lies on the opposite side of the mean phenO plane from the Cu atom. The displacement of the Cu atom from the ligand plane, together with the strict planarity of the equatorial CuN_2O_2 unit, leads to the adoption of a 'stepped' structure (Holm & O'Connor, 1971) characterized by the angle θ between the planes of the ligand and the chromophore of 33.77 (14)° and/or by the step s (defined as the distance between the ligand planes) of 1.570 (4) Å.

The complex and water molecules are held together by van der Waals interactions and hydrogen bonds (see Table 2). There are intermolecular Cl···H (water) contacts involving H(11) and H(12) of 2.24 (6) and 2.72 (9) Å and between the water oxygen O(2) and H(6), H(7) and H(8) atoms [O(2)···H 2.78 (6), 2.60 (4) and 2.27 (5) Å respectively]. Other contacts correspond to the sum of the van der Waals radii for the atoms involved.

References

Baran, P., Koman, M., Valigura, D. & Mrozinski, J. (1991). *J. Chem. Soc. Dalton Trans.* pp. 1385–1390.

Gažo, J., Bersuker, I. B., Garaj, J. Kabešová, M., Kohout, J., Langfelderová, H., Melník, M., Serátor, M. & Valach, F. (1976). *Coord. Chem. Rev.* **19**, 253–297.

Holm, R. H. & O'Connor, M. J. (1971). *Prog. Inorg. Chem.* **14**, 241–401.

Johnson, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Koman, M., Baran, P. & Valigura, D. (1991). *Acta Cryst.* **C47**, 2529–2531.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Nardelli, M., Fava, G., Boldrini, P. & Giraldi, G. (1965). *Acta Cryst.* **19**, 491–500.

Pavkovic, S. F. & Brown, J. N. (1982). *Acta Cryst.* **B38**, 274–276.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Stephens, F. S., Vagg, R. S. & Williams, P. A. (1977). *Acta Cryst.* **B33**, 438–443.

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Structure of an Aminodicarbonyldiiodo(triphenylphosphine)osmium Complex

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Abstract. $[OsI_2(CO)_2(C_3H_9N)(C_{18}H_{15}P)]$, $M_r = 821.4$, monoclinic, $P2_1/n$, $a = 15.011$ (3), $b = 11.316$ (4), $c = 16.155$ (2) Å, $\beta = 106.55$ (1)°, $V = 2630$ (1) Å^3, $Z = 4$, $D_x = 2.07$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 7.25$ mm^{-1}, $F(000) = 1528$, $T = 298$ K, $R = 0.058$, $wR = 0.051$ for 2432 observed reflections. The Os atom is six coordinate in a slightly distorted octahedral geometry. Two I ligands and two CO groups are mutually in a *cis* form. The Os—C(2) bond length [1.75 (2) Å] is significantly shorter than that of Os—C(1) [1.82 (2) Å]. Two Os—I bond distances [2.698 (2), 2.705 (3) Å] are among the shortest Os—I bond lengths reported in the literature.

Introduction. In the previous paper (Lu, Chen, Lin & Peng, 1988) we reported the synthesis of (μ-I)$Os_2(CO)_6$(μ-OCNHCHMe$_2$)I_2, (1). Since halides have been employed as promoters in many catalytic (Dombek, 1981) or stoichiometric reactions (Morrison, Geoffroy & Rheingold, 1985), we were interested in the chemical behavior of the cluster in the presence of halogen. In this work, the crystal structure of the product, $Os(CO)_2[NH_2CH(CH_3)_2](PPh_3)I_2$, (2), from the reaction of (1) with PPh_3 is determined.

Experimental. Synthesis of the title compound was achieved by reacting the carboxamidotriiododiosmium complex (μ-I)$Os_2(CO)_6$(μ-OCNHCHMe$_2$)I_2 with PPh_3 in refluxing chloroform solution. Crystals of the yellow complex were grown by slow evaporation of a saturated dichloromethane solution of the complex at room temperature. CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$. Crystal 0.20 × 0.20 × 0.30 mm. Unit-cell parameters from 24 reflections with $18.78 < 2\theta < 24.72°$, data collected by $\omega/2\theta$-scan method with scan width of $2(1.0 + 0.35\tan\theta)°$ and variable scan speed of 20/2–20/

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13° min^{-1}, variation of standard reflections checked every 2 h, <2%. $2\theta_{max} = 50°$, $-17 \le h \le 17$, $0 \le k \le 13$, $0 \le l \le 19$, 4617 unique reflections (out of 4805 total number of measured reflections), 2432 observed with $I > 2.5\sigma(I)$. Empirical absorption correction based on azimuthal rotation from three reflections (North, Phillips & Mathews, 1968); transmission factors 0.60–1.00. Structure solved by heavy-atom method. The function minimized in least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, $\sigma(F_o)$ from counting statistics. 254 parameters with anisotropic temperature factors for non-H atoms. H atoms were included with calculated positions. There was a residual peak in the neighborhood of C(2)—O(2) at a distance of 2.73 (3) Å away from Os. It was modeled as 0.05 of the I atom, I′. There may be 0.05 CO group around either I(1) or I(2); however, it is small compared with the electron density of the I atom. Thus all I′, C(2) and O(2) parameters were not refined in the least-squares process. $R = 0.058$, $wR = 0.051$, $S = 2.790$, $(\Delta/\sigma)_{max} = 0.022$ in the final cycle. $\Delta\rho_{max} = 2.01$ e Å^{-3} near Os. Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computing programs: *NRCVAX* package on MicroVAX III computer (Gabe, Lee & Le Page, 1985).

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

B_{iso} is the mean of the principal axes of the thermal ellipsoids.

	x	*y*	*z*	B_{iso}
Os	0.24164 (7)	0.01855 (9)	0.07497 (5)	2.96 (4)
I(1)	0.13158 (14)	−0.02776 (20)	−0.08546 (10)	6.14 (11)
I(2)	0.15982 (16)	−0.16905 (19)	0.12716 (13)	6.49 (12)
P(1)	0.3052 (4)	0.1811 (6)	0.0206 (3)	3.2 (3)
C(1)	0.3126 (15)	0.0368 (21)	0.1864 (13)	4.3 (12)
O(1)	0.3590 (11)	0.0495 (15)	0.2569 (8)	5.6 (9)
C(2)	0.32361	0.91822	0.05854	4.26
O(2)	0.38145	0.84644	0.05860	7.46
N(1)	0.1279 (13)	0.1197 (14)	0.0903 (10)	3.3 (10)
C(3)	0.1346 (14)	0.1912 (19)	0.1713 (13)	3.5 (12)
C(4)	0.0620 (17)	0.2873 (25)	0.1500 (15)	5.8 (16)
C(5)	0.1214 (18)	0.1151 (21)	0.2431 (13)	4.8 (14)
C(11)	0.3266 (15)	0.1648 (23)	−0.0837 (12)	4.2 (13)
C(12)	0.3225 (18)	0.2636 (23)	−0.1381 (14)	5.0 (15)
C(13)	0.3435 (18)	0.248 (3)	−0.2151 (14)	7.0 (18)
C(14)	0.3674 (20)	0.142 (3)	−0.2396 (16)	8.4 (21)
C(15)	0.3664 (24)	0.044 (3)	−0.1906 (15)	8.9 (22)
C(16)	0.3503 (18)	0.0585 (21)	−0.1123 (14)	4.9 (14)
C(21)	0.4178 (14)	0.2308 (19)	0.0908 (13)	3.4 (11)
C(22)	0.4263 (16)	0.2669 (22)	0.1748 (13)	4.2 (13)
C(23)	0.5056 (15)	0.3131 (24)	0.2243 (14)	5.3 (14)
C(24)	0.5810 (17)	0.315 (3)	0.1933 (16)	8.1 (19)
C(25)	0.5772 (18)	0.283 (3)	0.1136 (17)	8.1 (20)
C(26)	0.4927 (15)	0.246 (3)	0.0587 (13)	6.0 (16)
C(31)	0.2352 (14)	0.3137 (20)	0.0070 (12)	3.3 (11)
C(32)	0.2606 (15)	0.4140 (20)	0.0499 (13)	4.3 (12)
C(33)	0.2081 (17)	0.509 (3)	0.0357 (12)	5.9 (15)
C(34)	0.1236 (22)	0.5116 (24)	−0.0202 (15)	7.5 (19)
C(35)	0.0899 (17)	0.417 (3)	−0.0665 (15)	6.4 (16)
C(36)	0.1457 (18)	0.3125 (21)	−0.0524 (14)	4.9 (14)
I′*	0.36500	0.85000	0.05800	3.16

* Occupancy 0.05.

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

Os—I(1)	2.6984 (19)	Os—I(2)	2.705 (3)
Os—P(1)	2.354 (7)	Os—C(1)	1.823 (22)
Os—C(2)	1.749	Os—N(1)	2.128 (19)
P(1)—C(11)	1.813 (23)	P(1)—C(21)	1.835 (21)
P(1)—C(31)	1.808 (25)	C(1)—O(1)	1.16 (3)
C(2)—O(2)	1.189	N(1)—C(3)	1.52 (3)
C(3)—C(4)	1.51 (4)	C(3)—C(5)	1.50 (3)
I(1)—Os—I(2)	86.49 (7)	I(1)—Os—P(1)	89.76 (14)
I(1)—Os—C(1)	174.7 (8)	I(1)—Os—C(2)	89.6
I(1)—Os—N(1)	85.6 (4)	I(2)—Os—P(1)	176.18 (15)
I(2)—Os—C(1)	88.3 (8)	I(2)—Os—C(2)	86.5
I(2)—Os—N(1)	86.3 (5)	P(1)—Os—C(1)	95.4 (8)
P(1)—Os—C(2)	94.2	P(1)—Os—N(1)	92.7 (5)
C(1)—Os—C(2)	89.1	C(1)—Os—N(1)	95.0 (8)
C(2)—Os—N(1)	171.6	Os—P(1)—C(11)	117.7 (9)
Os—P(1)—C(21)	114.1 (8)	Os—P(1)—C(31)	114.2 (8)
C(11)—P(1)—C(21)	103.3 (10)	C(11)—P(1)—C(31)	102.8 (11)
C(21)—P(1)—C(31)	102.9 (10)	Os—C(1)—O(1)	178.8 (21)
Os—C(2)—O(2)	171.3	Os—N(1)—C(3)	121.9 (13)
N(1)—C(3)—C(4)	108.8 (17)	N(1)—C(3)—C(5)	111.7 (18)
C(4)—C(3)—C(5)	110.0 (20)	P(1)—C(11)—C(12)	120.6 (20)
P(1)—C(11)—C(16)	122.3 (19)	P(1)—C(21)—C(22)	120.4 (18)
P(1)—C(21)—C(26)	120.9 (16)	P(1)—C(31)—C(32)	125.1 (16)
P(1)—C(31)—C(36)	118.8 (17)		

Discussion. The molecular structure of the title complex is shown in Fig. 1. The atomic coordinates and B_{eq} values are listed in Table 1.* Selected interatomic distances and angles are given in Table 2. In this complex, the Os metal center is coordinated in a slightly distorted octahedral geometry with two carbonyl ligands, two I atoms, one isopropylamine and one triphenylphosphine group. Two I ligands and two CO groups are both in a mutually *cis* form. The C(2)—Os—N(1) bond angle [171.6 (8)°] deviates significantly from 180°; this might be due to the steric hindrance of the bulkier triphenylphosphine ligands. Two methyl groups of the isopropylamine are oriented away from the phosphine ligand. The Os—C(2) bond length [1.75 (2) Å] is significantly

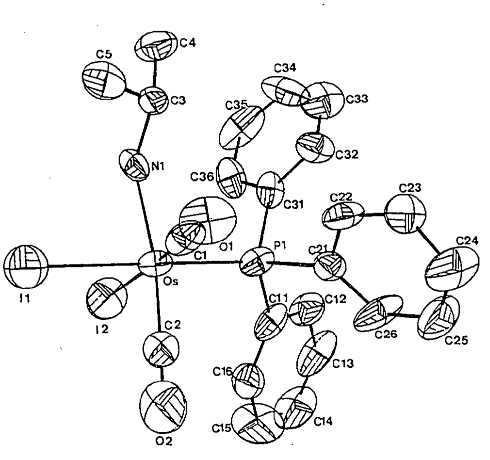

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of $Os(CO)_2[NH_2CH(CH_3)_2](PPh_3)I_2$.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54520 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0511]

shorter than that of Os—C(1) [1.82 (2) Å]. The Os—C(2) bond is strengthened by a strong electron donor in the *trans* position. Two Os—I bond lengths [2.698 (2), 2.705 (3) Å] are relatively short compared with that of other Os complexes. To our knowledge these are among the shortest Os—I bond lengths reported in the literature. We previously reported the crystal structure of $Os(CO)_3[NH_2C(CH_3)_3]I_2$ in which the ligands are also in a *cis* orientation to Os—I with distances of 2.735 (1) and 2.736 (1) Å (Lu, Chen, Lin & Peng, 1988). The structural difference between the two molecules is that, in (2), a triphenylphosphine ligand which is a better σ donor, replaces one of the carbonyl ligands of $Os(CO)_3(NH_2\text{-}i\text{Pr})I_2$. This causes remarkable shortening of the Os—I distance. Therefore the electronic effect is likely to be a key factor in determining the bond length. The shortest Os—I distance of 2.662 Å is found in tetraphenylarsonium nitridotetraiodoosmate(VI) which bears a negative charge on the Os metal center and has the same *cis* orientation for the I ligands (Phillips, Skapski & Withers, 1975). In our case, complex (2) is a neutral compound. Studies on the relationship between the Os—I distance and the Os coordinated environment are underway.

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References

Dombek, B. D. (1981). *J. Am. Chem. Soc.* **103**, 6508–6510.

Gabe, E. J., Lee, F. L. & Le Page, Y. (1985). *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Kruger & R. Goddard, pp. 167–174. Oxford: Clarendon Press.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lu, K. L., Chen, J. L., Lin, Y. C. & Peng, S. M. (1988). *Inorg. Chem.* **27**, 1726–1730.

Morrison, E. D., Geoffroy, G. L. & Rheingold, A. L. (1985). *J. Am. Chem. Soc.* **107**, 254–255.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–354.

Phillips, F. L., Skapski, A. C. & Withers, M. J. (1975). *Transition Met. Chem.* **1**, 28–34.

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Copper(I) Reoxygenation Products: the Structures of Di-μ-hydroxy-bis(di-2-pyridylamine)bis(tetrafluoroborato)dicopper(II) and μ-Aqua-di-μ-hydroxy-bis(di-2-pyridylamine)dicopper(II) Dichloride Dihydrate

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Abstracts. (I) $[Cu_2(FBF_3)_2(OH)_2(C_{10}H_9N_3)_2]$, $C_{20}H_{20}B_2Cu_2F_8N_6O_2$, $M_r = 677.11$, triclinic, $P\bar{1}$, $a = 9.686\ (2)$, $b = 9.429\ (2)$, $c = 7.414\ (3)$ Å, $\alpha = 69.90\ (1)$, $\beta = 97.53\ (2)$, $\gamma = 106.97\ (3)°$, $V = 607.97\ (3)$ Å^3, $Z = 1$, $D_m = 1.70\ (4)$, $D_x = 1.85$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.781$ mm^{-1}, $F(000) = 338$, room temperature. (II) $[Cu_2(OH)_2(H_2O)(C_{10}H_9N_3)_2]Cl_2.2H_2O$, $C_{20}H_{22}Cu_2N_6O_3^{2+}.2Cl^-.2H_2O$, $M_r = 628.47$, orthorhombic, $Cmc2_1$, $a = 15.675\ (3)$, $b = 8.563\ (1)$, $c = 18.115\ (3)$ Å, $V = 2431.49$ Å^3, $Z = 4$, $D_m = 1.67\ (5)$, $D_x = 1.717$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.946$ mm^{-1}, $F(000) = 1280$, room temperature. With 1750 and 1045 unique reflections $R = 0.0474$ and 0.0309 for (I) and (II), respectively. Both complexes contain a dinuclear $[(dpyam)Cu(OH)_2Cu(dpyam)]^{2+}$ unit, dpyam = 2,2′-bipyridylamine, with near planar CuN_2O_2 chromophores. In (I) the centrosymmetric dinuclear unit is approximately planar, but each CuN_2O_2 chromophore has a tetrahedral twist, dihedral angle 24.0°. An F atom from a monodentate $[BF_4]^-$ anion completes a distorted square pyramidal CuN_2O_2F chromophore with a Cu—F distance of *ca* 2.745 (7) Å. In (II) the dinuclear unit has a roof-top structure (140.6°), with an additional single water molecule bridging both copper(II) cations at a Cu—O′ distance of 2.419 (5) Å, to give a square pyramidal CuN_2O_2O' chromophore. The Cu—Cu distances are 2.919 (5) and 2.799 (1) Å in (I) and (II), respectively. Both (I) and (II) are ESR silent, but while the room-temperature magnetic moment of (I) is normal (0.90 BM) that of (II) is slightly low (1.75 BM).

Introduction. Copper metal reduction of the $[Cu^{II}(dpyam)_2][BF_4]_2$ complex, by refluxing in air in acetonitrile solution then reoxygenation in air, yields steel-blue crystals of $[Cu^{II}_2(dpyam)_2(OH)_2(FBF_3)_2]$, (I)

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