Oxo-complexes of Osmium and Ruthenium with Organic Ligands

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The stoicheiometries and vibrational spectra of a number of oxo-osmium complexes and an oxoruthenium complex with pyridine, and also of oxo-osmium esters of glycol and pinacol have been studied.

OSMIUM tetroxide has long been used as a *cis*-hydroxylating reagent for olefinic double bonds,[1] and has extensive uses in electron microscopy for tissue staining and fixation.[2] In both these applications the intermediate formation of a cyclic ester in which an OsO_2 unit adds across a C=C double bond appears to be involved. Criegee *et al.*,[3] studied the reactions of a wide range of olefins with osmium tetroxide and isolated both mono- and di-esters, but neither the stoicheiometries or structures are fully established since only osmium analyses and oxidation state determinations were made.[3] Here we report analytical data, and studies of the vibrational spectra of the esters formed by ethylene and tetramethylethylene, these olefins being chosen so that the spectra would be as simple as possible to permit structural information to be obtained. We preface this work with a similar examination of the complexes obtained by reaction of osmium tetroxide with pyridine; these were studied because they are likely to have simple 'model' structures, and since osmium tetroxide–pyridine solutions are often used to prepare some of the esters. We also report on the nature of the reaction product [4] of ruthenium tetroxide with pyridine.

Oxo-osmium Pyridine Complexes.—Reaction between osmium tetroxide and pyridine in an inert solvent gives yellow crystals of a complex formulated as OsO_4,py,[3] and the same reaction when conducted in the presence of ethanol gives green-brown platelets of OsO_3,py_2, both regarded as being five-co-ordinate. We have repeated the preparations and found that these formulae are correct; OsO_4,py is monomeric in benzene, but we were unable to measure the molecular weight of OsO_3,py_2 as it was either insufficiently soluble in, or decomposed by, solvents appropriate for the measurements. Study of the vibrational spectra of the complexes in the 750—1000 cm^{-1} region (see the Table) should help in establishing their structures since osmium-oxo (Os=O) stretching modes are found in this range [5,6] but co-ordinated pyridine does not absorb strongly in the region.[7]

In the case of OsO_4,py the Raman spectra of the solid and its benzene solutions are very similar, suggesting that the complex retains its five-co-ordination in the solid state. Both the Raman and i.r. spectra show four sharp bands in the 750—1000 cm^{-1} region which we assign to Os=O stretches.

The likely molecular structures for OsO_4,py are trigonal pyramidal or square-based pyramidal, and in either case the pyridine may occupy an axial or an equatorial position. The skeletal molecular symmetries would then be respectively C_{3v} or C_{2v} (trigonal bipyramid) and C_{4v} or C_s (square-based pyramid). The appearance of four Raman and four (coincident) i.r. bands excludes C_{4v} and C_{3v} since these would give fewer bands than observed; for C_{2v} we expect two polarised Raman bands and for C_s, three. It appears that three of the Raman bands are polarised, though the 907 cm^{-1} band is too weak for fully reliable polarisation measurements. On

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Vibrational spectra of oxo-osmium and -ruthenium complexes

	OsO_4,py *		Os_2O_6,py_4		$RuO_2(OH)_2py_2$ †		OsO_2,$py_2(C_2H_4O_2)$	
	I.r.	R	I.r.	R	I.r.	R	I.r.	R
M–O modes								
ν^{as} (MO_2)	885m	886(1)	833s	830(1)	790s		824s	
ν^{s} (MO_2)	926w 915s 908s	928(1) 916(6) 907(1)	875w	875(9)		850w		870(10)
δ (MO_2)	360m 298w	378(7) 316(3)	346m 300s	332(3)			292s	
ν (MO)			448m	640(3) 420(3)			518s 456w	519(2) 456(1)
H_2O, OH modes					3300s			
Other modes [c]								
py	3040s 3000s		3100m 2970s		3100s 3000s		3050m 2950s	
eg, tmg							2850s	
py	1600s		1595s		1605s		1595s	
py, eg, tmg	1470m 1435s		1440s		1450s		1470m 1445s	
py	1333m		1333m		1340m		1350s	
eg, tmg							1237w	
py, eg, tmg	1204w 1150w 1035m 1051m	1040(2) 1015(2)	1202m 1144w 1045m 1015m	1015(10)	1225m 1165s 1080s 990w	995(6)	1204w 1145w 1070m 1015m 935m	1018(4)
tmg							894s	
py	758s 697s		775s 690s		730w 715m		769s 690s	
eg, tmg, py	633s	657(1)	606s 591s				633s 592s	660(½) 591(3)
py	266w	304(6)		297(2)			270m	

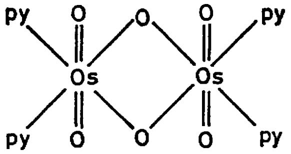
	$Cs_2[IrpyCl_5]$	$[OsO_2(Me_4C_2O_2)]_n$	$K_2[OsO_2(C_2H_4O_2)_2]$		$[OsO(C_2H_4O_2)_2]_n,nH_2O$	$[CoCl_2\{C_2H_4(OH)_2\}_2]$
	I.r.[a]	I.r.	I.r.	R	I.r.	I.r.[b]
M–O modes						
ν^{as} (MO_2)			803s			
ν^{s} (MO_2)				859(10)		
δ (MO_2)			330s			
ν (MO)		485m	469s	460(1) 431(1)	436m	
HO_2, OH modes					3400s 1630b	3170s
Other modes [c]						
py	3112s 3051m					
eg, tmg		2979s 2900s	2940s		2940s 2880s	2920s
py	1600s					
py, eg, tmg	1472m 1440s	1440m	1485m		1440m	1471s 1449s
py						
eg, tmg		1298w	1299m		1220w	1307s 1276m
py, eg, tmg	1230m 1150m 1070s 1060m	1150m 1112s 981s	1218w 1064s 1038s		1204w 1031m 1010m 985m	1212s 1062s 1027s
tmg		943m 854s	893m 880m	899(½)	895s 865m	892s 881m
py	760s 690s	714s 659s 629s	645m		689m 625s	
eg, tmg, py	469m	585s	547s	539(3)	571s	
eg, tmg		391s 340s	386s		309s	
py		309m				

[a] Ref. 7. [b] Ref. 14. [c] py = Pyridine; eg = co-ordinated ($C_2H_4O_2$) group; tmg = co-ordinated ($Me_4C_2O_4$) group. All spectra measured in samples in the solid state: † Raman spectrum of $RuO_2(OH)_2py_2$ (700—1000 cm^{-1}): 995w, 850w.

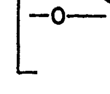
* Raman spectrum of OsO_4,py in CCl solution (700—1000 cm^{-1}): 934(10)p; 921(5)p; 907(1)p; 887(½)dp.

the basis of these data we then propose a square-based pyramidal structure for OsO_4,py with the pyridine ligand in the equatorial plane; this arrangement of oxo-ligands about the osmium atom is the most likely since four oxo-ligands in a plane would compete for two *d* orbitals, but with one ligand perpendicular to the plane all three t_{2g} orbitals are brought into use.[6] There is such an arrangement of oxo-ligands in *cis*-$[OsO_4X_2]^{2-}$ (X = F or OH) and in $[ReO_4(OH)_2]^{3-}$, and for the $[OsO_4X_2]^{2-}$ species the observed profile [6] of the Raman spectrum in the 750—1000 cm^{-1} region is very similar to that of OsO_4,py.

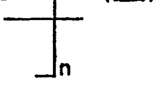
In ' OsO_3,py_2 ' both the Raman and i.r. spectra in the same region are much simpler than in OsO_4,py: there is only one strong Raman band at 875 cm^{-1} and an i.r. one at 833 cm^{-1}, and there are few Raman–i.r. coincidences over the whole spectrum. The positions and intensities of the 875 and 833 bands are strongly suggestive of the presence of an ' osmyl ' (*trans* O=Os=O) grouping; for such species, the Raman-active symmetric stretch $\nu^s(OsO_2)$ is found in the range 850—900 cm^{-1} and the i.r.-active asymmetric stretch $\nu^{as}(OsO_2)$ and deformation $\delta(OsO_2)$ are found in the 790—850 and 300—350 cm^{-1} regions respectively.[6] The presence of these bands and the general lack of Raman and i.r. coincidences suggests a centrosymmetric structure with bridging oxo-ligands, so that the complex should be formulated as Os_2O_6,py_4. The above type of structure (centrosymmetric, with D_{2h} skeletal symmetry) has been shown to be that in the anion of $K_4[Os_2O_6(NO_2)_4]$, nitro-ligands replacing pyridine,[8] and we find that prolonged action of an aqueous solution of potassium nitrite on Os_2O_6,py_4 gives $K_4[Os_2O_6(NO_2)_4]$. The Os_2O_2 bridge system in $K_4[Os_2O_6(NO_2)_4]$, and also a number of other M_2O_2 bridge systems have symmetric (Raman-active) stretches *ca.* 600 cm^{-1} and asymmetric (i.r.-active) stretches *ca.* 450 cm^{-1}; [6] the bands at 640 (Raman) and 448 (i.r.) in Os_2O_6,py_4, not found in OsO_4,py, may perhaps be assigned to these modes.



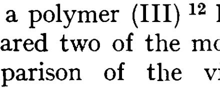
The action of ruthenium tetroxide in carbon tetrachloride on pyridine is to give a dark green solid, formulated by Koda as RuO_4,py_2.[4] We find that this is monomeric in benzene and is diamagnetic, but its i.r. spectrum is quite different from that of OsO_4,py in the 750—1000 cm^{-1} region. The only band which is unlikely to arise from pyridine modes is that at 790 cm^{-1}; we propose that this may be due to a *trans*-O=Ru=O asymmetric stretch, $\nu^{as}(RuO_2)$. This mode is found at 814 cm^{-1} in *trans*-$[RuO_2Cl_4]^{2-}$.[9] There is a very weak Raman band at 850 cm^{-1} which may be due to $\nu^s(RuO_2)$. Since there are no strong bands between 850 and 1000 cm^{-1} reported for the species formulated as RuO_4,bipy,-$3H_2O$ [10] we suggest that this may also contain a *trans* O=Ru^{VI}=O unit; the diamagnetism for such d^2 systems presumably arises from the very axially distorted ligand field, as in ' osmyl ' complexes.[11]



(I)



(II)



(III)

Oxo-osmium(VI) *Monoesters*.—Various structures have been proposed for those monoesters which do not contain pyridine: *viz.*, (I),[2,3] (II),[2] and, in the case of the cyclopentene ester, a polymer (III) [12] linked by oxo-bridges. We have prepared two of the mono-esters reported by Criegee. Comparison of the vibrational spectra of $OsO_2,py_2(C_2H_4O_2)$, OsO_4,py, and Os_2O_6,py_4 allows assignment of the pyridine modes; the remaining i.r. bands are very similar in frequency to those observed in ethylene glycol [13] and its complexes $MCl_2\{C_2H_4(OH)_2\}_2$ (M = Co or Ni),[14] except that no O–H stretches are observed in the osmium ester. The appearance of a very strong Raman band at 870 cm^{-1} and an intense i.r. band at 824 cm^{-1} suggests the presence of a *trans* O=Os=O grouping as in Os_2O_6,py_4. The Raman and i.r. bands *ca.* 456 cm^{-1} may be the Os–O stretch of the co-ordinated $(C_2H_4O_2)$ ligands; such bands are not found in OsO_4,py, Os_2O_6,py_4, or in ethylene glycol,[13] but Os–O (single bond) stretches are found *ca.* 500 cm^{-1}.[15] We therefore propose the simple octahedral structure for the complex with two *trans*-oxo-ligands.

The complex obtained by reaction of tetramethylethylene with osmium tetroxide in cyclohexane was formulated by Criegee [3] as $OsO_2(Me_4C_2O_2)$, with a structure of type (I) above. Our analyses are consistent with this formula but the implied tetrahedral co-ordination with *cis*-oxo-ligands is unlikely for osmium(VI) which in all its other complexes has octahedral co-ordination. The complex is black, which prevents measurement of its Raman spectrum, and insoluble in

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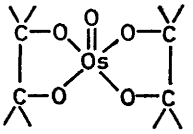
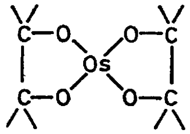
organic solvents, suggesting a possible polymeric structure. Comparison of its i.r. spectrum with that of $OsO_2py_2(C_2H_4O_2)$ and of the ethyleneglycol diesters discussed below suggests that no bands in the Os=O stretching region (800—1150 cm^{-1}) can be assigned to osmium–oxygen stretches. Mono-oxo-osmium(VI) species of type (III) have not been established previously; we suggest that the compound is a polymer, $[OsO_2(Me_4C_2O_2)]_n$, with the organic ligand occupying two *cis*-sites on octahedrally co-ordinated osmium(VI), there being zig-zag Os_2O_2 bridges linking the metal atoms to give a polymer chain with no Os=O double bonds.

Oxo-osmium(VI) *Diesters*.—These are made by procedures similar to those for the monoesters. Two main structural types have been proposed: a five-co-ordinate complex with a single Os=O bond (IV) [2,3,16] and a four-co-ordinate species involving tetravalent osmium (V).[17] An *X*-ray powder study on the pinacol complex formulated as $OsO(Me_4C_2O_2)_2$ has been reported [18] but no structural data were obtained.


(IV)


(V)

We have prepared $K_2[OsO_2(C_2H_4O_2)_2]$ from ethylene glycol and $K_2[OsO_2(OCH_3)_4]$ in the manner described by Criegee,[3] and also the acid hydrolysis product of this, originally formulated as $OsO(C_2H_4O_2)_2$.[3] Although the potassium salt was not analysed by the original workers, we find it to have the stoicheiometry above, and its vibrational spectra clearly suggest that it contains the *trans*-O=Os=O ' osmyl ' grouping; the Raman band at 859 cm^{-1} is probably $\nu^s(OsO_2)$ and the i.r. bands at 803 and 330 cm^{-1} may be assigned to $\nu^{as}(OsO_2)$ and $\delta(OsO_2)$ respectively. The Raman and i.r. bands *ca.* 460 cm^{-1} may arise as before from Os–O single-bond stretches of the co-ordinated bidentate organic ligands. The i.r. spectrum is very similar to that for $MCl_2\{C_2H_4(OH)_2\}_2$ ($M = $ Ni or Co),[14] for ethylene glycol,[13] and for the above monoesters, but again no O–H stretches are seen.

Our analyses of the diester made by acidification of this potassium salt suggest that it is $OsO(C_2H_4O_2)_2,H_2O$ [or $Os(OH)_2(C_2H_4O_2)_2$, but this is less likely as the complex appears to be polymeric]. It is very dark in colour and we were unable to record its Raman spectrum for this reason; the i.r. spectrum is very similar to that of the above potassium salt but it does have bands *ca.* 3400 and 1600 cm^{-1} which could be due to water. We do not observe the strong bands *ca.* 1000 cm^{-1} ascribed to terminal Os=O groups said to arise in diesters of proposed structure (IV),[19] and so we tentatively propose that it is polymeric with Os–O–Os bridges, or possibly dimeric with an Os_2O_2 bridge system as in Os_2O_6,py_4. We hope to examine this complex and $[OsO_2(Me_4C_2O_2)]_n$ at a later date with oxygen-18 substitution in order to clarify the structures.

$K[OsO_2(CH_3COO)_3]$.—This dark blue material is obtained by the action of acetic acid on $K_2[OsO_2(OMe)_4]$,[3] and from its formula is apparently five-co-ordinate. The i.r. spectrum is very complex in the 1600 cm^{-1} region suggesting that not all the acetate ligands are unidentate. Using the i.r. criteria for co-ordinated acetates of Curtis *et al.*,[20] we may assign the 1585 cm^{-1} band to unidentate, and those at 1660 and 1626 cm^{-1} to bridging or chelating acetate groups. It therefore seems likely that the complex is indeed octahedral with one chelating or bridging acetate group per osmium atom. The i.r. bands at 845 and 316 cm^{-1} may provisionally be assigned to $\nu^{as}(OsO_2)$ and $\delta(OsO_2)$ of the ' osmyl ' unit (as may the bands at 825 and 316 cm^{-1} in $K_2[OsO_2(OMe)_4]$).

EXPERIMENTAL

Tetraoxo(*pyridine*)*osmium*(VIII), OsO_4,py.—This was made as bright yellow crystals by reaction of pyridine with a solution of osmium tetroxide in pyridine [3] [Found: C, 17·8; H, 1·7; O, 19·7; N, 4·3. $C_5H_5NO_4Os$ requires C, 18·0; H, 1·5; O, 19·2; N, 4·2%; *M* (benzene) found: 323; required for OsO_4,py 333·2].

Di-μ-oxo-tetraoxotetrakis(*pyridine*)*diosmium*(VI), $Os_2O_6py_4$.—This was made in the same manner as OsO_4,py [3] but in the presence of ethanol. The compound forms dark green-brown platelets (Found: C, 30·3; H, 2·5; O, 12·1; N, 7·1. $C_{20}H_{20}N_4O_6Os_2$ requires C, 30·5; H, 2·6; O, 12·3; N, 7·2%).

Dihydroxodioxobis(*pyridine*)*ruthenium*(VI), $RuO_2(OH)_2py_2$.—This was prepared by the method of Koda,[4] pyridine being mixed with a solution of RuO_4 in carbon tetrachloride. The latter solution was made by Nakata's [21] procedure [Found: C, 36·5; H, 4·1; N, 7·8; O, 19·6; Ru, 30·9. $C_{10}H_{12}O_4N_2Ru$ requires C, 37·1; H, 3·7; N, 8·7; O, 19·8; Ru, 31·3%; *M* (methanol) 305; requires 323·0].

Ethane-1,2-*diolatodioxobis*(*pyridine*)*osmium*(VI), $OsO_2py_2(C_2H_4O_2)$.—This was prepared [3] from a solution of OsO_4 in cyclohexane and pyridine under a current of ethylene. It formed dark brown crystals (Found: C, 32·6; H, 3·4; N, 6·5; O, 14·6. $C_{12}H_{14}N_2O_4Os$ requires C, 32·7; H, 3·2; N, 6·3; O, 14·5%).

Poly[*di-μ-oxo-tetramethylethane*-1,2-*diolato-osmium*(VI)] $[OsO_2(Me_4C_2O_2)]_n$.—This was made [3] as glittering black needles from tetramethylethylene and a solution of OsO_4 in cyclohexane (Found: C, 21·4; H, 3·7; O, 19·0. $C_6H_{12}O_4Os$ requires C, 21·3; H, 3·6; O, 18·9%).

Dipotassiumbis(*ethane*-1,2-*diolato*)*dioxo-osmate*(VI), $K_2[OsO_2(C_2H_4O_2)_2]$.—This was made as very hygroscopic rose-coloured crystals by the action of ethylene glycol on $K_2[OsO_2(OCH_3)_4]$ [3] (Found: C, 11·2; H, 2·9; O, 22·3. $C_4H_{12}O_6K_2Os$ requires C, 11·4; H, 2·3; O, 22·8%).

Poly[*μ-oxo-bis*(*ethane*-1,2-*diolato*)*osmium*(VI)], $[OsO(C_2H_4O_2)_2]_n nH_2O$.—This was made [3] by acidification of the above potassium salt; it formed dark brown crystals (Found: C, 14·4; H, 2·6; O, 28·9. $C_4H_{10}O_6Os$ requires C, 14·0; H, 2·9; O, 27·9%).

Dipotassium Tetramethoxodioxo-osmate(VI), $K_2[OsO_2$-

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$(OCH_3)_4]$.—This was made [3] as brown crystals by the action of methanolic potassium hydroxide on a solution of OsO_4 in methanol.

I.r. spectrum: 3150m, 2800s, 1610s, 1420w, 1270w, 1177m, 1130w, 1060m, 1045m, 1030m, 955m, 875m, 825s, 755w, 535s, 400m, 316m, 300s cm^{-1}.

Potassium Trisacetatodioxo-osmate(VI), $K[OsO_2(CH_3COO)_3]$.—This was prepared as a dark blue solid [3] by reaction of glacial acetic acid with $K_2(OsO_2(OCH_3)_4)$ (Found: C, 16·6; H, 2·2; O, 29·0. $C_6H_9O_8KOs$ requires C, 16·4; H, 2·1; O, 29·2%).

I.r. spectrum: 2925s, 1660s, 1626s, 1585m, 1485m, 1370m, 1325m, 1285s, 1265s, 1042w, 1020m, 930m, 845vs, 536s, 400m, 316s, 300s cm^{-1}.

Raman spectra were measured on a Cary 81 instrument with red (helium–neon, 6328 Å) or yellow (krypton, 5628 Å) irradiation, on powdered samples over the range 1100—300 cm^{-1}. I.r. spectra were measured as Nujol or hexachlorobutadiene mulls on a Grubb–Parsons Spectromaster (4000—400 cm^{-1}) with potassium bromide plates, and over the range 500—200 cm^{-1} with vaseline in Polythene plates on a Grubb–Parsons DM 4 instrument. Microanalyses were performed by Alfred Bernhardt.

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