Studies on Transition-metal Oxo- and Nitrido-complexes. Part 3.[1] Complexes of Osmium Tetraoxide with Tertiary Amines, and their Reactions with Alkenes

By **Michael J. Cleare** and **Paul C. Hydes**, Johnson Matthey Research Centre, Sonning Common, Reading RG4 9NH
William P. Griffith * and **Michael J. Wright**, Inorganic Chemistry Research Laboratories, Imperial College of Science & Technology, London SW7 2AY

Osmium tetraoxide reacts with multidentate tertiary amines to give $L\cdot 2OsO_4$ (L = hexamethylenetetramine, 1,4-diazabicyclo[2.2.2]octane, pyrazine, or 5-methylpyrimidine) and with other amines to give $L\cdot OsO_4$ (L = quinuclidine, isoquinoline, phthalazine, or pyridazine). Reactions of these adducts with monoalkenes R give the oxo-osmium(VI) esters $L\cdot[OsO_2(O_2R)]$ (L = hexamethylenetetramine, quinuclidine, isoquinoline, or phthalazine) and $L\cdot 2[OsO_2(O_2R)]$ (L = 1,4-diazabicyclo[2.2.2]octane). The structures of these compounds are discussed.

OSMIUM TETRAOXIDE forms unstable 1 : 1 adducts with ammonia[2] and pyridine,[3] and a much more stable but incompletely characterised complex with hexamethylenetetramine(1,3,5,7-tetra-azatricyclo$[3.3.1.1^{3,7}]$decane) has been reported.[4] We recently prepared some stable

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[1] Part 2, D. Pawson and W. P. Griffith, *J.C.S. Dalton*, 1975, 417.

[2] M. L. Hair and P. L. Robinson, *J. Chem. Soc.*, 1960, 2775.

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

[4] L. Chugaev and J. Chernyaev, *Z. anorg. Chem.*, 1928, **172**, 216.

adducts of OsO_4 with tertiary amines, and as part of our continuing work [5] on the interaction of OsO_4 with double bonds we have investigated their reactions with alkenes.

RESULTS AND DISCUSSION

Preparation and Properties of Adducts of OsO_4 *with Amines.*—Reaction of aqueous solutions of OsO_4 with excess of the amine gave the products listed in the Table. They are orange or yellow diamagnetic solids which, with the exception of the pyrazine ($1,4\text{-}C_4H_4N_2$) and 5-methylpyrimidine ($C_5H_6N_2$) adducts, produce no appreciable vapour pressure of OsO_4 at room temperatures. The adducts with the cage ligands hexamethylenetetramine ($C_6H_{12}N_4$), 1,4-diazabicyclo[2.2.2]-octane [$C_6H_{12}N_2$ (triethylenediamine)], and quinuclidine ($C_7H_{13}N$) are chemically more stable than those with aromatic amines such as isoquinoline (C_9H_7N), phthalazine ($C_8H_6N_2$), and pyridazine ($1,2\text{-}C_4H_4N_2$). The compound $C_6H_{12}N_4{\cdot}2OsO_4$ was made and given this formula by Chugaev and Chernyaev [4] on the basis, however, of incorrectly calculated theoretical analytical figures.

Analytical and spectroscopic data

Adduct	M.p. (θ_c/°C)	Colour	Analysis (%) [a]					Infrared and Raman spectra (cm^{-1}) [c]	
			C	H	N	O	M [a,b]	$\nu(OsO_4)$	$\delta(OsO_4)$
(*i*) Amine–OsO_4 adducts									
$C_6H_{12}N_4{\cdot}2OsO_4$ [d]	175—185 [e]	Orange	11.3	1.6	8.7	18.4	621, 641	930, 917, 909	364, 352, 308
			(11.1)	(1.9)	(8.6)	(19.7)	(648)	*930, 919, 907*	*379, 369, 311*
($C_6{}^2H_{12}N_4$ form)								925, 915, 905	369, 351, 304
								929, 919, 906	*378, 368, 306*
$C_6H_{12}N_4{\cdot}2OsO_4$	180—185 [e]	Orange	11.6		4.5	20.3	627, 630	927, 910, 905	370, 365, 305
			(11.6)		(4.5)	(20.6)	(620)	*926, 914, 906*	*381, 373*
$1,4\text{-}C_4H_4N_2{\cdot}2OsO_4$	96—99	Yellow	8.4		4.9			930, 925, 918	368, 355, 310
			(8.2)		(4.7)				
$C_5H_6N_2{\cdot}2OsO_4$	81—84	Yellow	10.0		4.7			930, 920, 895	365, 350, 300
			(10.0)		(4.8)				
$C_7H_{13}N{\cdot}OsO_4$	130—132	Orange	23.0		3.8	17.3		925, 910, 900	364
			(23.0)		(3.8)	(17.5)		*930, 922, 904*	*382, 370, 307*
$C_9H_7N{\cdot}OsO_4$	90—92 [e]	Yellow	28.6		3.7	16.4	470	918, 910	368, 352
			(28.2)		(3.7)	(16.7)	(447)	*925, 908*	
$C_8H_6N_2{\cdot}OsO_4$	122—125 [e]	Yellow	25.6		7.5	16.8		935, 915, 910	368, 350
			(25.0)		(7.3)	(16.7)		*926, 914, 906*	
$1,2\text{-}C_4H_4N_2{\cdot}OsO_4$	88—89	Yellow	14.3		8.4	18.6		920, 905, 890	
			(14.4)		(8.4)	(19.2)			
(*ii*) Aminedioxo-osmium(VI) adducts									
$C_6H_{12}N_4{\cdot}[OsO_2(O_2C_2Me_4)]$	205 [e]	Green	30.4	4.9	11.7	13.8	481 [f]	832, 824	297
			(30.1)	(5.0)	(11.7)	(13.4)	(478)	*882*	
($C_6{}^2H_{12}N_4$ form)								835, 828	295
$C_6H_{12}N_4{\cdot}[OsO_2(O_2C_5H_8)]$	192 [e]	Green	28.6	4.0	11.9	13.4		835, 822	295
			(28.6)	(4.3)	(12.1)	(13.9)		*883*	
$C_6H_{12}N_4{\cdot}[OsO_2(O_2C_6H_{12})]$		Green	29.8	4.7	11.0	14.3		832, 825	290
			(30.1)	(5.0)	(11.7)	(13.4)		*884*	
$C_6H_{12}N_4{\cdot}[OsO_2(O_2C_7H_{13})]$	155 [e]	Green	31.3	4.7	10.9	13.2	586	835, 825	285, 280
			(31.8)	(4.9)	(11.4)	(13.1)	(490)	*883*	
$C_6H_{12}N_4{\cdot}[OsO_2(O_2C_8H_{16})]$	189 [e]	Green	33.1	5.4	11.1	12.4	526 [f]	835, 822	290, 280
			(32.2)	(5.5)	(11.1)	(12.6)	(506)	*883*	
($C_6{}^2H_{12}N_4$ form)								835, 828	285, 280
$C_6H_{12}N_2{\cdot}2[OsO_2(O_2C_2Me_4)]$	206 [e]	Green	27.1	4.4	3.7	15.9	615 [f]	890, 882	325, 310
			(27.4)	(4.6)	(3.6)	(16.2)	(788)		
$C_6H_{12}N_2{\cdot}2[OsO_2(O_2C_5H_8)]$		Brown	25.4	3.9	3.9	18.1		900	330, 295
			(25.4)	(3.7)	(3.7)	(16.9)			
$C_6H_{12}N_2{\cdot}2[OsO_2(O_2C_8H_{16})]$		Green	31.8	5.3	3.1			890	325
			(31.3)	(5.2)	(3.3)				
$C_9H_7N{\cdot}[OsO_2(O_2C_2Me_4)]$		Brown	38.0	4.0	3.1	13.7	454 [f]	898	310
			(38.5)	(4.1)	(3.0)	(13.7)	(467)		
$[Os(NC_9H_7)_2O_2(O_2C_2Me_4)]$		Brown	49.2	4.9	4.6			826	310, 285
			(48.1)	(4.7)	(4.7)				
$C_8H_6N_2{\cdot}[OsO_2(O_2C_2Me_4)]$		Brown	34.8	3.7	5.6	13.5		875	
			(35.9)	(3.8)	(5.9)	(13.7)			
$C_7H_{13}N{\cdot}[OsO_2(O_2C_2Me_4)]$		Green	34.6	5.4	3.5	14.3	474 [f]	900	320
			(34.7)	(5.6)	(3.1)	(14.3)	(447)		
$C_7H_{13}N{\cdot}[OsO_2(O_2C_7H_{12})]$		Green	36.8	5.7	3.0			895	330
			(36.4)	(5.4)	(3.0)				

[a] Calculated values are given in parentheses. [b] In benzene. [c] Only the strongest bands are quoted; Raman modes are italicised. [d] Infrared bands in CCl_4 solution at 955 and 917 cm^{-1}; Raman bands in solution at 960 and 924 cm^{-1} (polarised). [e] Melts with decomposition. [f] In chloroform.

Although they are virtually insoluble in water, the adducts dissolve readily in most organic solvents and are particularly soluble in tetrahydrofuran (thf), dimethylformamide (dmf), and 1,4-dioxan; solutions of $C_6H_{12}N_4{\cdot}2OsO_4$ in these latter solvents, on addition of water, dissociate to give aqueous solutions of OsO_4. Iodimetric titration shows that they are osmium(VIII) species.

The reactions of the adducts with monoalkenes are

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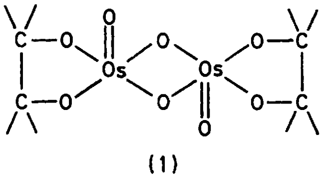
[5] R. J. Collin, W. P. Griffith, and J. Jones, *J.C.S. Dalton*, 1974, 1094.

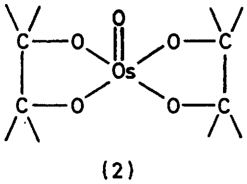
discussed later. We found that $C_6H_{12}N_4{\cdot}2OsO_4$ can be used in the same way as OsO_4 for the *cis*-hydroxylation of alkenes, and have shown this by preparation of *cis*-9,10-dihydrophenanthrene-9,10-diol from phenanthrene using the method of Criegee *et al.*[3] It seems that these adducts could be used in place of OsO_4 for such *cis*-hydroxylations, being in a more convenient form and safer to handle than OsO_4. The presence of the nitrogen-donor ligand may accelerate the reaction of alkenes with OsO_4, since such effects have been observed with osmium tetraoxide–pyridine and –2,2′-bipyridyl mixtures.[6,7] The adducts could have applications as fixatives and stains for electron microscopy since OsO_4 is widely used for this.

Structures and Spectra of the Adducts.—Preliminary *X*-ray studies on $C_6H_{12}N_4{\cdot}2OsO_4$ and $C_7H_{13}N{\cdot}OsO_4$ show that the OsO_4 units are distorted from tetrahedral to trigonal-bipyramidal, the fifth ligand in the latter being an axial nitrogen atom (Os–N *ca.* 2.4 Å).[8] In $C_6H_{12}N_4{\cdot}2OsO_4$ the organic ligand functions as a bridge between two OsO_4 moieties, but only two of its four nitrogen atoms are co-ordinated, and all our attempts to make $C_6H_{12}N_4{\cdot}4OsO_4$ resulted in formation again of $C_6H_{12}N_4{\cdot}2OsO_4$. The reluctance of the complexed hexamethylenetetramine to use its remaining nitrogen atoms may be due to unfavourable bond angles at these sites: it has been found that bond lengths and angles around the unco-ordinated nitrogen atoms in $C_6H_{12}N_4{\cdot}2Br_2$, which contains two linear N–Br–Br groups, differ considerably from those in the free ligand.[9,10] Although there are two nitrogen-donor sites in phthalazine and pyridazine, steric considerations make it unlikely that $L{\cdot}2OsO_4$ would be formed with these amines. No such constraints operate with 1,4-diazabicyclo[2.2.2]octane, pyrazine, and 5-methylpyrimidine.

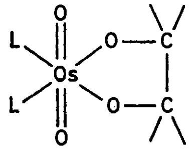
Vibrational spectra of the solids (Table) show, in addition to bands due to the co-ordinated amines, strong absorptions in the 900—960 and 300—380 cm^{-1} regions, essentially unshifted by deuteriation of the ligand in the case of $C_6H_{12}N_4$. These we assign to Os=O stretching and deformation modes respectively: we have previously proposed similar assignments for bands in $NH_3{\cdot}OsO_4$[11] and $C_5H_5N{\cdot}OsO_4$.[12] The similarities in band profiles of the i.r. spectra of the new species (and also the similarities between their Raman spectra) suggest similar environments for the OsO_4 group, *i.e.* a distortion from tetrahedral to trigonal bipyramidal. The i.r. and Raman spectra of the species in carbon tetrachloride solution are similar to, but simpler than, those of the solids; bands of moderate intensity at *ca.* 950 cm^{-1} were observed in the solutions only, arising probably from some OsO_4 formed by slight dissociation of the compounds, molecular-weight data notwithstanding.

Reactions of $L{\cdot}2OsO_4$ *and of* $L{\cdot}OsO_4$ *with Alkenes.*—Osmium tetraoxide reacts with alkenes R to give dimeric monoesters $[Os_2O_4(O_2R)_2]$ (1) and, in some cases, monomeric diesters $[OsO(O_2R)_2]$ (2). These all contain


(1)


(2)

square-based pyramidal Os^{VI} with cyclic ester rings.[3,5,13,14] In the presence of an excess of pyridine or isoquinoline (L) the octahedral *trans*-$[OsL_2O_2(O_2R)]$ (3) species are formed.[3,12] It is of interest then to examine the reactions of $L{\cdot}2OsO_4$ and $L{\cdot}OsO_4$ with alkenes since the initial L : Os ratio is fixed by the stoicheiometries of the reactants.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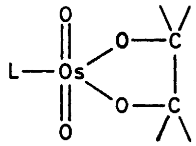
(4)

With $C_6H_{12}N_4{\cdot}2OsO_4$ and alkenes R [R = tetramethylethylene (C_2Me_4), cyclopentene (C_5H_8), *trans*-hex-3-ene (C_6H_{12}), cycloheptene (C_7H_{12}), or 2,4,4-trimethylpent-1-ene (C_6H_{16})], products of stoicheiometry $C_6H_{12}N_4{\cdot}[OsO_2(O_2R)]$ together with the corresponding monoesters $[Os_2O_4(O_2R)_2]$ can be isolated (quantitatively in the case of C_2Me_4). The overall reaction is (1). In the case of

$$2C_6H_{12}N_4{\cdot}2OsO_4 + 4R \longrightarrow [Os_2O_4(O_2R)_2] + 2\{C_6H_{12}N_4{\cdot}[OsO_2(O_2R)]\} \quad (1)$$

the adduct $C_6H_{12}N_2{\cdot}2OsO_4$ the ligand retains its bridging role to give $C_6H_{12}N_2{\cdot}2[OsO_2(O_2R)]$ (R = C_2Me_4, C_5H_8, or C_8H_{16}). (This is supported by the ^{1}H n.m.r. spectrum of the C_2Me_4 adduct which shows two resonances in a 1 : 2 ratio.) With $L{\cdot}OsO_4$ (L = isoquinoline, phthalazine, or quinuclidine) the products have the formulae $L{\cdot}[OsO_2(O_2R)]$. Iodimetric titration of some of these compounds shows the osmium to be in the oxidation state VI. The compounds are diamagnetic as expected for oxo-osmium(VI) species.[5,12] Molecular-weight data were difficult to obtain owing to the low solubility of the compounds, but suggest that the $L{\cdot}[OsO_2(O_2R)]$ species are monomeric. Electronic spectra of $C_6H_{12}N_2{\cdot}2[OsO_2(O_2R)]$ (R = C_2Me_4) and of $L{\cdot}[OsO_2(O_2R)]$ (L = $C_6H_{12}N_4$, $C_7H_{13}N$, or C_9H_7N; R = C_2Me_4) in the

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[7] F. B. Daniel and E. J. Behrman, *J. Amer. Chem. Soc.*, 1975, **97**, 7352.

[8] J. Mant, F. L. Phillips, A. C. Skapski, and P. B. Williams, unpublished work.

[9] G. Eia and O. Hassel, *Acta Chem. Scand.*, 1956, **10**, 139.

[10] M. Horak and P. Tvarutzek, *Coll. Czech. Chem. Comm.*, 1975, **40**, 2741.

[11] W. P. Griffith, *J. Chem. Soc.* (*A*), 1966, 899.

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[14] R. Collin, W. P. Griffith, F. L. Phillips, and A. C. Skapski, *Biochim. Biophys. Acta*, 1974, **354**, 152; F. L. Phillips and A. C. Skapski, *Acta Cryst.*, 1975, **B31**, 1814.

400—800 nm region are similar, whereas spectra of $C_9H_7N\cdot[OsO_2(O_2C_2Me_4)]$ and $[Os(NC_9H_7)_2O_2(O_2C_2Me_4)]$ [known [3,12] to have structure (3)] are different in this region. The i.r. spectra of the compounds show, in addition to modes of co-ordinated L, bands typical of $Os(O_2R)$ rings.[5] There are also strong bands in the 830—890 cm^{-1} region and weaker ones at *ca.* 300 cm^{-1} (unshifted by deuteriation of $C_6H_{12}N_4$ in its C_2Me_4 and C_8H_{16} esters). These we assign to the asymmetric stretching [$\nu_{asym}(OsO_2)$] and bending modes [$\delta(OsO_2)$] of a *trans*-O=Os=O ' osmyl ' group; such modes are seen in the spectra of other ' osmyl ' compounds [15] and also for species of structure (3).[12] In the $C_6H_{12}N_4$ species these bands are at 830 cm^{-1} in the solid state and at 870 cm^{-1} in chloroform solution. The Raman spectra of the same compounds have bands at *ca.* 890 cm^{-1} which could arise from the symmetric stretch [$\nu_{sym}(OsO_2)$] of an osmyl unit.[15]

We tentatively propose that the compound $L\cdot[OsO_2(O_2R)]$ and also the $OsNO_2(O_2R)$ unit in $L\cdot2[OsO_2(O_2R)]$ have structure (4) with five-co-ordinate Os^{VI}, probably trigonal bipyramidal with a *trans*-O=Os=O skeleton as the axis. If this is so, the somewhat higher Os=O stretching frequencies found in these species compared with those of structure (3) probably arise from the higher effective electronegativity of the osmium atom in the five-co-ordinate species, there being only three equatorial σ-donor ligands as against four in the octahedral type (3) species. These are then the first five-co-ordinate compounds to contain a *trans*-osmyl group, although five-co-ordinate osmium(VI) complexes containing one doubly bonded oxo-ligand [5,12-14] or triply bonded nitride ligand [16] are well established.

EXPERIMENTAL

Amine–Osmium Tetraoxide Adducts.—These were made by the following general method unless otherwise noted.

To a solution of OsO_4 (1 g) in water (25 cm^3) was added an aqueous solution or emulsion of the amine. The solution was stirred for 5 min and the yellow or orange product was filtered off, washed with water, and dried *in vacuo*, yield 70—90%. The products with hexamethylenetetramine ($C_6H_{12}N_4$) and quinuclidine were recrystallised from CCl_4 as bright red needles and platelets respectively. The deuteriated $C_6H_{12}N_4$ adduct was made from $C_6{}^2H_{12}N_4$ and OsO_4 in ^2H_2O. The quinuclidine *adduct* $C_7H_{13}N\cdot OsO_4$ was similarly made, a solution of quinuclidine hydrochloride (0.6 g) in water (1 cm^3) being neutralised with Na[OH] before addition to OsO_4 solution. Drying of the pyrazine and 5-methylpyrimidine *species*, $C_4H_4N_2\cdot2OsO_4$ and $C_5H_6N_2\cdot2OsO_4$, led to appreciable loss of material owing to their volatilities.

Aminedioxo-osmium(VI) *Esters.*—The preparation of these species followed similar procedures.

Hexamethylenetetramine species. The preparation of $C_6H_{12}N_4\cdot[OsO_2(O_2C_2Me_4)]$ is typical. Finely powdered $C_6H_{12}N_4\cdot2OsO_4$ (0.25 g) was dissolved in tetrahydrofuran (thf) or chloroform (3 cm^3) and a slight excess of C_2Me_4 (0.1 g) was added. The greenish black microcrystalline precipitate was filtered off after 5 min, washed with thf (1 cm^3) and then copiously with diethyl ether to remove $[Os_2O_4(O_2C_2Me_4)_2]$, and finally dried in air to give the pale green product (75%). The $C_6{}^2H_{12}N_4$ derivative was made similarly from $C_6{}^2H_{12}N_4\cdot2OsO_4$ and tetramethylethylene. In a separate experiment, the by-product of the reaction, $[Os_2O_4(O_2C_2Me_4)_2]$, was recovered in 80% yield by using the above procedure but omitting the addition of diethyl ether. The filtrate after separation of $C_6H_{12}N_4\cdot[OsO_2(O_2C_2Me_4)]$ was passed down a silica column and eluted with chloroform. Concentration of the eluate gave shiny black crystals of $[Os_2O_4(O_2C_2Me_4)_2]$.

1,4-*Diazabicyclo*[2.2.2]*octane species.* The preparation of $C_6H_{12}N_2\cdot2[OsO_2(O_2C_2Me_4)]$ is typical. The adduct $C_6H_{12}N_2\cdot2OsO_4$ (0.25 g) was dissolved in thf (3 cm^3) and tetramethylethylene (0.1 g) was added with stirring. The dark green precipitate was filtered off after 5 min, washed with thf (1 cm^3) then diethyl ether (5 cm^3), and dried in air, yield 90%.

Quinuclidine species. These were made from $C_7H_{13}N\cdot OsO_4$ (0.5 g) in thf (1 cm^3) on addition of the alkene (0.15 g). The deep green solutions were reduced in volume to precipitate the products. The tetramethylethylene ester was recrystallised from CH_2Cl_2 and light petroleum.

Isoquinoline and phthalazine species. The adduct $C_9H_7N\cdot[OsO_2(O_2C_2Me_4)]$ was made from $C_9H_7N\cdot OsO_4$ (0.5 g) in CCl_4 (10 cm^3) and tetramethylethylene (0.15 g). The solution was allowed to evaporate slowly to give the dark brown product in 60% yield. Octahedral $[Os(NC_9H_7)_2O_2(O_2C_2Me_4)]$ was made according to Criegee *et al.*[3] The adduct $C_8H_6N_2\cdot[OsO_2(O_2C_2Me_4)]$ was made from $C_8H_6N_2\cdot OsO_4$ (0.5 g) and tetramethylethylene (0.15 g) in chloroform, and the pale brown product was dried in air (70%).

Analytical and molecular-weight data are given in the Table. They were obtained by the Microanalytical Department, Imperial College, A. Bernhardt (Munich), and F. Pascher (Bonn). Iodimetric titrations were carried out by the literature method.[17] Infrared spectra were recorded (200—4 000 cm^{-1}) on Perkin-Elmer 457 and 325 instruments as Nujol mulls with caesium iodide plates, and in various solvents using potassium bromide cells. Raman spectra were obtained (200—1 000 cm^{-1}) on a Cary 81 instrument with a Coherent Radiation 52 krypton laser using excitation at 6 471, 5 682, and 5 308 Å.

One of us (M. J. W.) thanks the S.R.C. for the award of a postgraduate studentship.

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