Crystal and Molecular Structure of Bis[μ-oxo-oxo(tetramethylethane-1,2-diolato)osmium(VI)]; a Dimeric Monoester Complex with Square-pyramidal Co-ordination

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The crystal structure of the title complex has been determined from *X*-ray diffractometer data, and has been refined to *R* 0.038 for 1 309 independent reflections. Crystals are monoclinic, with unit-cell dimensions a = 8.145(3), b = 14.008(3), c = 7.811(3) Å, β = 93.24(3)°; space group $P2_1/n$, Z = 2.

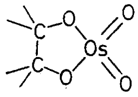
This structure differs from those hitherto accepted for osmium(VI) monoester complexes in that it is dimeric and has $\bar{1}$ (S_2) crystallographic symmetry. A square-pyramidal co-ordination is found for osmium, two of the basal oxygen atoms being from a chelate ester [mean Os–O(ester) 1.87 Å], and the other two from a dioxo-bridge [mean Os–O(br) 1.92 Å]. A terminal oxo-ligand occupies the apical position, with a short Os–O(term) distance of 1.675 Å. Electronic repulsion by this π-donating ligand causes the large O(apical)–Os–O(basal) mean angle of 111.1°, such that the osmium atom is 0.68 Å above the basal plane.

The monoester is discussed as a model compound for the staining and fixation of unsaturated membrane lipids by osmium tetroxide.

OSMIUM tetroxide has two important uses: as a reagent in organic chemistry for the *cis*-specific hydroxylation of ethylenic double bonds,[1] and as a staining and fixation agent in the examination of biological tissue components by electron microscopy.[2,3]

The *cis*-hydroxylation reaction is thought to proceed *via* a cyclic monoester intermediate which on hydrolysis yields the *cis*-diol. Hitherto the most generally accepted structure [4,5] for the monoester intermediate has involved four-co-ordinate osmium(VI), and is often quoted in textbooks [6] as (I); such a structure would imply tetrahedral osmium(VI), for which no crystallographically proved example exists. Other structures involving octahedral co-ordination have also been suggested.[7,8]

The most widely held theory for the staining and fixation of biological tissue by osmium tetroxide has as the initial step an attack on olefinic double bonds which results in the formation of osmium(VI) mono- or di-esters; the evidence for the two possible intermediate species is summarised in ref. 2. A striking departure from current orthodoxy has been the suggestion [9] that OsO_4 simply


(I)

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[1] J. F. Cairns and H. L. Roberts, *J. Chem. Soc.* (*C*), 1968, 640.

[2] J. C. Riemersma, ' Some Biological Techniques in Electron Microscopy,' Academic Press, New York, 1970, pp. 69—99.

[3] M. A. Hayat, ' Principles and Techniques of Electron Microscopy,' vol. 1, Van Norstrand, London, 1970, p. 36.

[4] R. Criegee, *Annalen*, 1936, **522**, 75.

[5] R. Criegee, B. Marchand, and H. Wannowius, *Annalen*, 1942, **550**, 99.

[6] See *e.g.* R. O. C. Norman, ' Principles of Organic Synthesis,' Methuen, London, 1968, pp. 502—503; F. A. Cotton and G. Wilkinson, ' Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 1003.

[7] R. Becker, quoted in ref. 2.

[8] W. P. Griffith and R. Rossetti, *J.C.S. Dalton*, 1972, 1449.

[9] R. B. Litman and R. J. Barnett, *J. Ultrastruct. Res.*, 1972, **38**, 63.

attaches itself to aliphatic side chains and proteins through hydrogen bonds. This, however, seems rather unlikely in view of the experimental evidence [10] that OsO_4 has negligible hydrogen-bonding properties.

From our *X*-ray structural studies on simple model mono- and di-ester osmium(VI) complexes, we find that in both the title compound, for which preliminary information has been published,[11] and the related di-ester complex, $OsO(O_2C_2H_4)_2$,[12,13] the metal atom has a square-pyramidal five-co-ordination. Apart from having a different metal co-ordination, the monoester complex differs from (I) in that it is dimeric. It has been shown [14] by chemical and spectroscopic methods that osmium(VI) monoesters of larger alkenes are also dimeric and of a similar nature to the title complex, which suggests that this structure-type has wider generality.

EXPERIMENTAL

Crystals of $[\{OsO_2(O_2C_2Me_4)\}_2]$ were obtained [14] from carbon tetrachloride as black elongated prisms. Accurate unit-cell dimensions were obtained from a least-squares calculation on 21 high-angle α_1 reflections measured on a diffractometer.

TABLE 1

Fractional atomic co-ordinates and anisotropic thermal parameters, with estimated standard deviations in parentheses

Atom	x	y	z	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Os(1)	0.565 53(4)	0.449 25(3)	0.347 03(5)	892(13)	299(4)	1 115(11)	28(2)	142(7)	29(3)
				$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
O(1)	0.453 6(10)	0.461 8(6)	0.161 8(6)	161(15)	80(6)	169(17)	18(6)	−11(12)	7(6)
O(2)	0.415 6(9)	0.433 8(4)	0.529 8(9)	136(11)	31(3)	187(14)	−3(5)	66(10)	−7(5)
O(3)	0.787 8(8)	0.463 4(4)	0.308 4(10)	112(11)	32(3)	222(15)	−3(5)	47(10)	−8(5)
O(4)	0.630 9(8)	0.323 7(4)	0.399 0(9)	104(10)	28(3)	199(13)	5(5)	34(9)	4(5)
C(3)	0.872 9(12)	0.374 4(7)	0.271 1(14)	108(15)	44(6)	200(20)	14(7)	46(14)	−24(9)
C(31)	1.054 8(13)	0.394 7(10)	0.304 2(21)	106(18)	69(8)	362(33)	2(9)	35(19)	−62(14)
C(32)	0.829 2(16)	0.347 1(9)	0.084 3(16)	210(23)	69(8)	185(22)	13(11)	49(18)	−2(11)
C(4)	0.808 1(12)	0.303 2(7)	0.397 3(13)	119(15)	39(5)	184(19)	25(8)	3(13)	−11(8)
C(41)	0.874 5(16)	0.317 3(9)	0.579 4(15)	212(23)	66(7)	178(21)	22(11)	−65(18)	−22(10)
C(42)	0.820 9(14)	0.197 0(8)	0.347 6(16)	163(20)	53(7)	221(24)	19(9)	−7(17)	−35(10)

Crystal Data.—$C_{12}H_{24}O_8Os_2$, $M = 676.6$, Monoclinic, $a = 8.145(3)$, $b = 14.008(3)$, $c = 7.811(3)$ Å, $\beta = 93.24(3)°$, $U = 889.8$ Å^3, $D_m = 2.50$ (by flotation), $Z = 2$, $D_c = 2.53$, $F(000) = 624$. Space group $P2_1/n$ (No. 14), Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 272.1 cm^{-1}.

A crystal *ca.* 0.28 × 0.26 × 0.27 mm was selected, and was mounted about its *a* axis on a Siemens off-line automatic four-circle diffractometer. Intensity measurement was carried out using a 'five-value' procedure [15] (one side of peak, background, full peak, background on other side of peak, other side of peak), with Cu-K_α radiation at a take-off angle of 3.0°, a nickel β filter, and a Na(Tl)I scintillation counter. Of 1 321 independent reflections measured in two concentric spheres (θ 0—45°, and 45—60°), 56 were judged 'unobserved' as the net count of each was $<2.58\sigma$. The intensity of the $34\bar{4}$ reflection, monitored every 50 reflections, was almost constant until about half-way through data collection, but by the end (*ca.* 40 h) the net count had dropped by *ca.* 15%. Data were scaled by use of the reference reflection, and Lorentz and polarisation corrections were applied.

Solution and Refinement of the Structure.—An updated version [16] of the '*X*-ray '63' system [17] was used for the solution of the structure, the refinement being carried out by use of the full-matrix least-squares program ORFLS. Calculations were performed on the University of London CDC 7 600 computer, while the structural illustrations were drawn with the Imperial College CDC 6 400 and a Kingmatic flat-bed plotter.

Solution of the structure was started as soon as the inner sphere of data had been collected. A three-dimensional Patterson synthesis gave the position of the osmium atom and after a few cycles of isotropic least-squares refinement *R* was 0.168. All other non-hydrogen atoms were located from the resulting difference-Fourier synthesis, and isotropic refinement reduced *R* to 0.075. When the atoms were allowed to refine with anisotropic thermal parameters *R* dropped to 0.062, but this rose to 0.069 when the remainder of the intensity data was included in the refinement.

At this point an absorption correction was applied according to the method of Busing and Levy [18] using a 10 × 10 × 10 grid with crystal pathlengths determined by the vector analysis procedure.[19] Refinement as previously gave *R* 0.048. The three strongest low-angle reflections judged to be suffering from extinction were removed from the data, and from a difference-Fourier synthesis ten of the twelve independent hydrogen atoms were located with a fair degree of confidence; the positions of the remaining two were calculated. Inclusion of these atoms as a fixed-atom contribution with isotropic temperature factors of their parent carbon atoms gave *R* 0.042. Introduction of a weighting scheme (*R* 0.040) and the removal of nine more extinguished reflections reduced *R* to its final value of 0.038.

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[10] R. J. Collin and W. P. Griffith, *J. Histochem. Cytochem.*, 1974, **22**, 992.

[11] R. J. Collin, W. P. Griffith, F. L. Phillips, and A. C. Skapski, *Biochim. Biophys. Acta*, 1973, **320**, 745.

[12] R. J. Collin, W. P. Griffith, F. L. Phillips, and A. C. Skapski, *Biochim. Biophys. Acta*, 1974, **354**, 152.

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

[14] R. J. Collin, J. Jones, and W. P. Griffith, *J.C.S. Dalton*, 1974, 1094.

[15] F. H. Allen, D. Rogers, and P. G. H. Troughton, *Acta Cryst.*, 1971, **B27**, 1325.

[16] Ref. 17, version of July 1970, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin.

[17] '*X*-ray '63' system of programs, J. M. Stewart, University of Maryland Technical Report TR 64 6.

[18] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[19] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[20] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[21] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[22] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[23] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

The Hughes weighting scheme[20] used had $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geqslant F^*$, with $F^* = 44$ as the final optimum value. Atomic scattering factors were taken from ref. 21 for non-hydrogen atoms and from ref. 22 for hydrogen, the correction for the real and the imaginary parts of anomalous dispersion for osmium being taken from ref. 23. Table 1 lists the fractional co-ordinates of the non-hydrogen atoms and the coefficients in the expression for the anisotropic temperature factor $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, while the unrefined co-ordinates of the hydrogen atoms are given in Table 2. Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21 528 (7 pp., 1 microfiche).*

TABLE 2

Fractional co-ordinates of the hydrogen atoms

Atom	*x*	*y*	*z*
H(311)	1.089	0.437	0.427
H(312)	1.122	0.332	0.317
H(313)	1.094	0.444	0.212
H(321)*	0.703	0.331	0.068
H(322)	0.904	0.278	0.038
H(323)	0.854	0.413	0.000
H(411)	0.975	0.311	0.625
H(412)	0.800	0.274	0.675
H(413)	0.858	0.388	0.633
H(421)	0.952	0.186	0.335
H(422)	0.771	0.183	0.242
H(423)*	0.758	0.125	0.417

* Calculated position.

Hydrogen atoms are numbered so that the first two digits correspond to the numbering of the carbon atoms to which they are bonded.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Figure 1 shows the molecular structure of the dimeric title complex, and the thermal vibration ellipsoids[24] of the non-hydrogen atoms. The molecule possesses $\bar{1}$ (S_2) crystallographic symmetry, and the asymmetric unit contains an osmium atom in a square-pyramidal environment. Of the four oxygen atoms forming the base of this pyramid, two derive from the chelating ester group while the other two are from a dioxo-bridge. A terminal oxygen atom forms the apex of the pyramid. The more important bonded and non-bonded intramolecular distances are listed in Table 3, and bond angles in Table 4.

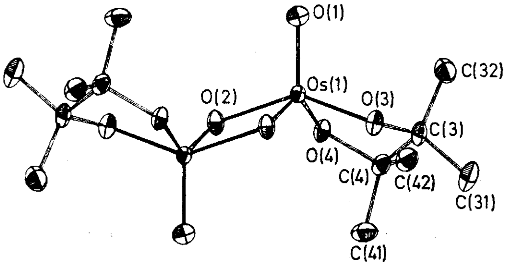

FIGURE 1 The binuclear centrosymmetric structure of [{OsO$_2$(O$_2$C$_2$Me$_4$)}$_2$]. Thermal vibration ellipsoids are scaled to enclose 20% probability

The short Os–O(term) bond length (1.675 Å) is indicative of a triple bond, and is virtually identical to that found (1.673 Å)[13] in the monomeric diester OsO(O$_2$C$_2$H$_4$)$_2$. It is *ca.* 0.1 Å shorter than Os–O(term) double-bond distances reported for six-co-ordinate complexes.[25–27] Of the four Os–O(basal) distances, the two Os–O(ester) bond lengths (mean 1.870 Å) are significantly shorter than the two Os–O(br) bonds (mean 1.922 Å). It is possible that some π-bonding interaction occurs between the osmium atom and the *p* orbitals of the ester oxygen atoms, and this is in line with the observed lengthening of the O–C(ester) bonds (mean 1.468 Å, as compared to a literature mean of 1.426 Å from ref. 28). Table 5 shows that in the metal–ester chelate system four of the atoms [Os(1), O(3), O(4), and C(4)] are reasonably planar, while C(3) is *ca.* 0.6 Å out of the least-squares plane.

TABLE 3

Interatomic distances (Å), with estimated standard deviations in parentheses

(*a*) Bonded distances

Os(1)–O(1)	1.675(7)		
Os(1)–O(2)	1.943(7)	Os(1)–O(3)	1.863(7)
Os(1)–O(2$^{\rm I}$)	1.901(6)	Os(1)–O(4)	1.876(6)
Mean Os–O(bridge)	1.922	Mean Os–O(ester)	1.870
O(3)–C(3)	1.463(12)	O(4)–C(4)	1.473(12)
C(3)–C(4)	1.518(15)		
C(3)–C(31)	1.517(14)	C(4)–C(41)	1.506(16)
C(3)–C(32)	1.531(16)	C(4)–C(42)	1.542(15)

(*b*) Non-bonded distances

O(1) · · · O(2)	2.935(11)	O(2) · · · O(2$^{\rm I}$)	2.371(13)
O(1) · · · O(2$^{\rm I}$)	2.964(10)	O(2) · · · O(4)	2.589(9)
O(1) · · · O(3)	2.893(10)	O(3) · · · O(2$^{\rm I}$)	2.579(10)
O(1) · · · O(4)	2.993(10)	O(3) · · · O(4)	2.463(9)
Mean O(apical) · · · O(basal)	2.946		
Mean O(basal) · · · O(basal)	2.501		
Os(1) · · · Os(1$^{\rm I}$)	3.026(2)		

Here and in subsequent Tables, Roman numeral superscript refers to atoms in the following position: I, $1 - x, 1 - y, 1 - z$

TABLE 4

Bond angles (°) with estimated standard deviations in parentheses

O(1)–Os(1)–O(2)	108.2(3)	O(1)–Os(1)–O(3)	109.6(4)
O(1)–Os(1)–O(2$^{\rm I}$)	111.8(4)	O(1)–Os(1)–O(4)	114.8(4)
Mean O(apical)–Os–O(basal)	111.1		
O(2)–Os(1)–O(2$^{\rm I}$)	76.1(4)	O(3)–Os(1)–O(4)	82.4(3)
O(2)–Os(1)–O(4)	85.4(3)	O(3)–Os(1)–O(2$^{\rm I}$)	86.5(3)
O(2)–Os(1)–O(3)	142.0(3)	O(2$^{\rm I}$)–Os(1)–O(4)	133.2(3)
Os(1)–O(2)–Os(1$^{\rm I}$)	103.9(4)		
Os(1)–O(3)–C(3)	114.6(5)	Os(1)–O(4)–C(4)	116.6(5)
O(3)–C(3)–C(4)	104.2(8)	O(4)–C(4)–C(3)	104.7(7)
O(3)–C(3)–C(31)	106.0(9)	O(4)–C(4)–C(41)	105.4(9)
O(3)–C(3)–C(32)	108.4(8)	O(4)–C(4)–C(42)	105.7(8)
C(4)–C(3)–C(31)	112.6(9)	C(3)–C(4)–C(41)	114.0(9)
C(4)–C(3)–C(32)	112.6(9)	C(3)–C(4)–C(42)	116.2(9)
C(31)–C(3)–C(32)	112.4(1.0)	C(41)–C(4)–C(42)	109.8(9)

As has been discussed for the analogous cases of the

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

[24] C. K. Johnson, ORTEP thermal ellipsoid plotting program, Oak Ridge National Laboratory, 1965, Report ORNL 3794.

[25] F. H. Kruse, *Acta Cryst.*, 1961, **14**, 1035.

[26] M. A. Porai-Koshits, L. A. Atovmyan, and V. G. Adrianov, *J. Struct. Chem. USSR*, 1961, **2**, 686.

[27] L. A. Atovmyan and O. A. L'yachenko, *J. Struct. Chem. USSR*, 1967, **8**, 143.

[28] *Chem. Soc. Special Publ.*, No. 18, 1965.

nitride ligand in $[OsNCl_4]^-$(ref. 29) and the terminal oxo-ligand in $OsO(O_2C_2H_4)_2$,[13] the extensive multiple-bonding character of the Os–O(term) linkage here causes a depression of the oxygen atoms constituting the base of the pyramid. The effect of the π-electronic repulsion must, of course, be counterbalanced by O(basal) ··· O(basal) interactions, and this occurs at the unusually large mean O(term)–Os–O(basal) angle of 111.1°. To illustrate this point one may consider the O ··· O non-bonded distances in the co-ordination polyhedron. The mean O(basal) ··· O(basal) separation is 2.501 Å; while one could argue that the O(bridge) ··· O(bridge) and O(ester) ··· O(ester) separations are subject to chelate-bonding constraints, no such restriction operates on the O(bridge) ··· O(ester) separations. The fact that the mean O(apical) ··· O(basal) distance (2.946 Å) is much longer than that of the mean O(bridge) ··· O(ester) (2.584 Å) shows the overriding influence of the π-bonding terminal ligand.

TABLE 5

Planarity of groups of atoms in the structure and (in square brackets) distances (Å) of relevent atoms from least-squares planes. Equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space

Plane (1): O(2)—(4), O(2^I)

$$3.99x - 1.15y + 6.55z = 4.70$$

[O(2) −0.066, O(2^I) 0.066, O(3) −0.064, O(4) 0.063, Os(1) −0.682, O(1) −2.357]

Plane (2): O(2)—(4), O(2^I)—(4^I)

$$4.07x - 0.95y + 6.51z = 4.82$$

[O(2) −0.087, O(2^I) 0.087, O(3) −0.042, O(3^I) 0.042, O(4) 0.042, O(4^I) −0.042, Os(1) −0.682, Os(1^I) 0.682, O(1) −2.356, O(1^I) 2.356]

Plane (3): Os(1), O(3), O(4), C(4)

$$0.85x + 3.94y + 7.39z = 4.79$$

[Os(1) 0.024, O(3) −0.018, O(4) −0.031, C(4) 0.025, C(3) −0.572]

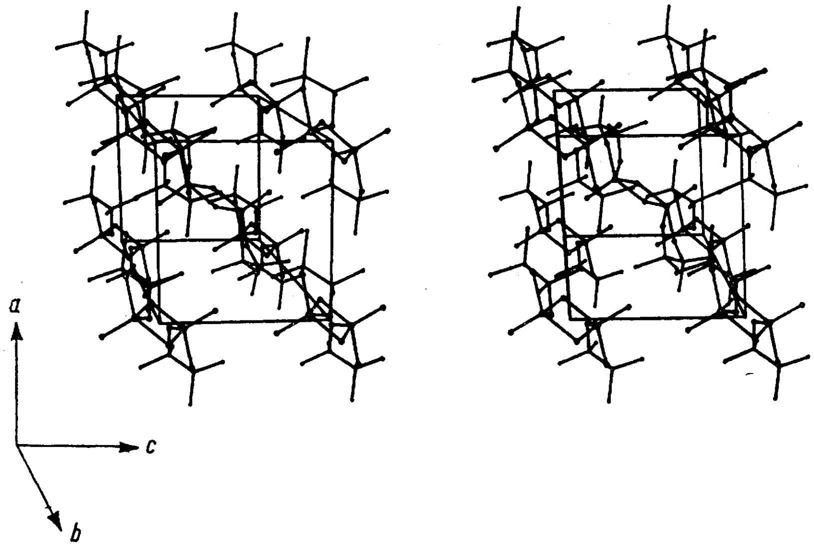

FIGURE 2 A stereoscopic view showing the packing of the dimeric molecules

The individual O(apical)–Os–O(basal) angles range from 108.2 to 114.8°. This scatter represents a slight deviation from square-pyramidal towards trigonal-bipyramidal co-ordination, although less than that observed for the diester complex.[13] A least-squares plane through the four basal oxygen atoms shows a mean deviation of 0.065 Å, with the osmium atom 0.68 Å above this plane (Table 5).

A stereoscopic pair of drawings [24] (Figure 2) shows the packing arrangement of the dimeric molecules. The closest intermolecular approach is across a centre of symmetry and involves the terminal oxygen atoms, O(1) ··· O(1^{II}), 2.885 Å (II at $1 - x, 1 - y, -z$). While this distance is rather short, it is readily explicable in terms of the withdrawal of the oxygen electron-density into the Os≡O triple bonds. All other distances are >3.2 Å and not particularly noteworthy.

As already stated, the structure of the title complex, in being dimeric and five-co-ordinate, differs from that most often quoted for osmium(VI) monoester species (I). Square-pyramidal co-ordination for osmium(VI) is not rare, having been established crystallographically for $(Ph_4As)[OsNCl_4]$,[29,30] and $(Ph_4As)[OsNI_4]$,[31] and also for the diester complex.[12,13] Furthermore, chemical and spectroscopic studies [14] indicate that osmium(VI) mono- and di-ester derivatives of a wide range of alkenes have structures similar to those of the two ester complexes[11-13] characterised by X-ray methods. While smaller alkenes gave both mono- and di-ester derivatives (II), for larger alkenes, such as cholesterol and ergosterol, only monoesters were obtained.[14] This seems reasonable in that in the dimeric monoester structure the presence

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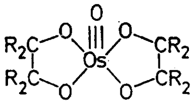
[29] F. L. Phillips and A. C. Skapski, *J. Cryst. Mol. Struct.*, 1975, **5**, 83.

[30] S. R. Fletcher, W. P. Griffith, D. Pawson, F. L. Phillips, and A. C. Skapski, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 1117.

[31] F. L. Phillips, A. C. Skapski, and M. J. Withers, *Transition Metal Chem.*, 1975, **1**, 32.

of an Os_2O_2 bridge helps to keep the bulkier ester groups apart and so minimises steric interactions. However, where the erstwhile double bond is reasonably exposed it may still be possible for the two alkene molecules to approach close enough for a monomeric diester complex to be formed, despite the size of the alkene, as indeed has been observed in the case of methyl oleate.[32]



(II)

Osmium tetroxide is the most commonly used reagent in the staining and fixation of biological tissue for electron microscopy. The situation occurring in a biological environment will, of course, be much more complicated than that found in controlled chemical experiments, and although the action of OsO_4 on tissue has been known for more than a century[33] the actual processes taking place are still a matter of conjecture. One of the points of dispute has been whether the initial attack of OsO_4 on olefinic double bonds leads to the formation of mono-[34] or di-esters.[32,35,36]

The cross-linking of lipid chains was first suggested by Wigglesworth[35] as an explanation of the fixation properties of OsO_4. Monoester structures of the type depicted by (I) clearly do not cross-link, and the wide acceptance of (I), therefore, helped to raise the importance given to diester species as bridging groups between lipid chains. The new model of the monoester species, as exemplified by the title compound (Figure 1), is now equally plausible as a bridging unit.*

The fact that in normal practice an excess of OsO_4 is used would tend to swing the balance in favour of the formation of monoester species, *i.e.* osmium–double-bond ratio 1 : 1 rather than 1 : 2. This, together with the results of Collin *et al.*,[14] would suggest that monoesters are the more likely intermediates. However, under favourable conditions diester formation could also occur. One important factor in deciding which species is formed will be the original disposition of double bonds in the lipids of the substrate before fixation, since each type of complex requires a characteristic separation between the erstwhile C=C bonds. This can be easily calculated from the geometry of the two model structures,[11,13] and is *ca.* 8 and 5 Å for the mono- and di-ester respectively. Because of these relatively inflexible separations OsO_4 may well cause disruption[37] of the substrate as double bonds are forced (towards or away from each other) into an orientation satisfactory for the osmium atoms.

Given a favourable disposition of double bonds, or a flexible molecule, one can also envisage the formation of intramolecular species of both types.

Apart from the unsaturated lipids, membrane proteins are a further potential site of OsO_4 attack, in particular at their terminal $-SH$ and $-NH_2$ groups.[2] Reaction here may lead to cross-linking, and in the modified Danielli model of the membrane, where the protein and lipid regions interpenetrate, more complicated osmium interactions with both protein and lipid may well be involved.

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* Where for steric reasons a dioxo-bridged intermediate with *trans*-terminal oxo-ligand is impossible, a *cis*-variant may be considered. Although a monoester dimer of this type is highly unlikely as a free unit, in a constrained situation, where both ester ends are anchored on the substrate, it may just be viable. *Note added at proof:* Since this paper was submitted two structures of binuclear molybdenum complexes with *cis*-terminal oxo-ligands have been reported: $[Mo_2O_4(O_2CMe)(NCS)_4]$ (T. Glowiak, M. Sabat, H. Sabat, and M. F. Rudolf, *J.C.S. Chem. Comm.*, 1975, 712) and $[Mo_2O_4(S_2CNEt_2)_2]$ (L. Ricard, C. Martin, R. Weist, and R. Weiss, *Inorg. Chem.*, 1975, **14**, 2300).

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