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Tetraphenylphosphonium *trans*-Aquatetrabromo(carbonyl)osmate(III), *trans*-[(C₆H₅)₄P][OsBr₄(CO)(H₂O)]

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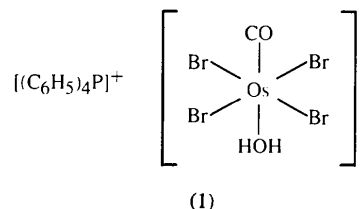
Abstract

The X-ray structure determination of tetraphenylphosphonium *trans*-aquatetrabromo(carbonyl)osmate(III), *trans*-[(C₆H₅)₄P][OsBr₄(CO)(H₂O)], at 293 K has revealed slightly distorted octahedral coordination of the osmium(III) atom, with H₂O *trans* to the almost linear carbonyl group. The distances are 1.795 (10) for Os—C, 2.181 (6) for Os—O_w and 1.164 (9) Å for C—O; among the Os—Br bond lengths two are shorter [2.4692 (8) and 2.4753 (10) Å] and two are longer [2.5042 (8) and 2.5072 (8) Å]. Centrosymmetric dimers of the complex anions are formed by intermolecular hydrogen bonding between the coordinated water molecule and the two Br ligands that form longer bonds to the central atom.

Comment

We are currently studying the mutual influences of different ligands in octahedral complexes on their spectroscopic and structural properties. The halogeno-carbonyl compounds of osmium(III) of the types [OsX₅(CO)]²⁻ (X = Cl, Br, I) and *trans*-[OsX₄(CO)₂]⁻ (X = Br, I) have been synthesized and well charac-

terized by vibrational spectroscopy (Cleare & Griffith, 1970; Johannsen & Preetz, 1977a) and in some cases by X-ray structure determination (Bergardt *et al.*, 1993a,b, 1994). The related aqua complexes of the type *trans*-[OsX₄(CO)(H₂O)]⁻ are formed by hydrolysis of the monocarbonylates (Johannsen & Preetz, 1977b; Bottomley, Lin & White, 1978). The substitution of the Br ligand *trans* to CO causes a shift of the carbonyl stretching frequency from 1949 to 1989 cm⁻¹ (10 K, KBr disc) in the title compound, (1).



(1) crystallizes in space group *P* $\bar{1}$ with all atoms located in general positions. The complex anion, which is represented in Fig. 1 with its labelling scheme, has almost *mm*4 (*C*_{4v}) local symmetry.

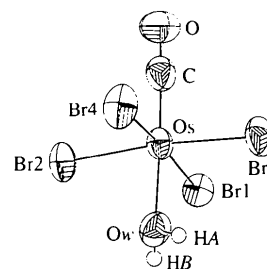


Fig. 1. View of the *trans*-[OsBr₄(CO)(H₂O)]⁻ anion showing 50% probability ellipsoids. H atoms are drawn as spheres of arbitrary size.

The Os—C distance in (1) of 1.795 (10) Å is slightly shorter than that in K₂[OsBr₅(CO)], (2) [1.84 (2) Å; Bergardt *et al.*, 1994], and significantly shorter than those in *trans*-(Bu₄N)[OsBr₄(CO)₂], (3) [1.90 (3) and 1.91 (4) Å; Bergardt *et al.*, 1993a]. On the other hand, the Os—O_w distance [2.181 (6) Å] in (1) is somewhat longer than the sum of the covalent radii of osmium and oxygen (2.03 Å; Pauling, 1960). These results are consistent with a decreasing *trans* influence of the ligands in the order CO > Br > H₂O. The effect on the C—O distances [1.164 (9) in (1), 1.16 (3) in (2), and 1.14 (4) and 1.21 (4) Å in (3)] is uncertain, due to lower accuracy of determination. The Os—C, Os—O_w and C—O distances in (1) are in good agreement with the corresponding averaged distances in *trans*-[(C₆H₅)₄P][OsCl₄(CO)(H₂O)], (4) (2.19, 1.81 and 1.16 Å; Gorbunova *et al.*, 1994), and the carbonyl stretching frequencies are virtually equal [1987 in (4),

1989 cm^{-1} in (1)]. Thus, if at all, the *cis* influence of the halogen ligands on the $(H_2O)–Os–(CO)$ axis is very small. As in other monocarbonyl complexes, the Os atom is slightly displaced from the best plane through the four Br ligands, by 0.115 (1) Å, towards the carbonyl group. Two of the Os–Br distances, Os–Br1 and Os–Br3 [2.5042 (8) and 2.5072 (8) Å, respectively], are considerably longer than the other two, Os–Br2 and Os–Br4 [2.4692 (8) and 2.4753 (10) Å, respectively]. The difference is probably caused by weak intermolecular hydrogen bonds from Br1 and Br3 to the water ligand of a neighbouring complex (Fig. 2). This is analogous to the situation in the structures of *trans*- $[(C_6H_5)_4P][OsCl_4(NS)(H_2O)]$ (Pandey, Roesky, Noltemeyer & Sheldrick, 1984) and $[H_9O_4][FeCl_4]$ (Gustafsson, 1986) in which Cl ligands involved in hydrogen bonds form longer bonds to the central atom by *ca* 0.02 Å. The $Br \cdots H$ hydrogen-bond distances are shorter than the sum of the van der Waals radii ($r_H = 1.2$, $r_{Br} = 1.85$ Å; Bondi, 1964). The $Br \cdots Ow$ distances and $Br \cdots H–Ow$ angles (Table 3) are comparable with those recently reported for $Br \cdots H–N$ hydrogen bonds in two organometallic bromide salts (Haber, Fábry & Petříček, 1995; Parker & Breneman, 1995).

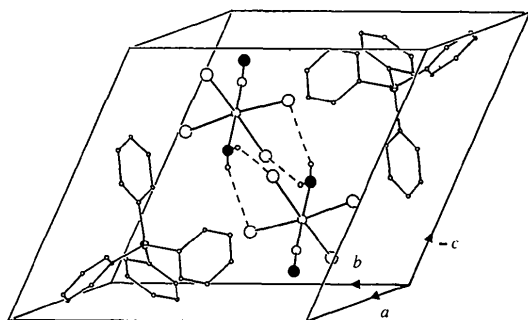


Fig. 2. View of the crystal packing almost along *a*. H atoms of the cations are omitted for clarity.

In the IR spectrum we have observed absorption bands at 3330 and 1615 cm^{-1} (10 K, KBr disc) and assigned them to O–H stretching and H–O–H bending vibrations of the coordinated water molecule (Nakamoto, 1986).

Experimental

The title compound was prepared by hydrolysis of $K_2[OsBr_5CO]$ in water at 293 K, subsequent precipitation using $[(C_6H_5)_4P][HSO_4]$, and recrystallization from dichloromethane/ether solution to give dark red single crystals.

Crystal data

$(C_{24}H_{20}P)[OsBr_4(CO)(H_2O)]$ Mo $K\alpha$ radiation
 $M_r = 895.24$ $\lambda = 0.71069$ Å

Triclinic

$P\bar{1}$
 $a = 10.5458$ (9) Å
 $b = 12.4347$ (10) Å
 $c = 12.5963$ (12) Å
 $\alpha = 65.749$ (9)°
 $\beta = 85.167$ (8)°
 $\gamma = 68.828$ (7)°
 $V = 1400.4$ (2) Å³
 $Z = 2$
 $D_x = 2.123$ Mg m⁻³

Cell parameters from 25 reflections

$\theta = 5.827–11.263$ °
 $\mu = 10.337$ mm⁻¹
 $T = 293$ (2) K
 Prismatic
 $0.30 \times 0.20 \times 0.20$ mm
 Dark red

Data collection

Enraf–Nonius CAD-4-Turbo
 four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 ψ scans (North, Phillips
 & Mathews, 1968)
 $T_{min} = 0.55$, $T_{max} = 1.00$
 5203 measured reflections
 4913 independent reflections

3507 observed reflections
 $[I > 2\sigma(I)]$
 $R_{int} = 0.0198$
 $\theta_{max} = 24.96$ °
 $h = -12 \rightarrow 12$
 $k = -13 \rightarrow 14$
 $l = 0 \rightarrow 14$
 3 standard reflections
 frequency: 240 min
 intensity decay: 3.9%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0298$
 $wR(F^2) = 0.0556$
 $S = 1.069$
 4912 reflections
 306 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0189P)^2 + 2.6281P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
 $\Delta\rho_{max} = 0.880$ e Å⁻³
 $\Delta\rho_{min} = -0.516$ e Å⁻³
 Extinction correction: none
 Atomic scattering factors
 from *International Tables
 for Crystallography* (1992,
 Vol. C, Tables 4.2.6.8 and
 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Os	0.67509 (3)	0.26071 (3)	0.66938 (3)	0.04705 (9)
Br1	0.77001 (7)	0.39423 (7)	0.49915 (6)	0.0543 (2)
Br2	0.74873 (8)	0.09705 (7)	0.59104 (7)	0.0631 (2)
Br3	0.58407 (10)	0.44174 (8)	0.72967 (7)	0.0710 (3)
Br4	0.56277 (10)	0.13595 (8)	0.82619 (8)	0.0812 (3)
C	0.8285 (10)	0.1882 (8)	0.7633 (7)	0.066 (2)
O	0.9266 (7)	0.1371 (6)	0.8264 (6)	0.091 (2)
Ow	0.4877 (5)	0.3419 (5)	0.5579 (5)	0.0628 (14)
P	0.8987 (2)	0.6842 (2)	0.73605 (15)	0.0421 (4)
C11	1.0067 (7)	0.7367 (6)	0.7900 (6)	0.045 (2)
C21	0.9993 (6)	0.5288 (6)	0.7463 (5)	0.043 (2)
C31	0.7567 (7)	0.6823 (6)	0.8240 (5)	0.046 (2)
C41	0.8325 (7)	0.7882 (6)	0.5880 (5)	0.043 (2)
C12	0.9680 (8)	0.7820 (7)	0.8749 (6)	0.059 (2)
C13	1.0559 (9)	0.8150 (8)	0.9194 (7)	0.068 (2)
C14	1.1820 (9)	0.8013 (7)	0.8820 (8)	0.069 (2)
C15	1.2237 (8)	0.7559 (7)	0.7983 (7)	0.063 (2)
C16	1.1371 (7)	0.7233 (7)	0.7522 (6)	0.055 (2)
C22	1.1049 (8)	0.4516 (7)	0.8311 (6)	0.062 (2)
C23	1.1857 (9)	0.3342 (7)	0.8373 (8)	0.074 (2)
C24	1.1590 (8)	0.2928 (7)	0.7599 (7)	0.067 (2)
C25	1.0545 (9)	0.3674 (7)	0.6766 (7)	0.068 (2)
C26	0.9709 (7)	0.4854 (7)	0.6691 (6)	0.054 (2)
C32	0.6620 (7)	0.7956 (7)	0.8212 (6)	0.053 (2)
C33	0.5588 (7)	0.7953 (8)	0.8960 (6)	0.059 (2)
C34	0.5478 (8)	0.6812 (8)	0.9696 (6)	0.063 (2)
C35	0.6366 (8)	0.5701 (8)	0.9720 (6)	0.062 (2)

C36	0.7433 (7)	0.5680 (7)	0.8980 (6)	0.051 (2)
C42	0.7051 (8)	0.8008 (7)	0.5504 (6)	0.059 (2)
C43	0.6553 (9)	0.8778 (8)	0.4383 (7)	0.068 (2)
C44	0.7317 (9)	0.9411 (7)	0.3630 (7)	0.063 (2)
C45	0.8568 (8)	0.9274 (6)	0.3978 (6)	0.057 (2)
C46	0.9095 (7)	0.8514 (6)	0.5107 (6)	0.047 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Os—C	1.795 (10)	Os—Br1	2.5042 (8)
Os—Ow	2.181 (6)	Os—Br3	2.5072 (8)
Os—Br2	2.4692 (8)	C—O	1.164 (9)
Os—Br4	2.4753 (10)		
C—Os—Ow	177.8 (3)	Br2—Os—Br1	88.70 (3)
C—Os—Br2	92.6 (2)	Br4—Os—Br1	174.91 (4)
Ow—Os—Br2	86.08 (14)	C—Os—Br3	93.0 (2)
C—Os—Br4	90.5 (3)	Ow—Os—Br3	88.42 (14)
Ow—Os—Br4	87.87 (15)	Br2—Os—Br3	173.97 (3)
Br2—Os—Br4	90.66 (3)	Br4—Os—Br3	91.60 (3)
C—Os—Br1	94.6 (3)	Br1—Os—Br3	88.55 (3)
Ow—Os—Br1	87.04 (15)	O—C—Os	177.4 (7)

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	H...A	D...A	D—H...A
Ow ¹ —HA...Br1	2.53 (5)	3.258 (5)	144 (7)
Ow ¹ —HB...Br3	2.67 (4)	3.452 (6)	156 (7)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

H atoms of the cation were refined using a riding model with a common displacement parameter. H atoms of the water molecule were found from a Fourier map and refined with a distance restraint of 0.85 (2) \AA for O—H and a fixed displacement parameter of 0.085 \AA^2 .

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diaquabis(4-amino-3-methyl-4,5-dihydro-1H-1,2,4-triazole-5-thione)nickel(II) Nitrate: a Sulfur–Nitrogen Chelate

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Abstract

The title compound, $[\text{Ni}(\text{C}_3\text{H}_6\text{N}_4\text{S})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$, is an octahedral complex of nickel(II) in which two triazole ligands are coordinated in a bidentate fashion through the amine and thione substituents. The coordination sphere has the two S atoms *trans* with respect to each other, while the N atoms and two water molecules are ligated in *cis* positions. The Ni—S and Ni—N bond lengths in the chelate are consistent with those in similar octahedral nickel complexes. The geometry of the