Novel Osmium-(V) and -(IV) Dioxo Complexes of Macrocyclic Tetradentate Tertiary Amines: Spectroscopic Studies and Reactivity of *trans*-$[Os^{V}(tmc)(O)_2]^+$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)

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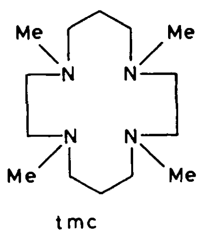
trans-$[Os^{V}(tmc)(O)_2]^+$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) was generated by the electrochemical reduction of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ in MeCN with an $E_{\frac{1}{2}}$ of the Os^{VI}/Os^{V} couple of −0·73 V *vs.* ferrocenium–ferrocene; the Os^{V} complex displayed two vibronic structured d–d bands in the 300—450 nm region.

High-valent *trans*-dioxo-osmium(VI) complexes such as *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)[1] and $[Os^{VI}(trpy)(OH)(O)_2]^+$ (trpy = 2,2′,2″-terpyridine)[2] have recently been shown to exhibit a reversible three-electron–proton redox couple of Os^{VI} to Os^{III}: $[Os^{VI}(O)_2] + 3H^+ + 3e^- \rightarrow [Os^{III}(OH)(OH_2)]$, in aqueous acidic medium. Although an Os^{V}–oxo species has been suggested as the possible kinetic intermediate,[1,2] its chemistry and properties remain virtually unknown. To the best of our knowledge, osmium complexes in the +5 oxidation state[3] are rare and no well characterized Os^{V}–oxo complex has ever been reported.[4] We describe here the preparation and spectroscopic characterization of the novel *trans*-$[Os^{V}(tmc)(O)_2]^+$; the isoelectronic *trans*-$[Ru^{V}(tmc)(O)_2]^-$ has recently been reported.[4]

The cyclic voltammogram of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ (Figure 1) in acetonitrile containing 0.1 M $Bu^n{}_4NClO_4$ displays two reversible-quasi-reversible redox couples, I and II, at −0.73 and −1.74 V *vs.* the $(cp)_2Fe^{+/0}$ (cp = cyclopentadienyl)



tmc

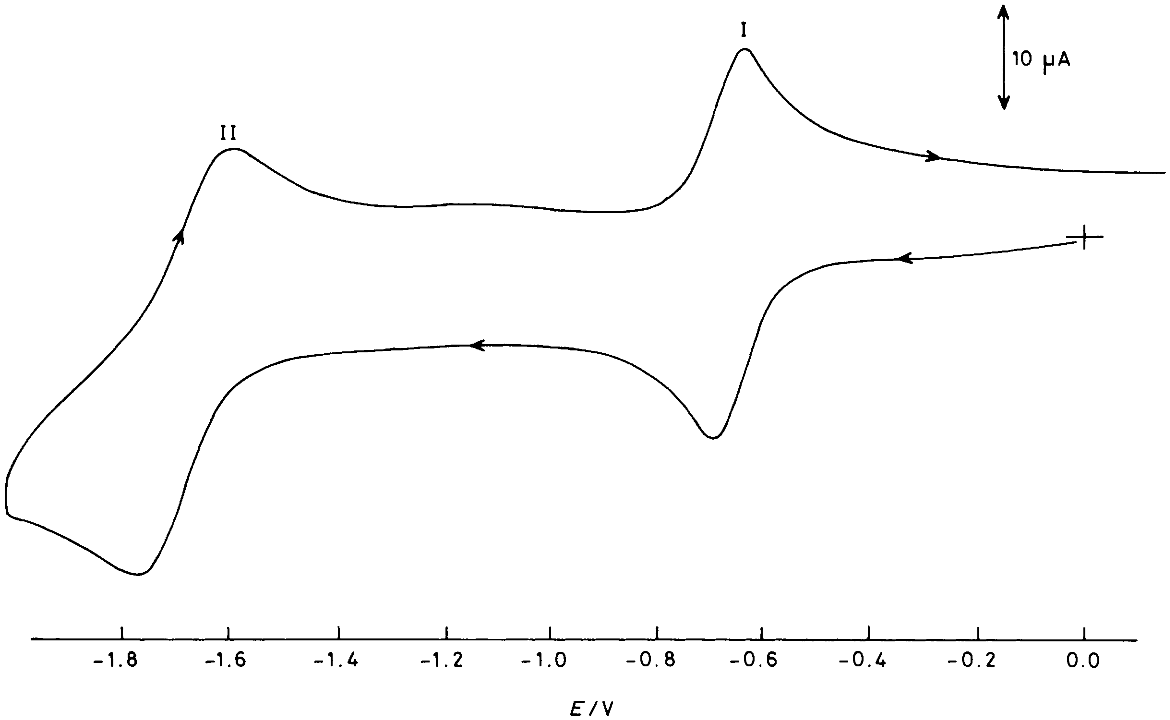


Figure 1. Cyclic voltammogram of *trans*-$[Os^{VI}(tmc)(O)_2][ClO_4]_2$ in MeCN; scan rate, 100 mV s^{-1}; working electrode, pyrolytic graphite; reference electrode, $Ag/AgNO_3$ 0.1 M in MeCN.

couple respectively. At a scan rate (ν) of less than 100 mV s^{-1}, the peak-to-peak (ΔE_p) value for couple I is 60—70 mV, as is commonly found for a reversible one-electron transfer process. Both the current function ($i_{pc}/\sqrt{\nu}$) and current ratio ($i_{pa}/i_{pc} \sim 1$) are independent of scan rate (10—100 mV s^{-1}).

Controlled potential coulometric experiments showed that the electrochemical stoicheiometry n is 1.00 ± 0.1 for couple I. As the magnitudes of i_{pa} (or i_{pc}) for couples I and II are the same, couple II also corresponds to a reversible one-electron redox wave and the electrode reactions are as shown.

$$\text{I: } trans\text{-}[Os^{VI}(tmc)(O)_2]^{2+} + e^- \rightarrow trans\text{-}[Os^{V}(tmc)(O_2)]^{+}$$

$$\text{II: } trans\text{-}[Os^{V}(tmc)(O_2)]^{+} + e^- \rightarrow trans\text{-}[Os^{IV}(tmc)(O)_2]$$

The generation of stable Os^V (d^3) and Os^{IV} (d^4) dioxo complexes has no precedent in the literature and demonstrates the usefulness of macrocyclic tertiary amines in the stabilization of transition metal complexes in unusual oxidation states. *trans*-$[Os^V(tmc)(O)_2]ClO_4$ was isolated by electrochemical reduction of *trans*-$[Os^{VI}(tmc)(O_2)]^{2+}$ in MeCN solution containing 0.1 M $Bu^n{}_4NClO_4$, followed by addition of diethyl ether. An acetonitrile solution of *trans*$[Os^V(tmc)(O)_2]^+$ is stable during a week under degassed and dry conditions. Solid *trans*-$[Os^V(tmc)(O)_2]ClO_4$ is air-sensitive and hygroscopic and easily air-oxidized back to the starting *trans*-$[Os^{VI}(tmc)(O)_2](ClO_4)_2$. Controlled potential electrochemical oxidation of an acetonitrile solution of *trans*-$[Os^V(tmc)(O)_2]ClO_4$ regenerated the Os^{VI} complex in 100% yield, indicating that the interconversion between Os^{VI} and Os^V dioxo complexes is a simple and reversible one-electron transfer process and proceeds without secondary chemical reactions. Its i.r. spectrum displays a doublet in the 840—860 cm^{-1} region, corresponding to the ν(Os=O) stretch. The u.v.-visible spectrum

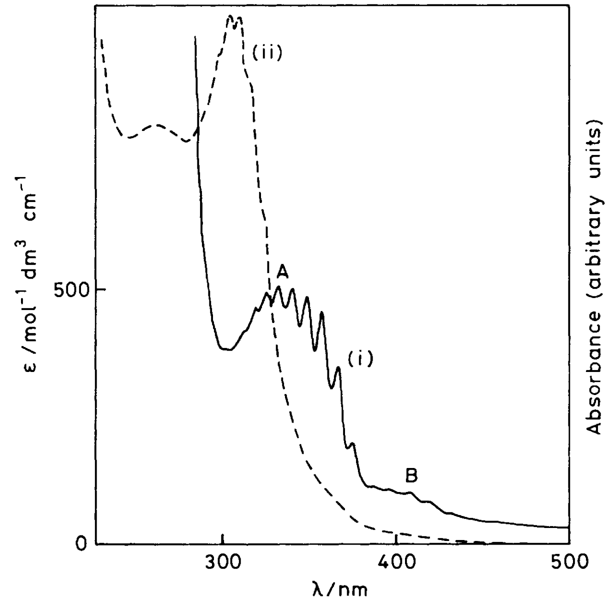


Figure 2. U.v.-visible spectra of (i) *trans*-$[Os^V(tmc)(O)_2]^+$ in MeCN; (ii) of the solution obtained after addition of one drop of CF_3CO_2H to solution (i).

[Figure 2(i)] obtained either by dissolving solid *trans*-$[Os^V(tmc)(O)_2]ClO_4$ or by constant potential reduction of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ in MeCN containing 0.1 M $Bu^n{}_4NClO_4$ exhibits two vibronic structured absorption bands, A and B, centred at 335 and 410 nm respectively. The measured low $\varepsilon_{max.}$ values for band A and B indicate that they are d–d transitions. As in the case of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$,† bands A and B arise primarily from the spin-allowed (A) and spin-forbidden (B) $d_{xy} \rightarrow d_\pi^*$ ($d_\pi^* = d_{xz}, d_{yz}$) transitions. In the analogous *trans*-$[Ru^V(tmc)(O)_2]^+$,[5] the spin-forbidden $d_{xy} \rightarrow d_\pi^*$ transition is not detectable in solution, and this is understandable as the spin–orbit coupling constant of Ru is much less than that of Os.

Addition of a small drop of CF_3CO_2H to an acetonitrile solution of *trans*-$[Os^V(tmc)(O)_2]^+$ leads to immediate disappearance of the vibronic structured 335 nm band and concomitant formation of the vibronic structured 315 and 355 nm bands of *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ [Figure 2(ii)]. A similar u.v.–visible spectrum was obtained by dissolving solid *trans*-$[Os^V(tmc)(O)_2]ClO_4$ in 0.1 M $HClO_4$. It appears that H^+ induces the disproportionation of the Os^V–oxo complex, as observed in high-valent chemistry of ruthenium.[5]

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† U.v.–visible data for *trans*-$[Os^{VI}(tmc)(O)_2]^{2+}$ in MeCN: $\lambda_{max.}$ ($\varepsilon_{max.}$)/nm: 312(1260) and 355(343); these are vibronic structured d–d bands.

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4 See, *e.g.*, K. J. Takeuchi, G. J. Samuels, S. W. Gersten, J. A. Gilbert and T. J. Meyer, *Inorg. Chem.*, 1983, **22**, 1407.

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