Inorg. Chem. **1984**, *23*, 393–397

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Crystal Structures of the Tetraphenylphosphonium Salts of Hexachloroosmate(V) and Hexachloroosmate(IV), $[(C_6H_5)_4P]OsCl_6$ and $[(C_6H_5)_4P]_2OsCl_6$

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Received September 14, 1982

The crystal structures of $[(C_6H_5)_4P]OsCl_6$ (compound I) and of $[(C_6H_5)_4P]_2OsCl_6$ (compound II) have been determined from single-crystal X-ray data. A total of 776 reflections, collected with a Nicolet $P2_1$ automated diffractometer, were used in the study of compound I and 2537 in the study of compound II. The crystals of compound I are tetragonal, space group $P4/n$, with $a = b = 12.957$ (3) Å and $c = 7.709$ (1) Å, $Z = 2$, d(measd) = 1.9 g·cm^{-3}, and d(calcd) = 1.905 g·cm^{-3}. The crystals of compound II are triclinic, space group $P\bar{1}$, with $a = 10.028$ (2) Å, $b = 11.228$ (2) Å, $c = 11.996$ (3) Å, $\alpha = 106.58$ (1)°, $\beta = 79.37$ (2)°, $\gamma = 101.24$ (1)°, $Z = 1$, and d(measd) = 1.52 g·cm^{-3}, and they contain one molecule of solvent (DMF) per formula unit of the hexachloroosmate(IV), giving d(calcd) = 1.525 g·cm^{-3}. Least-squares refinement gave R values of 0.023 and 0.053 for compounds I and II, respectively. Both crystals contain octahedral $OsCl_6$ anions and tetrahedral $(C_6H_5)_4P^+$ cations. In compound I, the Os–Cl distance is 2.284 Å (av), and the $OsCl_6^-$ octahedron is slightly distorted so that the osmium atom lies 0.026 Å below the plane of the equatorial chlorine atoms. This distortion is interpreted as being a result of electrostatic repulsion between neighboring $OsCl_6^-$ ions. There is an extremely short contact distance of 3.184 Å between chlorine atoms along the z axis. In compound II, the $OsCl_6^{2-}$ octahedron is nearly regular, with a Os–Cl distance of 2.332 Å (av). The ionic radii resulting from the two structures are 0.47 Å for Os(V) and 0.52 Å for Os(IV). The $(C_6H_5)_4P^+$ ions display a wide variation of the angles of rotation of the phenyl groups around the P–C bond, from 1° to 88° out of the C–P–C plane, indicating a very low rotational energy barrier for these groups.

Introduction

The successful preparation of the tetraphenylphosphonium salt of the $OsCl_6^-$ ion in crystalline form[1] prompted a structure determination of the compound, especially because structural information about osmium in the V oxidation state is very scarce. Only two structural studies have been reported: (a) that of the $OsCl_5$ dimer,[2] from powder data, in which only Os positions were refined and Cl positions were taken from the isomorphous Re_2Cl_{10} structure, and (b) several studies of OsF_6^-, also from powder data.[3–6]

After completion of the $[(C_6H_5)_4P]OsCl_6$ structure, it became apparent that the structure $[(C_6H_5)_4P]_2OsCl_6$ would need to be done as well if explanations of the distortions in the hexachloroosmate(V) ion were to be attempted. Consequently, the structure of the Os(IV) salt is reported as well, even though many structures containing osmium in the IV oxidation state are reported in the literature.

Experimental Section

(a) Preparation and Physical Properties. Tetraphenylphosphonium hexachloroosmate(V), $[(C_6H_5)_4P]OsCl_6$ (hereafter designated as compound I), was prepared by following the procedure described in the preceding paper.[1] The greenish-black crystalline product was washed with a small volume of cold acetonitrile and dried with a stream of air. The density was determined to be 1.9 g·cm^{-3} at 23 °C by using flotation in mixtures of bromoform and carbon tetrachloride. Other physical properties, complete spectral data, and the chemical analysis for the compound are given in the preceding paper.[1]

The preparation of tetraphenylphosphonium hexachloroosmate(IV), $[(C_6H_5)_4P]_2OsCl_6$ (hereafter designated as compound II), by precipitation from saturated solutions of $(NH_4)_2OsCl_6$ and $(C_6H_5)_4PBr$, is also described in the preceding paper.[1] The orange-yellow product was recrystallized from *N*,*N*-dimethylformamide (DMF). The density, determined as for compound I, was 1.52 g·cm^{-3}.

(b) Data Collection. The crystals obtained in the preparation of compound I were directly usable for X-ray data collection. A well-formed greenish-black crystal of size 0.15 × 0.15 × 0.20 mm^3 was mounted on the end of a glass fiber with epoxy cement, placed on an xyz goniometer head, and optically centered on a Nicolet $P2_1$ diffractometer equipped with a molybdenum tube ($\lambda(K\alpha) = 0.71069$ Å) and a graphite monochromator. Unit cell parameters were obtained from 15 centered reflections of the crystal at angles $10° < 2\theta < 23°$. The reciprocal lattice showed fourfold symmetry around the c^* axis. Systematic absences were found for $hk0$ with $h + k = 2n + 1$, indicating the space group $P4/n$ (no. 85 in the International Tables[7]). Unit cell parameters are given in Table I along with other crystal data and information about the data collection. A total of 3780 reflections, including check reflections, were measured at 21 °C over a 2θ range of 2–45°. This set was reduced to 939 unique reflections, of which 766 had $I > 3\sigma$. Two check reflections were measured after every 38 reflections to monitor experimental consistency; for both reflections there was no observable decay. The intensities were corrected for Lorentz and polarization effects, but no absorption correction was applied since the absorption coefficient for Mo radiation of 59.1 cm^{-1} gives rise to a range of μr from 0.44 to 0.59 or absorption A^* between 1.90 and 2.35.

Table I. Summary of Crystal Data

	compd I	compd II
formula weight	742.3	1150.7
d(measd), g·cm^{-3}	1.9	1.52
d(calcd), g·cm^{-3}	1.905	1.525
space group	$P4/n$	$P\bar{1}$
Z	2	1
cryst size, mm^3	0.15 × 0.15 × 0.20	0.08 × 0.10 × 0.24
axis of cryst orientation	0.20	0.24
a, Å	12.957 (3)	10.028 (2)
b, Å	12.957 (3)	11.228 (2)
c, Å	7.709 (1)	11.996 (3)
α, deg	90.0	106.58 (1)
β, deg	90.0	79.37 (2)
γ, deg	90.0	101.24 (1)
V, Å^3	1294.2 (4)	1257.6 (4)
temp of data collection, °C	21 ± 1	20 ± 1
wavelength of X-radiation, Å	0.71069	1.5418
scan range, deg	2.0–2.1	2.0–2.1
scan rate, deg min^{-1}	2.0–29.3	1.0–29.3
ratio, bkgd time/scan time	0.5	0.5
max 2θ, deg	45.0	100.0
no. of reflcns measd	3780	5344
no. of unique reflcns	939	2577
no. of unique reflcns with $I > 3\sigma$	766	2537
std reflcns/decay	$(2\bar{4}0)$; $(3\bar{1}4)$/none	(052); (403)/none

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Table II. Atomic Coordinates for Compound I[a]

atom	*x*	*y*	*z*
Os	0.2500	0.2500	0.1552 (1)
Cl(1)	0.2500	0.2500	0.4500 (4)
Cl(2)	0.2500	0.2500	−0.1370 (5)
Cl(3)	0.4185 (1)	0.3045 (1)	0.1586 (3)
P	0.2500	0.7500	0.0000
C(1)	0.3519 (4)	0.7073 (4)	0.1410 (7)
C(2)	0.3948 (5)	0.6120 (5)	0.1306 (9)
C(3)	0.4712 (6)	0.5801 (6)	0.2459 (9)
C(4)	0.5038 (6)	0.6499 (7)	0.3728 (10)
C(5)	0.4603 (6)	0.7445 (7)	0.3847 (10)
C(6)	0.3846 (5)	0.7749 (5)	0.2711 (8)
H(2)	0.385 (4)	0.579 (4)	0.045 (7)
H(3)	0.504 (4)	0.510 (4)	0.237 (7)
H(4)	0.560 (6)	0.610 (6)	0.458 (9)
H(5)	0.483 (6)	0.772 (6)	0.474 (9)
H(6)	0.343 (4)	0.850 (4)	0.289 (7)

[a] Standard deviations are in parentheses.

Table III. Atomic Coordinates for Compound II[a]

atom	*x*	*y*	*z*
Os	0.0	0.0	0.0
Cl(1)	0.1559 (3)	−0.1492 (2)	0.0598 (2)
Cl(2)	−0.0661 (3)	−0.0616 (3)	0.1750 (2)
Cl(3)	−0.1660 (3)	−0.1548 (2)	−0.0890 (3)
P	0.5211 (2)	0.3005 (2)	0.6365 (2)
C(11)	0.6692 (9)	0.3245 (9)	0.5317 (7)
C(12)	0.7360 (9)	0.4445 (9)	0.5268 (9)
C(13)	0.8461 (11)	0.4587 (12)	0.4457 (11)
C(14)	0.8923 (12)	0.3549 (15)	0.3643 (10)
C(15)	0.8290 (13)	0.2382 (13)	0.3668 (9)
C(16)	0.7155 (12)	0.2204 (10)	0.4523 (10)
C(21)	0.3707 (10)	0.2430 (9)	0.5591 (9)
C(22)	0.3842 (13)	0.2303 (11)	0.4431 (9)
C(23)	0.2721 (12)	0.1928 (11)	0.3855 (10)
C(24)	0.1463 (17)	0.1647 (12)	0.4434 (15)
C(25)	0.1276 (13)	0.1794 (14)	0.5630 (17)
C(26)	0.2452 (12)	0.2220 (12)	0.6233 (12)
C(31)	0.5524 (9)	0.1935 (8)	0.7113 (8)
C(32)	0.6816 (10)	0.1959 (9)	0.7299 (9)
C(33)	0.7055 (12)	0.1190 (12)	0.7941 (11)
C(34)	0.6028 (13)	0.0443 (10)	0.8411 (9)
C(35)	0.4730 (11)	0.0396 (10)	0.8223 (11)
C(36)	0.4443 (10)	0.1152 (10)	0.7589 (9)
C(41)	0.4947 (9)	0.4466 (8)	0.7410 (8)
C(42)	0.4016 (14)	0.5165 (12)	0.7309 (11)
C(43)	0.3858 (16)	0.6308 (12)	0.8095 (12)
C(44)	0.4606 (14)	0.6759 (10)	0.8956 (10)
C(45)	0.5586 (14)	0.6092 (11)	0.9072 (10)
C(46)	0.5728 (12)	0.4945 (10)	0.8321 (10)
O(9)	0.060 (2)	0.572 (2)	0.210 (2)
C(9)	−0.004 (4)	0.594 (4)	0.119 (3)
N(9)	0.004 (3)	0.507 (3)	0.028 (2)
C(91)	0.086 (3)	0.412 (3)	−0.022 (3)
C(92)	−0.072 (4)	−0.468 (3)	−0.075 (3)
H(12)	0.714	0.525	0.586
H(13)	0.884	0.555	0.447
H(14)	0.965	0.376	0.322
H(15)	0.832	0.170	0.325
H(16)	0.645	0.137	0.478
H(22)	0.447	0.242	0.407
H(23)	0.287	0.172	0.290
H(24)	0.056	0.142	0.395
H(25)	0.027	0.172	0.599
H(26)	0.213	0.215	0.675
H(32)	0.740	0.245	0.710
H(33)	0.786	0.137	0.797
H(34)	0.613	0.004	0.899
H(35)	0.380	−0.002	0.847
H(36)	0.354	0.117	0.758
H(42)	0.330	0.485	0.650
H(43)	0.320	0.685	0.799
H(44)	0.447	0.745	0.965
H(45)	0.606	0.639	0.979
H(46)	0.620	0.466	0.851

[a] Standard deviations are in parentheses.

A crystal from the preparation of II measuring 0.20 × 0.20 × 0.18 mm^3 was used for the data collection of II. The method of data collection was similar to that of I, except that in this case the radiation used was copper ($\lambda(K\alpha) = 1.54178$ Å). For this case, μr lies between 0.86 and 1.45. It was found in the later stages of the refinement that absorption is high enough so that it cannot be neglected. Consequently, the data between $2\theta = 2{-}40°$ were recollected completely by using a crystal of dimensions 0.08 × 0.10 × 0.24 mm^3, mounted along the needle axis, which is small enough that no absorption corrections need to be applied. The crystals are triclinic, space group $P\bar{1}$. Unit cell parameters were determined from 15 reflections in the range $2\theta = 36{-}50°$. The cell volume of 1257.6 Å^3, combined with the measured density of 1.52 g·cm^{-3} and $Z = 1$, led to a formula weight of 1150.7, compared with a molecular weight of 1081.6 for the unsolvated II. it is therefore highly likely that the compound crystallizes with one molecule of the solvent DMF ($M_r = 73$). The crystal data given in Table I apply to the formulation of $[(C_6H_5)_4P]_2OsCl_6{\cdot}DMF$ for II. The structure determination should then give evidence for the presence of the solvent in the crystal.

(c) Structure Determinations. Compound I. Initial coordinates for Os, the three crystallographically independent Cl atoms, and P were easily determined from a three-dimensional Patterson function, particularly since Os, Cl(1), and Cl(2) must lie in special positions $^1/_4$, $^1/_4$, z and P in $^1/_4$, $^3/_4$, 0. An electron-density map revealed positions for all the carbon atoms, and subsequent least-squares refinement and a difference Fourier map showed unambiguous positions for all the phenyl hydrogen atoms. Final full-matrix least-squares refinement with anisotropic thermal motion for all non-hydrogen atoms and isotropic thermal motion for the hydrogen atoms converged to values for R $((\sum||F_o| - |F_c||)/\sum|F_o|) = 0.023$ and R_w $([\Sigma w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}) = 0.028$, weights being taken as $w = [\sigma(F_o)]^{-1/2}$. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The average shift/error in positional parameters in the last cycle was 0.085.

Compound II. The Os atom was placed at 0, 0, 0. Initial positions for the three chlorine atoms and for phosphorus were again determined from a Patterson map, and all 24 carbon atoms were located from a difference Fourier map. After several cycles of least-squares refinement, tentative positions for the atoms of the solvent molecule were found. Since there is only one DMF molecule per cell, lying across the inversion center at 0, $^1/_2$, 0, the molecule is disordered, and the multiplicities of the atoms of this molecule are each equal to 0.5. Further refinement, with anisotropic temperature factors for all atoms except those of the solvent molecule, led to an R factor of 0.064. At that point the hydrogen atoms of all four phenyl rings could be located from a difference Fourier map. They were included in the final stages of the calculations at the positions in which they were found, but no refinement of their positional and thermal parameters was attempted. Ultimate refinement, with anisotropic thermal parameters for all non-hydrogen atoms except those of the solvent (which were treated isotropically), led to a value of $R = 0.053$ and $R_w = 0.070$.

In both structure determinations, atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann[8] and for hydrogen atom from Stewart et al.[9] All computations were done by using the program X-ray 76.[10] Positional and thermal atomic parameters for the two structures are listed in Tables II and III, and values of F_o and F_c are given in Tables IV and V.[11]

Description of Structures

Both structures I and II consist of octahedral $OsCl_6$ anions and tetrahedral $P(C_6H_5)_4{}^+$ cations.

Compound I. In the Os(V) structure, the weighted average Os–Cl distance is 2.284 Å with a mean deviation of 0.015 Å (see Table VI for the important interatomic distances and

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(11) See paragraph at the end of paper regarding supplementary material.

Table VI. Interatomic Distances and Angles

$OsCl_6$ Octahedron

	Distance(Å) I	Distance(Å) II		Angle(deg) I	Angle(deg) II
Os -Cl(1)	2.273(3)	2.332(3)	Cl(1)-Os-Cl(3)	89.35(5)	89.65(10)
-Cl(2)	2.252(4)	2.338(3)	Cl(2)-Os-Cl(3)	90.65(5)	89.17(11)
-Cl(3)	2.295(2)	2.325(3)	Cl(3)-Os-Cl(3) (diag)	178.7(6)	
Cl(1)-Cl(2)	4.525(5)	3.277(4)	Cl(3)-Os-Cl(3) (edge)	90.00(7)	
Cl(1)-Cl(3)	3.212(3)	3.283(5)	Cl(1)-Os-Cl(2)		89.14(10)
Cl(2)-Cl(3)	3.234(3)	3.321(5)			
Cl(3)-Cl(3) (edge)	3.246(3)				
Cl(3)-Cl(3) (diag)	4.589(5)				

$P(C_6H_5)_4^+$ Cation[a]

	Distance(Å) I	Distance(Å) II		Angle(deg) I	Angle(deg) II
P -C(1)	1.797(6)	1.802(9)	C(1)-P-C(1)'	105.6(3)	108.5(5)
C(1)-C(2)	1.356(9)	1.364(15)	C(1)-P-C(1)"	111.4(3)	111.1(5)
C(2)-C(3)	1.394(10)	1.360(13)	P-C(1)-C(2)	123.1(5)	120.3(8)
C(3)-C(4)	1.397(11)	1.361(21)	C(6)-C(1)-P	117.6(4)	119.2(9)
C(4)-C(5)	1.353(12)	1.375(21)	C(6)-C(1)-C(2)	119.3(5)	120.3(10)
C(5)-C(6)	1.373(10)	1.399(18)	C(1)-C(2)-C(3)	121.5(6)	119.9(11)
C(6)-C(1)	1.398(9)	1.384(12)	C(2)-C(3)-C(4)	118.0(7)	121.3(15)
C(2)-H(2)	0.80(6)	1.08(4)	C(3)-C(4)-C(5)	120.6(7)	119.8(12)
C(3)-H(3)	1.01(6)	1.08(4)	C(4)-C(5)-C(6)	120.9(7)	119.5(13)
C(4)-H(4)	1.11(8)	1.06(5)	C(5)-C(6)-C(1)	119.6(6)	119.0(12)
C(5)-H(5)	0.83(7)	1.02(4)	C-C-H (av.)	119(6)	120(7)
C(6)-H(6)	1.12(6)	1.07(4)			

[a] For compound II: average value of four independent values is given.

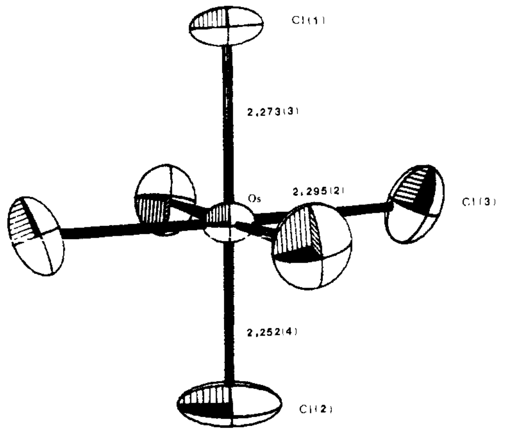

Figure 1. $OsCl_6$ octahedron of compound I showing the atom numbering of the atoms and interatomic distances. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of the electron density.

angles in the two structures). In spite of the fact that the octahedron is located on a fourfold axis (atoms Cl(1), and Os, and Cl(2) lie on the axis), the geometry of the octahedron is not precisely regular (Figure 1):

(1) The Os atom does not lie exactly in the plane of the four equatorial Cl(3) atoms, but is shifted below that plane by the small but significant distance of 0.026 Å. The standard deviation in the z coordinate of Cl(3) is only 0.002 Å; thus the shift is greater than 10 standard deviations.

(2) The distances Os–Cl(1) and Os–Cl(2), both parallel to the z axis, are 2.273 and 2.252 Å, again significantly different, the difference being 5 times the standard deviation in the Os–Cl(2) distance. These small deviations from strict regularity of the octahedron also show up, of course, in the interatomic angles, in particular in the value of 178.7° for the diagonal Cl(3)–Os–Cl(3) angle.

(3) The U_{ij} values for Cl(1), Cl(2), and Cl(3) indicate that there is a considerable libration of the $OsCl_6^-$ group about the central Os, but the values of U_{11} and U_{22} for Cl(2) are exceptionally large. This indicates that the Cl(2) vibrates strongly in a plane perpendicular to the z axis.

These distortions seemed surprising, yet they must be taken as real, since Os and Cl are the heaviest atoms in the structure and their positions should be least subject to error. We applied several modifications to the least-squares refinement in order to eliminate any doubts concerning the correctness of the final determination:

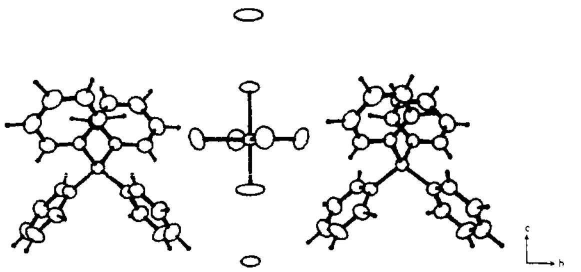

Figure 2. Compound I: environment of $OsCl_6^-$ by $(C_6H_5)_4P^+$ groups. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of the electron density. All the hydrogen atoms are given an arbitrary value of $U = 0.04$ Å^2.

(1) A refinement was done that included a variable population parameter for Cl(2) to test the possibility that the large thermal motion found for this atom was in fact a result of a slight deviation from exact stoichiometry of the crystal; at the start of this calculation, the values of U_{ij} of Cl(2) were set equal to those of Cl(1), and all parameters were allowed to vary, as in the original refinement. After three cycles of refinement, the value of R was back to 0.023, the U_{ij} values of Cl(1) and Cl(2) were identical with those determined originally, and the population parameter of Cl(2) was 1.003.

(2) A calculation was done in which the population parameter of Cl(2) was the only variable, its U_{ij} values being fixed to be equal to those of Cl(1) as given in Table II. The value of R rose to 0.038 after three cycles, and the population parameter became 0.75. The latter value disagrees with the chemical analysis of I and with the charge of the $OsCl_6^-$ ion, which are reported in the preceding paper.[1]

(3) A refinement in which all parameters were allowed to vary, except that the values of U_{ij} for Cl(2) were constrained to be equal to those of Cl(1), led to a R value of 0.051. As a result of these unsuccessful modifications, it was concluded that the distortions of the $OsCl_6^-$ octahedron are real and that they are either a consequence of the packing of the ions or an inherent property of the $OsCl_6^-$ ion (see Discussion).

The geometry of the $P(C_6H_5)_4^+$ ion is close to tetrahedral. The site symmetry of phosphorus is $\bar{4}$, the angles correspond to a tetrahedron that is slightly elongated along the z axis, and the P–C distance of 1.797 Å is very close to that reported for other structures: 1.792,[12] 1.80,[13] and 1.775 (av).[14] The atoms C(4)–C(1)–P–C(1)′–C(4)′ are coplanar (plane 1), the largest deviation from the least-squares plane being 0.027 Å for C(1) and C(1)′. The average C–C distance in the phenyl ring is 1.379 Å, with a mean deviation of 0.018 Å. The six carbon atoms are coplanar (plane 2); the largest deviation from the least-squares plane is 0.008 Å. The least-squares plane through the six carbon atoms, the five hydrogens, and the phosphorus atom was also calculated. One hydrogen atom (H(2)) deviates from this plane by 0.10 Å; all other atoms are within 0.06 Å. The dihedral angle between planes 1 and 2 is 53.7°. The geometry of the $P(C_6H_5)_4^+$ ion and the packing in the crystal are shown in Figure 2.

Compound II. The octahedral $OsCl_6^{2-}$ ion (see Table VI for distances and angles) has an average Os–Cl distance of 2.332 Å, with a mean deviation of 0.005 Å. The octahedron in this case is clearly more regular than that in $OsCl_6^-$, and the thermal parameters do not show the abnormalities that

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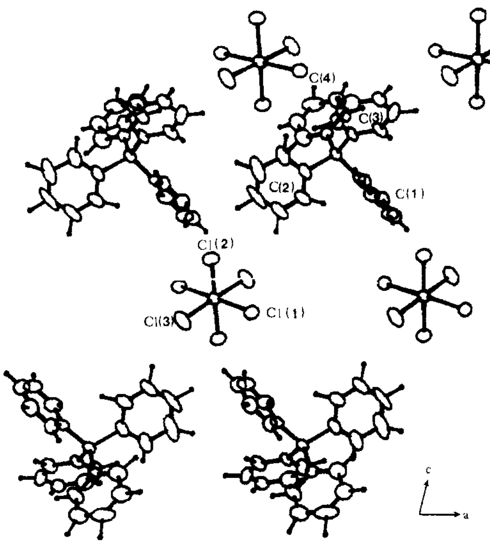

Figure 3. Compound II: arrangement of ions in the cell. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of the electron density. The atom numbering scheme is also given. All the hydrogen atoms are given an arbitrary value of $U = 0.05$ Å^2.

were found in the $OsCl_6^-$ ion. Figure 3 shows the $OsCl_6^{2-}$ ion in its environment of $P(C_6H_5)_4^+$ ions.

The tetraphenylphosphonium ion in this structure has no imposed symmetry, the phosphorus atoms lying in a general position, and the ion is not as regular as that in the structure of I. A calculation of all the least-squares planes in the ion reveals that (1) the two C(4)–C(1)–P–C(1)′C(4)′ arrays are planar with a maximum deviation of 0.027 Å from the plane; (2) the four independent phenyl groups are planar with a maximum carbon atom deviation of 0.017 Å from the plane; (3) the angle between the two C(4)–C(1)–P–C(1)′–C(4)′ planes is 86.9° rather than the ideal value of 90°; and (4) the dihedral angles between the appropriate C(4)–C(1)–P–C(1)′–C(4)′ and the phenyl rings designated as 1, 2, 3, and 4 (Table III) are 70.8°, 1.0°, 87.5°, and 37.2°, respectively.

The positions for the atoms of the disordered solvent DMF could not be determined with any accuracy. The molecule lies across the inversion center at 0, $^1/_2$, 0, but reliable interatomic distances could not be obtained. The difference Fourier map still shows some low positive areas in the region of that molecule. However, this ambiguity does not appear to affect the positions of the other atoms: their coordinates remained the same through all the calculations that were done to locate the solvent molecule.

Discussion

Compound I. To our knowledge this is the first single-crystal structure determination of a compound containing Os(V). The structures reported previously[2–6] (see above) were determined from powder data. Nevertheless, some interesting comparisons between these structures and the present study can be made. Os_2Cl_{10}[2], the dimer of $OsCl_5$, contains terminal Os–Cl distances of 2.24 Å and bridging Os–Cl distances of 2.42 Å. No standard deviations for the distances are reported, and it should be noted again that only Os positions were refined, the Cl positions having been taken without change from the isomorphous Re_2Cl_{10} structure.[15] Therefore, while these distances may be subject to some error, the value of 2.24 Å, and especially the weighted average distance of 2.30 Å, compares well with the Os–Cl distance of 2.284 Å (av) found by us.

Three different structural types have been reported for compound $M^+OsF_6^-$. For M = Li and Na, the structure is rhombohedral,[4] of the type of $LiSbF_6$,[5] and the OsF_6^- octahedron is regular, without perceptible distortions. For M = K, Rb, Cs, the structure is also rhombohedral[3] but of a type different from the first one. The OsF_6^- octahedra are compressed along one of the threefold axes such that there are two types of F–Os–F angles, 85.9° and 93.9°, respectively. For M = Ag, the structure is tetragonal,[4] of the type of $KNbF_6$[6]. In this case the OsF_6^- octahedron is distorted into a bisphenoid. In all of these three structural types, the Os–F distances are found to be equal, their value being 1.82–1.83 Å. If the Pauling radii[16] of F^- and Cl^- are taken as 1.36 and 1.81 Å, respectively, the studies of OsF_6^- lead to a radius of Os(V) of 0.46–0.47 Å, while our study gives a value of 0.47 Å. Thus, the ionic radius of Os(V) can be taken to be 0.47 Å.

The three structural types of $MOsF_6$ show clearly that the basic OsX_6^- octahedron can be quite easily distorted to a considerable extent, depending upon crystal environment. We believe that the distortion of the $OsCl_6^-$ octahedron in the present study is also a result of interactions in the crystal, specifically of repulsions between neighboring $OsCl_6^-$ groups. The reasons for this conclusion are the following:

(1) A spontaneous distortion from symmetry O_h to C_{4v} in the solid must be discarded. There is no evidence of such a deformation in solution (see the preceding paper), and there are no theoretical reasons why this should happen.

(2) A calculation of contact distances between the chlorine atoms of $OsCl_6^-$ and the hydrogen atoms of neighboring phenyl rings shows two relatively close contacts for Cl(1) (of 3.14 and 3.52 Å) and seven for Cl(3) (ranging from 2.94 to 3.68 Å). The hydrogen atom closest to Cl(2) is 3.93 Å away. The interactions of the hydrogen atoms with Cl(3) are predominantly from above (i.e., from the direction in which Cl(1) is located), and they would therefore, if anything, tend to repel the Cl(3) atoms downward. This is contrary to the result of the structure determination, which shows the Os atom to lie below the plane of the four Cl(3) atoms.

(3) Each Cl(3) atom at $z = 0.1586$ has a nearest Cl(3) at $z = -0.1586$, at a distance of 6.009 Å, and another one at $z = 0.8414$ at a distance of 7.605 Å. Thus, the Cl(3) at $z = 0.1586$ experiences an appreciably larger electrostatic repulsive force from the Cl atom below it than from the one above (by a factor of 1.6). We believe that it is this electrostatic repulsion between chlorine atoms that is the cause of the small distortion of the $OsCl_6^-$ ions from their ideal octahedral geometry. It is of course the reason for many cases of distortion from the ideal geometry in structures where ions are not surrounded symmetrically by their counterparts, including the distortions mentioned above for the OsF_6^- ion.

A noteworthy feature of this structure is the exceedingly short contact distance between Cl(1) and Cl(2), along the z axis, of 3.183 Å. This corresponds to a van der Waals radius of chlorine of 1.592 Å, compared to the normal value of about 1.8 Å. The low values of U_{33} for both Cl(1) and Cl(2) are consistent with this short contact. It is even shorter than the Cl(1)–Cl(2) distance of 3.26 Å in NH_4HgCl_3,[17] and it tends to show that the high positive charge of the central osmium ion draws considerable electron density from the chlorine atom into the region between chlorine and osmium.

The contact distances between Cl and H (see above) show that there is no hydrogen atom close to Cl(2), so that this atom should experience very little steric hindrance toward vibration. This was indeed found in the exceptionally high thermal parameters of Cl(2), and it can be seen in Figure 2.

Compound II. Structures containing $OsCl_6^{2-}$, OsF_6^{2-}, and $OsBr_6^{2-}$ are well-known. M_2OsF_6 with M = Na, K, Cs is

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hexagonal;[18,19] K_2OsCl_6 and K_2OsBr_6 are cubic with K_2PtCl_6 structure.[20] The Os–Cl distance in K_2OsCl_6 is 2.36 Å compared with our determined value of 2.332 Å (av). Assuming as before an ionic radius of Cl^- of 1.81 Å, the radius of Os(IV) becomes 0.52 Å. In spite of the low (triclinic) crystal symmetry, the $OsCl_6^{2-}$ octahedron is almost undistorted. Another related structure is that of $OsCl_4$,[21] which contains endless chains of linked $OsCl_6$ octahedra. In this structure the terminal Os–Cl distance is 2.262 Å and the bridging Os–Cl is 2.378 Å, with a weighted average Os–Cl distance of 2.339 Å.

It is of interest to note that the dihedral angles, i.e., the angles of rotation of the phenyl groups in $(C_6H_5)_4P^+$ out of the appropriate C(4)–C(1)–P–C(1)′–C(4)′ plane, have totally differing values of 1°, 37°, 71°, and 88°. The corresponding value in I is 54°. The energy barrier to rotation of these groups must be exceedingly low since the ring can clearly adopt any rotational angle from almost parallel to almost perpendicular to the carbon–phosphorus plane, depending upon influences from the environment. In the structure of $(C_6H_5)_4PI$,[13] the experimental value for the dihedral angle is 62°, and it is claimed that the optimum value for minimum steric hindrance is 38°. In two other papers,[12,14] the dihedral angles are not given at all, but from a figure in ref 14 on $[(C_6H_5)_4P]CuCl_3$ it would seem that two of them are almost 0° and two close to 90°, again indicating the variability of these angles.

Registry No. I, 86365-50-6; II, 86392-81-6.

Supplementary Material Available: Tables of observed and calculated structure factors and thermal parameters for compounds I and II (27 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Reversible Photochemical/Thermal Interconversion of η^1- and η^2-Bridged (Aryldiazo)triosmium Clusters. Crystal Structure of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-N=NPh})$[1]

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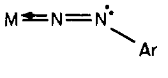
Received January 11, 1983

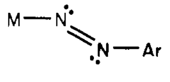
$H_2Os_3(CO)_{10}$ reacts with $ArN_2^+BF_4^-$ (Ar = Ph, $p\text{-}C_6H_4F$, $p\text{-}C_6H_4CH_3$) in refluxing dichloromethane to produce, after neutralization, the compounds $HOs_3(CO)_{10}(N_2Ar)$ (**1**), in which the aryldiazo ligand bridges one edge of the osmium triangle through one nitrogen atom. UV photolyses of **1** produce the isomeric series of compounds **2**, in which the aryldiazo ligand bridges one edge of the osmium triangle through both nitrogen atoms. This isomerization is reversible thermally. Quantum yields for the photoisomerization at 313 and 366 nm, 0.06 and 0.006, respectively, indicate that higher energy light is more efficient at causing the transformation. The structure of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^1\text{-N=N-}p\text{-}C_6H_4CH_3)$ has been previously determined by a single-crystal X-ray diffraction study. The results of a crystallographic study on $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-N=Ph})$ are reported herein. This complex crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ with a = 9.482 (2) Å, b = 12.542 (3) Å, c = 17.588 (4) Å, V = 2091.6 (7) Å^3, and Z = 4. The structure was solved by a combination of Patterson, difference-Fourier, and full-matrix least-squares refinement. All non-hydrogen atoms were located; final discrepancy indices are R_F = 7.7% and R_{wF} = 7.4% for all 2114 independent data. The $(\mu\text{-}\eta^2\text{-N=NPh})$ ligand spans the Os(2)–Os(3) linkage, with Os(3)–N(1) R_F 2.14 (2) Å, Os(2)–N(2) = 2.11 (3) Å, and N(1)–N(2) = 1.20 (4) Å. The (μ-hydrido, μ-aryldiazo) dibridged Os(2)–Os(3) distance is 2.895 (2) Å as compared to Os(1)–Os(2) = 2.868 (2) Å and Os(1)–Os(3) = 2.862 (2) Å.

Introduction

Mononuclear aryldiazo (N_2Ar) complexes may have the $M\text{-}N_\alpha\text{-}N_\beta$ group bent at N_β only (I) or at both N_α and N_β (II).[2-6] In the former case, the neutral ligand is a 3-electron



I



II

donor to the metal; in the latter case, it is a 1-electron donor, in direct analogy with compounds of the isoelectronic nitrosyl ligand. Although many monomolecular aryldiazo complexes are known, polynuclear compounds remain rather rare. The three[7-9] structurally characterized examples have η^1-bridging aryldiazo ligands (III). Two different bridging modes (IV[10]

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