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Single Crystal X-Ray Study of Mo_6Se_8-Type Selenides Containing Partially Substituted $(Mo,Me)_6$ Clusters (Me = Ru,Re)[1]

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Atomic coordinates for rhombohedral $Mo_4Ru_2Se_8$ and $Mo_{\sim 1.5}Re_{\sim 4.5}Se_8$ are reported. The metal atom octahedra (point symmetry $\bar{3}$) are significantly smaller and less elongated (d(metal–metal) = 2.66 and 2.71 Å ($Mo_4Ru_2Se_8$); 2.63 and 2.67 Å ($Mo_{\sim 1.5}Re_{\sim 4.5}Se_8$)) than those in Mo_6Se_8 (2.69 and 2.84 Å). The apparent contraction exceeds that expected from atomic size considerations and confirms the correlation between the valence electron concentration on the metal atom cluster and the strength of the metal–metal bonds. The bond order sums calculated from the expression $n = (d(1)/d(n))^5$ lead to a more coherent description of the metal–metal bonding than those calculated from $d(n) = d(1) - 0.6 \log(n)$.

Introduction

Structural data of the rhombohedral cluster chalcogenides Mo_6X_8 (X = S, Se, Te) and their ternary derivatives MMo_6X_8 (M = Cu, Ag, Ni, Fe, rare earth, etc.) suggest (*1*) that there exists a correlation between the size and elongation of the Mo atom octahedra and the number of valence electrons per Mo atom available for metal–metal bonding. As the valence electron concentration (VEC) on the metal atoms is increased the Mo_6 octahedra contract and become more regular. This behavior was interpreted by assuming a gradual filling of Mo d orbitals having *bonding* character, and an energy-band effect arising from the presence of *two* Mo d bands at the Fermi level. Recent theoretical band-structure calculations (*2*) and the discovery of structural phase transformations in the sulfides MMo_6S_8 (M = Eu, Ca, Sr, Ba) at low temperature (*3*) due to a Jahn–Teller distortion of the Mo_6 clusters have supported this view.

Unfortunately, the apparent contraction of the metal atom octahedra due to this *electronic effect* is often obscured by other effects which are of a geometrical nature and arise mainly from the anion matrix. Insertion (or substitution) of the ternary metal cations M, or substitution of the nonmetal component X by other anions leads to changes in the anion packing which influence the metal–metal bonds *via* the network of metal–nonmetal (Mo–X) bonds. These perturbations, together with others have been summarized as *matrix effect* and discussed recently by Corbett (*4*) who concluded that this effect was mainly responsible for the anomalies in size and shape of

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the Mo_6 octahedra as reported in this class of compounds.

In this communication we attempt to arrive at a better understanding of the interplay between the *electronic effect* and the *matrix effect*. For this purpose a structural study of pseudobinary compounds $(Mo, Me)_6X_8$ containing mixed-metal $(Mo,Me)_6$ clusters (Me = transition metal) was thought to be of particular interest because the substitution *on* the metal atom clusters allows one to change the VEC within a wide range, while the anion packing and thus the main part of the *matrix effect* can be kept essentially unchanged. The compounds chosen for this study are rhenium and ruthenium substituted selenides of composition $Mo_4Ru_2Se_8$ and $Mo_2Re_4Se_8$. They both contain 88 valence electrons per formula unit, i.e., four electrons more than binary Mo_6Se_8 (84*e*), and they are the most electron-rich compounds of this structural class reported as yet. Both have been characterized previously by X-ray powder diffraction analysis (*5*, *6*). They were reported to crystallize with the rhombohedral Mo_6Se_8 structure type (*7*), but atomic parameters were not given.

Experimental and Results

Single crystals of the ruthenium based compound $Mo_4Ru_2Se_8$ were isolated from a compact sample which was supplied by R. Baillif. It had been prepared by sintering a stoichiometric mixture of high purity elements in sealed quartz tube at 1470 K, followed by melting at 1970 K in a high pressure (0.7 GPa) argon furnace (*8*). The weight loss during melting was small (only ~3 wt% (*9*)). As shown by X-ray (Guinier photographs and metallographic inspection the sample contained almost exclusively the rhombohedral phase, the estimated amount of impurity phases (nonidentified) being only ~4 at.%.

Single crystals of the rhenium based compound $Mo_2Re_4Se_8$ could not be obtained by using the procedure described above, presumably because the rhombohedral phase decomposed before melting (*9*). Thus the crystals used in this study were taken from a sintered specimen of nominal composition $Mo_2Re_4Se_8$ (supplied by B. Lachal) which was annealed in quartz tubes for several days at 1320 K. In contrast to $Mo_4Ru_2Se_8$, the sample contained a significant amount of β-$MoSe_2$ (2H) phase (*10*). Its concentration was estimated by comparison with calibrated X-ray Guinier films and found to be about 10 at.%. Since no other impurity phases were detected in this sample, the crystals of the rhombohedral phase were expected to be Se deficient and/or more Re rich than the $Mo_2Re_4Se_8$ compound reported previously (*5*).

The cube-shaped crystals were mounted on glass fibers and measured on an automated four-circle diffractometer using graphite-monochromated Ag$K\alpha$ radiation (λ = 0.5608 Å). Their Bravais lattice and point symmetry were checked, and confirmed to be of type R and $\bar{3}$, respectively. No additional reflections indicative of a possible superstructure were observed. The lattice parameters were determined by accurately centering 20 reflections. The values obtained by least-squares analysis are listed in Table I. They do not differ significantly from those reported previously (*5*,

TABLE I

CRYSTAL DATA FOR Mo_6Se_8, $Mo_4Ru_2Se_8$, AND $Mo_{1.5}Re_{4.5}Se_8$ (SPACE GROUP $R\bar{3}$, No 148 (*12*))

	Mo_6Se_8[a]	$Mo_4Ru_2Se_8$[b]	$Mo_{1.5}Re_{4.5}Se_8$[b]
a_{hex} (Å)	9.545(16)	9.680(1)	9.674(1)
c_{hex} (Å)	11.210(6)	10.850(3)	10.752(2)
c/a	1.174	1.121	1.111
a_{rh} (Å)	6.658	6.657	6.636
α_{rh} (°)	91.58	93.28	93.58
V_{hex} (Å^3)	884.5(34)	880.5(4)	871.4(2)
d_{cal} (g · cm^{-3})	4.095	4.148	5.555

[a] From Ref. (*7*).
[b] This work.

6). Intensity data were collected by continuous θ–2θ scans ($Mo_4Ru_2Se_8$: 1132 reflections, of which 895 with $I_0 \geq 3\sigma(I_0)$; $Mo_2Re_4Se_8$: 1058 (997) reflections). The data ($2\theta_{max} = 60°$) were corrected for absorption for a sphere ($Mo_4Ru_2Se_8$: $\mu(AgK\alpha) = 9.8\ cm^{-1}$, $\bar{d} = 0.0096$ cm; $Mo_2Re_4Se_8$: $\mu(AgK\alpha) = cm^{-1}$, $\bar{d} = 0.0048$ cm) and processed by the subroutines of the XRAY computer program system (*11*). The atomic scattering factors used were those for neutral atoms (*12*). Structural refinement was performed by least-squares analysis, using as starting values the atomic coordinates of Mo_6Se_8 (*7*) and assuming occupational disorder on the metal atom site. While refinement of the Ru-based compound converged within a few cycles (agreement factor $R = 0.048$) the structure of the Re-based compound could not be refined below $R = 0.17$. Inspection of its Patterson map revealed unexpected peaks which could only be interpreted if the crystal was assumed to be twinned. The twinning showed two domains which were oriented such that the peaks of the majority component I appeared at positions $u_i^I v_i^I w_i^I$ and the corresponding peaks of the minority component II at $v_i^{II} u_i^{II} w_i^{II}$. The volume ratio, $k = V^{II}/V^{I}$, was estimated to be $k \sim 0.2$. Although reliable atomic coordinates were obtained from a refinement based on ($h0l$) reflections only ($R = 0.055$, 150 reflections) a search for possibly untwinned crystals was made. Among six specimens examined no such crystal was found. Thus an attempt was made to perform a least-squares refinement of the intensities using the complete (hkl) data set and a local modification of CRYLSQ (*11*). The constraining equations were

$$F^2_{obs}(hkl) = (1 - k) * F^2_{cal,I}(hkl) + k * F^2_{cal,II}(kh\bar{l})$$

$$F^2_{obs}(kh\bar{l} = k * F^2_{cal,I}(kh\bar{l}) + (1 - k) * F^2_{cal,II}(hk\bar{l})$$

(merohedric twin of case I (*13*)).

Refinement converged within a few cycles ($R = 0.056$, all data) and the atomic parameters obtained agreed within 2 e.s.d.'s with those obtained from the ($h0l$) data. The twinning ratio refined to $k = 0.163(3)$, which is close to the value estimated from the Patterson map.

In view of the substantial amount of impurity phase $MoSe_2$ found in the $Mo_2Re_4Se_8$ sample, additional refinements were performed by letting the Mo/Re ratio on the metal atom site vary, while the occupancy factors of the chalcogen atom sites were fixed at unity. As expected the Mo/Re ratio decreased from its nominal value of 0.5, indicating that the metal atom clusters may contain more than 4 Re atoms and less than 2 Mo atoms on the average. Convergence was obtained at a Mo/Re ratio corresponding to the formula $Mo_{1.5}Re_{4.5}Se_8$ ($R = 0.054$, 1058 reflections, 24 variables, significance level (*14*) $\alpha \sim 10^{-6}$). The Mo deficiency on these clusters is consistent with the amount of $MoSe_2$ impurity phase found in the $Mo_2Re_4Se_8$ sample (~10%), as can be seen from the following mass balance equation.

$$2Mo + 4Re + 8Se \rightarrow 0.89Mo_{1.5}Re_{4.5}Se_8 + 0.44MoSe_2 + 0.22Mo.$$

According to this reaction small amounts of unreacted Mo metal were expected in our $Mo_2Re_4Se_8$ samples, which however could not be detected experimentally, presumably because of overlap of the X-ray lines in the powder pattern.

Clearly, another possibility to interpret the lower Mo/Re ratio found by the X-ray structure refinement would be to assume vacancies on the Se atom sites. In fact, the proposed formula $Mo_{1.5}Re_{4.5}Se_8$ is crystallographically indistinguishable from the composition $Mo_2Re_4Se_{7.6}$, which is characterized by a Mo/Re ratio of 0.5 and ~5% Se vacancies.[4] However, such a high concen-

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[4] Assuming equal distribution over both Se atom sites.

tration of Se defects appears to be unlikely in view of the large number of MMo_6X_8 compounds which have been studied so far by single crystal X-ray diffraction, metallurgical methods, and density measurements, and for which no significant deviation from the ideal Mo/X ratio 6/8 has been detected with certainty as yet. Also, the assumption of a Mo/Re ratio of 0.5 in the rhombohedral phase is not consistent with the presence of the relatively large amount of $MoSe_2$ phase in our $Mo_2Re_4Se_8$ sample. Thus the Re substituted crystal studied in this work is very likely more Re rich than indicated by the nominal composition $Mo_2Re_4Se_8$. It will be designated by the formula $Mo_{1.5}Re_{4.5}Se_8$, keeping in mind, however, that direct evidence for this stoichiometry is still lacking. For the ruthenium substituted crystal, the Mo/Ru ratio could not be verified by refinement of the occupancy factors, because of the similar scattering power of the two metals. However, in view of the very small concentration of impurity phases found in the melted $Mo_4Ru_2Se_8$ sample (a few vol%, as judged from metallographic inspection) its value can be safely assumed close to the nominal ratio Mo/Ru = 2. Final electron density difference maps showed no peaks higher than $3e/\text{Å}^3$ for $Mo_4Ru_2Se_8$ (all data) and $Mo_{1.5}Re_{4.5}Se_8$ (*h*0*l*) data only. A vector difference map for $Mo_{1.5}Re_{4.5}Se_8$ (all data) showed no peaks higher than 2% of the origin peak height. Thus the structural models for both compounds describe well their actual structure and possible deviations due to anharmonic thermal vibrations and/or static displacements of some chalcogen atoms (possibly Se(2)) can be assumed to be small. Also a possible occupancy of interstitial sites in the chalcogen atom network by significant amounts of metal atoms can be excluded. The atomic parameters of both compounds are listed in Table II, and a list of bond distances is given in Table III. Tables I and III also contain the corresponding values of binary Mo_6Se_8 for comparison. The distance labels in Table III refer to the bonds shown in the structural drawing of Fig. 1. A graphic representation of the metal–metal bond lengths as a function of the VEC is given in Fig. 2.

Discussion

Comparing the metal–metal bond distances of $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$ in Fig. 2 with those of binary Mo_6Se_8 and ternary selenides MMo_6Se_8 one observes the following characteristic trends:

(i) Electron rich compounds have smaller and more regular metal atom octahedra than electron poor compounds (see decrease of bond lengths d_1 and d_2 as a function of the number of valence electrons on the metal cluster in Fig. 2a).

(ii) As the number of valence electrons is

TABLE II

$Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$: ATOMIC AND THERMAL PARAMETERS ($\times 10^4$ Å^2)[a]

Atom	Pos.	Occ.[c]	x	y	z	$U_{eq.}$[b]	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo/Ru	18f	$\frac{2}{3}/\frac{1}{3}$	0.0161(1)	0.1660(1)	0.3971(1)	67(3)	72(3)	73(3)	60(3)	39(2)	−4(2)	−4(2)
Se(1)	18f	1	0.3227(1)	0.2835(1)	0.4107(1)	97(3)	90(4)	84(4)	99(4)	30(3)	8(2)	12(2)
Se(2)	6c	1	0	0	0.2136(1)	117(21)	140(10)	U_{11}	71(6)	$\frac{1}{2}U_{11}$	0	0
Re/Mo	18f	0.76(2)/0.24	0.0156(1)	0.1643(1)	0.3978(1)	42(3)	50(4)	45(4)	30(3)	24(4)	−1(3)	1(3)
Se(1)	18f	1.00(1)	0.3254(3)	0.2839(3)	0.4103(2)	62(7)	70(9)	68(9)	47(7)	34(7)	9(6)	15(6)
Se(2)	6c	1.00(2)	0	0	0.2113(3)	73(5)	96(10)	U_{11}	29(12)	$\frac{1}{2}U_{11}$	0	0

[a] Space group $R\bar{3}$, No. 148 (*12*); the U_{ij} are defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$.

[b] U_{eq} is the equivalent isotropic temperature factor.

[c] Occupancy.

TABLE III

BOND DISTANCES (Å)

		Mo_6Se_8[a]	$Mo_4Ru_2Se_8$[b]	$Mo_{1.5}Re_{4.5}Se_8$[b]
Me	$-2Me$[c]	2.685(4)	2.659(1)	2.632(1)
	$-2Me$[d]	2.837(2)	2.710(2)	2.672(1)
	$-Me$[e]	3.266(3)	3.386(1)	3.406(1)
	$-Me$[f]	3.905(5)	3.797(1)	3.749(2)
	–Se(1)	2.587(5)	2.598(1)	2.621(3)
	–Se(1)	2.545(2)	2.522(2)	2.523(3)
	–Se(1)	2.572(5)	2.526(1)	2.526(3)
	–Se(1)[g]	2.598(3)	2.623(2)	2.635(3)
	–Se(2)	2.547(3)	2.514(1)	2.516(3)
Se(1)	$-Me$	2.587(5)	2.598(1)	2.621(3)
	$-Me$	2.545(2)	2.522(2)	2.523(3)
	$-Me$	2.572(5)	2.526(1)	2.526(3)
	$-Me$[g]	2.598(3)	2.623(2)	2.635(3)
Se(2)	$-3Me$	2.547(3)	2.514(1)	2.516(3)
$\bar{d}$(Se	–Se)[h]	3.61	3.59	3.58
d[Se(1)–Se(2)][i]		3.380(5)	3.449(2)	3.411(3)

[a] From Ref. (*7*).

[b] This work.

[c] d_2.

[d] d_1.

[e] d_3 in Figs. 1 and 3.

[f] Diagonal intracluster bond, d_4.

[g] Intercluster bond (d_{Me-Se} in Fig. 1).

[h] Average Se–Se contact.

[i] Shortest Se–Se contact (that *between* different Mo_6Se_8 units).

increased the metal atom octahedra contract mainly along the $\bar{3}$ axis and little perpendicular to this direction (bond length reduction $\Delta d_1 \gg \Delta d_2$).

(iii) The shortest separation between the metal atom clusters, d_3 (Fig. 1) does not only depend on the number of valence electrons on the metal cluster (Fig. 2b), but also on the rhombohedral cell parameter a_{rh} and thus the cell volume (Fig. 2c). A very similar correlation (not represented here) is also found for the metal–selenium *inter*cluster bonds, d_{Me-Se}.

Clearly, the apparent contraction of the metal atom octahedra in the mixed-cluster compounds $Mo_4Ru_2Se_8$ (No. 10 in Fig. 2a) and $Mo_{1.5}Re_{4.5}Se_8$ (No. 11) relative to those in Mo_6Se_8 (No. 1) exceeds the size reduction expected from considerations of atomic radii. Using, for instance, Pauling's single-bond radii (*15*) as a basis of comparison (Mo: 1.30 Å, Ru: 1.25 Å, Re: 1.28 Å) one expects for both species of mixed metal clusters [Mo_4Ru_2] and [$Mo_{1.5}Re_{4.5}$] an average *isotropic* bond length reduction of about 0.03 Å. The observed reduction, however, is much larger, as six metal–metal bonds (d_1) are shortened by 0.13 Å ($Mo_4Ru_2Se_8$) and 0.17 Å ($Mo_{1.5}Re_{4.5}Se_8$). Furthermore, the contraction is strongly *anisotropic*, and the metal atom octahedra in the Re based compound are significantly smaller than those in the Ru based compound. These observations, together with the consistent trend shown by the ternary MMo_6Se_8 selenides in Fig. 2a confirm the important role played by the valence electron concentration (*electronic effect*) for the size and shape of the metal atom octahedra.

As suggested previously, the amount of metal–metal bonding, and also many physical properties of these compounds depend critically on the *cluster*-VEC (*16*). This quantity is a measure of the average formal oxidation state of the metal atoms on the

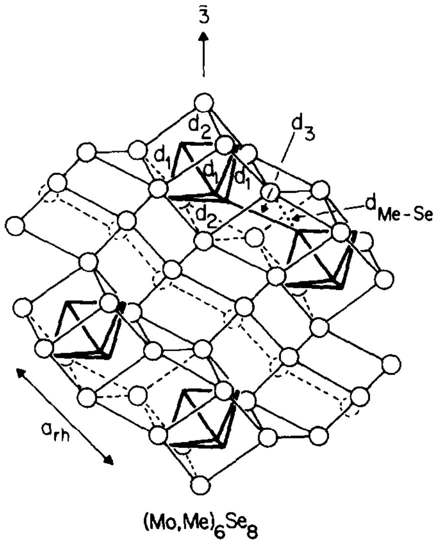

FIG. 1. The rhombohedral structure of pseudobinary $(Mo,Me)_6Se_8$ (Me = Ru,Re), projected approximately perpendicular to the ternary axis. Metal atom octahedra: heavy lines, Se atoms: circles. The bond labels refer to the bond lengths shown in Fig. 2 and listed in Table III.

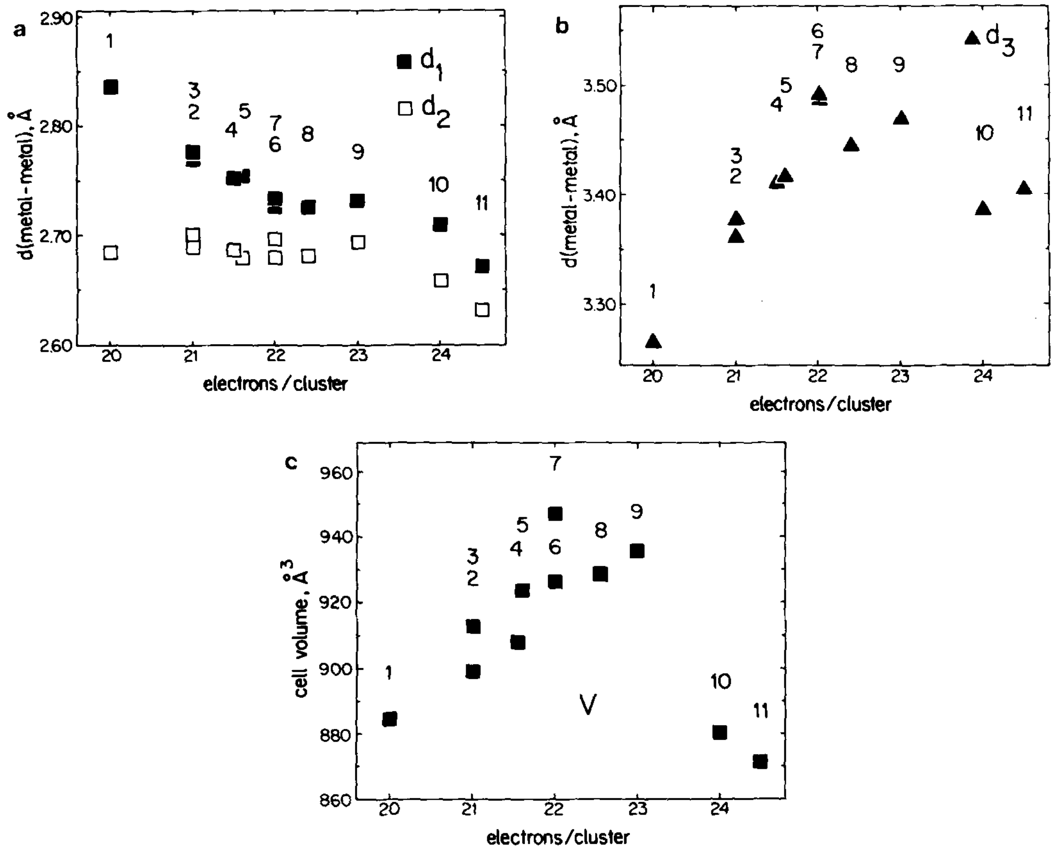

FIG. 2. The metal–metal intracluster bond distances d_1 and d_2 (a), the intercluster bond distance d_3 (b), and the hexagonal cell volume, V (c), in Mo_6Se_8 (1), $Mo_4Ru_2Se_8$ (10), $Mo_{1.5}Re_{4.5}Se_8$ (11), and MMo_6Se_8 selenides ($M = Cu^+$ (2), Ag^+ (3), $Cu^+_{1.5}$ (4) $Sn^{2+}_{0.8}$ (5), Cu_2^+ (6), Pb^{2+} (7), $La^{3+}_{0.8}$ (8), In^{3-} (9), as a function of the number of valence electrons on the metal atom cluster (≡ cluster-VEC, for definition see text). Data are taken from (*1*).

cluster, and it can be derived by assuming that the nonmetal (X) p states are completely filled by charge transfer from the metal atom states (those of the ternary metal component M plus those of the cluster components Mo, Re, Ru). The *cluster* VEC values defined in this way vary between the limits 20*e* (Mo_6Se_8) and 23*e* (e.g., $LaMo_6Se_8$) per metal atom cluster in those known selenides which are based on Mo only (*1*). In particular they do not reach in these compounds the "magic" number of 24*e* (as they do in certain sulfides, such as $Cu_4Mo_6S_8$), which corresponds to an energy gap in their electronic band structure (*2*). Clearly, higher values are reached in the selenides which contain mixed-metal clusters, such as $Mo_4Ru_2Se_8$ (24*e*) and $Mo_{1.5}Re_{4.5}Se_8$ (24.5*e*). The latter compound is particularly intriguing because it appears to be the first example of a member of the MMo_6X_8 class of compounds which contains *more* than 24 valence electrons per metal cluster.[5]

From a valence-bond theory point of

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[5] As pointed out earlier in the text the exact composition of this compound still needs to be confirmed by independent methods. However, note that a Se deficient crystal of composition $Mo_2Re_4Se_{7.6}$ would also have more than 24*e* per metal atom cluster.

view one anticipates for compounds with a low cluster-VEC value electron deficient and thus relatively long metal–metal intracluster bonds. For compounds having a high cluster-VEC these bonds are more saturated and are therefore expected to be shortened. As can be seen in Fig. 2a this behavior corresponds qualitatively to the observed experimental trend. It also correlates with some of the known physical properties since binary Mo_6Se_8 and the more reduced ternary MMo_6Se_8 selenides are metallic at room temperature (*17*) whereas the 24-electron compounds $Mo_4Ru_2Se_8$ and $Mo_2Re_4Se_8$ are thought to be semiconducting and diamagnetic (*5, 6*). Clearly, the latter properties would be consistent with the assumption of 12 covalent (2 center–2 electron) bonds which can formally be located near the edges of the metal atom octahedra.

However, a closer inspection of the bond lengths listed in Table II, and in particular a calculation of the metal–metal bond order sums, Σn_i, using Pauling's (*15*) relation

$$d(n) = d(1) - 0.6 \log_{10}(n) \qquad (1)$$

(n = bond order = number of valence electrons/number of nearest neighbors, $d(1)$ = sum of single-bond radii) shows that the number of cluster electrons obtained by (1) does not correspond to that expected. As has been discussed recently in detail (*4, 18*) the Σn_i values calculated from (1) are systematically too low for the $(M)Mo_6X_8$ compounds, and the discrepancies do not disappear if different sets of "single-bond" radii are used, or if metal-to-nonmetal bonds are included in the bond order summation. This led to the conclusion that the metal–metal bonds in this class of compounds are stretched beyond their "normal" value by the influence of the nonmetal matrix. This observation has already been made some years ago by Schäfer and Von Schnering while studying other classes of metal cluster compounds (*19*). One way of estimating the importance of this effect is to relate the metal–metal bond order sums calculated by (*1*) to the expected number of valence electrons on the metal atom cluster. The corresponding Pauling Bond Order per electron-*pair* values, PBO/*e* (4), have been calculated for the known $(M)Mo_6Se_8$ selenides and plotted as a function of the cluster electron count in Fig. 3. One can see that they fall considerably short of the expected value of unity, and vary within relatively narrow limits ($0.75 < PBO/e < 0.80$). This is also true for the mixed-cluster compounds $Mo_4Ru_2Se_8$ (PBO/e = 0.68) and $Mo_{1.5}Re_{4.5}Se_8$ (PBO/e = 0.76) for which the PBO/*e* values are definitely below unit, although that of the rhenium based compound appears to be anomalously high with

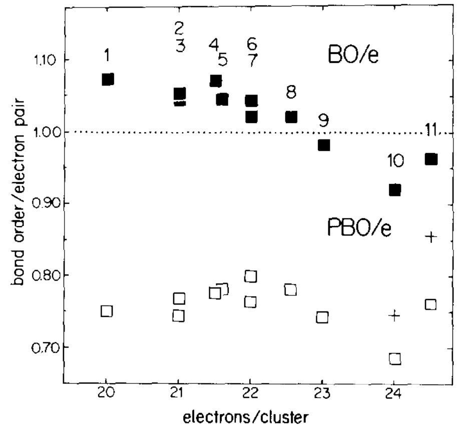

FIG. 3. The metal–metal bond order sums per electron pair, PO/*e* and PBO/*e*, vs the cluster-VEC in $(M)Mo_6Se_8$-type selenides. Lower curve: calculated using Pauling's logarithmic relation (1), upper curve: Donnay–Allmann relation (2). Bonds included in the summation: d_1 (6x), d_2 (6x), d_3 (3x), and d_4 (3x). Numbering as in Fig. 2. The reference distances $d(1)$ used for the metal–metal bonds are 2.619 Å (Mo_6Se_8 and MMo_6Se_8), 2.578 Å ($Mo_4Ru_2Se_8$), and 2.582 Å ($Mo_{1.5}Re_{4.5}Se_8$). They correspond to the weighted average of the single-bond distance which were derived from the elemental structures of the metals by using relation (1) and the metal valency 6 for Mo, Re, and Ru (*15*). Assuming metal valencies of 6 (Mo), 7 (Re), and 8 (Ru) larger $d(1)$ values are found (2.603 Å ($Mo_4Ru_2Se_8$) and 2.612 Å ($Mo_{1.5}Re_{4.5}Se_8$)) and thus higher PBO/*e* values (crosses).

respect to that of the ruthenium based compound. Thus in terms of bond orders as defined by (*1*) a *matrix effect* can also be assumed in these very electron rich compounds. This conclusion is consistent with the observed elongation of their metal atom octahedra which, although reduced, is still apparent.

Based on these observations one may describe the interplay between the *electronic* and the *matrix effect* as follows. The *electronic effect* is strongest in electron poor compounds such as Mo_6Se_8. This can be seen from the quasi-exponential decrease of the metal–metal bond distances d_1 in Fig. 2a, which corresponds formally to logarithmic relation (1). It influences mainly one type of intracluster bonds (d_1) for which it leads to a mean *contraction* of about 0.17/4 = 0.04 Å per electron added to the cluster. The *matrix effect,* by comparison, does not vary much as a function of the cluster electron count. It causes an *expansion* of both types of intracluster bonds (d_1 and d_2) although the bonds perpendicular to the ternary axis (d_2) appear to be less affected. From the bond order reduction shown in Fig. 3 and the size of the metal atom clusters in electron rich compounds (Fig. 2a) one can estimate this expansion to be of the order of 0.1 Å. However, this value applies mainly to selenides, and it should be considered only as a crude estimate. In fact the PBO/*e* values shown in Fig. 3 exhibit some scattering which could be related to slight differences in the *matrix effect.* Such differences are conceivable for the ternary MMo_6Se_8 compounds which contain cations M of different size and charge, but they can hardly be responsible for the difference between the PBO/*e* values of the two pseudobinary compounds $Mo_4Ru_2Se_8$ (0.68) and $Mo_{1.5}Re_{4.5}Se_8$ (0.76) which have practically the same anion matrix (as judged from the average and shortest Se–Se distances listed in Table III) and differ only little with respect to their VEC. This difference is more likely to be of electronic origin. It could indicate, for instance, that the ordering of the metal *d* bonding states in mixed-metal cluster compounds differs significantly from that in the Mo-based compounds Mo_6X_8 and MMo_6X_8 (*2*). If this is true, the *24-electron rule* which correlates well with the position of the forbidden-energy gap in the Mo based compounds may not necessarily correlate with the true compositions of semiconducting compounds such as those reported in the mixed-cluster series $(Mo,Me)_6X_8$ (Me = Re,Ru) (*5, 6*).

Finally, it is useful to point out that the above bond order analysis and in particular the discussion of the *matrix effect* depends critically on the choice of the analytical function and its parameters. Although the prelog constant of 0.6 Å used in Eq. (1) has shown to yield satisfactory results for a wide range of inorganic compounds (*15*) it may not be the best choice for this class of compounds. As shown for instance in oxide structures (*20*) higher values (up to 1.1 Å) yield more consistent results, and for some compounds (for instance, borates (*21*), or sulfides (*22*)) different analytical functions may be applied with equal success, such as the relation

$$n = [d(1)/d(n)]^5 \qquad (2)$$

originally proposed by Donnay and Allmann (*20, 21*). Although relation (2) does not seem to have been applied systematically to metal–metal bonds as yet, an attempt was made to use it for calculating bond order sums in the MMo_6X_8 class of compounds. Taking the *same* reference radii and observed metal–metal bond distances as those used for calculating PBO/*e* values with relation (1) one obtains for the selenides Bond Order per electron pair values, BO/*e*, which are consistently higher than the corresponding PBO/*e* values and come much closer to unity (see upper data points in Fig. 3). Interestingly, this relation yields BO/*e* values close to unity also for the sulfides Mo_6S_8 and MMo_6S_8 ($0.95 < BO/e < 1.10$ as compared to $0.70 < PBO/e < 0.85$ (*4*)) and the telluride Mo_6Te_8 ($BO/e = 1.02$, $PBO/e = 0.70$ (misprinted as 0.65 in (*4*) and (*23*)), and also for many other metal cluster compounds for which a *matrix effect* has been found (*23*). As far as the $(M)Mo_6X_8$ chalcogenides are concerned the reason for the general increase of the bond order sums is mainly due to the heavier weight received by the long metal–metal bonds *between* the metal atom clusters (d_3) in relation (2) as compared to that in relation (1). This could be an indication that the relatively "soft" potential implied by (2) is a more adequate approximation to describe the metal–metal bonding in this class of compounds than the relatively "hard" potential implied by the logarithmic relation (1). It must be kept in mind, however, that the above bond order analysis is somewhat arbitrary because it makes combined use of *two* relations, i.e., (1) for calculating single-bond distances $d(1)$ from the metals (*15*), and (2) for calculating bond orders n from experimentally observed bond lengths $d(n)$ (*20*). Although this procedure leads to a more coherent description of the metal–metal bonding in this class of compounds, it has the disadvantage that any simple relationship to the bonding in metals is lost.

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