

Fig. 6. SCHAKAL (Keller, 1986) stereo plots of the structure of $\text{Cu}(\text{OH})_2$ based on atomic parameters of (a) the centrosymmetric refinement of single-crystal data, corresponding to the structure reported from X-ray powder data (Jaggi & Oswald, 1961), (b) non-centrosymmetric refinement.

involving H atoms, since the hydrogen bonds observed are much too weak to suggest such a transition mechanism.

Gratitude is expressed to the Swiss National Science Foundation for financial support under No. 2000-5.422.

Acta Cryst. (1990). C46, 2284–2287

Structure of $\text{Cs}_5\text{Mo}_{21}\text{Se}_{23}$ Containing Mo_{21} Clusters

BY P. GOUGEON, M. POTEL AND M. SERGENT

Laboratoire de Chimie Minérale B, Unité de Recherche Associée au CNRS n° 254, Université de Rennes I, Avenue du Général Leclerc–35042 Rennes CEDEX, France

(Received 3 November 1989; accepted 11 May 1990)

Abstract. Pentacaesium hencosamolybdenum tricosaselenium, $\text{Cs}_5\text{Mo}_{21}\text{Se}_{23}$, $M_r = 4495.35$, hexagonal, $P6_3/m$, $a = 9.6513(7)$, $c = 29.939(6)$ Å, $V = 2415.1(5)$ Å³, $Z = 2$, $D_x = 6.181$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 259.9$ cm⁻¹, $F(000) = 3878$, $T = 295$ K, $R = 0.034$ for 1290 observed. The main building block of the title compound is the new cluster unit $\text{Mo}_{21}\text{Se}_{23}$ whose Mo core consists of six

0108-2701/90/122284-04\$03.00

References

- CUDENNEC, Y., LECERF, A., RIOU, A. & GERAULT, Y. (1988). *Eur. J. Solid State Inorg. Chem.* **25**, 351–358.
- DUBLER, E., HESS, R. & OSWALD, H. R. (1976). *Z. Anorg. Allg. Chem.* **421**, 61–70.
- DUBLER, E., KORBER, P. & OSWALD, H. R. (1973). *Acta Cryst.* **B29**, 1929–1933.
- FLEET, M. E. (1975). *Acta Cryst.* **B31**, 183–187.
- GAZO, J., BERSUKER, I. B., GARAJ, J., KABESOVA, M., KOHOUT, J., LANGFELDEROVA, H., MELNIK, M., SERATOR, M. & VALACH, F. (1976). *Coord. Chem. Rev.* **19**, 253–297.
- GRICE, J. D. & GASPARRINI, E. (1981). *Can. Mineral.* **19**(2), 337–340.
- GÜNTER, J. R. & OSWALD, H. R. (1970). *J. Appl. Cryst.* **4**, 21–26.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- HATHAWAY, B. J. (1984). *Struct. Bonding (Berlin)*, **57**, 55–118.
- HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210–214.
- JAGGI, H. & OSWALD, H. R. (1961). *Acta Cryst.* **14**, 1041–1045.
- KARLE, I. L., DRAGONETTE, K. S. & BRENNER, S. A. (1965). *Acta Cryst.* **19**, 713–716.
- KELLER, E. (1986). *SCHAKAL. Chem. Unserer Zeit*, **20**, 178–181.
- MARSH, R. E. (1981). *Acta Cryst.* **B37**, 1985–1988.
- MELLINI, M. & MERLINO, S. (1979). *Z. Kristallogr.* **149**, 249–257.
- OSWALD, H. R. & ASPER, R. (1977). In *Preparation and Crystal Growth of Materials with Layered Structures*, edited by R. M. A. LIETH, pp. 71–140. Dordrecht, Boston: D. Reidel.
- OSWALD, H. R. & FEITKNECHT, W. (1964). *Helv. Chim. Acta*, **47**, 272–289.
- PARISE, J. B. & HYDE, B. G. (1986). *Acta Cryst.* **C42**, 1277–1280.
- SCHOMAKER, V. & MARSH, R. E. (1983). *Acta Cryst.* **A39**, 819–820.
- SCHÖNENBERGER, U. W., GÜNTER, J. R. & OSWALD, H. R. (1971). *J. Solid State Chem.* **3**, 190–193.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1985). *SHELXS86*. In *Crystallographic Computing 3*, edited by G. M. SHELDRIK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
- VORONOVA, A. A. & VAINSHTEIN, B. K. (1958). *Sov. Phys. Crystallogr.* **3**, 445–451.

face-linked Mo_6 octahedra. These cluster units are linked to each other through Mo—Se interunit bonds and delimit large voids and channels where the Cs ions reside in a tri- or tetra-capped trigonal prismatic Se environment.

Introduction. In a recent systematic survey of the lower ternary chalcogenides of molybdenum with the

Table 1. *Positional parameters and equivalent isotropic thermal parameters*

	$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			$B_{eq}(\text{\AA}^2)$
	x	y	z	
Mo(1)	0.5195 (1)	0.1653 (1)	0.52395 (3)	0.60 (2)
Mo(2)	0.6847 (1)	0.1834 (1)	0.60037 (3)	0.50 (1)
Mo(3)	0.5184 (1)	0.1647 (1)	0.67488 (3)	0.50 (1)
Mo(4)	0.6878 (2)	0.1859 (2)	0.750	0.52 (2)
Se(1)	0.0440 (1)	0.3376 (1)	0.47042 (4)	0.67 (2)
Se(2)	0.6236 (1)	-0.0063 (1)	0.09918 (4)	0.76 (2)
Se(3)	0.7097 (1)	0.0439 (1)	0.67533 (4)	0.76 (2)
Se(4)	0.6223 (2)	0.0003 (2)	0.250	0.68 (3)
Se(5)	0.667	0.333	0.45672 (6)	0.80 (2)
Cs(1)	0.667	0.333	0.16787 (5)	1.59 (2)
Cs(2)	0.000	0.000	0.250	1.87 (3)
Cs(3)	0.000	0.000	0.09476 (6)	1.94 (2)

heavy alkali metals (Rb, Cs), new compounds containing various molybdenum clusters were synthesized: $Cs_{0.6}Mo_6S_7$ comprising octahedral Mo_6 clusters (Gougeon, Padiou, Potel, Sergent & Couach, 1984) and the homologous series of general formula $M_{2n-2}Mo_6nX_{6n+2}$ ($M = Rb, Cs; X = S, Se; n = 2, 3, 4, 5$ and ∞) based on the condensed clusters Mo_{12} , Mo_{18} , Mo_{24} , Mo_{30} and on the infinite chain $[Mo_{6/2}]_{\infty}^1$ (Gougeon, 1984; Gougeon, Potel, Padiou & Sergent, 1987, 1988). Recently, the odd-membered Mo_{15} cluster was obtained in the two isostructural compounds $Rb_3Mo_{15}Se_{17}$ (Gougeon, Potel & Sergent, 1989a) and $Cs_3Mo_{15}Se_{17}$ (Gougeon, Potel & Sergent, 1989b). We now report the crystal structure of $Cs_5Mo_{21}Se_{23}$ comprising the new Mo_{21} cluster. This compound constitutes with the Mo_{15} materials the first two members of a family of general formula $M_{2n-1}Mo_{6n+3}X_{6n+5}$.

Experimental. Single crystals were obtained by heating a stoichiometric mixture of $Cs_2Mo_6Se_6$ and Mo_6Se_8 at about 2000 K for one hour in a sealed molybdenum crucible, then cooled to 1873 K at 20 K h⁻¹ and finally furnace cooled.

The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated $Mo K\alpha$ radiation. The dimensions of the crystal fragment were 0.06 × 0.07 × 0.10 mm. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with $6 \leq \theta \leq 15^\circ$. 3010 observed reflections were recorded over the range $1 \leq \theta \leq 35^\circ$ with $0 \leq h \leq 15$, $0 \leq k \leq 15$, $0 \leq l \leq 48$; ω - 2θ scan method was used with scan width $\Delta\omega = (0.8 + 0.35 \tan \theta)^\circ$ and counter aperture $\Delta l = (2 + 0.5 \tan \theta)$ mm. Three orientation and three intensity control reflections were checked every 250 reflections and every hour, respectively, and showed no significant variation. Data were corrected for Lorentz-polarization and an empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was

Table 2. *Selected interatomic distances (Å)*

Intratriangle distances		Intertriangle distances	
Mo(1)—Mo(1)	2 × 2.652 (2)	Mo(1)—Mo(2)	2.744 (1)
Mo(2)—Mo(2)	2 × 2.669 (2)	—Mo(2)	2.768 (2)
Mo(3)—Mo(3)	2 × 2.665 (2)	Mo(2)—Mo(3)	2.701 (2)
Mo(4)—Mo(4)	2 × 2.660 (3)	—Mo(3)	2.721 (1)
		Mo(3)—Mo(4)	2.721 (1)
		—Mo(4)	2.727 (2)
Intercluster distances		Cs environment	
Mo(1)—Mo(1)	3.342 (3)	Cs(1)—Se(2)	3 × 3.713 (2)
Mo—Se distances		—Se(3)	3 × 3.643 (1)
Mo(1)—Se(1)	2.601 (2)	—Se(4)	3 × 3.897 (2)
—Se(1)	2.611 (2)	—Se(5)	3.730 (3)
—Se(1)	2.646 (2)		
—Se(2)	2.686 (2)	Cs(2)—Se(3)	6 × 3.770 (1)
—Se(5)	2.529 (2)	—Se(4)	3 × 3.647 (2)
Mo(2)—Se(1)	2.575 (2)	Cs(3)—Se(1)	3 × 3.636 (2)
—Se(2)	2.586 (2)	—Se(2)	3 × 3.606 (1)
—Se(2)	2.602 (2)	—Se(3)	3 × 3.877 (2)
—Se(3)	2.690 (2)		
Mo(3)—Se(1)	2.694 (2)	Cs(1)···Cs(1)	4.918 (3)
—Se(3)	2.606 (2)	Cs(2)···Cs(3)	4.648 (2)
—Se(3)	2.631 (2)	Cs(3)···Cs(3)	5.674 (4)
—Se(4)	2.697 (2)		
Mo(4)—Se(3)	2 × 2.685 (2)		
—Se(4)	2.609 (3)		
—Se(4)	2.634 (3)		

applied to isotropically refined data. The minimum and maximum corrections were 0.883 and 1.048. After averaging ($R_{int} = 0.047$), 2717 unique data were used to solve the structure with the aid of *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier synthesis. The function minimized in the least-squares program was $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/|\sigma^2(F_o^2) + (0.05F_o^2)^2|$.

The refinement of all atoms anisotropically and an extinction coefficient (79 variables) converged to $R = 0.034$, $wR = 0.042$, $S = 0.984$ for 1290 reflections with $F_o^2 > 2\sigma(F_o^2)$. In the final cycle of refinement, the largest shift/e.s.d. was < 0.01 and the largest residuals on final difference map were $+1.57$ and -2.26 e Å⁻³; final value of g was 2.25×10^{-8} (Stout & Jensen, 1968).

Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). All the calculations were performed on a PDP 11/60 using the *SDP* programs (Frenz, 1985). Final atomic coordinates and equivalent isotropic thermal parameters with their e.s.d.'s are given in Table 1* and selected interatomic distances in Table 2.

* Lists of structure factors, anisotropic thermal parameters and bond distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53233 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The crystal structure of the title compound shown in Fig. 1 is obviously closely related to that of $\text{Rb}_3\text{Mo}_{15}\text{Se}_{17}$ and can be deduced from this by a simple replacement of the $\text{Mo}_{15}\text{Se}_{17}$ cluster unit centered on the $2(c)$ position by the new $\text{Mo}_{21}\text{Se}_{23}$ unit (Fig. 2), which results from the condensation of six Mo_6Se_8 units instead of four for the $\text{Mo}_{15}\text{Se}_{17}$ unit. Consequently, the environment of the Mo atoms as well as the inter-unit connectivity is similar to that previously described for the Mo_{15} compounds (Gougeon *et al.*, 1989*a,b*). The distances between Mo atoms related through the threefold axis (intra-triangle distances in Table 1) are distributed in a narrow range (2.652–2.669 Å) whereas those between Mo atoms of adjacent Mo_3 triangles (noted inter-triangle in Table 1) vary from 2.701 to 2.768 Å. The spacing between Mo_3 triangles is alternately long

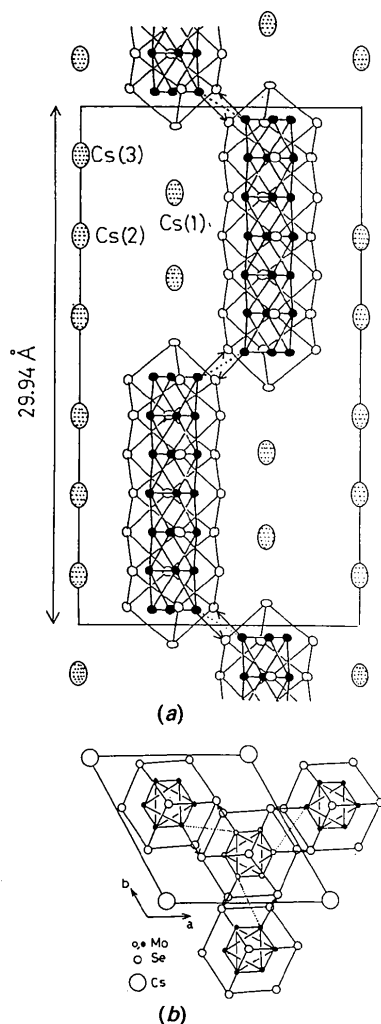


Fig. 1. Projection of the structure of $\text{Cs}_5\text{Mo}_{21}\text{Se}_{23}$ on the hexagonal planes (a) $(11\bar{2}0)$ and (b) (0001) . Filled circles: Mo atoms; empty circles: Se atoms. The thin lines define the Se polyhedra surrounding the Mo_{21} cluster. Arrows show the Mo—Se inter-unit bonds, the dotted lines the intercluster bonds.

[2.290 and 2.248 Å for $\Delta(1)$ – $\Delta(2)$ and $\Delta(3)$ – $\Delta(4)$] and short [2.230 Å for $\Delta(2)$ – $\Delta(3)$] as already observed in the even-membered clusters Mo_{6n} ($n = 2, 3, 4$ and 5) (Gougeon, 1984). The shortest Mo—Mo intercluster distance which occurs between Mo(1) atoms is 3.342 Å and is responsible for the metallic behaviour of $\text{Cs}_5\text{Mo}_{21}\text{Se}_{23}$. The Mo—Se bond distances range from 2.529 to 2.697 Å with the shortest of these involving the ending Se(5) atoms which are only linked to three Mo atoms. These values are similar to those reported for $\text{Rb}_3\text{Mo}_{15}\text{Se}_{17}$ and $\text{Cs}_3\text{Mo}_{15}\text{Se}_{17}$ (Gougeon *et al.*, 1989*a,b*).

The cations occupy either the tunnels running along the c axis or the inter-unit voids centered on the $(\frac{1}{3}, \frac{1}{3}, \frac{1}{4})$ position. The latter, because of the larger size of the $\text{Mo}_{21}\text{Se}_{23}$ cluster unit, are now occupied by two mirror-related Cs(1) atoms separated by 4.917 Å. Each Cs(1) atom is surrounded by ten Se atoms: six [three Se(2) and three Se(4)] form a trigonal prism and the remaining four cap the three rectangular [three Se(3)] and one triangular [Se(5)] faces. The Cs(1)—Se distances vary between 3.643 and 3.897 Å. The environments of the Cs(2) and Cs(3) atoms are nearly identical and consist of nine Se atoms at the corners of a tricapped trigonal prism. However, the symmetry of the Cs(2) site is a little higher than that of the Cs(3) site ($\bar{6}$ and 3, respectively). For these two sites, the Cs—Se distance ranges from 3.647 to 3.770 Å and from 3.606 to 3.877 Å, respectively. Moreover, the polyhedra around Cs(2) and Cs(3) form tunnels extended along the c axis in which the spacing between Cs(2) and Cs(3) is 4.648 Å and Cs(3)—Cs(3) is 5.674 Å.

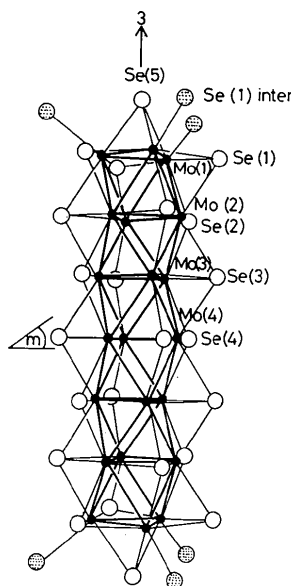


Fig. 2. $\text{Mo}_{21}\text{Se}_{23}$ units with the numbering scheme. Cross-hatched atoms belong to neighbouring units.

References

- FRENZ, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.
- GOUGEON, P. (1984). Thesis, Univ. of Rennes, France.
- GOUGEON, P., PADIOU, J., POTEL, M., SERGENT, M. & COUACH, M. (1984). *Ann. Chim. Fr.* **9**, 1083–1086.
- GOUGEON, P., POTEL, M., PADIOU, J. & SERGENT, M. (1987). *Mater. Res. Bull.* **22**, 1087–1093.
- GOUGEON, P., POTEL, M., PADIOU, J. & SERGENT, M. (1988). *Mater. Res. Bull.* **23**, 453–460.
- GOUGEON, P., POTEL, M. & SERGENT, M. (1989a). *Acta Cryst.* **C45**, 182–185.
- GOUGEON, P., POTEL, M. & SERGENT, M. (1989b). *Acta Cryst.* **C45**, 1413–1415.
- MAIN, P., FISKE, S., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- STOUT, G. & JENSEN, L. H. (1968). *X-ray Structure Determination*. London: Macmillan.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1990). **C46**, 2287–2291

Structure of Antimony Lead Selenide, $\text{Pb}_4\text{Sb}_4\text{Se}_{10}$, a Selenium Analogue of Cosalite

BY A. SKOWRON AND I. D. BROWN

Institute for Materials Research, McMaster University, 1280 Main St West, Hamilton, Ontario, Canada L8S 4M1

(Received 18 December 1989; accepted 26 March 1990)

Abstract. $M_r = 2105.36$, orthorhombic, $Pnam$, $a = 24.591(8)$, $b = 19.757(8)$, $c = 4.166(8)$ Å, $V = 2024$ Å³, $Z = 4$, $D_x = 6.91$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 543.9$ cm⁻¹, $F(000) = 3487$, room temperature, $R = 0.064$ for 1562 unique reflections. The crystal was prepared by slow cooling in vacuum sealed ampoules. The structure is isotypic with cosalite, $\text{Pb}_4\text{Bi}_4(\text{Ag,Cu})\text{S}_{10}$, and is composed of ribbons built up of square pyramidal (Pb,Sb)Se₅ groups. The distribution of Sb/Pb atomic positions was determined by site occupancy refinement and, independently, by bond-valence analysis.

Introduction. We have previously undertaken determinations to establish the structural details, including cation distributions, of specific lead antimony sulfides (Skowron & Brown, 1990a,b,c). Here, the structure of a lead antimony selenide is investigated and compared with an isotypic lead bismuth sulfide. To obtain a broader view, the results are taken together with those from other works, and cation environments in a number of selenides and sulfides compared.

Experimental. Single crystals of $\text{Pb}_4\text{Sb}_4\text{Se}_{10}$ were prepared from elemental lead, antimony and selenium of 'Specpure' grade, supplied by Johnson Matthey Ltd. Six samples were prepared by weighing the elements in the proportions corresponding to 50–75 mol % of PbSe. The samples were then sealed in evacuated silica tubes, melted at 1073 K and subsequently slowly cooled over a period of two weeks

to 823 K. Extensive phase separation into regions of acicular crystals was observed in all the ampoules. A needle-shaped crystal, $0.1 \times 0.2 \times 0.5$ mm, which was chosen from the ampoule with the initial composition 55 mol % PbSe, was mounted with the needle axis along the goniometer axis for the X-ray study.

The unit-cell parameters were refined from the Bragg angles of 15 well centered reflections in the range $15 < 2\theta < 30^\circ$ measured on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å. Intensities of 5308 reflections were measured in the range $2\theta < 50^\circ$ and $0 \leq h \leq 26$, $-20 \leq k \leq 20$, $-4 \leq l \leq 4$ with a $\theta/2\theta$ scan. Two standard reflections ($62\bar{1}$, $10\bar{4}\bar{2}$), measured every 50 reflections, varied by $\pm 2.1\%$. The systematic absences, $0kl: k+l=2n+1$; $h0l: h=2n+1$, found using precession photographs, indicate space groups $Pnam$ or $Pna2_1$. The former was chosen and led to a satisfactory refinement. The absorption correction was based on ψ scans of 13 reflections (maximum correction was 6.29 for the intensity of the $1\bar{2}2$ reflection). The intensities were corrected for Lorentz and polarization effects. Equivalent reflections were averaged ($R_{\text{int}} = 0.159$ before and $R_{\text{int}} = 0.049$ after the absorption correction) to give 1562 unique reflections.

The initial atomic positions, found by direct methods using *SHELXS* (Sheldrick, 1986), were refined using *SHELX76* (Sheldrick, 1976) by full-matrix least squares with anisotropic atomic displacement parameters for all the atoms and with mixed occupancies for the metal sites. Complex scat-