The Structure of Di-μ-iodohexacarbonyldiosmium(I)

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The compound $Os_2(CO)_6I_2$ has been prepared and characterized, and the structure determined by X-ray crystallography. Crystals of the compound are monoclinic, space group $P2_1/m$, with a *= 6.453(3) Å,* b *= 14.017(7) Å,* c *= 7.328(4) Å, β = 91.03(2)° and Z = 2. Intensities were obtained using $\omega-2\theta$ scan techniques with a Philips PW 1100 four-circle diffractometer using graphite-monochromated MoKα radiation. The structure was solved by conventional heavy-atom methods, and least-squares refinement of structural parameters led to a conventional* R *factor of 0.079 for 1048 reflections. The molecular structure of $Os_2(CO)_6I_2$ shows a butterfly-type arrangement with two six-coordinate osmium atoms joined by a metal–metal bond and two bridging iodine ligands at the apices of the wings. Three terminal carbonyl groups are attached to each osmium atom. The reactivity of this molecule is also briefly discussed.*

Introduction

Catalytic reactions that occur on metal surfaces can involve processes requiring adjacent metal atoms. Examples of such processes are the migration of substrate from one metal atom to another and the interaction of a substrate with more than one metal atom. It is not possible to model such processes using mononuclear metal complexes. The analogy between chemisorbed species on metal surfaces and metal cluster complexes is now well known [1], and this has in part led to the rapid expansion of the study of such cluster complexes. Binuclear complexes are, however, the simplest species with more than one metal atom and should therefore serve as particularly useful models for processes involving adjacent metal atoms. Consequently, there is considerable current interest in binuclear metal complexes [2, 3].

The chemistry and structure of complexes containing three or more osmium atoms has been investigated in detail [4–6], but there have been few studies on binuclear osmium complexes. In contrast, studies on Fe_2 complexes are fairly common [2]. Since metal–metal bonds are generally more robust for third series transition metals, an Os–Os bond may remain intact during chemical transformations whereas similar Fe–Fe bonds, for example, may be cleaved. Thus, binuclear osmium complexes may be good models for reactions occuring on metal surfaces. With this in mind, we have undertaken a study on the structure and chemical reactivity of binuclear osmium complexes, and now report on the synthesis and structure of $Os_2(CO)_6I_2$.

Experimental

IR spectra were recorded on a Perkin-Elmer 180 grating spectrophotometer; mass spectra were recorded using a VG micromass 16F spectrometer operating at 70 eV ionizing voltage (1 eV = 1.60 × 10^{-19} J), samples were introduced into the instrument as solids using the direct probe. The complex $Os_2(CO)_8I_2$ was prepared by the reaction of $Os_3(CO)_{12}$ with iodine in benzene [7]. Reactions were carried out under an atmosphere of nitrogen.

Preparation of $Os_2(CO)_6I_2$ from $Os_2(CO)_8I_2$

$Os_2(CO)_8I_2$ (0.11 g, 0.13 mmol) was dissolved in dry nitrogen-saturated heptane (12 cm^3) and the solution heated under reflux for 40 mins. The solvent was removed under reduced pressure to give $Os_2(CO)_6I_2$ as a yellow solid (0.082 g, 80%). The product was purified by sublimation m.p. 82–87 °C; IR ν(CO) (cyclohexane) 2097 m, 2067 vs, 2014 vs, 2008 vs, 2002 m cm^{-1}; a parent ion with the expected isotope pattern is observed in the mass spectrum (lit. [8] m.p. 87 °C; IR ν(CO) (cyclohexane) 2098, 2068, 2016, 2010 and 2004 cm^{-1}). Orange crystals suitable for X-ray crystallographic analysis were obtained by sublimation (60 °C/0.01 mm Hg) for three days.

Crystal and Intensity Data

Preliminary photographs (CuKα radiation, λ = 1.542 Å) indicated that the compound had crystallized in either of the two monoclinic space groups $P2_1$ or $P2_1/m$. Accurate cell dimensions were obtained by least-squares analysis from the settings of 25 high order reflections measured on a Philips PW 1100 four-circle diffractometer with graphite-monochromated MoKα radiation (λ = 0.7107 Å). Intensities were collected by the $\omega-2\theta$ scan technique.

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The intensities of three reference reflections were examined after every 68 measured reflections to monitor the stability of the crystal. Lorentz-polarization corrections were applied but no correction was made for absorption effects. Crystal data and experimental details of the data collection and final refinement are listed in Table I.

TABLE I. Crystal Data and Experimental and Refinement Parameters for the Crystal Structure of [Di-μ-iodohexacarbonyldiosmium(I)], $Os_2(CO)_6I_2$.

Molecular Formula	$Os_2C_6O_6I_2$
M_r	802.27 g
Space Group	$P2_1/m$
a/Å	6.453(3)
b/Å	14.017(7)
c/Å	7.328(4)
β/°	91.03(2)
V/Å^3	661
Z	2
D_c/Mgm^{-3}	4.03
μ(MoKα)/mm^{-1}	22.85
F(000)	688
Data Collection	
Crystal dimensions/mm	0.8 × 0.4 × 0.5
Scan Mode	$\omega-2\theta$
Scan Width/°θ	1.4
Scan Speed/°θ s^{-1}	0.047
Range Scanned (2θ)/°	6–52
Stability of Standard Reflections/%	0.81
Number of Reflections Collected	1170
Number of Observed Reflections	1048 with $I_{rel} > 2\sigma I_{rel}$
Refinement	
Number of Variables	46
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.079
$R_w = \Sigma w^{1/2}\|\|F_o\| - \|F_c\|\|/\Sigma w^{1/2}\|F_o\|$	0.086
Weighting Scheme w	$(\sigma^2F + 2 \times 10^{-3}F^2)^{-1}$

Solution and Refinement of the Structure

An examination of the E-statistics on data reduction, indicated a centrosymmetric space group; hence $P2_1/m$ was chosen and subsequent refinement of the structure vindicated this choice. A Patterson map revealed the osmium atom lying on a general position and subsequent weighted difference syntheses revealed two independent iodines on special positions and the carbonyls on positions of general symmetry. The final full-matrix least-squares refinement was carried out with the Os and I atoms treated anisotropically and the C and O atoms, isotropically. The weighting schemes were chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F_o, as shown by analyses of variance, computed after the final cycles. In the final cycle, the mean e.s.d. in the atomic parameters was more than 100 times the average parameter shift, while the final difference map was smooth, except close to the osmium atom where the largest residual peaks were 4 electrons Å^{-3}. Table II lists the final fractional atomic coordinates and temperature factors for all the atoms. Scattering factors for all atoms were taken from Cromer and Mann [9] with dispersion corrections from Cromer and Liberman [10]. All computations were performed at the computer centre of the University of Cape Town on a Univac 1100/81 computer with SHELX [11] (data reduction, structure solution and refinement), and PLUTO [12] (illustrations).

Results and Discussion

The paucity of data on Os_2 complexes is partly due to the lack of convenient synthetic routes for such complexes. We have now found that the complexes $Os_2(CO)_8X_2$, (X = Cl, Br or I), which are a convenient starting point for a study of Os_2 complexes, can be obtained in good (70–80%) yields by the reaction of the halogens with $Os_3(CO)_{12}$ under controlled conditions. Details of these syntheses will be the subject of a later paper [7]. Previously, the compounds $Os_2(CO)_8X_2$, where X = Cl or Br have been obtained from the fairly inaccessible hydride $H_2Os_2(CO)_8$ [13] or where X = I, by the reactions of iodine or CF_3I with $Os_3(CO)_{12}$ in sealed evacuated tubes over several days [8]. We obtained $Os_2(CO)_6I_2$ by heating a heptane solution of $Os_2(CO)_8I_2$ under reflux and isolated the hexacarbonyl complex in 80% yield. A similar method has previously been reported for the synthesis of $Os_2(CO)_6X_2$ from $Os_2(CO)_8X_2$ (X = Cl or Br) [13]. Thus, the complexes $Os_2(CO)_8X_2$ and $Os_2(CO)_6X_2$ are available for further study. Two interesting pathways for reaction of $Os_2(CO)_6X_2$ complexes are (i) oxidation of the Os–Os bond with the retention of the halogen bridges to give $Os_2(CO)_6X_2Y_2$ (where Y = halogen for example) and (ii) ligand addition with cleavage of the halogen bridges but retention of the Os–Os bond to give complexes of the type $Os_2(CO)_6L_2X_2$. In this regard, we find that $Os_2(CO)_6I_2$ reacts rapidly with PPh_3 under mild conditions to give $Os_2(CO)_6(PPh_3)_2I_2$, the product of a ligand addition reaction in which we believe that the iodine bridges are cleaved but the Os–Os bond is retained [7].

Description of the Structure

The molecular structure of $Os_2(CO)_6I_2$ (*I*) shows the two equivalent osmium atoms bonded together by a metal–metal bond which is bridged by two iodine atoms with three terminal carbonyl ligands on each osmium atom (see Figs. 1 and 2). This structure (which formally has a single bond between the two Os atoms) enables the metal atoms to obey the 18 electron rule. This type of structure had previously

TABLE II. Fractional Atomic Coordinates (× 10^4) and Temperature Factors ($Å^2$ × 10^3) with Estimated Standard Deviations in Parentheses.

Atoms	*x/a*	*y/b*	*z/c*	U_{iso}
Os_1	2478(1)	1529(1)	2824(1)	*
I_1	5617(3)	2500(1)	4605(3)	*
I_2	3892(4)	2500(1)	−121(3)	*
C_1	1207(44)	1282(20)	5039(44)	37(6)
O_1	413(38)	1090(18)	6362(39)	60(6)
C_2	70(46)	1195(21)	1534(46)	41(7)
O_2	−1413(36)	974(17)	716(35)	57(6)
C_3	3894(41)	302(20)	2526(39)	35(6)
O_3	4648(35)	−402(17)	2465(34)	58(6)

*Anisotropic Temperature Factors

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os_1	22(1)	27(1)	7(1)	1(1)	−2(1)	−1(1)
I_1	20(1)	44(1)	12(1)	0(1)	−7(1)	0(1)
I_2	44(1)	45(2)	3(1)	0(1)	5(1)	0(1)

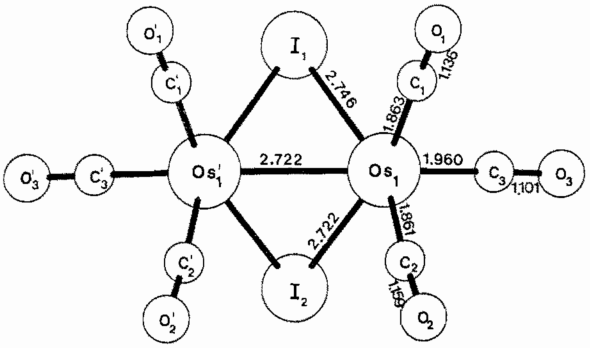

Fig. 1. A perspective view of $Os_2(CO)_6I_2$. The bond distances (Å) and atom-numbering scheme are shown.

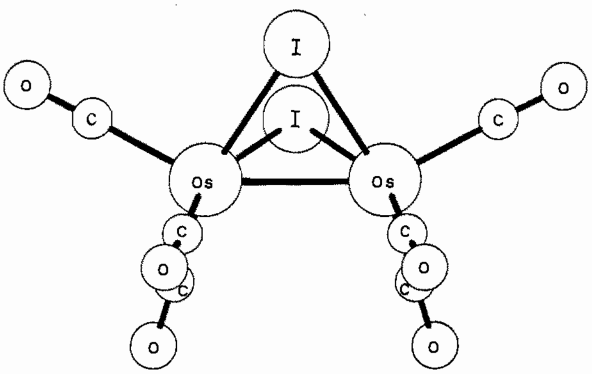

Fig. 2. A perspective view of $Os_2(CO)_6I_2$ illustrating the butterfly structure.

been proposed for the complexes $Os_2(CO)_6X_2$ (X = Cl, Br or I) on the basis of IR and mass spectral data [8, 13] and has been previously found for a related ruthenium complex $Ru_2Cl_2(CO)_4$(P-*t*-Bu_2-*p*-tolyl$)_2$ [14]. The coordination about the Os atoms is distorted octahedral if we assume a bent metal–metal bond. $Os_2(CO)_6I_2$ can be described as having a butterfly structure with iodine atoms at the apices of the wings (see Fig. 2). Bond lengths and angles are given in Tables III and IV. The Os–Os distance of 2.722(2) Å is shorter than that found in $Os_3(CO)_{12}$ (2.88 Å) [15] and $Os_3(CO)_{12}I_2$ (2.93 Å) [16], longer than that in bulk osmium metal (2.70 Å) [17] but similar to that in $Os_2(CO)_6(CH_3COO)_2$ (2.731 Å) [18].

TABLE III. Bond Lengths (Å) for $Os_2(CO)_6I_2$ with the Estimated Standard Deviations in Parentheses.

Os_1–Os_1'	2.722(2)	C_1–O_1	1.136(38)
Os_1–I_1	2.746(2)	C_2–O_2	1.159(37)
Os_1–I_2	2.722(2)	C_3–O_3	1.101(34)
Os_1–C_1	1.863(30)		
Os_1–C_2	1.861(31)		
Os_1–C_3	1.960(27)		

Os_1–Os_1 non-bonded distance 6.251(2) Å

The Os–I distances in $Os_2(CO)_6I_2$ are 2.722(2) and 2.746(2) Å (average 2.734(2) Å) which is shorter than the terminal Os–I distance of 2.77 Å in $Os_3(CO)_{12}I_2$. This is somewhat surprising, since in similar compounds, the terminal Os–I distance would be expected to be shorter than the bridging Os–I distance. As a general result, terminal M–X bonds are usually shorter than bridging M–X bonds, as is found in $[OsCl_2(C_{10}H_{14})]_2$ [19] and $Ru_2(CO)_6Br_4$ [20]. However, the average Os–I distance of 2.734 Å in (*I*) is not unreasonable for a bridging Os–I distance since in the compounds $[Os_{10}C(CO)_{24}I]^-$ and $Os_{10}C(CO)_{24}I_2$ the bridging Os–I distances range

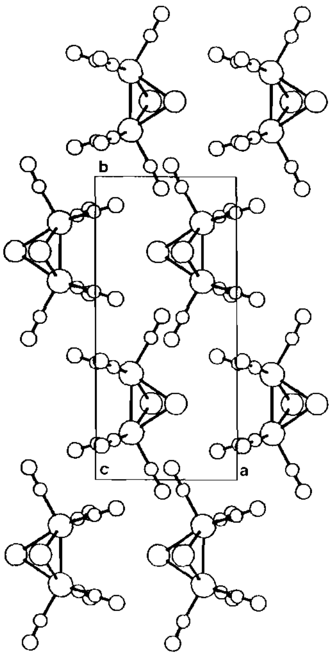

Fig. 3. A projection of the packing in the unit cell.

TABLE IV. Bond Angles (°) for $Os_2(CO)_6I_2$ with the Estimated Standard Deviations in Parentheses.

C_1–Os_1–I_1	90.5(9)
C_1–Os_1–I_2	160.4(9)
C_2–Os_1–I_1	164.8(9)
C_2–Os_1–I_2	90.6(10)
C_2–Os_1–C_1	91.2(13)
I_2–Os_1–I_1	82.9(1)
C_3–Os_1–I_1	98.5(8)
C_3–Os_1–I_2	100.8(8)
C_3–Os_1–C_1	98.4(12)
C_3–Os_1–C_2	96.1(12)
Os_1–I_1–Os_1'	59.4(1)
Os_1–I_2–Os_1'	60.0(1)
Os_1–C_1–O_1	176.9(27)
Os_1–C_2–O_2	178.9(27)
Os_1–C_3–O_3	175.6(27)

from 2.717–2.746 Å although in these deca-osmium complexes there is no Os–Os bond connecting the Os atoms bridged by the iodine atoms [5]. The Os–C distances in (*I*) vary; thus Os–C_3 (pseudo axial) distances are longer at 1.960(27) Å than the other Os–C distances (1.861(31) and 1.863(30) Å). Similar variation is found in Os–C distances in $Os_2(CO)_6(CH_3COO)_2$ [18] and in Fe–C distances in $Fe_2(CO)_6X_2$ (X = SMe, S, NH_2 or NMe) [21]. The C–O distances in (*I*) are in the range 1.101(34)–1.159(37) Å. These distances can be compared to the average C–O bond lengths of 1.14 Å found in $Os_3(CO)_{12}I_2$ [16] and 1.114 Å in $Os_3(CO)_{12}$ [15]. Figure 3 shows a projection of the packing in the unit cell.

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