Inorg. Chem. **1990**, *29*, 3197-3199 **3197**

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Further Studies of $Os_2X_8^{2-}$ Ions: $[PMePh_3]_2Os_2Cl_8$ with Eclipsed, Disordered Anions and the First $Os_2I_8^{2-}$ Compound

F. Albert Cotton* and K. Vidyasagar

Received January 16, 1990

The compound $[PMePh_3]_2Os_2Cl_8$ has been structurally characterized by X-ray crystallography. It is isomorphous with the corresponding rhenium compound and contains an eclipsed $Os_2Cl_8^{2-}$ ion with an Os–Os unit disordered unequally (63/37) in two orientations. A new triply bonded compound $[TBA]_2Os_2I_8$ has been prepared by treating its chloro analogue with HI gas at 0 °C. Dark brown crystals of composition $[TBA]_2Os_2I_8{\cdot}CH_2Cl_2$ grown by layering a dichloromethane solution of the compound with toluene have been studied by X-ray crystallography. It contains the $Os_2I_8^{2-}$ ion with a staggered conformation (torsion angle is 46.7°) similar to the $Os_2X_8^{2-}$ ions in $[TBA]_2Os_2X_8$ (X = Cl, Br). Crystallographic data are as follows. $[PMePh_3]_2Os_2Cl_8$: space group $P2_1/n$, a = 10.853 (2) Å, b = 11.893 (3) Å, c = 16.167 (3) Å, β = 93.33 (2)°, V = 2083 (2) Å^3, Z = 2. $[TBA]_2O_2I_8{\cdot}CH_2Cl_2$: space group $P\bar{1}$, a = 12.833 (5) Å, b = 20.095 (4) Å, c = 12.331 (3) Å, α = 95.95 (2)°, β = 109.16 (2)°, γ = 106.03 (2)°, V = 2802 (4) Å^3, Z = 2. A comparison of important structural dimensions of staggered $[Os_2X_8]^{2-}$ ions shows that they are completely homologous.

Introduction

The first reports of $Os_2X_8^{2-}$ ions appeared about 5 years ago[1,2] and dealt with the chloro and bromo species. These were shown to occur in both staggered and eclipsed rotomeric forms in keeping with the presence of a net triple Os–Os bond in which no barrier to rotation was expected. Several years later,[3] in an attempt to obtain the iodo analogue, we isolated instead a condensed dimer, $[Os_2I_6(\mu\text{-}I)_2Os_2I_6]^{2-}$. We can now report that by changing the conditions, though not the essential features of the preparative procedure, which entails treatment of a solution of an $Os_2Cl_8^{2-}$ compound with gaseous HI, we have obtained a crystalline compound containing the staggered octaiodo anion, $[NBu_4]_2Os_2I_8$. In addition, we have structurally characterized the previouslyy mentioned $[PMePh_3]_2Os_2Cl_8$ and shown it to be isomorphous with the rhenium analogue. It has a rigorously eclipsed conformation and displays a disordered packing of the quasicubic anions.

Experimental Section

Synthesis. The octachlorodiosmate(III) complexes $A_2Os_2Cl_8$ (A = $(C_4H_9)_4N$ (TBA), $PMePh_3$) were prepared according to the procedures described in the literature.[1-3] Hydrogen iodide gas was purchased from Matheson Gas Products. All solvents were dried and freshly distilled prior to use.

Crystals of $[PMePh_3]_2Os_2Cl_8$ suitable for X-ray diffraction, were grown by layering a dichloromethane solution of the compound with toluene.

Preparation of $[TBA]_2Os_2I_8{\cdot}CH_2Cl_2$. A sample of $[TBA]_2Os_2Cl_8$ (0.08 g, 0.07 mmol) was dissolved in 15 mL of dichloromethane and cooled in an ice bath. HI gas was passed through this cold CH_2Cl_2 solution until the color changed to dark greenish brown. The solvent was removed under vacuum to leave behind a dark residue, and about 15 mL of CH_2Cl_2 was added to the residue. The mixture was stirred for 5 min and then filtered. The dark green filtrate was layered with toluene. Dark brown crystals of $[TBA]_2Os_2I_8{\cdot}CH_2Cl_2$, suitable for diffraction were formed after several days. Yield was 0.10 g (73%).

X-ray Crystallography. $[PMePh_3]_2Os_2Cl_8$. A block-shaped crystal was mounted at the end of a glass fiber with epoxy glue. Geometric and intensity data were taken with an automated diffractometer (Nicolet P3) by following procedures described previously.[4] Lattice dimensions and Laue symmetry were verified by axial photography. Intensity data, gathered by the 2θ–ω method, were reduced by routine procedures.[5] Absorption corrections were applied, based on azimuthal scans of several reflections with the diffractometer angle χ near 90°.[6]

Table I. Crystal Data for $[PMePh_3]_2[Os_2Cl_8]$ and $[TEA]_2[Os_2I_8]{\cdot}CH_2Cl_2$

	$[PMePh_3]_2[Os_2Cl_8]$	$[TBA]_2[Os_2I_8]{\cdot}CH_2Cl_2$
formula	$Os_2Cl_8P_2C_{38}H_{36}$	$Os_2I_8Cl_2N_2C_{33}H_{74}$
fw	1218.683	1965.509
space group	$P2_1/n$	$P\bar{1}$
syst abs	$(h0l)$ $h + l \neq$ 2n; $(0k0)$ $k \neq 2n$	none
a, Å	10.853 (2)	12.833 (5)
b, Å	11.893 (3)	20.095 (4)
c, Å	16.167 (3)	12.331 (3)
α, deg	90	95.95 (2)
β, deg	93.33 (2)	109.16 (2)
γ, deg	90	106.03 (2)
V, Å^3	2083 (2)	2802 (4)
Z	2	2
d_{calc}, g/cm^3	1.943	2.315
cryst size, mm	0.50 × 0.30 × 0.15	0.30 × 0.20 × 0.20
μ(Mo Kα), cm^{-1}	67.244	89.611
data colln instrum	Nicolet P3	Rigaku AFC5R
radiation monochromated in incident beam (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
orientation reflcns: no.; range (2θ), deg	25; 27.51 ≤ 2θ ≤ 30.87	25; 26.02 ≤ 2θ ≤ 31.65
temp, °C	21 ± 1	21 ± 1
scan method	2θ–ω	2θ–ω
no. of unique data; tot. with $F_o^2 > 3\sigma(F_o^2)$	3675; 3103	7475; 4273
no. of params refined	236	332
transm factors, %: max; min	99.9; 45.5	99.9; 68.6
R^a	0.056	0.054
R_w^b	0.081	0.081
quality-of-fit indicator^c	1.902	1.707
largest shift/esd, final cycle	0.01	0.46
largest peak, e/Å^3	0.623	1.905

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(|F_o|) + 0.001(|F_o|)^2]$. [c] Quality-of-fit $= [\sum w(|F_o| - |f_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Half of the Os_2Cl_8 moiety was located near an inversion center ($^1/_2$, 0, 0) via Patterson maps. From the Patterson map a second pair of osmium atoms was also found, centered about the same point as the principal pair, with the Os–Os vector roughly perpendicular to that of the primary dimer. The site-occupation factors of the two sites were refined with the constraint that their sum be 1.0; the values refined quickly to 0.63 and 0.37 for the major and the minor orientations, respectively. The rest of the structure was developed by an alternating sequence of least-squares refinements and difference Fourier maps. All the atoms were refined anisotropically, giving a data to parameter ratio

---

(1) (a) Fanwick, P. E.; Tetrick, S. M.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 4546. (b) Fanwick, P. E.; King, M. K.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5009.

(2) Agaskar, P. A.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1985**, *108*, 4850.

(3) Cotton, F. A.; Vidyasagar, K. *Inorg. Chim. Acta* **1989**, *166*, 109.

(4) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. J. *J. Organomet. Chem.* **1973**, *50*, 227.

(5) Calculations were carried out on a Local Area VAX cluster (VMS V4.6), with the programs SHELXS-86 and SHELX-76 and the commercial package SDP/V V3.0.

(6) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr. Theor, Crystallogr.* **1968**, *24*, 351.

0020-1669/90/1329-3197$02.50/0

Table II. Positional Parameters and Their Estimated Standard Deviations for $[PMePh_3]_2[Os_2Cl_8]$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Os(1)[b]	0.41953 (5)	0.05228 (5)	0.01360 (4)	2.72 (1)
Os(2)[c]	0.54364 (9)	0.01747 (8)	0.06225 (6)	2.89 (2)
Cl(1)	0.2522 (2)	−0.0562 (2)	−0.0333 (2)	4.30 (6)
Cl(2)	0.3772 (3)	0.1542 (2)	−0.1064 (2)	4.35 (6)
Cl(3)	0.5041 (3)	0.2134 (2)	0.0742 (2)	4.83 (7)
Cl(4)	0.3821 (2)	−0.0046 (3)	0.1477 (2)	4.98 (7)
P	0.4701 (2)	0.2271 (2)	0.4137 (2)	3.48 (6)
C(1)	0.3332 (9)	0.1409 (9)	0.3910 (6)	3.6 (2)
C(2)	0.2201 (9)	0.1822 (9)	0.4092 (7)	4.3 (2)
C(3)	0.118 (1)	0.111 (1)	0.3984 (7)	4.6 (3)
C(4)	0.130 (1)	0.004 (1)	0.3695 (7)	4.6 (3)
C(5)	0.246 (1)	−0.0364 (9)	0.3487 (7)	4.4 (3)
C(6)	0.350 (1)	0.0330 (9)	0.3590 (6)	4.2 (2)
C(7)	0.4902 (9)	0.2428 (8)	0.5238 (6)	3.7 (2)
C(8)	0.586 (1)	0.3116 (9)	0.5576 (8)	4.8 (3)
C(9)	0.604 (1)	0.323 (1)	0.6414 (8)	5.6 (3)
C(10)	0.529 (1)	0.270 (1)	0.6954 (8)	5.8 (3)
C(11)	0.435 (1)	0.199 (1)	0.6622 (7)	4.9 (3)
C(12)	0.4157 (9)	0.1879 (9)	0.5768 (6)	4.0 (2)
C(13)	0.6022 (8)	0.1579 (9)	0.3731 (6)	3.5 (2)
C(14)	0.611 (1)	0.160 (1)	0.2890 (7)	5.3 (3)
C(15)	0.709 (1)	0.103 (1)	0.2553 (9)	6.8 (4)
C(16)	0.795 (1)	0.045 (1)	0.308 (1)	6.0 (4)
C(17)	0.786 (1)	0.048 (1)	0.3927 (8)	4.9 (3)
C(18)	0.6872 (9)	0.1053 (9)	0.4273 (7)	4.1 (2)
C(19)	0.488 (1)	0.364 (1)	0.3671 (8)	5.3 (3)

[a] All atoms were refined anisotropically and they are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Site modeled as 0.626 Os. [c] Site modeled as 0.374 Os.

Table III. Positional Parameters and Their Estimated Standard Deviations for $[TBA]_2[Os_2I_8]\cdot CH_2Cl_2$

atom	*x*	*y*	*z*	*B*, Å^2
Os(1)	0.45967 (8)	0.31530 (5)	0.20439 (7)	4.71 (3)
Os(2)	0.35696 (9)	0.21215 (5)	0.07890 (7)	4.83 (3)
I(1)	0.3067 (2)	0.3653 (1)	0.2519 (2)	8.09 (8)
I(2)	0.5074 (2)	0.2833 (1)	0.4137 (1)	7.33 (7)
I(3)	0.6788 (2)	0.3321 (1)	0.2323 (2)	7.64 (7)
I(4)	0.4728 (2)	0.40910 (9)	0.0713 (1)	7.72 (7)
I(5)	0.1847 (2)	0.23962 (9)	−0.0781 (1)	6.79 (6)
I(6)	0.1988 (2)	0.1468 (1)	0.1601 (2)	7.92 (7)
I(7)	0.4735 (2)	0.12717 (9)	0.1654 (2)	8.02 (8)
I(8)	0.4503 (2)	0.2126 (1)	−0.0824 (1)	7.55 (7)
N(1)	0.769 (2)	0.1172 (9)	−0.079 (2)	5.7 (7)
C(1)	0.859 (3)	0.183 (2)	−0.012 (3)	10 (1)
C(2)	0.838 (4)	0.233 (3)	0.076 (5)	22 (3)
C(3)	0.948 (3)	0.299 (2)	0.142 (5)	15 (2)
C(4)	0.952 (5)	0.345 (3)	0.079 (7)	24 (4)
C(5)	0.814 (2)	0.065 (2)	−0.144 (2)	8 (1)
C(6)	0.856 (3)	0.091 (2)	−0.233 (2)	9 (1)
C(7)	0.914 (3)	0.039 (1)	−0.270 (3)	10 (1)
C(8)	0.947 (3)	0.061 (2)	−0.371 (3)	12 (2)
C(9)	0.680 (3)	0.142 (2)	−0.179 (3)	8 (1)
C(10)	0.584 (3)	0.090 (2)	−0.271 (3)	10 (1)
C(11)	0.511 (3)	0.115 (2)	−0.362 (3)	11 (1)
C(12)	0.432 (5)	0.072 (3)	−0.479 (4)	19 (3)
C(13)	0.708 (3)	0.082 (2)	−0.011 (2)	8 (1)
C(14)	0.779 (3)	0.062 (2)	0.090 (3)	10 (1)
C(15)	0.717 (4)	0.027 (2)	0.170 (3)	13 (2)
C(16)	0.776 (4)	−0.006 (3)	0.260 (3)	19 (3)
N(2)	0.719 (1)	0.6178 (7)	0.359 (1)	6.8 (7)
C(17)	0.787 (2)	0.590 (1)	0.468 (2)	12 (1)*
C(18)	0.746 (4)	0.516 (1)	0.455 (3)	18 (2)*
C(19)	0.784 (4)	0.497 (2)	0.565 (3)	17 (1)*
C(20)	0.882 (5)	0.475 (3)	0.578 (5)	24 (3)*
C(21)	0.729 (2)	0.582 (1)	0.244 (2)	13 (1)*
C(22)	0.834 (2)	0.583 (2)	0.228 (2)	14 (1)*
C(23)	0.808 (3)	0.544 (3)	0.115 (3)	23 (2)*
C(24)	0.912 (3)	0.550 (2)	0.095 (3)	17 (1)*
C(25)	0.585 (2)	0.596 (2)	0.342 (3)	18 (2)*
C(26)	0.513 (2)	0.631 (1)	0.275 (2)	9.8 (8)*
C(27)	0.394 (2)	0.591 (2)	0.245 (4)	17 (2)*
C(28)	0.322 (3)	0.629 (2)	0.186 (3)	13 (1)*
C(29)	0.774 (3)	0.701 (1)	0.381 (3)	20 (2)*
C(30)	0.773 (3)	0.739 (2)	0.483 (3)	15 (1)*
C(31)	0.800 (4)	0.812 (2)	0.480 (3)	20 (2)*
C(32)	0.906 (5)	0.851 (2)	0.574 (5)	24 (3)*
C	0.216 (2)	−0.235 (2)	−0.481 (2)	15 (1)*
Cl(1)	0.149 (1)	−0.2597 (8)	−0.627 (1)	18.7 (5)*
Cl(2)	0.122 (3)	−0.223 (1)	−0.422 (2)	33 (1)*

[a] Starred values denote atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

of 13.1 and residuals of $R = 0.056$ and $R_w = 0.081$.

$[TBA]_2Os_2I_8\cdot CH_2Cl_2$. X-ray crystallographic data employed were gathered from two crystals of similar shape and size with an automated diffractometer (Rigaku AFC5R). The first crystal used was a block-shaped one mounted on the tip of a glass fiber with epoxy glue. The data set on this crystal was gathered for 2θ from 4 to 35° in 44 h during which a decay of 15% was observed from three intensity standard reflections monitored throughout the data collection time. This data set was corrected for absorption, based on azimuthal scans of several reflections with diffractometer angle χ near 90°,[6] and for the decay observed. The second crystal used was mounted in a thin-walled capillary surrounded by a mixture of mineral oil and mother liquor. The data set gathered on this crystal consisted of all reflections with 2Θ from 35 to 50° and about 500 reflections common to both data sets. Three intensity standard reflections monitored throughout the data collection period showed no sign of crystal decay. After correction for absorption, this data set was merged with the first one by using the SHELX-76 program[5] to give an agreement factor of 0.044. In the merged data set there were 4273 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ to be used in least-squares calculations.

Positions of all the atoms of the $Os_2I_8^{2-}$ moiety were found from Patterson maps. The rest of the structure was developed by an alternating sequence of least-squares and difference Fourier maps. The crystallographic asymmetric unit was found to contain one formula unit of $[TBA]Os_2I_8$ and one molecule of solvent, CH_2Cl_2. All the atoms of CH_2Cl_2 and the carbon atoms of the second TBA moiety were refined isotropically, and restraints on their interatomic distances were added in least-squares refinements. In the final cycle, 332 parameters were refined, giving a data to parameter ratio of 12.9 and residuals of $R = 0.054$ and $R_w = 0.081$. In the final difference Fourier map, there were six peaks above 1 e/Å^3. The first peak was 1.96 Å away from the CH_2Cl_2 carbon atom indicating a possible disorder of Cl(2) over two sites, each with the site-occupation factor of $^1/_2$. Our efforts to include such a disorder in the refinement were not successful, and so we left the structure at this stage. The remaining five peaks were ghosts of existing atoms.

Pertinent crystallographic data for both compounds are given in Table I. Positional parameters for the two compounds are presented in Tables II and III, and selected bond distances and angles are given in Tables IV and V.

Results and Discussion

The composition of the pink starting material for the preparation of $[PMePh_3]_2Os_4I_{14}$ was assumed but never shown to be $[PMePh_3]_2Os_2Cl_8$.[3] This assumption of composition as a dimer has been in doubt because the final product is a tetramer. An X-ray crystal structure determination was carried out to clarify this doubt and also to see whether $Os_2Cl_8^{2-}$, if present, would adopt an eclipsed or a staggered conformation.

The present study has shown that the pink solid is indeed $[PMePh_3]_2Os_2Cl_8$, similar to other pink $Os_2Cl_8^{2-}$ salts known in the literature,[1a] and that it is isomorphous with the corresponding rhenium compound.[7] It has an eclipsed conformation for $Os_2Cl_8^{2-}$ ion, and as in most of the eclipsed M_2X_8 quasi-cubic moieties, the Os–Os units are disordered in two orientations (as shown in Figure 1) with one of them predominating (63%). Os–Os bond distances for the major and minor orientations in this compound are not different from one another and also are the same as those in the other structurally characterized $[Os_2Cl_8]^{2-}$ compound with eclipsed conformation,[1a] $[PPN]_2[Os_2Cl_8]$.

The conditions employed in the preparation of $[TBA]_2Os_2I_8$ and $[PMePh_3]_2Os_4I_{14}$[3] are similar, and the only noteworthy difference is in temperature. The reason for the present conversion of $Os_2Cl_8^{2-}$ to $Os_2I_8^{2-}$ rather than $Os_4I_{14}^{2-}$ could be either low

---

(7) Cotton, F. A.; Price, A. C.; Torralba, R. C.; Vidyasagar, K. *Inorg. Chim. Acta*, in press.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[PMePh_3]_2[Os_2Cl_8]$[a]

Bond Distances			
Os(1)–Os(1)	2.209 (1)	Os(2)–Cl(2)	2.311 (3)
Os(1)–Cl(1)	2.319 (3)	Os(2)–Cl(3)	2.379 (3)
Os(1)–Cl(2)	2.310 (3)	Os(2)–Cl(4)	2.309 (3)
Os(1)–Cl(3)	2.317 (3)	P–C(1)	1.824 (10)
Os(1)–Cl(4)	2.329 (3)	P–C(7)	1.790 (10)
Os(2)–Os(2)	2.214 (1)	P–C(13)	1.809 (10)
Os(2)–Cl(1)	2.337 (3)	P–C(19)	1.808 (12)
Bond Angles			
Os(1)–Os(1)–Cl(1)	103.59 (7)	Os(2)–Os(2)–Cl(4)	102.89 (8)
Os(1)–Os(1)–Cl(2)	104.42 (7)	Cl(1)–Os(2)–Cl(2)	84.0 (1)
Os(1)–Os(1)–Cl(3)	104.56 (8)	Cl(1)–Os(2)–Cl(3)	90.1 (1)
Os(1)–Os(1)–Cl(4)	101.79 (8)	Cl(1)–Os(2)–Cl(4)	154.7 (1)
Cl(1)–Os(1)–Cl(2)	84.5 (1)	Cl(2)–Os(2)–Cl(3)	154.9 (1)
Cl(1)–Os(1)–Cl(3)	151.9 (1)	Cl(2)–Os(2)–Cl(4)	89.8 (1)
Cl(1)–Os(1)–Cl(4)	88.1 (1)	Cl(3)–Os(2)–Cl(4)	85.2 (1)
Cl(2)–Os(1)–Cl(3)	88.6 (1)	C(1)–P–C(7)	108.1 (5)
Cl(2)–Os(1)–Cl(4)	153.7 (1)	C(1)–P–C(13)	109.0 (5)
Cl(3)–Os(1)–Cl(4)	86.1 (1)	C(1)–P–C(19)	109.7 (5)
Os(2)–Os(2)–Cl(1)	102.44 (8)	C(7)–P–C(13)	110.8 (4)
Os(2)–Os(2)–Cl(2)	104.28 (8)	C(7)–P–C(19)	109.0 (5)
Os(2)–Os(2)–Cl(3)	100.82 (8)	C(13)–P–C(19)	110.3 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for $[TBA]_2[Os_2I_8]\cdot CH_2Cl_2$[a]

Bond Distances			
Os(1)–Os(2)	2.217 (1)	N(1)–C(1)	1.44 (3)
Os(1)–I(1)	2.632 (3)	N(1)–C(5)	1.59 (4)
Os(1)–I(2)	2.641 (2)	N(1)–C(9)	1.61 (4)
Os(1)–I(3)	2.638 (2)	N(1)–C(13)	1.45 (4)
Os(1)–I(4)	2.631 (2)	N(2)–C(17)	1.59 (3)
Os(2)–I(5)	2.650 (2)	N(2)–C(21)	1.59 (3)
Os(2)–I(6)	2.642 (2)	N(2)–C(25)	1.59 (3)
Os(2)–I(7)	2.652 (2)	N(2)–C(29)	1.58 (3)
Os(2)–I(8)	2.637 (2)		
Bond Angles			
Os(2)–Os(1)–I(1)	106.06 (6)	I(5)–Os(2)–I(8)	86.20 (7)
Os(2)–Os(1)–I(2)	104.59 (6)	I(6)–Os(2)–I(7)	86.73 (8)
Os(2)–Os(1)–I(3)	104.87 (7)	I(6)–Os(2)–I(8)	149.25 (6)
Os(2)–Os(1)–I(4)	104.71 (5)	I(7)–Os(2)–I(8)	86.58 (8)
I(1)–Os(1)–I(2)	86.18 (7)	C(1)–N(1)–C(5)	114 (2)
I(1)–Os(1)–I(3)	149.05 (6)	C(1)–N(1)–C(9)	103 (2)
I(1)–Os(1)–I(4)	85.52 (8)	C(1)–N(1)–C(13)	112 (2)
I(2)–Os(1)–I(3)	87.39 (7)	C(5)–N(1)–C(9)	108 (2)
I(2)–Os(1)–I(4)	150.70 (6)	C(5)–N(1)–C(13)	111 (2)
I(3)–Os(1)–I(4)	85.45 (7)	C(9)–N(1)–C(13)	109 (2)
Os(1)–Os(2)–I(5)	103.92 (6)	C(17)–N(2)–C(21)	109 (2)
Os(1)–Os(2)–I(6)	105.99 (6)	C(17)–N(2)–C(25)	109 (2)
Os(1)–Os(2)–I(7)	103.05 (5)	C(17)–N(2)–C(29)	110 (2)
Os(1)–Os(2)–I(8)	104.76 (6)	C(21)–N(2)–C(25)	109 (2)
I(5)–Os(2)–I(6)	86.32 (7)	C(21)–N(2)–C(29)	109 (2)
I(5)–Os(2)–I(7)	153.03 (6)	C(25)–N(2)–C(29)	110 (2)
Torsional Angles			
I(1)–Os(1)–Os(2)–I(5)	46.45 (8)		
I(1)–Os(1)–Os(2)–I(6)	−43.68 (8)		
I(2)–Os(1)–Os(2)–I(6)	46.51 (9)		
I(2)–Os(1)–Os(2)–I(7)	−43.80 (9)		
I(3)–Os(1)–Os(2)–I(7)	47.36 (8)		
I(3)–Os(1)–Os(2)–I(8)	−42.51 (8)		
I(4)–Os(1)–Os(2)–I(5)	−43.07 (9)		
I(4)–Os(1)–Os(2)–I(8)	46.62 (9)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

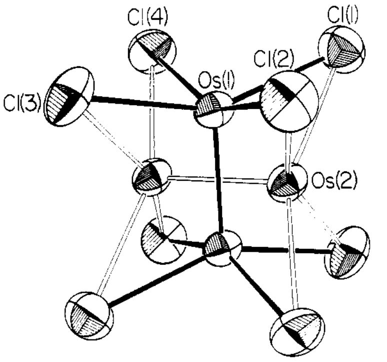

Figure 1. ORTEP diagram of the eclipsed $Os_2Cl_8^{2-}$ ion in $[PMePh_3]_2Os_2Cl_8$ showing the 2-fold disorder. The major orientation is shown in thick lines. Unlabeled atoms are related to those labeled by inversion.

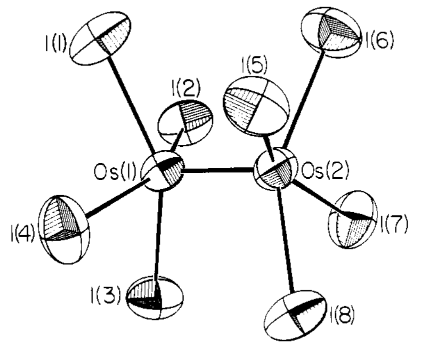

Figure 2. ORTEP diagram of staggered $[Os_2I_8]^{2-}$ ion in $[TBA]_2Os_2I_8\cdot CH_2Cl_2$.

Table VI. Comparison of Dimensions of Staggered $[Os_2Cl_8]^{2-}$, $[Os_2Br_8]^{2-}$, $[Os_2I_8]^{2-}$, and $[Os_4I_{14}]^{2-}$ Ions

	$[Os_2Cl_8]^{2-}$[a]	$[Os_2Br_8]^{2-}$[a]	$[Os_2I_8]^{2-}$[b]	$[Os_4I_{14}]^{2-}$[c]
Os–Os, Å	2.182	2.196	2.217	2.231
av Os–X, Å	2.322	2.444	2.640	2.648
calc Os–X,[d] Å	2.308	2.458	2.648	2.648
av Os–Os–X angle, deg	104.2	104.3	104.7	104.2
av X–Os–Os–X torsion angle, deg	49.0	46.7	46.7	46.0
r_{vdw} of X,[e] Å	1.80	1.95	2.15	2.15

[a] $[(n\text{-}Bu)_4N]_2[Os_2X_8]$.[2] [b] This work. [c] $[PMePh_3]_2[Os_4I_{14}]$.[3] [d] Assuming constant r_{Os} of 1.318 and covalent radii for X of 0.99, 1.14, and 1.33 for X = Cl, Br, and I. [e] van der Waals radius of halogen.

temperature or the cation used, or both. At present, we cannot choose between these possibilities.

$[TBA]_2Os_2I_8\cdot CH_2Cl_2$ is not isomorphous, as it might have been, with $[TBA]_2Os_2X_8$ (X = Cl, Br) compounds[2] but has the same structural features. The $Os_2I_8^{2-}$ ion with an approximate symmetry of D_{4d} (as shown in Figure 2) sits on a general position and possesses no crystallographic symmetry elements. The mean torsion angle is 46.7°.

With the preparation and characterization of a compound containing the $Os_2I_8^{2-}$ ion, the series of $Os_2X_8^{2-}$ ions with X = Cl, Br, and I is complete. For the $Re_2X_8^{2-}$ series, the corresponding three species as well as $Re_2F_8^{2-}$ are known, but in no other case is the iodide known. Most certainly, this makes it all the more remarkable that no $Ru_2X_8^{n-}$ compound has yet been prepared.

With completion of the $Os_2X_8^{2-}$ series, the principal structural dimensions for the Cl, Br, and I species can be compared. Important structural dimensions of $Os_2X_8^{2-}$ ions with staggered conformation and $Os_4I_{14}^{2-}$ ion are given in Table VI. It can be seen that they form a uniform homologous set, differing only as expected due to the differences in the sizes of the halogen atoms, and there is constancy of the effective covalent radius of the osmium atom.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Full tables of bond distances and angles, tables of anisotropic thermal displacement parameters, and unit cell diagrams (11 pages); tables of structure factors (42 pages). Ordering information is given on any current masthead page.