Journal of Alloys and Compounds 262–263 (1997) 311–315

Journal of ALLOYS AND COMPOUNDS

New experimental and theoretical studies on condensed molybdenum chalcogenide cluster compounds

Régis Gautier, Patrick Gougeon, Jean-François Halet*, Michel Potel, Jean-Yves Saillard

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Université de Rennes 1, F-35042 Rennes, France

Abstract

New theoretical investigations using density functional theory calculations on condensed molybdenum chalcogenide cluster compounds $A_{n-2}Mo_{3n}X_{3n+2}$ (A = alkali metal) suggest that it should be possible to reduce them with several electrons without changing their structural arrangement. Experimental work on several examples such as $Cs_2Mo_{12}Se_{14}$ confirms these conclusions. © 1997 Elsevier Science S.A.

Keywords: Molybdenum; Chalcogenide cluster compounds; Selenium

1. Introduction

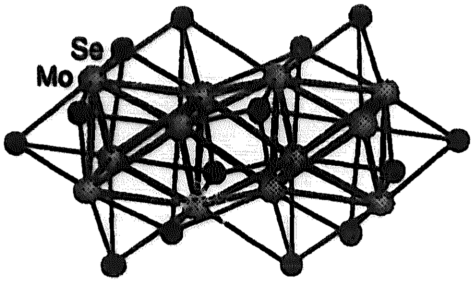
Since their discovery in the early 1970s, the Chevrel phases have constituted a fascinating set of ternary molybdenum chalcogenide materials of varying dimensionality and interesting physical properties [1–3]. The most representative example is $PbMo_6S_8$ which contains discrete face-capped octahedral $M_6(\mu_3\text{-}S)_8$ units connected by metal-chalcogenide bridges [4]. Also included in this family are finite condensed clusters such as the $Mo_{12}Se_{14}$ (Fig. 1) entity present in $Cs_2Mo_{12}Se_{14}$, which is made of face-sharing octahedra surrounded by bridging selenide ligands [5]. Described as built by the successive insertion of additional Mo_3X_3 planar fragments between chalcogens that form the apices of oligomers, Mo_6Se_8 and $Mo_{12}Se_{14}$ are members of a series of chain-like compounds which can be formulated $Mo_{3n}X_{3n+2}$. Different oligomers with X = S, Se, and Te, and n = 2–8, 10, ∞ have been achieved. They are listed in Table 1. Metal-metal and metal-chalcogen separations in these clusters are comparable to those measured in Mo_6X_8 compounds ($2.6 \le d_{Mo\text{-}Mo} \le 2.8$ Å) with intra-layer Mo-Mo distances somewhat shorter (~0.1 Å) than inter-layer distances. Just as in Mo_6X_8 compounds, the large clusters assemble themselves in the solid state in such a way that outer Mo atoms of the clusters are linked to chalcogen atoms of neighboring clusters.

The examination of both the crystal and electronic structures indicates a weak metal-metal bonding between clusters and a significant metal-metal bonding within the clusters. The study of the electronic structure of isolated $Mo_{3n}X_{3n+2}$ oligomers is then a good starting point to understand the bonding properties of these materials. Assuming an oxidation state of −II for the X ligands, the number of metallic electrons (ME) is often ($13n - 6$) (see Table 1). However, regarding the chemical bonding in these clusters based on Extended Hückel (EH) calculations, theoretical considerations performed by Hughbanks and Hoffmann revealed that a significant gap between M-M bonding and antibonding sets is kept as n increases.

---

*Corresponding author. Fax: +33 2 99635704; e-mail: halet@univ-rennes1.fr

0925-8388/97/$17.00 © 1997 Elsevier Science S.A. All rights reserved
PII S0925-8388(97)00413-1



1

The filling of all the bonding molecular orbitals leads to an optimal electron count of (13n − 2) for even n and (13n − 3) or (13n − 1) for odd n [12,13]. More electron-rich oligomers should probably be stable [12,13].

Fenske and others have shown that the structural principle of face-sharing condensation of octahedral units can be extended to the more electron-rich transition metals. Molecular $M_{3n}X_{3n+2}$ and $M_{3n}X_{3n}$ compounds such as $Co_9Se_{11}(PPh_3)_6$ (59 MEs) [14], $[Ni_9S_9(PEt_3)_6]^{2+}$ (70 MEs) [15], $Ni_{12}Se_{12}(PEt_3)_6$ (96 MEs) [16], $Ni_{15}S_{15}(PPh_3)_6$ (120 MEs) [17] and $Ni_{15}Se_{15}(PPh_3)_6$ (120 MEs) [16] were synthesized. Although structurally related to the solid state molybdenum chalcogenide materials, these compounds are considerably electronically different, with extra electrons occupying metal-metal antibonding MOs (Gautier et al., unpublished results). Considering this, it is somewhat puzzling that at least the occupation of all the metal-metal bonding levels is not generally achieved for the condensed Chevrel phases. It is why we have decided to revisit both theoretically and experimentally the chemistry of the molybdenum chalcogenides. We have concentrated our efforts on the molybdenum selenide compounds.

Table 1
Ternary molybdenum chalcogenides $A_xMo_{3n}X_{3n+2}$ characterized by X-ray diffraction[a]

n[b]	Compound	Cluster	ME[c]	Reference
3	h-Mo_9Se_{11}	Mo_9Se_{11}	32 (13n − 7)	—[d]
	$Ag_{2.3}CsMo_9Se_{11}$	$Mo_9Se_{11}^{3.3-}$	35.3 (13n − 3.7)	[6]
	$Ag_{4.4}ClMo_9Se_{11}$	$Mo_9Se_{11}^{3.4-}$	35.4 (13n − 3.6)	[6]
4	$KMo_{12}S_{14}$	$Mo_{12}S_{14}^{-}$	45 (13n − 7)	—[d]
	$K_{2.3}Mo_{12}S_{14}$	$Mo_{12}S_{14}^{2.3-}$	46.3 (13n − 5.7)	—[d]
	$Rb_2Mo_{12}Se_{14}$	$Mo_{12}X_{14}^{2-}$	46 (13n − 6)	—[d]
	$Cs_2Mo_{12}Se_{14}$			[5]
	$Cs_2Mo_{12}Te_{14}$			—[d]
5	$Rb_3Mo_{15}Se_{17}$	$Mo_{15}X_{17}^{3-}$	59 (13n − 6)	[7]
	$Cs_3Mo_{15}Se_{17}$			[8]
	$Cs_3Mo_{15}Te_{17}$			—[d]
6	$Rb_4Mo_{18}Se_{20}$	$Mo_{18}X_{20}^{4-}$	72 (13n − 6)	[9]
	$Cs_4Mo_{18}Se_{20}$			—[d]
	$Cs_4Mo_{18}Te_{20}$			—[d]
7	$Cs_5Mo_{21}S_{23}$	$Mo_{21}X_{23}^{5-}$	85 (13n − 6)	[10]
	$Rb_5Mo_{21}Se_{23}$			—[d]
	$Cs_5Mo_{21}Se_{23}$			[11]
8	$Cs_6Mo_{24}S_{26}$	$Mo_{24}X_{26}^{6-}$	98 (13n − 6)	[6]
	$Cs_6Mo_{24}Se_{26}$			[6]
	$Cs_6Mo_{24}Te_{26}$			—[d]
10	$Cs_8Mo_{30}S_{32}$	$Mo_{30}X_{32}^{8-}$	124 (13n − 6)	[6]
	$Cs_8Mo_{30}Se_{32}$			[6]

[a] Compounds containing a 'mixture' of different oligomers are not listed here.
[b] Number of Mo_3X_3 layers.
[c] Metallic electron count.
[d] Gougeon et al., unpublished results.

2. Theoretical considerations

Density functional theory (DFT) calculations were performed on different isolated models $(Mo_9Se_{11})^-$, $(Mo_{12}Se_{14})^{2-}$, and $(Mo_{15}Se_{17})^{3-}$ with (13n − 6) MEs.[1] Geometry optimization was made under the symmetry constraint D_{3h}, D_{3d}, and D_{3h}, respectively. The molecular orbital diagrams of these optimized $Mo_{3n}Se_{3n+2}$ oligomers are illustrated in Fig. 1. The energy levels are labeled in the symmetry subgroup C_{3v} in order to allow a comparison between clusters with odd and even values of n. As noted previously by Hughbanks and Hoffmann for the $Mo_{12}S_{14}$ model [12], low-lying MOs (26e and $6a_2$) remain partially or fully empty for the observed electron count of 46 (13n = 6), that is for $(Mo_{12}Se_{14})^{2-}$. The 26e and $6a_2$ MOs, which are strongly metallic in character, are Mo-Mo non-bonding overall. Assuming a 'rigid MO' model, electron count up to 50 (13n − 2) should be possible without altering much the oligomer architecture. In agreement with this result, a comparison of the optimized geometries for 46 and 50 MEs indicates a slight change in the Mo-Mo distances upon addition of electrons (see Table 2). Note that although the six 'terminal' Se^{2-} ligands tethered to the outer Mo atoms in the solid state were not taken into account in the calculations, the Mo-Mo distances computed for $(Mo_{12}Se_{14})^{2-}$ compare rather well with the corre-

---

[1] Density functional theory calculations were carried out on different $(Mo_{3n}Se_{3n+2})^{n-}$ oligomers using the Amsterdam Density Functional (ADF) program [18] developed by Baerends and co-workers [19–22]. Electron correlation was treated within the local density approximation [23]. The geometry optimization procedure was based on the method developed by Versluis and Ziegler [24]. The atom electronic configurations were described by a triple-ζ STO basis set for Mo 4d and 5s, augmented with a single-ζ 5p polarization function, and a triple-ζ STO basis set for Se 4s and 4p, augmented with a single-ζ 4d polarization function. A frozen-core approximation was used to treat the core electrons of Mo and Se.

Table 2
Comparison of experimental and optimized Mo-Mo bond distances (Å) for different $(Mo_{3n}X_{3n+2})^{m-}$ oligomers

Distances	Exp.(m = 3.3)[a]	Exp.(m = 3.4)[b]	m = 1	m = 4
$Mo_9Se_{11}{}^{m-}$				
Intra-layer:				
Mo_o-Mo_o	2.627	2.609	2.577	2.570
Mo_i-Mo_i	2.732	2.739	2.648	2.792
Inter-layer:				
Mo_o-Mo_i	2.715	2.716	2.689	2.713
Distances	Exp.(m = 2)		m = 2	m = 6
$Mo_{12}Se_{14}{}^{m-}$				
Intra-layer:				
Mo_o-Mo_o	2.656		2.554	2.596
Mo_i-Mo_i	2.682		2.745	2.769
Inter-layer:				
Mo_o-Mo_i	2.777		2.706	2.704
Mo_i-Mo_i	2.682		2.747	2.838
Distances	Exp.(m = 3)		m = 3	m = 6
$Mo_{15}Se_{17}{}^{m-}$				
Intra-layer:				
Mo_o-Mo_o	2.658		2.560	2.586
Mo_i-Mo_i	2.670/2.667		2.732/2.723	2.768/2.716
Inter-layer:				
Mo_o-Mo_i	2.752		2.734	2.711
Mo_i-Mo_i	2.714		2.760	2.798

[a] $Ag_{2.3}CsMo_9Se_{11}$.
[b] $Ag_{4.4}ClMo_9Se_{11}$.

sponding bond lengths measured experimentally in $Cs_2Mo_{12}Se_{14}$ for instance (see Table 2). A deviation smaller than ~0.1 Å is observed.

Based on EH calculations, Hughbanks and Hoffmann proposed an optimal electron count of either 36 ($13n-3$) or 38 ($13n-1$) for the cluster Mo_9S_{11} [12]. These results were partially confirmed by our DFT calculations on $(Mo_9Se_{11})^-$ and $(Mo_{15}Se_{17})^{3-}$. As shown in Fig. 1, an open-shell electronic configuration is found for the electron count of ($13n-6$), with low-lying MOs partially or fully empty. Electron counts of 36 and 62 seem optimal for Mo_9Se_{11} and $Mo_{15}Se_{17}$, respectively. Although situated in the middle of a large energy gap, the possible occupation of the $5a_2$ MO and the $8a_2$ MO in Mo_9Se_{11} and $Mo_{15}Se_{17}$, respectively, which would lead to electron counts of 38 and 64, seems unlikely. Indeed, these MOs, which are strongly localized on the metal atoms, are metal-metal antibonding overall and rather high in energy. Therefore, we think that the optimal electron count for the $Mo_{3n}Se_{3n+2}$ oligomers is ($13n-3$) for odd values of n.

The partially and/or fully unoccupied low-lying MOs in $(Mo_9Se_{11})^-$ and $(Mo_{15}Se_{17})^{3-}$ are Mo-Mo non-bonding overall. As for $Mo_{12}Se_{14}$, addition of extra electrons should not alter much the structural arrangement of these oligomers. This is confirmed by optimization of the models $(Mo_9Se_{11})^{4-}$ and $(Mo_{15}Se_{17})^{6-}$ which yields geometries comparable to those of $(Mo_9Se_{11})^-$ and $(Mo_{15}Se_{17})^{3-}$ (see Table 2).

It is important to note that not all of the characterized oligomers obey the rule of ($13n-6$) MEs (see Table 1). For instance, the Mo_9Se_{11} cluster contained in $Ag_{2.3}CsMo_9Se_{11}$ [6] and $Ag_{4.4}ClMo_9Se_{11}$ [6] has ($13n-3.7$) and ($13n-3.6$) MEs, respectively, an electron count close to the optimal count of ($13n-3$), with the 20e MO nearly fully occupied. This is why a better agreement is observed between the experimental structures and the optimized $(Mo_9Se_{11})^{4-}$ geometry rather than the $(Mo_9Se_{11})^-$ geometry (see Table 2).

In summary, a good agreement is obtained between the experimental and optimized interatomic distances in these materials. This provides compelling evidence that the computational method used here is reliable for predicting the bond lengths of such systems, and confirms the previous EH results.

The conclusions obtained from calculations on isolated clusters remain valid in the solid state. Extended Hückel tight-binding calculations on the su-

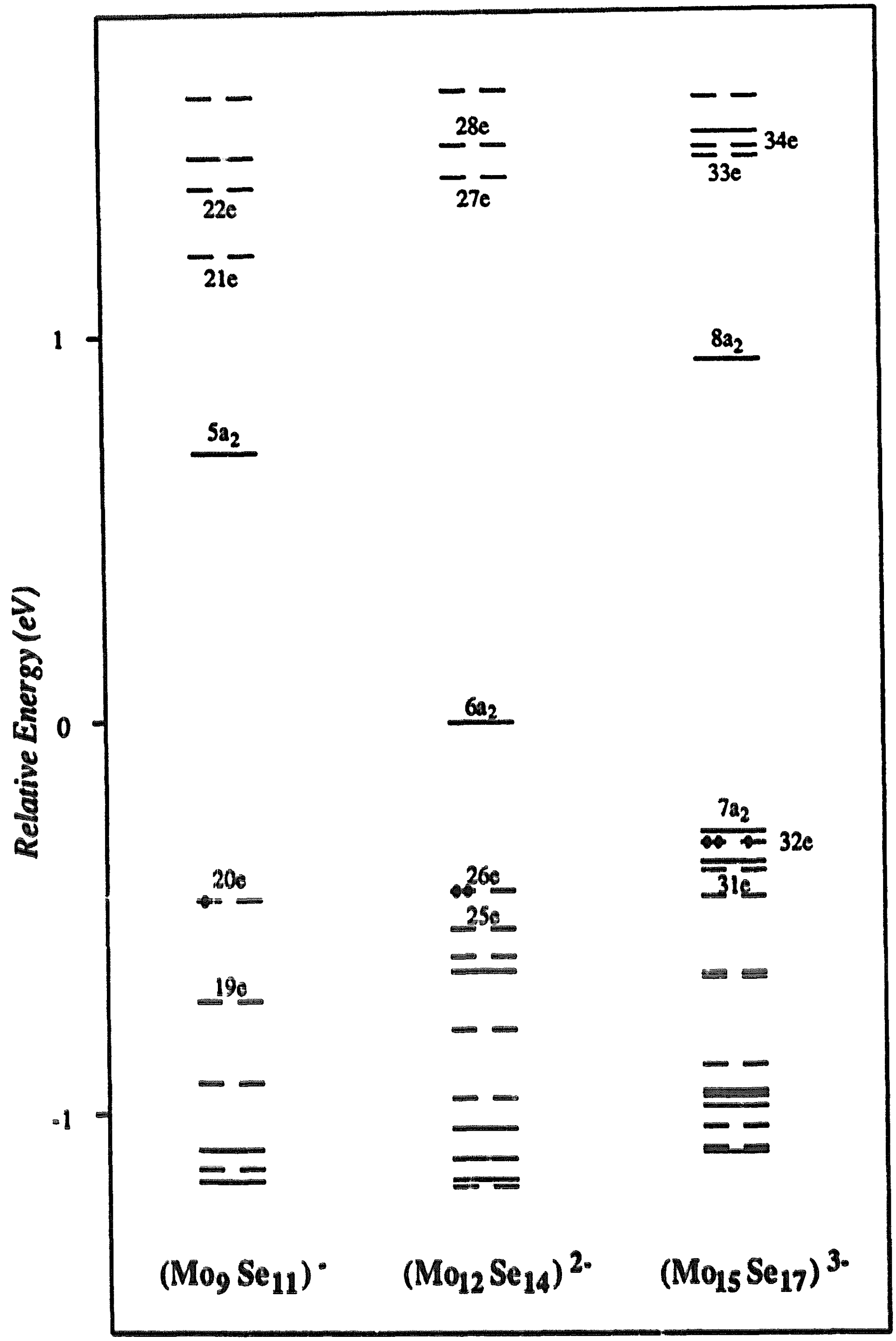


Fig. 1. Density functional theory molecular orbital diagrams for isolated optimized $(Mo_9Se_{11})^-$, $(Mo_{12}Se_{14})^{2-}$, and $(Mo_{15}Se_{17})^{3-}$ clusters.

perconducting material $Cs_2Mo_{12}Se_{14}$ for instance indicate rather low-lying flat bands crossed by the Fermi level, largely separated from upper bands in the density of states. With these theoretical results in mind, the chemistry of different $Mo_{3n}X_{3n+2}$ oligomers was reinvestigated in order to explore the possibility of synthesizing stable species with electron counts larger than $(13n-6)$. Results concerning the oligomer $Mo_{12}Se_{14}$ are reported here.

3. Experimental studies

In $Cs_2Mo_{12}Se_{14}$, which crystallizes in space group $R\bar{3}$, the 'packing' of the $Mo_{12}Se_{14}$ units leads to the creation of large voids in which are located the Cs cations [5]. Nevertheless, small-size crystallographic sites remain empty. Therefore, among the different possibilities for increasing the number of electrons on the $Mo_{12}Se_{14}$ units, insertion of a small reducing transition-metal element was chosen. Attempts to introduce silver were unproductive. On the other hand, insertion of Cu and Zn was successful leading to new materials, namely $Cu_{1.4}Cs_2Mo_{12}Se_{14}$ and $Zn_{1.9}Cs_2Mo_{12}Se_{14}$.[2] X-ray measurements performed on single-crystals indicate that Cu^+ and Zn^{2+} cations occupy trigonal and tetrahedral interstices between $Mo_{12}Se_{14}$ units, respectively. A comparison of selected Mo-Mo distances found in $Cs_2Mo_{12}Se_{14}$, $Cu_{1.4}Cs_2Mo_{12}Se_{14}$, and $Zn_{1.9}Cs_2Mo_{12}Se_{14}$ is given in Table 3. As expected from theoretical geometry optimization, the same architecture is kept for the reduced oligomers $(Mo_{12}Se_{14})^{3.4-}$ and $(Mo_{12}Se_{14})^{5.8-}$ encountered in $Cu_{1.4}Cs_2Mo_{12}Se_{14}$ and $Zn_{1.9}Cs_2Mo_{12}Se_{14}$ (see Table 2 and Table 3). Preliminary experiments on $Cs_3Mo_{15}Se_{17}$ indicate that larger electron-deficient $Mo_{3n}X_{3n+2}$ oligomers can also be reduced without altering their structural arrangement.

Further work is in progress in order to evaluate the change of the physical properties upon addition of electrons to these clusters.

The new results indicate that in turn, the $(13n - 6)$ electron rule may not particularly be favored thermodynamically but rather depends upon the choice of the elements and the method of preparation.

Table 3
Selected Mo-Mo bond distances (Å) measured in $Cs_2Mo_{12}Se_{14}$, $Cu_{1.4}Cs_2Mo_{12}Se_{14}$, and $Zn_{1.9}Cs_2Mo_{12}Se_{14}$

Distances	$Cs_2Mo_{12}Se_{14}$	$Cu_{1.4}Cs_2Mo_{12}Se_{14}$	$Zn_{1.9}Cs_2Mo_{12}Se_{14}$
Intra-layer:			
Mo_o-Mo_o	2.656	2.617	2.635–2.666–2.623
Mo_i-Mo_i	2.682	2.686	2.683–2.700–2.705
Inter-layer:			
Mo_o-Mo_i	2.758	2.719	2.657–2.668–2.686
	2.796	2.743	2.665-2.686–2.690
Mo_i-Mo_i	2.682	2.692	2.755–2.761–2.793

Acknowledgements

Thanks are expressed to the Centre de Ressources Informatiques (CRI) of the University of Rennes and the Institut de Développement et de Ressources en Informatique Scientifique (IDRIS-CNRS) of Orsay for computing facilities.

References

[1] R. Chevrel, M. Sergent, in: Ø. Fischer, M.B. Maple (Eds.), Superconductivity in Ternary Compounds I, Springer, Berlin, 1982, p. 25.
[2] R. Chevrel, M. Sergent, in: J. Rouxel (Ed.), Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures, D. Reidel, 1986, p. 315.
[3] A. Simon, in: G. Schmid (Ed.), Metal Clusters and Colloids, Weinheim, Verlag, 1994, p. 373.
[4] R. Chevrel, M. Sergent, J. Prigent, J. Solid State Chem. 3 (1971) 515.
[5] P. Gougeon, M. Potel, J. Padiou, M. Sergent, Mater. Res. Bull. 22 (1987) 1087.
[6] P. Gougeon, Thesis, Rennes, 1984.
[7] P. Gougeon, M. Potel, M. Sergent, Acta Cryst. C45 (1989) 182.
[8] P. Gougeon, M. Potel, M. Sergent, Acta Cryst. C45 (1989) 1413.
[9] P. Gougeon, M. Potel, J. Padiou, M. Sergent, Mater. Res. Bull. 23 (1988) 453.
[10] P. Gougeon, S. Picard, M. Potel, Acta Cryst. (1997) (in press).
[11] P. Gougeon, M. Potel, M. Sergent, Acta Cryst. C46 (1990) 2284.
[12] T. Hughbanks, R. Hoffmann, J. Am. Chem. Soc. 105 (1983) 1150.
[13] T. Hughbanks, Prog. Solid State Chem. 19 (1989) 329.
[14] D. Fenske, J. Ohmer, Angew. Chem., Int. Ed. Engl. 26 (1987) 148.
[15] C.A. Ghilardi, S. Midollini, L. Saccini, J. Chem. Soc., Chem. Commun. (1981) 47.
[16] D. Fenske, J. Ohmer, J. Hachgenei, Angew. Chem., Int. Ed. Engl. 24 (1985) 993.
[17] M. Hong, Z. Huang, H. Liu, J. Chem. Soc., Chem. Commun. (1990) 1210.
[18] Amsterdam Density Functional (ADF) program, release 2.0.1, Vrije Universiteit, Amsterdam, Netherlands, 1996.
[19] E.J. Baerends, D.E. Ellis, P. Ros, Chem. Phys. 2 (1973) 41.
[20] E.J. Baerends, P. Ros, Int. J. Quantum Chem. S12 (1978) 169.
[21] P.M. Boerrigter, G. te Velde, E.J. Baerends, Int. J. Quantum Chem. 33 (1988) 87.
[22] G. te Velde, E.J. Baerends, J. Comput. Phys. 99 (1992) 84.
[23] S.D. Vosko, L. Wilk, M. Nusair, Can. J. Chem. 58 (1990) 1200.
[24] L. Versluis, T. Ziegler, J. Chem. Phys. 88 (1988) 322.

---

[2] Preparation. $Cu_{1.4}Cs_2Mo_{12}Se_{14}$: a mixture of $Cs_2Mo_{12}Se_{14}$ crystals and an excess of Cu powder was heated at 800°C for 100 h in an evacuated silica tube, followed by slow cooling down to room temperature at 10°C/h. $Zn_{1.9}Cs_2Mo_{12}Se_{14}$: the same procedure was used at 450°C. Crystallographic data. $Cu_{1.4}Cs_2Mo_{12}Se_{14}$: $R\bar{3}$, $a = 9.900$ (1), $c = 24.370$ (1) Å, $V = 2068.7$ (9) Å^3, $Z = 3$, $R(F) = 0.039$, $R_w(F) = 0.041$ (based on 1457 reflections with $I > 2\sigma(I)$). $Zn_{1.9}Cs_2Mo_{12}Se_{14}$: $P\bar{1}$, $a = 9.942$ (2), $b = 9.940$ (2), $c = 9.915$ (2) Å, $\alpha = 61.76$ (2), $\beta = 60.06$ (2), $\gamma = 57.15$ (2), $V = 685.2$ (3) Å^3, $Z = 1$, $R(F) = 0.042$, $R_w(F) = 0.043$ (based on 2273 reflections with $I > 2\sigma(I)$). Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Accurate cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections. Structures were solved with the aid of MOLEN programs (K. Fair, ENRAF-NONIUS, Delft, The Netherlands, 1990).