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The Synthesis and Molecular Structure of Diiodooctacarbonyldiosmium(I), [$Os_2(CO)_8I_2$]

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Abstract

The compound, diiodooctacarbonyldiosmium(I), [$Os_2(CO)_8I_2$], has been prepared by a route involving only atmospheric pressures. Its structure has been determined by X-ray crystallography. The crystals are tetragonal with $a = 11.791(2)$, $c = 23.583(4)$ Å, $Z = 8$, $D_c = 3.48$ Mg m^{-3}. A total of 1637 reflections were collected out to $\theta = 25°$ on a CAD4 diffractometer in ω–2θ mode using Mo Kα ($\lambda = 0.7107$ Å) radiation. Lp and empirical absorption corrections were applied. The structure was solved in the space group $I4_1cd$ using conventional heavy atom methods and refined to $R = 0.0477$ [$R_w = 0.0424$, $w = (\sigma^2 F)^{-1}$]. The molecule of [$Os_2(CO)_8I_2$] has two crystallographically equivalent halves joined by a single Os–Os bond of length 2.947(3) Å. There are no bridging ligands. The geometry about each osmium is pseudo-octahedral and the iodine atoms occupy equatorial positions with an Os–I distance of 2.767(3) Å. The equatorial ligands on one osmium atom are staggered with respect to the equatorial ligands on the other osmium atom.

Introduction

Bimetallic systems are of considerable current interest in the development of organotransition metal chemistry. They are useful models for processes involving adjacent metal atoms and fundamental studies of their addition, insertion and elimination reactions will help our understanding of polymetallic or cluster catalyzed reactions [1–3]. The chemistry of binuclear transition metal complexes is also of value in mechanistic studies of certain reactions previously believed to take place at a single metal site [4–6]. Finally their interest as a group of organometallic compounds as yet much less well studied than monomeric or cluster compounds, cannot be ignored. We are particularly interested in binuclear osmium complexes whose metal–metal bonds are expected to be more robust than those in analogous compounds of metals of the 1st and 2nd row transition series. Os–Os bonds can exist without the support of any bridging ligands and thus the Os–Os bond may be retained through a variety of chemical transformations and as such may allow better modelling of reactions taking place on metal surfaces. Binuclear carbonyl halide complexes of osmium have been known for a number of years. Thus Hieber and Stallman [7] reported complexes of the type [$Os(CO)_4Br$]$_2$ in 1943; however the complexes were not fully characterized at that time. [$Os_2(CO)_8I_2$] was first characterized by Bruce *et al.* [8], as a product of the reaction of [$Os_3(CO)_{12}$] with iodine or CF_3I. The compounds [$Os_2(CO)_8X_2$] (where X = Cl or Br) were reported by Moss and Graham [9, 10] as products of the reactions of [$Os_2(CO)_8H_2$] with CX_4 (X = Cl or Br). On the basis of the IR spectra in the ν(CO) region and on the effective atomic number rule, the structure **2** was suggested for these carbonyl halides [8–10]. Although the structure of [$Os_2(CO)_8Cl_2$] was determined and found to be in agreement with these proposals, the details were never published [11]. Since compounds of the type [$Os_2(CO)_8X_2$] (X = Cl, Br or I) are important precursors to both binuclear compounds such as [$Os_2(CO)_8H_2$] [10, 12] and [$Os_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}I)$] [13] as well as mononuclear cyclopentadienyl compounds of the type [$CpOs(CO)_2I$] (where Cp = η^5-C_5H_5 or η^5-C_5Me_5) [14]. We now wish to report the synthesis of [$Os_2(CO)_8I_2$] by a method which does not require the use of high pressure apparatus, as well as the X-ray crystal structure of this compound which is a rare example of a binuclear carbonyl halide which has a metal–metal bond unsupported by any bridging ligands.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 180 grating spectrophotometer; mass spectra were recorded using a VG micromass 16F spectrometer operating at an ionizing voltage of 70 eV (1 eV = 1.60×10^{-19} J); samples were introduced into the instrument as solids using the direct probe. Melting

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points were determined on a hot-stage microscope (Reichert Thermovar) and are uncorrected. Reactions were carried out using standard Schlenk tube techniques. Benzene was dried by distillation over anhydrous calcium chloride. Hexane was distilled from sodium wire. Column chromatography was carried out using silica gel (BDH, 40–60 mesh) made up as a slurry with 20% CH_2Cl_2 and 80% hexane. $[Os_3(CO)_{12}]$ was prepared by A. J. Deeming or purchased from Strem Chemicals. $[Os_2(CO)_6I_2]$ was prepared as described previously [15].

Preparation of $[Os_2(CO)_8I_2]$

(a) $[Os_3(CO)_{12}]$ (0.23 g, 0.25 mmol) was heated in benzene (250 ml) under reflux until dissolved. Iodine (0.22 g, 0.89 mmol) was added to the hot solution at 80 °C. The hot reaction solution was placed in direct, bright sunlight for 20 min with intermittent swirling of the glass reaction flask. The solvent was removed *in vacuo* to leave a brown–yellow solid which was dissolved in a minimum of CH_2Cl_2 (*ca.* 10 ml) and passed through a chromatography column. Elution with a 30% CH_2Cl_2/n-hexane solution caused a red and a yellow band to separate on the column. The eluant ahead of the red band was collected and evaporated to dryness to give, in low yield, a colourless solid, IR ν(CO) (hexane) 2071 cm^{-1} and the mass spectrum shows a parent ion at *m/e* 462 corresponding to $[Os(CO)_4I_2]^+$ with sequential loss of four CO groups; *trans*-$[Os(CO)_4I_2]$ shows one very strong ν(CO) band at 2073 cm^{-1} [16]. The solvent and excess iodine were removed under reduced pressure from the red band to give a yellow, microcrystalline solid (0.11 g, 51%) melting point (m.p.) 137–140 °C; far-IR (Nujol): ν(Os–I) 162 cm^{-1}, which was identified as $[Os_2(CO)_8I_2]$ on the basis of its IR spectrum in the ν(CO) region and its mass spectrum (lit. m.p. 138 °C) [8]. Elution with CH_2Cl_2 gave a yellow band which, on removal of solvent gave *cis*-$[Os(CO)_4I_2]$ as a yellow solid (0.24 g, 57%) m.p. 320–330 °C; far-IR (Nujol): ν(OS–I) 164 cm^{-1}; mass spectrum shows a parent ion at *m/e* 462; the IR spectrum in the ν(CO) region was identical to that previously reported [16].

(b) $[Os_3(CO)_{12}]$ (0.23 g, 0.25 mmol) was finely crushed and heated in benzene (200 ml) under reflux until it dissolved. Iodine (0.22 g, 0.87 mmol) was added to the hot solution at 80 °C and this hot solution transferred to a 1 litre Hanovia photochemical reactor. The solution was then irradiated for 15 min with stirring, after which the temperature of the solution was 30 °C. The solvent was removed *in vacuo* to leave a brown–yellow solid. Chromatography of this solid as in (a) gave a low yield of *trans*-$[Os(CO)_4I_2]$ and a yellow solid which was mainly $[Os_2(CO)_8I_2]$. Fractional recrystallization of this yellow solid from n-hexane gave $[Os_2(CO)_8I_2]$ (0.09 g, 42%) and *cis*-$[Os(CO)_4I_2]$ (0.02 g, 5%). Elution of the column with methanol gave $[Os_2(CO)_6I_4]$ (0.06 g, 23%) IR (CH_2Cl_2) ν(CO) 2119s, 2050s cm^{-1} and *M* (mass spectrometry) 1058.

Reaction of $[Os_2(CO)_6I_2]$ *with CO*

CO was bubbled through a solution of $[Os_2(CO)_6I_2]$ (0.05 g, 0.06 mmol) in hexane (125 cm^3) at room temperature and under an atmosphere of CO for 2 days. The bright yellow colour of the solution had paled over this period. An IR spectrum in hexane of a portion of the reaction solution showed ν(CO) bands of both $[Os_2(CO)_6I_2]$ and $[Os_2(CO)_8I_2]$. Complete conversion to $[Os_2(CO)_8I_2]$ was not observed under the conditions employed.

Preparation of $[Os_2(CO)_6I_4]$ *from cis-*$[Os(CO)_4I_2]$

A solution of *cis*-$[Os(CO)_4I_2]$ (0.08 g, 0.14 mmol) in light petroleum ether (b.p. 100–120 °C) (20 cm^3) was heated under reflux for 4 h. A yellow product crystallized out of the solution on cooling. Removal of the solvent yielded a bright yellow microcrystalline solid which we believe to be $[Os_2(CO)_6I_4]$ (0.88 g, 54%) m.p. 225–235 °C which was washed with hexane (2 × 10 cm^3) and recrystallized from benzene. The IR spectrum (CCl_4) shows ν(CO) 2119s, 2116sh, 2049s, 2025sh cm^{-1}. After a 2 h period, the IR spectrum showed only two ν(CO) bands at 2119s, 2049s cm^{-1}; lit. [17] 2119s, 2151s cm^{-1}. We believe these latter ν(CO) bands are due to the interaction of $[Os_2(CO)_6I_4]$ with H_2O present in the CCl_4 solvent. Far-IR (Nujol) shows bands at 159 and 139 cm^{-1}, which we assign to ν(Os–I). The mass spectrum of this yellow solid revealed a molecular ion at *m/e* 1058, providing further evidence for the compound being of the formulation $[Os_2(CO)_6I_4]$.

Reaction between $[Os_2(CO)_6I_2]$ *and* I_2

Iodine (0.004 g, 0.034 mmol) dissolved in hexane was added to a solution of $[Os_2(CO)_6I_2]$ (0.027 g, 0.034 mmol) in hexane (10 cm^3) with stirring. The almost immediate formation of a yellow precipitate was observed. This precipitate was washed with hexane and recrystallized from benzene to give a bright yellow solid (0.02 g, 49%) m.p. 225 °C. IR (CCl_4): ν(CO) 2115s, 2025vs cm^{-1}. Lit. [17] 2119s, 2051s cm^{-1}. (We believe the bands at 2119 and 2051 cm^{-1} are due to a monomeric species present in solution, possibly $[Os(CO)_3I_2(H_2O)]$ formed by the interaction of $[Os_2(CO)_6I_4]$ with H_2O in the CCl_4 solvent.) The mass spectrum showed a molecular ion for $[Os_2(CO)_6I_4]^+$ at *m/e* 1058, with sequential loss of 6 carbonyl groups, to give an ion at *m/e* 890, corresponding to $[Os_2I_4]^+$.

Reaction of $[Os_3(CO)_{12}Br_2]$ *with Bromine*

$[Os_3(CO)_{12}Br_2]$ (0.17 g, 0.16 mmol) was dissolved in CH_2Cl_2 with warming. Bromine (0.08 cm^3, 0.16 mmol) was added to the solution and the reaction mixture left to stand at ambient temperature under laboratory light conditions for 3 h. Removal of the solvent *in vacuo* afforded a yellow solid. Extraction with hexane (3 X 20 cm^3) gave a yellow solution and an off-white insoluble solid. The solvent was removed from the hexane solution to yield a yellow microcrystalline solid shown to be [$Os_2(CO)_8Br_2$] by IR and mass spectroscopy and by melting point, all data found to be in agreement with the literature [10] (0.09 g, 72%) m.p. 126–132 °C. The hexane-insoluble solid was shown to be *cis*-[$Os(CO)_4Br_2$] by IR and mass spectral and melting point data in agreement with the literature [18] (0.07 g, 30%) m.p. 275–295 °C.

Crystal and Intensity Data

Yellow single crystals of [$Os_2(CO)_8I_2$], suitable for X-ray determination were obtained after recrystallization of the compound from hexane. Preliminary photographs (Cu Kα radiation, $\lambda = 1.542$ Å) were consistent with the tetragonal space group $I4_1cd$. Accurate cell parameters were determined by a least-squares analysis of the setting angles of 24 reflections ($16° \leqslant \theta \leqslant 17°$) which were automatically located and centred on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). The intensities were collected with an ω–2θ scan mode [$\Delta\omega = (1.04 + 0.35 \tan\theta)°$] with an aperture of vertical length 4 mm and ($1.57 + 1.05 \tan\theta$) mm wide, a final acceptance limit of 20σ at 20° min^{-1} in ω and a maximum recording time of 40 s. A total of 1637 reflections were collected out to $\theta = 25°$. The data were Lp processed and an empirical absorption correction applied [19]. In the solution and refinement of the structure, 578 reflections (with $I_{rel} > 2\sigma I_{rel}$) were considered observed. Further crystal data and experimental details of the data collection are listed in Table I.

Solution and Refinement of the Structure

A Patterson map was generated from the data, and a single heavy atom, the osmium, located in a general position (multiplicity = 16 in this space group). As $Z = 8$, this implies that the asymmetric unit comprises one half the chemical species. The remaining iodine, four carbon and four oxygen atoms were revealed in subsequent difference syntheses. In the final refinements, the osmium and iodine atoms were treated anisotropically, and all other atoms isotropically. A weighting scheme was employed to reduce the systematic variation of $\omega\Delta^2$ with the magnitude of F_o, as shown by analyses of variance computed after the final cycle. Shift/e.s.d. for the positional and thermal parameters <0.2, indicated satisfactory convergence. In the final difference map, maximum and minimum electron density were found to be 1.75 and -1.76 e Å^{-3} respectively. Further details of the final refinement are shown in Table I. Fractional atomic coordinates and temperature factors are shown in Table II. Scattering factors were taken from Cromer and Mann [20] with dispersion corrections from Cromer and Liberman [21]. All computations were carried out at the Computer Centre of the University of Cape Town on a Sperry 1100/81 computer with SHELX [22] (data reduction, structure solution and refinement) and PLUTO [23] (illustrations).

TABLE I. Crystal Data, Data Collection and Refinement Procedures for [$Os_2(CO)_8I_2$]

Crystal data	
Molecular formula	$C_8O_8I_2Os_2$
M_r (g)	858.3
Space group	$I4_1cd$
a (Å)	11.791(2)
b (Å)	23.583(4)
V (Å^3)	3278.6(1)
D_c (Mg m^{-3}) (for $Z = 8$)	3.48
μ(Mo Kα) (mm^{-1})	18.44
F(000)	2960
Data collection	
Crystal dimensions (mm)	0.10 x 0.10 x 0.20
Range scanned (θ) (°)	1–25
Stability of standard reflections (%)	< 1
Final refinement	
No. reflections 'observed'	578 (with $I_{rel} > 2\sigma I_{rel}$)
No. parameters	50
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0477
$R_w = \Sigma w^{1/2}\|\|F_o\| - \|F_c\|\|/\Sigma w^{1/2}\|F_o\|$	0.0424
Weighting scheme w	$(\sigma^2 F)^{-1}$

TABLE II. Fractional Atomic Coordinates (X 10^4) and Temperature Factors (Å^2 X 10^3)[a]

Atoms	x/a	y/b	z/c	U_{iso}
Os_1	5191(1)	1235(1)	0	aniso.
I_1	7322(2)	1049(2)	−482(2)	aniso.
C_1	5428(29)	2796(30)	−37(18)	57(10)
O_1	5478(22)	3797(25)	−12(20)	85(9)
C_2	4524(36)	1203(37)	−851(18)	67(13)
O_2	4128(33)	1097(33)	−1246(16)	107(12)
C_3	5992(34)	1047(35)	740(17)	63(12)
O_3	6363(26)	909(28)	1160(14)	77(9)
C_4	3684(33)	1386(33)	374(16)	61(12)
O_4	2871(28)	1521(28)	610(14)	36(9)

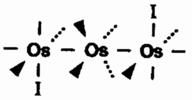
Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Anisotropic temperature factors						
Os_1	38(1)	35(1)	43(1)	−3(1)	1(1)	2(1)
I_1	54(2)	62(2)	94(2)	−2(2)	29(2)	−2(2)

[a] e.s.d.s given in parentheses.

Results and Discussion

The reactions of [$Os_3(CO)_{12}$] with Iodine

It has been known for some time that the reaction of [$Os_3(CO)_{12}$] with iodine using a short reaction time gives the trinuclear di-iodide [$Os_3(CO)_{12}I_2$] (**1**) in high yield [24] and the structure of this trinuclear compound has been determined by X-ray crystallography [25].



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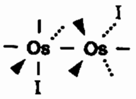

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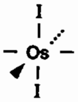

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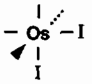

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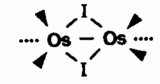

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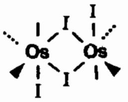

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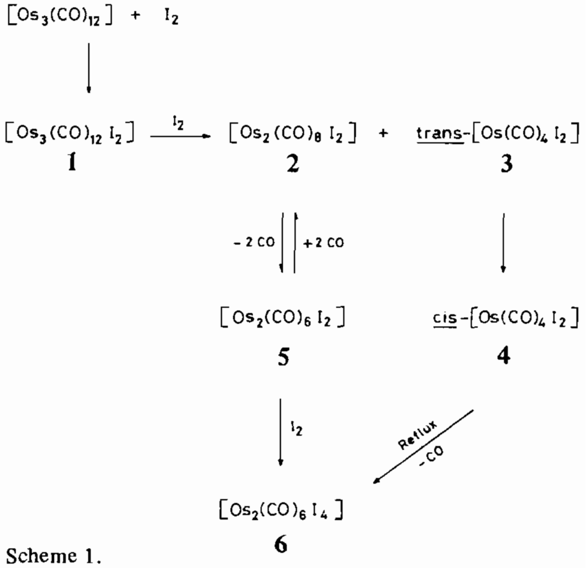
We were interested in finding a convenient synthetic route to the dinuclear complex [$Os_2(CO)_8I_2$] at atmospheric pressure. We thus investigated the reaction of [$Os_3(CO)_{12}$] with iodine under various conditions and we monitored the reaction by IR spectroscopy. We find that the initial reaction gives **1** but that further reaction of **1** with iodine readily occurs to cause cleavage of another Os–Os bond and resulting in a mixture of [$Os_2(CO)_8I_2$] (**2**) and [$Os(CO)_4I_2$]. We also demonstrated that the analogous compound [$Os_3(CO)_{12}Br_2$] reacted with bromine (1:1 mole ratio) to give [$Os_2(CO)_8Br_2$] and *cis*-[$Os(CO)_4Br_2$] as the main products. In the reaction of [$Os_3(CO)_{12}$] with I_2 we observe IR evidence for *trans*-[$Os(CO)_4I_2$] (**3**) being formed which then is readily converted to the more stable *cis*-[$Os(CO)_4I_2$] (**4**). The separation of **2** and **4** can be readily effected by recrystallization and/or column chromatography. The reaction of [$Os_3(CO)_{12}$] with I_2 is further complicated however by the fact that **2** can not only react with I_2 to cleave the remaining Os–Os bond to give [$Os(CO)_4I_2$] but it can lose 2 moles of CO to give [$Os_2(CO)_6I_2$] (**5**). Compound **5** can also react with I_2 to give [$Os_2(CO)_6I_4$] (**6**) and this same compound is also formed if **4** is heated under reflux at about 100 °C for 4 h. These transformations are shown in Scheme 1 and new ones are described in 'Experimental'.

Thus the reaction of [$Os_3(CO)_{12}$] with I_2 is complicated and can lead to at least six products. We find that the reaction of [$Os_3(CO)_{12}$] with iodine (molar ratio 1:3.5) as a benzene solution in the presence of sunlight for 20 min, as described in 'Experimental', leads to the optimum yields of pure [$Os_2(CO)_8I_2$] (**2**) (50%) (yield based on [$Os_3(CO)_{12}$] used) along with *cis*-[$Os(CO)_4I_2$] (**4**) (57%) which can be separated from other minor products and purified.



Scheme 1.

Since the structure of a compound of the type [$Os_2(CO)_8X_2$] (where X = halogen) had not been reported previously and to compare the structure with that of the related, but structurally different compound, [$Os_2(CO)_6I_2$] we then determined the crystal and molecular structure of [$Os_2(CO)_8I_2$].

Description of Structure and Discussion

A perspective view of the molecule, with atomic labelling is shown in Fig. 1 and bond lengths and angles are given in Tables III and IV respectively. The two equivalent osmium atoms are linked by a single metal–metal bond and each has one terminal iodide in an equatorial position and four terminal carbonyls

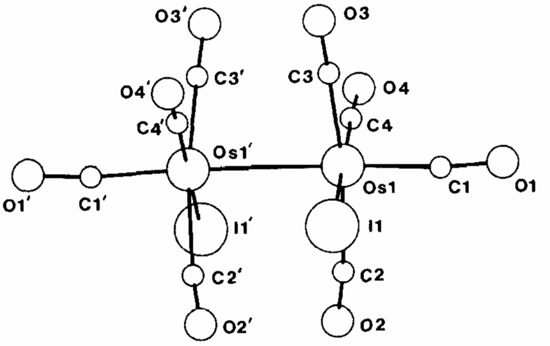


Fig. 1. Perspective view of [$Os_2(CO)_8I_2$] with atomic labelling.

TABLE III. Bond Lengths (Å) for $[Os_2(CO)_8I_2]$ [a]

Os_1-Os_1' [b]	2.947(3)
Os_1-I_1	2.767(3)
Os_1-C_1	1.86(4)
Os_1-C_2	2.16(4)
Os_1-C_3	2.00(4)
Os_1-C_4	1.99(4)
C_1-O_1	1.18(4)
C_2-O_2	1.05(5)
C_3-O_3	1.10(4)
C_4-O_4	1.12(5)

[a] e.s.d.s given in parentheses. [b] Translated by symmetry element $-x + 1, -y, z$.

TABLE IV. Bond Angles (°) for $[Os_2(CO)_8I_2]$ [a]

$C_1-Os_1-I_1$	86(1)
$C_2-Os_1-I_1$	87(1)
$C_2-Os_1-C_1$	92(2)
$C_3-Os_1-I_1$	86(1)
$C_3-Os_1-C_1$	95(2)
$C_3-Os_1-C_2$	170(2)
$C_4-Os_1-I_1$	178(1)
$C_4-Os_1-C_1$	94(2)
$C_4-Os_1-C_2$	95(2)
$C_4-Os_1-C_3$	93(2)
$O_1-C_1-Os_1$	172(4)
$O_2-C_2-Os_1$	172(5)
$O_3-C_3-Os_1$	175(4)
$O_4-C_4-Os_1$	175(4)
$Os_1'-Os_1-C_2$	86(1)
$Os_1'-Os_1-C_3$	88(1)
$Os_1'-Os_1-C_4$	87(1)

[a] e.s.d.s given in parentheses.

in an irregular octahedral geometry; thus, for each osmium, the effective atomic number rule is obeyed. As shown in Fig. 2, the ligands on one osmium are staggered with respect to the ligands on the other osmium, with the iodine atoms being as far away from each other as possible. This type of staggered conformation would be expected to be most sterically favourable. Indeed, a similar staggered conformation has been found for the related molecules $[M_2(CO)_{10}]$ (M = Mn, Re [26] and M = Tc [27] and for $[Re_2(CO)_8L_2]$) (L = $CNC_6H_3Me_2$-2,6) [28].

The Os–Os bond length of 2.947(3) Å is similar to that found in $[Os_3(CO)_{12}I_2]$ (2.93 Å) [25] and $[Os_3(CO)_{12}]$ (2.88 Å) [29] but longer than that in $[Os_2(CO)_6(CH_3COO)_2]$ (2.73 Å) [30] and $[Os_2(CO)_6I_2]$ (2.72 Å) [15]; in the latter two compounds the shorter metal–metal bond most likely derives from the fact that osmium atoms are spanned by bridging ligands. The terminal Os–I distance of 2.767(3) Å in $[Os_2(CO)_8I_2]$ is identical to 2.77 Å found for the terminal Os–I in the triosmium homologue $[Os_3(CO)_{12}I_2]$ [25] and a little longer than 2.74 Å for the terminal Os–I distance in the anionic cluster $[Os_5(CO)_{15}I]$PPN (PPN = bis(triphenylphosphine)iminium cation) [31]. In some cases, terminal M–X bonds are shorter than corresponding bridging M–X bonds. Examples of this are the two complexes $[OsCl_2(C_{10}H_{14})]_2$ [32] and $[Ru_2(CO)_6Br_4]$ [33]; however it should be noted that neither of these complexes possesses a metal–metal bond. In $[Os_2(CO)_6I_2]$ [15], the mean Os–I bridging distance of 2.74 Å is however shorter than the Os–I terminal distance of 2.767 Å in $[Os_2(CO)_8I_2]$. This presumably is a consequence of the metal–metal bond in $[Os_2(CO)_6I_2]$. Short bridging Os–I bonds are also found in $[Os_4(CO)_{12}H_3I]$ (2.75 Å) [34] and in $[Os_{10}C(CO)_{24}I_2]$ and $[Os_{10}C(CO)_{24}I]^-$ (2.717–2.746 Å) [35]. Concerning the Os–C bonds in $[Os_2(CO)_8I_2]$, the range (1.86(4)–2.16(4) Å) is much greater than the range found in $[Os_3(CO)_{12}I_2]$ (1.91(3)–1.97(3) Å) [25], with the shortest Os–C distance being the axial one, *trans* to the Os–Os bond. Similarly, the shortest M–C bond in $[M_2(CO)_{10}]$ (M = Mn, Tc or Re) is that *trans* to the metal–metal bond [26, 27]. The C–O bond lengths in $[Os_2(CO)_8I_2]$ are unremarkable and in the range 1.05(5)–1.18(4) Å with the longest C–O distance corresponding to the carbonyl group in the axial position.

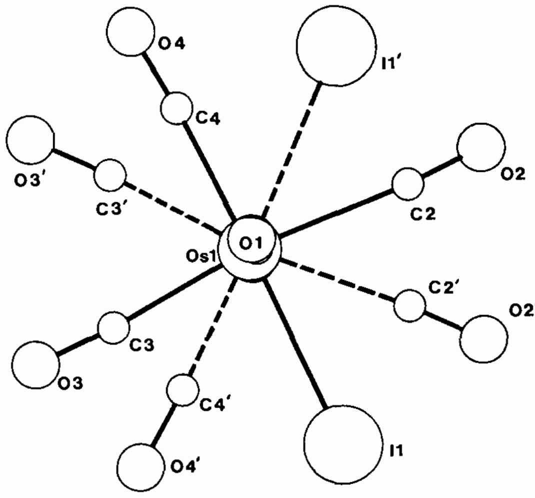


Fig. 2. View of the molecule along the Os–Os bond showing the staggering of the ligands.

Os–C–O angles are close to being linear and lie in the range 172(4) to 175(4)°; such deviations from linearity are observed in other similar compounds [26, 25]. The Os–Os–C equatorial angles are acute and lie in the range 86–88°; thus, the equatorial CO ligands bend in towards the centre of the molecule. This behaviour is often observed for dinuclear compounds of the type $[M_2(CO)_8L_2]$ (where M = Mn or Re, L = CO, PR_3 or RNC) [36], as well as in the trinuclear $[Os_3(CO)_{12}I_2]$ [25]. Reasons for this bending-in have previously been discussed [37]. However this behaviour is not always observed, for example in $[Os_3(CO)_{12}(SiCl_3)_2]$ which has a linear $SiOs_3Si$ backbone, no significant bending-in of the equatorial CO groups on the terminal Os atoms towards the centre of the molecule was seen [38].

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Supplementary Material

Structure factors may be obtained from the authors on request.

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