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A Binuclear Tetrolato Complex of Osmium(VI): X-Ray Crystal Structure of $Os_2O_4(O_4C_6H_{12})py_4 \cdot 4H_2O$

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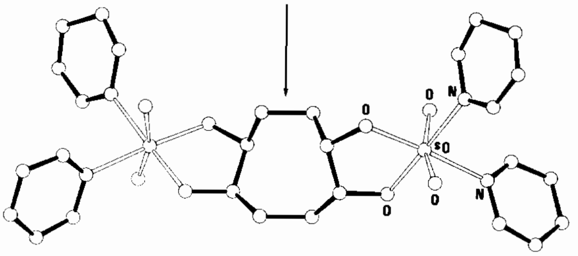

Fig. 1. Molecular structure of $Os_2O_4(O_4C_8H_{12})py_4$. The arrow indicates the direction of the twofold axis which passes through the centre of the molecule.

We have shown recently that osmium tetraoxide, OsO_4, reacts with non-conjugated dienes R in the presence of excess pyridine (py) to give 1:1 complexes $OsO_2(O_2R)py_2$ or 2:1 complexes $Os_2O_4(O_4R)py_4$, depending on the ratio of OsO_4:diene used in the reaction. Hydrolysis of the complexes yields ene-diols and tetrols respectively [1]. We report here the X-ray structure of the 2:1 complex formed between OsO_4, pyridine and cycloocta-1,5-diene, the first such structural determination of a reaction product between OsO_4 and a diene, and the first example of a tetrolato osmium(VI) complex.

Experimental

Reaction of OsO_4 in diethyl ether with cycloocta-1,5-diene in a 2:1 mole ratio in the presence of excess pyridine yields the brown diamagnetic product. Recrystallisation from diethyl ether and dichloromethane in the presence of atmospheric moisture gave dark brown crystals of the product.

The crystals of formula $Os_2O_4(O_4C_8H_{12})py_4 \cdot 4H_2O$ are orthorhombic, with unit-cell dimensions $a = 8.363(1)$, $b = 14.546(1)$, $c = 14.441(1)$ Å, $U = 1756.8$ Å^3 (at 12 °C), space group $P222_1$ and $Z = 2$. Intensity data were collected on a Siemens automatic four-circle diffractometer using Cu-K$_\alpha$ radiation. A total of 1980 independent reflections were measured (to $\theta = 70°$), of which 41 were judged to be 'unobserved'. The structure was solved by Patterson and Fourier methods and least-squares refinement has reached $R = 0.062$. A degree of disorder affects at least one of the independent pyridine ligands.

Results and Discussion

The molecule is binuclear and its structure is shown in Fig. 1. A crystallographic diad axis passes through the centre of the molecule where a cyclooctan-1,2,5,6-tetrolato moiety bridges the two osmium atoms. A somewhat distorted octahedral coordination is found for the metal atoms, with two *cis* pyridine ligands, two *cis* diolato oxygen atoms, and two *trans* oxo ligands, the latter forming the familiar 'osmyl' unit. The mean Os=O distance of 1.72 Å, and the mean Os–O (tetrolato) distance of 1.95 Å are comparable with those found in monomeric diolato species of the form $OsO_2(O_2R)py_2$ [2–5], and also those in the dimeric complex $Os_2O_4(O_2C_6H_{10})_2(C_7H_{13}N)_2$ [6].

The markedly non-linear O=Os=O angle of 163.5(7)° and the direction of bending, away from the oxygen atoms (mean O(tetrolato)–Os–O(terminal) angle of 96.0°) and towards the nitrogen atom (mean N(pyridine)–Os–O(terminal) angle of 84.3°), are in line with the results discussed by Kistenmacher *et al.*, [3] for analogous 'osmyl' systems.

The longest bonds in the osmium coordination sphere are to pyridine, with a mean Os–N distance of 2.19 Å which is typical of literature values [2–5], but some 0.2 Å shorter than the Os–N distances found in the partially coordinated OsO_4 adducts with quinuclidine and hexamethylenetetramine [7].

The arrangement of the four tetrolato oxygen atoms relative to the central eight-membered ring is best described as 1,2,5,6-*syn-anti-syn,* while the conformation of the central ring itself is essentially that of a skewed chair-boat form. This conformation is a result of the constraints placed on the ring by formation of the two five-membered metal–diolato ring systems.

Neither of the two crystallographically independent water molecules is coordinated to the osmium atom. These molecules, however, take part in a series of hydrogen bonds, both between themselves and also to coordinated oxygen atoms, with medium-length O···O distances of 2.70–2.76 Å.

The molecular weight of the complex in dichloromethane indicates that it retains its molecularity in solution. On reductive hydrolysis (using potassium sulphite in water–ethanol, a procedure similar to that used by Criegee [8]), cyclooctan-1,2,5,6-tetrol is formed. This is fully consistent with the observed structure, since it is well established that hydrolysis of the diolato complexes $OsO_2(O_2R)py_2$ derived from mono-alkenes R gives *cis*-diols [9].

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