X-Ray Molecular Structure of the Asymmetrically Bridged Ester Complex Di-μ-oxo-bis[(cyclohexane-1,2-diolato)oxo(quinuclidine)osmium(VI)], $[OsO_2(O_2C_6H_{10})(C_7H_{13}N)]_2$

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Summary An *X*-ray structure determination of the title compound has shown it to be a dimer involving a novel asymmetric Os_2O_2 bridge system; in solution the bridge breaks to give a pentaco-ordinate monomer $[OsO_2(O_2C_6H_{10})(C_7H_{13}N)]$.

Osmium tetraoxide (OsO_4) and quinuclidine (L) form an adduct, $OsO_4{\cdot}C_7H_{13}N$, which reacts with mono-alkenes R to give diamagnetic products of stoicheiometry $OsO_4{\cdot}R{\cdot}L$.[1] Such complexes are of interest as models for the products formed by reaction of OsO_4, during its fixation of plant tissue, with those unsaturated alkaloids which contain quinuclidine units (*e.g.*, quinine or cinchonine). We present data on the complex formed from cyclohexene which show it to be dimeric in the solid and monomeric in solution, the O=Os=O unit deviating considerably from linearity in both cases.

The adduct $OsO_4{\cdot}C_7H_{13}N$ was treated with cyclohexene (C_6H_{10}) in a 1 : 1 molar ratio in diethyl ether, and the solution was allowed to evaporate slowly. Dark green crystals of a dimeric compound were deposited, which proved to be orthorhombic, with $a = 23{\cdot}394$, $b = 10{\cdot}303$, $c = 11{\cdot}743$ Å, space group *Pbca*, $Z = 4$. Intensity data were collected on a Siemens four-circle off-line automatic diffractometer. A total of 1784 independent reflections were measured to $\theta = 55°$, of which 139 were judged to be 'unobserved.' The structure was solved by Patterson and Fourier methods, and least-squares refinement has reached $R = 0{\cdot}059$.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

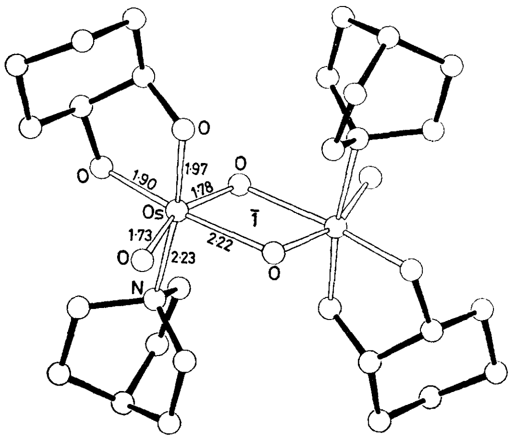

FIGURE. Dimeric structure of $[OsO_2(O_2C_6H_{10})(C_7H_{13}N)]_2$. Standard deviations of bond lengths are *ca.* 0·01 Å

The Figure shows the structure of the dimeric molecule, in which the two halves are related by a centre of symmetry. A notable feature of the molecule is the presence of an asymmetric Os_2O_2 bridge system, the two independent bridge distances being 1·78 and 2·22 Å. The shorter bond differs only slightly in length from the terminal oxo-ligand (1·73 Å) and clearly has appreciable multiple bond character. The terminal Os=O bond length is comparable to those found in other oxo-osmium complexes, *e.g.*, $[Os_2O_4(O_2C_2Me_4)_2]$[2] and $[OsO(O_2C_2H_4)_2]$.[3] The longer 2·22 Å linkage, while weak, is clearly sufficient to hold the dimer together on crystallisation. Although asymmetry has been found in the single oxo-bridged species $[Na(NH_4)\{MoO_3(C_2O_4)\}]_n$ (bridge distances 1·878 and 2·230 Å),[4] ours is the first example of a complex containing an asymmetric M_2O_2 bridge. The Os–O(ester) bond lengths are unexceptional, while the relatively long Os–N distance of 2·23 Å is comparable with those found in $[OsO_2(O_2\text{-methylthymine})(py)_2]$[5] (py = pyridine).

The complex is monomeric in chloroform $\{M\ 465$; calc.for $[OsO_2(O_2C_6H_{10})(C_7H_{13}N)]$, $447\}$ indicating that the weak bridge has broken. Vibrational spectra of the complex in chloroform show two pairs of bands which may be assigned to O=Os=O stretches: a strong, polarised Raman shift at 923 cm^{-1} (weak i.r. counterpart at 919 cm^{-1}) which we assign to the symmetric stretch $\nu_{sym}(OsO_2)$, and a weak, depolarised Raman shift at 881 cm^{-1} (strong i.r. counterpart at 879 cm^{-1}), ascribed to the asymmetric stretch $\nu_{asym}(OsO_2)$. Activity of both the symmetric and asymmetric bands in the Raman and i.r. spectra indicates, as it does with *cis* dioxo-species,[6] a non-linear arrangement of the OsO_2 unit. We suggest that the solute has a trigonal bipyramidal structure with the terminal oxo-ligands in the equatorial plane and an axial quinuclidine ligand. An equatorial arrangement of oxo-ligands is found in $[RuO_3(OH)_2]^{2-}$,[7] but ours is the first example of such a d^2 dioxo-system. This proposed solute structure is closely related to that established for the solid; in the latter, the co-ordination about the osmium atoms may be thought of as arising from two weakly linked trigonal bipyramidal species, where the approach of one terminal Os=O group from each molecule creates the asymmetric double bridge, opening out the erstwhile equatorial O=Os=O angle to 154°.

We thank the S.R.C. for a Research Studentship (to B. A. C.) and the S.R.C. and Johnson, Matthey Limited for a C.A.S.E. Award (to M. S.).

(*Received*, 20*th July* 1978; *Com.* 781.)

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[1] M. J. Cleare, P. C. Hydes, W. P. Griffith, and M. J. Wright, *J.C.S. Dalton*, 1977, 941.

[2] F. L. Phillips and A. C. Skapski, *J.C.S. Dalton*, 1975, 2586.

[3] F. L. Phillips and A. C. Skapski, *Acta Cryst.*, 1975, **B31**, 1814.

[4] L. O. Atovmyan and G. B. Bokii, *J. Struct. Chem.*, 1963, **4**, 524.

[5] T. J. Kistenmacher, L. G. Marzilli, and M. Rossi, *Bioinorg. Chem.*, 1976, **6**, 347.

[6] W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 211.

[7] G. Nowogrocki, F. Abraham, J. Tréhaux, and D. Thomas, *Acta Cryst.*, 1976, **B32**, 2413.