Syntheses, Spectroscopy, and Electrochemistry of High-valent Osmium-(v) and -(vi) Oxo Complexes of Macrocyclic Tertiary Amine Ligands

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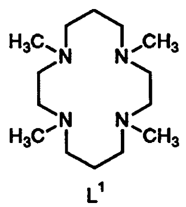
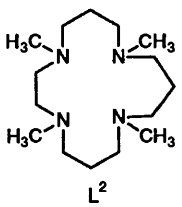
Osmium has been inserted into macrocyclic tertiary amine ligands [L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane, 1,4,8,12-tetramethyl-1,4,8,12-tetra-azacyclopentadecane, 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane, and *meso*-2,3,7,11,12-pentamethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene] to give *trans*-$[Os^{III}LCl_2]^+$, which could be oxidized to *trans*-$[Os^{VI}L(O)_2]^{2+}$ by H_2O_2. The *trans*-$[Os^{VI}L(O)_2]^{2+}$ complexes show one intense $\nu_{asym}(OsO_2)$ stretch at 870—880 cm^{-1}. Their u.v.–visible spectra display two vibronic structured electronic absorption bands centred at *ca.* 310 and 350 nm, assignable to the spin-allowed and spin-forbidden $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_\pi{}^*)^1$ transitions $(d_\pi{}^* = d_{xz}, d_{yz})$. Room-temperature photoluminescence with emission maxima in the region 620—710 nm from *trans*-$[Os^{VI}L(O)_2]^{2+}$ has been observed. In acetonitrile, *trans*-$[Os^{VI}L(O)_2]^{2+}$ displays reversible Os^{VI}–Os^{V} and Os^{V}–Os^{IV} couples with $E^\ominus$ ranging from −0.67 to −0.73 and −1.48 to −1.74 V *vs.* ferrocenium–ferrocene, respectively. The complexes *trans*-$[Os^{V}L(O)_2]^+$ have been characterized by u.v.–visible spectroscopy and magnetic susceptibility measurements. In aqueous solutions, pH-dependent and reversible Os^{VI}–Os^{III} couples have been observed. Thermally, *trans*-$[Os^{VI}L(O)_2]^{2+}$ complexes are poor oxidants for alkene oxidation.

The chemistry of osmium macrocyclic amine complexes remains relatively unexplored despite the rich co-ordination chemistry found for the ruthenium analogues in recent years.[1,2] An extension of our recent work on macrocyclic ruthenium oxo complexes[2] is to study the chemistry of the osmium analogues, which are anticipated to possess novel photochemical and electrochemical properties.[3,4] In a recent paper, we reported a modified procedure for the synthesis of *trans*-dichloro(tetra-amine)osmium(III) complexes,[5] which are precursors for the synthesis of high-valent osmium oxo complexes. Herein are described the synthesis, spectroscopic, and electrochemical behaviour of a series of *trans*-dioxo-osmium complexes of macrocyclic tertiary amine ligands, L.



L^1



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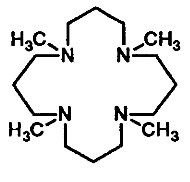

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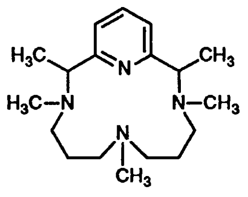

L^4

Experimental

Reagents and Materials.—The salt $Na_2[OsCl_6]$ was purchased from Johnson and Matthey Co. Ltd. The macrocyclic tertiary amine ligands, 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L^1),[6] 1,4,8,12-tetramethyl-1,4,8,12-tetra-azacyclopentadecane (L^2),[7] 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane (L^3),[8] and *meso*-2,3,7,11,12-pentamethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^4)[9] were prepared by the published methods. All reagents and solvents used were of analytical grade. Acetonitrile (Mallinckrodt Chrom AR) used for electrochemical studies was distilled twice over CaH_2 under argon. Deionized water used in electrochemical studies was purified by passing through an ion-exchange resin purification train (Barnstead Nanopure). Tetra-n-butylammonium hexafluorophosphate (Electrometric Grade, Southwestern Analytical Chemicals) was dried under vacuum at 100 °C for 48 h before use. Trifluoroacetic acid (99%, Aldrich) was purified by distillation under nitrogen. Perchloric acid (70%, Merck), sodium perchlorate (GR, Merck), and sodium trifluoroacetate (99%, Aldrich) were used as received.

Physical Measurements and Instrumentation.—U.v.–visible electronic absorption spectra were recorded on a Shimadzu UV-240 spectrophotometer, i.r. spectra as Nujol mulls on a Perkin-Elmer 577 spectrophotometer (4 000—200 cm^{-1}). Conductivity measurements were conducted by using a Radiometer model CDH2 conductivity meter with 0.1 mol dm^{-3} KCl as calibrant. Magnetic moments were measured by the Evans method. Elemental analyses of the new complexes were performed by the Microanalytical Unit of the Australian Mineral Development Laboratory.

Cyclic voltammetric measurements were perfomred by using a Princeton Applied Research (PAR) universal programmer (model 175), potentiostat (model 173), and digital coulometer (model 179). For electrochemical studies in non-aqueous solution (acetonitrile), the ferrocenium–ferrocene couple was used as the internal standard to which the E° values are referenced to.[10] The working electrodes were either glassy carbon (Atomergic Chemetals V25) or pyrolytic graphite (basal or edge plane, Union Carbide). Treatment of the electrode surfaces was as reported elsewhere.[11] Controlled-potential electrolysis was performed by using a PAR coulometric cell system (model 9610) equipped with a synchronous stirring motor (model 377). A glassy carbon crucible (Atomergic Chemetals V25-12) was used as the working electrode. All solutions for electrochemical studies were deaerated with argon gas. In cases where the u.v.–visible spectral changes of the solution during constant-potential electrolysis were to be monitored, aliquots of the solution were withdrawn periodically with a micropipette and the spectra recorded immediately.

Emission lifetime measurements were performed using a time-resolved laser system. The excitation source was the 355-nm output (third harmonic) of a Quanta-Ray Q-switched DCR-3 pulsed Nd:YAG laser (10 Hz, G-resonator). Luminescence decay signals were recorded either on a Tektronix model 2430 digital oscilloscope or a Tektronix model 7912AD transient recorder with a 7B90P programmable time base, a 7A19 vertical amplifier, and a type 602 display unit. The waveforms were acquired and analyzed using a program for exponential fits. Steady-state emission spectra were recorded on a Hitachi 650–60 fluorescence spectrophotometer. All solutions for photochemical studies were prepared under vacuum in a 10-cm^3 round-bottomed flask with a side-arm 1-cm fluorescence cuvette and sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze–pump–thaw cycles.

Syntheses of Osmium Complexes.—*trans*-$[\mathrm{Os^{VI}L^1(O)_2}]\mathrm{Y_2}$ ($\mathrm{Y = ClO_4^-}$ *or* $\mathrm{PF_6^-}$). An ethanolic solution of $\mathrm{Na_2[OsCl_6]}$ (0.5 g in 200 cm^3) was added dropwise to a refluxing and vigorously stirred ethanolic solution of $\mathrm{L^1}$ (0.5 g in 150 cm^3) in the presence of tin foil (2 g). The addition took 5 h to complete and the reaction mixture was refluxed overnight. It was then filtered and the filtrate rotary evaporated to dryness. The yellow residue was dissolved in hot deionized water (30 cm^3) and heated to about 80 °C for 20 min. The resulting yellow solution was filtered, and hydrogen peroxide (30%, 3 cm^3) was slowly added to the filtrate which was kept at *ca.* 60 °C for 5 min. The solution was cooled in an ice-water bath. Upon addition of a saturated solution of $\mathrm{NaClO_4}$ yellow microcrystalline *trans*-$[\mathrm{OsL^1(O)_2}][\mathrm{ClO_4}]_2$ slowly deposited. It was collected by filtration and recrystallized from hot $\mathrm{HClO_4}$ (0.1 mol dm^{-3} 60 °C). The hexafluorophosphate salt was similarly prepared using $\mathrm{NH_4PF_6}$ instead of $\mathrm{NaClO_4}$, and was recrystallized from hot $\mathrm{CF_3CO_2H}$ (0.1 mol dm^{-3}, 60 °C). Yield: 25% {Found: C, 24.8; H, 4.7; Cl, 10.5; N, 8.3. Calc. for *trans*-$[\mathrm{OsL^1(O)_2}][\mathrm{ClO_4}]_2$: C, 24.3; H, 4.9; Cl, 10.7; N, 8.1%}. I.r. (Nujol mull): ν_asym(Os=O) 876 cm^{-1}. Molar conductivity (in water at 298 K): Λ_M 268 Ω^{-1} cm^2 mol^{-1}. Magnetic moment (at 298 K): $\mu_\mathrm{eff.}$ 0.

trans-$[\mathrm{OsL^2(O)_2}]\mathrm{Y_2}$ ($\mathrm{Y = ClO_4^-}$ *or* $\mathrm{PF_6^-}$]. These complexes were prepared similarly as for *trans*-$[\mathrm{OsL^1(O)_2}]\mathrm{Y_2}$. Yield: 40% {Found: C, 26.1; H, 4.9; Cl, 10.3, N, 8.1. Calc. for *trans*-$[\mathrm{OsL^2(O)_2}][\mathrm{ClO_4}]_2$: C, 26.2; H, 5.3; Cl, 10.0; N, 8.0%}. I.r. (Nujol mull): ν_asym(Os=O) 875 cm^{-1}. Molar conductivity (in water at 296 K): Λ_M 259 Ω^{-1} cm^2 mol^{-1}. Magnetic moment (at 298 K): $\mu_\mathrm{eff.}$ 0.

trans-$[\mathrm{OsL^3(O)_2}]\mathrm{Y_2}$ ($\mathrm{Y = ClO_4^-}$ *or* $\mathrm{PF_6^-}$]. These complexes were prepared similarly as for *trans*-$[\mathrm{OsL^1(O)_2}]\mathrm{Y_2}$. Yield: 35% {Found: C, 27.2; H, 5.4; Cl, 10.1; N, 7.9. Calc. for *trans*-$[\mathrm{OsL^3(O)_2}][\mathrm{ClO_4}]_2$: C, 26.9; H, 5.4; Cl, 10.4; N, 7.7%}. I.r. (Nujol mull): ν_asym(Os=O) 872 cm^{-1}. Molar conductivity (in water at 296 K): Λ_M 248 Ω^{-1} cm^2 mol^{-1}. Magnetic moment (at 298 K): $\mu_\mathrm{eff.}$ 0.

trans-$[\mathrm{OsL^4(O)_2}]\mathrm{Y_2}$ ($\mathrm{Y = ClO_4^-}$ *or* $\mathrm{PF_6^-}$]. These complexes were prepared similarly as for *trans*-$[\mathrm{OsL^1(O)_2}]\mathrm{Y_2}$. Yield: 45% {Found: C, 30.4; H, 4.5; Cl, 9.2; N, 8.6. Calc. for *trans*-$[\mathrm{OsL^4(O)_2}][\mathrm{ClO_4}]_2$: C, 30.6; H, 4.5; Cl, 9.5; N, 8.5%}. I.r. (Nujol mull): ν_asym(Os=O) 875 cm^{-1}. Molar conductivity (in water at 296 K): Λ_M 239 Ω^{-1} cm^2 mol^{-1}. Magnetic moment (at 298 K): $\mu_\mathrm{eff.}$ 0.

trans-$[\mathrm{Os^VL^1(O)_2}]\mathrm{ClO_4}$. This complex was prepared electrochemically by constant-potential reduction of *trans*-$[\mathrm{OsL^1(O)_2}][\mathrm{ClO_4}]_2$ (1 mmol) in MeCN (30 cm^3, 0.1 mol dm^{-3} $\mathrm{NBu_4ClO_4}$). The electrolysis was conducted at −0.750 V *vs.* ferrocenium–ferrocene. Upon completion of the electrolysis, the MeCN solution was evaporated to 10 cm^3 and *trans*-$[\mathrm{OsL^1(O)_2}]\mathrm{ClO_4}$ was precipitated upon addition of diethyl ether. Yield: 90%. I.r. (Nujol mull): ν_asym(Os=O) 879 and 873 cm^{-1}. Magnetic moment (at 298 K): $\mu_\mathrm{eff.}$ 1.89.

trans-$[\mathrm{Os^{II}L^1(MeCN)_2}][\mathrm{PF_6}]_2$. The complex *trans*-$[\mathrm{OsL^1(O)_2}][\mathrm{PF_6}]_2$ (0.5 g) and triphenylphosphine (0.7 g) were refluxed in acetonitrile (100 cm^3) with stirring for 12 h. The solution was rotary evaporated to 20 cm^3. Addition of anhydrous diethyl ether to the resulting solution precipitated *trans*-$[\mathrm{OsL^1(MeCN)_2}][\mathrm{PF_6}]_2$ as a pale yellow solid, which was recrystallized by vapour diffusion of diethyl ether into acetonitrile. Yield: 25%. {Found: C, 27.0; H, 4.8; F, 27.7; N, 9.9; P, 7.9. Calc. for *trans*-$[\mathrm{OsL^1(MeCN)_2}][\mathrm{PF_6}]_2$: C, 26.4; H, 4.6; F, 27.9; N, 10.3; P, 7.6%}. I.r. (Nujol mull): ν(C≡N) 2 230 cm^{-1}. Magnetic moment (at 298 K): $\mu_\mathrm{eff.}$ 0.

trans-$[\mathrm{OsL^4(MeCN)_2}][\mathrm{PF_6}]_2$. The complex *trans*-$[\mathrm{OsL^4(O)_2}][\mathrm{PF_6}]_2$ (0.5 g) and triphenylphosphine (0.7 g) were refluxed in acetonitrile (100 cm^3) with stirring for 12 h. The solution was rotary evaporated to 20 cm^3. Addition of anhydrous diethyl ether to the resulting solution precipitated *trans*-$[\mathrm{OsL^4(MeCN)_2}][\mathrm{PF_6}]_2$ as a pale yellow solid, which was recrystallized by vapour diffusion of diethyl ether into acetonitrile. Yield: 35%. {Found: C, 30.2; H, 4.5; F, 26.1; N, 9.8; P, 7.4. Calc. for *trans*-$[\mathrm{OsL^4(MeCN)_2}][\mathrm{PF_6}]_2$: C, 30.5; H, 4.4; F, 26.3; N, 9.7; P, 7.2%}. I.r. (Nujol mull): ν(C≡N) 2 230 cm^{-1}. Magnetic moment (at 298 K): $\mu_\mathrm{eff.}$ 0.

Results and Discussion

Known *trans*-dioxo(tetra-amine)osmium(VI) complexes include *trans*-$[\mathrm{Os(NH_3)_4(O)_2}]^{2+}$ and *trans*-$[\mathrm{Os(en)_2(O)_2}]^{2+}$ (en = 1,2-diaminoethane), which can be prepared from the reaction of $\mathrm{K_2[Os(OH)_4(O)_2]}$ with the primary amine.[12] However, the procedure had been found to be unsuccessful for macrocyclic tertiary amine ligands. The dropwise addition of an ethanolic solution of $\mathrm{Na_2[OsCl_6]}$ to a refluxing suspension of tin and $\mathrm{L^1}$—$\mathrm{L^4}$ in ethanol results in a facile metal-insertion reaction, whereby a low-valent osmium complex that is reactive in the insertion reaction may be generated *in situ*. Oxidation of the residue obtained from this insertion with hydrogen peroxide produces a series of stable *trans*-dioxo-osmium(VI) complexes of macrocyclic tertiary amine ligands.

trans-Dioxo-osmium(V) complexes, *trans*-$[\mathrm{OsL(O)_2}]^+$, have been prepared by electrochemical reduction of the corresponding *trans*-dioxo-osmium(VI) complexes in acetonitrile. Acetonitrile solutions of the osmium(V) complexes are stable for more than 1 week if kept in a well stoppered flask at 5 °C, as evidenced by u.v.–visible spectrophotometry. To our knowledge, the generation of stable *trans*-dioxo-osmium(V) complexes has no precedent in the literature. This demonstrates the usefulness of utilizing macrocyclic tertiary amines in stabilizing transition-metal centres in unusual oxidation states.

All the *trans*-dioxo-osmium(VI) complexes are air-stable solids and exist as 1:2 electrolytes in solution. Magnetic susceptibility measurements show that they are diamagnetic, consistent with the $(d_{xy})^2$ ground-state electronic configuration in a D_{4h} symmetry. The magnetic susceptibility of *trans*-$[\mathrm{OsL^1(O)_2}]^+$ is 1.89, in accordance with the $(d_{xy})^2(d_\pi{}^*)^1$ ground-state electronic configuration. A similar magnetic

Table 1. U.v.-visible spectral data for *trans*-dioxo complexes of osmium-(VI) and -(V) in acetonitrile

Complex	λ/nm (ε/dm^3 mol^{-1} cm^{-1})	
	Band I	Band II
$[OsL^1(O)_2]^{2+}$	312 (1 260)	355 (340)
$[OsL^2(O)_2]^{2+}$	307 (1 815)	347 (475)
$[OsL^3(O)_2]^{2+}$	306 (1 915)	346 (345)
$[OsL^4(O)_2]^{2+}$	307 (1 935)	365 (365)
	Band III	Band IV
$[OsL^1(O)_2]^{+}$	335 (490)	410 (100)
$[OsL^2(O)_2]^{+}$	332 (540)	410 (120)
$[OsL^3(O)_2]^{+}$	330 (550)	410 (160)
$[OsL^4(O)_2]^{+}$	330 (980)	415 (200)

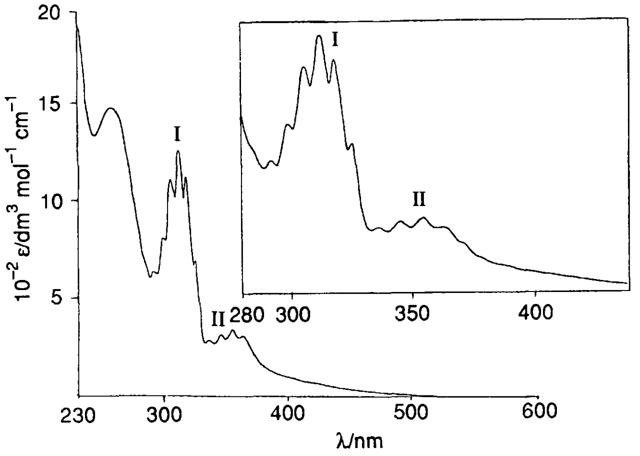

Figure 1. U.v.-visible spectrum of *trans*-$[OsL^1(O)_2][ClO_4]_2$ in acetonitrile

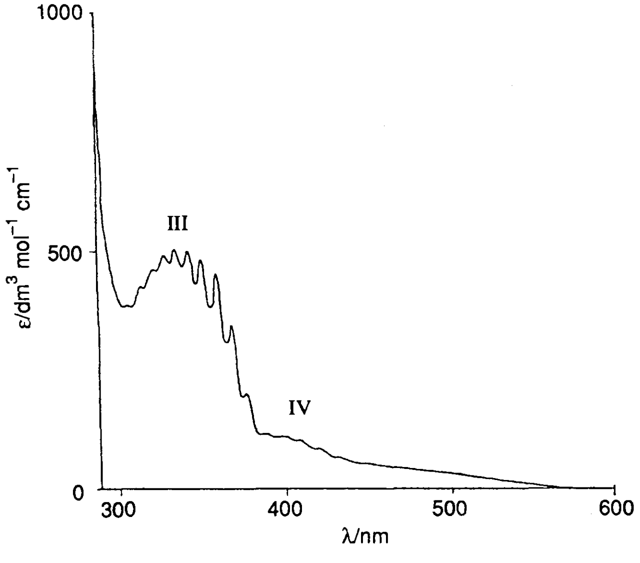

Figure 2. U.v.-visible spectrum of *trans*-$[OsL^1(O)_2]^+$ in acetonitrile

moment of 1.93 has been reported for the ruthenium analogue, *trans*-$[RuL^1(O)_2]ClO_4$.[2e]

All *trans*-dioxo-osmium(VI) complexes exhibit a strong i.r. absorption band at *ca.* 875 cm^{-1}, assignable as the asymmetric $Os(O)_2$ stretch. The observed stretching frequencies are comparable to those found for *trans*-$[Os(NH_3)_4(O)_2]Cl_2$[13] and *trans*-$[Os(en)_2(O)_2]Cl_2$.[14] On the other hand, *trans*-($[OsL^1(O)_2]ClO_4$ exhibits two intense i.r. bands at 873 and 879 cm^{-1}, possibly assignable to the $\nu_{asym}[Os(O)_2]$ stretch. The observation of two bands possibly arises as a result of solid-state splitting due to low site symmetry. However, in the absence of ^{18}O-labelling studies the assignment is only tentative.

Electronic Absorption Spectroscopy.—The u.v.–visible absorption spectra of *trans*-$[Os^{VI}L(O)_2][ClO_4]_2$ in acetonitrile exhibit two distinct vibronic structured bands, I and II (Figure 1). The spectral data are in Table 1. Simple ligand-field analysis[4a,15] shows that both bands arise from the $d_{xy} \longrightarrow d_\pi^*$ ($d_\pi^* = d_{xz}$, d_{yz}) transition, which is vibronically coupled to the $A_{2u}[\nu(Os{=}O)]$ vibrational stretching mode. Assuming D_{4h} symmetry for the molecule, bands I and II are assigned as the respective $^1A_{1g} \longrightarrow {}^1E_g$ and $^1A_{1g} \longrightarrow E_g(^3E_g)$ transitions. Very weak absorptions are also observed in the low-energy tail of band II, possibly attributed to transitions from $^1A_{1g}$ to the spin–orbit sublevels of the ^3E_g state. The relative insensitivity of the $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_\pi^*)^1$ transitions to the nature of the equatorial ligands is in accord with the lack of involvement of d_σ^* electrons. Similar observations were made for the analogous *trans*-dioxoruthenium(VI) system.[2e] The occurrence and the much higher absorption coefficients of the $^1A_{1g} \longrightarrow E_g(^3E_g)$ transition for the osmium complexes over that of ruthenium, which appears as a weak shoulder at 455 nm ($\varepsilon_{max.}$ = 50 dm^3 mol^{-1} cm^{-1}) for *trans*-$[RuL^1(O)_2][ClO_4]_2$, have been attributed to the larger spin–orbit coupling constant for the heavier osmium atom. The smaller ν(Os=O) stretching frequency of the ^1E_g and ^3E_g excited-state levels (*ca.* 700—730 cm^{-1}, estimated from the vibrational spacing in bands I and II) than that of the $^1A_{1g}$ ground state (ν_{sym} 917, ν_{asym} 875 cm^{-1}) indicates that the Os–O bond is weakened upon excitation by light. This is expected as excitation results in a transition that places an electron into the antibonding d_π^* orbitals, and a lengthening of the Os–O bond.

The u.v.–visible absorption spectra of *trans*-dioxo-osmium(V) complexes in acetonitrile also exhibit two vibronic structured absorption bands III and IV, centred at *ca.* 335 and 410 nm, respectively (Figure 2). The spectral data are summarized in Table 1. The measured low $\varepsilon_{max.}$ values for bands III and IV suggest that they are derived from *d–d* transitions. As in the case of *trans*-dioxo-osmium(VI), bands III and IV arise from the respective spin-allowed and -forbidden $d_{xy} \longrightarrow d_\pi^*$ transitions. The red shift of bands III and IV in the *trans*-dioxo-osmium(V) system relative to bands I and II in the osmium(VI) counterpart is probably attributed to splitting of the doubly degenerate d_π^* orbitals of d^3 osmium(V). Moreover, occupancy of an electron in the antibonding d_π^* orbitals of osmium(V) may also lower its energy level. Similar red shifts of the u.v.–visible absorption bands have been reported for the isoelectronic d^2 *trans*-$[Re^V(en)_2(O)_2]^+$–d^3 *trans*-$[Re^{IV}(en)_2(O)_2]$[16] and the analogous ruthenium-(VI) and -(V) systems.[2e]

An interesting characteristic property of the *trans*-$[Os^{VI}L(O)_2][ClO_4]_2$ complexes is that they all exhibit long-lived room-temperature phosphorescence at 620—710 nm (lifetime *ca.* 0.9—1.6μs) upon excitation at 350—400 nm.[3d,e] Details of the photophysical properties of this class of compounds will be published subsequently.[3e]

Electrochemistry.—The cyclic voltammogram of *trans*-$[OsL^1(O)_2]^{2+}$ in acetonitrile displays two reversible quasi-reversible redox couples, I and II, at −0.73 and −1.64 V *vs.* ferrocenium–ferrocene (Figure 3). At a scan rate (v) of less than 100 mV s^{-1} the peak-to-peak (ΔE_p) separation for couple I is

Table 2. Cyclic voltammetric data (E°/V) for *trans*-dioxo-osmium(VI) complexes in acetonitrile and in aqueous solutions

	a		*b*	
Complex	Os^{VI}–Os^{V}	Os^{V}–Os^{IV}	Os^{VI}–Os^{III}	Os^{III}–Os^{II}
trans-$[OsL^1(O)_2]^{2+}$	−0.73	−1.64	+0.04	−0.64[c]
trans-$[OsL^2(O)_2]^{2+}$	−0.72	−1.70	+0.05	−0.68[c]
trans-$[OsL^3(O)_2]^{2+}$	−0.70	−1.66	+0.05	−0.70[c]
trans-$[OsL^4(O)_2]^{2+}$	−0.67	−1.48	+0.14	−0.54[c]

[a] In acetonitrile (0.1 mol dm^{-3} $NBu^n{}_4PF_6$). Working electrode: glassy carbon. [b] In 0.1 mol dm^{-3} CF_3CO_2H–0.1 mol dm^{-3} CF_3CO_2Na(pH1). Working electrode: basal-plane pyrolytic graphite. [c] Irreversible wave.

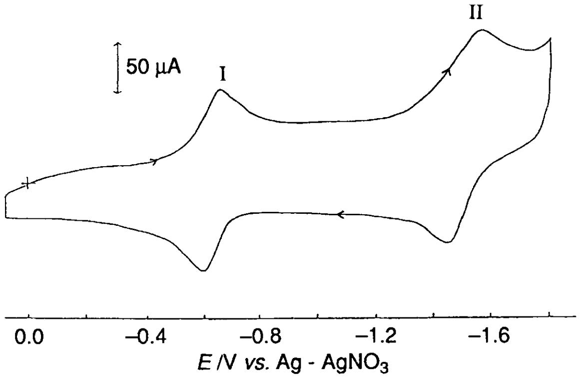

Figure 3. Cyclic voltammogram of 1 mmol dm^{-3} *trans*-$[OsL^1(O)_2]^{2+}$ in 0.1 mol dm^{-3} $NBu^n{}_4PF_6$–MeCN. Scan rate 100 mV s^{-1}; working electrode, edge-plane pyrolytic graphite

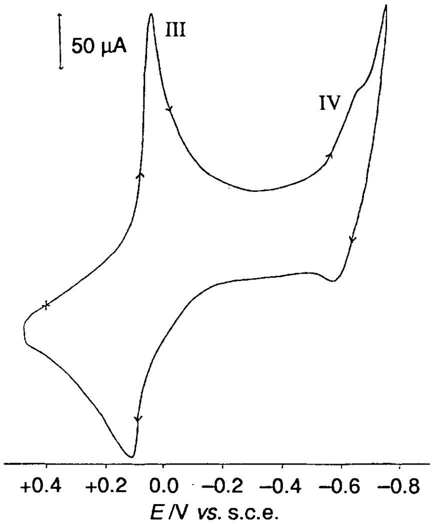

Figure 4. Cyclic voltammogram of 1 mmol dm^{-3} *trans*-$[OsL^1(O)_2]^{2+}$ in 0.1 mol dm^{-3} CF_3CO_2H–0.1 mol dm^{-1} CF_3CO_2Na. Scan rate 100 mV s^{-1}; working electrode, basal-plane pyrolytic graphite

60—70 mV, as is commonly found for a reversible one-electron transfer process. Both the current function ($i_{p_a}/\sqrt{v}$) and current ratio ($i_{p_a}/i_{p_c} \approx 1$) are independent of scan rate (10—100 mV s^{-1}). Controlled-potential coulometric experiments showed that the electrochemical stoicheiometry (n) is 1.0 ± 0.1 for couple I. Rotating-disc voltammetric studies also support $n = 1$ for couple I, with a linear Levich plot and a calculated diffusion coefficient (D) of 1.75×10^{-6} cm^2 s^{-1}. Couple II also exhibits a linear Levich plot with $n = 1$. The electrode reactions for couples I and II are as shown in equations (1) and (2).

$$\text{Couple I: } trans\text{-}[Os^{VI}L(O)_2]^{2+} + e^- \longrightarrow trans\text{-}[Os^{V}L(O)_2]^{+} \quad (1)$$

$$\text{Couple II: } trans\text{-}[Os^{V}L(O)_2]^{+} + e^- \longrightarrow trans\text{-}[Os^{IV}L(O)_2] \quad (2)$$

The electrochemically generated *trans*-$[Os^{V}L(O)_2]^{+}$ complexes have been characterized by u.v.–visible spectroscopy, and can be reoxidized back to the starting osmium(VI) complex quantitatively. The observed reversibility of the Os^{V}–Os^{IV} couple suggests that *trans*-$[Os^{IV}L(O)_2]$ is at least stable in fluid solution on the time-scale of cyclic voltammetric experiments. To our knowledge, no trans-dioxo-osmium(IV) complex has been reported in the literature. Reversible Os^{VI}–Os^{V} and Os^{V}–Os^{IV} couples have also been observed for the other *trans*-$[Os^{VI}L(O)_2]^{2+}$ complexes (Table 2). The change in the macrocyclic ring size of L has only a slight effect on the E° values. However, substitution of a tertiary nitrogen by a pyridyl group as in L^4 shifts the redox potential toward more positive values. This is understandable since the π-acceptor ability of the pyridyl group would preferentially stabilize the electron-rich lower valent state of osmium.

The cyclic voltammogram of *trans*-$[OsL^1(O)_2]^{2+}$ in acetonitrile in the presence of 3 molar equivalents of CF_3CO_2H displays two irreversible reductive waves at −0.55 and −1.20 V *vs.* ferrocenium–ferrocene, respectively. Controlled-potential reduction of *trans*-$[OsL^1(O)_2]^{2+}$ at −0.60 V *vs.* Ag–$AgNO_3$ (0.1 mol dm^{-3} in MeCN) led to a stoicheiometry of $n = 3$, indicating a direct reduction of Os^{VI} to Os^{III}: [equation (3)].

$$trans\text{-}[Os^{VI}L^1(O)_2]^{2+} + 3e^- + 3\,H^+ \longrightarrow trans\text{-}[Os^{III}L^1(OH)(H_2O)]^{2+} \quad (3)$$

Further electrochemical reduction at potential of −1.30 V *vs.* Ag–$AgNO_3$ (0.1 mol dm^{-3} in MeCN) has been found to generate *trans*-$[Os^{II}L^1(MeCN)_2]^{2+}$ identified by the reversible redox wave at +0.19 V, ascribed to the $[Os^{III}L^1(MeCN)_2]^{3+/2+}$ couple.

In an aqueous medium (pH 1) the cyclic voltammogram of *trans*-$[OsL^1(O)_2]^{2+}$ showed a reversible three-electron couple at +0.035 V (couple III), and an irreversible one-electron couple at −0.64 V *vs.* saturated calomel electrode (couple IV) (Figure 4). The three-electron nature of couple III has been confirmed by controlled-potential coulometry at −0.20 V *vs.* s.c.e. and a ΔE_p value of 20—30 mV at scan rates of less than 100 mV s^{-1}. Both the current function and current ratio are independent of scan rate.

The redox potential of couple III is found to shift cathodically as the pH of the medium is raised. A pourbaix plot is shown in Figure 5, with slopes of −60 and −42 mV per pH unit in the ranges pH 1.0—3.2 and 3.2—6.7, respectively. The electrode reactions occurring are (3) at pH 1.0—3.2 and (4) at pH 3.2—6.7.

$$trans\text{-}[Os^{VI}L^1(O)_2]^{2+} + 3e^- + 2\,H^+ \longrightarrow trans\text{-}[Os^{III}L^1(OH)_2]^{+} \quad (4)$$

The complex *trans*-$[Os^{III}L^1(OH)(H_2O)]^{2+}$ has been characterized spectroscopically [$\lambda_{max.}$/nm ($\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}): 270 (2 900)] and can be quantitatively reoxidized (electrochemically or aerially) back to *trans*-$[Os^{VI}L^1(O)_2]^{2+}$. Controlled-potential reduction of *trans*-$[OsL^1(O)_2]^{2+}$ at pH 5.73 at −0.35 V *vs.* s.c.e. generated *trans*-$[OsL^1(OH)_2]^{+}$ [$\lambda_{max.}$/nm ($\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}): 267 (2 900)].

At pH > 7 couple III splits into two waves (couples V and VI) (Figure 6) corresponding to the electrode reactions (5) and (6). As expected, the redox potential for couple V (−0.225 V *vs.* s.c.e.) is pH-independent. For couple VI a linear plot of E°

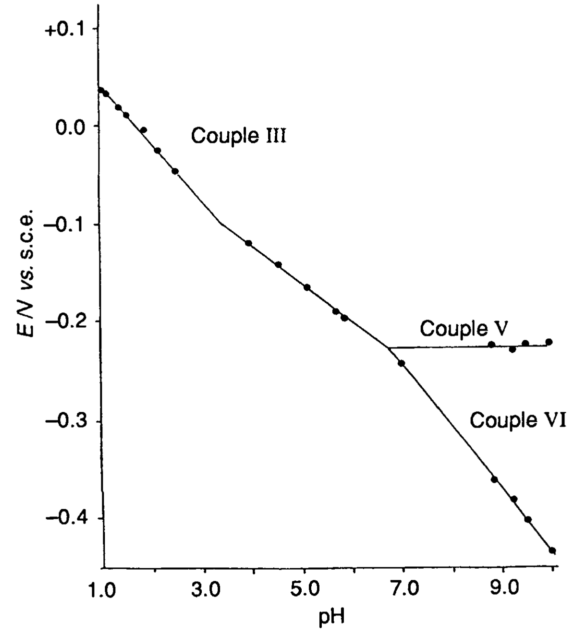

Figure 5. A Pourbaix plot for couple V of *trans*-$[\mathrm{OsL^1(O)_2}]^{2+}$ in aqueous buffer solutions

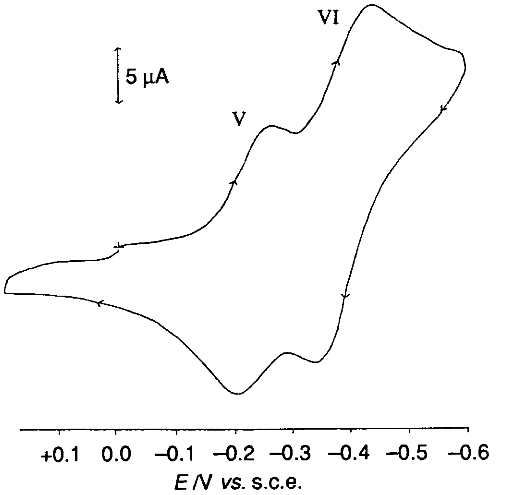

Figure 6. Cyclic voltammogram of 0.5 mmol dm^{-3} *trans*-$[\mathrm{OsL^1(O)_2}]^{2+}$ in pH 9.26 buffer. Scan rate 50 mV s^{-1}, working electrode basal-plane pyrolytic graphite

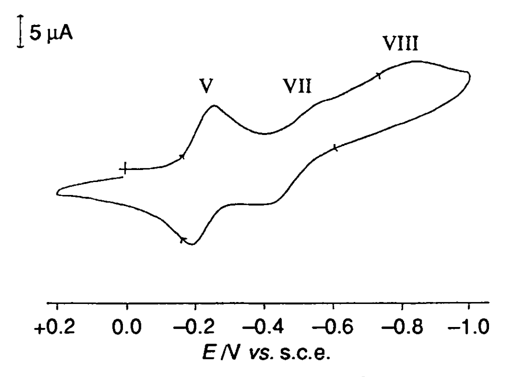

Figure 7. Cyclic voltammogram of 0.5 mmol dm^{-3} *trans*-$[\mathrm{OsL^1(O)_2}]^{2+}$ in pH 11.3 buffer. Scan rate 50 mV s^{-1}, working electrode, basal-plane pyrolytic graphite

$$\text{Couple V: } trans\text{-}[\mathrm{Os^{VI}L^1(O)_2}]^{2+} + e^- \longrightarrow trans\text{-}[\mathrm{Os^{V}L^1(O)_2}]^{+} \quad (6)$$

$$\text{Couple VI: } trans\text{-}[\mathrm{Os^{V}L^1(O)_2}]^{+} + 2e^- + 2\,\mathrm{H^+} \longrightarrow trans\text{-}[\mathrm{Os^{III}L^1(OH)_2}]^{+} \quad (7)$$

versus pH with a slope of −60 mV/pH unit obtained is in agreement with a two-proton two-electron transfer process. The direct two-electron reduction of Os$^{\mathrm{V}}$ to Os$^{\mathrm{III}}$ indicates that the osmium(IV) oxo species is unstable and undergoes rapid disproportionation in water (see later).

The irreversible reduction wave, couple IV at pH 1.0, has been ascribed to the reduction of Os$^{\mathrm{III}}$ to Os$^{\mathrm{II}}$.

The cyclic voltammogram of *trans*-$[\mathrm{OsL^1(O)_2}]^{2+}$ at pH 11.3 is shown in Figure 7. Couple VI splits into two, VII and VIII. By comparing the current magnitudes with that for couple V it is believed that couples VII and VIII correspond to two discrete one-electron transfers. The peak-to-peak separation (ΔE_p) for couple VII is *ca.* 100 mV while that for couple VIII is very broad and essentially irreversible. It is reasonable to assume that couples VII and VIII correspond to Os$^{\mathrm{V}}$–Os$^{\mathrm{IV}}$ and Os$^{\mathrm{IV}}$–Os$^{\mathrm{III}}$ couples, respectively. Further attempts to follow the pH dependence of these two couples were unsuccessful.

Proton-coupled electron-transfer reactions have also been observed for polypyridyl ruthenium and osmium oxo complexes.[17,18] Meyer and co-workers[18] also reported a reversible three-electron Os$^{\mathrm{VI}}$–Os$^{\mathrm{III}}$ couple with $[\mathrm{Os^{VI}(terpy)(OH)(O)_2}]^+$ (terpy = 2,2′ = 6′,2″-terpyridine) using an activated glassy carbon electrode. It appears that the direct reduction of Os$^{\mathrm{VI}}$ to Os$^{\mathrm{III}}$ is a general feature of *trans*-dioxo-osmium(VI) complexes in acidic media, provided that the intermediate osmium-(V) and -(IV) species are stable enough with regard to dissociation and μ-oxo dimerization processes.

The electrochemical data for other *trans*-$[\mathrm{Os^{VI}L(O)_2}]^{2+}$ complexes in aqueous media are summarized in Table 2. It is interesting that the change in macrocyclic ring size again has little effect on the redox potentials.

Disproportionation of Dioxo-osmium(V).—Addition of a small drop of $\mathrm{CF_3CO_2H}$ to an acetonitrile solution of *trans*-$[\mathrm{OsL^1(O)_2}]^+$ led to an immediate disappearance of the vibronic structured bands at 335 and 410 nm, and concomitant formation of the vibronic structured bands at 315 and 355 nm of *trans*-$[\mathrm{OsL^1(O)_2}]^{2+}$. It appears that protons induce disproportionation of the *trans*-$[\mathrm{OsL^1(O)_2}]^+$ complex [equation (7)]. No isosbestic point was found when different amounts of $\mathrm{CF_3CO_2H}$ were added to an acetonitrile solution of *trans*-$[\mathrm{OsL^1(O)_2}]^+$. This contrasts with *trans*-$[\mathrm{RuL^1(O)_2}]^+$ which undergoes a simple disproportionation reaction to give *trans*-$[\mathrm{RuL^1(O)_2}]^{2+}$ and *trans*-$[\mathrm{RuL^1(O)(H_2O)}]^{2+}$ as the final products.[1] It is believed that oxo-osmium(IV) is unstable and disproportionates in a protic medium.

$$3\,trans\text{-}[\mathrm{Os^{V}L^1(O)_2}]^{+} + 3\,\mathrm{H^+} \longrightarrow 2\,trans\text{-}[\mathrm{Os^{VI}L^1(O)_2}]^{2+} + 2trans\text{-}[\mathrm{Os^{III}L^1(OH)(H_2O)}]^{2+} \quad (7)$$

These observations are in agreement with the results obtained in cyclic voltammetric experiments. In cyclic voltammetry, the direct reduction of Os$^{\mathrm{VI}}$ to Os$^{\mathrm{III}}$ in an acidic medium (pH < 6.7) implies that the osmium-(V) and -(IV) species, though important as kinetic intermediates, are thermodynamically unstable with respect to disproportionation under these conditions. That is, the Os$^{\mathrm{IV}}$–Os$^{\mathrm{III}}$ and Os$^{\mathrm{V}}$–Os$^{\mathrm{IV}}$ couples occur at more positive potentials than that of the Os$^{\mathrm{VI}}$–Os$^{\mathrm{V}}$ couple so that thermodynamically no Os$^{\mathrm{V}}$ and Os$^{\mathrm{IV}}$ can build up in solution to a significant extent.

The osmium(V) state is stabilized with respect to disproportionation as the pH is increased (pH > 6.7), as evidenced by the observation of a distinct Os^{VI}–Os^{V} couple (couple V) in the cyclic voltammogram of *trans*-$[OsL^1(O)_2]^{2+}$. The existence of the Os^V–Os^{III} couple (couple VI) implies that the osmium(IV) state is thermodynamically unstable with respect to disproportionation to Os^V and Os^{III} even under alkaline conditions.

Reactivity.—Complexes *trans*-$[Os^{VI}L(O)_2]^{2+}$ have been found to be poor oxidants. No reaction with norborn-2-ene, styrene, and *cis*- and *trans*-stilbenes was found. Cyclohexene was oxidized to 2-cyclohexen-1-one and 2-cyclohexen-1-ol after prolonged reaction for 40 h at room temperature. The reaction between *trans*-$[Os^{VI}L(O)_2]^{2+}$ and PPh_3 was very slow at room temperature. However, upon prolonged refluxing in acetonitrile, *trans*-$[Os^{II}L(MeCN)_2]^{2+}$ and $O{=}PPh_3$ (identified by its i.r. band at 1 195 cm^{-1}) were formed. The formation of *trans*-$[OsL(MeCN)_2]^{2+}$ as the final product indicated that the $Os^{IV}{=}O$ intermediate was also capable of transferring an oxygen atom to PPh_3. Similar results have been observed for other *trans*-dioxo-osmium(VI) complexes.[19]

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