

[99.6 (1)°] and  $\text{Ge}_2\text{Se}_6^{4-}$  [95.4 (1)°]. Among the nonbonding  $\text{S}\cdots\text{S}$  and  $\text{Se}\cdots\text{Se}$  distances the common edges of the tetrahedra are, as expected, by far the shortest. It is, however, remarkable that in  $\text{SiSe}_2$  the clear distinction between the shorter  $\text{Se}\cdots\text{Se}$  distances within the edges of the tetrahedra and the much longer ones outside the tetrahedra gets partly lost, the interchain distances  $\text{Se}\cdots\text{Se}^{\text{IV}}$  and  $\text{Se}\cdots\text{Se}^{\text{V}}$  being of the same order as the intratetrahedral distances.

The thermal parameters (Table 1) for  $\text{SiSe}_2$  are roughly twice as large as those for  $\text{SiS}_2$  in accordance with the higher temperature for the measurements. The significantly smaller values of  $U_{33}$  compared to  $U_{11}$  and  $U_{22}$  for both  $\text{SiS}_2$  and  $\text{SiSe}_2$  indicate, as expected, librational motion of the quasi-rigid  $(\text{SiS}_2)_n$  and  $(\text{SiSe}_2)_n$  chains around [001] rather than translational motion parallel to this direction.

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for substantial support of our work.

#### References

BÜSSEM, W., FISCHER, H. & GRUNER, E. (1935). *Naturwissenschaften*, **23**, 740.

- DITTMAR, G. & SCHÄFER, H. (1975). *Acta Cryst.* **B31**, 2060–2064.  
 DITTMAR, G. & SCHÄFER, H. (1976). *Acta Cryst.* **B32**, 2726–2728.  
 EULENBERGER, G. (1978). *Acta Cryst.* **B34**, 2614–2616.  
 HILLEL, R. & CUEILLERON, J. (1971). *Bull. Soc. Chim. Fr.* pp. 394–398.  
*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99 ff. Birmingham: Kynoch Press.  
 KREBS, B. & MANDT, J. (1977). *Z. Naturforsch. Teil B.* **32**, 373–379.  
 KREBS, B. & MÜLLER, H. (1982). *Z. Anorg. Allg. Chem.* Submitted.  
 KREBS, B., POHL, S. & SCHIWY, W. (1972). *Z. Anorg. Allg. Chem.* **393**, 241–252.  
 MANDT, J. & KREBS, B. (1976). *Z. Anorg. Allg. Chem.* **420**, 31–39.  
 PETERS, J., MANDT, J., MEYRING, M. & KREBS, B. (1981). *Z. Kristallogr.* **156**, 90–91.  
 PREWITT, C. T. & YOUNG, H. S. (1965). *Science*, **149**, 535–537.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 WEISS, A. & WEISS, A. (1952). *Z. Naturforsch. Teil B.* **7**, 483–484.  
 ZINTL, A. & LOOSEN, K. (1935). *Z. Phys. Chem. (Leipzig)*, **A174**, 301–311.

*Acta Cryst.* (1982). **B38**, 1272–1274

## Structure of 1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3,2,3-di- $\mu$ -chloro-triangulo-triosmium

BY FREDERICK W. B. EINSTEIN, TERRY JONES AND KENNETH G. TYERS

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

(Received 24 July 1981; accepted 25 November 1981)

**Abstract.**  $\text{Os}_3\text{Cl}_2(\text{CO})_{10}$ ,  $[(\mu\text{-Cl})_2\text{Os}_3(\text{CO})_{10}]$ ,  $M_r = 921.61$ , orthorhombic, *Pbca*,  $a = 25.580$  (8),  $b = 22.832$  (6),  $c = 12.036$  (3) Å,  $V = 7029.5$  Å<sup>3</sup>,  $Z = 16$ ,  $D_c = 3.483$ ,  $D_m = 3.25$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 21.7$  mm<sup>-1</sup>. The structure was solved by direct methods and refined by block-diagonal least squares to a final *R* value of 0.041 for 2838 independent reflections,  $I > 2.3\sigma(I)$ . There are two crystallographically independent molecules with similar geometry in the asymmetric unit. The triosmium core defines an isosceles triangle with the dibridged non-bonding, osmium–osmium vector being 3.233 (2) Å, compared to the non-bridged bond distance of 2.852 (2) Å (av.).

**Introduction.** A yellow crystal, 0.25 × 0.30 × 0.22 mm, was obtained by recrystallization from hexane and used for the diffraction studies.

Weissenberg and precession photographs taken with Cu  $K\alpha$  radiation showed the crystal to be orthorhombic and systematic absences  $0kl: k = 2n + 1$ ,  $h0l: l = 2n + 1$ ,  $hk0: h = 2n + 1$ , uniquely defined the space group as *Pbca*.

Data were collected on a Picker FACS-1 automated four-circle diffractometer with Mo  $K\alpha$  radiation ( $\lambda K\alpha_1 = 0.7093$  Å) using a graphite monochromator and a scintillation counter with pulse-height discrimination. Cell dimensions were obtained from a least-squares refinement of 26 accurately centered reflexions with  $2\theta > 23^\circ$ . Intensity data were collected using a scan rate of 2° min<sup>-1</sup>, a symmetrical scan width of  $(1.2 + 0.692 \times \tan \theta)^\circ$  and background counts of 10% of the total scan time at each scan limit. Peak-profile analyses were performed on all reflections (Grant & Gabe, 1978). Two standards were measured after every 70 reflec-

tions and showed a small gradual overall decline (4%) in average intensity; the data were scaled accordingly. The intensities of 4619 unique reflections with  $3^\circ < 2\theta < 45^\circ$  were measured and of these 2838 were regarded as observed with  $I > 2.3\sigma(I)$  [ $\sigma(I)$  is the e.s.d. derived from counter statistics and a precision factor of 0.03].

The Os atoms were located by direct methods. Full-matrix least-squares refinement of the scale factor

Table 1. Atom coordinates ( $\times 10^4$ ) and isotropic temperature factors ( $\text{\AA}^2 \times 10$ )

	x	y	z	$B_{\text{eq}}$ * or $B_{\text{iso}}$
Os(1)	2517.3 (4)	1274.5 (4)	6779.0 (8)	28.7 (4)*
Os(2)	1644.0 (3)	782.3 (4)	7913.9 (8)	25.3 (4)*
Os(3)	2628.3 (4)	1398.4 (4)	9127.9 (8)	29.6 (5)*
Os(4)	318.8 (4)	1826.2 (4)	3263.2 (8)	24.3 (4)*
Os(5)	-598.2 (3)	1400.4 (4)	2194.6 (8)	26.4 (4)*
Os(6)	480.0 (3)	657.1 (4)	2507.9 (8)	25.5 (4)*
Cl(1)	2284 (2)	393 (3)	9252 (5)	34 (3)*
Cl(2)	1689 (2)	1642 (3)	9145 (5)	35 (3)*
Cl(3)	-426 (2)	457 (3)	3136 (5)	33 (3)*
Cl(4)	4 (2)	969 (3)	830 (5)	34 (3)*
C(11)	2303 (10)	1103 (11)	5282 (21)	39 (5)
O(11)	2163 (7)	971 (9)	4461 (16)	59 (5)
C(21)	3138 (10)	1643 (11)	6421 (21)	40 (6)
O(21)	3563 (9)	1847 (10)	6214 (19)	82 (6)
C(31)	2858 (10)	535 (11)	6979 (22)	42 (6)
O(31)	3054 (7)	91 (8)	7095 (15)	54 (4)
C(41)	2126 (10)	2009 (11)	6827 (21)	41 (6)
O(41)	1910 (7)	2436 (9)	6831 (16)	61 (5)
C(12)	1080 (9)	469 (11)	8789 (20)	37 (5)
O(12)	768 (7)	252 (8)	9345 (15)	56 (4)
C(22)	1199 (11)	1179 (11)	6932 (22)	45 (6)
O(22)	908 (8)	1443 (9)	6375 (16)	58 (5)
C(32)	1704 (10)	164 (11)	6954 (20)	37 (5)
O(32)	1746 (7)	-241 (8)	6375 (15)	49 (4)
C(13)	2650 (9)	1435 (11)	10709 (20)	37 (5)
O(13)	2692 (7)	1474 (8)	11658 (15)	49 (4)
C(23)	2855 (11)	2144 (12)	8836 (24)	52 (7)
O(23)	2973 (8)	2636 (9)	8761 (18)	69 (5)
C(33)	3299 (11)	1119 (12)	8982 (23)	49 (6)
O(33)	3733 (8)	954 (9)	8883 (16)	59 (5)
C(14)	74 (10)	2563 (12)	3565 (21)	43 (6)
O(14)	-91 (8)	3043 (9)	3763 (17)	70 (5)
C(24)	999 (9)	1913 (10)	3872 (19)	33 (5)
O(24)	1401 (7)	1976 (8)	4269 (14)	51 (4)
C(34)	46 (9)	1488 (10)	4579 (18)	29 (5)
O(34)	-123 (6)	1250 (7)	5364 (13)	42 (4)
C(44)	552 (9)	2064 (11)	1791 (19)	35 (5)
O(44)	687 (6)	2218 (7)	936 (14)	44 (4)
C(15)	-971 (9)	1696 (10)	3386 (19)	33 (5)
O(15)	-1195 (7)	1874 (7)	4142 (14)	46 (4)
C(25)	-636 (9)	2120 (10)	1522 (19)	33 (5)
O(25)	-662 (7)	2577 (9)	1121 (16)	57 (5)
C(35)	-1189 (9)	1078 (10)	1449 (20)	34 (5)
O(35)	-1561 (7)	933 (8)	986 (15)	54 (4)
C(16)	563 (10)	-108 (12)	1950 (21)	44 (6)
O(16)	617 (8)	-594 (9)	1644 (17)	68 (5)
C(26)	1109 (9)	921 (11)	2013 (20)	37 (5)
O(26)	1511 (7)	1081 (8)	1662 (15)	53 (4)
C(36)	754 (10)	513 (11)	3873 (20)	37 (5)
O(36)	946 (7)	383 (8)	4704 (15)	52 (4)

\*  $B_{\text{eq}} = 8\pi^2(U_{11}^2 + U_{22}^2 + U_{33}^2)/3|^{1/2}$ .

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for Os<sub>3</sub>Cl<sub>2</sub>(CO)<sub>10</sub>

Os(1)–Os(2)	2.849 (2)	Os(4)–C(44)	1.95 (3)
Os(1)–Os(3)	2.855 (2)	Os(5)–C(15)	1.85 (2)
Os(2)–Os(3)	3.233 (2)	Os(5)–C(25)	1.83 (2)
Os(4)–Os(5)	2.846 (2)	Os(5)–C(35)	1.91 (2)
Os(4)–Os(6)	2.850 (2)	Os(6)–C(16)	1.88 (3)
Os(5)–Os(6)	3.260 (2)	Os(6)–C(26)	1.82 (2)
Os(2)–Cl(1)	2.461 (6)	Os(6)–C(36)	1.82 (3)
Os(2)–Cl(2)	2.462 (6)	C(11)–O(11)	1.09 (3)
Os(3)–Cl(1)	2.462 (6)	C(21)–O(21)	1.21 (3)
Os(3)–Cl(2)	2.467 (6)	C(31)–O(31)	1.14 (3)
Os(5)–Cl(3)	2.473 (6)	C(41)–O(41)	1.12 (3)
Os(6)–Cl(3)	2.479 (6)	C(12)–O(12)	1.15 (3)
Os(5)–Cl(4)	2.457 (6)	C(22)–O(22)	1.17 (3)
Os(6)–Cl(4)	2.463 (6)	C(32)–O(32)	1.16 (3)
Os(1)–C(11)	1.92 (3)	C(13)–O(13)	1.15 (3)
Os(1)–C(21)	1.85 (3)	C(23)–O(23)	1.17 (3)
Os(1)–C(31)	1.91 (3)	C(33)–O(33)	1.18 (3)
Os(1)–C(41)	1.95 (3)	C(14)–O(14)	1.20 (3)
Os(2)–C(12)	1.92 (2)	C(24)–O(24)	1.14 (3)
Os(2)–C(22)	1.87 (3)	C(34)–O(34)	1.17 (3)
Os(2)–C(32)	1.83 (2)	C(44)–O(44)	1.14 (3)
Os(3)–C(13)	1.91 (2)	C(15)–O(15)	1.15 (3)
Os(3)–C(23)	1.83 (3)	C(25)–O(25)	1.15 (3)
Os(3)–C(33)	1.84 (3)	C(35)–O(35)	1.15 (3)
Os(4)–C(14)	1.83 (3)	C(16)–O(16)	1.18 (3)
Os(4)–C(24)	1.90 (2)	C(26)–O(26)	1.17 (3)
Os(4)–C(34)	1.90 (2)	C(36)–O(36)	1.15 (3)
Os(1)–Os(2)–Os(3)	55.56 (3)	Os(2)–Os(3)–Cl(2)	48.9 (1)
Os(1)–Os(3)–Os(2)	55.39 (3)	Os(1)–Os(3)–Cl(1)	86.1 (2)
Os(2)–Os(1)–Os(3)	69.06 (4)	Os(1)–Os(3)–Cl(2)	86.2 (2)
Os(4)–Os(5)–Os(6)	55.13 (3)	Os(3)–Os(2)–Cl(1)	49.0 (1)
Os(4)–Os(6)–Os(5)	55.04 (3)	Os(3)–Os(2)–Cl(2)	49.1 (1)
Os(5)–Os(4)–Os(6)	69.83 (4)	Os(4)–Os(5)–Cl(3)	86.8 (1)
Os(2)–Cl(1)–Os(3)	82.1 (2)	Os(4)–Os(5)–Cl(4)	85.5 (1)
Os(2)–Cl(2)–Os(3)	82.0 (2)	Os(4)–Os(6)–Cl(3)	86.6 (1)
Os(5)–Cl(3)–Os(6)	82.3 (2)	Os(4)–Os(6)–Cl(4)	85.4 (1)
Os(5)–Cl(4)–Os(6)	83.0 (2)	Os(5)–Os(6)–Cl(3)	48.8 (1)
Os(1)–Os(2)–Cl(1)	86.3 (2)	Os(5)–Os(6)–Cl(4)	48.4 (1)
Os(1)–Os(2)–Cl(2)	86.4 (2)	Os(6)–Os(5)–Cl(3)	48.9 (1)
Os(2)–Os(3)–Cl(1)	48.9 (1)	Os(6)–Os(5)–Cl(4)	48.6 (1)

along with the positional and isotropic thermal parameters for the Os atoms led to  $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.16$  and  $R' = (\sum w|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2} = 0.19$ . Subsequent difference maps revealed the chlorine and carbonyl groups. Further refinement with anisotropic temperature factors for the Os and Cl, isotropic for C and O, gave  $R = 0.059$  and  $R' = 0.074$ . At this stage an analytical absorption correction was applied to the data (transmission coefficients = 0.070–0.039); further refinement resulted in  $R = 0.041$  and  $R' = 0.049$ . A final difference Fourier synthesis based on all data revealed no chemically significant peaks and no evidence of anisotropy around the carbonyl groups; consequently no further refinement was carried out. All shift-to-error ratios were less than 0.1 in the final cycle.

The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma(F)^2 + 0.0008F^2$ , and the average  $\sum w\Delta^2$  showed no major variations as a function of

$|F_o|$ ,  $\sin \theta/\lambda$ , or identity of Miller indices. Neutral-atom scattering factors and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974). Computer programs (Gabe, Larsen, Lee & Wang, 1979) were run on an in-house PDP-8e computer. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1, bond lengths and angles in Table 2.\*

**Discussion.** The present structural analysis completes the investigation of  $(\mu\text{-H})_{0-2}(\mu\text{-Cl})_{2-0}\text{Os}_3(\text{CO})_{10}$  complexes (Allen, Mason & Hitchcock, 1977; Churchill & Lashewycz, 1979). A comparison of the important bond distances and angles within the species  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ ,  $(\mu\text{-H})(\mu\text{-Cl})\text{Os}_3(\text{CO})_{10}$  and  $(\mu\text{-Cl})_2\text{Os}_3(\text{CO})_{10}$  is reported in Table 3.

The two molecules in the asymmetric unit did not differ significantly. Fig. 1 shows the atomic-labeling scheme and a view of the molecule projected onto its triosmium plane.

\* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36572 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Distances (Å) and angles (°) within the complexes  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ ,  $(\mu\text{-H})(\mu\text{-Cl})\text{Os}_3(\text{CO})_{10}$ , and  $(\mu\text{-Cl})_2\text{Os}_3(\text{CO})_{10}$

	$(\mu\text{-H})_2$ compound <sup>a</sup>	$(\mu\text{-H})(\mu\text{-Cl})$ compound <sup>b</sup>	$(\mu\text{-Cl})_2$ compound <sup>c</sup>
Bridged Os—Os	2.682 (1)	2.846 (1)	3.233 (2)
Non-bridged Os—Os(av.)	2.815 (1)	2.833 (1)	2.852 (2)
Os—Cl(av.)	—	2.456 (3)	2.463 (3)
Os—Cl—Os (av.)	—	70.83 (9)	82.04 (8)

(a) Allen, Mason & Hitchcock (1977). (b) Churchill & Lashewycz (1979). (c) This work.

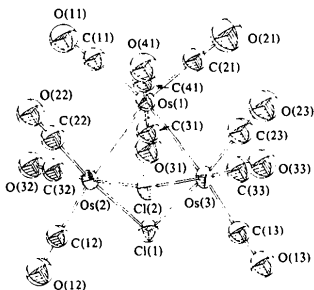


Fig. 1. ORTEP (Johnson, 1976) diagram of 1,1,1,1,2,2,2,3,3,3-decacarbonyl-2,3,2,3-di- $\mu$ -chloro-triangulo-triosmium showing the atom labeling. Thermal ellipsoids indicate 45% probability levels.

The three Os atoms in  $(\mu\text{-Cl})_2\text{Os}_3(\text{CO})_{10}$  essentially define an isosceles triangle. One atom, Os(1), has four terminal carbonyl ligands while Os(2) and Os(3) each have three terminal carbonyl groups and are bridged by two chloride ligands. The angle at the unique osmium, Os(2)—Os(1)—Os(3), is  $69.06(4)^\circ$  while the angles defined by Os(1)—Os(2)—Os(3) and Os(1)—Os(3)—Os(2) are  $55.56(3)$  and  $55.39(3)^\circ$  respectively. This compares with the 'close to' equilateral triangle found for  $(\mu\text{-H})(\mu\text{-Cl})\text{Os}_3(\text{CO})_{10}$  (Churchill & Lashewycz, 1979). The dibridged osmium—osmium distance increases from 2.682 (2) to 2.846 (2) to 3.233 (2) Å as Cl is substituted for H as the bridging ligand. This increase in Os—Os length reflects the decrease in Os—Os bond order from 2 in  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$  to 1 in  $(\mu\text{-H})(\mu\text{-Cl})\text{Os}_3(\text{CO})_{10}$  to 0 in  $(\mu\text{-Cl})_2\text{Os}_3(\text{CO})_{10}$ . As shown in Table 3, there is an increase in the non-bridged osmium—osmium distance which parallels that of the dibridged osmium—osmium length. This was not seen in the series  $(\mu\text{-H})_{0-2}(\mu\text{-OMe})_{2-0}\text{Os}_3(\text{CO})_{10}$  (Churchill & Wasserman, 1980).

The bridging Cl atoms are bound to the triosmium core *via* Os(2) and Os(3) with an average bond length of 2.461 (3) Å. The Os(2)—Cl—Os(3) angle of  $82.04(8)^\circ$  {avg;  $\sigma = \left[ \sum_N (d_i - \bar{d})^2 / N(N-1) \right]^{1/2}$ } is much larger than the acute value of  $70.83(9)^\circ$  reported for  $(\mu\text{-H})(\mu\text{-Cl})\text{Os}_3(\text{CO})_{10}$ . The Os—C [1.83 (2)—1.95 (3) Å] and C—O [1.09 (3)—1.21 (3) Å] distances are normal and the Os—C—O angles are close to linear [172.4 (25)—178.8 (23)°].

We thank Dr R. K. Pomeroy of this Department for supplying the crystals and for helpful discussion. Financial aid in the form of an operating grant from the Natural Sciences and Engineering Research Council of Canada is also acknowledged.

## References

- ALLEN, V. F., MASON, R. & HITCHCOCK, P. B. (1977). *J. Organomet. Chem.* **140**, 297–304.
- CHURCHILL, M. R. & LASHEWYCZ, R. A. (1979). *Inorg. Chem.* **18**, 1926–1930.
- CHURCHILL, M. R. & WASSERMAN, H. J. (1980). *Inorg. Chem.* **19**, 2391–2395.
- GABE, E. J., LARSEN, A. C., LEE, F. L. & WANG, Y. (1979). *the NSERC PDP-8e Crystal Structure System*.
- GRANT, D. F. & GABE, E. J. (1978). *J. Appl. Cryst.* **11**, 114–117.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.