2·963 (2) Å, unbridged 2·822 (1) Å] (Churchill & Hollander, 1980).

The presence of edge-bridging hydrides in $Os_4(CO)_{12}H_4$ is as expected from simple electron-counting considerations. This complex is an 'electron precise' 60 electron system with the correct number of electrons to form two two-centre two-electron Os—Os bonds and four three-centre two-electron Os—H—Os bonds. $Re_4(CO)_{12}H_4$ has only 56 electrons, and it appears to be more favourable to form four four-centre two-electron Re_3H bonds; hence the difference in structure between $Re_4(CO)_{12}H_4$ and $Os_4(CO)_{12}H_4$.

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Di-μ₃-selenido-tris(tricarbonylosmium)(2Os—Os)

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Abstract. [$Os_3(CO)_9Se_2$], triclinic, $P\bar{1}$, $a = 6\cdot804$ (3), $b = 9\cdot620$ (5), $c = 13\cdot527$ (6) Å, $\alpha = 94\cdot206$ (21), $\beta = 95\cdot570$ (24), $\gamma = 110\cdot469$ (25)°, $U = 820\cdot1$ Å³, $Z = 2$, $D_c = 3\cdot968$ Mg m⁻³, μ(Mo $K\alpha$) = 27·62 mm⁻¹. The structure refined to $R = 0\cdot042$ for 4106 unique observed diffractometer data. The Os atoms define a triangle with one long non-bonding edge [Os···Os 3·791 (1) Å]. The Se atoms cap this triangle on both sides to give a trigonal bipyramidal cluster core. Three terminal carbonyl groups are also bonded to each metal.

Introduction. In trinuclear and square-planar tetra-nuclear clusters which are capped by ligands on both sides there is the possibility of a bonding interaction between the ligands. In the structure of $Co_4(\mu_2\text{-}CO)_2(CO)_8(\mu_4\text{-PPh})_2$ (Ryan & Dahl, 1975) the P···P distance of 2·544 (3) Å indicates the presence of a bonding interaction between these atoms. There is less evidence for such an interaction in the S analogue

$Co_4(\mu_2\text{-CO})_2(CO)_8(\mu_4\text{-S})_2$ (Wei & Dahl, 1975) or in the complex $Fe_3(CO)_9S_2$ (Wei & Dahl, 1965). During the reaction of $Os_3(CO)_{12}$ with elemental Se under reflux, in *n*-octane, $Os_3(CO)_9Se_2$ was isolated as one of the products (Johnson, Lewis, Lodge, Raithby, Henrick & McPartlin, 1979). It was decided to undertake this crystal-structure analysis in order to determine the molecular parameters, and to establish whether an increase in the size of the capping atom increases ligand–ligand bonding interaction.

Deep-yellow platelets of the title compound were obtained by slow crystallization from hexane. 4948 reflections were measured for $3\cdot0 < 2\theta < 60\cdot0°$ on a Stoe four-circle diffractometer with graphite-mono-chromated Mo $K\alpha$ radiation, an ω–θ scan technique, and a crystal $0\cdot34 \times 0\cdot29 \times 0\cdot10$ mm. Lp corrections and a semi-empirical absorption correction based on a pseudo-ellipsoid model with 292 azimuthal scan data from 12 independent reflections were applied; trans-mission factors ranged from 0·026 to 0·081. The data

were averaged to give 4106 unique observed reflections [$F > 4\sigma(F)$]. Cell dimensions were derived from angular measurements of 20 strong reflections in the range $20 < 2\theta < 30°$.

The three Os atoms were located by multisolution Σ_2 sign expansion, and the Se, C, and O atoms from a subsequent difference synthesis. The structure was refined by blocked-cascade least squares with all atoms assigned anisotropic thermal parameters. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) were employed, with the weighting scheme $w = [\sigma^2(F) + 0.00054|F_o|^2]^{-1}$ for the final stages of refinement. The final residuals were $R = 0.042$ and $R' = \sum w^{1/2} \Delta / \sum w^{1/2}|F_o| = 0.045$. Final atomic coordinates and equivalent isotropic temperature factors are presented in Table 1, bond lengths and angles in Tables 2 and 3.*

Discussion. The structure of Os$_3$(CO)$_9$Se$_2$ (Fig. 1) is similar to that of Fe$_3$(CO)$_9$S$_2$ (Wei & Dahl, 1965). The metal atoms define an isosceles triangle with one edge lengthened to such an extent [Os(2)$\cdots$Os(3) 3.791 (1) Å] that there can be little direct metal—metal bonding. The dimensions of the triangle are similar to those found in Os$_3$(CO)$_8$(CS)S$_2$ (Broadhurst, Johnson, Lewis & Raithby, 1980) [Os(1)—Os(2), 2.830 (2);

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36070 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2 $\times 10^3$)

U_{eq} equals $\frac{1}{3}$ of the trace of the orthogonalized U matrix.

	x	y	z	U_{eq}
Os(1)	2811 (1)	6928 (1)	3424 (1)	31 (1)
Os(2)	1096 (1)	3960 (1)	2437 (1)	32 (1)
Os(3)	4294 (1)	7642 (1)	1570 (1)	32 (1)
Se(1)	4898 (1)	6530 (1)	2496 (1)	32 (1)
Se(2)	545 (1)	6141 (1)	1730 (1)	34 (1)
C(11)	5137 (18)	8757 (11)	3884 (7)	43 (5)
O(11)	6488 (14)	9842 (9)	4188 (6)	61 (5)
C(12)	2875 (18)	5857 (12)	4550 (7)	47 (5)
O(12)	2910 (20)	5270 (12)	5245 (6)	84 (7)
C(13)	802 (18)	7694 (13)	3879 (7)	48 (5)
O(13)	−418 (15)	8173 (12)	4105 (8)	74 (6)
C(21)	1919 (17)	2675 (11)	3278 (7)	46 (5)
O(21)	2377 (15)	1902 (10)	3767 (7)	68 (6)
C(22)	−1801 (17)	3103 (11)	2670 (8)	46 (5)
O(22)	−3481 (14)	2513 (12)	2798 (8)	76 (6)
C(23)	698 (19)	2731 (11)	1210 (7)	47 (5)
O(23)	499 (17)	2081 (11)	464 (6)	76 (6)
C(31)	7247 (18)	8830 (11)	1836 (7)	47 (5)
O(31)	8963 (14)	9521 (11)	2002 (7)	69 (6)
C(32)	3658 (20)	9334 (11)	1207 (8)	50 (6)
O(32)	3275 (17)	10326 (10)	997 (8)	79 (6)
C(33)	4446 (17)	6943 (11)	258 (7)	47 (5)
O(33)	4391 (16)	6450 (11)	−558 (6)	68 (6)

Table 2. *Bond lengths* (Å)

Os(1)—Os(2)	2.847 (1)	Os(1)—C(11)	1.921 (9)
Os(1)—Os(3)	2.836 (1)	Os(1)—C(12)	1.906 (11)
Os(1)—Se(1)	2.551 (2)	Os(1)—C(13)	1.895 (14)
Os(1)—Se(2)	2.539 (2)	Os(2)—C(21)	1.924 (11)
Os(2)—Se(1)	2.513 (2)	Os(2)—C(22)	1.920 (11)
Os(2)—Se(2)	2.497 (1)	Os(2)—C(23)	1.904 (10)
Os(3)—Se(1)	2.509 (2)	Os(3)—C(31)	1.914 (10)
Os(3)—Se(2)	2.493 (1)	Os(3)—C(32)	1.909 (13)
C(11)—O(11)	1.138 (11)	Os(3)—C(33)	1.877 (10)
C(12)—O(12)	1.134 (15)	C(23)—O(23)	1.119 (13)
C(13)—Os(1)	1.895 (14)	C(31)—O(31)	1.113 (13)
C(21)—O(21)	1.133 (16)	C(32)—O(32)	1.122 (17)
C(22)—O(22)	1.121 (14)	C(33)—O(33)	1.161 (13)

Table 3. *Bond angles* (°)

Os(2)—Os(1)—Os(3)	83.7 (1)	Os(1)—Se(1)—Os(2)	68.4 (1)
Os(2)—Os(1)—Se(1)	55.2 (1)	Os(1)—Se(1)—Os(3)	68.2 (1)
Os(3)—Os(1)—Se(1)	55.2 (1)	Os(2)—Se(1)—Os(3)	98.0 (1)
Os(2)—Os(1)—Se(2)	54.9 (1)	Os(1)—Se(2)—Os(2)	68.8 (1)
Os(3)—Os(1)—Se(2)	54.9 (1)	Os(1)—Se(2)—Os(3)	68.6 (1)
Os(1)—Os(2)—Se(1)	56.4 (1)	Os(2)—Se(2)—Os(3)	98.9 (1)
Os(1)—Os(2)—Se(2)	56.3 (1)	Os(2)—Os(1)—C(11)	152.0 (4)
Os(1)—Os(3)—Se(1)	56.6 (1)	Os(3)—Os(1)—C(11)	80.9 (3)
Os(1)—Os(3)—Se(2)	56.5 (1)	Os(2)—Os(1)—C(12)	80.7 (3)
Se(1)—Os(1)—Se(2)	79.5 (1)	Os(3)—Os(1)—C(12)	147.1 (4)
Se(1)—Os(2)—Se(2)	81.0 (1)	Os(2)—Os(1)—C(13)	115.3 (3)
Se(1)—Os(3)—Se(2)	81.1 (1)	Os(3)—Os(1)—C(13)	119.4 (3)
Se(1)—Os(1)—C(11)	96.9 (4)	Os(1)—Os(2)—C(21)	108.4 (3)
Se(2)—Os(1)—C(11)	128.8 (3)	Os(1)—Os(2)—C(22)	108.0 (3)
Se(1)—Os(1)—C(12)	92.3 (4)	Os(1)—Os(2)—C(23)	145.5 (3)
Se(2)—Os(1)—C(12)	131.0 (3)	C(21)—Os(2)—C(23)	96.2 (5)
Se(1)—Os(1)—C(13)	167.7 (3)	C(22)—Os(2)—C(23)	94.6 (5)
Se(2)—Os(1)—C(13)	88.6 (3)	Os(1)—Os(3)—C(31)	107.9 (3)
Se(1)—Os(2)—C(21)	90.7 (3)	Os(1)—Os(3)—C(32)	108.4 (4)
Se(2)—Os(2)—C(21)	164.7 (3)	Os(1)—Os(3)—C(33)	147.1 (3)
Se(1)—Os(2)—C(22)	164.2 (3)	C(11)—Os(1)—C(12)	100.1 (4)
Se(2)—Os(2)—C(22)	92.8 (4)	C(11)—Os(1)—C(13)	92.7 (5)
Se(1)—Os(2)—C(23)	100.7 (3)	C(12)—Os(1)—C(13)	93.5 (5)
Se(2)—Os(2)—C(23)	98.0 (3)	C(21)—Os(2)—C(22)	91.8 (5)
Se(1)—Os(3)—C(31)	90.6 (4)	C(31)—Os(3)—C(32)	90.8 (5)
Se(2)—Os(3)—C(31)	164.4 (3)	C(31)—Os(3)—C(33)	94.1 (4)
Se(1)—Os(3)—C(32)	164.5 (4)	C(32)—Os(3)—C(33)	95.0 (5)
Se(2)—Os(3)—C(32)	93.7 (4)	Os(1)—C(11)—O(11)	177.6 (9)
Se(1)—Os(3)—C(33)	100.3 (4)	Os(1)—C(12)—O(12)	177.1 (11)
Se(2)—Os(3)—C(33)	100.4 (3)	Os(1)—C(13)—O(13)	176.6 (10)
Os(2)—C(21)—O(21)	179.0 (6)	Os(3)—C(31)—O(31)	179.2 (10)
Os(2)—C(22)—O(22)	175.4 (11)	Os(3)—C(32)—O(32)	179.6 (10)
Os(2)—C(23)—O(23)	176.0 (10)	Os(3)—C(33)—O(33)	175.2 (9)

Os(2)—Os(3), 2.780 (2) Å; Os(1)—Os(2)—Os(3), 81.0 (1)°] and Os$_3$(CO)$_7$H$_2$(CS)S$_2$ (Broadhurst, Johnson, Lewis, Orpen, Raithby & Thornback, 1980) [Os(1)—Os(2), 2.813 (1); Os(1)—Os(3), 2.808 (1) Å; Os(2)—Os(1)—Os(3), 82.8 (1)°]. The two Se atoms μ_3-cap the Os$_3$ triangle on either side; the distances of Se(1) and Se(2) from the Os$_3$ plane are 1.64 (1) and 1.62 (1) Å respectively. The Se—Se distance of 3.254 (1) Å is *ca* 0.9 Å longer than the sum of the covalent radii so there seems to be no significant bonding interaction between these atoms. The Os—Se distances show that the Se atoms lie closer to the non-bonding Os(2)—Os(3) edge than to Os(1). These distances are slightly shorter than the range of bond lengths [2.537 (1)—2.576 (1) Å] found in
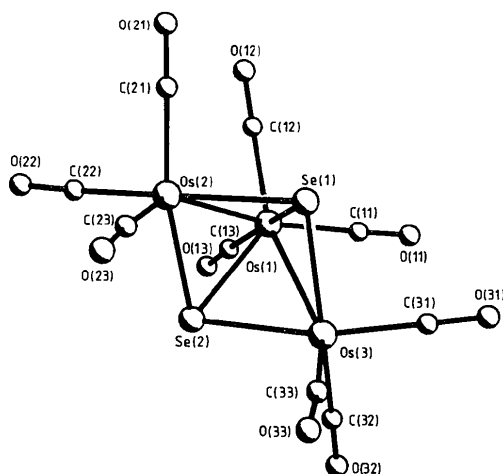
Fig. 1. The molecular structure of $Os_3(CO)_9Se_2$ showing the atom-numbering scheme.

$Os_4(CO)_{12}H_2Se_2$ (Johnson *et al.*, 1979) where the Se atoms also bond to three Os atoms.

The three carbonyl groups bonded to each Os atom are staggered with respect to the metal–metal bonds. The carbonyls are all essentially linear, and the average Os–C and C–O bond lengths of 1·91 (1) and 1·13 (1) Å are similar to those found in $Os_3(CO)_8(CS)S_2$ (Broadhurst, Johnson, Lewis & Raithby, 1980).

In terms of electron counting, with the Se atoms acting as four-electron donors, the title compound is a

50 electron complex. This has two more electrons than the 'electron precise' 48 electron system, and the inclusion of an additional electron pair requires the cleavage of a metal–metal bond, in this case Os(2)–Os(3).

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Structure of Arrojadite, $KNa_4CaMn_4Fe_{10}Al(PO_4)_{12}(OH,F)_2$

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Abstract. $KNa_4CaMn_4Fe_{10}Al(PO_4)_{12}(OH,F)_2$, monoclinic, $C2/c$, $a = 16·526$ (4), $b = 10·057$ (3), $c = 24·730$ (5) Å, $\beta = 105·78$ (3)°. The structure was solved by direct and Fourier methods. An isotropic full-matrix least-squares refinement, followed by anisotropic block-diagonal least-squares cycles, led to a final $R = 0·084$ for 6910 reflections with $I > 3\sigma(I)$.

The structure analysis indicated the ideal crystal chemical formula $KNa_4CaMn_4Fe_{10}Al(PO_4)_{12}(OH,F)_2$.

Introduction. The name arrojadite was first proposed by Guimaraes (1925) for a phosphate of Fe, Mn and Na from Sierra Branca pegmatite, Brazil. Lindberg (1950) identified arrojadite as the unnamed Na, Fe, Mn