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A Compound Containing Two $[Os_2I_8]^{2-}$ Ions Fused to Form a $[Os_4I_{14}]^{2-}$ Ion Containing Os≡Os Triple Bonds

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Abstract

The series of $Os_2X_8^{2-}$ ions, previously known only with X = Cl and Br, has now been extended to include the iodide, albeit with a centrosymmetric tetranuclear anion consisting of two staggered Os_2I_8 units joined by sharing of two iodine atoms that form an edge approximately perpendicular to the metal–metal bonds. The complete formula of the compound is $[PMePh_3]_2Os_4I_{14}$. The Os–Os distance, 2.231 Å, is the longest Os–Os distance yet reported in $Os_2X_8^{2-}$ species. The compound was made by treating the pink '$[PMePh_3]_2Os_2Cl_8$' (obtained from $Os_2(OAc)_4Cl_2$) with HI gas at room temperature. Crystallographic data: space group $P\bar{1}$, $a = 12.617(2)$, $b = 14.421(2)$, $c = 9.386(2)$ Å, $\alpha = 91.32(1)$, $\beta = 100.32(1)$, $\gamma = 113.97(1)^\circ$, $V = 1526(1)$ Å^3, $Z = 1$.

Introduction

The first compound containing a triply-bonded Os_2^{6+} unit, reported only in 1980, was $Os_2(hp)_4Cl_2$, and it was characterized crystallographically in two differently solvated crystal forms [1]. Within the next few years a series of carboxylato-bridged species, $Os_2(O_2CR)_4X_2$, was reported [2–5] and several of them were characterized crystallographically [4, 5]. They have since been well studied by resonance Raman spectroscopy [6]. In 1984 it was found that these carboxylato-bridged species undergo a remarkable reaction with triphenylphosphine in which two carboxylato ligands are replaced by $Ph_2P(o\text{-}C_6H_4)$ ligands [7]. Amidato compounds, $Os_2(PhCONH)_4Cl_2$ and $Os_2(PhCONH)_4Br_2$, were also prepared and structurally characterized [8] before 1985, as well as an interesting, rather unsymmetrical compound, $Os_2Cl_3(PhNpy)_3$, where PhNpy represents the 2-(phenylamino)pyridine anion [9].

In 1986 the $Os_2Cl_4(chp)_2L$ (L = H_2O, py and chp = anion of 2-hydroxy-6-chloropyridine) species, the first diosmium compounds to have any halide ions (along with other ligands) in equatorial sites, were reported [10], and in 1987 the compound $Os_2Cl_4(Ph_2PC_6H_4)_2$, which has a unique, very unsymmetrical structure, but nevertheless a short Os–Os bond (2.231(1) Å), was reported [11]. The only other well-established Os_2^{6+} compound (other than the $Os_2X_8^{2-}$ species to be discussed presently) is the compound $Os_2(CH_2CMe_3)_4(\eta^3\text{-}C_3H_5)_2$ which is a kind of Os_2X_8 species in which the $\eta^3\text{-}C_3H_5^-$ ligands may be considered to be bidentate ones occupying pairs of *cis* positions on each end; the entire torsional conformation is then effectively eclipsed and the Os–Os distance, 2.194(3) Å, is the shortest known [12].

For the sake of completeness, it may be mentioned that the porphyrin (P) complexes, Os_2P_2, for which no structural data are yet available, are the only reported Os_2^{4+} complexes [13]. It is also well known that complexes of Os_2^{5+} can exist [14] and for several of these the structures are available, viz. $Os_2Cl_4(O_2CCH_3)(Ph_2Ppy)_2$ [15], $Os_2(chp)_4Cl$ [16] and $Os_2(fhp)_4Cl$ [17].

A specially important advance in the study of Os_2^{6+} complexes was the discovery by Walton and coworkers [18], in 1985, of the $Os_2Cl_8^{2-}$ and $Os_2Br_8^{2-}$ ions. Following this, there have been further chemical [19, 20], structural [19, 21] and theoretical [21] studies. These studies support the view that these are triply-bonded, $\sigma^2\pi^4\delta^2\delta^{*2}$, systems in which there is no inherent electronic barrier to rotation about the Os–Os bond. The $Os_2Cl_8^{2-}$ ion has shown mean torsion angles ranging from 0° for the brown form of $(PPN)_2Os_2Cl_8$ through 11.5 and 39.8 to 41.0°. The one structure of the $Os_2Br_8^{2-}$ has a torsion angle of 43.3°. The Os–Os distances in these species range from 2.182(1) Å for the staggered $Os_2Cl_8^{2-}$ ion to 2.212(1) Å for the eclipsed form of the same ion. The staggered $Os_2Br_8^{2-}$ ion shows an Os–Os distance of 2.196(1) Å.

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Experimental

Synthesis of [$PMePh_3$]$_2$[Os_4I_{14}]

A weighed amount of $Os_2(O_2CCH_3)_4Cl_2$ (0.25 g, 0.364 mmol) was added to HCl-saturated ethanol (12.5 ml) and this mixture was refluxed for 1.5 h to give a green solution. After cooling to room temperature, it was filtered and then treated with a solution of $PMePh_3Br$ (0.53 g, 1.48 mmol) in ethanol (1 ml). This led to the immediate formation of a salmon pink precipitate, which was washed with ethanol and ether, filtered and then vacuum dried. The pink solid was dissolved in 20 ml of dichloromethane to give a green homogeneous solution, through which HI was passed until the color changed to dark green or almost black. The solvent was removed under vacuum to leave behind a black residue. This was redissolved in 5 ml of dichloromethane, filtered and then layered with 10 ml of ethanol. After a few days, black crystals of $[PMePh_3]_2[Os_4I_{14}]$ were formed: yield 0.429 g (75% based on Os). The crystals thus obtained were used for X-ray crystallographic studies.

X-ray Crystallography

A plate-like crystal of $[PMePh_3]_2[Os_4I_{14}]$ was mounted at the end of a glass fiber and covered with epoxy glue. Geometric and intensity data were taken with an automated diffractometer (Nicolet P3) by following procedures described previously [22]. Pertinent crystallographic data are given in Table 1. Lattice dimensions were verified by axial photography. Intensity data, gathered by the $2\theta-\omega$ method, were reduced by routine procedures. (Calculations were carried out using a Micro-Vax II (Micro VMS V4.5) with programs SHELXS-86 and the commercial package SDP/V, V3.0.) Absorption corrections were applied, based on azimuthal scans of several reflections with the diffractometer angle χ near 90° [23].

All the atoms of the Os_4I_{14} moiety were located via Patterson maps. The rest of the structure was developed by an alternating sequence of least-squares refinements and difference Fourier maps. After convergence of isotropic refinement, additional absorption corrections were applied according to the method of Walter and Stuart [24]. Then all the atoms were anisotropically refined, giving a data to parameter ratio of 16.9. The final difference Fourier map had seven peaks above 1 e/Å^3, all of which were ghosts of existing heavy atoms, Os and I. Positional parameters are presented in Table 2 and selected bond distances, bond angles and torsion angles are given in Table 3.

Results and Discussion

TABLE 1. Crystal data for $[PMePh_3]_2[Os_4I_{14}]$

Formula	$Os_4I_{14}P_2C_{38}H_{36}$
Formula weight	3092.12
Space group	$P\bar{1}$
Systematic absences	none
a (Å)	12.617(2)
b (Å)	14.421(2)
c (Å)	9.386(2)
α (°)	91.32(1)
β (°)	100.32(1)
γ (°)	113.97(1)
V (Å^3)	1526(1)
Z	1
D_{calc} (g/cm^3)	3.364
Crystal size (mm)	0.70 × 0.20 × 0.05
μ(Mo Kα) (cm^{-1})	153.99
Data collection instrument	Nicolet P3
Radiation monochromated in incident beam (λ, Å)	Mo Kα (0.71073)
Orientation reflections number, range (2θ) (°)	25, $27 \leq 2\theta \leq 31$
Temperature (°C)	21 ± 1
Scan method	$2\theta-\omega$
Data collection range, 2θ (°)	$4 \leq 2\theta \leq 50$
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	4359, 4144
No. parameters refined	262
Transmission factors (%) maximum, minimum	99.9, 22.9
R [a]	0.034
R_w [b]	0.048
Quality-of-fit indicator[c]	1.069
Largest shift/e.s.d., final cycle	0.05
Largest peak (e/Å^3)	1.270

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2\{|F_o|\}$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

Our initial plan was to make $[PMePh_3]_2Os_2Cl_8$ by following the method of Walton and coworkers [18, 19], and then to convert it to the corresponding iodide by treating it with HI in analogy to the conversion of $Re_2Cl_8^{2-}$ to $Re_2I_8^{2-}$ [25]. Our purpose in making a new compound, $[PMePh_3]_2Os_2Cl_8$, instead of using one of the already known salts of $[Os_2Cl_8]^{2-}$, was to avoid the type of crystallographic problem normally encountered with nBu_4N salts, namely disorder of the four-carbon chains. The fact that the final product contains $[Os_4I_{14}]^{2-}$ and not $[Os_2I_8]^{2-}$ raises a doubt concerning the composition of the pink solid, which was assumed (but never shown) to be $[PMePh_3]_2Os_2Cl_8$. The nature of the pink solid is now under investigation.

Turning now to the structure of the $[Os_4I_{14}]^{2-}$ ion itself, it is clear from Fig. 1 that it consists of two of the desired $Os_2I_8^{2-}$ ions fused together on a common edge. Why this fused species was formed rather than the intended product is not known, but we shall attempt to get the latter by suitable modification of the reaction conditions. The planar rectangle formed by Os(2), Os(2)′, I(7) and I(7)′ has

TABLE 2. Positional parameters and their e.s.d.s for $[PMePh_3]_2[Os_4I_{14}]$

Atom	*x*	*y*	*z*	*B* (Å^2)
Os(1)	0.22119(3)	0.81462(3)	0.40724(4)	2.612(8)
Os(2)	0.39545(3)	0.86858(3)	0.56298(4)	2.499(8)
I(1)	0.25487(7)	0.95501(6)	0.22183(9)	4.39(2)
I(2)	0.09530(6)	0.89659(6)	0.5144(1)	4.44(2)
I(3)	0.08630(8)	0.64143(7)	0.4971(1)	5.37(2)
I(4)	0.23776(7)	0.69948(6)	0.19808(9)	4.87(2)
I(5)	0.44015(6)	0.70509(5)	0.57901(9)	4.13(2)
I(6)	0.34381(6)	0.84874(6)	0.82407(8)	3.97(2)
I(7)	0.54716(5)	0.93240(5)	0.38544(8)	3.28(1)
P	0.8416(2)	0.6960(2)	0.8518(3)	3.49(6)
C(1)	0.8187(8)	0.7918(8)	0.951(1)	3.2(2)
C(2)	0.7026(9)	0.7841(9)	0.934(1)	4.2(3)
C(3)	0.680(1)	0.8520(9)	0.022(2)	4.7(3)
C(4)	0.228(1)	0.0730(9)	0.879(2)	5.2(3)
C(5)	0.111(1)	0.065(1)	0.860(2)	5.6(4)
C(6)	0.090(1)	0.1352(9)	0.947(1)	4.3(3)
C(7)	0.763(1)	0.5782(9)	0.919(1)	4.9(3)
C(8)	0.180(1)	0.451(1)	0.958(2)	6.3(4)
C(9)	0.252(1)	0.544(1)	0.899(2)	7.5(4)
C(10)	0.631(2)	0.401(1)	0.036(2)	8.4(5)
C(11)	0.574(1)	0.430(1)	0.920(2)	8.1(5)
C(12)	0.641(1)	0.520(1)	0.861(2)	6.5(4)
C(13)	0.7878(9)	0.6914(9)	0.659(1)	3.7(3)
C(14)	0.7832(9)	0.7777(9)	0.605(1)	4.1(3)
C(15)	0.246(1)	0.224(1)	0.551(1)	4.7(3)
C(16)	0.264(1)	0.309(1)	0.639(1)	4.9(3)
C(17)	0.261(1)	0.397(1)	0.579(2)	7.2(5)
C(18)	0.766(1)	0.602(1)	0.571(2)	5.2(4)
C(19)	1.001(1)	0.729(1)	0.876(2)	6.1(4)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \text{gamma})\beta_{12} + ac(\cos \text{beta})\beta_{13} + bc(\cos \text{alpha})\beta_{23}]$.

a crystallographic inversion center at its midpoint and the two halves of the tetranuclear ion are equivalent. The fusing together of the two Os_2I_8 units leads to surprisingly slight perturbations from the D_{4h} symmetry that a discrete $Os_2I_8{}^{2-}$ ion would be expected to have. The Os(1)–Os(2)–I(7) and I(7)′ angles are only about 2° smaller than the other six Os–Os–I angles, the I(7)–Os(2)–I(7)′ angle is contracted by only about 3° compared to the others of its type, and the Os(2)–I(7), and Os(2)–I(7)′ bond lengths are only about 0.02 Å longer than the other Os–I bond lengths.

The rotational conformation about the Os–Os bond is almost perfectly staggered, with a mean torsion angle (for individual angles, see Table 3) of 46.0°.

Since the Os_2I_8 portion of the anion is so little perturbed from D_{4h} symmetry, it seems reasonable to compare it with the other $Os_2X_8{}^{2-}$ species, as though it were a discrete $Os_2I_8{}^{2-}$ ion. This is done in Table 4. It is clear that all three $Os_2X_8{}^{2-}$ ions show

TABLE 3. Selected bond distances (Å), bond angles (°) and torsion angles (°) for $[PMePh_3]_2[Os_4I_{14}]$

Atom 1	Atom 2	Distance
Bond distances		
Os(1)	Os(2)	2.231(0)
Os(1)	I(1)	2.653(1)
Os(1)	I(2)	2.642(1)
Os(1)	I(3)	2.647(1)
Os(1)	I(4)	2.633(1)
Os(2)	I(5)	2.639(1)
Os(2)	I(6)	2.640(1)
Os(2)	I(7)	2.660(1)
Os(2)	I(7)	2.668(1)
P	C(I)	1.795(13)
P	C(7)	1.780(12)
P	C(13)	1.803(11)
P	C(19)	1.832(13)

Atom 1	Atom 2	Atom 3	Angle
Bond angles			
Os(2)	Os(1)	I(1)	104.05(2)
Os(2)	Os(1)	I(2)	106.70(2)
Os(2)	Os(1)	I(3)	104.72(3)
Os(2)	Os(1)	I(4)	104.51(3)
I(1)	Os(1)	I(2)	85.96(3)
I(1)	Os(1)	I(3)	151.21(3)
I(1)	Os(1)	I(4)	85.90(3)
I(2)	Os(1)	I(3)	86.80(3)
I(2)	Os(1)	I(4)	148.78(3)
I(3)	Os(1)	I(4)	86.01(3)
Os(1)	Os(2)	I(5)	103.97(2)
Os(1)	Os(2)	I(6)	105.32(2)
Os(1)	Os(2)	I(7)	101.83(2)
Os(1)	Os(2)	I(7)	102.16(2)
I(5)	Os(2)	I(6)	89.83(3)
I(5)	Os(2)	I(7)	87.51(3)
I(5)	Os(2)	I(7)	153.51(2)
I(6)	Os(2)	I(7)	152.55(2)
I(6)	Os(2)	I(7)	87.43(3)
I(7)	Os(2)	I(7)	82.97(2)
Os(2)	I(7)	Os(2)	97.03(3)
C(1)	P	C(7)	106.5(6)
C(1)	P	C(13)	110.4(6)
C(1)	P	C(19)	109.8(6)
C(7)	P	C(13)	111.3(5)
C(7)	P	C(19)	112.6(8)
C(13)	P	C(19)	106.2(7)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
Torsional angles				
I(1)	Os(1)	Os(2)	I(7)	−41.26 (0.03)
I(1)	Os(1)	Os(2)	I(7)′	43.99 (0.03)
I(2)	Os(1)	Os(2)	I(6)	44.70 (0.03)
I(2)	Os(1)	Os(2)	I(7)′	−45.96 (0.03)
I(3)	Os(1)	Os(2)	I(5)	47.36 (0.04)
I(3)	Os(1)	Os(2)	I(6)	−46.37 (0.04)
I(4)	Os(1)	Os(2)	I(5)	−42.28 (0.03)
I(4)	Os(1)	Os(2)	I(7)	48.09 (0.03)

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 4. Comparison of dimensions of $[Os_2Cl_8]^{2-}$, $[Os_2Br_8]^{2-}$ and $[Os_4I_{14}]^{2-}$ ions

	$[Os_2Cl_8]^{2-\,a}$	$[Os_2Br_8]^{2-\,a}$	$[Os_4I_{14}]^{2-\,b}$
Os–Os (Å)	2.182	2.196	2.231
Average Os–X (Å)	2.322	2.444	2.648
Calculated Os–X (Å)[c]	2.308	2.458	2.648
Average Os–Os–X angle (°)	104.2	104.3	104.2
Average X–Os–Os–X torsion angle (°)	49.0	46.7	46.0
r_{vdw} of X (Å)[d]	1.80	1.95	2.15

[a] $[(n\text{-}Bu)_4N]_2[Os_2X_8]$; ref. 21. [b] This work. [c] Assuming constant r_{Os} of 1.318 and X covalent radii of 0.99, 1.14 and 1.33 for Cl, Br and I. [d] van der Waals radius of halogen.

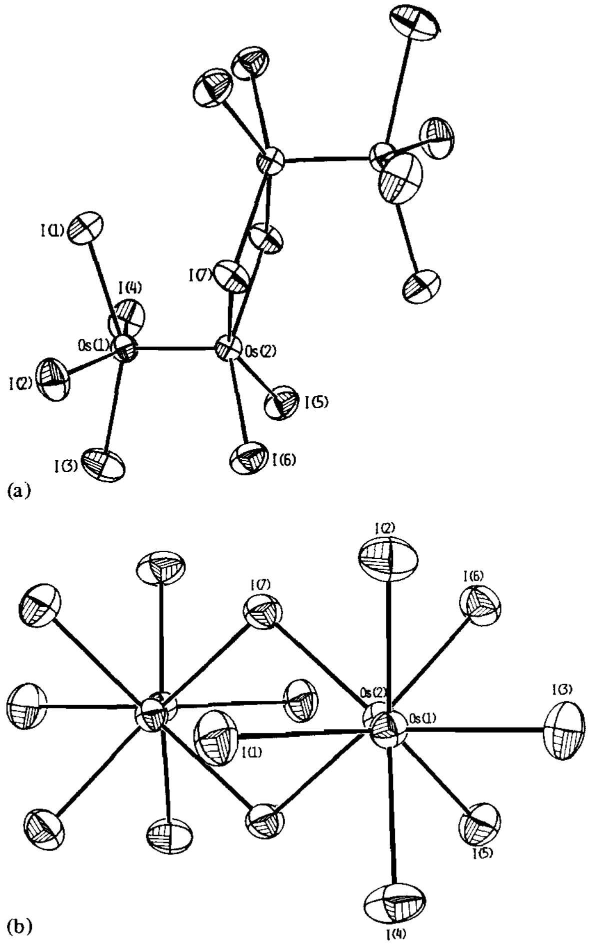

Fig. 1. An ORTEP drawing of the $[Os_4I_{14}]^{2-}$ ion. Labelled and unlabelled Os_2I_7 moieties are related by a center of inversion. (a) View showing the Os–Os bond. (b) View along the Os–Os bond showing the staggered configuration.

good homology, with the only slight deviation being the larger Os–Os distance in the iodide. This may have either a steric origin (owing to the van der Waals radius of I increasing relatively more its covalent radius) or an electronic one (owing to a greater interaction of π orbitals on I with the Os–Os π* orbitals to weaken the bond). We presently have no basis for choosing between these possibilities.

Supplementary Material

Tables of anisotropic displacement parameters and structure factors (24 pages) are available from author F.A.C.

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