Complexes of Osmium(VI) with Catechol and Substituted Catechols

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Osmium tetraoxide reacts with catechols, $R(OH)_2$-*o*, to give the tris(catecholato)-species $[Os(O_2R)_3]$ and the polymers $[\{OsO(O_2R)_2\}_n]$, while in the presence of pyridine or substituted pyridines (L) *trans*-$[OsO_2(O_2R)L_2]$ complexes are formed. Reaction of *cis*-$[OsO_4(OH)_2]^{2-}$ or *trans*-$[OsO_2(OH)_4]^{2-}$ with catechols yields salts of *trans*-$[OsO_2(O_2R)_2]^{2-}$. The Raman, i.r., ^1H and ^{13}C n.m.r., and mass spectra of the products are reported and the structures deduced. The relevance of some of these complexes to the reaction of OsO_4 with phenolic material in plant tissue is briefly discussed.

THE reaction of osmium tetraoxide and some phenols to give deep blue solutions has long been known.[1-3] (Tennant, in his original paper announcing the discovery of osmium, used the blue colour formed with gallic acid as a test for OsO_4.) However, the reaction products have not hitherto been isolated or characterised, nor has the nature of the phenols required to give the reaction established. Work on plant-tissue fixation and staining by OsO_4 for optical or electron microscopy[3-5] suggests that those areas of tissue-containing phenols are osmiophilic, but no reaction specificity has been established. This study, part of our continuing work on the reactions of OsO_4 with organic substrates,[6,7] was made to establish the nature of the reaction with phenols and the structures of the products.

RESULTS AND DISCUSSION

We find that osmium tetraoxide reacts rapidly in non-aqueous or aqueous solution only with those phenols containing *o*-dihydroxy-groups (*i.e.* catechol or substituted catechols). There is no reaction under such conditions with monohydroxy phenols (*e.g.* phenol, *p*-cresol, guaiacol, or vanillin), *m*-dihydroxy phenols (*e.g.* resorcinol), *o*-dimethoxy phenols (*e.g.* veratrole), or those containing one hydroxy- and one carboxyl group (*e.g.* *m*- or *p*-hydroxy-benzoic acid or salicylic acid). Prolonged reaction with these species gives insoluble materials of variable composition, but it is only with catechols that there is reaction to give characterisable species. This occurs because the *cis* oxygen-donor atoms in catechols, as demonstrated below, give stable five-membered chelate rings with Os^{VI}. Previous work on the reaction of OsO_4 with glycols, where the *cis*-hydroxy- groups do not form part of a conjugated system, shows that there is only slow reaction to give osmium(VI) esters.[6,7] Co-ordination of some glycols to OsO_4 without reduction to Os^{VI} has also been proposed.[8]

(*a*) *Tris(catecholato)-species*, $[Os(O_2R)_3]$.—Reaction of OsO_4 in non-polar solvents such as benzene or carbon tetrachloride with 4-t-butyl-, 3,5-di-t-butyl-, or 4-t-octyl-catechol gave deep blue solutions from which the tris-chelates were obtained in 60—80% yield after chromatography. These are the first neutral tris-(catecholates) to be isolated. Similar blue solutions were obtained with catechol and 4-methylcatechol, but the yields of tris-complexes in these cases were very low (*ca.* 10%): the main products were insoluble species of approximate stoicheiometry $[Os_2O(O_2R)_5]\cdot nH_2O$.

The complexes are deep blue air-stable solids, very soluble in non-polar solvents to give deep blue solutions, but only slightly soluble in polar solvents such as acetone or methanol. They are monomeric in benzene and chloroform, and diamagnetic in the solid state and in solution. They do not react with dilute acids or bases, or after prolonged refluxing with pyridine.

X-*Ray data.* Preliminary single-crystal *X*-ray data on the catechol and 3,5-di-t-butylcatechol complexes $[Os(O_2C_6H_4)_3]$ and $[Os(O_2C_{14}H_{20})_3]$ show that these are indeed tris(catecholato)-species.[9] The Os–O bond lengths are 1.95(1) Å and the O–Os–O angles 80(2)°, the OSO_2R rings being essentially planar. The structure is then essentially similar to that found for the anion in $K_3[Cr(O_2C_6H_4)_3]\cdot 1.5H_2O$,[10] and the Os–O distances are close to those found in $[Os_2O_4(O_2C_2Me_4)_2]$.[11] The distortion from octahedral to approximate D_3 local symmetry with a small O–Os–O angle about the metal

[1] S. Tennant, *Phil. Trans.*, 1804, **94**, 419.
[2] G. F. Bahr, *Expt. Cell Res.*, 1954, **7**, 457.
[3] H. Schultz and M. Rudneff, *Arch. Mikr. Anat.*, 1865, **1**, 299.
[4] C. H. Beckman and W. C. Mueller, *Phytopathology*, 1970, **60**, 79.
[5] P. S. Baur and C. H. Walkinshaw, *Canad. J. Bot.*, 1974, **52**, 615.
[6] R. J. Collin, J. Jones, and W. P. Griffith, *J.C.S. Dalton*, 1974, 1094.
[7] M. J. Cleare, P. C. Hydes, W. P. Griffith, and M. J. Wright, *J.C.S. Dalton*, 1977, 941.
[8] N. A. Milas, J. H. Trepagnier, J. T. Nolan, and M. Iliopulos, *J. Amer. Chem. Soc.*, 1959, **81**, 4730.
[9] M. Hursthouse, unpublished work.
[10] K. N. Raymond, S. S. Isied, L. D. Brown, F. R. Fronzek, and J. H. Nibert, *J. Amer. Chem. Soc.*, 1976, **98**, 1767.
[11] F. L. Phillips and A. C. Skapski, *J.C.S. Dalton*, 1975, 2586.

atom probably accounts for the diamagnetism of these complexes.

Vibrational spectra. Infrared spectra of chloroform solutions of the complexes were recorded from 700 to 4 000 cm^{-1}, and Raman spectra of acetone solutions from 700 to 1 000 cm^{-1} (Table 1). No bands in the O–H stretching region (3 000—4 000 cm^{-1}) are seen. The strong band near 1 250 cm^{-1} in catechol and catechol complexes assigned [12] to ν(C–O) is still prominent but depolarised shifts near 530 cm^{-1} close to the i.r. bands. For complexes of skeletal D_3 symmetry we expect one polarised Raman mode (A_1) inactive in the i.r. and three depolarised bands ($A_2 + 2E$) active also in the i.r.; probably an A_2 and an E mode overlap. A similarly high frequency for the A_1 mode is found in other comparable D_3 complexes {*e.g.*[13] at 570 cm^{-1} in $[Ir(C_2O_4)_3]^{3-}$}.

Hydrogen-1 and ^{13}C n.m.r. spectra. The ^1H n.m.r. spectra show well defined ABX patterns in the aromatic

TABLE 1

Analytical and spectroscopic data for osmium(VI) catecholato-complexes

Ligand	Analyses [a] (%) C	H	*M* [a,b]	Vibrational spectra (selected bands) (cm^{-1}) [c] ν(C–O)	ν(Os–O)	δ(OsO_2)
(*a*) tris(catecholato)-complexes $[Os(O_2R)_3]$						
Catecholate	42.4 (42.0)	2.3 (2.3)	514, *514* (514)	1 110vs	520m *549*p, *524*dp	
4-t-Butylcatecholate	52.3 (52.8)	5.5 (5.3)	689 (689)	1 180vs	540m	
3,5-Di-t-butylcatecholate	59.2 (59.3)	6.9 (7.1)	868, *851* (851)	1 150vs	500m *587*p, *508*dp	
4-t-Octylcatecholate	58.8 (58.3)	7.0 (7.1)	835, *852* (851)	1 180vs	530m *548*p, *512*dp	
	C	H	P			
(*b*) *trans*-Bis(catecholato)dioxo-complexes $[PPh_4]_2[OsO_2(O_2R)_2]\cdot nH_2O$						
Catecholate (n = 3)	61.0 (61.5)	4.4 (4.6)	5.3 (5.3)	1 250vs	824vs, *864*s	290w
4-Methylcatecholate (n = 1) [d]	30.0 (30.2)	2.2 (2.5)		1 263vs	828vs	318w
4-Methylcatecholate	65.2 (66.0)	4.9 (4.6)	5.4 (5.4)	1 263vs	822vs	295w
4-t-Butylcatecholate	66.9 (66.4)	5.2 (5.2)	4.4 (5.0)	1 250vs	818vs, *862*s	
4-Nitrocatecholate (n = 1) [e]	59.8 (59.7)	4.0 (3.8)	5.6 (5.1)	1 260vs	828vs, *872s*	250w
4-Methyldaphnetinate (n = 2)	61.6 (62.0)	3.9 (4.3)	4.2 (4.7)	1 260vs	820vs, *866s*	240w
	C	H	O			
(*c*) *catena*-μ-Oxo-bis(catecholato)-complexes $[\{[OsO(O_2R)_2]\cdot nH_2O\}_x]$						
4-Methylcatecholate (n = 0.5)	36.9 (37.0)	2.8 (2.8)	19.1 (19.1)	1 135s	475b	
4-t-Butylcatecholate (n = 1)	43.4 (43.5)	4.8 (4.7)		1 170s	540b	
3,5-Di-t-butylcatecholate	51.7 (52.0)	6.1 (6.2)		1 165s	506b	
D-Catechinate (n = 3)	43.4 (43.1)	3.6 (3.6)		1 120	545b	
Gallate (n = 3)	28.5 (28.2)	2.5 (2.4)		1 175s		
Digallate (n = 3.5)	36.9 (37.0)	2.7 (2.5)	39.6 (39.6)	1 170s		
Caffeate (n = 2)	35.8 (36.1)	2.7 (2.7)			528b	
(*d*) *trans*-Catecholatodioxobis(pyridine) complexes [f] $[OsO_2(O_2R)L_2]\cdot nH_2O$	C	H	N			
Catecholate	38.7 (39.3)	3.0 (2.9)	5.5 (5.7)	1 248s	838vs	302w
4-Methylcatecholate	48.6 (48.8)	5.1 (5.2)	4.1 (4.5)	1 264s	840vs, *875s*	307w
Gallate (n = 1)	35.9 (36.6)	2.7 (2.8)	4.8 (4.9)	1 213vs	843vs, *882*s	278w
Quercetinate	44.4 (44.1)	2.9 (2.7)	4.1 (4.1)	1 262s	840vs, *882*s	325w

[a] Calculated figures are given in parentheses. [b] For chloroform solutions (osmometric); mass-spectral values are italicised. [c] Raman bands are italicised. Data for chloroform (i.r.) or acetone (Raman) solutions for (*a*), on solids for (*b*)—(*d*). [d] Potassium salt. [e] N, 2.4 (2.3%). [f] L = Pyridine for all except 4-methylcatecholate (L = 4-t-butylpyridine).

shifted to somewhat lower frequencies. {We find a similar effect in the i.r. spectrum of $K_3[Cr(O_2C_6H_4)_3]\cdot 1.5H_2O$.} Bands due to aromatic C–H and C–C stretches are seen near 3 000 and 1 640 cm^{-1} respectively in the complexes, and there are also strong absorptions near 1 580 cm^{-1} which may arise from increased ring conjugation brought about by co-ordination to the metal atom. In the Os–O stretching region (300—650 cm^{-1}) one or two i.r. modes are observed for the solid complexes which do not appear in the free ligands, and we assign them to Os–O stretches [bands near 550 cm^{-1} are found for these in osmium(VI) mono- and di-esters [6]]. The Raman spectra of the solutions in acetone show a strong polarised shift near 580 cm^{-1} (*p ca.* 0.05) and two region, with protons (H_a and H_b) adjacent to the donor oxygen atoms shifted downfield from the remaining aromatic protons by *ca.* 0.8 p.p.m. This would be expected as a result of electron drain *via* the oxygen ligands to osmium. In the ^{13}C n.m.r. spectra a downfield shift is found for the *o*-substituted carbon atoms in the complexes as compared with the free ligands. The position of these resonances appears to be sensitive to substituent effects: in particular, the *o*-substituted carbon atom *ortho* to a Bu^t group experiences a large upfield shift. Steric or electronic factors could be

[12] P. A. Wicklund and D. G. Brown, *Inorg. Chem.*, 1976, **15**, 397.

[13] J. Gouteron, *J. Inorg. Nuclear Chem.*, 1976, **38**, 55.

responsible for these effects, but we note that no such steric effects are present in the spectrum of the free ligand.

Mass spectra. For $[Os(O_2C_6H_4)_3]$, well defined molecular ions M^+ and $[M - O_2C_6H_4]^+$ are seen but none due to $[M - 2O_2C_6H_4]^+$; a similar phenomenon is found for $[Os(pd)_3]$ (pd = pentane-2,-4-dionate).[14] For the alkyl-substituted-catechol complexes, fragments due to the loss of methyl groups occur both for $[Os(O_2R)_3]$ and $[Os(O_2R)_2]$. The other features of these complex spectra seem to arise from species synthesised in the spectrometer as a result of fragmentation of the aromatic ring. Thus, for $[Os(O_2C_6H_4)_3]$, species attributable to $[Os(O_2C_6H_4)(C_4H_4)]^+$, $[Os(O_2C_6H_4)(C_2H_2)]^+$, $[Os(C_4H_4)]^+$, $[Os(C_2H_2)_2]^+$, and $[Os(C_2H_2)]^+$ can be seen. The cleaved ligands appear to protonate in the spectrometer since the ion of $C_6H_4(OH)_2$ is seen as a major peak and of $C_6H_4O_2$ as a very minor one.

which resulted could also be made from the catechol in aqueous sodium phosphate or sodium dimethylarsenate buffers at pH 6.8 with OsO_4. Owing to their lower solubilities, tetraphenylphosphonium salts are easier to crystallise than the potassium salts. They are slightly soluble in dichloromethane but practically insoluble in other organic solvents, so the spectral data in Table 1 refer to solids only. In addition to bands due to the cation, the main features of the corresponding tris-(catecholato)-species are observed, although the Os–O stretching bands near 500 cm^{-1} are weaker. In addition, very strong bands for the solids near 830 (i.r.) and 880 cm^{-1} (Raman) are observed, as in other complexes containing the *trans*-O=Os=O ' osmyl ' group;[6,17,18] these we assign to the asymmetric and symmetric $\nu_{asym}(OsO_2)$ and $\nu_{svm}(OsO_2)$ stretching modes respectively. The $\delta(OsO_2)$ deformation mode is observed as a weak to moderate intensity band in the i.r. near 300 cm^{-1}. Both

TABLE 2

Hydrogen-1 and ^{13}C n.m.r. spectra for $[Os(O_2R)_3]$

Complexed ligand (O_2R)	^1H (δ/p.p.m. *versus* $SiMe_4$)				^{13}C (δ/p.p.m. *versus* $SiMe_4$) [a]			
	H_a	H_b	H_c	Others	C–O	C–C	C–H	Alkyl C–H, C–C
Catecholate	6.40—6.68 (m)		7.38—7.68 (m)		171.5 (145.0)		124.0, 117.1 (122,1. 117.3)	
4-t-Butylcatecholate	7.40, 7.56 (d)	7.61 (d)	6.51, 6.65 (d)	1.43 (s) Bu^t	171.3, 169.9 [b] (144.9, 142.8)	148.2 (140.8) [b]	120.7, 116.1, 115.7 (117.8, 115.0, 113.0)	33.4, 33.1, 32.6 (34.0, 31.3)
3,5-Di-t-butyl-catecholate		7.50 (d)	6.68 (d)	1.32, 1.38 (2 s) Bu^t	172.5, 184.9 (142.2, 140.5) [b]	138.4 (135.6) [b]	117.2, 111.0 (116.1, 110.5)	34.9, 33.5, 32.6 29.9 (34.5, 34.0, 31.6, 29.7)
4-t-Octylcatecholate	7.35, 7.49 (d)	7.58 (d)	6.47, 6.63 (2 d)	0.77 (s) Bu^t 1.46 (s) Me 1.83 (s) CH_2	171.4, 170.0 (143.7, 142.6) [b]	147.9 (140.5) [b]	121.6, 115.6, 114.1 (118.7, 114.7, 113.7)	58.2, 37.4, 32.8, 32.3, 31.8 (56.9, 37.9, 32.2, 31.6, 31.5)

[a] Shifts for the free ligands are given in parentheses. [b] Tentative assignment only.

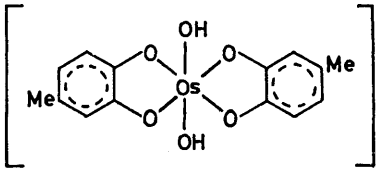
Polarography. Polarographic reduction of the catecholato- and 3,5-di-t-butyl-catecholato complexes in acetone at a dropping mercury electrode shows two reversible one-electron waves {reversibility established both from $\log[(i_d - i)/i]$ and from $E_{3/4} - E_{1/4}$ values} with $E_{\frac{1}{2}}$ (*versus* a silver electrode) at 0.04 and −0.72 V for $[OsCO_2C_6H_4)_3]$ and $E_{\frac{1}{2}}$ 0.04 and −0.85 V for $[Os(O_2C_{14}H_{20})_3]$ (the second wave of the latter exhibited a slight maximum). The shift of $E_{\frac{1}{2}}$ to more negative potentials when electron-donating substituents are attached to pentane-2,4-dionate ligands has also been observed for $[Os(pd)_3]$.[15] It seems likely that an electron-transfer series $[Os(O_2R)_3]^n$ exists, of which these polarographically reduced species are the n = −1 and −2 members; similar series have been found with other catecholato-complexes.[16]

(*b*) *The* trans-*Bis(catecholato)dioxo-osmate*(VI) *Ions*, $[OsO_2(O_2R)_2]^{2-}$.—Salts containing these ions were formed by reactions of the catechols with $K_2[cis\text{-}OsO_4(OH)_2]$ or $K_2[trans\text{-}OsO_2(OH)_4]$ in water, or $K_2[trans\text{-}OsO_2(OMe)_4]$ in methanol. The characteristically red-brown solutions $\nu_{asym}(OsO_2)$ and $\nu_{sym}(OsO_2)$ are sensitive to the nature of the substituents on the catechol ring, increasing in frequency the more electron-withdrawing the substituent, consistent with a greater degree of Os=O multiple bonding. The complexes are diamagnetic, as are other ' osmyl ' species.[6,17]

These salts are stable in alkaline solution or in aqueous phosphate or dimethylarsenate buffer at pH 6.8, but in acid there is immediate formation of the polymeric species $[\{OsO(O_2R)_2\}_n]$ discussed below [section (*C*)]. Such reaction occurs if acid is added to the solutions, or excess of catechol, or the addition of acidic cations (*e.g.* tetraphenylarsonium hydrochloride). In one reaction we were able to isolate a *trans*-dihydroxo-complex (1). This complex is blue and soluble in chloroform or acetone. It has i.r. bands at 3 450 [ν(OH)] and 540 cm^{-1} [ν(Os–OH)] in addition to the modes observed in $[Os(O_2C_6H_3Me)_3]$. Attempted recrystallisation or storage of a solution of the complex gave the polymer $[\{OsO(O_2R)_2\}_n]$. Attempts to acetylate the hydroxy-groups with acetic anhydride and pyridine or to methylate them

[14] C. G. MacDonald and J. S. Shannon, *Austral. J. Chem.*, 1966, **19**, 1545.
[15] G. S. Patterson and R. H. Holm, *Inorg. Chem.*, 1972, **11**, 2285.
[16] F. Rohrschedi, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, 1966, **5**, 1542.
[17] W. P. Griffith and R. Rossetti, *J.C.S. Dalton*, 1972, 1449.
[18] W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 211.

with diazomethane resulted in decomposition. It seems that the *trans*-dioxo-groups in these species are easily protonated and that the resulting hydroxo-species then eliminate water to form *catena*-[{OsO-$(O_2R)_2$}$_n$]; intermediates such as (1) may be formed in all



(1)

these reactions. A similar elimination of water occurs for the d^2 species $[MoO_2(CN)_4]^{3-}$ which on acidification gives $[Mo_2O_3(CN)_8]^{6-}$.[19]

(*c*) catena-*μ-Oxo-bis*(*catecholato*)*osmium*(VI), [{OsO-$(O_2R)_2$}$_n$]·xH_2O.—Reaction of OsO_4 in aqueous acetone with the catechol or acidification as described above of solutions of *trans*-$[OsO_2(O_2R)_2]^{2-}$ yields deep blue diamagnetic solids of empirical formula $[OsO(O_2R)_2]$·xH_2O. Formation of these from OsO_4 and the catechol in pure acetone is very slow, but addition of only a trace amount of water caused the reaction to proceed to completion. The complexes are diamagnetic as expected for osmium(VI) complexes of low symmetry.[6,20] They are chemically very inert and do not react with refluxing pyridine.

The insolubility of these species in most solvents made characterisation very difficult. One, however, the 3,5-di-t-butyl species, was sufficiently soluble in benzene to enable a molecular weight of 2 797 to be determined, suggesting in this case a tetrameric structure. The same complex gave a mass spectrum showing the molecular ion $[OsO(O_2R)_2]^+$. Their i.r. spectra are very similar to those of the corresponding $[Os(O_2R)_3]$ complexes, although of much poorer quality due probably to the intense colours of the polymers. No Raman spectra could be recorded. A very broad i.r. absorption in the 500—700 cm^{-1} region could be due to Os–O · · · Os–O · · · Os chains such as are observed in other chain metal oxo-[21] and nitrido-systems.[22] We propose tentatively that these are ring or chain complexes with bridging oxo-ligands.

Other catecholato-oxo-species of sexivalent metals have been prepared, *e.g.* $[WO_2(O_2C_6H_4)_2]^{2-}$ and $[WO_3(O_2C_6H_4)(OH_2)]^{2-}$,[23,24] but there is no reason to suppose that these contain bridging oxo-ligands.

(*d*) trans-*Catecholatodioxobis*(*pyridine*)*osmium* (VI) *Complexes*, $[OsO_2(O_2R)L_2]$ (L = *Pyridine* or 4-t-*Butylpyridine*).—Reaction of OsO_4 in chloroform or dichloromethane with the pyridine and the catechol gave red-brown solutions from which the complexes precipitated. Only a few could be obtained pure, however, since the products are light-sensitive and in some cases contaminated by quinone oxidation products. Recrystallisation was not possible owing to the low solubility of the products in organic solvents such as acetone or methanol and the instability of such solutions. The use of 4-t-butylpyridine in a 2 : 1 ratio with OsO_4 in an inert atmosphere gave purer products. One such complex, $[OsO_2(O_2C_6H_4)(py)_2]$, has previously been reported.[25]

The i.r. spectra show the main features of those of $[Os(O_2R)_3]$, although the expected Os–O bands near 550 cm^{-1} are obscured by pyridine vibrations. In addition, bands due to the *trans*-O=Os=O 'osmyl' grouping near 830 cm^{-1} [$\nu_{asym}(OsO_2)$] and 320 cm^{-1} [$\delta_{asym}(OsO_2)$] are prominent, as in *trans*-$[OsO_2(O_2R)_2]^{2-}$. We were able to record the Raman spectrum of $[OsO_2(O_2C_6H_4)(py)_2]$ in acetone and show that the band at 878 cm^{-1} is polarised, as expected for $\nu_{sym}(OsO_2)$. As with the $[OsO_2(O_2R)_2]^{2-}$ salts, both $\nu_{asym}(OsO_2)$ and $\nu_{sym}(OsO_2)$ are higher in frequency the more electron-withdrawing are the substituents on the catechol. The complexes are all diamagnetic as are other 'osmyl' complexes.[6,17]

A number of species with L = 4Bu^t-py were made but could not be isolated pure. They were, however, characterised by ^1H n.m.r. and i.r. spectra; the former clearly showed the presence of one catecholato- and two 4Bu^t-py ligands. Donation of electrons from the ligand to osmium is reflected by a downfield shift of the α protons by some 0.4 p.p.m. as compared with the free ligand, while the more distant β protons or γ Bu^t groups show smaller shifts. A similar effect has been observed in $[OsO_2(O_2C_2Me_4)(py)_2]$.[26] As found for $[Os(O_2R)_3]$, the effect of co-ordination of the catecholato-ligands to osmium is to shift the *ortho* (to oxygen) catecholate protons downfield from the remaining aromatic protons, all the resonances showing the expected ABX splitting pattern. In the cases of 4-methyldaphnetin and 4-methylesculetin, which contain double bonds with which OsO_4 might have been expected to react, the ^1H n.m.r. spectra show that these bonds remain intact: *i.e.* these ligands function purely as catecholato-groups. Some deactivation of the double bond seems to have occurred in these ligands, since acetylation of the hydroxy-groups of 4-methylesculetin followed by addition of OsO_4 and 4Bu^t-py gave only a slow reaction, despite the known effect of pyridines[27] of increasing the rate of reaction of OsO_4 with double bonds.

(*e*) *Tissue Staining of Phenolic Materials*.—We have demonstrated that OsO_4 reacts with those phenols which are of the catechol type, *i.e.* which contain *o*-dihydroxy-units. Under the normal conditions of cytochemical

[19] D. L. Toppen and R. K. Murmann, *Inorg. Chem.*, 1973, **12**, 1611.
[20] K. A. K. Lott and M. C. R. Symons, *J. Chem. Soc.*, 1966, 973.
[21] W. P. Griffith, *J. Chem. Soc.*, 1964, 5248.
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[23] L. Fernandes, *Gazzetta*, 1925, **55**, 434.
[24] R. Weinland, A. Babel, K. Gross, and H. Mai, *Z. anorg. Chem.*, 1926, **150**, 177.
[25] R. Criegee, B. Marchand, and B. Wannowius, *Annalen*, 1942, **550**, 99.
[26] L. G. Marzilli, B. E. Hanson, T. J. Kistenmacher, L. A. Epps, and R. C. Stewart, *Inorg. Chem.*, 1976, **15**, 1661.
[27] L. R. Subbaraman, J. Subbaraman, and E. J. Behrman, *Inorg. Chem.*, 1972, **11**, 2621.

fixation, OsO_4 is used in an aqueous buffer solution (usually sodium phosphate or dimethylarsenate at pH 6.8), such reaction being allowed to proceed only for 1 h at 0—20 °C before removal of OsO_4 by washing. In these circumstances only catechol-like phenols would react, and are likely to give species of the *trans*-$[OsO_2(O_2R)_2]^{2-}$ type initially. With removal of the buffer, these species would undoubtedly polymerise to $[\{OsO_2(O_2R)_2\}_n]\cdot xH_2O$, and the stability of these complexes is such that it is likely that no further reactions will occur. Naturally occurring plant catechols which we have shown to undergo these reactions are quercirin, D-catechin, caffeic acid, and the dihydroxycoumarin compounds 4-methyldaphnetin and 4-methylesculetin.

Complexes of the type *trans*-$[OsO_2(O_2R)_2]^{2-}$ and *trans*-$[OsO_2(O_2R)(py)_2]$ could themselves perhaps be introduced as stains for electron microscopy, utilising catechols containing substituents designed to react with specific tissue components. Such a process is probably involved in the extra staining [28] of tissues using polyphenolic materials.

EXPERIMENTAL

Analyses and molecular-weight data are given in Table 1.

Preparation of Complexes.—All the catechols were purified by sublimation or recrystallisation as appropriate immediately prior to use.

(*a*) *Tris*(*catecholato*)*osmium*(VI) *complexes*, $[Os(O_2R)_3]$. The preparation of the 3,5-di-t-butylcatecholato-complex is typical. Osmium tetraoxide (0.1 g, 0.4 mmol) was dissolved in chloroform (15 cm³) and the ligand (0.26 g, 1.2 mmol) added. The mixture was allowed to stand under argon for 3 d. The solvent was then removed and the residue chromatographed on a silica gel column and eluted with chloroform until the column became a clear light blue. The complex was obtained as dark blue prisms after recrystallisation from methylene dichloride–methanol (1 : 1) (yield 75%).

With catechol and 4-methylcatechol the above procedure led to formation of dark blue precipitates which were filtered off, and the filtrate was then chromatographed as above; yields *ca.* 10%. The product with 4-methylcatechol could not be obtained analytically pure although the appropriate mass spectrum was observed.

(*b*) trans-*Bis*(*catecholato*)*dioxo-osmate*(VI) *salts*, $A^2[OsO_2(O_2R)_2]\cdot nH_2O$. *Method* (1): *from* cis-$K_2[OsO_4(OH)_2]$ *trans*-$K_2[OsO_2(OMe)_4]$, *or* trans-$K_2[OsO_2(OH)_4]$. A solution containing the catechol (0.54 mmol) in water (10 cm³) was added slowly to a stirred solution of any of the above salts (0.27 mmol) in water (10 cm³); methanol or acetone was added for water-insoluble catechols. The resulting deep red solution was allowed to stand for 1 h and filtered into a stirred solution of tetraphenylphosphonium chloride (0.3 g) in water (10 cm³). The solid salt was filtered off and recrystallised from a methylene chloride–n-hexane mixture where possible. The *catena*-μ-oxo-bis(catecholato)osmium(VI) species often result if the above sequence of operations is not followed.

Method (2): *from* OsO_4. The preparation of the catechol complex is typical. To a solution of OsO_4 (0.05 g, 0.19 mmol) in acetone (1 cm³) was added an aqueous solution of a sodium phosphate buffer (0.1 mol dm⁻³, pH 6.8, 5 cm³) or sodium dimethylarsenate buffer (0.1 mol dm⁻³, pH 6.8, 10 cm³) and the mixture added to a solution of catechol (0.043 g, 0.39 mmol) in water (5 cm³). The resulting red solution was filtered into a solution of $[PPh_4]Cl$ as above.

The salt *trans*-$K_2[OsO_2(O_2C_6H_3Me\text{-}4)_2]$ was made by method (1) using just enough water to dissolve the reactants, and filtering off the resulting solid.

(*c*) catena-μ-*Oxo-bis*(*catecholato*)*osmium*(VI) *complexes*. *Method* (1). The preparation of the 4-methylcatechol complex is typical. To a solution of 4-methylcatechol (0.048 g, 0.4 mmol) in acetone (2 cm³) was added OsO_4 (0.05 g, 0.2 mmol) in acetone (2 cm³) followed by several drops of water, whereupon the solution became deep blue. The mixture was allowed to stand overnight, and the solid was filtered off, washed with acetone, and dried *in vacuo*.

Method (2). A red solution of the *trans*-$[OsO_2(O_2R)_2]^{2-}$ species prepared as already described was filtered into stirred aqueous hydrochloric acid (20 cm³ of water containing *ca.* 8 drops of concentrated HCl). The deep blue precipitate was filtered off, washed with acetone, and dried.

The bis[dihydroxy(4-methylcatecholato)osmium(VI)] complex was made from a solution of $K_2[OsO_2(O_2C_6H_3Me_2)]$ in water to which one drop of concentrated HCl had been added. The blue precipitate was filtered off and dried *in vacuo* (Found: C, 35.7; H, 3.1. $C_{14}H_{14}O_6Os$ requires C, 35.9; H, 3.0%). The i.r. spectrum of the solution in acetone includes bands at 3 500 (O–H str.), 1 100 [ν(C–O)], and 540 and 475 cm⁻¹ [ν(Os–O)].

(*d*) trans-*Catecholatodioxobis*(*pyridine*)*osmium*(VI) *complexes*, $[OsO_2(O_2R)(py)_2]$. Osmium tetraoxide (0.1 g, 0.4 mmol) in methylene dichloride (5 cm³) was added to a solution of the pyridine (0.8 mmol), and the mixture was degassed, sealed under argon, and allowed to stand for 10 min. To this yellow solution was added the catechol (0.4 mmol) in methylene dichloride (10 cm³) (acetone was used for catechols insoluble in CH_2Cl_2). The resulting brown solution was allowed to stand. If the complex had not precipitated within 1 h, n-hexane was added and the solid was filtered off and dried *in vacuo*.

trans-(4-*Methyldaphnetinato*)*dioxobis*(4-*t-butylpyridine*)-*osmium*(VI) was obtained as a brown precipitate by the above procedure, 4-t-butylpyridine replacing pyridine. The i.r. spectrum (KBr disc) included bands at 1 720 [ν(C=O)], 1 020 (py), 1 065 [ν(C–O)], and 845 cm⁻¹ [$\nu_{asym}(OsO_2)$]. The ^1H n.m.r. spectra in $CDCl_3$ had peaks at δ 1.32 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 5.99 (s, 1 H, C=CH), 6.94 (s, 2 H, aromatics), 7.28—7.62 (m, 4 H, py β), and 8.60—8.80 (m, 4 H, py β).

trans-(4-*Methylesculetinato*)*dioxobis*(4-*t-butylpyridine*)-*osmium*(VI) was made in analogous fashion. The i.r. spectrum (KBr disc) included bands at 1 800 [ν(C=O)], 1 020 (py), 845 [$\delta_{asym}(OsO_2)$] and 332 [$\delta(OsO_2)$]. The ^1H n.m.r. spectrum in $CDCl_3$ had peaks at δ 1.37 (s, 9 H, CH_3), 2.13 (s, 3 H, CH_3), 5.90—6.10 (m, 1 H, C=CH), 6.79 and 7.06 (2 s, 2 H, aromatics), 7.32—7.75 (m, 4 H, py β) and 8.42—8.90 (m, 4 H, py α).

Analytical data were obtained by the Microanalytical Department, Imperial College; oxygen analyses were from F. 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 on KBr discs or Nujol mulls

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between caesium iodide plates, and in chloroform or methylene dichloride using KBr cells. Raman spectra were obtained on a Spex Ramalog 5 instrument with a DPC-2 detector using a krypton-ion laser (6 471 Å excitation); solids were scanned as 5% sample—95% KBr spun discs. Hydrogen-1 n.m.r. spectra were recorded on a 60-mHz Perkin-Elmer R-12 spectrometer, ^{13}C spectra on an XL 100-12 instrument. Mass spectra were obtained on a VG-7070 instrument. Polarographic measurements were made on a Beckman Electroscan 30 instrument using a dropping mercury electrode. Magnetic-susceptibility measurements were made on a Gouy balance for solids and using the Evans method [29] for solutions.

We thank Johnson, Matthey Ltd. for loans of OsO_4, the S.R.C. for the award ot a postdoctoral research assistantship (to A. J. N.), and Dr. A. F. Masters for help and advice with the polarographic measurements.

[29] D. F. Evans, *J. Chem. Soc.*, 1959 2003.

[7/2287 *Received*, 29*th December*, 1977]