The Crystal Structure of a Dinitrosyl Complex of Osmium(II)

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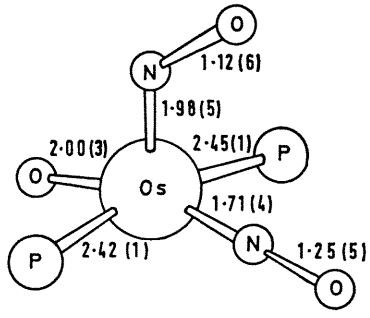
Summary The crystal structure of the compound $[Os(OH)(NO)_2(PPh_3)_2][PF_6]$ reveals the tetragonal pyramidal configuration for osmium with nitrosyl groups co-ordinated in both a linear and a bent manner.

THE preparation of the osmium dinitrosyl cation $[Os(OH)(NO)_2(PPh_3)_2]^+$ has recently been reported[1] and from the i.r. spectrum the presence of both a bent and a linear nitrosyl group was suggested. We report here the result of a single crystal *X*-ray diffraction study on the $[PF_6]^-$ salt.

The brown crystals, which were supplied by Dr. W. R. Roper of the University of Auckland, have cell parameters $a = 18{\cdot}949(11)$, $b = 10{\cdot}696(13)$, $c = 18{\cdot}446(9)$ Å, $\beta = 91{\cdot}90(3)°$; space group $P2_1/a$, $Z = 4$. The structure was solved by Patterson and Fourier methods from *X*-ray data recorded by a Hilger–Watts four-circle automatic diffractometer with Mo-K_α radiation. At the current stage of least-squares refinement $R = 0{\cdot}101$ for the 1855 independent reflexions observed to be greater than $2{\cdot}5\sigma$.

The structure of the osmium dinitrosyl cation is that of a tetragonal pyramid, in which two *trans* phosphorus atoms, the hydroxy-group, and one nitrosyl group make up the base (Figure). The second nitrosyl group is located at the apex with the osmium atom displaced 0·30 Å towards it. As was found in the similar ruthenium complex, $[RuCl(NO)_2(PPh_3)_2]^+$,[2] the apical nitrosyl is co-ordinated in a bent manner with the longer metal–nitrogen distance of 1·98(5) Å. The nitrosyl lying in the base of the pyramid is essentially linear with the shorter metal–nitrogen distance of 1·71(4). However, in contrast to the ruthenium dinitrosyl complex with its ruthenium–nitrogen–oxygen angle of 136·0(1·6)° the osmium complex has an osmium–nitrogen–angle which is smaller, 127·5(2·0)°. This is more in line with the corresponding angles of 124·1(9) and 125(3)°, respectively, found in the square pyramidal mono-nitrosyl complexes $[IrCl(CO)(NO)(PPh_3)_2]^+$ [3] and $[IrI(CO)(NO)(PPh_3)_2]^+$.[4] The two nitrogen–oxygen distances of 1·12(6) (bent) and 1·25(5) Å (linear) do not differ significantly from one another and are in accord with previously reported values.[3–5]



FIGURE

(*Received, March 15th*, 1971; *Com.* 263.)

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