Structures of Bis(triphenylphosphonium) Hexabromoosmate(IV) and Bis(triphenylphosphonium) Hexachloroosmate(IV)

By P. D. Robinson

Department of Geology, Southern Illinois University, Carbondale, IL 62901, USA

and C. C. Hinckley,* M. Matusz and P. A. Kibala

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, USA

Abstract. (I) $[HP(C_6H_5)_3]_2[OsBr_6]$, $M_r = 1196.22$, monoclinic, $P2_1/n$, $a = 10.167$ (1), $b = 13.873$ (4), $c = 13.962$ (2) Å, $\beta = 90.74$ (1)°, $V = 1969$ (1) Å^3, $Z = 2$, $D_x = 2.02$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 99.82$ cm^{-1}, $F(000) = 1128$, $T = 295$ K, $R = 0.044$, 3612 unique reflections measured, 1565 observed $[I > 3\sigma(I)]$. Prepared from di(tetra-*n*-butylammonium) hexabromoosmate(IV) and triphenylphosphine by precipitation from an acetic acid/acetic anhydride solution. (II) $[HP(C_6H_5)_3]_2[OsCl_6]$, $M_r = 929.51$, monoclinic, $P2_1/n$, $a = 9.875$ (2), $b = 13.875$ (3), $c = 13.664$ (3) Å, $\beta = 90.17$ (2)°, $V = 1872$ (1) Å^3, $Z = 2$, $D_x = 1.65$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 41.43$ cm^{-1}, $F(000) = 912$, $T = 295$ K, $R = 0.072$, 3420 unique reflections measured, 1788 observed $[I > 3\sigma(I)]$. Prepared from OsO$_4$ by reflux in concentrated HCl followed by cold addition of acetic anhydride and triphenylphosphine dissolved in acetic anhydride, yielding a yellow precipitate which was purified by recrystallization from methanol. The molecular conformation of the two isostructural compounds can be described as an octahedral Os hexahalogen ion about which two triphenylphosphonium ions are symmetrically disposed.

Introduction. These compounds were prepared as part of a study of osmium–phosphine chemistry in which triphenylphosphine acts as a reducing agent, a role that is unusual for this substance. In one example, $OsBr_6^{2-}$ reacts with triphenylphosphine in mixed acetic acid/ acetic anhydride in the presence of acetate to yield an Os^{III} complex (Hinckley, Matusz, Kibala & Robinson, 1987). Other reduced osmium products, for example $OsBr_2(CO)_2[P(C_6H_5)_3]_2$, are obtained when acetate is not present (Robinson, Hinckley, Kibala & Ikuo, 1988). The triphenylphosphine salts prepared in this study are believed to be precursors of the reduced products.

Experimental. Compounds prepared in an acetic acid/ acetic anhydride solvent. The nature of products derived from hexahaloosmium ions in this solvent is sensitively dependent upon conditions. Mild conditions employed avoid reductive processes. Preparation of compound (I) by dissolution of di(tetra-*n*-butylammonium) hexabromoosmate(VI) (0.5 g, 0.43 mmol) and triphenylphosphine (1.0 g, 3.82 mmol) in 20 ml of CH$_2$Cl$_2$; 25 ml of glacial acetic acid and 2.5 ml of acetic anhydride added and mixture placed in a 328–333 K oil bath for three days. Red-brown crystals separated from the solution by filtration (yield: 0.15 g). Compound (II) prepared from OsO$_4$ (4.0 g, 15.7 mmol) dissolved in 80 ml of concentrated HCl (12.1 *M*) and refluxed for 1 h. Red reaction mixture concentrated under N$_2$ gas to about 40 ml. Solution cooled in an ice bath, 160 ml of acetic anhydride added dropwise over 1.5 h period. A solution of triphenylphosphine (8.0 g, 30.5 mmol) dissolved in 80 ml of acetic anhydride added; resultant yellow precipitate separated by filtration and air dried (yield: 10.60 g). To purify the product, 10.0 g of precipitate refluxed for 1.5 h in 800 ml of methanol; undissolved solid (5.46 g) separated from the yellow methanol solution and again refluxed in 800 ml of methanol. The two methanol solutions were placed in a freezer (253 K); yellow crystals which formed in the cooled solutions separated by filtration and washed with diethyl ether. Solids combined and again recrystallized from methanol to obtain crystals suitable for X-ray diffraction study. Crystals used for data collection 0.28 × 0.25 × 0.01 mm, red, platy (I) and 0.35 × 0.19 × 0.03 mm, green, platy (II). Rigaku AFC5S diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scans, scan speeds 3 (I) and 6° min^{-1} (II), maximum of three scan repetitions to obtain $\sigma(F)/F < 0.10$, $(\sin\theta)/\lambda_{(max)} = 0.595$ Å^{-1}. Lattice parameters from least-squares fit of 25 reflections in 2θ range 8–23 (I) and 6–21° (II). For (I), 3759 reflections measured (h −11 to 11, k 0 to 16, l 0 to 16), 3612 unique, 1565 observed $[I > 3\sigma(I)]$, $R_{int} = 2.2\%$ for 147 equivalent reflec-

* Author to whom correspondence should be addressed.

tions. Three standard reflections (11$\bar{2}$, 12$\bar{1}$ and $\bar{1}$1$\bar{4}$) decreased by 14·3, 12·5 and 13·8% respectively; decay correction applied. For (II), 3565 reflections measured (h −11 to 11, k 0 to 16, l 0 to 16), 3420 unique, 1788 observed [$I > 3\sigma(I)$], $R_{int} = 2\cdot0$% for 145 equivalent reflections. Three standard reflections (0$\bar{2}$$\bar{2}$, 1$\bar{1}$$\bar{2}$ and 11$\bar{2}$) decreased by 4·8, 5·2 and 4·6%, respectively; decay correction applied. Data for both structures corrected for Lorentz, polarization and absorption [numerical method, transmission ranges 0·25–0·89 (I) and 0·43–0·88 (II)]. Direct methods used to locate Os, (Br,Cl), P, and most of the phenyl-ring C atoms; remainder located by Fourier and difference Fourier syntheses. Some difficulty in locating several of the phenyl-ring C atoms in compound (II) due to disorder. Full-matrix least-squares refinement of F magnitudes for both structures, atomic scattering factors and anomalous-dispersion corrections from Cromer & Waber (1974), extinction corrections not applied. Compound (I) refined with 209 variables including a scale factor, positional parameters, anisotropic thermal parameters of non-H atoms and an isotropic thermal parameter for the phosphonium H atom. Phenyl-ring H atoms placed in geometrically correct positions (C—H = 0·95 Å) after anisotropic convergence of all other atoms, structure again refined to convergence and H-atom positions regenerated. H generation/refinement repeated until parameter shifts became insignificant. B's of phenyl-ring H atoms fixed at 1·2 × B_{eq} of associated C atom. Compound (II) refined with 115 variables including a scale factor, positional parameters, anisotropic thermal parameters for Os, Cl and P atoms, and isotropic thermal parameters for the C atoms; H atoms not included in the model due to significant phenyl-ring disorder which could not be described in terms of partially occupied C sites. Convergence of (I) yielded $R = 0\cdot044$, $wR = 0\cdot046$, $S = 1\cdot14$ and $(\Delta/\sigma)_{max} = 0\cdot07$ while (II) converged at $R = 0\cdot072$, $wR = 0\cdot085$, $S = 2\cdot05$ and $(\Delta/\sigma)_{max} = 0\cdot09$ [$w = 1/\sigma^2(|F_o|)$]. Final difference Fourier syntheses showed $(\Delta\rho)_{max} = 0\cdot97$ and $(\Delta\rho)_{min} = -1\cdot21$ e Å^{-3} for (I) and $(\Delta\rho)_{max} = 2\cdot18$ and $(\Delta\rho)_{min} = -2\cdot37$ e Å^{-3} for (II). Maximum and minimum difference Fourier excursions located near the Os atom for both (I) and (II). All computer programs from the *TEXSAN* crystal structure analysis package (Molecular Structure Corporation, 1985).*

Discussion. Atomic coordinates and temperature factors for the two isostructural compounds are presented

---

Table 1. *Positional and equivalent isotropic thermal parameters for the non-H atoms and their e.s.d.'s*

$$B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33} + 2U_{12}\cos\gamma + 2U_{13}\cos\beta + 2U_{23}\cos\alpha).$$

	x	y	z	$B_{eq}(\text{Å}^2)$
(I)				
Os	½	½	½	2·92 (4)
Br(1)	0·4030 (2)	0·5234 (1)	0·3366 (1)	4·21 (9)
Br(2)	0·5929 (2)	0·6659 (1)	0·4929 (1)	4·40 (9)
Br(3)	0·7030 (2)	0·4323 (1)	0·4289 (1)	4·15 (9)
P	0·7100 (4)	0·6490 (4)	0·2366 (3)	4·3 (2)
C(1)	0·871 (2)	0·681 (1)	0·279 (1)	3·7 (8)
C(2)	0·922 (2)	0·634 (1)	0·359 (1)	6 (1)
C(3)	1·045 (2)	0·654 (2)	0·387 (1)	6 (1)
C(4)	1·125 (2)	0·715 (1)	0·337 (2)	6 (1)
C(5)	1·075 (2)	0·761 (2)	0·260 (2)	8 (1)
C(6)	0·946 (2)	0·746 (2)	0·228 (1)	6 (1)
C(7)	0·602 (2)	0·750 (1)	0·218 (1)	4 (1)
C(8)	0·510 (2)	0·751 (2)	0·150 (2)	8 (1)
C(9)	0·423 (2)	0·830 (3)	0·146 (2)	10 (2)
C(10)	0·437 (3)	0·903 (2)	0·206 (3)	9 (2)
C(11)	0·532 (2)	0·901 (1)	0·276 (2)	6 (1)
C(12)	0·614 (2)	0·824 (1)	0·280 (1)	5 (1)
C(13)	0·715 (2)	0·580 (2)	0·130 (1)	6 (1)
C(14)	0·773 (2)	0·616 (2)	0·045 (2)	8 (2)
C(15)	0·768 (4)	0·560 (3)	−0·038 (2)	11 (2)
C(16)	0·718 (4)	0·472 (2)	−0·035 (2)	10 (2)
C(17)	0·652 (2)	0·438 (2)	0·043 (2)	8 (1)
C(18)	0·652 (2)	0·494 (2)	0·126 (1)	6 (1)
H(1)	0·66 (1)	0·57 (1)	0·30 (1)	6 (4)*
(II)				
Os	½	½	½	2·95 (4)
Cl(1)	0·4054 (5)	0·5240 (4)	0·3447 (4)	4·1 (3)
Cl(2)	0·5897 (6)	0·6555 (4)	0·4947 (4)	5·2 (3)
Cl(3)	0·6962 (5)	0·4385 (5)	0·4292 (4)	4·8 (3)
P	0·7049 (6)	0·6493 (9)	0·2409 (5)	8·7 (5)
C(1)	0·874 (2)	0·685 (2)	0·279 (2)	5·8 (6)*
C(2)	0·924 (3)	0·628 (2)	0·358 (2)	6·2 (6)*
C(3)	1·060 (3)	0·659 (2)	0·390 (2)	7·1 (7)*
C(4)	1·134 (3)	0·718 (2)	0·338 (2)	7·0 (7)*
C(5)	1·077 (3)	0·773 (2)	0·259 (3)	8·9 (9)*
C(6)	0·941 (3)	0·750 (2)	0·225 (2)	8·7 (8)*
C(7)	0·594 (3)	0·755 (3)	0·223 (3)	8·2 (8)*
C(8)	0·488 (5)	0·757 (4)	0·144 (3)	14 (1)*
C(9)	0·416 (3)	0·854 (3)	0·153 (2)	7·3 (7)*
C(10)	0·430 (5)	0·915 (4)	0·214 (4)	14 (1)*
C(11)	0·518 (5)	0·913 (3)	0·288 (3)	13 (1)*
C(12)	0·604 (3)	0·823 (3)	0·282 (3)	8·9 (9)*
C(13)	0·699 (3)	0·567 (3)	0·129 (3)	9·0 (9)*
C(14)	0·769 (4)	0·626 (3)	0·054 (4)	13 (1)*
C(15)	0·763 (5)	0·566 (4)	−0·029 (4)	15 (2)*
C(16)	0·716 (5)	0·477 (3)	−0·036 (3)	13 (1)*
C(17)	0·649 (4)	0·417 (3)	0·045 (3)	12 (1)*
C(18)	0·649 (3)	0·488 (3)	0·129 (2)	9·2 (8)*

* Isotropic temperature factor.

in Table 1; selected interatomic distances and angles are given in Table 2. Fig. 1 illustrates the molecular configuration of compound (I), along with atomic designations and thermal vibrations. A drawing of compound (II) would differ only in the representation of the thermal motion and is thus not presented. Two triphenylphosphonium ions are located opposite trigonal faces on either side of the octahedral hexahalo-osmium ion. H atoms bound to the P atoms are directed towards the trigonal face to a point near the center of the triangle formed by the three halogens. Distances between the H(1) atom and the three halogens range from 2·7 (2) to 3·0 (1) Å (I) and are thus too long for covalent bonding. The orientation of the phenyl groups of the triphenylphosphonium ions is between the halogen atoms of the trigonal faces.

Table 2. *Selected bond distances (Å), bond angles (°), and their e.s.d.'s*

	(I)	(II)
Os–Br,Cl(1)	2·495 (2)	2·340 (5)
Os–Br,Cl(2)	2·490 (2)	2·334 (6)
Os–Br,Cl(3)	2·486 (2)	2·330 (5)
P–C(1)	1·79 (2)	1·82 (3)
P–C(7)	1·80 (2)	1·85 (3)
P–C(13)	1·78 (2)	1·91 (4)
P–H(1)	1·5 (1)	
Br,Cl(3)–Os–Br,Cl(2)	90·89 (6)	90·6 (2)
Br,Cl(3)–Os–Br,Cl(1)	90·25 (6)	90·3 (2)
Br,Cl(2)–Os–Br,Cl(1)	89·36 (6)	89·5 (2)
C(13)–P–C(1)	111·9 (8)	115 (1)
C(13)–P–C(7)	109 (1)	111 (2)
C(1)–P–C(7)	114·3 (9)	111 (1)
H(1)–P–C(1)	106 (6)	
H(1)–P–C(7)	116 (6)	
H(1)–P–C(13)	100 (6)	

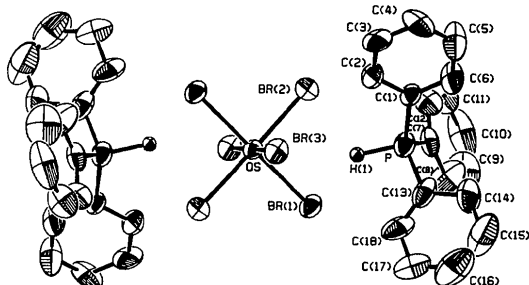

Fig. 2. Stereoview of the molecular packing.

Fig. 1. Molecular structure and numbering scheme for compound (I); thermal ellipsoids at the 50% probability level.

It is interesting to note that the *a* and *c* axial dimensions of (I) are significantly larger than those of (II) while the *b* dimension remains essentially constant. Examination of the molecular packing, as shown by Fig. 2, indicates that the larger $OsBr_6^{2-}$ ions are responsible for the lattice expansion in the *a* and *c* direction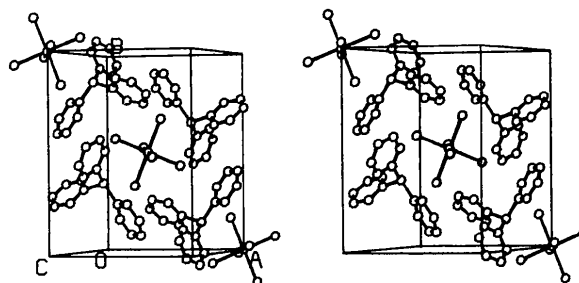s; however, the *b* dimension appears to be controlled by the end-to-end packing of the phosphonium ions and thus remains constant.

Hexahaloosmium ions in both lattices are essentially octahedral, exhibiting only slight differences in bond distances and angles. Bond distances and angles for the triphenylphosphonium ions are regular with the exception of one C–P–C angle in each compound [114·3 (9)° for (I), 115 (1)° for (II)], which deviates significantly from the expected tetrahedral geometry.

References

CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV, p. 71 (scattering factors), p. 148 (anomalous dispersion). Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

HINCKLEY, C. C., MATUSZ, M., KIBALA, P. A. & ROBINSON, P. D. (1987). *Acta Cryst.*, C43, 1880–1882.

Molecular Structure Corporation (1985). *TEXSAN Structure Analysis Package*. MSC, 3304 Longmire Drive, College Station, TX 77840, USA.

ROBINSON, P. D., HINCKLEY, C. C., KIBALA, P. A. & IKUO, A. (1988). In preparation.

Structure of Bis(2-acetylcyclohexanonato)copper(II)

By Amalia Tobon-Cervantes, R. A. Toscano, Maria J. Rosales, Juan M. Fernandez-G.* and Margarita I. Bernal-Uruchurtu

Instituto de Quimica de la Universidad Nacional Autonoma de México, Ciudad Universitaria, Circuito Exterior, Coyoacan 04510, Mexico DF

Abstract. [Cu(C$_8$H$_{11}$O$_2$)$_2$], $M_r = 341·9$, orthorhombic, *Pbca*, $a = 15·273$ (7), $b = 6·369$ (2), $c = 15·687$ (6) Å, $V = 1526$ (1) Å^3, $Z = 4$, $D_x = 1·486$ g cm^{-3}, λ(Mo $K\alpha$) $= 0·71069$ Å, $\mu = 14·45$ cm^{-1}, $F(000) = 716$, $T = 293$ K, $R = 0·0516$ for 862 observed reflections. The complex exhibits a square planar coordination around the metal atom. The ligand acts as a bidentate monoanion. The chelate ring is nearly planar while the

* Address correspondence to this author.