Crystal Structure of Dodecacarbonyldi-iodotriosmium

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Crystals of $[Os_3(CO)_{12}I_2]$ are monoclinic, space group $P2_1/n$, with $Z = 2$ in a unit cell of dimensions $a = 10.329(7)$, $b = 11.579(11)$, $c = 9.334(7)$ Å, and $\beta = 100.07(2)°$. The structure has been elucidated by heavy-atom methods from 2 015 diffracted intensities measured on a four-circle diffractometer, and refined to R 0.062. The molecule is required crystallographically to be centrosymmetric. It comprises a straight chain of three osmium atoms, with the iodine atoms occupying equatorial sites, *trans* to one another, on the terminal Os atoms. Each Os atom has an octahedral configuration and, apart from the two iodine atoms, all the other sites are occupied by carbonyl ligands. The equatorial ligands on the terminal atoms are staggered with respect to the four carbonyl groups on the central Os atom, while the two terminal carbonyl groups are collinear with the molecular axis. The Os–Os distance is 2.93, Os–I 2.77, and the mean Os–C and C–O distances are 1.95 and 1.14 Å. As has been observed in other compounds of this type, the equatorial carbonyl groups on the terminal metal atoms lean inwards towards the central metal atom.

THE title compound was obtained by reaction of iodine with dodecacarbonyl-*triangulo*-triosmium in methylene chloride, the molar ratio of reactants being maintained at 1 : >10 at 0 °C in absence of light.[1] Earlier studies of the reaction between halogens and polynuclear carbonyls [2,3] have led to the formulation of the osmium dihalides $[Os_3(CO)_{12}X_2]$ as linear molecules of D_{4h} symmetry containing the atom sequence X–Os–Os–Os–X, mainly on the basis of mass-spectral and i.r. evidence.[3] According to Moss and Graham,[4] however, such a conclusion is based on an over-simplistic interpretation of the i.r. spectrum.[5] Because of the possi-

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[1] J. Maher, personal communication.

[2] J. P. Candlin and J. Cooper, *J. Organometallic Chem.*, 1968, **15**, 230.

[3] B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc.* (*A*), 1968, 2859.

[4] J. R. Moss and W. A. G. Graham, unpublished work and personal communication.

[5] J. R. Moss and W. A. G. Graham, *J. Organometallic Chem.*, 1970, **23**, C47; *Chem. Comm.*, 1969, 800.

bility that the D_{4h} structure might be incorrect, and because of the intrinsic interest of knowing whether the carbonyl ligands adopt an eclipsed or staggered relative orientation, an *X*-ray determination of the structure has been carried out.

EXPERIMENTAL

The conditions of preparation of $[Os_3(CO)_{12}I_2]$ used by us are considerably milder than those reported in ref. 3, and unfortunately the i.r. spectrum of the compound described in ref. 3 is not given in sufficient detail (' three strong bands ') to enable us to establish beyond doubt whether that compound is identical to ours. We therefore repeated the preparation described in ref. 3 and have shown, by determination of the crystallographic unit-cell parameters, that the two materials are identical. The i.r. spectrum of the title compound in CCl_4 shows absorptions at 2 147w, 2 117s, 2 090w(sh), 2 062vs, 2 032s, 2 026w(sh), and 2 006m cm^{-1}.

Crystals of $[Os_3(CO)_{12}I_2]$ grow from toluene as yellow prisms. The dimensions of the one chosen for *X*-ray diffraction were $0.30 \times 0.15 \times 0.05$ mm. This crystal was mounted on a Syntex $P2_1$ four-circle diffractometer and intensities were collected for $2.9 < 2\theta < 55.0°$ according to methods described earlier.[6] Of the total (2 997) reflections, 2 014 independent intensities having $I > 2.5\sigma(I)$ were deemed ' observed ', and only these were used in the solution and refinement of the structure.

Crystal Data.—$C_{12}I_2O_{12}Os_3$, $M = 1\ 160.4$, Monoclinic, $a = 10.329(7)$, $b = 11.579(11)$, $c = 9.334(7)$ Å, $\beta = 100.07(2)°$, $D_c = 3.56$ g cm^{-3}, $Z = 2$, $D_m = 3.3$ g cm^{-3}, $F(000) = 1\ 004$. Space group $P2_1/n$. Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å; μ(Mo-K_α) = 212.2 cm^{-1}.

TABLE 1

Atomic positional (fractional co-ordinates) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Os(1)	0.500 00	0.500 00	0.500 00
Os(2)	0.721 90(9)	0.647 79(8)	0.460 26(10)
I	0.561 45(19)	0.828 09(16)	0.344 49(24)
C(1)	0.830(3)	0.521(2)	0.539(3)
O(1)	0.895(2)	0.445(2)	0.587(3)
C(2)	0.704(2)	0.591(2)	0.259(3)
O(2)	0.685(2)	0.565(2)	0.138(2)
C(3)	0.870(3)	0.746(2)	0.440(3)
O(3)	0.957(2)	0.802(2)	0.431(2)
C(4)	0.713(2)	0.705(2)	0.655(3)
O(4)	0.691(3)	0.739(2)	0.763(2)
C(5)	0.576(5)	0.468(2)	0.704(3)
O(5)	0.631(2)	0.455(2)	0.817(2)
C(6)	0.590(2)	0.365(2)	0.437(3)
O(6)	0.645(2)	0.290(2)	0.399(2)

Solution and Refinement of the Structure.—The iodine and osmium atoms were located by vector methods, and because $Z = 2$ the molecule is required crystallographically to be centrosymmetric, with the central osmium atom at a centre of inversion. The carbon and oxygen atoms were located by successive electron-density difference syntheses. The structure was refined by full-matrix least squares with anisotropic thermal parameters for all the atoms. Weights were applied according to the scheme $w = xy$, where $x = 1$ for $\sin\theta \geqslant b$ and $(\sin\theta)/b$ for $\sin\theta < b$, $y = 1$ for $F_o \leqslant c$ and c/F_o for $F_o > c$, with two parameters $b = 0.29$, and $c = 65.0$. This gave a satisfactory weight analysis following the final cycles of refinement. The refinement converged to R 0.062 (R' 0.077) with a maximum shift-to-error ratio of 0.4 : 1 in the final cycle. Final electron-density difference syntheses showed peaks of *ca.* +4 and −4 eÅ^{-3} in the neighbourhood of the Os atoms, with general background levels very much less than this. Atomic scattering factors were those of ref. 7 for C, O, and I, and of ref. 8 for osmium, corrected for anomalous dispersion in the case of osmium and iodine (Os: $\Delta f' = -1.816$, $\Delta f'' = 7.605$; I: $\Delta f' = -0.726$, $\Delta f'' = 1.812$). The intensities were corrected for the effects of *X*-ray absorption,[9] and all the computational work was carried out at the University of London Computing Centre with the ' *X*-Ray ' system of programs.[9] Observed and calculated structure factors together with the thermal parameters are listed in Supplementary Publication No. SUP 22093 (12 pp., 1 microfiche).*

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances			
Os(1)–Os(2)	2.935(2)	Os(1)–C(6)	1.96(3)
Os(2)–I	2.772(3)	C(1)–O(1)	1.15(3)
Os(2)–C(1)	1.91(3)	C(2)–O(2)	1.15(3)
Os(2)–C(2)	1.97(3)	C(3)–O(3)	1.12(3)
Os(2)–C(3)	1.94(3)	C(4)–O(4)	1.14(3)
Os(2)–C(4)	1.95(3)	C(5)–O(5)	1.12(3)
Os(1)–C(5)	1.97(3)	C(6)–O(6)	1.13(3)
(*b*) Angles			
C(5)–Os(1)–C(6)	90.6(12)	C(1)–Os(2)–C(2)	93.6(11)
C(5)–Os(1)–Os(2)	92.7(13)	C(1)–Os(2)–C(3)	94.0(11)
C(6)–Os(1)–Os(2)	89.7(7)	C(1)–Os(2)–C(4)	91.0(11)
Os(1)–Os(2)–I	93.6(1)	C(2)–Os(2)–C(3)	92.6(9)
Os(1)–Os(2)–C(1)	85.5(8)	C(2)–Os(2)–C(4)	172.2(8)
Os(1)–Os(2)–C(2)	89.0(6)	C(3)–Os(2)–C(4)	93.3(10)
Os(1)–Os(2)–C(3)	178.4(7)	Os(2)–C(1)–O(1)	180(3)
Os(1)–Os(2)–C(4)	85.1(7)	Os(2)–C(2)–O(2)	174(2)
I–Os(2)–C(1)	179.1(8)	Os(2)–C(3)–O(3)	178(2)
I–Os(2)–C(2)	86.0(6)	Os(2)–C(4)–O(4)	171(2)
I–Os(2)–C(3)	86.8(7)	Os(1)–C(5)–O(5)	172(4)
I–Os(2)–C(4)	89.3(6)	Os(1)–C(6)–O(6)	178(2)

RESULTS AND DISCUSSION

The *X*-ray analysis (Tables 1 and 2) of $[Os_3(CO)_{12}I_2]$ establishes that the molecule has the overall structure shown in Figure 1. The spine of the molecule comprises the linear sequence O–C–Os–Os–Os–C–O, and the iodine atoms occupy equatorial sites, *trans* to one another, on the terminal Os atoms. The molecule is required crystallographically to be centrosymmetric. Each Os atom has an octahedral configuration, and, apart from the two iodine atoms, all the other sites are occupied by carbonyl ligands. The equatorial ligands on the terminal atoms are staggered with respect to the four carbonyl groups on the central Os atom. This feature is illustrated in Figure 2, which shows a projection of the molecule as seen along the molecular axis. The Os–Os [2.935(2) Å], Os–I [2.772(3) Å], and mean Os–C and C–O distances [1.95(3) and 1.14(3) Å] are all within expected

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[6] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

[9] Technical Report TR 192, The Computer Science Centre, University of Maryland, June 1972.

ranges. (The 18-electron rule predicts a closed shell for each osmium atom if a two-centre electron-pair osmium–osmium bond is assumed.) Reasons for the occurrence of staggered, rather than eclipsed, arrangement of carbonyl groups on adjacent metal atoms have been discussed in connection with several polynuclear carbonyl species [10] and need not be repeated here. Unlike $[\{Ru(SnMe_3)(CO)_4\}_2]$,[11] $[Os_3(CO)_{12}I_2]$ has the expected staggered configuration. Such molecules often reveal two other features: (*i*) the axial M–CO bonds are shorter than the equatorial M–CO bonds; and (*ii*) the equatorial carbonyl groups on the terminal metal atoms tend to lean inwards towards the central metal atom. In the title compound, the M–CO distances listed in Table 2 do not differ significantly from one another, but of course any real differences may be disguised because of the large standard deviations. The interbond angles, however, clearly show an inward lean for carbonyl groups (1), (2), and (4), and it is interesting to note that the iodine atom leans a little the opposite way. The Os–C–O bonds are almost linear, although the deviations appear to be just significant on the errors given. The shortest intermolecular contact occurs between O(1) at *x, y, z* and O(4) at $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$, a distance of 2.98 Å.

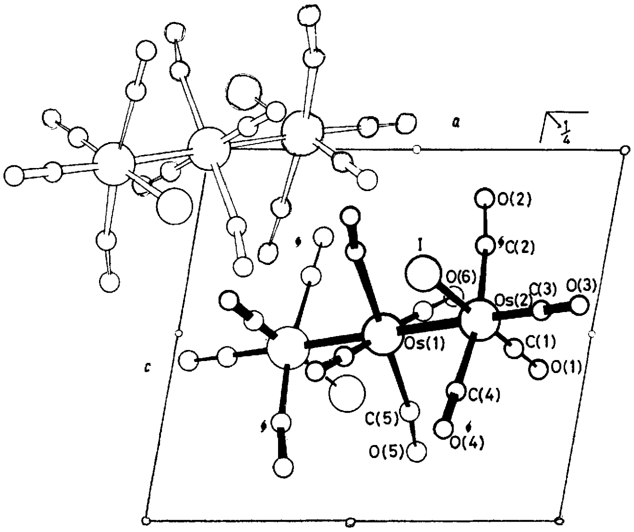

FIGURE 1 Molecular structure of $[Os_3(CO)_{12}I_2]$ seen in projection down the *b* axis of the monoclinic unit cell. The atom-numbering system is also shown

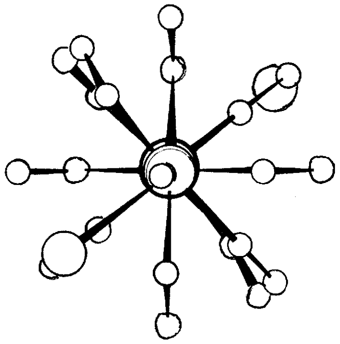

FIGURE 2 View of $[Os_3(CO)_{12}I_2]$ along the molecular axis, showing the staggered relationship of carbonyl groups on adjacent Os atoms

The table of anisotropic thermal parameters * shows an unusually low value of U_{11} for C(2) and an unusually high one for C(5). We attach no physical significance to these values. The electron-density difference maps showed no existence of disorder, but the absorption-correction factor is very large [μ(Mo-K_α) 212 cm^{-1}], and in view of the difficulty of measuring the crystal dimensions sufficiently accurately, small errors in the refined parameters are not unexpected.

A similar structure to that of $[Os_3(CO)_{12}I_2]$ has been postulated [12] on the basis of spectroscopic evidence for $[Os_3(CO)_{12}Me_2]$; our results tend to support this postulation.

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* See Supplementary publication.

[10] R. Bau, S. W. Kirtley, T. N. Sorrell, and S. Winarko, *J. Amer. Chem. Soc.*, 1974, **96**, 988 and refs. therein.

[11] J. A. K. Howard, S. C. Kellett, and P. Woodward, *J.C.S. Dalton*, 1975, 2332.

[12] J. Evans, S. J. Okrasinski, A. J. Pribula, and J. R. Norton, personal communication.