Crystal and Molecular Structure of Hydroxodinitrosylbis(triphenylphosphine)osmium(II) Hexafluorophosphate

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The crystal and molecular structure of the title compound has been determined from three-dimensional *X*-ray data collected by counter methods. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 18{\cdot}433(2)$, $b = 10{\cdot}654(1)$, $c = 18{\cdot}952(4)$ Å and $\beta = 91{\cdot}80(2)°$. Block-diagonal least-squares refinement has led to a final R of 0·057 for 3646 observed reflections. The geometry about the metal is that of a tetragonal pyramid with two *trans*-phosphorus atoms, a hydroxo and a linear nitrosyl group forming the basal plane; the apical position is occupied by a bent nitrosyl group.

CO-ORDINATION of the nitrosyl group in both linear and bent bonding modes is well established. When found in the linear form this ligand is best formulated as NO^+ and is regarded as a strong π-acceptor as shown by the relatively short metal–nitrogen bond distances (1·57—1·77 Å)[1] which have been observed. In contrast the bent nitrosyl group is best formulated as NO^-, a ligand which acts primarily as a σ-donor and for which longer metal–nitrogen distances (1·89—1·97 Å)[1] have been found. The sp^2 hybridisation of the nitrogen atom in co-ordinated NO^- normally results in an angle of *ca.* 120° with the metal.

Closely related to the nitrosyl bonding mode in five-co-ordinate complexes of Group VIII metals is the configuration of the central metal. Thus, formally d^6 metal complexes are found with the tetragonal pyramidal arrangement and a bent nitrosyl group {*e.g.* $[IrI(CO)(NO)(PPh_3)_2]^+$ (ref. 2), $[IrCl_2(NO)(PPh_3)_2]$ (ref. 3), and $[IrIMe(NO)(PPh_3)_2]$ (ref. 4)} whereas the trigonal

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[1] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1479.

[2] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1282.

[3] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1035.

[4] D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1043.

bipyramidal geometry and linear nitrosyl-bonding mode are associated with d^8 metals {*e.g.* $[Ru(NO)(NO_2)_4(OH)]^{2-}$ (ref. 5) and $[Os(CO)_2(NO)(PPh_3)_2]^+$ (ref. 6)}. The metal configuration and nitrosyl geometry is, however, sensitive to the electronegativity and steric requirements of the other ligands present so that the introduction of the hydrido-group, with its low electronegativity and minimal steric requirement, results in the formation [1] of the trigonal bipyramidal iridium(I) complex, $[IrH(NO)(PPh_3)_3]^+$ with a linear nitrosyl group. The effect on the metal configuration and nitrosyl bonding of including two nitrosyl groups in a five-co-ordinate complex was investigated by preparing $[Os(OH)(NO)_2(PPh_3)_2]^+$ from the reaction between $[Os(NO)_2(PPh_3)_2]$ and oxygen in the presence of HPF_6 or HBF_4.[7] Co-ordination of the nitrosyl groups in both bonding modes was suspected from the i.r. evidence which showed two distinct bands at 1842 and 1632 cm^{-1} for the BF_4^- salt.

To determine unequivocally the nitrosyl bonding and also to investigate the co-ordination geometry of the osmium atom we have carried out a single-crystal analysis of $[Os(OH)(NO)_2(PPh_3)_2]PF_6$.

EXPERIMENTAL

Unit-cell constants for the orange-brown crystals were determined from a least-squares refinement [8] of the setting angles of twelve reflections centred on a Hilger and Watts automatic four-circle diffractometer.

Crystal Data.—$C_{36}H_{31}N_2O_3OsP_2{}^+F_6P^-$, $M = 936·8$, Monoclinic, $a = 18·433(2)$, $b = 10·654(1)$, $c = 18·952(4)$ Å, $\beta = 91·80(2)°$, $U = 3720$ Å^3, $D_m = 1·67$, $Z = 4$, $D_c = 1·67$. Space group $P2_1/c$. Mo-K_α radiation, $\lambda = 0·7107$ Å; μ(Mo-K_α) $= 38·2$ cm^{-1}. The ω—2θ technique was used to record 3646 independent reflections for which $I > 3\sigma(I)$. The intensity data were processed according to the procedure of Ibers [9] with $p = 0·05$ and absorption corrections were applied.[10]

A 'sharpened' Patterson synthesis revealed the sites of the osmium and two phosphorus atoms. A structure-factor calculation based on the osmium atom alone returned a conventional reliability factor, R, of 0·28, whereas all three atoms gave R as 0·24. From an electron-density map based on the second calculation, the remaining forty-eight non-hydrogen atoms were located (R 0·18). The atomic scattering factors used for the osmium atom were those of ref. 11 and for all other atoms from ref. 12.

Five cycles of block-diagonal least-squares refinement assuming isotropic motion lowered R to 0·104 and R' to 0·103 $[R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2$, where the weight, w, is given by $4F_o{}^2/\sigma^2(F_o{}^2)]$; the function minimised is $\Sigma w(|F_o| - |F_c|)^2$. All atoms other than those of the phenyl groups and the oxygen of the hydroxo-group were assigned anisotropic thermal parameters and after a further four cycles, which included the effects of anomalous dispersion in the calculation of F_c (the values of $\Delta f'$ and $\Delta f''$ for osmium were from ref. 13), the refinement converged with R 0·057 and R' 0·062. At this stage the average parameter shift was $< 0·3\sigma$. No attempt was made to include hydrogen-atom positions in the calculations. Analysis of the weighting scheme used showed that the function $\langle w\Delta F^2\rangle$ was approximately constant over a range of $|F_o|$ values thus justifying the value chosen for p.

TABLE 1

Atomic co-ordinates and isotropic temperature parameters, with standard deviations in parentheses

Atom	x/a	y/b	z/c	B/Å^2
Os	0·22516(2)	0·29666(5)	0·38029(3)	
P(1)	0·1239(2)	0·1827(3)	0·4289(2)	
P(2)	0·3455(2)	0·3528(3)	0·3412(2)	
P(3)	0·7128(3)	0·4091(5)	0·3087(3)	
F(1)	0·6354(8)	0·4644(16)	0·3110(12)	
F(2)	0·6972(12)	0·3256(16)	0·2452(9)	
F(3)	0·7401(10)	0·5138(14)	0·2610(8)	
F(4)	0·7857(8)	0·3538(17)	0·3203(14)	
F(5)	0·7263(10)	0·4973(14)	0·3728(8)	
F(6)	0·6823(9)	0·3043(14)	0·3598(8)	
O(1)	0·1696(6)	0·2760(12)	0·2376(6)	
O(2)	0·1646(6)	0·5370(10)	0·3688(7)	
O(3)	0·2705(4)	0·2673(8)	0·4723(4)	3·1(2)
N(1)	0·1941(6)	0·2874(13)	0·2987(7)	
N(2)	0·1947(7)	0·4583(12)	0·4015(7)	
C(111)	0·0468(7)	0·1670(13)	0·3701(7)	3·9(3)
C(112)	0·0149(9)	0·2780(17)	0·3456(9)	6·0(4)
C(113)	−0·0504(10)	0·2709(18)	0·3001(10)	6·6(4)
C(114)	−0·0804(10)	0·1563(18)	0·2844(10)	6·6(4)
C(115)	−0·0489(9)	0·0457(17)	0·3088(9)	5·8(4)
C(116)	0·0161(9)	0·0486(16)	0·3530(9)	5·2(4)
C(121)	0·0879(8)	0·2532(13)	0·5071(8)	3·8(3)
C(122)	0·0147(9)	0·2352(15)	0·5220(9)	5·2(4)
C(123)	−0·0136(9)	0·2905(20)	0·5842(9)	6·3(4)
C(124)	0·0296(9)	0·3675(16)	0·6245(9)	5·3(4)
C(125)	0·1021(9)	0·3826(17)	0·6112(9)	5·6(4)
C(126)	0·1326(8)	0·3278(14)	0·5525(8)	4·5(3)
C(131)	0·1563(8)	0·0264(14)	0·4511(8)	4·1(3)
C(132)	0·1437(8)	−0·0278(14)	0·5163(8)	4·2(3)
C(133)	0·1713(9)	−0·1484(16)	0·5323(9)	5·4(4)
C(134)	0·2117(9)	−0·2094(18)	0·4823(9)	5·8(4)
C(135)	0·2248(10)	−0·1570(17)	0·4186(10)	6·4(4)
C(136)	0·1953(9)	−0·0359(15)	0·3994(9)	5·1(3)
C(211)	0·3385(7)	0·3795(13)	0·2475(7)	3·4(3)
C(212)	0·3512(8)	0·2816(15)	0·2018(8)	4·7(3)
C(213)	0·3335(8)	0·2973(17)	0·1291(8)	5·0(3)
C(214)	0·3067(9)	0·4122(16)	0·1068(9)	5·3(4)
C(215)	0·2925(9)	0·5116(16)	0·1507(9)	5·4(4)
C(216)	0·3105(8)	0·4930(14)	0·2245(8)	4·1(3)
C(221)	0·4077(7)	0·2239(12)	0·3589(7)	3·4(3)
C(222)	0·4823(9)	0·2430(15)	0·3488(9)	5·2(4)
C(223)	0·5304(10)	0·1405(19)	0·3615(10)	6·7(4)
C(224)	0·5058(11)	0·0246(20)	0·3788(11)	7·1(5)
C(225)	0·4303(12)	0·0048(23)	0·3833(12)	8·5(6)
C(226)	0·3818(10)	0·1089(19)	0·3757(10)	6·5(4)
C(231)	0·3873(7)	0·4899(12)	0·3842(7)	2·9(2)
C(232)	0·4348(9)	0·5620(16)	0·3480(9)	5·1(4)
C(233)	0·4727(9)	0·6620(17)	0·3816(9)	5·9(4)
C(234)	0·4588(10)	0·6818(18)	0·4545(10)	6·4(4)
C(235)	0·4106(9)	0·6091(18)	0·4922(9)	6·0(4)
C(236)	0·3735(8)	0·5090(15)	0·4542(8)	4·6(3)

Final atomic co-ordinates and isotropic temperature factors together with their estimated standard deviations are listed in Table 1;* anisotropic thermal parameters together with their estimated standard deviations are

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* Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21202 (32 pp., 1 microfiche). For details, see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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[13] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

listed in Table 2. The numbering scheme and a perspective view of the molecule are shown in Figures 1 and 2 respectively. Bond distances and angles together with their estimated standard deviations are listed in Tables 3 and 4. The root-mean-square amplitudes of vibration of the anisotropic atoms are given in Table 5. Planes of 'best fit' through various groups of atoms have been calculated and their equations with the displacements of relevant atoms from them are listed in Table 6.

TABLE 2

Anisotropic thermal parameters * ($\times 10^4$), with standard deviations in parentheses

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Os	18·3(1)	61·7(3)	28·5(1)	−8·1(6)	2·2(2)	8·1(7)
P(1)	22(1)	70(4)	35(1)	−17(3)	7(2)	0(4)
P(2)	21(1)	62(3)	31(1)	−5(3)	7(2)	3(3)
P(3)	52(2)	92(5)	62(2)	5(5)	5(4)	8(6)
F(1)	59(6)	257(23)	193(13)	41(20)	−4(15)	112(29)
F(2)	188(13)	244(22)	81(7)	−143(27)	2(15)	−100(20)
F(3)	185(10)	157(16)	101(6)	−36(21)	156(11)	63(17)
F(4)	58(5)	271(23)	270(18)	135(17)	24(16)	74(34)
F(5)	110(8)	230(18)	84(6)	−54(22)	8(12)	−110(18)
F(6)	115(7)	142(14)	111(7)	−17(21)	81(11)	16(21)
O(1)	41(4)	147(14)	51(5)	−21(13)	8(7)	−16(14)
O(2)	46(4)	78(11)	74(6)	27(12)	−24(8)	−6(14)
N(1)	42(4)	96(12)	38(4)	6(15)	37(6)	−18(15)
N(2)	31(4)	101(14)	46(5)	31(13)	16(8)	−3(15)

* The scattering factor is of the form: $f = f_0 \exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

TABLE 3

Bond distances (Å), with standard deviations in parentheses

Os–P(1)	2·432(4)	C(133)–C(134)	1·38(2)
Os–P(2)	2·436(3)	C(134)–C(135)	1·36(3)
Os–N(1)	1·63(1)	C(135)–C(136)	1·44(2)
Os–N(2)	1·86(1)	C(211)–C(212)	1·38(2)
Os–O(3)	1·935(8)	C(211)–C(216)	1·38(2)
P(1)–C(111)	1·79(1)	C(212)–C(213)	1·42(2)
P(1)–C(121)	1·80(1)	C(213)–C(214)	1·38(2)
P(1)–C(131)	1·81(2)	C(214)–C(215)	1·38(2)
P(2)–C(211)	1·80(1)	C(215)–C(216)	1·44(2)
P(2)–C(221)	1·81(1)		
P(2)–C(231)	1·83(1)	C(221)–C(222)	1·41(2)
O(1)–N(1)	1·24(2)	C(221)–C(226)	1·36(2)
O(2)–N(2)	1·17(2)	C(222)–C(223)	1·42(3)
C(111)–C(112)	1·39(2)	C(223)–C(224)	1·36(3)
C(111)–C(116)	1·42(2)	C(224)–C(225)	1·41(3)
C(112)–C(113)	1·46(3)	C(225)–C(226)	1·43(3)
C(113)–C(114)	1·37(3)	C(231)–C(232)	1·37(2)
C(114)–C(115)	1·39(3)	C(231)–C(236)	1·37(2)
C(115)–C(116)	1·44(2)	C(232)–C(233)	1·41(2)
C(121)–C(122)	1·40(2)	C(233)–C(234)	1·43(3)
C(121)–C(126)	1·42(2)	C(234)–C(235)	1·39(3)
C(122)–C(123)	1·43(2)	C(235)–C(236)	1·45(2)
C(123)–C(124)	1·36(3)	P(3)–F(1)	1·54(2)
C(124)–C(125)	1·38(2)	P(3)–F(2)	1·52(2)
C(125)–C(126)	1·39(2)	P(3)–F(3)	1·53(2)
C(131)–C(132)	1·39(2)	P(3)–F(4)	1·48(2)
C(131)–C(136)	1·40(2)	P(3)–F(5)	1·55(2)
C(132)–C(133)	1·41(2)	P(3)–F(6)	1·59(2)

TABLE 4

Bond angles (°), with standard deviations in parentheses

P(1)–Os–P(2)	162·8(1)
P(1)–Os–O(3)	83·8(3)
P(1)–Os–N(1)	94·4(5)
P(1)–Os–N(2)	98·0(4)
P(2)–Os–O(3)	86·7(3)
P(2)–Os–N(1)	91·3(5)
P(2)–Os–N(2)	97·0(4)
O(3)–Os–N(1)	166·1(5)
O(3)–Os–N(2)	94·6(5)
N(1)–Os–N(2)	99·3(6)
Os–P(1)–C(111)	114·5(5)
Os–P(1)–C(121)	114·2(5)
Os–P(1)–C(131)	107·1(5)
Os–P(2)–C(211)	107·5(5)
Os–P(2)–C(221)	109·6(4)
Os–P(2)–C(231)	115·8(4)
Os–N(1)–O(1)	177·6(1·2)
Os–N(2)–O(2)	133·6(1·2)
C(111)–P(1)–C(121)	104·2(7)
C(111)–P(1)–C(131)	108·0(7)
C(121)–P(1)–C(131)	108·6(7)
C(211)–P(2)–C(221)	109·1(6)
C(211)–P(2)–C(231)	109·2(6)
C(221)–P(2)–C(231)	105·5(6)
P(1)–C(111)–C(112)	116·6(1·1)
P(1)–C(111)–C(116)	122·0(1·1)
P(1)–C(121)–C(122)	119·3(1·1)
P(1)–C(121)–C(126)	120·7(1·1)
P(1)–C(131)–C(132)	121·6(1·1)
P(1)–C(131)–C(136)	116·5(1·1)
P(2)–C(211)–C(212)	119·4(1·1)
P(2)–C(211)–C(216)	117·7(1·0)
P(2)–C(221)–C(222)	118·7(1·1)
P(2)–C(221)–C(226)	120·1(1·2)
P(2)–C(231)–C(232)	119·5(1·1)
P(2)–C(231)–C(236)	117·4(1·0)
C(112)–C(111)–C(116)	121(1)
C(111)–C(112)–C(113)	119(2)
C(112)–C(113)–C(114)	120(2)
C(113)–C(114)–C(115)	122(2)
C(114)–C(115)–C(116)	120(2)
C(111)–C(116)–C(115)	118(1)
C(122)–C(121)–C(126)	120(1)
C(121)–C(122)–C(123)	119(1)
C(122)–C(123)–C(124)	119(2)
C(123)–C(124)–C(125)	121(2)
C(124)–C(125)–C(126)	121(2)
C(121)–C(126)–C(125)	119(1)
C(132)–C(131)–C(136)	122(1)
C(131)–C(132)–C(133)	120(1)
C(132)–C(133)–C(134)	119(2)
C(133)–C(134)–C(135)	122(2)
C(134)–C(135)–C(136)	121(2)
C(131)–C(136)–C(135)	116(2)
C(212)–C(211)–C(216)	122(1)
C(211)–C(212)–C(213)	119(1)
C(212)–C(213)–C(214)	118(1)
C(213)–C(214)–C(215)	125(2)
C(214)–C(215)–C(216)	116(2)
C(211)–C(216)–C(215)	120(1)
C(222)–C(221)–C(226)	121(1)
C(221)–C(222)–C(223)	118(1)
C(222)–C(223)–C(224)	122(2)
C(223)–C(224)–C(225)	119(2)
C(224)–C(225)–C(226)	120(2)
C(221)–C(226)–C(225)	120(2)
C(232)–C(231)–C(236)	123(1)
C(231)–C(232)–C(233)	121(1)
C(232)–C(233)–C(234)	116(2)
C(233)–C(234)–C(235)	123(2)
C(234)–C(235)–C(236)	117(2)
C(231)–C(236)–C(235)	119(1)
F(1)–P(3)–F(2)	95(1)
F(1)–P(3)–F(3)	93(1)
F(1)–P(3)–F(4)	170(1)
F(1)–P(3)–F(5)	83(1)
F(1)–P(3)–F(6)	85(1)
F(2)–P(3)–F(3)	91(1)
F(2)–P(3)–F(4)	92(1)
F(2)–P(3)–F(5)	178(1)
F(2)–P(3)–F(6)	91(1)
F(3)–P(3)–F(4)	94(1)
F(3)–P(3)–F(5)	88(1)
F(3)–P(3)–F(6)	178(1)
F(4)–P(3)–F(5)	90(1)
F(4)–P(3)–F(6)	88(1)
F(5)–P(3)–F(6)	90(1)

TABLE 5

Root-mean-square amplitudes of vibration (Å)

Atom	Minimum	Intermediate	Maximum
Os	0·168	0·193	0·229
P(1)	0·173	0·217	0·253
P(2)	0·181	0·195	0·237
P(3)	0·229	0·299	0·336
F(1)	0·301	0·379	0·605
F(2)	0·283	0·427	0·589
F(3)	0·239	0·364	0·627
F(4)	0·233	0·441	0·703
F(5)	0·287	0·421	0·462
F(6)	0·281	0·367	0·513
O(1)	0·255	0·287	0·317
O(2)	0·199	0·273	0·380
N(1)	0·187	0·241	0·315
N(2)	0·193	0·261	0·294

TABLE 6

Planes of best fit. The equations of the planes are referred to an orthogonal set of axes and are given in the form $AX + BY + CZ + D = 0$, where A, B, and C are the direction cosines. Distances (Å) of the atoms from the plane are in square brackets

Plane (1): P(1), P(2), N(1), O(3)

$$0{\cdot}3284X - 0{\cdot}9250Y - 0{\cdot}1909Z - 2{\cdot}7416 = 0$$

[Os −0·27, P(1) 0·06, P(2) 0·06, N(1) −0·05, N(2) −2·13, O(1) 0·14, O(3) −0·06]

Plane (2): C(111)—(116)

$$0{\cdot}5815X - 0{\cdot}0463Y - 0{\cdot}8123Z - 5{\cdot}4063 = 0$$

[C(111) 0·003, C(112) −0·009, C(113) 0·011, C(114) −0·007, C(115) 0·001, C(116) 0·001]

Plane (3): C(121)—(126)

$$0{\cdot}2306X - 0{\cdot}8039Y + 0{\cdot}5482Z + 3{\cdot}4088 = 0$$

[C(121) −0·008, C(122) −0·012, C(123) 0·031, C(124) −0·031, C(125) 0·011, C(126) 0·009]

Plane (4): C(131)—(136)

$$0{\cdot}8259X + 0{\cdot}4211Y + 0{\cdot}3750Z + 5{\cdot}4711 = 0$$

[C(131) 0·009, C(132) 0·005, C(133) −0·010, C(134) 0·000, C(135) 0·015, C(136) −0·019]

Plane (5): C(211)—(216)

$$-0{\cdot}9304X - 0{\cdot}3401Y + 0{\cdot}1366Z - 6{\cdot}4041 = 0$$

[C(211) 0·001, C(212) −0·006, C(213) 0·012, C(214) −0·013, C(215) 0·008, C(216) −0·002]

Plane (6): C(221)—(226)

$$0{\cdot}0659X + 0{\cdot}2266Y + 0{\cdot}9718Z + 7{\cdot}6110 = 0$$

[C(221) 0·017, C(222) −0·032, C(223) 0·012, C(224) 0·022, C(225) −0·037, C(226) 0·017]

Plane (7): C(231)—(236)

$$-0{\cdot}7353X + 0{\cdot}6267Y - 0{\cdot}2581Z - 3{\cdot}6878 = 0$$

[C(231) 0·000, C(232) −0·002, C(223) 0·003, C(234) −0·001, C(235) −0·001, C(236) 0·002]

TABLE 7

Comparison of bond lengths (Å) and angles (°) in the two dinitrosyl complexes

		$[Os(OH)(NO)_2(PPh_3)_2]^+$	$[RuCl(NO)_2(PPh_3)_2]^+$
M–N	bent	1·86(1)	1·85(2)
	linear	1·63(1)	1·74(2)
N–O	bent	1·17(2)	1·17(2)
	linear	1·24(2)	1·16(2)
M–N–O	bent	134(1)	138(2)
	linear	178(1)	178(2)

P(1)–Os–P(2)	162·8(1)	P(1)–Ru–P(2)	159·6(2)
N(1)–Os–O(3)	166·1(5)	N(2)–Ru–Cl	155·8(2)
N(2) · · · P(1)	3·26(2)	N(1) · · · P(1)	3·34(2)
N(2) · · · P(2)	3·24(2)	N(1) · · · P(2)	3·22(2)
N(2) · · · N(1)	2·67(2)	N(1) · · · N(2)	2·80(3)
N(2) · · · O(3)	2·79(2)	N(1) · · · Cl	3·30(2)

RESULTS AND DISCUSSION

The crystal structure analysis of $[Os(OH)(NO)_2(PPh_3)_2]PF_6$ shows it to be monomeric. The co-ordination geometry of the cation is that of a tetragonal pyramid with two *trans*-phosphorus atoms, the hydroxo- and a linear nitrosyl group forming the basal plane; the apical position is occupied by a bent nitrosyl group. The osmium is displaced from the basal plane by 0·27 Å in the direction of this last group (see Table 6). Because of the presence of both nitrosyl bonding modes (NO^+ and NO^-) the complex should be formulated as osmium(II), the tetragonal pyramidal geometry being consistent with the d^6 configuration.

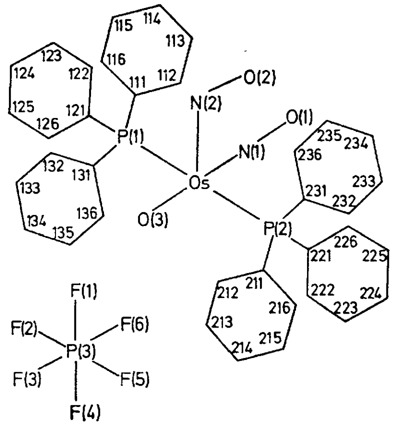

FIGURE 1 Diagram showing the numbering system of the molecule

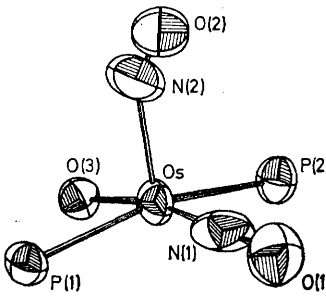

FIGURE 2 A perspective drawing of the inner co-ordination sphere of the cation

The bond lengths and angles associated with the two nitrosyl groups in the cation compare favourably with those found in the similar cation $[RuCl(NO)_2(PPh_3)_2]^+$ (see Table 7).[14] The linear nitrosyl group is characterised by a short metal–nitrogen bond, that in the osmium complex being shorter than in the similar ruthenium one. The difference presumably reflects the greater *trans*-effect of chloride relative to hydroxo {the osmium–nitrosyl distance is also shorter than that found in $[OsCl_2(HgCl)(NO)(PPh_3)_2]$ [1·81(5) Å] in which the nitrosyl group occupies the *trans*-position to chloride}.[15] The metal–nitrogen bond lengths associated

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[14] C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 1972, **11**, 1088.

[15] G. A. Bentley, K. R. Laing, W. R. Roper, and J. M. Waters, *Chem. Comm.*, 1970, 998.

with the bent nitrosyl are equivalent in the osmium and ruthenium complexes and are much longer than those for the linear nitrosyl, since NO^- is a much poorer π-acceptor. Both values found for the hydroxo-complex lie approximately in the range observed in iridium complexes for linear (1·57—1·77 Å) and bent (1·89—1·97 Å) nitrosyl groups.[1] The two bent metal–nitrogen–oxygen angles are equivalent for the two metals, but are significantly different from other bent nitrosyls such as $[IrCl(CO)(NO)(PPh_3)_2]^+$ where an iridium–nitrogen–oxygen angle of 124·1(9)° is observed.[16] In the ruthenium complex, it was suggested that the nitrosyl angle of 138(2)° was the result of an interaction between a filled metal d_π orbital and a π^* function of the apical nitrosyl group.[14] In the hydroxo-complex, the bent nitrosyl lies in the hydroxo–osmium–linear-nitrosyl plane and is orientated towards the linear nitrosyl. This is in line with the view that the bent nitrosyl in tetragonal complexes is oriented towards the ligand of greatest π-bonding ability [14] and there thus appears to be a weak donor–acceptor interaction between the lone pair of the apical nitrosyl oxygen and the π^*(NO) orbital of the linear nitrosyl. The nitrogen–oxygen distances [1·24(2) and 1·17(2) Å] are normal for linear and bent nitrosyls and are comparable with those found elsewhere.

The osmium–phosphorus bond lengths [2·432(4) and 2·436(3) Å] do not differ from one another and are comparable with similar reported distances.[15,17] The mean phosphorus–carbon bond length is 1·80(2) Å and mean carbon–carbon bond is 1·40(3) Å, both standard deviations being calculated from a statistical range of values. The mean angles: Os–P–C 112(4), C–P–C 107(2), P–C–C 119(2), and C–C–C 120(2)° are all as expected and agree with those found in comparable complexes.[3]

Planes of 'best fit' through the phenyl rings [planes (2)—(7), Table 6] show that these are approximately planar.

No suitable site for the hydroxo-hydrogen was found in this analysis. The osmium–oxygen bond length of 1·935(8) Å is similar to the metal–oxygen distance found [18] in $Na_2[Ru(NO_2)_4(NO)(OH)],2H_2O$ [1·950(5) Å], which is thought to be a normal value. This ruthenium compound was studied by neutron diffraction and the hydrogen atom was located, to give an O–H distance of 0·921(9) Å and Ru–O–H 108·1(7)°. There appears to be no hydrogen bonding in this structure.

The angles around the osmium in the basal plane are not all equivalent. The two P–Os–O angles are less than the two P–Os–N(1) angles causing the triphenylphosphine groups to crowd around the hydroxo-group. The distortion in the present cation can be compared with that found in $[RuCl(NO)_2(PPh_3)_2]^+$ (see Table 7).[14] These values show that the N · · · N distance is shorter in the osmium complex and also that in this osmium complex the *trans*-phosphorus bond angle is less than the other *trans* bond angle of the basal plane. This is the opposite to the case in previous observations.[3] As the M–N(ax) bond length decreases it has been shown that the *trans*-phosphorus bond angle deviates less from linearity than the other *trans* bond angle in the basal plane. It was thought that the distortion minimised the non-bonded repulsions between the axial nitrogen atom and the non-phosphine basal ligands.

The plane of 'best fit' through P(1), P(2), N(1), and O(3) [plane (1), Table 6] shows that the osmium atom is displaced from this plane towards the apical nitrogen by 0·27 Å. The data also show that the linear nitrosyl and hydroxide are displaced slightly towards the apical nitrosyl whereas the two phosphorus atoms are displaced slightly away from the apex of the tetragonal pyramid.

The hexafluorophosphate anion does not adopt a perfect octahedral arrangement and has bond lengths ranging from 1·48(2) to 1·59(2) Å and *trans* angles of 170(1), 178(1), and 178(1)°. Since the fluorine atoms have large anisotropic temperature parameters the anion appears to be disordered and the co-ordinates of the atoms are therefore only approximate. The bond lengths have been corrected for the effects of thermal motion by the method of Cruickshank [19] (see Table 8).

TABLE 8

Bond distances (Å) in the hexafluorophosphate anion

	Uncorrected bond length	Correction
P(3)–F(1)	1·54(2)	0·05
P(3)–F(2)	1·52(2)	0·05
P(3)–F(3)	1·53(2)	0·05
P(3)–F(4)	1·48(2)	0·06
P(3)–F(5)	1·55(2)	0·05
P(3)–F(6)	1·59(2)	0·04

Individual values are in line with those already observed [20] and any differences among the six are not thought to be significant.

Non-bonded intramolecular distances <3·40 Å are listed in Table 9 (excluding C · · · C interactions, none of which represents a significant interaction). Many involve the fluorine atoms of the anion, but none of these are less than the van der Waals distances,[21] and are therefore unlikely to represent hydrogen-bonding interactions. The more important of the inter- and intra-molecular contacts involve the hydroxo-oxygen and phenyl-ring carbon atoms (Table 10). In addition, positions have been calculated for the hydrogen

TABLE 9

Intramolecular distances <3·40 Å

P(1) · · · O(3)	2·94	O(3) · · · N(2)	2·79
P(1) · · · N(1)	3·03	O(3) · · · C(126)	3·07
P(1) · · · N(2)	3·26	O(3) · · · C(131)	3·33
P(2) · · · O(3)	3·02	O(3) · · · C(226)	3·26
P(2) · · · N(1)	2·96	O(3) · · · C(236)	3·22
P(2) · · · N(2)	3·24	N(1) · · · N(2)	2·67
O(2) · · · N(1)	3·03		

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[16] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2345.

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[19] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 757.

[20] H. Bode and G. Teufer, *Acta Cryst.*, 1956, **9**, 825.

[21] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968.

atoms associated with these carbon atoms, in an attempt to investigate any possible hydrogen bonding with the hydroxo-group. Relevant data are also listed in Table 10.

TABLE 10

Close approaches to the hydroxyl oxygen atom (distances in Å, angles in °); primed atoms are at x, $\frac{1}{2} - y$, $\frac{1}{2} + z$)

(1)	O(3) · · · C(126)	3·07	O(3) · · · H(126)	2·25
			H(126)–C(126)	0·98
			O(3) · · · $\hat{\mathrm{H}}$(126)–C(126)	141
(2)	O(3) · · · C(213′)	3·23	O(3) · · · H(213′)	2·65
			H(213′)–C(213′)	0·98
			O(3) · · · $\hat{\mathrm{H}}$(213′)–C(213′)	118
(3)	O(3) · · · C(214′)	3·24	O(3) · · · H(214′)	2·62
			H(214′)–C(214′)	0·98
			O(3) · · · $\hat{\mathrm{H}}$(214′)–C(214′)	121
(4)	O(3) · · · C(226)	3·26	O(3) · · · H(226)	2·74
			H(226)–C(226)	0·98
			O(3) · · · $\hat{\mathrm{H}}$(226)–C(226)	114
(5)	O(3) · · · C(236)	3·22	O(3) · · · H(236)	2·37
			H(236)–C(236)	0·98
			O(3) · · · $\hat{\mathrm{H}}$(236)–C(236)	145

A test for the presence of hydrogen bonding is that the O · · · C and O · · · H distances be <3·0 and 2·6 Å, respectively and that the O · · · H–C angle is >150°.[21] If these criteria are applied here then hydrogen bonds can certainly be ruled out for contacts (2)—(4) (Table 10). For the contacts (1) and (5) however the O · · · H–C angles are only a little less than the critical value, and the O · · · H distance is considerably so. Moreover H(126) and H(236) occupy two positions of a distorted tetrahedron about O(3) [angles Os–O(3)–H(126) 101, Os–O(3)–H(236) 97, and H(126)–O(3)–H(236) 94°]. Thus in these two instances geometrical considerations do not clearly rule out the occurrence of hydrogen bonding. However the involvement of aromatic carbon atoms in these contacts suggests that the approaches result from the close packing of triphenylphosphine groups.

We thank Dr. W. R. Roper for supplying crystals of the complex, and Professor B. R. Penfold for the ORTEP diagram.

[4/1529 *Received*, 23*rd July*, 1974]