1}$) of the tetragonal hollandite structure, e.g. BaMn$_8$O$_{16}$. A view of the structure looking down the unique tunnel axis, in this case the *c*-axis, is shown in figure 6. The structural framework is built up from infinite chains of rhomboidal cluster units running parallel to the *c*-axis. The chains are then woven together in the indicated square pattern by Mo–O–Mo cross-linking to form the tunnels in which the Ba$^{2+}$ cations are located. A view of one of the individual cluster chains is shown in figure 7. From the mode of interlinking of cluster units along the chains and sharing of O atoms between chains, the connectivity formula for the individual cluster units can be written as Mo$_4$O$_2$O$_{\frac{8}{2}}$O$_{\frac{6}{3}}$ = Mo$_4$O$_8$.

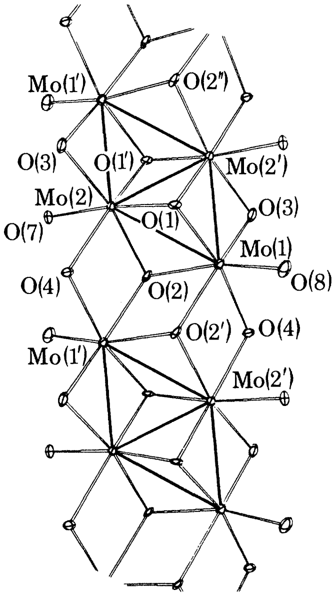

Figure 7. View of a segment of one infinite chain in the structure of Ba$_{1.14}$Mo$_8$O$_{16}$, showing the discrete rhomboidal cluster units. The atom labelling scheme is that used in the text.

In the P$\bar{1}$ space group the infinite chains are related in pairs. Thus, of the four chains forming the sides of each tunnel, there are two non-equivalent pairs. These non-equivalent pairs contain non-equivalent rhomboidal clusters, which will be referred to as regular and distorted units. With reference to figure 7 the Mo(1)–Mo(2), Mo(1)–Mo(2′) and Mo(2)–Mo(2′) distances are, respectively, 2.616(1), 2.578(1) and 2.578(1) Å for the regular cluster units, and 2.847(1), 2.546(1) and 2.560(1) Å for the distorted units. We see that the distortion results from the elongation of two sides of the rhomboid from 2.616 Å in the regular units to 2.847 Å in the distorted units, whereas the dimensions of the other bonds of the two rhomboids remain comparable. The change in bond order associated with this bond lengthening is approximately from 1.0 to 0.5, which suggests that the Mo(1)–Mo(2) bonds in the distorted units are one-electron bonds. It all other Mo–Mo bonds are taken as normal two-electron bonds, then the total m.c.e. count in the regular clusters is ten, and that in the distorted clusters is approximately eight. Based on these considerations the compound may be reformulated as Ba$_{1.14}$(Mo$_4$O$_8^{2-}$)(Mo$_4$O$_8^{0.28-}$).

Although the rhomboidal units are the first of their kind found in oxide systems, regular, ten-electron clusters are strictly analogous to the rhomboidal cluster units found in the halide compounds M$^{\mathrm{I}}$Nb$_4$X$_{11}$ (M$^{\mathrm{I}}$ = Rb, Cs; X = Cl, Br) (Broll *et al.* 1969). Moreover, almost simultaneously with our discovery of Ba$_{1.14}$Mo$_8$O$_{16}$, the compound W$_4$(OEt)$_{16}$ was discovered by Chisholm *et al.* (1981 *b*). The latter molecular cluster also contains eight m.c.es and is distorted in exactly the same way as the $Mo_4O_8^{0.28-}$ units in $Ba_{1.14}Mo_8O_{16}$. Cotton & Fang (1982) have ascribed the observed distortion of these clusters to a second-order Jahn–Teller effect. This seems quite plausible for the distortion in the molecular $W_4(OEt)_{16}$, but is questionable for the distorted units in $Ba_{1.14}Mo_8O_{16}$, where other solid-state effects complicate the interpretation. In particular the Mo(1)–O(8) bond contracts from 2.022(6) Å in the regular cluster to 1.894(6) Å in the distorted cluster. Evidently the atomic orbital utilized on Mo(1) to form the Mo(1)–Mo(2) bond becomes more strongly involved as a $\pi$-acceptor orbital towards O(8) when the m.c.e. count is lowered from ten to eight.

Future work will doubtlessly uncover other examples of structures of this type. Indeed, it may be possible to design compounds with a range of m.c.e. counts from eight to ten or greater in the rhomboidal units by the proper selection of cations incorporated into the channels and the replacement of molybdenum with transition elements of differing valence-electron population. Although in $Ba_{1.14}Mo_8O_{16}$ the regular and distorted units appear to be incorporated in separate chains, other arrangements can be envisaged where varying patterns of both types are included in the same chain. Some evidence for such arrangements has been obtained from the structures of mixed-cation compounds $Li_xBaMo_8O_{16}$ and $Na_xBaMo_8O_{16}$, with $x < 1$ (McCarley & Lii 1982).

## INFINITE-CHAIN COMPOUNDS

The discovery of this family of compounds was quite unintentional and resulted from a most innocent experiment. Having determined that the $Li^+$ and $Zn^{2+}$ ions in $LiZn_2Mo_3O_8$ were scrambled among themselves in both octahedral and tetrahedral sites, attempts were planned for preparation of the $Na^+$-substituted isomorph $NaZn_2Mo_3O_8$. It was expected that $Na^+$ could only occupy octahedral sites and hence would induce an ordered arrangement in the cation positions. Since sodium salts commonly cause devitrification of fused silica, the mixture containing $Na_2MoO_4$, ZnO, $MoO_2$ and Mo was sealed in a Mo tube and the reaction conducted at 1100 °C for several days. Upon opening the Mo tube, thin air-stable needles with silvery lustre were found growing from the walls of the tube. The structural determination of one of these needles indicated that the actual composition was $NaMo_4O_6$, and electron microprobe analysis confirmed the absence of zinc in the crystals. A subsequent reaction,

$$Na_2MoO_4 + 4MoO_2 + 3Mo \xrightarrow[\text{1100 °C}]{\text{Mo tube}} 2NaMo_4O_6, \tag{17}$$

provided essentially pure, highly crystalline $NaMo_4O_6$.

The structure of this compound was astonishing and unprecedented among metal oxide systems (Torardi & McCarley 1979). A view of the structure looking down the $c$-axis of the tetragonal crystal system ($a = 9.570(3)$, $c = 2.8634(8)$ Å) is shown in figure 8. This view shows infinite chains composed of $Mo_4O_6$ repeat units interlinked through Mo–O–Mo bonds to form the square pattern and tunnels in which the $Na^+$ ions are located. A detailed view of a segment of one of the infinite chains, shown in figure 9, reveals that the chain consists of condensed octahedral cluster units $Mo_6O_{12}$ fused on opposite edges by sharing Mo and O atoms with adjacent units. Including the Mo–O bonds to atoms of neighbouring chains the connective formula $Na[(Mo_2Mo_{\frac{4}{2}}O_{\frac{8}{2}}O_{\frac{2}{2}})O_{\frac{2}{2}}]$ is derived. It is undoubtedly the strong metal–metal bonding along the chains that dictates this structure. The metal–metal distances parallel to the chain axis for both the crystallographically independent apex and waist Mo atoms of the octahedral units are equal to the $c$ lattice dimension, 2.8618(2) Å, as required by the space group P4/mbm. All other Mo–Mo distances within the octahedral units are much shorter; these are enumerated in table 3 for comparison with other structures.

Because of the infinite metal–metal bonded chains parallel to the *c*-axis, with much larger metal–metal spacings between chains, $NaMo_4O_6$ is expected to behave as a highly anisotropic, nearly one-dimensional conductor. A simple two-probe resistivity measurement along the *c*-axis of a single crystal provided a value of *ca.* $10^{-4}$ Ω cm, indicative of metallic behaviour. A relatively

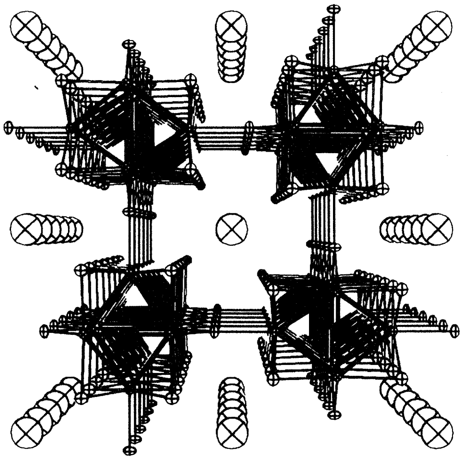

FIGURE 8. A three-dimensional representation of the structure of $NaMo_4O_6$ as viewed down the tetragonal *c*-axis with the eye directly over the central stack of Na atoms.

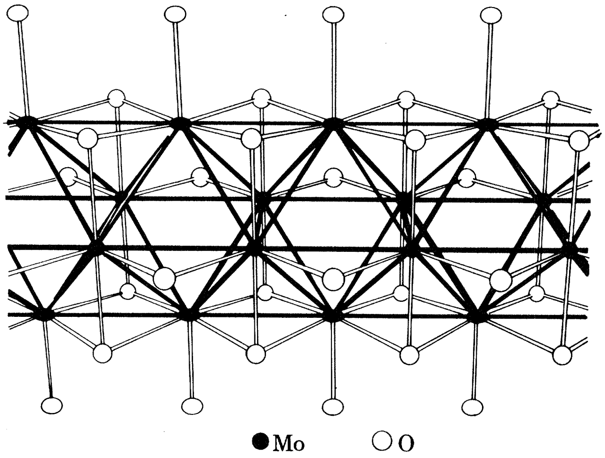

FIGURE 9. Structure of a segment of one infinite chain containing the octahedral cluster units fused on opposite edges by sharing of Mo atoms between repeat units in the compound $NaMo_4O_6$. Mo–Mo bonds are represented by heavy filled lines and Mo–O bonds by unfilled lines.

TABLE 3. A COMPARISON OF Mo–Mo BOND DISTANCES (ÅNGSTRÖMS) IN COMPOUNDS WITH INFINITE CHAIN STRUCTURES

| bond type | $NaMo_4O_6$ | $Sc_{0.75}Zn_{1.25}Mo_4O_7$ | $Ti_{0.5}Zn_{1.5}Mo_4O_7$ |
|---|---|---|---|
| apex–apex | 2.8618 (2) | 2.623 (2)<br>3.140 (2) | 2.790 (2)<br>2.992 (2) |
| apex–waist | 2.780 (2) | 2.749 (1)<br>2.782 (1) | 2.741 (1)<br>2.757 (1) |
| (waist–waist)$_{\parallel}$ | 2.8618 (2) | 2.8857 (5) | 2.8928 (5) |
| (waist–waist)$_{\perp}$ | 2.753 (3) | 2.818 (2) | 2.785 (2) |

high density of states at the Fermi level as determined from ultraviolet photoelectron spectroscopic measurements on freshly prepared and carefully handled material also confirms the metallic character. However, measurements on pressed and sintered pellets over the range 2–300 K provide much higher resistivity values, e.g. *ca.* $10^{-2}\,\Omega$ cm at 298 K, which decrease with increasing temperature, and show a maximum at *ca.* 11 K. The higher resistivity for a polycrystalline sample is consistent with the expected anisotropy, but the temperature dependence is not understood.

In $NaMo_4O_6$ there are 13 m.c.es per $Mo_4O_6^-$ repeat unit. That all 13 m.c.es enter into bonding interactions between the Mo atoms is confirmed by the Pauling bond order sum (Corbett 1981 *c*) for the 13 net Mo–Mo bonds within each octahedral unit. The expected bond order sum for 13 electrons and 13 bonds is 6.50, and that derived from summing bond orders computed from the individual Mo–Mo distances is 6.36. We may then ask: To what extent is the electron count for such a chain structure variable? What is the total range of electrons per repeat unit possible in stable structures, and what is the limiting number of electrons in bonding states? To some extent the question of stability of the chain structure is related to the matching between van der Waals radii of the non-metallic and metallic bond radii of the metallic constituents. This is a consequence of the requirement that the average metal–metal and non-metal–non-metal spacings along the chain axis must be equal. A large mismatch of these radii is likely to destabilize the structure relative to another with greater bonding and packing efficiency. Thus, metals with large metallic radii and low valence electron count will require a large M–M distance (low net bond order) matched by relatively large anions for equal anion–anion spacing. Chains constructed from such constituents will have low m.c.e. counts. Compounds with such chain structures meeting these conditions were the first discovered, e.g. $Gd_2Cl_3(Gd_4Cl_6)$, $ScCl_2^+Sc_4Cl_6^-(Sc_5Cl_8)$ and others listed in table 1. So far the lower limit of m.c.e. per repeat unit established from known compounds is six, as in the structural variants represented by $Gd_2Cl_3$ and $Tb_2Br_3$. The anion chain $Sc_4Cl_6^-$ found in $Sc_5Cl_8$ is slightly more tightly bound, with seven m.c.es per repeat unit.

If the lower limit of m.c.e.s per repeat unit is about six, then what is the upper limit? Is it possible to go beyond the 13 m.c.es of $NaMo_4O_6$? Subsequent synthetic and structural work in this laboratory has answered this question in the affirmative. Experiments designed to prepare new $M_xMo_4O_6$ chain structures with M = di-, tri- or tetra-positive cations are in progress. Early success has been found with the preparation and structure determination of $Ba_5(Mo_4O_6)_8$, $Sc_{0.75}Zn_{1.25}Mo_4O_7$ and $Ti_{0.5}Zn_{1.50}Mo_4O_7$. The structure of $Ba_5(Mo_4O_6)_5$ is a low-symmetry (orthorhombic) version of that of $NaMo_4O_6$ (Torardi & McCarley 1981). A small net contraction of the average Mo–Mo bond distance in the repeat units of the chains indicates that all 13.25 m.c.es in the repeat units of $Ba_5(Mo_4O_6)_8$ do indeed reside in bonding states.

The discovery of $Sc_{0.75}Zn_{1.25}Mo_4O_7$ and $Ti_{0.5}Zn_{1.50}Mo_4O_7$ was again serendipitous (Brough *et al.* 1982). During attempts to grow single crystals of $ScZnMo_3O_8$ (see above), this material was subjected to heating at increasing temperatures. At *ca.* 1450 °C, $ScZnMo_3O_8$ decomposed or underwent reaction with the molybdenum container and beautiful gem-like crystals of the new product were formed. Likewise, $Ti_{0.5}Zn_{1.5}Mo_4O_7$ was formed at *ca.* 1450 °C in a reaction between $TiO_2$, ZnO, $MoO_2$ and Mo held in a Mo tube for several days. The composition of the new compounds was established from electron microprobe analyses of single crystals and the subsequent X-ray structure determination. Both compounds crystallize with orthorhombic unit cells in the space group Imam. Although the compounds are isomorphous there are some significant differences in Mo–Mo bond distances, signifying differences in m.c.es per repeat unit as discussed below.

Some important structural features of $Sc_{0.75}Zn_{1.25}Mo_4O_7$ are evident from a view parallel to the *c*-axis shown in figure 10. This view illustrates the octahedral cluster units $Mo_4O_7^{n-}$ of infinite chains running parallel to the *c*-axis. The chains are interlinked in the *ac* plane by Mo–O–Mo bridge bonding, and in the *b*-direction by Mo–O–Sc and Mo–O–Zn bonding. If the infinite chains can be regarded as cylinders of infinite length the overall structure can be regarded as a closest-stacking of these cylinders with $Sc^{3+}$ and $Zn^{2+}$ located in sites along the narrow channels created by the cylinder stacking. The sites for these cations are of two types, namely tetrahedral sites occupied only by $Zn^{2+}$, and octahedral sites occupied by either $Zn^{2+}$(25 %) or $Sc^{3+}$(75 %).

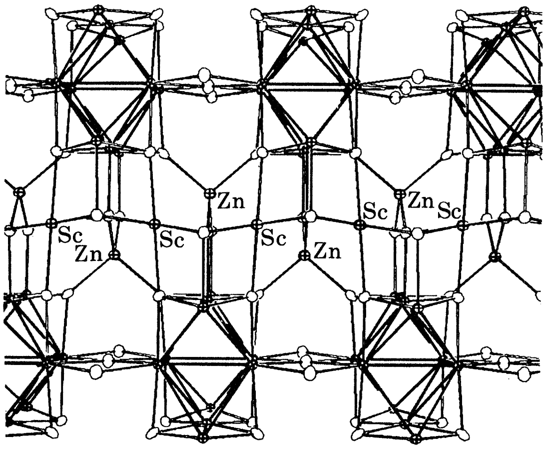

FIGURE 10. A three-dimensional representation of the structure of $Sc_{0.75}Zn_{1.25}Mo_4O_7$ as viewed down the orthorhombic *c*-axis. The positions of Sc and Zn atoms are labelled. The $Mo_4O_7$ cluster units show the Mo–Mo bonds with heavy filled lines.

Within the infinite chains the sharing of Mo and O atoms between adjacent units is much like that found in $NaMo_4O_6$. However, an extra O atom is inserted in the terminal positions on the apex Mo atoms along the chain for bonding to the Zn and Sc atoms. Because of alternate short and long Mo–Mo distances between apex atoms along the chains, the true repeat unit contains two individual cluster units. These considerations are then represented by the connective formula $Sc_{1.5}Zn_{2.5}[(Mo_6Mo_{\frac{4}{2}}O_4O_{\frac{4}{2}}O_{\frac{2}{2}})O_4]$. Assuming complete electron transfer from Sc and Zn to the cluster chains the m.c.e. count in the individual octahedral units becomes 14.75 for $Sc_{0.75}Zn_{1.25}Mo_4O_7$.

One effect of the increased m.c.e. count can be seen in the view of the cluster chains perpendicular to the chain direction, as shown in figure 11. The alternate short and long distances between apex Mo atoms is clearly evident, whereas the distances between waist Mo atoms remains perfectly regular. A comparison of Mo–Mo distances for $NaMo_4O_6$, $Sc_{0.75}Zn_{1.25}Mo_4O_7$ and $Ti_{0.5}Zn_{1.5}Mo_4O_7$ is given in table 3. The most notable feature of this comparison is that the distortion of the apex–apex bonding is quite severe in $Sc_{0.75}Zn_{1.25}Mo_4O_7$. In fact the short apex–apex distance agrees well with that expected for a Mo–Mo single bond, and the long distance is so great that it must be essentially non-bonding. A similar but less severe distortion is evident for the titanium compound. Again, Pauling bond-order values are instructive in the comparison between these structures. However, the titanium compound presents a special problem because the oxidation state of the Ti atom in this structure is not clear, and hence the number of electrons transferred to the anion chains is uncertain. For the scandium compound it is reasonably certain that this element is present as $Sc^{3+}$ and the bond-order sum computed from the Mo–Mo distances for the individual cluster units is 6.74, a value greater by 0.38 units than that of $NaMo_4O_6$. It thus appears that additional electrons have been fed into bonding states. The increase results predominantly from the formation of the short apex–apex bonds. This is demonstrated by comparing the bond-order sum for the short and long apex–apex distances with that of two waist–waist bonds in the scandium compound. The derived values for the apex–apex and waist–waist sums are 1.10 and 0.70, respectively. The difference of 0.40 shows that the net Mo–Mo bonding is strengthened by the distortion and accommodates additional electrons in the structure. Similar considerations for the titanium compound indicate that fewer electrons are donated to the anion chains. This in turn suggests that Ti is present as $Ti^{3+}$ and not as $Ti^{4+}$.

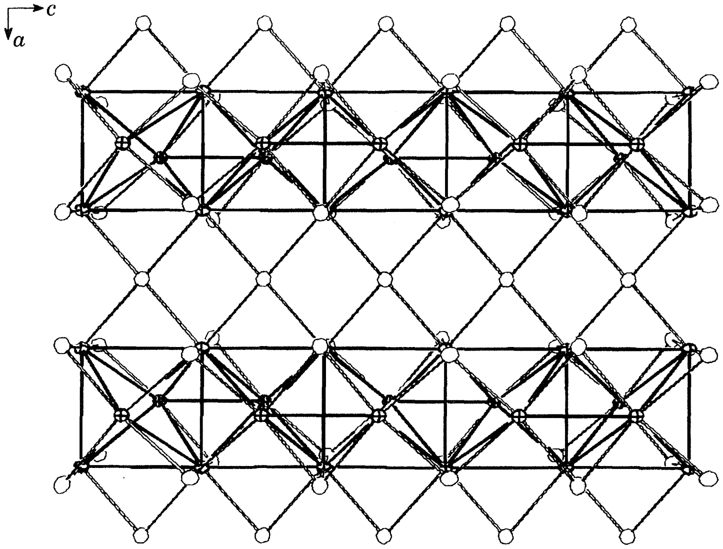

FIGURE 11. A view of the infinite chains containing octahedral cluster units fused on opposite edges in the compound $Sc_{0.75}Zn_{1.25}Mo_4O_7$. In this view the alternate short and long Mo–Mo distances between apex Mo atoms of the octahedral cluster units can be seen and the Mo–O–Mo bridge bonding connecting one chain to its neighbours also is illustrated.

I conclude by noting that this venture into the study of reduced ternary and quaternary molybdenum oxides has been most surprising and rewarding. In retrospect it is astonishing that before this work structurally characterized oxide compounds containing molybdenum in an oxidation state less than 4+ were unknown. The potential for further interesting compounds in this class is considerable, not only for molybdenum but for other heavy transition metals as well

I give special thanks to all my coworkers, past and present, who contributed to the work reported here, and without whom I would have had little to write. Their contributions are noted in the references. Thanks also go to the U.S. Department of Energy, Basic Energy Sciences, for their continuing support of this work through the Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under contract no. W-7405-Eng-82. This research was supported by the Assistant Secretary for Energy Research, Office of Basic Energy Sciences, no. WPAS-KC-02-03.

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