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Partial Coordination in Amine Adducts of Osmium Tetraoxide: X-Ray Molecular Structure of Quinuclidinetetraoxo-osmium(VIII)

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Of the few complexes of osmium(VIII) which are known, the two in the literature which have been structurally characterised (osmium tetraoxide [1, 2], OsO_4, and the osmiamate ion [3], $[OSO_3N]^-$) are both tetrahedral. We have shown that OsO_4, which is extensively used for *cis*-hydroxylation of alkenes and for biological tissue fixation, forms stable adducts with tertiary amines such as quinuclidine and triethylenediamine [4]. These adducts retain the chemical reactivity of OsO_4, but do not possess the dangerously high vapour pressure at room temperature of the toxic tetraoxide. We have studied the quinuclidine adduct crystallographically, and this is the first structural report of a non-tetrahedral osmium(VIII) complex.

The adduct is made by reaction of quinuclidine and OsO_4 in aqueous solution, followed by recrystallisation of the product from carbon tetrachloride. It forms bright red platelets which are monoclinic, with a = 9.514(1), b = 9.346(1), c = 6.123(1) Å, β = 115.94(1)° (at 12 °C), space group $P2_1/m$ and Z = 2. A total of 547 independent reflections were measured (to θ = 50°) on a Siemens four-circle diffractometer, of which 43 were judged to be 'unobserved'. The structure was solved by Patterson and Fourier methods, and full-matrix least-squares refinement has now reached R = 0.029.

Figure 1 shows the structure of the adduct molecule. It lies on a crystallographic mirror plane, but as the conformation of the OsO_4 group relative to the quinuclidine moiety is staggered, the adduct has approximate $3m(C_{3v})$ point symmetry. An unusual coordination is found for the osmium atom, which is between the tetrahedral of the free OsO_4 molecule, and the trigonal-bipyramidal in which one oxygen and the quinuclidine nitrogen are axial, and the remaining three oxygens are equatorial. The mean O(axial)–Os–O(equatorial) angle of 100.6° suggests that the coordination lies slightly nearer tetrahedral (angle 109.47°) than trigonal-bipyramidal (angle 90°). The O(axial)–Os–N angle is 180.0°.

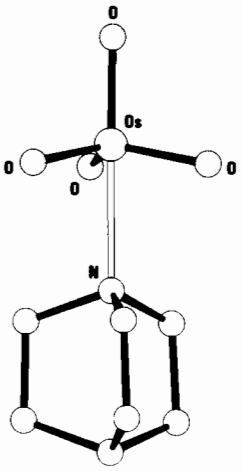

Figure 1. Structure of the 1:1 adduct of OsO_4 and quinuclidine.

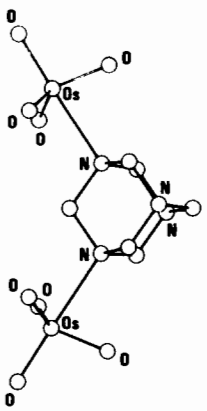

Figure 2. Structure of the 2:1 adduct of OsO_4 and hexamethylenetetramine.

Os–O bond lengths in the adduct are in the range 1.697–1.722 Å with a mean of 1.706 Å, in close agreement with 1.712 Å found [1] for OsO_4 itself. This suggests that, except for the angular distortion caused by the splaying apart of three oxygens to make room for a weak Os–N bond *trans* to the fourth oxygen, the OsO_4 molecule is not materially altered. Indeed, chemically the adduct behaves in a very similar fashion to OsO_4.

The most surprising aspect of the structure is that the Os–N distance of 2.37 Å is far longer than would be expected for a single bond (*ca.* 2.0 Å), yet this partial coordination suffices to hold the adduct together in the solid state and in solution in organic solvents (molecular weight and spectroscopic data show there to be very little dissociation in chloroform, and both Raman and infrared spectra indicate

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that the structure of the solid and solute are very similar [4]).

An analogous situation exists for the hexamethylenetetramine (HMT) adduct $C_6H_{12}N_4 \cdot 2OsO_4$ shown in Figure 2. Here two OsO_4 units are attached to two of the four donor atoms of the amine, again with very long Os–N bonds (2.42 Å), with again the OsO_4 groups being distorted from tetrahedral almost halfway towards trigonal-bipyramidal geometry [5]. The slightly shorter Os–N bond in the title compound is consistent with its lower vapour pressure of OsO_4 as compared to $HMT \cdot 2OsO_4$.

The latter adduct, which has long been known [6], is now successfully being used [7] as a fixation reagent for biological tissue, on which it has the same effect as OsO_4. The adducts react with alkenes to give cyclic osmium(VI) esters which can be hydrolysed to *cis* glycols [4], just as can other osmium(VI) cyclic esters [8]. The simulation by these adducts of the two most useful properties of OsO_4 – *i.e.* tissue fixation and alkene hydroxylation – is likely to arise from the fact that the partial coordination of the amine disturbs the structure of the OsO_4 moiety so little that the reactivity of the latter is not changed.

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