

3.117 Å listed in Table 2(a) represents only the overall average distance between the atoms involved in that entry in this disordered crystal rather than any specific distance in the unit cell. As explained above, the (Ca, Na)-Cl distance would be shorter than 3.117 Å.

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The Crystal and Molecular Structure of Oxobis(ethane-1,2-diolato)osmium(VI): a Five-Coordinate Diester Complex

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Oxobis(ethane-1,2-diolato)osmium(VI), $\text{OsO}(\text{O}_2\text{C}_2\text{H}_4)_2$, a model compound for the staining and fixation of unsaturated membrane lipids by OsO_4 , is orthorhombic with $a = 10.950$ (2), $b = 8.376$ (2), $c = 7.735$ (2) Å, space group $Pbcn$, $Z = 4$. Full-matrix least-squares refinement with 655 independent reflexions gave $R = 0.030$. The molecule possesses C_2 crystallographic symmetry, and a short Os-O(terminal) bond, of length 1.670 Å, lies along the twofold axis. An essentially square-pyramidal coordination is found for Os, in which four O atoms from the two chelating esters form the base of the pyramid, with a mean Os-O(ester) distance of 1.885 Å. Os lies 0.64 Å above the base. A feature of the molecule is the large O(apical)-Os-O(basal) mean angle of 110.1° . This is a consequence of the electronic repulsion by the strongly π -donating oxo ligand upon the ester O atoms.

Introduction

Osmium tetroxide is a specific reagent in organic chemistry for the *cis*-hydroxylation of olefinic double bonds (Cairns & Roberts, 1968), and it is widely used as a staining and fixation agent for the examination of biological tissues by electron microscopy (Hayat, 1970; Riemersma, 1970). Although the action of OsO_4 on tissue has been known for a long time (*e.g.* Branell, 1849), the exact nature of the processes taking place has been a subject of controversy and is still not fully understood. The most widely accepted theory involves the initial attack of OsO_4 on unsaturated tissue components with the formation of Os^{VI} mono- or diesters. The issue of whether mono- or diesters are formed has, however, been the subject of some debate, and evidence for both sides of the question has been summarized by

Riemersma (1970). A more recent theory has been put forward by Litman & Barnett (1972) who suggested that OsO_4 attaches itself by means of hydrogen bonds to aliphatic side chains and proteins in the tissue. This theory has been refuted by Collin & Griffith (1974), who showed that OsO_4 has negligible hydrogen-bonding properties.

We have carried out an X-ray structural study on relatively simple mono- and diester complexes of Os^{VI} which could serve as model compounds for the staining and fixation of unsaturated membrane lipids. We first determined the structure of a monoester complex (Collin, Griffith, Phillips & Skapski, 1973), and found this compound, $[\text{OsO}_2(\text{O}_2\text{C}_2\text{Me}_4)]_2$, to be five-coordinate and dimeric, and to have a structure quite different from that hitherto accepted. A study of the equivalent diester, $\text{OsO}(\text{O}_2\text{C}_2\text{Me}_4)_2$ (tetragonal, $a =$

10·224, $c=7\cdot265$ Å), proved to be inconclusive because of the sensitivity of the crystals to X-rays and the apparent presence of molecular disorder. We have, however, determined the structure of the closely related title complex, $\text{OsO}(\text{O}_2\text{C}_2\text{H}_4)_2$, and have published the preliminary details (Collin, Griffith, Phillips & Skapski, 1974).

Experimental

Oxobis(ethane-1,2-diolato)osmium(VI) was obtained in the form of black prisms by the prolonged action (over a period of some eight weeks) of OsO_4 on ethylene glycol at room temperatures (Collin, Jones & Griffith, 1974). Preliminary oscillation and Weissenberg photographs showed the crystals to be orthorhombic, with systematic absences $0kl: k=2n+1$, $h0l: l=2n+1$, and $hk0: h+k=2n+1$. These absences uniquely determine the space group as $Pbcn$ (No. 60).

Measurement of some high-angle α_1 and α_2 reflexions on a diffractometer gave $a=10\cdot950$ (2), $b=8\cdot376$ (2), $c=7\cdot735$ (2) Å, $U=709\cdot4$ Å³, $D_{\text{obs}}=3\cdot05$ (by flotation), $D_{\text{calc}}=3\cdot07$ g cm⁻³ for $Z=4$ and a molecular formula $\text{C}_4\text{H}_8\text{O}_5\text{Os}$, M.W. 326·3, $F(000)=592$.

Intensities were measured on a Siemens off-line automatic four-circle diffractometer. A crystal of approximate dimensions $0\cdot14 \times 0\cdot10 \times 0\cdot08$ mm was mounted with \mathbf{b} parallel to the φ axis of the diffractometer, and Cu $K\alpha$ radiation ($\lambda=1\cdot5418$ Å) at a take-off angle of $3\cdot0^\circ$, a Ni β filter and a Na(Tl)I scintillation counter were used. The θ - 2θ scan technique was employed with a 'five-value' measuring procedure: one side of peak, background, full peak, background on other side of peak, other side of peak (Allen, Rogers & Troughton, 1971). 676 independent reflexions were measured (to $\theta=70^\circ$), of which 177 were judged to be 'unobserved' as the net count of each was less than $2\cdot58\sigma$. This unusually high proportion of 'unobserved' reflexions is a consequence of the position of the Os atom on a twofold axis, so that most reflexions with $h+k=2n+1$ were very weak. The 800 reflexion was monitored as a reference every 50 reflexions. Towards the end of the period of data collection (*ca* 30 h), a decrease of *ca* 7% was observed in the intensity of the reference reflexion. The reflexion intensities were scaled by use of the reference reflexion, and Lorentz and polarization corrections were applied.

Solution and refinement of the structure

An updated version of July 1970 of the X-RAY 63 System (Stewart, 1964) was used for the solution and refinement of the structure. Refinement was carried out with the full-matrix *ORFLS* program throughout. The calculations were performed on the University of London CDC 7600 computer, while the structural illustrations were drawn with the aid of the Imperial College CDC 6400.

It was obvious from the intensity distribution on

Weissenberg photographs that the Os atom lay on a twofold axis, and a Patterson synthesis gave the y coordinate of this atom. A few cycles of least-squares refinement based only on Os gave $R=0\cdot207$. All non-hydrogen atoms were located from a difference Fourier synthesis and isotropic refinement reduced R to $0\cdot139$. Anisotropic refinement of the same atoms gave $R=0\cdot096$.

Although the crystal used was fairly small, the linear absorption coefficient was high [$\mu(\text{Cu } K\alpha)=341\cdot9$ cm⁻¹], so data were now corrected for absorption by the Gaussian integration method (Busing & Levy, 1957), with a $12 \times 12 \times 12$ grid, and with crystal path lengths determined by the vector analysis procedure of Coppens, Leiserowitz & Rabinovich (1965). Refinement as previously gave $R=0\cdot074$: heavy damping was required at this stage for convergence. It was clear that quite severe extinction effects were present, and when a weighting scheme was introduced into the refinement, R dropped to $0\cdot054$. Nine strong low-angle reflexions most affected by extinction were now removed from the refinement to give $R=0\cdot038$.

The four independent H atoms were located from a difference Fourier synthesis, and when they were included as a fixed-atom contribution with isotropic temperature factors of the parent C atoms, R diminished to $0\cdot034$. 12 more extinguished reflexions were now removed from the refinement, and the weighting scheme was adjusted to give a final R of $0\cdot030$.

In the later stages of refinement the weighting scheme (Hughes, 1941) was $w=1$ for $F < F^*$, $\sqrt{w}=F^*/F$ for $F \geq F^*$, with $F^*=39$ as the final optimum value. Atomic scattering factors used were those tabulated by Cromer & Waber (1965), except those for H (Stewart, Davidson & Simpson, 1965), while the anomalous dispersion correction for Os was that

Table 1. *The observed and the calculated structure amplitudes* ($\times 10$)

Reflexions marked with an asterisk were unobserved, and those marked with an *E* are thought to be affected by extinction.

hkl	Observed	Calculated	Remarks
000	592	592	
100	100	100	
200	100	100	
300	100	100	
400	100	100	
500	100	100	
600	100	100	
700	100	100	
800	100	100	
900	100	100	
110	100	100	
210	100	100	
310	100	100	
410	100	100	
510	100	100	
610	100	100	
710	100	100	
810	100	100	
910	100	100	
120	100	100	
220	100	100	
320	100	100	
420	100	100	
520	100	100	
620	100	100	
720	100	100	
820	100	100	
920	100	100	
130	100	100	
230	100	100	
330	100	100	
430	100	100	
530	100	100	
630	100	100	
730	100	100	
830	100	100	
930	100	100	
140	100	100	
240	100	100	
340	100	100	
440	100	100	
540	100	100	
640	100	100	
740	100	100	
840	100	100	
940	100	100	
150	100	100	
250	100	100	
350	100	100	
450	100	100	
550	100	100	
650	100	100	
750	100	100	
850	100	100	
950	100	100	
160	100	100	
260	100	100	
360	100	100	
460	100	100	
560	100	100	
660	100	100	
760	100	100	
860	100	100	
960	100	100	
170	100	100	
270	100	100	
370	100	100	
470	100	100	
570	100	100	
670	100	100	
770	100	100	
870	100	100	
970	100	100	
180	100	100	
280	100	100	
380	100	100	
480	100	100	
580	100	100	
680	100	100	
780	100	100	
880	100	100	
980	100	100	
190	100	100	
290	100	100	
390	100	100	
490	100	100	
590	100	100	
690	100	100	
790	100	100	
890	100	100	
990	100	100	
200	100	100	
300	100	100	
400	100	100	
500	100	100	
600	100	100	
700	100	100	
800	100	100	
900	100	100	
1000	100	100	

given by Cromer (1965). The final difference Fourier synthesis was featureless except for a few regions of electron density of up to $0.7 \text{ e } \text{Å}^{-3}$ in the immediate vicinity of the Os atom.

Table 1 lists the observed and the calculated structure amplitudes. Atomic coordinates are given in Table 2; those of the H atoms are unrefined. The coefficients in the expression for the anisotropic temperature factor,

$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and the root-mean-square amplitudes of vibration along

Table 2. Atomic coordinates with estimated standard deviations in parentheses

The hydrogen atom positions are unrefined, and these atoms are numbered such that the first digit corresponds to that of the parent carbon atom.

	x	y	z
Os(1)	0	0.27229 (6)	$\frac{1}{2}$
O(1)	0	0.4716 (14)	$\frac{1}{2}$
O(2)	0.1573 (5)	0.1857 (11)	0.2650 (8)
O(3)	-0.0106 (5)	0.2050 (10)	0.4835 (10)
C(2)	0.1955 (7)	0.1298 (12)	0.4334 (12)
C(3)	0.1097 (8)	0.2046 (13)	0.5642 (12)
H(21)	0.190	0.001	0.439
H(22)	0.293	0.164	0.456
H(31)	0.133	0.308	0.617
H(32)	0.110	0.134	0.679

the principal axes of the thermal ellipsoids are listed in Table 3.

Description of the structure and discussion

The structure determination has shown this diester complex to be a five-coordinate species, and a view of the molecular structure appears in Fig. 1. This diagram also shows the thermal vibration ellipsoids of the non-hydrogen atoms (Johnson, 1965). Both the Os atom and the terminal O atom lie on a twofold axis, and molecules have C_2 crystallographic symmetry. The two chelating ester groups complete an essentially square-pyramidal coordination about Os. Table 4 summarizes the more important interatomic distances, both intra- and intermolecular, and also the bond angles.

The Os—O(terminal) bond, which forms the apex of the pyramid, has a length of 1.670 Å , and is very similar to that (1.673 Å) found in the dimeric monoester $[\text{OsO}_2(\text{O}_2\text{C}_2\text{Me}_4)]_2$ (Collin, Griffith, Phillips & Skapski, 1973). Bond lengths of Os—O(terminal) double bonds in six-coordinate species are in general *ca* 0.1 Å longer, *e.g.* 1.75 Å in $\text{K}_2[\text{OsO}_2\text{Cl}_4]$ (Kruse, 1961), 1.77 Å in $\text{K}_2[\text{OsO}_2(\text{OH})_4]$ (Porai-Koshits, Atovmyan & Adrianov, 1961), and 1.79 Å in $\text{K}_4[\text{Os}_2\text{O}_6(\text{NO}_2)_4]$ (Atovmyan & L'yachenko, 1967). The terminal bond in the title compound corresponds

Table 3. Anisotropic thermal parameters ($\text{Os} \times 10^5$; $\text{C}, \text{O} \times 10^4$) and root-mean-square amplitudes of vibration (Å)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Min.	Inter.	Max.
Os(1)	454 (6)	1140 (10)	1544 (12)	0	35 (5)	0	0.166	0.201	0.217
O(1)	121 (10)	177 (19)	331 (27)	0	-23 (13)	0	0.251	0.265	0.322
O(2)	46 (4)	240 (12)	166 (11)	-4 (7)	3 (5)	-4 (11)	0.166	0.224	0.292
O(3)	54 (5)	267 (15)	156 (11)	-8 (7)	1 (6)	-12 (11)	0.181	0.217	0.309
C(2)	57 (6)	201 (17)	190 (16)	-5 (9)	-21 (9)	-6 (16)	0.177	0.246	0.268
C(3)	62 (7)	260 (21)	132 (14)	-20 (10)	-23 (9)	-2 (16)	0.167	0.219	0.306

Table 4. Interatomic distances (Å) and bond angles ($^\circ$) with estimated standard deviations in parentheses

Superscripts refer to atoms in the following positions:

i	-x	y	$\frac{1}{2}-z$	ii	$x-\frac{1}{2}$	$\frac{1}{2}-y$	$1-z$
iii	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$z-\frac{1}{2}$	iv	-x	$1-y$	$1-z$

(a) Intramolecular

Os(1)—O(1)	1.670 (12)	C(2)—O(2)	1.446 (11)
Os(1)—O(2)	1.873 (7)	C(3)—O(3)	1.457 (11)
Os(1)—O(3)	1.896 (8)	C(2)—C(3)	1.516 (13)
Mean Os—O(ester)	1.885		
Mean C—O(ester)	1.452		
O(1)···O(2)	2.953 (13)	O(1)···O(3)	2.875 (12)
O(2)···O(3)	2.503 (9)	O(2)···O(3 ⁱ)	2.511 (9)
Mean O(terminal)···O(ester)	2.914		
Mean O(ester)···O(ester)	2.507		
O(1)—Os(1)—O(2)	112.8 (3)	O(1)—Os(1)—O(3)	107.3 (3)
Mean O(terminal)—Os—O(ester)	110.1		
O(2)—Os(1)—O(3)	83.2 (3)	O(2)—Os(1)—O(3 ⁱ)	83.5 (3)
O(2)—Os(1)—O(2 ⁱ)	134.4 (4)	O(3)—Os(1)—O(3 ⁱ)	145.4 (4)
Os(1)—O(2)—C(2)	116.6 (5)	Os(1)—O(3)—C(3)	110.7 (5)
O(2)—C(2)—C(3)	106.8 (7)	O(3)—C(3)—C(2)	106.0 (7)

(b) Intermolecular

O(3)···H(22 ⁱⁱ)	2.46	O(3)···C(2 ⁱⁱⁱ)	3.562 (12)
O(2)···H(31 ⁱⁱⁱ)	2.56	O(2)···C(3 ⁱⁱⁱ)	3.125 (11)
O(1)···H(31 ^{iv})	2.57	O(1)···C(3 ^{iv})	3.296 (14)

to a triple bond. A likely bonding scheme is one in which Os forms σ bonds with the five $d_{x^2-y^2}sp^3$ hybrid orbitals, and the vacant d_{yz} and d_{zx} orbitals can then form π bonds with the donor p orbitals of the terminal O, leaving the d_{xy} orbital to accommodate the non-bonding $5d$ electron pair of Os^{VI}.

Four O atoms from the chelating ester ligands constitute the base of the pyramid. The two independent Os–O(ester) distances are 1.873 and 1.896 Å, compared to a mean of 1.869 Å in [OsO₂(O₂C₂Me₄)₂]. These bond lengths are somewhat shorter than one would expect for an Os–O single bond, e.g. Os–OH of 2.00 Å in square-pyramidal [Os(OH)(NO)₂(PPh₃)₂](PF₆) (Waters & Whittle, 1971), and it may be that some π bonding interaction occurs between the Os and the p orbitals of the ester O atoms. The C–O(ester) mean length of 1.452 Å is marginally longer than the literature mean of 1.426 Å (Sutton, 1965); this is what one would expect if the Os–O(ester) bonds were of bond order > 1. In the ester chelate ring system, Os(1), O(2), O(3) and C(2) are reasonably planar (Table 5), while C(3) is *ca* 0.6 Å out of the least-squares plane.

A significant feature of the molecular structure is the large mean O(apical)–Os–O(basal) angle of 110.1°. The two independent angles involved are 107.3 and

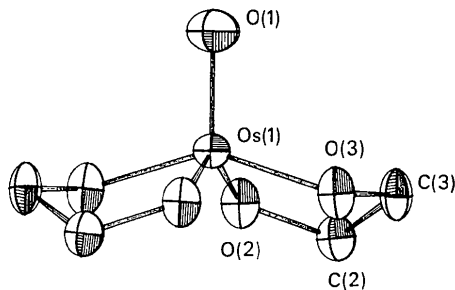


Fig. 1. Molecular structure of OsO(O₂C₂H₄)₂. Thermal vibration ellipsoids are scaled to enclose 30% probability.

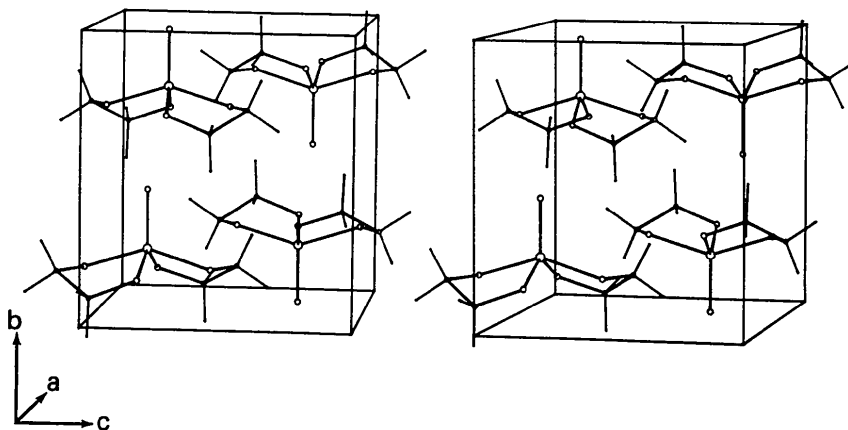


Fig. 2. A stereoscopic view showing the packing of OsO(O₂C₂H₄)₂ molecules. (The hydrogen atoms are also included in the molecular skeleton.)

Table 5. Planarity of groups of atoms in the structure and distances from least-squares planes

The equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space. Superscripts have the same meaning as in Table 4.

<i>P</i>	<i>Q</i>	<i>R</i>	<i>S</i>	Deviation (Å) of atoms from plane			
0.00	8.38	0.00	1.64	O(2)	−0.081	O(3)	0.081
				O(2')	−0.081	O(3')	0.081
Not defining plane:				Os(1)	0.645	O(1)	2.314
3.54	7.58	2.13	2.57	Os(1)	0.029	O(2)	−0.039
				O(3)	−0.021	C(2)	0.031
Not defining plane:				C(3)	0.573		

112.8°, and the difference between them represents a slight deviation from square-pyramidal towards trigonal-bipyramidal coordination. A least-squares plane through the four ester O atoms shows them to be ± 0.08 Å from the plane (Table 5), with the Os atom 0.64 Å above the base of the pyramid.

The large O(apical)–Os–O(basal) angles are a consequence of electronic repulsion by the strongly π -donating oxo ligand pushing the ester O atoms as far as O(basal)···O(basal) steric interactions will allow. This system is a particularly favourable example for showing these effects. Thus the four basal atoms form an almost perfect square of sides 2.50–2.51 Å, while their mean distance from the apical atom is much greater at 2.91 Å. A very similar situation obtains in the monoester complex [OsO₂(O₂C₂Me₄)₂], and in (Ph₄As)[OsNCl₄] (Fletcher, Griffith, Pawson, Phillips & Skapski, 1973). The electronic repulsion effects of the terminal nitrido ligand in the latter complex have been discussed in greater detail (Phillips & Skapski, 1975).

Fig. 2 shows a stereoscopic view (Johnson, 1965) of the packing of the molecules in the cell. It can be seen from Table 4 that three H···O distances are less than 2.6 Å, *i.e.* the van der Waals contact distance suggested by Pauling (1960). If, however, one takes the value for

this distance of 2.4 Å, as suggested by Ramachandran, Ramakrishnan & Sasisekharan (1963), then all three H...O distances are greater than this. It is unlikely therefore that any of these contacts represents a C-H...O hydrogen bond.

Of a number of structures suggested for Os^{VI} diesters, it is the original proposal of Criegee and his coworkers which has proved to be correct (Criegee, 1936; Criegee, Marchand & Wannowius, 1942). They suggested a five-coordinate cyclic diester, without specifying a preference for square-pyramidal or trigonal-bipyramidal stereochemistry. The monomeric structure of the diester and the dimeric structure of the monoester (Collin, Griffith, Phillips & Skapski, 1973) are both consistent with the cross-linking of lipid chains first suggested by Wigglesworth (1957) as an explanation of the fixation properties of OsO₄ in biological tissue.

Whether mono- or diesters are formed will to some extent depend on the disposition in the lipid chains of the C=C double bonds which are the original sites of OsO₄ attack. Some idea of the separation of double bonds needed to allow bridging by Os can be obtained by calculating the distance between the midpoints of the C-C bonds in the mono- and diester structures. In the title complex this distance is *ca* 5.1 Å, while in [OsO₂(O₂C₂Me₄)₂]₂, where two Os atoms are separated by a dioxo bridge, it is *ca* 7.7 Å. As these distances are essentially controlled by the Os environments, they are not likely to alter significantly with different lipid substrates. Since these distances seem to be relatively predetermined, it may be that it is the lipid chains which have to readjust their positions. Another factor will therefore be the extent to which the chains can move away from or towards each other so as to bring the double bonds to a required separation to allow bridging by Os. It is because of this that attack by OsO₄ may cause some disruption of the substrate. A third factor in determining the balance of mono- and diester species will, of course, be the relative concentration of OsO₄.

It has not yet proved possible to obtain crystalline esters of lipids comparable in size with those found in biological systems. However, there is chemical and spectroscopic evidence (Collin, Jones & Griffith, 1974) to show that esters formed by large unsaturated molecules, such as cholesterol and ergosterol, have structures which are similar to those of the simple model compounds discussed here.

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