Macrocyclic amine complexes of iron, ruthenium and osmium

Chi-Ming Che and Chung-Kwong Poon

Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

Abstract – High-Valent ruthenium and osmium complexes are stabilized by macrocyclic tertiary amine ligands. The structures, properties and reactivities of some ruthenium(VI) and osmium(VI) oxo complexes of 14-TMC(1,4,8,11-tetra-methyl-1,4,8,11-tetraazacyclotetradecane) are described. In aqueous solutions with pH>8, trans-$[Ru^{VI}(14\text{-}TMC)O_2]^{2+}$ and trans-$[Os^{VI}(14\text{-}MTC)O_2]^{2+}$ undergo a reversible one-electron reduction to trans-$[Ru^{V}(14\text{-}TMC)O_2]^{+}$ and trans-$[Os^{V}(14\text{-}TMC)O_2]^{+}$ with $E_{\frac{1}{2}}$ values at 0.33V and -0.23V v.s. S.C.E. respectively. In acidic solution, the electrochemical reduction of trans-$[Os^{VI}(14\text{-}TMC)O_2]^{2+}$ is a reversible three-electron three-proton transfer process. Trans-$[Ru^{VI}(14\text{-}TMC)O_2][ClO_4]_2$ does not react with norbornene or styrene in acetonitrile even at 50°C but selectively oxidizes allylic and benzylic C-H bonds.

The syntheses of Iron, Ruthenium and Osmium with a series of quadridentate macrocyclic amines are described. The iron(III) complexes, trans-$[Fe(L)Cl_2]^{+}$ [L = 1,4,8,11-tetraazacyclotetradecane (14aneN$_4$) and its 15-membered analogue, 15aneN$_4$] were prepared by aerial oxidation of methanolic solutions of FeCl$_2$ and the amines (ref. 1). Reactions of trans-$[Fe(14aneN_4)Cl_2]^{+}$ and NaX (X = Br and SCN) in methanol yielded trans-$[Fe(14aneN_4)X_2]^{+}$. These species are high-spin (μ_{eff} = 2.35 to 3.90 B.M.), substitutionally labile and easily undergo demetallation upon dissolution in protic solvents (ref. 2). The electrochemical oxidation of trans-$[Fe(L)X_2]^{+}$ in acetonitrile is completely irreversible. All attempts to prepare iron(III) and high-valent iron complexes of saturated macrocyclic tertiary amines such as 14-TMC and 15-TMC (1,4,8,11-tetra-methyl-1,4,8,11-tetraazacyclotetradecane and its 15-membered analogue respectively) were unsuccessful.
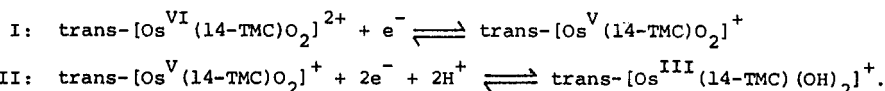
Macrocyclic tertiary amine ligands, 14-TMC, 15-TMC, and 16-TMC were prepared by N-methylation of the corresponding secondary cyclic amines with a mixture of formic acid and formaldehyde (ref. 3). Trans-$[Os^{III}(L)Cl_2]^{+}$ complexes (L = 14aneN$_4$, 14-TMC, 15aneN$_4$, 15-TMC, 16aneN$_4$ and

14aneN$_4$ ' 14-TMC   15-TMC   ' 16-TMC
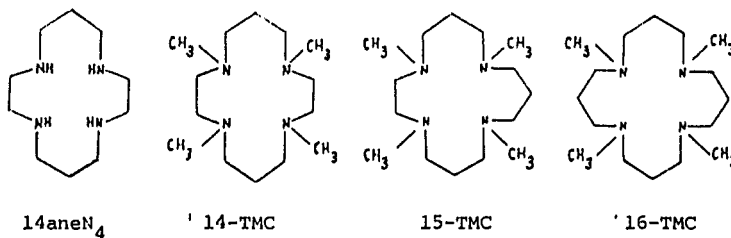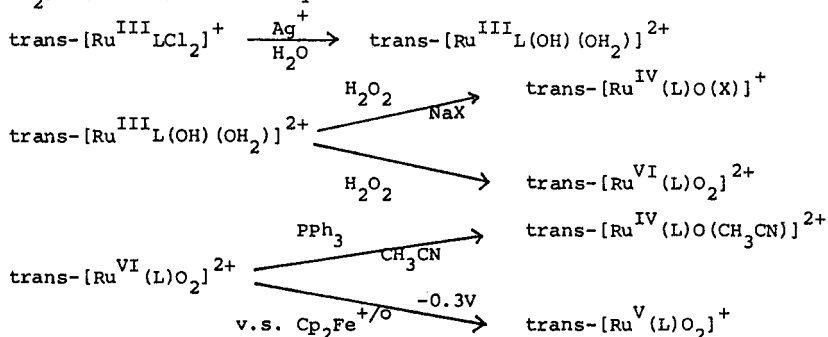
Structure of Tetraaza-macrocycles.

16-TMC) were prepared by refluxing ethanolic solutions of Na$_2$[OsCl$_6$] and L in the presence of tin plates for 24h (ref. 3). Oxidation of trans-$[Os^{III}(n\text{-}TMC)Cl_2]^{+}$ (n = 14,15, or 16) with H$_2$O$_2$ in water gave the corresponding trans-$[Os^{VI}(n\text{-}TMC)O_2]^{2+}$ (ref. 4). These trans-dioxoosmium(VI) complexes exhibit an intense i.r. stretch, $\nu(\dot{O}sO_2)$, at $\sim$870 cm^{-1} and show vibronic structured spin-allowed and spin-forbidden $(d_{xy})^2 \rightarrow (d_{xy})^1(d_{\pi}^*)^1$ $(d_{\pi}^* = d_{xz}, d_{yz})$ transitions at 300 and 350 nm respectively (ref. 4). They are non-oxidizing and do not react with benzyl alcohol or styrene even at 70°C. However, refluxing an acetonitrile solution of trans-$[Os(14\text{-}TMC)O_2]^{2+}$ with excess PPh$_3$ for 24h yielded trans-$[Os^{II}(14\text{-}TMC)(CH_3CN)_2]^{2+}$ and O=PPh$_3$ in high yield (over 70%). Attempts to isolated Os(IV)=O complexes of n-TMC have not been successful. In general, the osmium macrocyclic amine complexes are inert towards ligand exchange reactions. For example, no detectable substitution reaction between trans-$[Os^{III}(14aneN_4)Cl_2]^{+}$ and NaBr was found even upon heating the solution at 80°C for 2h. Novel trans-dichloroosmium(IV) of macrocyclic tertiary amines were prepared by electrochemical oxidation of trans-$[Os(n\text{-}TMC)Cl_2]^{+}$ (n = 14, 15 or 16)

in acetonitrile (ref. 3). Unlike the case of trans-$[Os^{IV}(NH_3)_4Cl_2]^{2+}$ which undergoes rapid disproportionation reaction in aqueous solution (ref. 5) electrochemical oxidation of trans-$[Os^{III}(16-TMC)Cl_2]^+$ to trans-$[Os^{IV}(16-TMC)Cl_2]^{2+}$ in aqueous solutions at pH = 1.1 and 7.0 is reversible ($E_{\frac{1}{2}}$ = 0.81V v.s. N.H.E. at pH = 1.1, ΔE_p = 60-70mV and $i_{pc}/i_{pa} \approx 1$). Trans-$[Os^{IV}(16-TMC)Cl_2]^{2+}$ has been characterized spectroscopically (Fig. 1). The 365nm band in Fig. 1 is attributed to LMCT transition, $p_\pi(Cl) \to d_\pi[Os(IV)]$, which is red-shifted from trans-$[Os^{III}(16-TMC)Cl_2]^+$ (304nm) (ref. 3). In aqueous solutions at pH = 1.1-6, the cyclic voltammogram (Fig. 2) of trans-$[Os^{VI}(14-TMC)O_2]^{2+}$ showed a reversible three-electron redox wave, corresponding to the reduction of trans-$[Os^{VI}(14-TMC)O_2]^{2+}$ to trans-$[Os^{III}(14-TMC)(OH)-(OH_2)]^{2+}$. At pH = 1.1, the $E_{\frac{1}{2}}$ value of the Os(VI)/Os(III) couple is 0.035V v.s. S.C.E. indicating that trans-$[Os^{VI}(14-TMC)O_2]^{2+}$ is not a strong oxidizing agent. At pH>7, the Os(VI)/Os(III) couple splits into two waves, I and II (Fig. 3), attributed to the following electrode reactions,
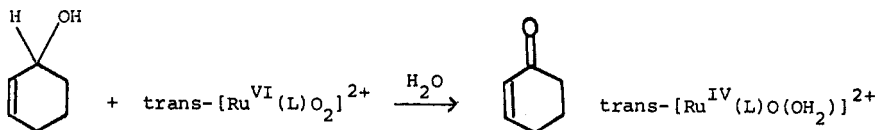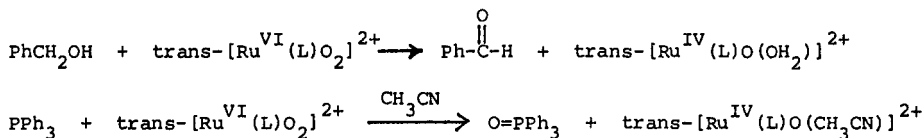
I: trans-$[Os^{VI}(14-TMC)O_2]^{2+}$ + e^- $\rightleftharpoons$ trans-$[Os^{V}(14-TMC)O_2]^+$

II: trans-$[Os^{V}(14-TMC)O_2]^+$ + $2e^-$ + $2H^+$ $\rightleftharpoons$ trans-$[Os^{III}(14-TMC)(OH)_2]^+$.

As expected, the $E_{\frac{1}{2}}$ value for the Os(VI)/Os(V) couple(I) at -0.23V v.s. S.C.E., is pH independent. The reversible redox interconversion between trans-$[Os^{V}(14-TMC)O_2]^+$ and trans-$[Os^{III}(14-TMC)(OH)_2]^+$ in alkaline solution is a two-proton two-electron transfer process, suggesting that the intermediate Os(IV)-oxo species is unstable and undergoes rapid disproportionation in water. Trans-$[Os^{V}(14-TMC)O_2]^+$ was prepared by electrochemical reduction of trans-$[Os^{VI}(14-TMC)O_2]^{2+}$ in acetonitrile; its optical absorption spectrum is shown in Fig. 4 in (ref. 6). Surprisingly, both trans-$[Os^{V}(14-TMC)O_2]^+$ and trans-$[Os^{III}-(14-TMC)(OH)(OH_2)]^{2+}$ were rapidly oxidized by air to trans-dioxoosmium(VI) species in acidic solutions. The inherent stability of the osmium complexes towards ligand exchange reactions or demetallation is in contrast to the iron system. Furthermore, the inability of the oxo-osmium macrocyclic tertiary amine complexes to participate in organic substrate oxidations seems to indicate that this class of complexes may not be useful in the future study of homogeneous catalysis of organic oxidation reactions.

Ruthenium-oxo complexes of L (n-TMC, n = 14, 15 or 16) were synthesized from trans-$[Ru^{III}L-Cl_2]^+$ (ref. 7) via the aquo intermediate as follow:

trans-$[Ru^{III}LCl_2]^+$ $\xrightarrow[H_2O]{Ag^+}$ trans-$[Ru^{III}L(OH)(OH_2)]^{2+}$

trans-$[Ru^{III}L(OH)(OH_2)]^{2+}$ $\xrightarrow[\text{NaX}]{H_2O_2}$ trans-$[Ru^{IV}(L)O(X)]^+$

$\xrightarrow{H_2O_2}$ trans-$[Ru^{VI}(L)O_2]^{2+}$

trans-$[Ru^{VI}(L)O_2]^{2+}$ $\xrightarrow[CH_3CN]{PPh_3}$ trans-$[Ru^{IV}(L)O(CH_3CN)]^{2+}$

$\xrightarrow[\text{v.s. } Cp_2Fe^{+/o}]{-0.3V}$ trans-$[Ru^{V}(L)O_2]^+$

These dioxoruthenium(VI) complexes are yellow solids. They are air stable, diamagnetic and have a short metal-oxo bonds. The d(Ru=O) distances, as determined by X-ray crystallography, lie between 1.70-1.71 Å (ref. 8). They are strong oxidants and easily undergo two-electron oxidation reactions in aqueous solutions, as illustrated by the following examples,

$PhCH_2OH$ + trans-$[Ru^{VI}(L)O_2]^{2+}$ $\longrightarrow$ $Ph\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H$ + trans-$[Ru^{IV}(L)O(OH_2)]^{2+}$

PPh_3 + trans-$[Ru^{VI}(L)O_2]^{2+}$ $\xrightarrow{CH_3CN}$ $O=PPh_3$ + trans-$[Ru^{IV}(L)O(CH_3CN)]^{2+}$

[cyclohexenol structure] + trans-$[Ru^{VI}(L)O_2]^{2+}$ $\xrightarrow{H_2O}$ [cyclohexenone structure] trans-$[Ru^{IV}(L)O(OH_2)]^{2+}$

However, they are poor epoxidation reagents since they do not seem to react with norbornene or styrene in acetonitrile even at 50°C. The strong Ru=O bonds found in trans-dioxo-ruthenium(VI) complexes suggest that this species favour hydride/hydrogen atom abstraction rather than oxo-transfer reactions. The observations that trans-$[Ru^{VI}(14-TMC)O_2]^{2+}$ reacted with cyclohexene to give cyclohexenone as the only product and oxidized toluene to give benzaldehyde are in agreement with this deliberation.
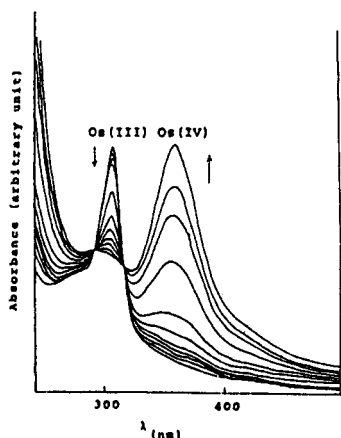
Figure 1. Optical spectral changes for the electrochemical oxidation of trans-$[Os^{III}(16\text{-}TMC)Cl_2]^+$ to trans-$[Os^{IV}(16\text{-}TMC)Cl_2]^{2+}$ in acetonitrile.
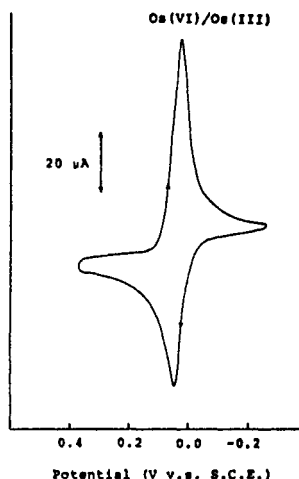
Figure 2. Cyclic voltammogram of trans-$[Os^{VI}(14\text{-}TMC)O_2]^{2+}$ in 0.1 M CF_3SO_3H, pH = 1.1. Working electrode, pyrolytic graphite; scan rate, 50 mVs^{-1}.
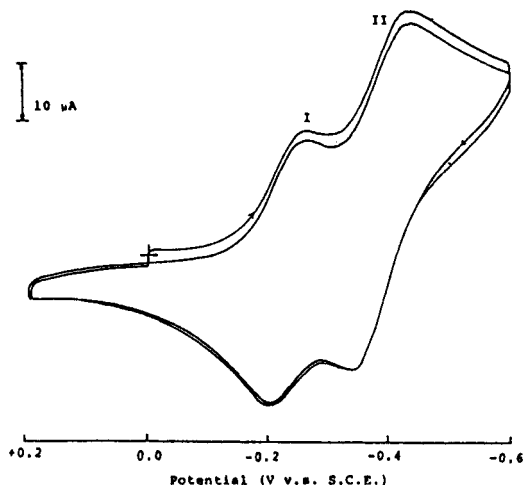
Figure 3. Cyclic voltammogram of trans-$[Os^{VI}(14\text{-}TMC)O_2]^{2+}$ in aqueous solution at pH = 10. Working electrode, pyrolytic graphite; scan rate, 50 mVs^{-1}.
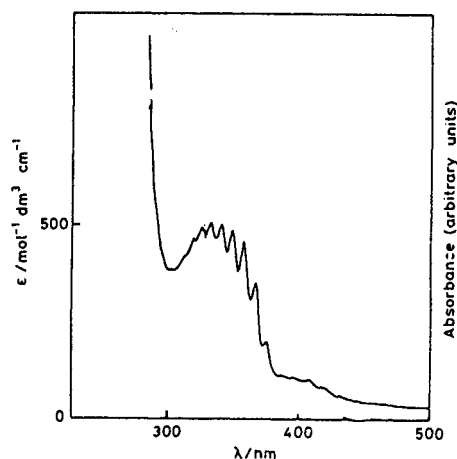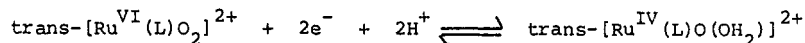

Figure 4. Optical spectrum of trans-$[Os^V(14\text{-}TMC)O_2]^+$ in acetonitrile.

In acidic solutions, the electrochemical reduction of trans-$[Ru^{VI}(L)O_2]^{2+}$ to trans-$[Ru^{IV}(L)\text{-}O(OH_2)]^{2+}$ is a reversible two-electron two-proton transfer reaction,

$$\text{trans-}[Ru^{VI}(L)O_2]^{2+} + 2e^- + 2H^+ \rightleftharpoons \text{trans-}[Ru^{IV}(L)O(OH_2)]^{2+}$$

At pH = 1.1, the $E_{\frac{1}{2}}$ values of the Ru(VI)/Ru(IV) couples lie between 0.66-0.67V v.s. S.C.E. (ref. 7). Thus trans-dioxoruthenium(VI) system is ∿630mV more oxidizing than its osmium analogue.

The Ru(IV)-oxo-tertiary amine complexes, which have a weaker Ru=O bond than trans-$[Ru^{VI}(L)\text{-}O_2]^{2+}$ complexes [d(Ru=O) for trans-$[Ru^{IV}(L)O(X)]^{n+}$ is 1.765 Å, being independent of the nature of axial ligand X], are milder oxidants (ref. 8). The oxidation of benzyl alcohol to benzaldehyde by trans-$[Ru^{IV}(L)O(X)]^{n+}$ required high temperature (e.g. 50°C) and they did not react with PPh_3 in acetonitrile at room temperature. However, they can be oxidized electrochemically and reversibly to mono-oxoruthenium(V) complexes in acetonitrile, (X = Cl,

$$\text{trans-}[Ru^{IV}(L)O(X)]^+ - e^- \rightleftharpoons \text{trans-}[Ru^V(L)O(X)]^{2+}$$
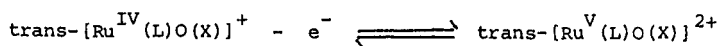
NCO & N_3). Typical cyclic voltammograms of trans-$[Ru^{IV}(14\text{-}TMC)O(NCO)]^+$ in acetonitrile and in the absence and presence of benzyl alcohol are shown in Fig. 5.
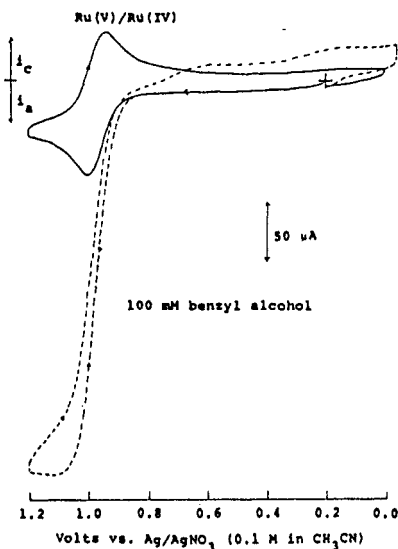
Figure 5. Cyclic voltammograms of trans-[Ru^{IV}(14-TMC)O(NCO)]$^+$ in acetonitrile in the presence and absence of benzyl alcohol. Working electrode, pyrolytic graphite; scan rate, 50 mVs^{-1}.

The $E_{\frac{1}{2}}$ values of trans-[Ru^V(14-TMC)O(X)]$^{2+}$ complexes in acetonitrile are 1.10, 0.89, 0.72V v.s. Cp$_2$Fe$^{+/0}$ for X = Cl, NCO and N$_3$ respectively. These Ru(V)-oxo complexes are active oxidants for the oxidation of benzyl alcohol as evident by the presence of large catalytic oxidative current shown in Fig. 5. The rate constants decrease in the same pattern as the formal reduction potentials. The second order rate constants are 2.1 x 10^2 and 1.4 x 10^2 M^{-1} s^{-1} for X = Cl and NCO respectively (ref. 9).

Strongly oxidizing trans-[Ru^{IV}(L)Cl$_2$]$^{2+}$ complexes (with $E_{\frac{1}{2}}$ values of 1.0-1.10V v.s. Cp$_2$Fe$^{+/0}$) could also be generated by electrochemical oxidation of trans-[Ru^{III}(L)Cl$_2$]$^+$ in acetonitrile (ref. 10). The reactivities of these Ru(IV) complexes in the oxidation of benzyl alcohol lie between Ru(IV)-oxo and Ru(V)-oxo complexes. The trans-[Ru^{VI}(L)O$_2$]$^{2+}$ complexes were found to catalyse the aerobic oxidation of benzyl alcohol at room temperature. However, the observed turn-over efficiency of the present Ru-oxo system is low (turn over number ∿3 for 24 h. reaction at 25°C).

CONCLUSION

The ruthenium-oxo complexes are in general more stable than the oxo-iron species but more oxidizing than the corresponding osmium analogues. The availability of oxo-ruthenium complexes with the central ruthenium ion in oxidation states IV, V and VI allows a more systematic study of electronic effects on the reactivies of metal-oxo complexes.

Acknowledgement

REFERENCES

1. P.K. Chan; C.K. Poon, J. Chem. Soc. Dalton Trans., 858-862 (1976).
2. C.K. Poon; A.W.M. To, Inorg. Chem., 18, 1277-1283 (1979).
3. C.M. Che, W.K. Cheng, T.F. Lai, C.K. Poon and T.C.W. Mak, Inorg. Chem., 26, 1678-1683 (1987).
4. C.M. Che; W.K. Cheng, J. Am. Chem. Soc., 108, 4644-4645 (1986).
5. J.D. Buhr; J.R. Winkler; H. Taube, Inorg. Chem., 19, 2416-2425 (1980).
6. C.M. Che; W.K. Cheng, J. Chem. Soc. Chem. Comm., 1519-1521 (1986).
7. C.M. Che; K.Y. Wong; C.K. Poon, Inorg. Chem., 24, 1797-1800 (1985).
8. C.M. Che; T.F. Lai; K.Y. Wong, Inorg. Chem., 26, 2289-2299 (1987).
9. K.Y. Wong; C.M. Che; F.C. Anson, Inorg. Chem., 26, 737-741 (1987).
10. C.M. Che; K.Y. Wong; C.K. Poon, Inorg. Chem., 25, 1809-1813 (1986).