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An Alkanolaminato Complex of Osmium(VI): X-ray Molecular Structure of $Os_2O_4(OCMe_2CH_2NBu^t)_2$

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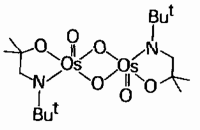
Osmium alkylimido complexes $OsO_3(NR)$ will react with alkenes R′ to give unidentified osmium-containing esters which, on reductive hydrolysis, give 1,2-hydroxyamines [1]. We report here the structure of the complex (**I**):



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formed by reaction of $OsO_3(NBu^t)$ with isobutylene and show that, as postulated [1], it contains a five-membered ring comprised of the metal atom together with coordinated nitrogen and oxygen atoms with the two carbon atoms of the erstwhile alkene. This ring system is analogous to the diolato rings found in monoester and diester complexes of osmium [2, 3], and this structural determination is the first to be made of an alkanolaminato complex.

Crystals of the deep brown complex where made by passing isobutylene gas into a solution of $OsO_3(NBu^t)$ in a chloroform-diethylether mixture, followed by slow evaporation of the solution.

The crystals are monoclinic, with $a = 8.184(1)$, $b = 11.475(2)$, $c = 12.100(2)$ Å, $\beta = 103.91(1)°$, $U = 1103.0$ Å^3 (at 20 °C), space group is $P2_1/c$ and $Z = 4$. Intensity data were collected on a Nicolet R3m/Eclipse S140 diffractometer system, using graphite-monochromated Cu Kα radiation. A total of 1124 independent reflections were measured (to $\theta = 50°$), of which 179 were judged to be 'unobserved'. The structure was solved by Patterson and Fourier methods, and least-squares refinement has now reached $R = 0.059$. A degree of conformational disorder affects the alkanolaminato rings. The program system SHELXTL [4] was used throughout the calculations.

Figure 1 shows the molecular structure of the dimeric title complex, in which a planar Os_2O_2 bridge links the two halves of the molecule. The dimer lies on a crystallographic centre of symmetry, and the coordination about the osmium atoms can best be described as square-pyramidal with a distortion towards the trigonal-bipyramidal. Using the square-pyramidal description, the terminal oxygen atom occupies the apical position, and the mean O(apical)–Os–O,N(basal) angle of 110°, the mean Os–O(bridging) distance of 1.92 Å, and the Os–O(terminal) of 1.67 Å, are all comparable to those found in the dimeric monoester complex $Os_2O_4(O_2C_2Me_4)_2$ [2]. The Os–N bond length is unexceptional at 1.91 Å.

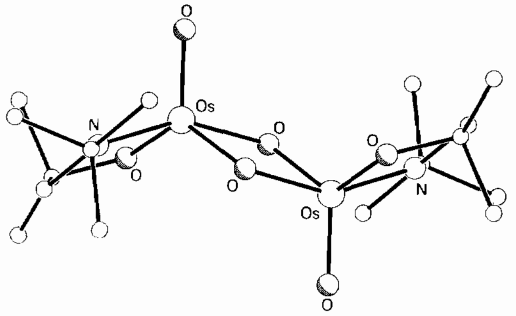

Fig. 1. Molecular structure of $Os_2O_4(OCMe_2CH_2NBu^t)_2$.

As with the dimeric diolato complexes $Os_2O_4(O_2R)_2$ [2] the complex is dimeric in solution (molecular weight in benzene 770, calculated for dimer 734). It exhibits a band in its infrared and Raman spectra at 960 cm^{-1} assigned to the terminal Os=O stretch, and a band at 660 cm^{-1} in the infrared assigned to a stretching vibration of the Os_2O_2 ring, similar to those found [5] for $Os_2O_4(O_2R)_2$ complexes. Although it is perhaps not surprising that the complex is dimeric in solution (since this is also the case for the diolato analogues), the diaminato complexes $OsO_2(NBu^t(CHCOOR)_2NBu^t)$ (R = Me, Et) [6] and the new complex $OsO_2(NBu^t(CHCN)NBu^t)_2$ (made from $OsO_2(NBu^t)_2$ and fumaronitrile) are monomeric in benzene. There is no obvious chemical or steric reason why alkanolaminato and alkanoldiaminato species should differ in their solution molecularity, and we hope to obtain a crystal structure of one of these diaminato complexes.

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