

regarded as observed. Data were corrected for Lorentz and polarization effects and absorption corrections were applied. The structural determination was carried out on a PDP 11/60 computer using the *SDP* package (Frenz, 1978). Scattering factors were from Cromer & Waber (1965). The structure was determined on the basis of isomorphism with  $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . Refinement was started with atomic coordinates reported by Tagaki, Mathew & Brown (1986). The four H atoms were refined isotropically. Full-matrix least-squares refinement was based on  $F$  and the function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w(F) = 1/\sigma^2(F)$ . The weighting scheme had a non-Poisson contribution with  $p = 0.050$ . Corrections were made for anomalous dispersion and secondary-extinction effects ( $g = 3.6 \times 10^{-7}$ ). During the last refinement cycle, the r.m.s. shift/e.s.d. was 0.39. The final difference Fourier map showed no features higher than  $0.78 \text{ e } \text{Å}^{-3}$ . In these conditions, the final  $R = 0.018$  and  $wR = 0.026$ . Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51834 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Related literature.** Little is known about cobalt phosphate hydrates. In a recent study (Cudennec, Lecerf, Riou & Gerault, 1987), we prepared crystals of  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . This solid phase belongs to the large vivianite family:  $M_3^{\text{II}}(\text{XO}_4)_2 \cdot 8\text{H}_2\text{O}$  with  $M^{\text{II}} = \text{Fe, Co, Ni, Zn, Mg}$  and  $\text{XO}_4 = \text{PO}_4, \text{AsO}_4$ . The structure of vivianite:  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , was proposed by Mori & Ito (1950), without refinement of the atomic coordinates. More recently Hill (1979) has determined the structure of köttigite:  $\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ , which was refined with the H atoms. Lastly, Tagaki *et al.* (1986) have determined the structure of  $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ .

#### References

- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.  
 CUDENNEC, Y., LECERF, A., RIOU, A. & GERAULT, Y. (1987). *Rev. Chim. Minér.* **24**, 234–247.  
 FRENZ, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution*. In *Computing in Crystallography*, edited by H. SCHENK, R. OLTJOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64–71. Delft Univ. Press.  
 HILL, R. J. (1979). *Am. Mineral.* **64**, 376–382.  
 MORI, H. & ITO, T. (1950). *Acta Cryst.* **3**, 1–6.  
 TAGAKI, S., MATHEW, M. & BROWN, W. E. (1986). *Am. Mineral.* **71**, 1229–1233.

*Acta Cryst.* (1989). **C45**, 1413–1415

## Structure of $\text{Cs}_3\text{Mo}_{15}\text{Se}_{17}$

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(Received 16 April 1989; accepted 11 May 1989)

**Abstract.** Caesium molybdenum selenide,  $\text{Cs}_3\text{Mo}_{15}\text{Se}_{17}$ ,  $M_r = 3180.14$ , hexagonal,  $P6_3/m$ ,  $a = 9.624$  (2),  $c = 20.898$  (8) Å,  $V = 1676.4$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 6.276 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 266.5 \text{ cm}^{-1}$ ,  $F(000) = 2746$ ,  $T = 293 \text{ K}$ ,  $R = 0.028$  for 1028 reflections with  $I \geq 2\sigma(I)$  and 58 parameters. The title compound is isostructural with  $\text{Rb}_3\text{Mo}_{15}\text{Se}_{17}$  and thus its structure contains as the main building block the  $\text{Mo}_{15}\text{Se}_{17}$  cluster unit whose Mo core is built up by four face-sharing  $\text{Mo}_6$  octahedra. Whereas the intracluster Mo—Mo distances as well as the Mo—Se ones are identical to within  $\pm 0.01$  Å in both compounds, owing to the same cationic charge transfer towards the  $\text{Mo}_{15}\text{Se}_{17}$  unit, a slight lengthening of the intercluster Mo—Mo dis-

tance from 3.268 to 3.318 Å is observed, as expected, when the size of the cation increases.

**Experimental.** Single crystals were obtained by heating a mixture of  $\text{CsMo}_3\text{Se}_3$  and  $\text{Mo}_3\text{Se}_4$  (3:2 ratio) in a sealed molybdenum crucible at about 2193 K for one hour and then cooling at  $100 \text{ K h}^{-1}$  to 1273 K.

Intensities were measured from a crystal fragment with dimensions  $0.06 \times 0.10 \times 0.12 \text{ mm}$  on an Enraf–Nonius CAD-4 diffractometer operating with graphite-monochromatized Mo  $K\alpha$  radiation. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with  $7 \leq \theta \leq 15^\circ$ . 5366 reflections were recorded over the range  $1 \leq \theta \leq 35^\circ$  with  $h: -15 \rightarrow 0$ ,  $k: 0 \rightarrow 15$ ,  $l: 0 \rightarrow$

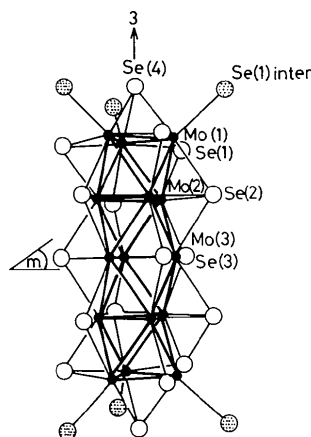
Table 1. Positional parameters and equivalent isotropic thermal parameters

$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

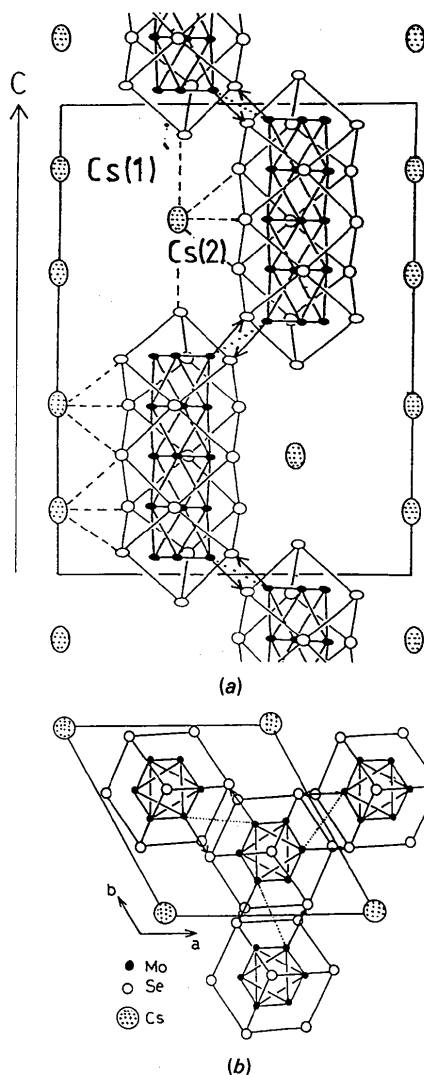
	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
Mo(1)	0.16414 (9)	0.51920 (8)	0.53385 (3)	0.41 (1)
Mo(2)	0.18303 (7)	0.68483 (7)	0.64305 (3)	0.34 (1)
Mo(3)	0.1643 (1)	0.5175 (1)	0.750	0.38 (2)
Se(1)	0.2928 (1)	0.33755 (9)	0.95787 (3)	0.53 (1)
Se(2)	-0.00596 (9)	0.62359 (9)	0.14170 (3)	0.58 (1)
Se(3)	0.0423 (1)	0.7076 (1)	0.750	0.57 (2)
Se(4)	0.667	0.333	0.56228 (7)	0.66 (2)
Cs(1)	0.000	0.000	0.36192 (6)	1.93 (2)
Cs(2)	0.667	0.333	0.750	1.70 (2)

Table 2. Selected interatomic distances (Å)

Mo(1)—Mo(1)	2 × 2.658 (2)	Mo(1)—Se(1)	2.589 (2)
Mo(2)	2.737 (1)	Se(1)	2.605 (1)
Mo(2)	2.767 (1)	Se(1)	2.632 (1)
Mo(2)—Mo(2)	2 × 2.670 (1)	Se(2)	2.682 (1)
Mo(3)	2.707 (1)	Se(4)	2.528 (1)
Mo(3)	2.722 (1)	Mo(2)—Se(1)	2.560 (1)
Mo(3)—Mo(3)	2 × 2.667 (1)	Se(2)	2.580 (1)
Mo(1)—Mo(1) <sub>intercluster</sub>	3.310 (2)	Se(2)	2.597 (1)
		Se(3)	2.678 (1)
		Mo(3)—Se(2)	2 × 2.687 (1)
		Se(3)	2.605 (2)
		Se(3)	2.622 (2)
Cs(1)—Se(1)	3 × 3.595 (1)	Cs(1)—Cs(1)	4.678 (3)
Se(2)	3 × 3.655 (1)	Cs(1)	5.771 (3)
Se(3)	3 × 3.834 (1)	Cs(1)—Cs(2)	6.029 (1)
Cs(2)—Se(2)	6 × 3.821 (1)		
Se(3)	3 × 3.609 (1)		
Se(4)	2 × 3.923 (1)		

Fig. 1. Mo<sub>15</sub>Se<sub>17</sub> units with the numbering scheme. Stippled atoms belong to neighbouring units.

33;  $\omega$ - $2\theta$  scan method was used with scan width  $\Delta\omega = (1 + 0.35\text{tg}\theta)^\circ$  and counter aperture  $\Delta l = (2 + 0.5\text{tg}\theta)$  mm. Three orientation and three intensity reference 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 applied to isotropically refined

Fig. 2. Projections of the structure of Cs<sub>3</sub>Mo<sub>15</sub>Se<sub>17</sub> 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<sub>15</sub> cluster. Arrows show the Mo—Se interunit bonds, dotted lines the intercluster bonds and dashed lines the Cs—Se bonds.

data. Min. and max. correction factors were 0.832 and 1.268. After averaging ( $R_{int} = 0.046$ ), 2277 unique reflections of which 1028 had  $I \geq 2\sigma(I)$  were used in subsequent calculations. The atomic coordinates of Rb<sub>3</sub>Mo<sub>15</sub>Se<sub>17</sub> (Gougeon, Potel & Sergent, 1989) were used as initial values in the first stage of the refinement. Anisotropic full-matrix least-squares refinement on  $F$  of all atoms led to final  $R = 0.028$  and  $wR = 0.026$  with  $w = 4F_o^2 / (\sigma^2 F_o^2 + 0.0004 F_o^4)$ ,  $S = 0.915$  using 1028 reflections with  $I \geq 2\sigma(I)$  and 58 variables. Final  $(\Delta/\sigma)_{max} \leq 0.01$ ; max. and min. heights in final  $\Delta\rho$  map 2.26 and  $-1.80 \text{ e \AA}^{-3}$  respectively; refined secondary-extinction value  $g = 1.3 \times 10^{-8}$ . Atomic scattering factors and

anomalous-dispersion correction from *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a PDP 11/60 using the *SDP* programs (B. A. Frenz & Associates Inc., 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; Fig. 1 shows the numbering scheme of the  $\text{Mo}_{15}\text{Se}_{17}$  cluster unit and Fig. 2 the packing arrangement.\*

**Related literature.**  $\text{Cs}_3\text{Mo}_{15}\text{Se}_{17}$  belongs to a large family of condensed Mo cluster compounds of general formula  $M_{n-2}\text{Mo}_{3n}\text{X}_{3n+2}$  ( $M = \text{Rb}, \text{Cs}; X = \text{S}, \text{Se}; n = 2, 3, 4, 5, 6, 7, 8, 10$  and  $\infty$ ). These series can be subdivided into two groups depending on the parity of  $n$ . The even members crystallize in the

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rhombohedral trigonal space group  $R\bar{3}$  and have a structure closely related to the ternary chalcogenides  $M\text{Mo}_6\text{X}_8$  (Gougeon, 1984; Gougeon, Potel, Padiou & Sergent, 1987, 1988). The odd members as well as the limiting compound  $M\text{Mo}_3\text{X}_3$  ( $n = \infty$ ) crystallize in the hexagonal space group  $P6_3/m$  (Potel, Chevrel & Sergent, 1980).

#### References

- B. A. FRENZ & ASSOCIATES INC. (1985). *SDP Structure Determination Package*. College Station, Texas, USA, and Enraf-Nonius, Delft, The Netherlands.
- GOUGEON, P. (1984). Thesis, Univ. of Rennes, France.
- 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. (1989). *Acta Cryst.* **C45**, 182–185.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- POTEL, M., CHEVREL, R. & SERGENT, M. (1980). *Acta Cryst.* **B36**, 1545–1548.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1989). **C45**, 1415–1417

## Structure of a Linear-Chain Chloro-Bridged Binuclear Platinum Complex, $(\text{NH}_4)_4[\text{Pt}_2\text{Cl}(\text{P}_2\text{O}_5\text{H}_2)_4]$

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(Received 13 March 1989; accepted 26 April 1989)

**Abstract.** Ammonium *catena-μ*-chloro-tetrakis( $\mu$ -diphosphonato-*P,P*-diplatinum(4-)),  $(\text{NH}_4)_4[\text{Pt}_2\text{Cl}(\text{P}_2\text{O}_5\text{H}_2)_4]$ ,  $M_r = 1073.61$ , orthorhombic,  $Pn\bar{n}m$ ,  $a = 9.660$  (5),  $b = 14.959$  (7),  $c = 8.215$  (4) Å,  $V = 1187$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 3.004$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 13.172$  mm<sup>-1</sup>,  $F(000) = 1010$ ,  $T = 296$  K,  $R = 0.025$  for 1507 reflections [ $|F_o| > 3\sigma(F_o)$ ]. The structure consists of a linear chain with a

$\dots\text{Pt}^{\text{II}}-\text{Pt}^{\text{II}}\dots\text{Cl}-\text{Pt}^{\text{III}}-\text{Pt}^{\text{III}}-\text{Cl}\dots$  repeating unit along the  $c$  axis. Two Pt atoms are bridged by four pyrophosphato ligands ( $\text{P}_2\text{O}_5\text{H}_2^-$ ) and the Pt—Pt separation is 2.830 (1) Å. The bridging Cl atom is disordered over two sites, giving short Pt—Cl [2.363 (4) Å] and long Pt—Cl [3.022 (4) Å] distances in the chain. The Pt dimers lie on  $2/m$  sites. The bridging O atoms of the  $\text{P}_2\text{O}_5\text{H}_2^-$  ligands deviate 0.298 (6) and 0.548 (5) Å from the planes defined by the two Pt atoms and the two P atoms of the ligand, respectively. No diffuse scattering could be observed on the X-ray photographs.

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