

title compound is isomorphous with the related Pd compound (Steffen & Palenik, 1976). The overall geometry of both compounds is the same: the major difference stems from shorter Ni—P and Ni—Cl distances (0.08 and 0.06 Å respectively).

The investigations were supported in part (ALS) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

References

- ALPER, H. (1975). *J. Organomet. Chem.* **84**, 347–350.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 GOSSELINK, J. W., BROUWERS, A. M. F., VAN KOTEN, G. & VRIEZE, K. (1982). *J. Chem. Soc. Dalton Trans.* pp. 397–406.
 GOSSELINK, J. W., BULTHUIS, H. & VAN KOTEN, G. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1342–1348.
 GOSSELINK, J. W., VAN KOTEN, G., VRIEZE, K., ZWANENBURG, B. & LAMMERINK, B. H. M. (1979). *J. Organomet. Chem.* **179**, 411–419.
 GOTZFRIED, F. & BECK, W. (1980). *J. Organomet. Chem.* **191**, 329–338.
 KRIEGE-SIMONDSSEN, J. & FELTHAM, R. D. (1983). *Inorg. Chim. Acta*, **71**, 185–194.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SPEK, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.
 STEFFEN, W. L. & PALENIK, G. J. (1976). *Inorg. Chem.* **15**, 2432–2438.

Acta Cryst. (1987). **C43**, 1880–1882

Structure of (Acetato)dibromobis(triphenylphosphine)osmium(III)

BY C. C. HINCKLEY,* M. MATUSZ AND P. A. KIBALA

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

AND P. D. ROBINSON

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

(Received 14 February 1987; accepted 13 May 1987)

Abstract. [OsBr₂(C₂H₃O₂)₂]{P(C₆H₅)₃]₂, *M_r* = 933.63, monoclinic, *P*2₁/*a*, *a* = 28.897 (8), *b* = 14.106 (5), *c* = 9.605 (4) Å, β = 93.21 (4)°, *V* = 3909 (4) Å³, *Z* = 4, *D_x* = 1.59 g cm⁻³, *Mo Kα*, λ = 0.71069 Å, μ = 57.33 cm⁻¹, *F*(000) = 1812, *T* = 295 K, *R* = 0.046, 3857 unique observed reflections. The complex was synthesized by refluxing an acetic acid/acetic anhydride solution containing OsBr₆²⁻, triphenylphosphine and sodium acetate. The central portion of the molecule contains a planar atomic array comprised of an Os atom bound to two *cis* Br atoms and a bidentate acetate ligand. Normal to the plane are two *trans* triphenylphosphine groups, bound to Os through their P atoms.

Introduction. (Acetato)dibromobis(triphenylphosphine)osmium(III) is an apparent member of a class of osmium complexes synthesized by Moore & Robinson (1979) with general formula [OsBr₂(O₂CR)₂]{P(C₆H₅)₃]₂, where *R* is aryl. Their preparation involved the air oxidation of [OsBr₂{P(C₆H₅)₃]₃] in the presence of the appropriate carboxylic acid. IR spectra indicated chelated arylcarboxylic ligands; a *trans* placement of

the Br ligands was proposed. The title compound was prepared in solution by reduction of the hexabromo-osmate(IV) ion, OsBr₆²⁻. The structure determination confirms the chelated binding of the carboxylate ligand, but the Br ligands are *cis* rather than *trans*.

Experimental. Preparation by dissolution of bis(tetra-*n*-butylammonium)hexabromoosmate(IV) (1.0 g, 0.87 mmol), triphenylphosphine (1.0 g, 3.8 mmol) and sodium acetate trihydrate (2.0 g, 14.7 mmol) in a mixture of 20.0 ml acetic acid and 20.0 ml acetic anhydride. Mixture refluxed for 10 min during which time yellow crystals appeared. Mixture cooled, filtered, and the solid washed with acetic acid and chilled ethyl ether (yield 0.68 g). Crystals obtained by dissolving the solid in dichloromethane and layering with *n*-hexane.

Crystal used for data collection was 0.21 × 0.11 × 0.05 mm, brown, bladed. Rigaku AFC5S diffractometer, graphite-monochromatized *Mo Kα* radiation, ω-2θ scans, scan speed 6° min⁻¹, maximum of 3 scan repetitions to obtain σ*F*/*F* < 0.10. Lattice parameters from least-squares fit of 16 reflections in 2θ range 9–22°. 7672 reflections measured (*h* = -34 to 34, *k* 0 to 16, *l* 0 to 11); 7212 reflections unique, 3857 observed

* Author to whom correspondence should be addressed.

($I > 3\sigma I$), $(\sin\theta)/\lambda_{\max} = 0.595 \text{ \AA}^{-1}$, $R_{\text{int}} = 1.3\%$ for 460 equivalent reflections. Three standard reflections (330, $\bar{3}\bar{3}0$, $2\bar{4}1$) varied by -1.11 , -0.63 and 0.96% respectively; thus no correction for decay was necessary. Data corrected for Lorentz and polarization. Numerical absorption correction performed (transmission range 0.54–0.74) using a modified version of the program *AGNOST* (Coppens, Leiserowitz & Rabinovich, 1965). Direct methods used to locate Os, Br and P atomic sites; Fourier and difference Fourier syntheses revealed all C-atom positions. Full-matrix least-squares refinement of F magnitudes performed on 407 variables including all non-H positional and anisotropic thermal parameters, one scale factor, and a secondary-extinction coefficient (0.70918×10^{-7}). Phenyl-ring H atoms placed in geometrically correct positions (C–H = 0.95 Å) but not refined. Two of the three methyl H atoms were located by a difference Fourier synthesis and the third H position was calculated; methyl H sites then geometrically optimized and fixed. H-atom B 's fixed at $1.2B_{\text{eq}}$ of associated C atom. Convergence yielded $R = 0.046$, $wR = 0.061$ [$w = 1/\sigma^2(|F_o|)$], $S = 1.48$ and $(\Delta/\sigma)_{\max} = 0.03$. Final difference synthesis showed twelve small intermolecular peaks (0.58 to 1.39 e Å⁻³) in geometrical configuration suggestive of minor disordered CH₂Cl₂ solvent; scanning-electron-microscope-based X-ray-energy spectroscopic analysis confirmed minor Cl presence. $(\Delta\rho)_{\min} = -0.72 \text{ e \AA}^{-3}$. Solvent peaks considered insignificant and were not included in the structural model. Atomic scattering factors and anomalous-dispersion corrections from Cromer & Waber (1974). All computer programs from the *TEXSAN* crystal structure analysis package (Molecular Structure Corporation, 1985).

Discussion. Positional and equivalent isotropic thermal parameters are given in Table 1; Table 2 presents selected interatomic distances and angles.*

In this complex the Os^{III} atom is bound to two *cis* Br atoms, two P atoms of *trans*-situated triphenylphosphine ligands, and a bidentate acetate ligand (Fig. 1). Acetate binding to the Os atom is slightly asymmetric with Os–O(1) and Os–O(2) bond distances of 2.109 (9) and 2.15 (1) Å, respectively. This bond-distance asymmetry is matched by a similar difference in the two Os–Br bonds, 2.450 (2) and 2.473 (2) Å. The longer Os–O bond is diametrically opposite to the shorter Os–Br bond. It is interesting to note that the average Os–O bond distance (2.130 Å) is shorter than

* Lists of structure factors, anisotropic thermal parameters, distances and angles involving the phenyl rings, H-atom coordinates and selected least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44050 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Os	0.304504 (20)	0.02128 (4)	0.86489 (5)	2.46 (2)
Br(1)	0.31612 (5)	-0.02357 (12)	0.62042 (14)	3.77 (7)
Br(2)	0.30365 (6)	0.19454 (10)	0.84694 (17)	3.92 (7)
P(1)	0.22261 (13)	0.00826 (25)	0.8167 (4)	2.7 (2)
P(2)	0.38658 (12)	0.0199 (3)	0.9099 (4)	3.1 (2)
O(1)	0.2947 (3)	0.0229 (8)	1.0808 (9)	3.5 (5)
O(2)	0.3012 (3)	-0.1112 (7)	0.9751 (11)	3.7 (5)
C(1)	0.1916 (5)	0.0997 (10)	0.7145 (15)	3.1 (7)
C(2)	0.2117 (5)	0.1447 (11)	0.6078 (14)	3.2 (7)
C(3)	0.1865 (7)	0.2127 (11)	0.5268 (16)	5 (1)
C(4)	0.1422 (6)	0.2342 (13)	0.5566 (20)	5 (1)
C(5)	0.1214 (6)	0.1892 (15)	0.6616 (22)	6 (1)
C(6)	0.1462 (6)	0.1235 (12)	0.7405 (20)	6 (1)
C(7)	0.1918 (5)	0.0031 (10)	0.9754 (14)	3.2 (7)
C(8)	0.1971 (6)	0.0782 (13)	1.0662 (18)	4.6 (9)
C(9)	0.1757 (7)	0.0833 (18)	1.1862 (22)	6 (1)
C(10)	0.1468 (8)	0.013 (2)	1.2223 (19)	8 (1)
C(11)	0.1398 (8)	-0.0655 (16)	1.1357 (25)	8 (1)
C(12)	0.1618 (6)	-0.0692 (13)	1.0081 (16)	4.8 (9)
C(13)	0.2079 (5)	-0.1012 (10)	0.7203 (14)	2.9 (7)
C(14)	0.1890 (6)	-0.0956 (11)	0.5846 (16)	4.2 (8)
C(15)	0.1811 (6)	-0.1779 (13)	0.5075 (16)	5 (1)
C(16)	0.1911 (6)	-0.2651 (13)	0.5688 (19)	5 (1)
C(17)	0.2085 (5)	-0.2718 (10)	0.7028 (16)	3.6 (7)
C(18)	0.2180 (5)	-0.1896 (11)	0.7781 (16)	3.7 (7)
C(19)	0.4160 (5)	-0.0824 (11)	0.8345 (15)	3.4 (7)
C(20)	0.3967 (6)	-0.1710 (11)	0.8482 (19)	4.8 (9)
C(21)	0.4184 (7)	-0.2482 (13)	0.7936 (23)	6 (1)
C(22)	0.4594 (8)	-0.2365 (16)	0.7221 (22)	7 (1)
C(23)	0.4779 (6)	-0.1475 (15)	0.7083 (19)	6 (1)
C(24)	0.4559 (6)	-0.0705 (12)	0.7643 (17)	4.3 (8)
C(25)	0.4028 (5)	-0.0114 (11)	1.0943 (14)	3.6 (7)
C(26)	0.4289 (6)	-0.0662 (12)	1.1522 (16)	4.3 (8)
C(27)	0.4377 (7)	-0.0726 (13)	1.2964 (18)	5 (1)
C(28)	0.4227 (6)	-0.0030 (17)	1.3787 (18)	6 (1)
C(29)	0.3974 (6)	0.0759 (15)	1.3258 (17)	6 (1)
C(30)	0.3875 (5)	0.0834 (12)	1.1831 (15)	4.1 (8)
C(31)	0.4180 (5)	0.1208 (10)	0.8507 (14)	3.3 (7)
C(32)	0.4524 (6)	0.1666 (12)	0.9323 (16)	4.6 (8)
C(33)	0.4778 (6)	0.2402 (13)	0.8821 (21)	5 (1)
C(34)	0.4683 (7)	0.2713 (13)	0.7463 (23)	6 (1)
C(35)	0.4352 (6)	0.2282 (13)	0.6633 (17)	5 (1)
C(36)	0.4107 (6)	0.1554 (12)	0.7145 (16)	4.3 (8)
C(37)	0.2958 (6)	-0.0670 (13)	1.0877 (17)	3.8 (8)
C(38)	0.2904 (7)	-0.1139 (14)	1.2229 (18)	6 (1)

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

Os	O(1)	2.109 (9)	P(1)	C(13)	1.84 (1)		
Os	O(2)	2.15 (1)	P(2)	C(31)	1.80 (1)		
Os	P(2)	2.387 (4)	P(2)	C(25)	1.81 (1)		
Os	P(1)	2.393 (4)	P(2)	C(19)	1.84 (2)		
Os	Br(2)	2.450 (2)	O(1)	C(37)	1.27 (2)		
Os	Br(1)	2.473 (2)	O(2)	C(37)	1.27 (2)		
P(1)	C(7)	1.81 (1)	C(37)	C(38)	1.47 (2)		
P(1)	C(1)	1.82 (1)					
O(1)	Os	O(2)	60.9 (4)	C(7)	P(1)	C(13)	106.2 (6)
O(1)	Os	P(2)	90.5 (3)	C(7)	P(1)	Os	111.6 (5)
O(1)	Os	P(1)	90.3 (3)	C(1)	P(1)	C(13)	103.3 (6)
O(1)	Os	Br(2)	93.3 (3)	C(1)	P(1)	Os	120.0 (5)
O(1)	Os	Br(1)	165.8 (3)	C(13)	P(1)	Os	111.1 (5)
O(2)	Os	P(2)	88.5 (3)	C(31)	P(2)	C(25)	104.7 (6)
O(2)	Os	P(1)	87.6 (3)	C(31)	P(2)	C(19)	104.1 (7)
O(2)	Os	Br(2)	154.2 (3)	C(31)	P(2)	Os	116.8 (5)
O(2)	Os	Br(1)	104.9 (3)	C(25)	P(2)	C(19)	103.5 (7)
P(2)	Os	P(1)	175.1 (1)	C(25)	P(2)	Os	112.1 (5)
P(2)	Os	Br(2)	91.5 (1)	C(19)	P(2)	Os	114.3 (5)
P(2)	Os	Br(1)	89.0 (1)	C(37)	O(1)	Os	92 (1)
P(1)	Os	Br(2)	93.3 (1)	C(37)	O(2)	Os	90.2 (9)
P(1)	Os	Br(1)	89.0 (1)	O(1)	C(37)	C(38)	119 (2)
Br(2)	Os	Br(1)	100.93 (6)	O(2)	C(37)	C(38)	124 (2)
C(7)	P(1)	C(1)	103.4 (7)	O(2)	C(37)	O(1)	117 (1)

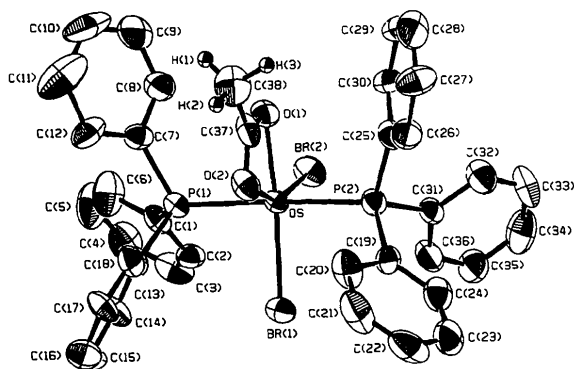


Fig. 1. Molecular structure and numbering scheme.

the mean Os—O distance of 2.148 Å reported by Behling, Capparelli, Skapski & Wilkinson (1982), for the bidentate acetate found in the Os^{VI} complex $K[OsO_2(O_2CMe)_3] \cdot 2MeCO_2H$. Least-squares cal-

culations reveal a near-perfect central plane composed of the Os atom, the acetate ligand, and two Br atoms. Triphenylphosphine ligands reside on either side of the central plane and exhibit a P(1)—Os—P(2) bond angle of 175.1 (1)°. The central plane forms a dihedral angle of 89.70° with the plane defined by P(1)—Os—P(2).

References

- BEHLING, T., CAPPARELLI, M. V., SKAPSKI, A. C. & WILKINSON, G. (1982). *Polyhedron*, **1**, 840–841.
 COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035.
 CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht, The Netherlands.)
 Molecular Structure Corporation (1985). *TEXSAN Structure Analysis Package*. MSC, 3304 Longmire Drive, College Station, TX 77840, USA.
 MOORE, D. S. & ROBINSON, S. D. (1979). *Inorg. Chem.* **18**, 2307–2309.

Acta Cryst. (1987). **C43**, 1882–1885

Structure of Tetrakis(biuret)samarium(III) Nitrate, $[Sm(NH_2CONHCONH_2)_4](NO_3)_3$

BY SALIM F. HADDAD

Department of Chemistry, The University of Jordan, Amman, Jordan

(Received 21 April 1987; accepted 18 May 1987)

Abstract. $[Sm(C_2H_5N_3O_2)_4](NO_3)_3$, $M_r = 748.69$, monoclinic, $C2/c$, $a = 17.256(2)$, $b = 7.090(1)$, $c = 20.545(2)$ Å, $\beta = 109.6(5)^\circ$, $V = 2368(8)$ Å³, $Z = 4$, $D_m = 2.090$, $D_x = 2.100$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 26.4$ cm⁻¹, $F(000) = 1484$, ambient temperature, $R = 0.0185$, $wR = 0.0252$ for 1526 reflections with $I_o > 3.0\sigma(I_o)$. Sm is located at site of symmetry 2. The two biuret ligands in the asymmetric unit are samarium-bonded as bidentates *via* the carbonyl O atoms with a twist (15.1, 15.7°) about the oxygen–oxygen line. One of the three nitrates in the molecular unit is centred at $\bar{1}$ and is disordered. The three O atoms of the disordered nitrate are distributed at eight positions, four with occupancy $\frac{1}{2}$ and four with occupancy $\frac{1}{4}$. The eight O-atom positions are imposed in part by hydrogen bonding. The CN = 8 coordination polyhedron is found by shape-parameter analysis to be closer to the square antiprism D_{4d} than the dodecahedron D_{2d} or the cube O_h . The twist angles, ϕ , in the dodecahedral *BAAB* trapezoids are 30.6 and 26.3°. The bidentate ligands span opposite edges of the rectangular faces of the square antiprism.

Introduction. Biuret (NH₂CONHCONH₂) was first reported as a decomposition product of urea and of urea nitrate (Wiedemann, 1848). Wiedemann also noted the formation of a characteristic red–violet colour as biuret is added to copper(II) sulfate in alkaline media, an observation which is the basis of the well known biuret reaction, where a violet–red colour is produced when cupric salts are added to proteins or polypeptides in alkaline media (Brücke, 1883; Schiff, 1898). With biuret, the colour is believed to be due to the violet hydroxy-bridged dimeric $K_2[Cu(NHCONHCONH)OH]_2 \cdot 4H_2O$ complex (McLellan & Melson, 1967), or due to the red $K_2[Cu(NHCONHCONH)_2] \cdot 4H_2O$ complex (Freeman, Smith & Taylor, 1961). In both the violet and the red complexes biuret behaves as a bidentate dianion bonding to Cu^{II} *via* the amide N atoms in a *cis-cis* configuration. In the solid state free biuret assumes a *trans-cis* configuration as found in the crystal structure of biuret hydrate (Hughes, Yakel & Freeman, 1961). It also assumes the *trans-cis* configuration in the crystal structure of bis(biuret)cadmium(II) chloride