Inorganica Chimica Acta, 44 (1980) L247–L248
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A Compound with an Osmium to Osmium Triple Bond

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Received December 17, 1979

Since the first recognition of the stabilities of Re=Re [1], Re≡Re [2] and Re$\equiv$Re [3] bonds over fifteen years ago, the chemistry of transition metal compounds containing multiple bonds (especially triple and quadruple ones) between metal atoms has developed broadly [4–6]. Today there are examples of such bonds, or closely related ones, for the metals V, Cr, Mo, W, Tc, Re and Ru, and for certain of these, especially molybdenum and rhenium, it is clear that in the absence of strongly π-acid ligands [7, 8] the formation of M–M multiple bonds plays a major role in their chemistry in one or more lower oxidation states. An obvious (and obviously important) question is what other elements are capable of forming such bonds.

We report here the preparation and structural characterization of the first compound containing a triple bond between osmium atoms, namely, $Os_2(hp)_4Cl_2$, where hp is the anion of Hhp, 2-hydroxypyridine(α-pyridone). This compound is obtained rather easily by reaction of $OsCl_3$ with Hhp in refluxing ethanol. After 12 hours the solution was cooled, solvent removed in vacuum, and the residue extracted with ether–CH_2Cl_2 from which a purple crystalline product, $Os_2(hp)_2Cl_2 \cdot Et_2O$, which is stable in air, was obtained.

The molecular structure has been established by X-ray crystallography* and is shown in Fig. 1. The molecules are chiral because of a twist of the ligands (about 17.5°) around the Os–Os axis. The packing in the crystal is disordered in two ways: (1) There is disordering of the two enantiomeric 'twistomers'; (2) the ligand orientations, 'up or down' relative to the Os–Os unit, are random. Enantiomer disordering [9] and ligand orientation disordering [10] have each been seen before (the latter with some frequency) but this is the first time both have occurred in the same crystal.

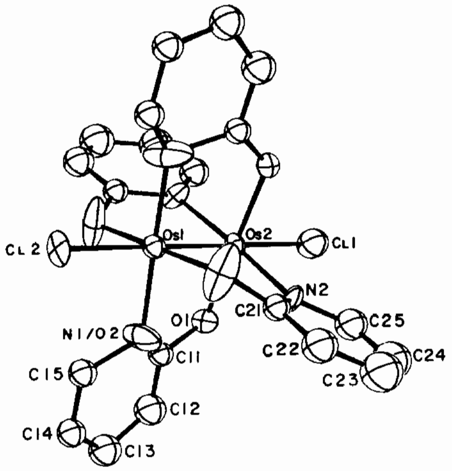

Fig. 1. An ORTEP drawing of one enantiomorph of the $Os_2(hp)_4Cl_2$ molecule.

TABLE I. Some Important Average Bond Lengths (A) and Angles (Deg) in $Os_2(hp)_4Cl_2$.

Os–Os	2.344(2)	Os–Os–N	88.4(5)
Os–Cl	2.484(12)	Os–Os–O	89.9(5)
Os–N	2.04(4)	Os–Os–Cl	180.0 (by symmetry)

The Os–Os distance, 2.344 Å, is consistent with the existence of an Os–Os triple bond, which is the bond order expected from simple reasoning, as explained below. A number of Ru–Ru bonds, which are believed to have bond orders of 2.5 [11] and which also have axial ligands, have Ru–Ru distances in the range 2.25–2.29 Å, and many W≡W [12] and Re≡Re [13] triple bonds have distances of *ca.* 2.30 Å. A consideration of the number of metal electrons available and comparison with the isoelectronic rhenium compounds of the type $Re_2X_4L_4$ make the assignment of a $\sigma^2\pi^4\sigma^2\sigma^{*2}$ configuration, which implies a net triple bond, a natural way to formulate the electronic structure. The absence of any net δ bond means that there is no inherent barrier to rotation about the Os–Os bond and the rotation observed may tentatively be attributed to a minimization of repulsions between hydrogen atoms at the 6-positions of the pyridine rings and the axial chlorine atoms.

The important bond lengths are listed in Table I. The arrangement of ligands within each molecule is such that on each metal atom the OsN_2O_2 moiety is *trans*. This can be inferred despite the disorder because it is not possible to satisfy the crystallographic *mm* symmetry using molecules with local *cis*-OsN_2O_2 groups.

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*The orthorhombic crystals are shown by systematic absences to belong to space group Pmmn or $Pmn2_1$, with unit cell dimensions a = 10.036(1) A, b = 12.114(1) A, c = 11.003(1) A and refinement was carried to convergence (R_1 = 0.037; R_2 = 0.047) in the former using 651 reflections with $I > 3\sigma(I)$. Empirical absorption corrections (psi scans at Chi = 90°) were made.

Acknowledgment

We are grateful to the National Science Foundation for support and Dr. T. R. Felthouse for assistance.

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