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Partial Coordination in an Adduct of an Osmium Imido Complex: X-ray Molecular Structure of $[OsO_3(NOct^t)]_2 \cdot N_2C_6H_{12}$

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We have shown in earlier work [1, 2] that osmium tetroxide OsO_4 will form adducts with bridgehead amines in which there is a very long Os–N(amine) bond; we have called this 'partial coordination' [1]. We now show that the tetrahedral oxo-imido complex $OsO_3(NOct^t)$, formed by reaction of OsO_4 with tert-octylamine [3], forms a 2:1 adduct with 1,4-diazabicyclo[2,2,2]octane ($N_2C_6H_{12}$) to give the new complex $[OsO_3(NOct^t)]_2 \cdot N_2C_6H_{12}$, in which there is an even longer Os–N(amine) bond.

The complex was made as orange needles by slow crystallisation from a solution of $OsO_3(NOct^t)$ (0.14 g, 0.4 mmol) and 1,4-diazabicyclo[2,2,2]octane (0.03 g, 0.2 mmol) in diethylether (5 cm^3).

The crystals are monoclinic with $a = 6.541(1)$, $b = 28.652(4)$, $c = 15.981(2)$ Å, $\beta = 92.82(1)$, $U = 2991.4$ Å^3 (at 19 °C), space group $P2_1/c$ and $Z = 4$. Intensity data were collected on a Nicolet R3m/Eclipse S140 diffractometer system, using graphite-monochromated Cu Kα radiation. A total of 3742 independent reflections were measured (to $\theta = 55°$), of which 1096 were judged to be 'unobserved'. The structure was solved by a combination of direct, Patterson, and Fourier methods, and least-squares refinement has now reached $R = 0.058$. The central portion of the molecule is subject to conformational disorder. Program system SHELXTL [4] was used throughout the calculations.

Figure 1 shows that the molecule is binuclear, with the amine bridging two $OsO_3(NOct^t)$ units. The osmium atoms have distorted trigonal bipyramidal coordination in which the equatorial positions are occupied by oxo ligands with a mean Os–O bond length of 1.71(1) Å, which is similar to that found in OsO_4 itself [5]. The axial positions are taken by the tert-octylimido ligand, with a mean Os–N(imido) bond length of 1.73(1) Å, comparable with such distances found in other osmium oxo-imido complexes [6], and by the bridging cage amine. Here the Os–N(amine) distances are very long with a mean of 2.45(1) Å, longer than the 2.37 Å distances observed in $OsO_4 \cdot NC_7H_{13}$ and 2.42 Å in $[OsO_4]_2 \cdot N_4C_6H_{12}$ [1]. This difference could well arise from the greater *trans* influence of the imido as compared with the oxo ligand.

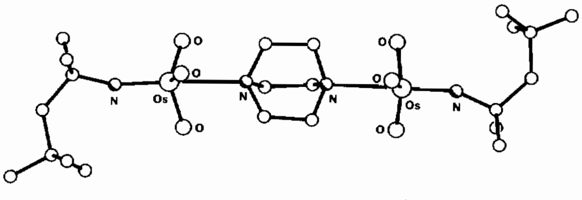

Fig. 1. Molecular structure of $[OsO_3(NOct^t)]_2 \cdot N_2C_6H_{12}$.

The vibrational spectra are fully consistent with this structure. Three ν_{OsO} stretches are observed in the infrared spectrum of the solid at 883, 873 and 845 cm^{-1}, with Raman bands at 887, 875 and 850 cm^{-1}; the ν_{OsN}(imide) stretch is at 1170 cm^{-1} in the infrared and Raman. In toluene or carbon tetrachloride solutions, however, two ν_{OsN} bands appear at 1210 and 1170 cm^{-1}, and in the ν_{OsO} regions there are infrared bands at 924, 914, 880 and 873 cm^{-1} (at 929, 912, 889 and 878 cm^{-1} in the Raman). The 1210 cm^{-1} band and the ν_{OsO} stretches above 900 cm^{-1} appear in solutions of OsO_3NOct^t also, and it is clear that dissociation has occurred, presumably to $OsO_3NOct^t \cdot N_2C_6H_{12}$ and to free OsO_3NOct^t. Such a conclusion is supported by molecular weight studies on the complex in benzene solution (found 488, calculated 841), clearly indicating dissociation. It is interesting that the analogous adduct with osmium tetroxide, $[OsO_4]_2 \cdot N_2C_6H_{12}$ retains its binuclear structure in benzene [2].

The $4f_{7/2}$ and $4f_{5/2}$ binding energies in the ESCA spectrum are at 53.0 and 55.7 eV respectively, consistent with the osmium being in the octavalent state (thus we find that for $K[OsO_3N]$ the corresponding binding energies are at 53.3 and 56.1 eV).

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References

1 W. P. Griffith, A. C. Skapski, K. A. Woode and M. J. Wright, *Inorg. Chim. Acta, 31*, L413 (1978).

2 M. J. Cleare, P. C. Hydes, W. P. Griffith and M. J. Wright, *J. Chem. Soc., Dalton Trans.*, 941 (1977).

3 N. A. Milas and M. I. Iliopulos, *J. Am. Chem. Soc., 81*, 6089 (1959).

4 G. M. Sheldrick, 'SHELXTL', an integrated system for solving, refining and displaying crystal structures from diffraction data, revision 4, Nicolet Instrument Ltd., Warwick, January 1983.

5 H. M. Seip and R. Stolevik, *Acta Chem. Scand., 20*, 385 (1966).

6 W. A. Nugent, R. L. Harlow and R. J. McKinney, *J. Am. Chem. Soc., 101*, 7265 (1979).

0020-1693/85/$3.30