

refined; final  $R = 0.042$ ,  $wR = 0.059$  and  $S = 1.41$  were obtained for 2248 unique reflections ( $R_{\text{int}} = 0.044$ ) with  $|F_o| > 3\sigma(|F_o|)$ ; weighting scheme  $w^{-1} = [\sigma^2(F_o) + (0.035|F_o|)^2]$ ;  $(\Delta/\sigma)_{\text{max}} < 0.01$ ;  $-1.0 \leq \Delta\rho \leq 3.0 \text{ e } \text{\AA}^{-3}$ . Scattering factors with anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed by using the UNICSIII program (Sakurai & Kobayashi, 1979) on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science. Final atomic parameters are listed in Table 1\* and selected bond distances and angles are in Table 2. Fig. 1 shows an ORTEP (Johnson, 1976) view of the discrete polyanion.

**Related literature.** Bond distances within some  $\text{XMo}_6\text{O}_{24}$  type polymolybdates incorporating transition metals are as follows: for  $[\text{H}_6\text{CrMo}_6\text{O}_{24}]^{3-}$ , Cr—O and Mo—O are in the ranges 1.968 (3)–1.986 (3) and 1.695 (3)–2.347 (3) Å, respectively (Perloff, 1970); for  $[\text{PtMo}_6\text{O}_{24}]^{5-}$ , Pt—O and Mo—O are in the ranges 1.99–2.04 and 1.68–2.34 Å, respectively (Lee & Sasaki, 1984); for  $[\text{H}_6\text{Cu}$

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53530 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

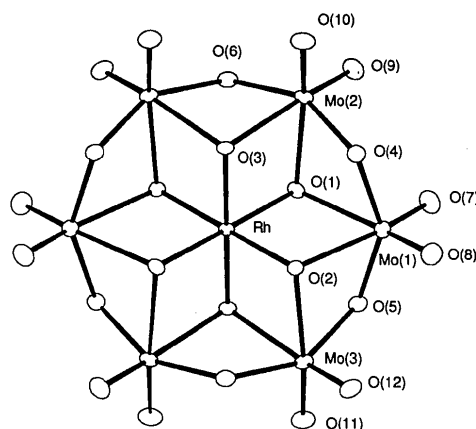


Fig. 1. ORTEP drawing of the discrete polyanion with 50% thermal probability level.

$\text{Mo}_6\text{O}_{24}]^{4-}$ , Cu—O and Mo—O are in the ranges 2.02 (1)–2.12 (1), and 1.70 (1)–2.25 (1) Å, respectively (Ito, Ozeki, Ichida, Miyamae & Sasaki, 1989).

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## Structure of Caesium Selenate

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**Abstract.**  $\text{Cs}_2\text{SeO}_4$ ,  $M_r = 408.77$ , orthorhombic,  $Pnam$ ,  $a = 8.3777$  (8),  $b = 11.276$  (2),  $c = 6.434$  (2) Å,  $V = 607.8$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 4.46 \text{ Mg m}^{-3}$ ,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 185.06 \text{ cm}^{-1}$ ,  $F(000) = 704$ ,  $T = 293 \text{ K}$ ,  $R = 0.048$ , 3348 observed reflections. Average values of the Se—O and Cs—O distances are 1.637 (4) and 3.387 (3) Å, respectively [range 3.038 (5)–3.872 (6) Å with 9 and 11 coordination of caesium by oxygen].

**Experimental.** Single crystals of  $\text{Cs}_2\text{SeO}_4$  were grown isothermally at 310 K from an aqueous solution (pH = 4.5), which contained the stoichiometric molar ratio of CsOH and  $\text{H}_2\text{SeO}_4$ . The colourless crystals obtained were of good optical quality.

A prismatic crystal of dimensions  $0.31 \times 0.15 \times 0.15 \text{ mm}$  was used to collect intensities with an Enraf-Nonius CAD-4 four-circle diffractometer, using graphite-monochromated  $\text{Mo } K\alpha$  radiation. A

Table 1. Atomic positional parameters and anisotropic thermal parameters ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Se	0.23482 (6)	0.41877 (3)	0.2500	0.0151 (2)	0.0133 (1)	0.0136 (2)	-0.0002 (1)	0	0
Cs(1)	0.17676 (4)	0.09001 (3)	0.2500	0.0232 (1)	0.0228 (1)	0.0195 (1)	0.00062 (9)	0	0
Cs(2)	-0.01048 (4)	0.70606 (3)	0.2500	0.0196 (1)	0.0185 (1)	0.0224 (1)	0.00031 (8)	0	0
O(1)	0.3032 (5)	0.3525 (3)	0.0418 (5)	0.043 (2)	0.034 (1)	0.020 (1)	0.007 (1)	0.005 (1)	-0.008 (1)
O(2)	0.3022 (6)	0.5546 (3)	0.2500	0.037 (2)	0.018 (1)	0.031 (2)	-0.010 (1)	0	0
O(3)	0.0392 (5)	0.4178 (5)	0.2500	0.017 (2)	0.044 (3)	0.047 (4)	-0.008 (2)	0	0

Table 2. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $\text{Cs}_2\text{SeO}_4$ 

Se—O(1)	1.638 (4)	Cs(1)—O(2) <sup>vii</sup>	3.247 (1)
Se—O(2)	1.633 (4)	Cs(1)—O(3)	3.872 (6)
Se—O(3)	1.639 (5)	Cs(1)—O(3) <sup>viii</sup>	3.038 (5)
		Cs(2)—O(1) <sup>ix</sup>	3.158 (4)
Cs(1)—O(1)	3.418 (3)	Cs(2)—O(1) <sup>x</sup>	3.044 (4)
Cs(1)—O(1) <sup>ii</sup>	3.465 (4)	Cs(2)—O(1) <sup>xi</sup>	3.044 (4)
Cs(1)—O(1) <sup>iii</sup>	3.275 (3)	Cs(2)—O(1) <sup>xii</sup>	3.158 (4)
Cs(1)—O(1) <sup>iv</sup>	3.418 (3)	Cs(2)—O(2)	3.128 (5)
Cs(1)—O(1) <sup>v</sup>	3.275 (3)	Cs(2)—O(2) <sup>xiii</sup>	3.122 (4)
Cs(1)—O(1) <sup>vi</sup>	3.465 (4)	Cs(2)—O(3)	3.276 (6)
Cs(1)—O(2) <sup>ii</sup>	3.536 (5)	Cs(2)—O(3) <sup>xiv</sup>	3.516 (3)
Cs(1)—O(2) <sup>iii</sup>	3.247 (1)	Cs(2)—O(3) <sup>xv</sup>	3.516 (3)

O(1)—Se—O(2)	107.9 (1)	O(1)—Se—O(1) <sup>i</sup>	109.8 (2)
O(1)—Se—O(3)	110.3 (2)	O(2)—Se—O(3)	110.6 (3)

Symmetry codes: (i)  $x, y, \frac{1}{2}-z$ ; (ii)  $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z$ ; (iii)  $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$ ; (iv)  $x, y, \frac{1}{2}-z$ ; (v)  $\frac{1}{2}-x, y-\frac{1}{2}, -z$ ; (vi)  $x-\frac{1}{2}, \frac{1}{2}-y, z$ ; (vii)  $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$ ; (viii)  $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$ ; (ix)  $-x, 1-y, \frac{1}{2}+z$ ; (x)  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$ ; (xi)  $\frac{1}{2}-x, \frac{1}{2}+y, -z$ ; (xii)  $-x, 1-y, -z$ ; (xiii)  $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z$ ; (xiv)  $-x, 1-y, 1-z$ .

total of 7198 measured reflections with  $2\theta_{\text{max}} = 100^\circ$  ( $hkl$  range:  $-18 < h < 18, 0 < k < 24, 0 < l < 13$ ).  $\theta$ - $2\theta$  scan mode [ $\Delta\omega = (0.65 + 0.35\tan\theta)^\circ$ ] with variable speed; three standard reflections measured every 7200 s without significant variation; absorption correction factors calculated by Gaussian integration (transmission max./min. = 0.1938/0.0904); 3348 reflections measured, and averaging yielded 2538 independent reflections with  $I > 3\sigma(I)$ . Unit-cell parameters refined from setting angles of 25 centered reflections ( $10 < \theta < 20^\circ$ ).

*XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the reduction of data and the refinement of the structure. The refinement was on *F*. Atomic scattering factors calculated by Cromer & Mann (1968) were assigned to Cs, Se and O; anomalous-scattering coefficients for Cs, Se and O (Cromer & Liberman, 1970).

The structure was refined with the starting coordinates from the  $\text{K}_2\text{SeO}_4$  compound (Kálmán, Stephens & Cruickshank, 1970). Refinement carried out by full-matrix least squares, with anisotropic displacement parameters for all atoms and an extinction correction in the last cycle.

The final agreement factors are  $R = 0.048$ ,  $wR = 0.063$  [ $w = 1/\sigma^2(F_o)$ ],  $S = 4.54$  and  $(\text{shift}/\text{e.s.d.})_{\text{max}} = 0.15$  with 41 variables. Maximum peaks in the final difference Fourier synthesis  $0.73 \text{ e \AA}^{-3}$ . The final

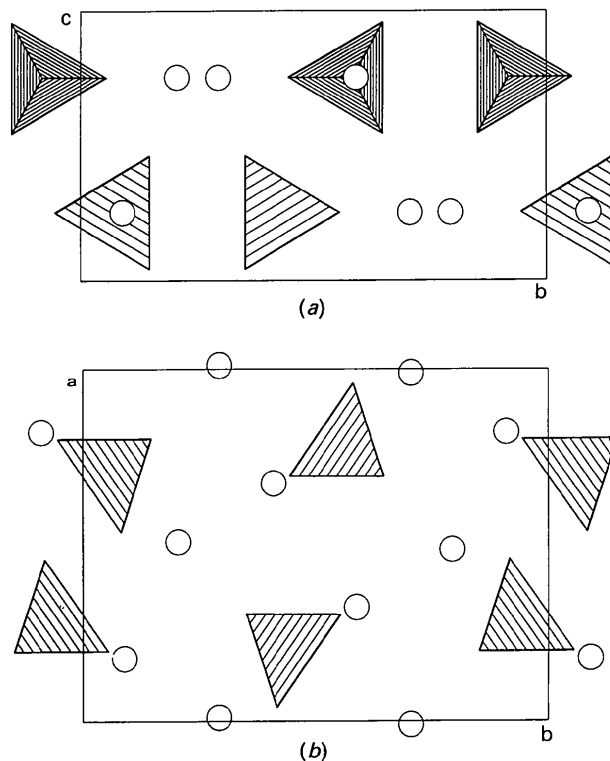


Fig. 1. (a), (b) Projections along the *a* and *c* axes of the structure of  $\text{Cs}_2\text{SeO}_4$ .  $[\text{SeO}_4]^{2-}$  anions and  $\text{Cs}^+$  cations are represented by tetrahedra and circles, respectively.

atom positional and equivalent isotropic displacement parameters are listed in Table 1,\* and selected bond distances and angles in Table 2. The  $\text{SeO}_4^{2-}$  anions are almost regular. A projection of the structure is shown in Fig. 1.

**Related literature.** Compounds of the  $A_2BX_4$  family ( $A = \text{K, Rb, Cs}$ ;  $B = \text{Zn, Co}$ ;  $X = \text{Cl, Br}$ ) together with  $\text{K}_2\text{SeO}_4$  exhibit structural phase transitions including commensurate and incommensurate phases (Cummins, 1990). All compounds have a common high-temperature phase with a prototype structure of the  $\beta$ - $\text{K}_2\text{SeO}_4$  type (Sasvári, 1963) and a similar

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structure for the incommensurate modulation. It has been claimed that some structural features of the prototype phase are the origin of these transitions (Kaltkanant, Edwardson, Hardy & Boyer, 1989). The lattice dynamic simulations performed for several  $A_2BX_4$  compounds confirm that the relative size of the  $A^+$  and  $BX_4^{2-}$  anions plays an important role in the sequence of transitions (Etxebarria, Pérez-Mato & Criado, 1990). In particular, calculations based on the static structural data reported here for  $Cs_2SeO_4$  exclude the existence of an incommensurate phase for this compound.

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## Structure of Di- $\mu$ -chloro-bis[dicarbonylrhodium(I)]

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**Abstract.**  $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ ,  $M_r = 388.76$ , tetragonal,  $I\bar{4}2d$ ,  $a = 14.279$  (4),  $c = 9.353$  (3) Å,  $V = 1907$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 2.708$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 3.666$  mm<sup>-1</sup>,  $F(000) = 1440$ ,  $T = 296$  K. Final  $R = 0.0398$  for 593 reflections [ $F_o > 3\sigma(F_o)$ ]. The unit cell contains eight molecules, which are bent in a V shape, with an Rh–Rh distance of 3.138 (1) Å. The coordination at one Rh atom is distorted from exact planarity. The molecules are connected to form zigzag chains with intermolecular Rh–Rh distances of 3.324 Å.

**Experimental.** Prepared according to the procedure given by Powell & Shaw (1968) by bubbling carbon monoxide through a refluxing ethanolic solution of rhodium trichloride trihydrate and extracting the dried residue with boiling light petroleum. A plate-like crystal with dimensions 0.044 × 0.192 × 0.300 mm and sealed in a Lindemann-glass capillary was used for the data collection on a Huber 511 four-circle diffractometer. Lattice constants were obtained from 18 reflections in the range  $20 \leq 2\theta \leq 25^\circ$ . 1455 reflections were measured [one octant,  $3 \leq$

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$2\theta \leq 60^\circ$ ,  $0 \leq h(k) \leq 20$ ,  $0 \leq l \leq 13$ ] leading to 593 unique reflections with  $F_o > 3\sigma(F_o)$  after numerical absorption correction ( $R_{\text{int}} = 0.0266$ , min., max. transmission factors 0.498, 0.851, 128 reflections unobserved). The intensity variation of three standard reflections measured every 2 h was < 1%. Structure solution with direct methods (Sheldrick, 1986). The refinement (56 parameters) with anisotropic thermal parameters and isotropic extinction ( $6 \times 10^{-4}$ ) on the basis of  $F$  (Sheldrick, 1976) converged at  $R = 0.0398$ ,  $wR = 0.0238$  [ $w = k/\sigma^2(F_o)$ ]. The ratio of max. least-squares shift to e.s.d. in the final refinement cycle was less than 0.01, max. and min. heights in the final difference Fourier synthesis were 1.42 and  $-1.0 \text{ e } \text{Å}^{-3}$ . The atomic scattering factors used were taken from Cromer & Mann (1968). Table 1 contains atomic parameters for (1). Bond distances and angles (Busing, Martin & Levy, 1971) are given in Table 2.† Fig. 1 shows the molecular structure of

† Lists of structure factors, anisotropic thermal parameters and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53496 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.