Osmium-(V), -(IV) and -(III) Complexes with Tetradentate Dianionic Chelating Ligands[†]

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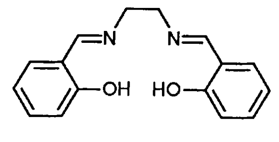
Osmium-(III) and -(IV) complexes of the ligands salen [H_2salen = ethylenebis(salicylidineimine)], bpb [H_2bpb = 1,2-bis(pyridine-2-carboxamido)benzene] and bpc [H_2bpc = 4,5-dichloro-1,2-bis(pyridine-2-carboxamido)benzene] were synthesised by reducing the corresponding *trans*-dioxoosmium(VI) complexes with PPh_3. The structure of [Os^{IV}(salen)(OPr^i)$_2$] has been determined by X-ray crystallography: monoclinic, space group *C*2/*c* (no. 15), *a* = 15.367(2), *b* = 7.847(1), *c* = 17.999(2) Å, β = 95.36(1)° and *Z* = 4. Electrochemical studies of *trans*-dialkoxyoosmium(IV) complexes in acetonitrile showed a reversible oxidation wave assignable to the oxidation of Os^{IV} to Os^{V}. Some *trans*-dialkoxyoosmium(V) complexes were characterised by UV/VIS spectroscopy. The osmium(III) complexes of salen, bpb and bpc were found to catalyse the oxidation of alkenes by iodosylbenzene.

As part of our program to study high-valent ruthenium and osmium complexes, we have been investigating the co-ordination chemistry of multianionic chelating ligands which are known to stabilise metal ions in high oxidation states.[1-3] In this context, Schiff base and amide ligands are of interest because their metal complexes function similarly to porphyrin analogues in catalysing organic oxidation reactions.[2b,c,4] Moreover, these ligands are relatively inexpensive and easily synthesised. Modification of them by adding different substituents allows variation of the chemical reactivities of the metal complexes. Herein is described the synthesis, characterisation and reactivities of osmium complexes with the dianionic ligands salen [H_2salen = ethylenebis(salicylideneimine), bpb [H_2bpb = 1,2-bis(pyridine-2-carboxamido)benzene and bpc [H_2bpc = 4,5-dichloro-1,2-bis(pyridine-2-carboxamido)benzene]. Part of this work has been communicated previously.[2c,5]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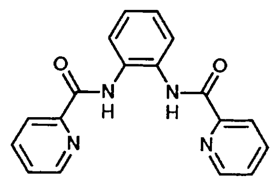
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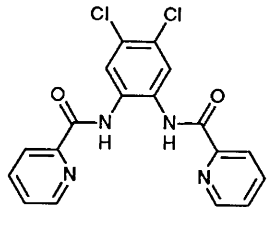
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Experimental

Synthesis of the Osmium Complexes.—Osmium tetraoxide was purchased from Johnson Matthey; $K_2[OsO_2(OH)_4]$ was prepared as described in the literature.[6] All reagents used were analytical grade. The ligands H_2salen, H_2bpb and H_2bpc were prepared by literature methods.[7,8] The complexes [Os^{VI}(salen)O_2], [Os^{IV}(salen)(OR)$_2$] (R = Me, Et or Pr^i) and [Os^{IV}(salen)(SPh)$_2$] were prepared as described previously.[5]

[Os^{III}(salen)(PPh_3)$_2$][CF_3CO_2]. A mixture of [Os^{VI}(salen)O_2] (0.5 g) and triphenylphosphine (1.4 g) in tetrahydrofuran–trifluoroacetic acid (3:1, 150 cm^3) was heated at 60 °C for 15 min. A deep green solution was formed. The reaction mixture was evaporated to dryness, and the residue purified on a silica gel column with methanol as eluent. A dark green microcrystalline solid of [Os^{III}(salen)(PPh_3)$_2$][CF_3CO_2] was obtained by vapour diffusion of diethyl ether into a dichloromethane solution of the crude product. Yield 60% (Found: C, 57.4; H, 4.4; N, 2.7. Calc. for $C_{54}H_{44}F_3N_2O_4OsP_2$: C, 57.5; H, 4.1; N, 2.4%); μ_{eff} = 2.17.

[Os^{VI}(H_2bpb)O_2]Cl_2. A mixture of $K_2[Os^{VI}O_2(OH)_4]$ (0.5 g) and H_2bpb (0.45 g) was stirred in methanol (150 cm^3) for 20 min. Hydrochloric acid was added dropwise until a yellowish green precipitate of [Os^{VI}(H_2bpb)O_2]Cl_2 was formed. The product was filtered off, washed with methanol–diethyl ether and dried in vacuum. Yield 85% (Found: C, 35.6; H, 2.7; N, 9.2. Calc. for $C_{18}H_{14}Cl_2N_4O_4Os$: C, 35.4; H, 2.3; N, 9.0%): μ_{eff} 0; $\nu_{asym}(OsO_2)$ 850, ν(N–H) 3170 and 3320 cm^{-1}.

[Os^{VI}(bpb)O_2]. A mixture of H_2bpb (0.45 g) and triethylamine (0.5 cm^3) in methanol (150 cm^3) was stirred at 30 °C for 20 min. The salt $K_2[OsO_2(OH)_4]$ (0.5 g) was added and the reaction mixture stirred for 15 min. The resulting reddish purple solution was filtered and the filtrate evaporated to 3 cm^3. A reddish purple solid of [Os^{VI}(bpb)O_2] was precipitated by addition of diethyl ether. The crude product was filtered off, washed with methanol–diethyl ether (1:10) and dried under vacuum. Yield 70% (Found: C, 39.4; H, 2.9; N, 10.0. Calc. for $C_{18}H_{12}N_4O_4Os$: C, 40.1; H, 2.2; N, 10.4%); μ_{eff} 0; $\nu_{asym}(OsO_2)$ 850 cm^{-1}.

[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Positional parameters for non-hydrogen atoms in $[\mathrm{Os(salen)(OPr^i)_2}]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Os	0.000	−0.091 54(2)	0.250
O(1)	0.122 1(2)	−0.085 0(3)	0.284 4(2)
O(2)	−0.023 6(2)	−0.273 4(3)	0.325 2(1)
N(1)	−0.020 3(2)	0.100 5(3)	0.318 9(2)
C(1)	−0.059 0(2)	−0.239 1(4)	0.387 7(2)
C(2)	−0.083 0(4)	−0.379 1(5)	0.430 9(3)
C(3)	−0.121 6(3)	−0.359 3(7)	0.496 0(3)
C(4)	−0.139 7(3)	−0.198 2(6)	0.521 9(2)
C(5)	−0.116 4(3)	−0.060 4(6)	0.482 7(2)
C(6)	−0.076 1(2)	−0.075 6(4)	0.415 1(2)
C(7)	−0.052 4(3)	0.083 9(4)	0.382 5(2)
C(8)	0.007 8(3)	0.266 7(4)	0.292 3(2)
C(9)	0.174 6(2)	−0.234 8(4)	0.295 7(2)
C(10)	0.200 0(3)	−0.255 5(6)	0.378 0(3)
C(11)	0.252 8(3)	−0.216 0(8)	0.251 6(3)

Table 2 Selected bond distances (Å) and angles (°) for $[\mathrm{Os(salen)(OPr^i)_2}]$ with e.s.d.s in parentheses

Os–O(1)	1.920(3)	N(1)–C(8)	1.468(4)
Os–O(2)	2.023(2)	C(8)–C(8)*	1.518(6)
Os–N(1)	1.995(3)	O(1)–C(9)	1.430(4)
O(1)–Os–O(1)*	176.93(8)	O(2)–Os–N(1)	94.0(2)
O(1)–Os–O(2)	91.9(1)	O(2)–Os–N(1)*	175.8(2)
O(1)–Os–O(2)*	90.2(1)	N(1)–Os–N(1)*	81.9(1)
O(1)–Os–N(1)	89.1(2)	O(2)–Os–O(2)*	90.24(9)
O(1)–Os–N(1)*	88.6(2)	Os–O(1)–C(9)	123.1(2)

* Symmetry code: $-x, y, \frac{1}{2} - z$.

$[\mathrm{Os^{VI}(H_2bpc)O_2]Cl_2}$. This was prepared as described for $[\mathrm{Os^{VI}(H_2bpb)O_2]Cl_2}$ except the ligand $\mathrm{H_2bpc}$ was used. Yield 55% (Found: C, 32.0; H, 2.2; N, 8.7. Calc. for $\mathrm{C_{18}H_{10}Cl_4N_4O_4Os}$: C, 31.8; H, 1.8; N, 8.2%); μ_{eff} 0; $\nu_{\mathrm{asym}}(\mathrm{OsO_2})$ 850 $\mathrm{cm^{-1}}$.

$[\mathrm{Os^{VI}(bpc)O_2}]$. This was prepared as described for $[\mathrm{Os^{VI}(bpb)O_2}]$ except that the ligand $\mathrm{H_2bpc}$ was used. Yield 65% (Found: C, 36.0; H, 1.9; N, 9.5. Calc. for $\mathrm{C_{18}H_{10}Cl_2N_4O_4Os}$: C, 35.6; H, 1.7; N, 9.2%); μ_{eff} 0; $\nu_{\mathrm{asym}}(\mathrm{OsO_2})$ 850 $\mathrm{cm^{-1}}$.

$[\mathrm{Os^{IV}(bpb)(OMe)_2}]$. A mixture of $[\mathrm{Os^{VI}(bpb)O_2}]$ (0.5 g) and $\mathrm{PPh_3}$ (1.0 g) was heated with stirring in methanol (25 $\mathrm{cm^3}$) at 50 °C for 25 min. The reddish brown solution obtained was filtered and the filtrate evaporated to dryness. The residue was dissolved in dichloromethane and purified on an alumina column. Triphenylphosphine was removed by eluting with $\mathrm{CH_2Cl_2}$ (300 $\mathrm{cm^3}$) and the osmium(IV) product was eluted as a brick-red band by dichloromethane–acetone (1:3 v/v). The crude product was recrystallised by vapour diffusion of hexane into dichloromethane. Yield 45% (Found: C, 42.4; H, 3.4; N, 10.2. Calc. for $\mathrm{C_{20}H_{18}N_4O_4Os}$: C, 42.3, H, 3.2; N, 9.9%).

$[\mathrm{Os^{IV}(bpb)(OEt)_2}]$. This complex was similarly prepared from $[\mathrm{Os^{VI}(bpb)O_2}]$ and ethanol. Yield 45% (Found: C, 44.2; H, 4.0; N, 9.4. Calc. for $\mathrm{C_{22}H_{22}N_4O_4Os}$: C, 44.3; H, 3.7; N, 9.4%).

$[\mathrm{Os^{IV}(bpb)(OPr^i)_2}]$. This complex was similarly prepared from $[\mathrm{Os^{VI}(bpb)O_2}]$ and propan-2-ol. Yield 42% (Found: C, 46.0; H, 4.0; N, 8.7. Calc. for $\mathrm{C_{24}H_{26}N_4O_4Os}$: C, 46.1; H, 4.2; N, 9.0%).

$[\mathrm{Os^{III}(bpb)Cl(PPh_3)}]$. A mixture of $[\mathrm{Os^{VI}(H_2bpb)O_2]Cl_2}$ (0.5 g) and $\mathrm{PPh_3}$ (1.0 g) in acetonitrile (30 $\mathrm{cm^3}$) was heated with stirring at 50 °C for 20 min. The deep green solution obtained was filtered and the filtrate evaporated to dryness. The residue was dissolved in dichloromethane and purified by column chromatography (silica gel). Triphenylphosphine was removed by eluting with $\mathrm{CH_2Cl_2}$ (300 $\mathrm{cm^3}$) and the osmium complex was eluted as a dark green band by dichloromethane–acetone (1:3 v/v). The crude product was recrystallised by vapour diffusion of diethyl ether into acetonitrile. Yield 50% (Found: C, 53.2; H, 3.4; N, 7.1. Calc. for $\mathrm{C_{36}H_{27}ClN_4O_2OsP}$: C, 53.7; H, 3.4; N, 7.0%); $\mu_{\mathrm{eff}} = 1.90$. The structure of this complex has been determined by X-ray crystallography.[2c]

$[\mathrm{Os^{III}(bpb)(PPh_3)(CF_3CO_2)}]$. A mixture of $[\mathrm{Os^{VI}(bpb)O_2}]$ (0.5 g) and $\mathrm{PPh_3}$ (1.0 g) in tetrahydrofuran–trifluoroacetic acid (3:1, 150 $\mathrm{cm^3}$) was heated at 60 °C for 15 min. A deep green solution was formed. The reaction mixture was boiled to remove the solvent and the residue dissolved in $\mathrm{CH_2Cl_2}$ and purified on a silica gel column. Triphenylphosphine was removed by eluting with $\mathrm{CH_2Cl_2}$ and the product was eluted as a green band by dichloromethane–acetone (4:1 v/v). The crude product was recrystallised by vapour diffusion of diethyl ether into a dichloromethane solution of the complex. Yield 45% (Found: C, 50.3; H, 3.0; N, 5.6. Calc. for $\mathrm{C_{38}H_{27}F_3N_4O_4OsP}$: C, 50.6; H, 3.4; N, 5.8%); $\mu_{\mathrm{eff}} = 2.0$.

$[\mathrm{Os^{IV}(bpc)(OMe)_2}]$. This was prepared from $[\mathrm{Os^{VI}(bpc)O_2}]$ in a similar manner as that used for $[\mathrm{Os^{IV}(bpb)(OMe)_2}]$. Yield 40% (Found: C, 38.0; H, 2.7; N, 9.0. Calc. for $\mathrm{C_{20}H_{16}Cl_2N_4O_4Os}$: C, 37.7; H, 2.5; N, 8.8%).

$[\mathrm{Os^{III}(bpc)Cl(PPh_3)}]$. This was prepared from $[\mathrm{Os^{VI}(H_2bpc)O_2]Cl_2}$ as described for $[\mathrm{Os^{III}(bpb)Cl(PPh_3)}]$. Yield 40% (Found: C, 49.9; H, 3.4; N, 6.7. Calc. for $\mathrm{C_{36}H_{25}Cl_3N_4O_2OsP}$: C, 49.5; H, 2.9; N, 6.4%).

Crystal Structure Determination of $[\mathrm{Os(salen)(OPr^i)_2}]$.—*Crystal data.* $M = 574.68$, monoclinic, space group $C2/c$ (no. 15), $a = 15.367(2)$, $b = 7.847(1)$, $c = 17.999(2)$ Å, $\beta = 95.36(1)°$, $U = 2160.9$ Å^3, $Z = 4$, $D_c = 1.766$ g cm^{-3}, μ(Mo-Kα) = 59.4 cm^{-1}, crystal size 0.16 × 0.21 × 0.42 mm, $F(000) = 1128$.

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710$ 73 Å). Intensity data were collected by the ω–2θ scan technique in the range $2 \leqslant 2\theta \leqslant 52°$. They were corrected for Lorentz, polarisation and absorption effects. The empirical absorption correction was based on azimuthal (ψ) scans of seven reflections with $80 < \chi < 90°$. A total of 3558 reflections were measured of which 2287 were independent and 2004 reflections having $I > 1.5\sigma(I)$ were considered observed. Atomic scattering factors were taken from ref. 9. All calculations were performed on a MicroVax II computer using the Enraf-Nonius SDP programs.[10]

The position of the osmium atom was determined from a Patterson function and the rest of the non-hydrogen atoms were obtained from subsequent Fourier maps. The osmium atom is located on a crystallographic two-fold axis which passes through the osmium atom and the midpoint of the C–C bond in the ethylene bridge of the salen ligand so that half a molecule occupies an asymmetric unit. The methyl hydrogen atoms were located from a difference map at a later stage and all other hydrogen atoms were included at calculated positions. The refinement was by full-matrix least squares and the quantity minimised was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$. During the final least-squares cycles 132 parameters were adjusted: atomic coordinates and anisotropic thermal parameters of all the non-hydrogen atoms and a scale factor. The hydrogen-atom parameters were not refined. The final $R = 0.022$, $R' = 0.026$ and $S = [\Sigma w(|F_o| - |F_c|)^2/(m - p)]^{\frac{1}{2}} = 1.03$, where m is the number of observed reflections and p the parameters refined. In the final difference map, apart from a peak of 3.35 e Å^{-3} at 2.38 Å from the osmium atom, the residual electron density varied from −0.48 to +0.40 e Å^{-3}. The peak which was located on the two-fold axis passing through the osmium atom might be the result of an imperfect absorption correction. Fractional atomic coordinates are given in Table 1, and selected bond distances and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom parameters, thermal parameters and remaining bond lengths and angles.

Catalytic Oxidation of Alkenes with Iodosylbenzene.—Nor-

Table 3 Summary of electronic spectral data for the osmium-(III) and -(IV) complexes

Complex	λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})
$[Os^{IV}(salen)(OMe)_2]$	540 (1600), 492 (3700), 413 (10 500), 352 (9900), 252 (8200)
$[Os^{IV}(salen)(OEt)_2]$	542 (1700), 490 (3800), 410 (17 700), 350 (15 500), 255 (15 100)
$[Os^{IV}(salen)(OPr^i)_2]$	540 (1700), 495 (3800), 417 (15 400), 355 (13 400), 260 (19 800)
$[Os^{IV}(salen)(SPh)_2]$	705 (13 300), 625 (11 500), 400 (10 300), 353 (19 100)
$[Os^{III}(salen)(PPh_3)_2][CF_3CO_2]$	600 (5600), 382 (35 500), 355 (29 500), 320 (20 400), 250 (55 000), 230 (85 100)
$[Os^{IV}(bpb)(OMe)_2]$	510 (5400), 380 (12 000), 345 (16 200), 290 (15 000), 262 (30 500), 228 (26 100)
$[Os^{IV}(bpb)(OEt)_2]$	512 (7000), 390 (15 500), 348 (23 900), 290 (20 500), 260 (40 400), 228 (35 100)
$[Os^{IV}(bpb)(OPr^i)_2]$	510 (7200), 390 (16 300), 345 (25 300), 285 (30 200), 263 (42 100), 228 (38 900)
$[Os^{IV}(bpc)(OMe)_2]$	510 (5500), 385 (12 500), 340 (16 500), 285 (16 000), 260 (31 500), 225 (27 000)
$[Os^{III}(bpc)Cl(PPh_3)]$	610 (4500), 415 (15 700), 320 (19 900), 260 (37 300), 212 (69 900)
$[Os^{III}(bpb)(PPh_3)(CF_3CO_2)]$	655 (5000), 425 (17 400), 330 (23 300), 300 (25 800), 260 (48 700)
$[Os^{III}(bpc)Cl(PPh_3)]$	620 (4700), 420 (16 500), 325 (19 000), 255 (38 500), 220 (70 000)

Table 4 Summary of ^1H NMR spectral data for the osmium(IV) complexes

	Chemical shift (δ)				
Complex	Aromatic	Azomethine	Ethylene bridge	Benzene bridge	Axial ligands
$[Os(salen)(OMe)_2]$	6.60–8.10 (m)	6.24 (s)	2.86 (s)		8.95 (s)
$[Os(salen)(OEt)_2]$	6.55–8.06 (m)	6.18 (s)	2.90 (s)		9.80 (q) −0.13 (t)
$[Os(salen)(OPr^i)_2]$	6.54–8.05 (m)	6.13 (s)	2.95 (s)		0.08 (s) 4.92 (spt)
$[Os(salen)(SPh)_2]$	5.78–8.26 (m)	12.0 (s)	2.80 (s)		br
$[Os(bpb)(OMe)_2]$	8.55–9.56 (m)			6.54–7.18 (m)	12.14 (s)
$[Os(bpb)(OEt)_2]$	8.50–9.57 (m)			6.67–7.17 (m)	14.53 (q) −0.39 (t)
$[Os(bpb)(OPr^i)_2]$	8.50–9.76 (m)			6.33–7.26 (m)	0.06 (d) 10.76 (spt)

Abbreviations: s = singlet; q = quartet; d = doublet; spt = septet; m = multiplet; br = broad.

bornylene (bicyclo[2.2.1]hept-2-ene) was purified by sublimation. The *cis-* and *trans*-stilbenes were purified by passage through a column of active alumina. Iodosylbenzene was prepared by hydrolysis of iodosylbenzene diacetate in NaOH solution. All other chemicals were of reagent grade used as received.

Catalytic reactions of osmium(III) complexes with organic substrates were performed by stirring iodosylbenzene (200 mg), organic substrate (200–500 mg) and the osmium catalyst (3 mg) in dichloromethane (2 cm^3). After 4–5 h when the reaction mixture had become a clear solution the organic products were analysed by gas chromatography–mass spectrometry; *trans-* and *cis*-stilbene oxide were analysed by NMR spectroscopy.

Instrumentation.—Electronic spectra were recorded on a Shimadzu UV-240 spectrophotometer, NMR spectra on a JEOL FX 90Q spectrometer (90 MHz). Chemical shifts were reported relative to tetramethylsilane. The magnetic susceptibility of the osmium complexes was determined by the Evans method. Cyclic voltammetry was performed with Princeton Applied Research instrumentation and a X-Y recorder. Gas chromatography was performed with a Varian 940 chromatograph with a 6 ft (*ca.* 1.8 m) 10% Carbowax 20M on Chromosorb W column. Elemental analyses were by the Microanalytical Unit of the Australian Mineral Development Laboratory.

Results and Discussion

Synthesis and Characterization of the Osmium Complexes.—The osmium(IV) complexes were easily prepared by PPh_3 reduction of *trans*-dioxoosmium(VI) in the presence of ROH or RSH. In a non-alcoholic medium similar reactions gave osmium(III) as the final products. For example, $[Os^{III}(salen)(PPh_3)_2][CF_3CO_2]$ and $[Os^{III}(bpb)(PPh_3)(CF_3CO_2)]$ were obtained by reduction of the corresponding *trans*-dioxoosmium(VI) complexes in tetrahydrofuran–trifluoroacetic acid (3:1).

The electronic spectra of the osmium(IV) complexes exhibit intense ligand-to-metal charge-transfer bands. Table 3 summarises the UV/VIS spectral data. The electronic spectra of the $[Os^{IV}(salen)(OR)_2]$ (R = Me, Et or Pr^i) complexes are very similar to each other as expected because the absorptions in the visible region should be dominated by the $p_\pi(OR) \longrightarrow d_\pi(Os)$ charge-transfer transition. The $[Os^{IV}(bpb)(OR)_2]$ system, is similar.

The osmium(IV) complexes gave well resolved NMR spectra and the data are summarised in Table 4. The bridging ethylene protons and the azomethine protons of $[Os^{IV}(salen)(OR)_2]$ are all equivalent and appear as singlets at δ 2.86–2.95 and δ 6.13–6.24 respectively. The observed downfield shift of the azomethine protons of $[Os^{IV}(salen)(SPh)_2]$ (δ 12.0) relative to $[Os^{IV}(salen)(OR)_2]$ is attributed to the larger shielding effect of the thiophenoxy group.

The proton signals for the alkoxy ligands of the Os^{IV}–bpb complexes are shifted downfield compared to those of the Os^{IV}-salen system. This is due to the larger shielding effect of the benzene bridge of bpb over the ethylene bridge of salen.

The magnetic moment of $[Os^{IV}(salen)(OMe)_2]$ was found to be 1.33, essentially independent of temperature from 263 to 303 K. This value is similar to that of 1.11 reported for $[Os^{IV}(oep)(OMe)_2]$ (H_2oep = 2,3,7,8,12,13,17,18-octaethylporphyrin)[11] but is significantly lower than those of 2.27 and 2.31 for $[Os^{IV}(tpp)(OMe)_2]$ and $[Os^{IV}(tpp)(OEt)_2]$ respectively (H_2tpp = 5,10,15,20-tetraphenylporphyrin).[12] For the dialkoxoosmium(IV) system a spin-only μ_{eff} of 2.83 is expected if the RO–Os–OR axis is linear. This is because if O–Os–O is taken to be the z axis, the d_{xz} and d_{yz} orbitals are destabilised relative to d_{xy} as a result of $p_\pi(O)$ and $d_{\pi^*}(Os^{IV})$ bonding interaction [$d_{\pi^*} = d_{xz},d_{yz}$] and hence a triplet ground state with the $(d_{xy})^2(d_{xz})^1(d_{yz})^1$ electronic configuration is expected. Antipas *et al.*[12] attributed the low μ_{eff} of $[Os^{IV}(oep)(OMe)_2]$ to

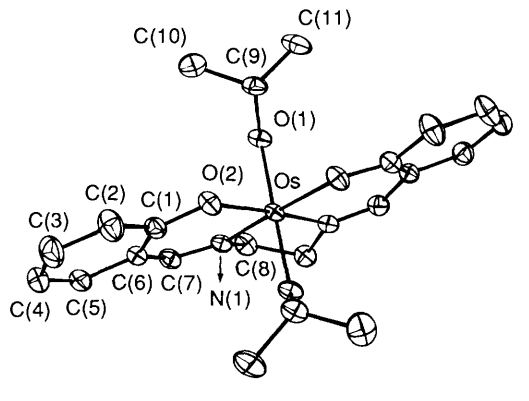

Fig. 1 An ORTEP[13] plot of [Os^{IV}(salen)(OPr^i)$_2$]

Table 5 Summary of E° for some osmium(III) and ruthenium(III) complexes in acetonitrile with 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate as supporting electrolyte. Working electrode, glassy carbon

Complex[a]	$E^{\circ b}$/V M^{IV}–M^{III}	 M^{III}–M^{II}
[Os(salen)(PPh_3)$_2$][CF_3CO_2]	0.40	−0.85
[Os(bpb)Cl(PPh_3)]	0.08	−1.05 (i)
[Os(bpb)(PPh_3)(CF_3CO_2)]	0.21	−0.73 (i)
[Os(bpc)Cl(PPh_3)]	0.26	−0.77 (i)
[Ru(salen)(PPh_3)(py)][ClO_4]	0.70	−0.53
[Ru(salen)Cl(PPh_3)]	0.39	−0.62

[a] py = Pyridine. [b] *vs.* ferrocenium–ferrocene; i = irreversible wave.

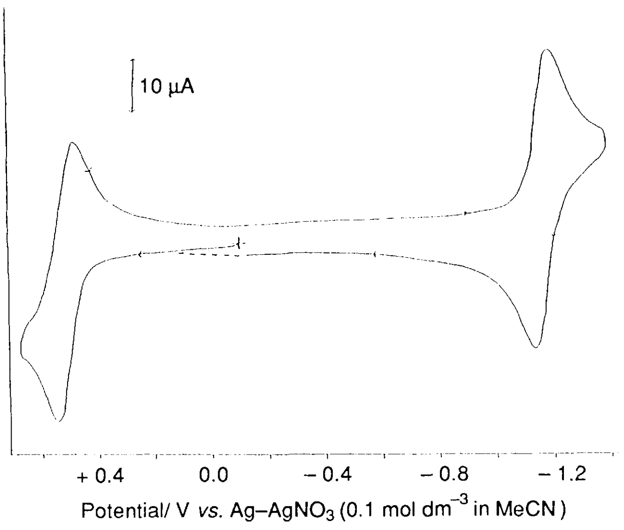

Fig. 2 Cyclic voltammogram of 1 mmol dm^{-3} [Os^{IV}(salen)(OMe)$_2$] in acetonitrile with 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate as supporting electrolyte. Scan rate: 100 mV s^{-1}. Working electrode, glassy carbon

a low-energy triplet excited state due to the bending of the CH_3O–Os–OCH_3 axis. However, the X-ray structure determination of [Os^{IV}(salen)(OPr^i)$_2$] described later indicates that the $(CH_3)_2CHO$–Os–$OCH(CH_3)_2$ moiety is essentially linear with a O–Os–O bond angle of 176.93(8)°. The reason(s) for the difference in the μ_{eff} values of [Os^{IV}(salen)(OMe)$_2$], [Os^{IV}(oep)(OMe)$_2$] and [Os^{IV}(tpp)(OMe)$_2$] remains uncertain. The μ_{eff} values of the Os^{III}–bpb complexes are slightly higher than the spin-only value of 1.73 for one unpaired electron.

Table 6 Summary of E° for some osmium(IV) complexes in acetonitrile with 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate as supporting electrolyte. Working electrode, glassy carbon

Complex	E°*/V Os^V–Os^{IV}	 Os^{IV}–Os^{III}
[Os(salen)(OMe)$_2$]	0.50	−1.19
[Os(salen)(OEt)$_2$]	0.46	−1.23
[Os(salen)(OPr^i)$_2$]	0.36	−1.31
[Os(bpb)(OMe)$_2$]	0.39	−1.08
[Os(bpb)(OEt)$_2$]	0.31	−1.15
[Os(bpb)(OPr^i)$_2$]	0.24	−1.23
[Os(salen)(SPh)$_2$]	0.33 (i)	−0.78
[Os(bpc)(OMe)$_2$]	0.57	−0.88

* *vs.* ferrocenium–ferrocene; i = irreversible wave.

X-Ray Crystal Structure of [Os^{IV}(salen)(OPr^i)$_2$].—A perspective view of [Os^{IV}(salen)(OPr^i)$_2$] is shown in Fig. 1. The structure constitutes the first reported example of a bis(dialkoxo)osmium(IV) complex. The co-ordination geometry of osmium is octahedral and the ethylene bridge of the salen ligand is in the *gauche* conformation. The most important structural features are the linearity of the $(CH_3)_2CHO$–Os–$OCH(CH_3)_2$ group [O–Os–O 176.93(8)°] and the short Os–O[$OCH(CH_3)_2$] distance of 1.920(3) Å. The latter bond distance is even shorter than that of 1.997(29) Å for Os–O(OCH_3) in [Os_2O(oep)$_2$(OMe)$_2$][14] indicating significant d_π(Os) and p_π[$OCH(CH_3)_2$] interaction. The co-ordination geometry of the salen ligand is normal.[5]

Electrochemistry.—In acetonitrile the osmium(III) complexes exhibit a reversible Os^{IV}–Os^{III} couple. The E° values are listed in Table 5. The fact that E° for this couple for [Os^{III}(bpb)Cl(PPh_3)] is higher than that for [Os^{III}(bpb)(PPh_3)(CF_3CO_2)] is in accordance with the stronger σ-donor strength of Cl over CF_3CO_2. Table 5 also shows that E° for [Ru^{III}(salen)Cl(PPh_3)] is 310 mV more anodic than that for the isoelectronic osmium(III) analogues, as expected for a metal-centred oxidation. The cyclic voltammogram of [Os^{III}(salen)(PPh_3)$_2$][CF_3CO_2] shows a reversible reduction at −0.85 V *vs.* ferrocenium–ferrocene assignable to the reduction of Os^{III} to Os^{II}; the salen ligand is electroinactive at this potential. In contrast, the electrochemical reduction of the Os^{III}–bpb and -bpc complexes is irreversible.

The cyclic voltammograms of the *trans*-dialkoxoosmium(IV) complexes in acetonitrile show a reversible reduction wave corresponding to the reduction of Os^{IV} to Os^{III}. However, the most interesting feature is the presence of a reversible oxidation wave assignable to the oxidation of Os^{IV} to Os^V. Fig. 2 shows the cyclic voltammetry of [Os^{IV}(salen)(OMe)$_2$]. The peak-to-peak separation of the Os^V–Os^{IV} couple is 60–65 mV at scan rate of 100 mV s^{-1}. Constant-potential coulometry showed that n = 1.0 for this couple. Rotating-disc voltammetry showed a linear Levich plot of plateau current *vs.* (rotation speed)$^{\frac{1}{2}}$ suggesting the electrochemical oxidation is a simple electron transfer without a preceding chemical step. The Os^V–Os^{IV} couple is reversible with a cathodic to anodic current ratio (i_{pc}/i_{pa}) = 1:1 at scan rates > 50 mV s^{-1}. At lower scan rates the couple becomes less reversible (at 20 mV s^{-1}, i_{pa} = 0.8:1). This indicates that the electrogenerated osmium(V) species is not very stable in acetonitrile. The E° values of the Os^V–Os^{IV} and Os^{IV}–Os^{III} couples are summarised in Table 6. The nature of the alkoxo ligands has been found to have little effect on the redox potential.

Spectroscopic Characterisation of the Osmium(V) Complexes.—The complex [Os^V(salen)(OMe)$_2$]$^+$ was generated chemically by the addition of 1 molar equivalent of

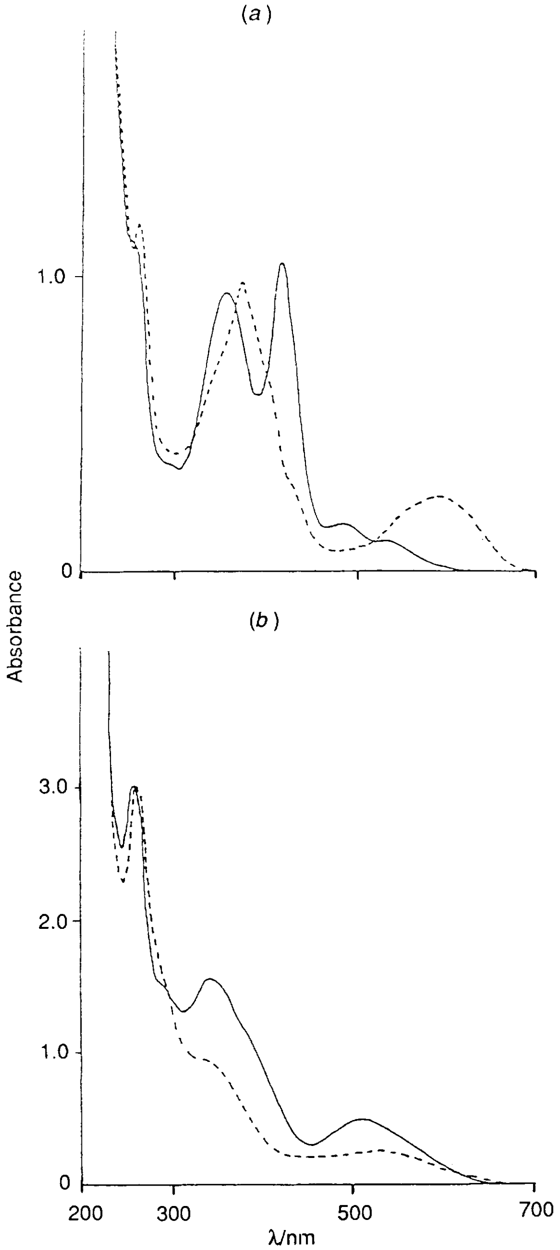

Fig. 3 UV/VIS spectra of (*a*) [Os^{IV}(salen)$(OMe)_2$] and (*b*) [Os^{IV}(bpb)$(OMe)_2$] in acetonitrile (——) and after addition of 1 mol equivalent of $[NH_4]_2[Ce(NO_3)_6]$ (- - -)

$[NH_4]_2[Ce(NO_3)_6]$ to a solution of [Os^{IV}(salen)$(OMe)_2$] in acetonitrile. The colour of the solution immediately changed from reddish purple to deep blue. Fig. 3(*a*) shows the UV/VIS spectral changes for the oxidation. The osmium(v) species could be reduced back to the starting osmium(iv) complex by $N_2H_4{\cdot}H_2O$ with over 90% recovery. The low-energy absorption band at 590 nm of [Os^V(salen)$(OMe)_2]^+$ can be assigned as the p_π (phenoxide) $\longrightarrow d_\pi$ (Os) charge-transfer transition. The complexes [Os^V(salen)$(OR)_2]^+$ are not very stable in acetonitrile solution at room temperature, the characteristic absorption at 590 nm slowly diminishing over 1 h. Our previous study on a *trans*-dioxoosmium(v) complex of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane indicated that it immediately disproportionated in the presence of acid.[15] In this work the UV/VIS spectrum of [Os^V(salen)$(OMe)_2]^+$ in the presence of a ten-fold excess of CF_3CO_2H has been measured and no immediately spectral change was observed. This indicates that the complex would not undergo rapid disproportionation in the presence of acid.

Attempts have also been made to generate [Os^V(salen)$(OMe)_2]^+$ by constant-potential electrochemical oxidation. The UV/VIS spectral changes of the electrochemical oxidation were followed but no isosbestic point was observed. Presumably the electrogenerated osmium(v) complex undergoes secondary reaction in acetonitrile on the time-scale for electrolysis. This is in accordance with the cyclic voltammetric studies where the Os^V–Os^{IV} couples becomes less reversible at slow scan rates.

Attempts have been made to isolate [Os^V(salen)$(OMe)_2]^+$ in solid form. Excess of ammonium cerium(iv) nitrate was added to a methanolic solution of [Os^{IV}(salen)$(OMe)_2$] in the presence of $LiClO_4$. The solution was evaporated to dryness under vacuum and deionised water was added. A blackish blue solid was obtained. Its IR spectrum showed absorption bands characteristic of the salen ligand as well as of the ClO_4 anion. However, this complex was unstable in MeCN or MeOH rendering purification difficult.

The [Os^V(bpb)$(OR)_2]^+$ complexes have also been characterised spectroscopically. Fig. 3(*b*) shows the UV/VIS spectrum of [Os^V(bpb)$(Me)_2]^+$ generated by cerium(iv) oxidation. Other [Os^V(salen)$(OR)_2]^+$ and [Os^V(bpb)$(OR)_2]^+$ complexes have been generated in acetonitrile and their electronic spectral data are summarised in Table 7.

Catalytic Oxidation of Alkenes with Iodosylbenzene.—Some studies were carried out to illustrate that the Os^{III}–salen and –bpb complexes are catalysts for the oxidation of alkenes by PhIO. The results are summarised in Table 8. No reaction was found in the absence of the osmium catalyst. For norbonylene, epoxidation occurs to give *exo*-norbornylene oxide. In the case of styrene, oxidative cleavage of the C=C bond to give benzaldehyde is the major reaction. Oxidative cleavage of the C=C bond also occurs in the reactions with *cis*- and *trans*-stilbenes.

The amount of epoxide and iodobenzene formed for the [Os^{III}(bpb)$(PPh_3)(CF_3CO_2)$]-catalysed oxidation of alkene was monitored by sampling at 20 min intervals. A plot of the amount of iodobenzene formed *vs.* time indicated an induction period of about 60 min during which insignificant quantity of oxidised organic products and iodobenzene were formed. The activity of the '[Os(bpb)Cl(PPh_3)] + PhIO' system ceased as all PhIO was consumed. This usually took about 2 h. Addition of more PhIO to the system replenished the activity instantaneously. The presence of an induction period was also observed in the '[Os^{III}(salen)$(PPh_3)_2]^+$ + PhIO' system.

Addition of PhIO to a dichloromethane solution of [Os^{III}(salen)$(PPh_3)_2]^+$ or [Os^{III}(bpb)$(PPh_3)(CF_3CO_2)$] resulted in no immediate change in the UV/VIS spectrum. However, the spectrum altered after the complex had been stirred with 1 equivalent of PhIO for 50 min. Attempts to characterise the oxidised osmium product were unsuccessful.

The effect of solvent on the catalytic system was studied. It was found that the time required for producing the same amount of epoxide in the oxidation of norbonylene decreases in the order pyridine (>24 h) > acetonitrile (≈ 6 h) > dichloromethane, acetone (≈ 4 h) which is the same as the order of co-ordinating strength. This suggests that better ligands such as pyridine could compete with PhIO for a co-ordinating site on the osmium complex.

Both M^V=O and M–O–I–Ph have been postulated as active intermediates in the metal-catalysed oxidation of alkenes by PhIO. In the present case it is difficult to assign unambiguously the active intermediate in the catalytic process.

Conclusion

The results clearly demonstrate the ability of the salen and bpb ligands to stabilise osmium in the +4 and +5 oxidation states. This can be attributed to the strong σ-donor strength of the phenoxide and N-co-ordinated organic amide groups. Since osmium complexes of chiral Schiff bases and amide ligands have

Table 7 Electronic spectral data for some osmium(V) complexes

Complex	λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})
$[Os(salen)(OMe)_2]^+$	590 (2500), 440 (2200), 390 (9800), 370 (12 000), 350 (7400), 260 (11 600)
$[Os(salen)(OEt)_2]^+$	605 (3900), 440 (3900), 395 (12 600), 372 (15 300), 350 (11 400), 260 (15 300)
$[Os(salen)(OPr^i)_2]^+$	600 (2800), 442 (2800), 395 (13 000), 375 (16 000), 350 (12 000), 260 (14 800)
$[Os(bpb)(OMe)_2]^+$	530 (2500), 343 (9800), 263 (31 500)
$[Os(bpb)(OEt)_2]^+$	535 (2700), 345 (12 400), 260 (33 200)
$[Os(bpb)(OPr^i)_2]^+$	535 (2650), 345 (11 000), 260 (32 000)

Table 8 Catalytic oxidation of alkenes by iodosylbenzene with osmium(III) catalysts

Catalyst	Substrate	Product[a] [yield[b] (%)]
$[Os(salen)(PPh_3)_2][CF_3CO_2]$	Norbornylene	*exo*-Norbornylene oxide [21]
	Styrene	Styrene oxide [4] Benzaldehyde [26]
	cis-Stilbene	*cis*-Stilbene oxide [1] *trans*-Stilbene oxide [2] Benzaldehyde [35]
	trans-Stilbene	*trans*-Stilbene oxide [2] Benzaldehyde [49]
$[Os^{III}(bpb)(PPh_3)(CF_3CO_2)]$	Norbornylene	*exo*-Norbornylene oxide [25]
	Styrene	Styrene oxide [6] Benzaldehyde [25]
	cis-Stilbene	*cis*-Stilbene oxide [2] *trans*-Stilbene oxide [6] Benzaldehyde [38]
	trans-Stilbene	*trans*-Stilbene oxide [5] Benzaldehyde [25]

[a] Reaction time 5 h. [b] Yields reported relative to the amount of iodobenzene formed.

recently been synthesised,[16] it is not difficult to envisage that these classes of complexes are potential catalysts for asymmetric alkene epoxidation.

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