Studies of Transition-metal Oxo- and Nitrido-complexes. Part 5.[1] Oxo-osmium Ester Complexes with Quinuclidine and Related Amines

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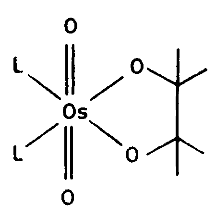
The osmium(VI) ester complexes $[\{OsO_2(O_2R)(NC_7H_{13})\}_2]$ formed by reaction of monoalkenes R (R = cyclohexene, ethylene, or stilbene) with the adduct $OsO_4{\cdot}NC_7H_{13}$ (NC_7H_{13} = quinuclidine) contain an asymmetric Os_2O_2 bridge; in solution they have five-co-ordinate monomeric structures. With tertiary amines L (L = pyridine, methylimidazole, 5,6-dimethylbenzimidazole, or quinuclidine) they give the corresponding *trans*-dioxo-complexes $[OsO_2(O_2R)(NC_7H_{13})L]$. The adduct $OsO_4{\cdot}NC_7H_{13}$ reacts with dienes R (R = cyclohexa-1,3-diene, cyclo-octa-1,5-diene, or 2,5-dimethylhexa-2,4-diene) to give products $[\{Os_2O_4(O_4R)(NC_7H_{13})_2\}_n]$ or $[\{OsO_2(O_2R)(NC_7H_{13})\}_2]$. With alkynes R they give $[\{Os_2O_4(O_4R)(NC_7H_{13})_2\}_n]{\cdot}nS$ (R = C_2H_2, S = benzene, toluene, or carbon tetrachloride) and $[\{Os_2O_4(O_4R)(NC_7H_{13})_2\}_n]$ (R = PhC_2H); these products have structures closely related to those of the complexes $[\{OsO_2(O_2R)L\}_2]$ derived from alkenes. Alkaloids such as strychnine and brucine which contain tertiary amine functions react with OsO_4 to give oxo-osmium(VI) esters. Structures for all these complexes are proposed on the basis of vibrational and ^1H n.m.r. spectra, and on that of an *X*-ray determination of the crystal structure of $[\{OsO_2(O_2C_6H_{10})(NC_7H_{13})\}_2]$.

ADDUCTS formed by reaction of OsO_4 with bulky amines such as quinuclidine or hexamethylenetetramine are useful since they do not possess the dangerously high vapour pressure of the toxic osmium tetraoxide (OsO_4) but, like the latter, will form oxo-osmium(VI) esters with alkenes which may then be hydrolysed to *cis*-glycols. In a previous paper [2] we suggested that such esters $[OsO_2(O_2R)L]$ formed from monoalkenes R and tertiary amines L were monomeric with *trans*-oxo-ligands. We show here that the quinuclidine (NC_7H_{13}) complexes of this type are in fact dimeric in the solid state and monomeric in solution. We also extend our earlier work [1] on the interaction of OsO_4 and amines with alkynes and dienes by studying reactions of $OsO_4{\cdot}NC_7H_{13}$ with these substrates. We have already briefly reported the crystal structures of $OsO_4{\cdot}NC_7H_{13}$ [3] and of the complex which it forms with cyclohexene, $[\{OsO_2(O_2C_6H_{10})(NC_7H_{13})\}_2]$.[4]

RESULTS AND DISCUSSION

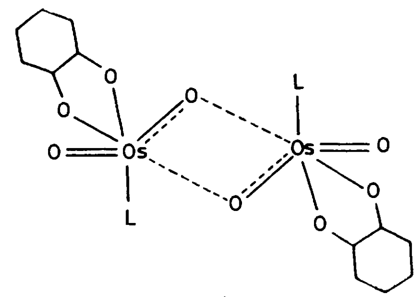
(*a*) *Aminediolatodioxo-osmium*(VI) *Complexes from Monoalkenes.*—Reaction of the adduct $OsO_4{\cdot}NC_7H_{13}$ (NC_7H_{13} = quinuclidine) with monoalkenes R [R = cyclohexene (C_6H_{10}), ethylene (C_2H_4), or stilbene $C_{14}H_{12}$] in a 1 : 1 mol ratio in carbon tetrachloride or diethyl ether gives green diamagnetic products of stoicheiometry



(1) L = quinuclidine

$[OsO_2(O_2R)(NC_7H_{13})]$; addition of more tertiary amine L [L = pyridine (NC_5H_5), methylimidazole ($N_2C_4H_6$), 5,6-dimethylbenzimidazole ($N_2C_9H_{10}$), or quinuclidine (NC_7H_{13})] gives the complexes $[OsO_2(O_2R)(NC_7H_{13})L]$. The vibrational spectra of these latter complexes (1) show bands in the Raman near 880 cm^{-1} and bands in the i.r. spectrum near 840 cm^{-1}, assigned to symmetric and asymmetric stretching vibrations [ν_{sym}- and ν_{asym}-(OsO_2)] of the OsO_2 unit respectively, as found in other complexes containing the *trans*-O=Os=O moiety.[1,5] We propose that these species have structure (1), as found in all other complexes of the type $OsO_2(O_2R)L_2$.[5-7]

The *X*-ray crystal structure [4] of the product $[OsO_2(O_2C_6H_{10})(NC_7H_{13})]$ shows that, in the solid state, the



(2)

complex is dimeric with an asymmetric Os_2O_2 bridge, the two independent Os–O bridge distances being 1.78 and 2.22 Å. The co-ordination about the metal is distorted octahedral (2). The terminal Os=O distance is 1.73 Å, and the angle between this and the Os$\overset{...}{-}$O bridge bond of 1.78 Å is 154°. The Os–O(ester) distances of 1.90 and 1.97 Å and the O(ester)–Os–O(ester) angle of 84° are comparable with those found in other oxo-osmium(VI) ester complexes;[8] the Os–N distance of 2.23 Å, while shorter than that (2.37 Å) found in the adduct $OsO_4{\cdot}NC_7H_{13}$, is comparable with Os–N distances in the complexes $[OsO_2(O_2R)(NC_5H_5)_2]$.[9] Infrared and Raman spectra of the solid complexes $[\{OsO_2(O_2R)(NC_7H_{13})\}_2]$ show strong bands in 800—900 cm^{-1} region which we assign, as before,[2] to Os=O stretching modes, and i.r. bands near 300 cm^{-1} assigned to the Os=O deformation. Infrared bands which may be tentatively assigned as being predominantly due to C–O and Os–O stretching vibrations are observed near 980 and 600 cm^{-1} respectively, as in other ester complexes [1,5] (Table 1).

Molecular-weight measurement of the products derived

TABLE 1

Analytical and spectroscopic data for oxo-osmium(VI) esters

	Analyses (%) [a]				^{1}H N.m.r. spectra [c]	Vibrational spectra: selected bands (cm^{-1}) [d]			
	C	H	N	M [a,b]		ν(C–O)	$\nu(OsO_2)$	ν(Os–O)	$\delta(OsO_2)$
(*a*) Diolato-complexes from alkenes									
$[\{OsO_2(O_2C_2H_4)(NC_7H_{13})\}_2]$	27.8 (27.5)	4.3 (4.4)	3.5 (3.6)	420 (395)		1 030s	890s *898s*	590m	296w
$[\{OsO_2(O_2C_6H_{10})(NC_7H_{13})\}_2]$	35.0 (34.9)	5.3 (5.2)	3.1 (3.1)	465 (449)	3.76 (2 H)	980s	903s *898*	618m	312w
$[\{OsO_2(O_2C_{14}H_{12})(NC_7H_{13})\}_2]$	46.2 (46.2)	4.9 (4.6)	2.5 (2.6)			1 008s	895s	615m	300m
$[OsO_2(O_2C_2H_4)(NC_7H_{13})_2]$	37.4 (38.1)	5.9 (6.0)	5.3 (5.6)			1 040s	835s *881m*	585m	320w
$[OsO_2(O_2C_6H_{10})(NC_7H_{13})_2]$	42.5 (43.0)	6.4 (6.5)	4.8 (5.0)			978s	835s *882s*	587m	315w
$[OsO_2(O_2C_6H_{10})(NC_7H_{13})(NC_5H_5)]$	41.2 (41.0)	5.3 (5.4)	5.3 (5.3)			978s	830s	590s	300m
$[OsO_2(O_2C_6H_{10})(NC_7H_{13})(N_2C_4H_6)]$	38.4 (38.5)	5.3 (5.5)	7.9 (7.9)			975s	822s	585m	310w
$[OsO_2(O_2C_6H_{10})(NC_7H_{13})(N_2C_9H_{10})]$	44.0 (44.5)	5.3 (5.6)	7.2 (7.1)			980s	828s	580m	312w
(*b*) Diolato-complexes from dienes									
$[\{Os_2O_4(O_4C_6H_8)(NC_7H_{13})_2\}_n]$	29.3 (29.6)	4.2 (4.2)	3.4 (3.5)	895 (811)	3.96 (4 H)	1 008m	870s	600m	315w
$[\{Os_2O_4(O_4C_8H_{12})(NC_7H_{13})_2\}_n]$	32.1 (31.5)	4.6 (4.6)	3.0 (3.0)	850 (839)	4.00 (4 H)	998m	872s		330w
$[\{Os_2O_4(O_4C_8H_{14})(NC_7H_{13})_2\}_n]$	31.8 (31.4)	4.8 (4.8)	3.3 (3.3)	789 (841)		1 018m	875s	625m	320w
$[\{OsO_2(O_2C_8H_{12})(NC_7H_{13})\}_2]$	38.3 (38.0)	5.3 (5.3)	2.8 (3.0)	465 (475)		967m	904s		300w
(*c*) Tetrolato-complexes from alkynes									
$[\{Os_2O_4(O_4C_2H_2)(NC_7H_{13})_2\}_n]\cdot nC_6H_6$ [e]	31.2 (31.6)	4.5 (4.1)	3.3 (3.4)		5.31 (2 H) 7.27 (6 H)	952m	905s *899s*	555m	279w
$[\{Os_2O_4(O_4C_2H_2)(NC_7H_{13})_2\}_n]\cdot nC_7H_8$	32.5 (32.5)	4.2 (4.4)	3.2 (3.3)		5.26 (2 H) 7.13 (5 H), 2.30 (3 H)	952m	903s *899s*	560m	280w
$[\{Os_2O_4(O_4C_2H_2)(NC_7H_{13})_2\}_n]\cdot nCCl_4$	22.1 (22.4)	3.2 (3.1)	3.1 (3.1)			952m	908s *900s*	540m	277w
$[\{Os_2O_4(O_4C_8H_6)(NC_7H_{13})_2\}_n]$	32.4 (31.7)	3.8 (3.9)	3.2 (3.4)			978m	872s	555m	305w
(*d*) Complexes from alkaloids									
$[\{OsO_2(O_6C_{23}H_{26}N_2)\}_2]$	40.5 (40.6)	3.8 (3.9)	4.1 (4.1)			1 008m	880s	548w	320w
$[\{OsO_2(O_2C_6H_{10})(O_4C_{23}H_{26}N_2)\}_2]$	47.1 (47.6)	4.7 (5.0)	4.2 (3.8)			1 010m	842s	550w	318w
$[\{OsO_2(O_4C_{21}H_{22}N_2)\}_2]\cdot 2H_2O$	40.9 (41.6)	4.0 (4.0)	4.4 (4.6)			1 005m	880s	540w	320w

[a] Calculated values are given in parentheses. [b] Molecular-weight measurements were for solutions in dichloromethane. [c] δ Values for protons adjacent to donor oxygen atoms (relative to tetramethylsilane, measured in C^2HCl_3). [d] Data for solids. Raman bands are italicised. [e] O, 15.5 (15.3%).

from ethylene and cyclohexene in chloroform or dichloromethane show the complexes to be monomeric in solution, suggesting that the long Os $\cdots$ O bonds in the Os_2O_2 bridge have been broken. The ^{1}H n.m.r. spectrum of $[OsO_2(O_2C_6H_{10})(NC_7H_{13})]$ in C^2HCl_3 shows a resonance due to protons adjacent to the donor oxygen atoms at δ 3.76 (2 H), as reported for other oxo-osmium(VI) complexes.[1]

Vibrational spectra of the complexes $[\{OsO_2(O_2C_6H_{10})(NC_7H_{13})\}_2]$ and $[\{OsO_2(O_2C_2H_4)(NC_7H_{13})\}_2]$ in chloroform, however, show two clearly discernible Raman-active and two i.r. active vibrations in the 800—950 cm^{-1} region which may be assigned to Os=O stretching vibrations. The ligands do not have interfering modes in this region. The coincidence in frequency of the strong, polarised, Raman mode with the weak i.r. band suggests that this arises from the symmetric stretching

TABLE 2

Vibrational spectra [a] of quinuclidineosmium(VI) ester complexes prepared from alkenes

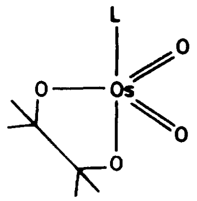
		Metal–oxygen stretching bands (cm^{-1})	
		$\nu_{sym}(OsO_2)$	$\nu_{asym}(OsO_2)$
Cyclohexene ester complexes			
$[\{OsO_2(O_2C_6H_{10})(NC_7H_{13})\}_2]$	i.r.	919m	879s
	Raman	923s (p)	881vw (dp)
$[OsO_2(O_2C_6H_{10})(NC_7H_{13})_2]$ [b]	i.r.		835s [c]
Ethylene ester complexes			
$[\{OsO_2(O_2C_2H_4)(NC_7H_{13})\}_2]$	i.r.	920w	878s
	Raman	926s (p)	880vw (dp)
$[OsO_2(O_2C_2H_4)(NC_7H_{13})_2]$ [b]	i.r.		835s [c]

[a] Recorded in chloroform in KBr and quartz cells. [b] Recorded in the presence of excess of quinuclidine to prevent dissociation of product. [c] The Raman spectrum could not be measured due to fluorescence of sample.

vibration $\nu_{sym}(OsO_2)$, while the weak depolarised Raman shift close to the strong i.r. band is assigned to the asymmetric stretching vibration $\nu_{asym}(OsO_2)$ (Table 2).

The presence of two rather than one Os=O stretching vibration in the i.r. and Raman suggests, as it does in *cis*-dioxo-complexes,[10] a non-linear arrangement of oxo-ligands. This is further supported by the observation that the complexes $[OsO_2(O_2R)(NC_7H_{13})_2]$, which involve a *trans* configuration of oxo-ligands, show in the solid and in solution only one Raman band in the 800—950 cm^{-1} region due to $\nu_{sym}(OsO_2)$ near 881 cm^{-1} and one i.r. band due to $\nu_{asym}(OsO_2)$ at 835 cm^{-1}; coincidence of Raman and i.r. frequencies would not be expected for a *trans*-O=Os=O unit.

The most likely structures of the monomeric solute species involve trigonal-bipyramidal (3) or square-based pyramidal (4) configurations:



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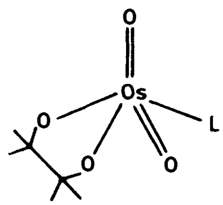
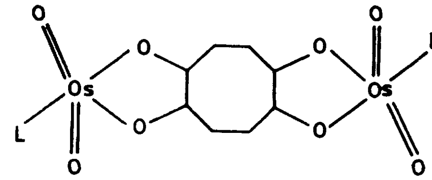


(4)

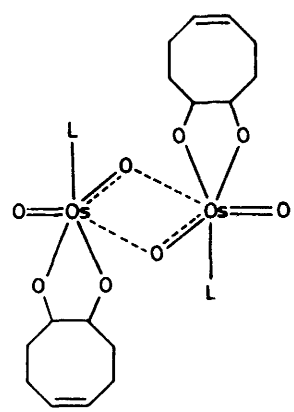
We prefer (3) to (4) since such a structure, involving electronically equivalent oxo-ligands, is closely related to that found for the solid, and a trigonal-bipyramidal co-ordination with three oxo-ligands in the equatorial positions has been reported for another d^2 complex, $Ba[RuO_3(OH)_2]$.[11] The fact that both ν_{sym}- and ν_{asym}-(OsO_2) occur at higher frequencies for the d^2 five-co-ordinate complexes than for the octahedral *trans*-$[OsO_2(O_2R)L_2]$ species may be due, as previously suggested, to electronegativity effects[2] or to the fact that there is more π-acceptor orbital overlap in the trigonal-bipyramidal structure (3)[12] than in a tetragonally distorted octahedron of type (1).[13]

(*b*) *Diolatodioxoquinuclidineosmium*(VI) *Complexes from Dienes*.—We have shown that OsO_4 reacts with dienes R in the presence of excess of pyridine or isoquinoline (L) to give 1 : 1 or 2 : 1 complexes, $[OsO_2(O_2R)L_2]$ or $[Os_2O_4(O_4R)L_4]$, depending on the reacting OsO_4: diene ratios.[1] We find that analogous species are formed if dienes react with the adduct $OsO_4{\cdot}NC_7H_{13}$. Thus, reaction of $OsO_4{\cdot}NC_7H_{13}$ with dienes R [R = cyclohexa-1,3-diene (C_6H_8), cyclo-octa-1,5-diene (C_8H_{12}), or 2,5-dimethylhexa-2,4-diene (C_8H_{14})] in a 2 : 1 ratio gives green diamagnetic complexes of stoicheiometry $[Os_2O_4(O_4R)(NC_7H_{13})_2]$. The vibrational and ^1H n.m.r. spectra of these complexes are very similar to those of the species $[\{OsO_2(O_2R)(NC_7H_{13})\}_2]$ described above, and it seems reasonable to formulate them as polymeric complexes $[\{Os_2O_4(O_4R)(NC_7H_{13})_2\}_n]$ with asymmetric bridges as in (2). Their molecular weights in dichloromethane suggests breakage of the Os_2O_2 bridge to give monomeric $[Os_2O_4(O_4R)(NC_7H_{13})_2]$ species. By analogy with the products $[\{OsO_2(O_2R)(NC_7H_{13})\}_2]$ prepared from alkenes, we suggest a similar structure for these complexes in solution. For example, we propose structure (5) for the complex derived from cyclo-octa-1,5-diene with the two oxo-ligands and one ester oxygen atom occupying equatorial positions of a trigonal bipyramid.



(5)

Reaction of $OsO_4{\cdot}NC_7H_{13}$ with a five-fold excess of cyclo-octa-1,5-diene gives a green diamagnetic product of stoicheiometry $[OsO_2(O_2C_8H_{12})(NC_7H_{13})]$. Although Raman and i.r. spectra of the solid show similar features to those for $[\{OsO_2(O_4C_8H_{12})(NC_7H_{13})_2\}_n]$, the ^1H n.m.r. spectra of the complex in C^2HCl_3 shows resonances due to alkenyl protons at δ 5.55 (2 H) in addition to protons adjacent to the donor oxygen atoms at δ 3.99 (2 H). It appears then that only one of the double bonds has reacted; we propose structures (6) and (7) for the species in the solid state and solution respectively:



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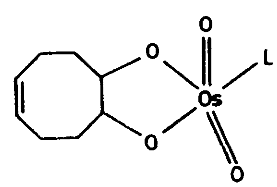
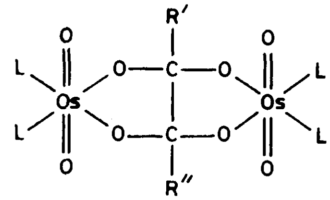


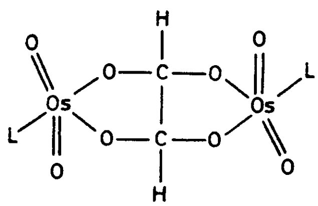
(7)

(*c*) *Aminedioxotetrolato-osmium*(VI) *Complexes from Alkynes*.—Osmium tetraoxide reacts with monoalkynes R in the presence of tertiary amines L (L = pyridine or isoquinoline) to give dioxotetrolato-osmium(VI) ester complexes $[Os_2O_4(O_4R)L_4]$ of structure (8).[1,5] These



(8)

products can be hydrolysed to give the corresponding α-diketones or, in some cases, carboxylic acids.[1] We find that $OsO_4{\cdot}NC_7H_{13}$ reacts with acetylene (C_2H_2) in a number of solvents S (S = benzene, toluene, or carbon tetrachloride) to give green diamagnetic products of stoicheiometry 2 $OsO_4{\cdot}C_2H_2{\cdot}2\ NC_7H_{13}{\cdot}S$, while reaction with phenylacetylene (C_8H_6) gives the product 2 $OsO_4{\cdot}C_8H_6{\cdot}2\ NC_7H_{13}$. The Raman and i.r. spectra of these species have similar features to those found for the complexes $[\{OsO_2(O_2R)(NC_7H_{13})\}_2]$ prepared from alkenes and dienes; the ^1H n.m.r. spectra of the complexes $[\{Os_2O_4(O_4C_2H_2)(NC_7H_{13})_2\}_n]{\cdot}nS$ show no alkynyl protons but do show protons adjacent to donor oxygen atoms at δ 5.3 (2 H) as well as resonances due to the solvent S. We formulate these as five-co-ordinate species in solution, in accordance with molecular-weight data; thus, for the acetylene complex in solution we propose structure (9):



(9)

These complexes are presumably polymeric in the solid state with asymmetric Os_2O_2 bridges.

(*d*) *Reactions of* OsO_4 *with Alkaloids*.—Many alkaloids contain cyclic tertiary amine groups or quinuclidine-like cages, and might be expected to form adducts with OsO_4 in the same way as quinuclidine and other tertiary amines.[2] We find that strychnine, brucine, quinine, sparteine, cinchonine, atropine, yohimbine, cocaine, and emetine react with OsO_4 in aqueous acetone to give red solutions which probably contain adducts of the $OsO_4{\cdot}L$ type. The red solution obtained from the reaction of OsO_4 with brucine ($C_{23}H_{26}N_2O_4$) reacts with cyclohexene to give a complex with similar vibrational spectra to $[\{OsO_2(O_2R)(NC_7H_{13})\}_2]$ in the 800—950 cm^{-1} region, so we formulate it as $[\{OsO_2(O_2C_6H_{10})(O_4C_{23}H_{26}N_2)\}_2]$ with a structure of type (2). If the red solutions of OsO_4 and L [L = brucine or strychnine ($C_{21}H_{22}N_2O_2$)] are allowed to stand, green diamagnetic complexes of stoicheiometry $OsO_2(O_2L)$ are deposited. Since both brucine and strychnine contain alkenyl groups it appears that an internal oxo-osmium(VI) ester of type (2) has been formed by an inter- or intra-molecular reaction of the $OsO_4{\cdot}L$ adduct with the double bond. Models show that such a reaction is sterically feasible. It is possible that, where alkaloids containing tertiary amine functions occur in plant tissue and are available for co-ordination, they could react with OsO_4 during fixation procedures involving that reagent to give $OsO_4{\cdot}L$ adducts. These might then react further with the double bonds to alkaloid substrates or unsaturated lipids.

EXPERIMENTAL

All manipulations involving osmium tetraoxide were carried out in a fume cupboard. The osmium tetraoxide-quinuclidine adduct, $OsO_4{\cdot}NC_7H_{13}$, was prepared by the previously reported method.[2]

(*a*) *Diolatodioxo(quinuclidine)osmium*(VI) *Complexes from Alkenes*, $[\{OsO_2(O_2R)(NC_7H_{13})\}_2]$.—The preparation and yield of $[\{OsO_2(O_2C_6H_{10})(NC_7H_{13})\}_2]$ are typical.

To a solution of the adduct $OsO_4{\cdot}NC_7H_{13}$ (0.5 g, 1.4 mmol) in diethyl ether (10 cm^3) was added dropwise with stirring a solution of cyclohexene (0.115 g, 1.4 mmol) in diethyl ether (5 cm^3). The reaction mixture was cooled to 0 °C and the dark green precipitate filtered off, washed with diethyl ether (10 cm^3), and dried *in vacuo*, yield 65%.

Diolatodioxobis(quinuclidine)osmium(VI) *Complexes from Alkenes*, $[OsO_2(O_2R)(NC_7H_{13})_2]$.—The preparation and yield of $[OsO_2(O_2C_6H_{10})(NC_7H_{13})_2]$ are typical.

To a solution of osmium tetraoxide (0.5 g, 2.0 mmol) in diethyl ether (10 cm^3) was added dropwise with stirring a solution of quinuclidine (0.44 g, 4.0 mmol) and cyclohexene (0.16 g, 2.0 mmol) in diethyl ether (10 cm^3). The reaction mixture was cooled to 0 °C and, if necessary, reduced in volume. The green precipitate was filtered off, washed with diethyl ether (5 cm^3), and dried *in vacuo*, yield 50%.

An alternative method of preparation was carried out by treating the complex $[\{OsO_2(O_2C_6H_{10})(NC_7H_{13})\}_2]$ (0.25 g, 0.28 mmol) in dichloromethane (10 cm^3) with quinuclidine (0.07 g, 0.63 mmol). The reaction mixture was reduced in volume and the product precipitated by the addition of diethyl ether (30 cm^3). The product was filtered off, washed with diethyl ether (10 cm^3), and dried *in vacuo*, yield 60%.

Bis(amine)diolatodioxo-osmium(VI) *Complexes from Alkenes*, $[OsO_2(O_2R)(NC_7H_{13})L]$.—The preparation and yield of $[OsO_2(O_2C_6H_{10})(NC_7H_{13})(NC_5H_5)]$ are typical.

To a solution of $[\{OsO_2(O_2C_6H_{10})(NC_7H_{13})\}_2]$ (0.25 g, 0.28 mmol) in dichloromethane (10 cm^3) was added pyridine (0.44 g, 0.56 mmol) in dichloromethane (5 cm^3). The reaction mixture was reduced in volume and the product precipitated by addition of diethyl ether (30 cm^3). The product was filtered off, washed with diethyl ether (10 cm^3), and dried *in vacuo*, yield 70%.

(*b*) *Diolato-oxo(quinuclidine)osmium*(VI) *Complexes from Dienes*.—$[\{Os_2O_4(O_4R)(NC_7H_{13})_2\}_n]$. The preparations of these complexes were carried out under a dry nitrogen atmosphere since the products were found to be hygroscopic. The preparation and yield of $[\{Os_2O_4(O_4C_8H_{14})(NC_7H_{13})_2\}_n]$ are typical.

To a solution of the adduct $OsO_4{\cdot}NC_7H_{13}$ (0.5 g, 1.4 mmol) in diethyl ether (15 cm^3) was added dropwise with stirring 2,5-dimethylhexa-2,4-diene (0.07 g, 0.6 mmol) in diethyl ether (10 cm^3). After 5 min the green precipitate was filtered off and washed with diethyl ether (10 cm^3). The product was recrystallised from dichloromethane and diethyl ether, yield 55%.

$[\{OsO_2(O_2C_8H_{12})(NC_7H_{13})\}_2]$. To a solution of cycloocta-1,5-diene (0.8 g, 7.4 mmol) in diethyl ether (15 cm^3) under nitrogen was added dropwise with stirring a solution of the adduct $OsO_4{\cdot}NC_7H_{13}$ (0.5 g, 1.4 mmol) in diethyl ether (10 cm^3). After 5 min the green precipitate was filtered off and washed with diethyl ether (10 cm^3). The product was recrystallised from dichloromethane and diethyl ether, yield 50%.

(*c*) *Oxo(quinuclidine)tetrolato-osmium*(VI) *Complexes from*

Alkynes, $[\{Os_2O_4(O_4C_2H_2)(NC_7H_{13})_2\}_n]\cdot nS$ (S = *benzene, toluene, or carbon tetrachloride and* $[\{Os_2O_4(O_4C_8H_6)(NC_7H_{13})_2\}_n]$.—The preparation and yield of $[\{Os_2O_4(O_4C_8H_6)(NC_7H_{13})_2\}_n]$ are typical.

To a solution of the adduct $OsO_4\cdot NC_7H_{13}$ (0.5 g, 1.4 mmol) in diethyl ether (10 cm^3) was added dropwise with stirring phenylacetylene (0.07 g, 0.7 mmol) in diethyl ether (10 cm^3). The reaction mixture was cooled to 0 °C and the dark green product filtered off, washed with diethyl ether (10 cm^3), and dried *in vacuo*, yield 40%.

(*d*) *Alkaloid Complexes*.—The preparation and yield of $[\{OsO_2(O_6C_{23}H_{26}N_2)\}_2]$ are typical.

Brucine (0.1 g, 0.23 mmol) in aqueous (1 : 1) acetone or $CHCl_3$ (5 cm^3) was added to OsO_4 (0.05 g, 0.23 mmol) in the same solvent. The initial brick-red solution turned green and a green crystalline solid was precipitated. The filtered product was washed with diethyl ether (20 cm^3) and dried *in vacuo*, yield 80%.

The complex $[\{OsO_2(O_2C_6H_{10})(O_4C_{23}H_{26}N_2)\}_2]$ was made by addition of excess of cyclohexene to the red solution obtained by mixing brucine (0.1 g, 0.23 mmol) and OsO_4 (0.05 g, 0.23 mmol) in chloroform (5 cm^3). Addition of light petroleum to the brown solution gave brown crystals of the product, yield 90%.

Analytical data were obtained by the Microanalytical Department, Imperial College; oxygen analyses were from Pascher (Bonn). Molecular weights were determined osmometrically on a Perkin-Elmer–Hitachi 115 instrument. Infrared spectra were recorded from 200 to 4 000 cm^{-1} on a Perkin-Elmer 457 instrument as Nujol mulls between caesium iodide plates, and in chloroform using potassium bromide cells. Raman spectra were obtained on a Spex Ramalog 5 instrument with a DPC-2 detector using a krypton-ion laser; solids were scanned as 5% sample–95% KBr spun discs, and solutions in a spinning solution cell. Hydrogen-1 n.m.r. spectra were recorded on a 60-MHz Perkin-Elmer R12B spectrometer, and magnetic susceptibility measurements were made on solids by the Gouy method and on solutions by Evans' method.[14]

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REFERENCES

[1] Part 4, M. Schröder and W. P. Griffith, *J.C.S. Dalton*, 1978, 1599.
[2] M. J. Cleare, P. C. Hydes, W. P. Griffith, and M. J. Wright, *J.C.S. Dalton*, 1977, 941.
[3] W. P. Griffith, A. C. Skapski, K. A. Woode, and M. J. Wright, *Inorg. Chim. Acta*, 1978, **31**, L413.
[4] B. A. Cartwright, W. P. Griffith, M. Schröder, and A. C. Skapski, *J.C.S. Chem. Comm.*, 1978, 853.
[5] R. J. Collin, J. Jones, and W. P. Griffith, *J.C.S. Dalton*, 1974, 1094.
[6] W. P. Griffith and R. Rossetti, *J.C.S. Dalton*, 1972, 1449.
[7] T. Prangé and C. Pacard, *Acta Cryst.*, 1977, **B33**, 621.
[8] F. C. Phillips and A. C. Skapski, *Acta Cryst.*, 1975, **B31**, 1814; *J.C.S. Dalton*, 1975, 2586.
[9] T. J. Kistenmacher, L. G. Marzilli, and M. Rossi, *Bioinorg. Chem.*, 1976, **6**, 347; S. Neidle and D. I. Stuart, *Biochim. Biophys. Acta*, 1976, **418**, 226.
[10] W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 211.
[11] G. Nowogrocki, F. Abraham, J. Tréhoux, and D. Thomas, *Acta Cryst.*, 1976, **B32**, 2413.
[12] A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 365.
[13] K. A. K. Lott and M. C. R. Symmons, *J. Chem. Soc.*, 1960, 973.
[14] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.