

## Redox properties of tetraaza-macrocycles of iron, ruthenium and osmium

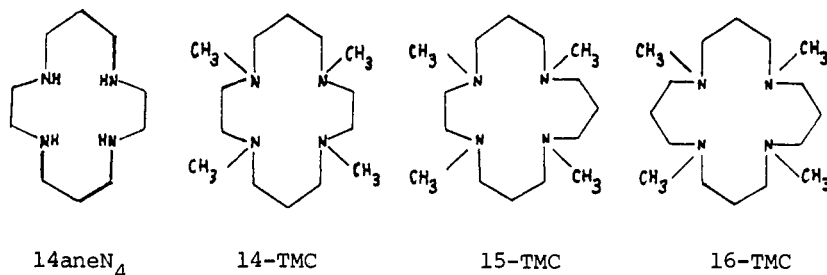
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**Abstract** - High-Valent ruthenium and osmium complexes are stabilized by macrocyclic tertiary amine ligands. The structures, properties and reactivities of some ruthenium(IV), (V) and (VI) oxo complexes of 14-TMC- (1,4,8,11-tetra-methyl-1,4,8,11-tetraazacyclotetradecane) and analogous 15- and 16-membered macrocycles are discussed. In acetonitrile, trans-[Ru<sup>VI</sup>(14-TMC)O<sub>2</sub>]<sup>2+</sup> undergoes a reversible one-electron reduction to trans-[Ru<sup>V</sup>(14-TMC)O<sub>2</sub>]<sup>+</sup> with E<sub>1/2</sub> value at -0.12 V (v.s. Cp<sub>2</sub>Fe<sup>+/0</sup>). In acidic solution, the electrochemical reduction of trans-[Ru<sup>VI</sup>(14-TMC)O<sub>2</sub>]<sup>2+</sup> to trans-[Ru<sup>IV</sup>(14-TMC)O(OH<sub>2</sub>)]<sup>2+</sup> is a reversible two-proton two-electron transfer process. Chemical reduction of trans-[Ru<sup>VI</sup>(14-TMC)O<sub>2</sub>]<sup>2+</sup> by cis-[Ru<sup>II</sup>(NH<sub>3</sub>)<sub>4</sub>(bpy)]<sup>2+</sup> (bpy = 2,2'-bipyridine) gives trans-[Ru<sup>IV</sup>(14-TMC)O<sub>2</sub>]<sup>+</sup>, which in the presence of H<sup>+</sup>, disproportionates into trans-[Ru<sup>V</sup>(14-TMC)O<sub>2</sub>]<sup>+</sup> and trans-[Ru<sup>IV</sup>(14-TMC)O(OH<sub>2</sub>)]<sup>2+</sup>.

### INTRODUCTION

High-valent metal-oxo complexes have long been intensively studied over the past decades (refs. 1 and 2). Classical oxidants, such as CrO<sub>3</sub> and MnO<sub>4</sub><sup>-</sup>, are often employed as oxidative catalysts in organic synthetic reactions, but their chemistry is still poorly understood. There is a clear need in establishing factors governing the reactivities of M=O complexes towards hydride abstraction and oxo-transfer reactions to facilitate the future design of chemo- and regio-selective oxidizing agents. The oxo complexes of iron family are of particular interest to us. Firstly, oxo-iron species has long been postulated as the active intermediate in the enzymatic reactions of cytochrome P-450, but its chemistry and also that of the ruthenium and osmium analogues are virtually unknown. Secondly, informations on the redox behaviour of Ru=O complexes are useful in understanding the chemistry and reactivities of RuO<sub>4</sub> and RuO<sub>2</sub>.XH<sub>2</sub>O (refs. 3 and 4), which have found useful applications in industrial processes. Macrocyclic tertiary amines, (L = 14-TMC, 15-TMC and 16-TMC) are known to stabilize transitional metal ions in unusual oxidation states (refs. 5 and 6). These ligands are chosen in our work because their metal complexes are stable towards demetallation. They have the additional advantage of being resistant towards oxidation and showing no low-energy charge-transfer bands in the UV-VIS region upon complexation to the metal ions. These complexes thus provide a better opportunity for the spectroscopic study of the electronic transitions from the M=O unit.



Structure of Tetraaza-macrocycles.

## DIHALOGENO MACROCYCLIC TERTIARY AMINE COMPLEXES OF RUTHENIUM(IV) AND OSMIUM(IV)

Although  $\text{trans-[M}^{\text{III}}(\text{14aneN}_4)\text{Cl}_2]^+$  complexes ( $M = \text{Fe, Ru and Os}$ ;  $\text{14aneN}_4 = 1,4,8,11\text{-tetra-azacyclotetradecane}$ ) undergo irreversible oxidation either chemically or electrochemically, electrochemical oxidation of  $\text{trans-[M}^{\text{III}}(\text{L})\text{X}_2]^+$  ( $M = \text{Ru, Os}$ ;  $\text{L} = 14\text{-TMC, 15-TMC and 16-TMC}$ ;  $\text{X} = \text{Cl, Br}$ ) to  $\text{trans-[M}^{\text{IV}}(\text{L})\text{X}_2]^{2+}$  has been found to be a simple and reversible one-electron transfer process (refs. 7 and 8). Some typical cyclic voltammograms of  $\text{trans-[Ru(16-TMC)-Cl}_2]^+$  and  $\text{trans-[Os(16-TMC)Cl}_2]^+$  in  $\text{CH}_3\text{CN}$  are given in Fig. 1. The electrochemically generated  $\text{trans-[M}^{\text{IV}}(\text{16-TMC)Cl}_2]^{2+}$  complexes have been characterized spectroscopically with  $p_\pi \rightarrow d_\pi(M)$  transitions at 410 and 365 nm for  $M = \text{Ru and Os}$  respectively (refs. 7 and 8). The  $\text{trans-[M}^{\text{IV}}(\text{16-TMC)Cl}_2]^{2+}$  species can also be quantitatively reduced back to the corresponding  $M(\text{III})$  complex by chemical means (for example, with  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ). Table 1 summarizes the  $E_{1/2}$  values of some  $M(\text{IV})/M(\text{III})$  couples of ruthenium and osmium tertiary amine complexes.  $\text{Trans-[Ru}^{\text{IV}}(\text{L})\text{Cl}_2]^{2+}$  complexes are usually more oxidizing than their osmium analogues by  $\sim 430$  mV, in agreement with a lower ionization potential of the osmium system. The generation of stable  $\text{Ru(IV)}$  and  $\text{Os(IV)}$  complexes containing no oxo ligand and having redox potentials as high as 1.23 V (v.s. ferrocene/ferrocenium couple,  $\text{Cp}_2\text{Fe}^{+/0}$ ) demonstrates the unusual structural feature of macrocyclic tertiary amines in the stabilization of highly oxidizing metal complexes.

TABLE 1.  $E_{1/2}$  values of some  $M(\text{IV})/M(\text{III})$  couples in acetonitrile

Complex	$E_{1/2}$ (v.s. $\text{Cp}_2\text{Fe}^{+/0}$ )
$\text{trans-[Os(16-TMC)Cl}_2]^+$	0.67
$\text{trans-[Ru(14-TMC)Cl}_2]^+$	1.21
$\text{trans-[Ru(15-TMC)Cl}_2]^+$	1.21
$\text{trans-[Ru(16-TMC)Cl}_2]^+$	1.22
$\text{trans-[Ru(14-TMC)Br}_2]^+$	1.23
$\text{trans-[Ru(15-TMC)Br}_2]^+$	1.18
$\text{trans-[Ru(14-TMC)(NCO)}_2]^+$	1.13

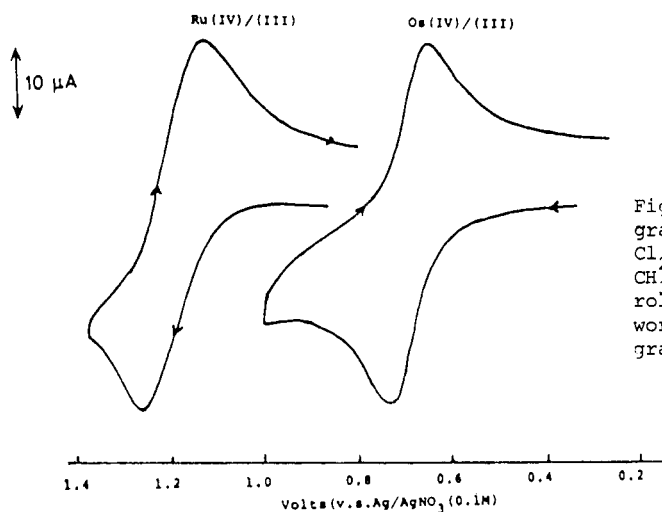
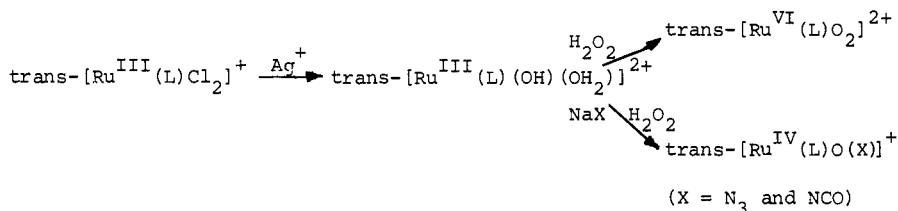
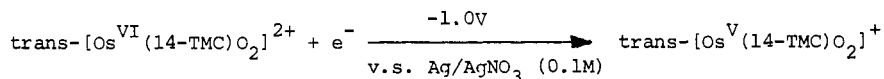
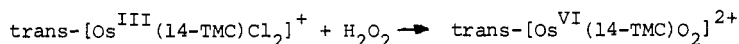
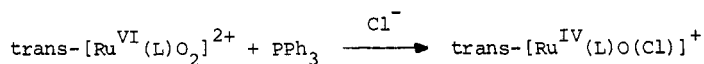
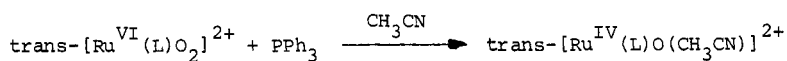
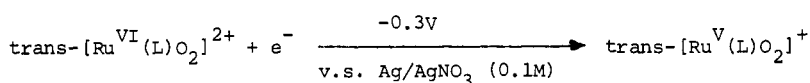


Fig. 1. Cyclic Voltammograms of  $\text{trans-[M(16-TMC)-Cl}_2]^+$  ( $M = \text{Ru and Os}$ ) in  $\text{CH}_3\text{CN}$ . Supporting electrolyte,  $0.1 \text{ M [Bu}_4\text{N]ClO}_4$ ; working electrode, pyrolytic graphite; scan rate,  $50\text{mVs}^{-1}$ .

## SYNTHESIS AND PROPERTIES OF RUTHENIUM AND OSMIUM OXO COMPLEXES OF MACROCYCLIC TERTIARY AMINES

The generalized synthetic methods leading to ruthenium and osmium oxo complexes of macrocyclic tertiary amines ( $\text{L} = 14\text{-TMC, 15-TMC and 16-TMC}$ ) are outlined as follows (refs. 7 - 13).





The stretching frequencies  $[\nu(\text{Ru}=\text{O})]$ , bond distances  $[\text{d}(\text{Ru}=\text{O})]$  and magnetic properties ( $\mu_{\text{eff}}$ ) of some ruthenium-TMC-oxo complexes are compiled in Table 2 (ref. 8). It is obvious from Table 2 that  $\text{Ru}^{\text{VI}}=\text{O}$  bond is stronger than the corresponding  $\text{Ru}^{\text{IV}}=\text{O}$  bond which is consistent with the ground state electron configurations of these species, viz.  $\text{Ru}^{\text{VI}}$ -dioxo ( $d_{xy}^2$ ),  $\text{Ru}^{\text{V}}$ -dioxo ( $d_{xy}^2(d_{xz}^* d_{yz}^*)^1$ ) and  $\text{Ru}^{\text{IV}}$ -monooxo ( $d_{xy}^2(d_{xz}^*)^1(d_{yz}^*)^1$ ) as predicted by the simplified molecular orbital diagram of Gray and coworkers (ref. 14). In any case, these  $\text{Ru}=\text{O}$  bonds are all in the range 1.70–1.765 Å indicating that they are short and strong. Experimentally, these Ru-TMC-oxo complexes are relatively unreactive towards C=C bond but are selective reagents for the oxidation of alcohol and activated C-H bonds. Selectivity has been observed for the reaction between the  $\text{trans-}[\text{Ru}^{\text{VI}}(14\text{-TMC})\text{O}_2](\text{PF}_6)_2$  and cyclohexene where cyclohexenone was found to be the only reaction product.

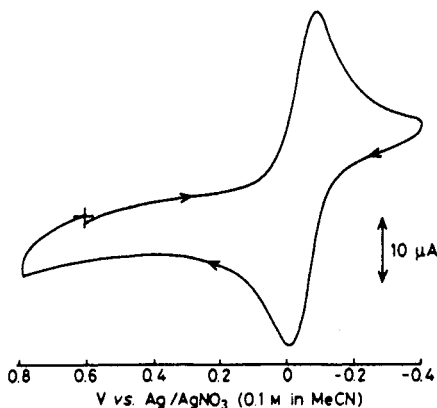
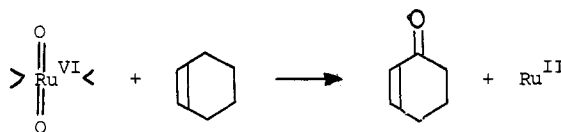


Fig. 2. Cyclic voltammogram of  $\text{trans-}[\text{Ru}^{\text{VI}}(14\text{-TMC})\text{O}_2](\text{ClO}_4)_2$  in  $\text{CH}_3\text{CN}$  - Supporting electrolyte, 0.1 M  $[\text{Bu}_4\text{N}]\text{ClO}_4$ ; working electrode, pyrolytic graphite; scan rate,  $50\text{mVs}^{-1}$ .

TABLE 2. A summary of magnetic moments,  $\text{Ru}=\text{O}$  bond distances and  $\nu(\text{Ru}=\text{O})$  stretching frequencies of some ruthenium-TMC-oxo complexes

Complex	$\text{d}(\text{Ru}=\text{O})$ (Å)	$\nu(\text{Ru}=\text{O})$ ( $\text{cm}^{-1}$ )	$\mu_{\text{eff}}$ (B.M.) at 25°C
$\text{Trans-}[\text{Ru}^{\text{VI}}(14\text{-TMC})\text{O}_2](\text{ClO}_4)_2$	-	850	0.00
$\text{Trans-}[\text{Ru}^{\text{VI}}(15\text{-TMC})\text{O}_2](\text{ClO}_4)_2$	1.718(5)	855	0.00
$\text{Trans-}[\text{Ru}^{\text{VI}}(16\text{-TMC})\text{O}_2](\text{ClO}_4)_2$	1.705(7)	860	0.00
$\text{Trans-}[\text{Ru}^{\text{V}}(14\text{-TMC})\text{O}_2]\text{ClO}_4$	-	840-860	1.94
$\text{Trans-}[\text{Ru}^{\text{IV}}(14\text{-TMC})\text{O}(\text{CH}_3\text{CN})](\text{PF}_6)_2$	1.765(5)	~815	2.93
$\text{Trans-}[\text{Ru}^{\text{IV}}(14\text{-TMC})\text{O}(\text{Cl})](\text{ClO}_4)$	1.765(5)	~815	2.80
$\text{Trans-}[\text{Ru}^{\text{IV}}(14\text{-TMC})\text{O}(\text{NCO})](\text{ClO}_4)$	1.765(5)	~815	2.70
$\text{Trans-}[\text{Ru}^{\text{IV}}(14\text{-TMC})\text{O}(\text{N}_3)](\text{ClO}_4)$	1.765(5)	~815	2.66
$\text{Trans-}[\text{Ru}^{\text{IV}}(15\text{-TMC})\text{O}(\text{CH}_3\text{CN})](\text{ClO}_4)_2$	-	~820	2.80
$\text{Trans-}[\text{Ru}^{\text{IV}}(15\text{-TMC})\text{O}(\text{Cl})](\text{ClO}_4)$	-	~820	2.70
$\text{Trans-}[\text{Ru}^{\text{IV}}(15\text{-TMC})\text{O}(\text{N}_3)](\text{ClO}_4)$	-	~820	2.70

## REDOX PROPERTIES OF RUTHENIUM AND OSMIUM OXO COMPLEXES OF MACROCYCLIC TERTIARY AMINES

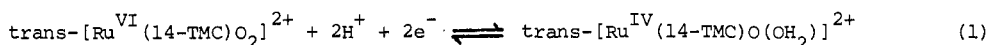
The electrochemical reductions of trans-dioxoruthenium(VI) complexes have been found to be solvent dependent. In aprotic medium, the redox interconversion between  $\text{trans-}[\text{Ru}^{\text{VI}}(\text{L})\text{O}_2]^{2+}$  ( $\text{L} = 14\text{-TMC}, 15\text{-TMC}$  and  $16\text{-TMC}$ ) and  $\text{trans-}[\text{Ru}^{\text{V}}(\text{L})\text{O}_2]^{+}$  is a simple one-electron reversible process, as exemplified by the cyclic voltammogram of  $\text{trans-}[\text{Ru}^{\text{VI}}(14\text{-TMC})\text{O}_2]^{2+}$  in  $\text{CH}_3\text{CN}$  (Fig. 2). This behaviour is insensitive to the nature of electrode surfaces. The reduction

TABLE 3.  $E_{1/2}$  values of some Ru-TMC-oxo complexes

Complex	$E_{1/2}$ values	
	Ru(VI)/Ru(V) couple in $\text{CH}_3\text{CN}$ (V v.s. $\text{Cp}_2\text{Fe}^+/\text{O}$ )	Ru(VI)/Ru(IV) couple (a) in aqueous solution at $\text{pH} = 1.1$ (V v.s. S.C.E.)
$\text{trans-}[\text{Ru}^{\text{VI}}(\text{14-TMC})\text{O}_2]^{2+}$	-0.12	0.66
$\text{trans-}[\text{Ru}^{\text{VI}}(\text{15-TMC})\text{O}_2]^{2+}$	-0.11	0.65
$\text{trans-}[\text{Ru}^{\text{VI}}(\text{16-TMC})\text{O}_2]^{2+}$	-0.09	0.66

(a) Electrode reaction:  $\text{trans-}[\text{Ru}^{\text{VI}}(\text{L})\text{O}_2]^{2+} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{trans-}[\text{Ru}^{\text{IV}}(\text{L})\text{O}(\text{OH}_2)]^{2+}$

potentials of  $\text{trans-}[\text{Ru}^{\text{VI}}(\text{L})\text{O}_2]^{2+}$  complexes are summarized in Table 3. The  $E_{1/2}$  values appear to be insensitive to the hole size of these macrocycles (14-TMC v.s. 16-TMC). The cyclic voltammograms of  $\text{trans-}[\text{Ru}^{\text{VI}}(\text{14-TMC})\text{O}_2]^{2+}$  in aqueous solutions at  $\text{pH}=1.1$  and  $11.0$  are given in Fig. 3a and 3b respectively. At  $\text{pH} = 1.0-7.6$ , the reduction of  $\text{trans-}[\text{Ru}^{\text{VI}}(\text{14-TMC})\text{O}_2]^{2+}$  to  $\text{trans-}[\text{Ru}^{\text{IV}}(\text{14-TMC})\text{O}(\text{OH}_2)]^{2+}$  is a reversible two-electron transfer process,



At higher  $\text{pH}$  ( $>7.6$ ), this Ru(VI)/Ru(IV) couple splits into two one-electron redox couples, corresponding to the following electrode reactions,

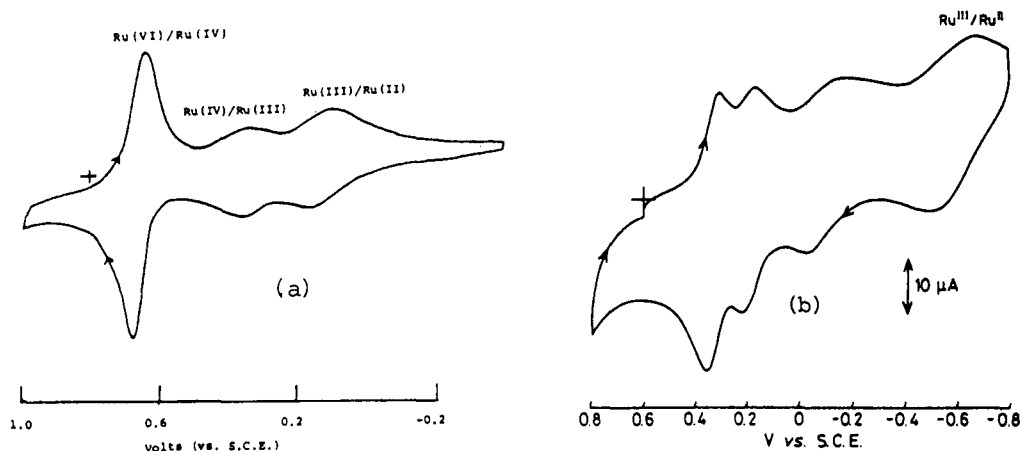
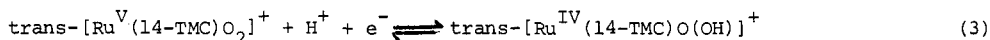
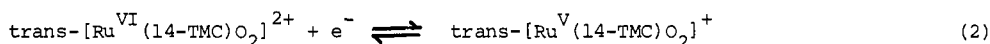


Fig. 3. Cyclic voltammograms of  $\text{trans-}[\text{Ru}^{\text{VI}}(\text{14-TMC})\text{O}_2][\text{ClO}_4]_2$  in aqueous solution at  $\text{pH} = 1.1$ (a) and  $10.0$ (b). Working electrode, basal plane pyrolytic graphite; scan rate,  $50\text{mVs}^{-1}$ .

As expected, the  $E_{1/2}$  of reactions (1) and (3) decrease by 60 mV per unit increase in  $\text{pH}$  whereas for reaction (2), it is independent of  $\text{pH}$ . The plots of  $E_{1/2}$  values versus  $\text{pH}$  for these various couples of  $\text{trans-}[\text{Ru}^{\text{VI}}(\text{14-TMC})\text{O}_2]^{2+}$  are shown in Fig. 4.

Unlike the Ru(VI)/Ru(V) couple in acetonitrile, the nature of electrode surfaces has a profound effect on reversibility of the Ru(VI)/Ru(IV) couple. Reversible/quasi-reversible reactions between  $\text{trans-}[\text{Ru}^{\text{VI}}(\text{14-TMC})\text{O}_2]^{2+}$  and  $\text{trans-}[\text{Ru}^{\text{IV}}(\text{14-TMC})\text{O}(\text{OH}_2)]^{2+}$  were observed only with edge-plane and basal plane pyrolytic graphite but not with glassy carbon and platinum electrodes.

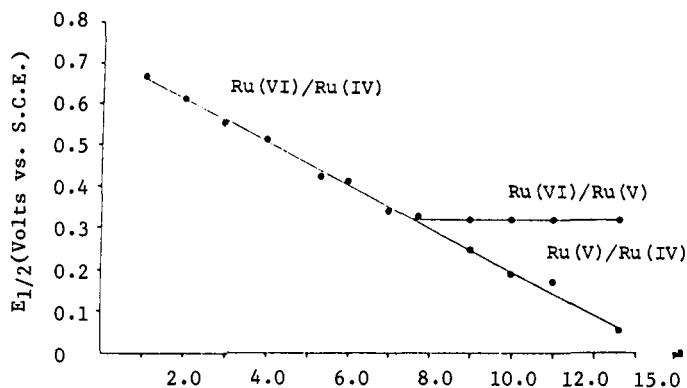


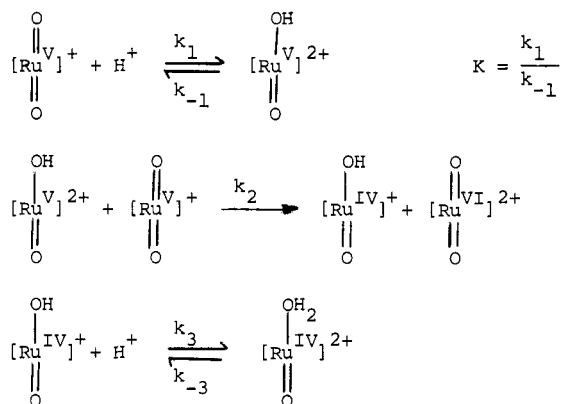
Fig. 4. The plots of  $E_{1/2}$  values versus pH for Ru(VI)/Ru(IV), Ru(VI)/Ru(V) and Ru(V)/Ru(IV) couples.

Anson and co-workers (ref. 15) recently found that the reversibility of Ru=O/Ru-OH<sub>2</sub> couple increases through the use of quinone modified electrode. These workers argued that the presence of phenolic groups on the electrode surface should facilitate the acid catalysed interconversion between Ru=O and Ru-OH<sub>2</sub> complexes.

The mechanism for the acid-catalysed two-electron reduction of trans-[Ru<sup>VI</sup>(14-TMC)O<sub>2</sub>]<sup>2+</sup> to trans-[Ru<sup>IV</sup>(14-TMC)O(OH<sub>2</sub>)]<sup>2+</sup> has also been investigated. At pH = 1-7, the rate of reduction of trans-[Ru<sup>VI</sup>(14-TMC)O<sub>2</sub>]<sup>2+</sup> by a one-electron reductant, cis-[Ru<sup>II</sup>(NH<sub>3</sub>)<sub>4</sub>(bpy)]<sup>2+</sup> (bpy = 2,3'-bipyridine) is independent of pH (ref. 16). This seems to suggest that trans-[Ru<sup>VI</sup>(14-TMC)O<sub>2</sub>]<sup>2+</sup> remains predominantly in the deprotonated form even in acid solutions with an unfavourable equilibrium constant for the following reaction,

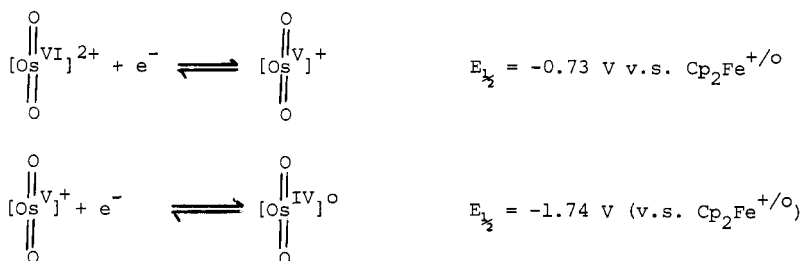


The reduced product, trans-[Ru<sup>V</sup>(14-TMC)O<sub>2</sub>]<sup>+</sup>, has been found to undergo rapid disproportionation probably through the following pathways,

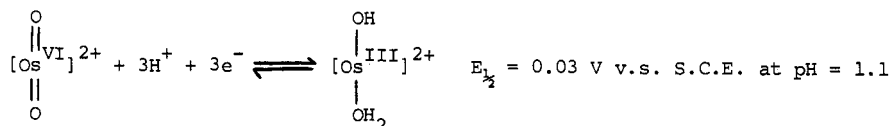


The rate of disproportionation has been found to obey the following rate law. Rate =  $k_{\text{obs}}[\text{Ru(V)}]^2$  with  $k_{\text{obs}} = k_2K[\text{H}^+]/(1+K[\text{H}^+])^2$  where  $k_2$  and  $K$  are  $2.69 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$  and 665(15) respectively at 25°C and 0.1 M ionic strength (ref. 16).

The redox chemistry of trans-[Os<sup>VI</sup>(14-TMC)O<sub>2</sub>]<sup>2+</sup> is similar to its ruthenium analogue (ref. 12). In acetonitrile, the electrochemical reductions of Os(VI) to Os(V) and Os(V) to Os(IV) are simple one-electron reversible process (red. 17).



In aqueous medium, the electrochemical reduction of trans-[Os<sup>VI</sup>(14-TMC)O<sub>2</sub>]<sup>2+</sup> to trans-[Os<sup>III</sup>(14-TMC)(OH)(OH<sub>2</sub>)]<sup>2+</sup> at pyrolytic graphite is a reversible (i<sub>pa</sub>/i<sub>pc</sub><sup>-1</sup>, ΔE<sub>p</sub> = 20-30 mV) three-proton three-electron transfer process,



The trans-[Os<sup>V</sup>(14-TMC)O<sub>2</sub>]ClO<sub>4</sub> complex, which is the intermediate in the acid-catalysed three-electron reduction of Os(VI) to Os(III), has been isolated and found to undergo rapid disproportionation in acidic solutions.

The redox chemistry of iron-oxo complexes still remains unknown. Given that the reduction potentials of trans-dioxoruthenium(VI) system can be tuned down to 0.66 V (v.s. S.C.E.) with the use macrocyclic tertiary amine ligands, it is anticipated that thermodynamically stable oxo-iron complexes can be obtained with the appropriate choice of ligands. The problem on the synthetic chemistry of iron-oxo complexes probability lies on the instability of the iron compounds toward demetallation. Recent work by Grove and co-workers (refs. 18 and 19) on [Fe<sup>IV</sup>(TMP)O] (H<sub>4</sub>TMP = tetramesitylporphyrin) showed that the oxidation chemistry of oxo-iron species could be as rich as its ruthenium and osmium analogues.

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