

Synthesis and Characterization of a Ruthenyl ($\text{Ru}^{\text{IV}}=\text{O}$) Complex with a Saturated Macrocyclic Tetramine

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The synthesis and characterization of a novel mono-oxo-ruthenium(IV) (ruthenyl) species of 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (tmc) are described; this ruthenyl cation, together with another high-valent $\text{Ru}^{\text{IV}}-\text{NCS}$ species of tmc, can also be generated electrochemically from $\text{trans}-[\text{Ru}(\text{tmc})\text{Cl}_2]^+$.

The chemistry of high-valent ruthenium(IV)-amine complexes, especially those containing the $\text{Ru}^{\text{IV}}=\text{O}$ (ruthenyl) unit, has received much attention in recent years in view of the potential usefulness of these complexes to function as oxidative catalysts and, for the ruthenyl species, as oxygen-atom-transfer agents.^{1,2} Though several ruthenyl polypyridine complexes have recently been reported,²⁻⁴ the existence of ruthenyl species in saturated macrocyclic amine complexes has never been observed. We now report the formation of the first stable ruthenyl complex of 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane [tmc, (1)].

The synthesis of $\text{trans}-[\text{Ru}(\text{tmc})\text{Cl}_2]^+$ and some of its substitutional, electrochemical, and chemical oxidative reactions are summarized in Scheme 1. Satisfactory elemental analyses have been found for products (2)–(5). Whereas products (2)–(4) are conventional Werner-type complexes, the yellow solid (5) has been shown to be a ruthenyl species by the presence of a very intense i.r. band at 855 cm^{-1} which is assignable to the $\nu(\text{Ru}=\text{O})$ stretch. This band is absent from the i.r. spectra of $\text{trans}-[\text{M}(\text{tmc})\text{Cl}_2]\text{Cl}$ ($\text{M} = \text{Ru}$ or Rh).⁵ Formulation of (5) as a ruthenyl species also came from its electronic absorption spectrum. A weak absorption band at $ca. 390\text{ nm}$ ($\epsilon_{\text{max}} ca. 550\text{ cm}^{-1}\text{ mol}^{-1}\text{ dm}^3$) with vibronic

structure is characteristic of the spin-forbidden $p_{\pi}(\text{oxygen}) \rightarrow d_{\pi}(\text{metal})$ transition commonly observed in most high-valent metal-oxo species, such as MnO_4^- and the vanadyl ion,^{6,7} although such a finding has not yet been encountered in other ruthenyl polypyridine complexes. In the present case, vibronic structure is observed even in fluid solution and at ambient temperature. The estimated value of $ca. 560\text{ cm}^{-1}$ for the $\nu(\text{Ru}=\text{O})$ stretch in the triplet ligand-to-metal charge-transfer excited state is reasonable in view of the decreased $\text{Ru}=\text{O}$ bond order in the excited state. The cyclic voltammogram (c.v.) of (5) gives rise to a quasi-reversible couple at $ca. 0.62\text{ V}$ vs. the saturated calomel electrode (s.c.e.), which is pH- and scan-rate-dependent. This couple can be attributed to a $\text{Ru}^{\text{IV}}/\text{Ru}^{\text{III}}$ couple by reference to other known ruthenyl complexes.²⁻⁴ Preliminary observations showed that (5) reacted with PPh_3 , resulting in the reduction of (5), and the disappearance of the $\text{Ru}=\text{O}$ group.

The same ruthenyl species of tmc could also be generated electrochemically from $\text{trans}-[\text{Ru}(\text{tmc})\text{Cl}_2]^+$ according to routes (iv) and (v) in Scheme 1.

The c.v. (Figure 1) of $[\text{Ru}(\text{tmc})(\text{NCS})\text{Cl}]^+$ in toluene-*p*-sulphonic acid (*p*-TSA) shows a quasi-reversible couple at

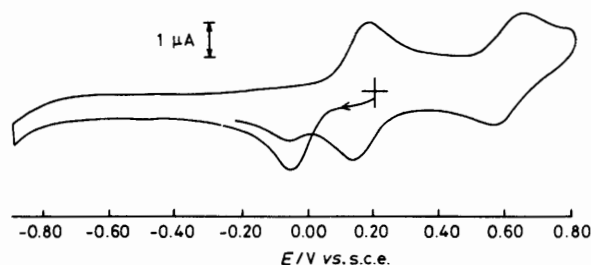
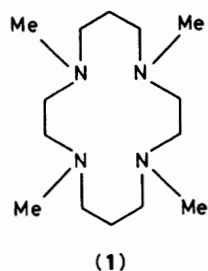
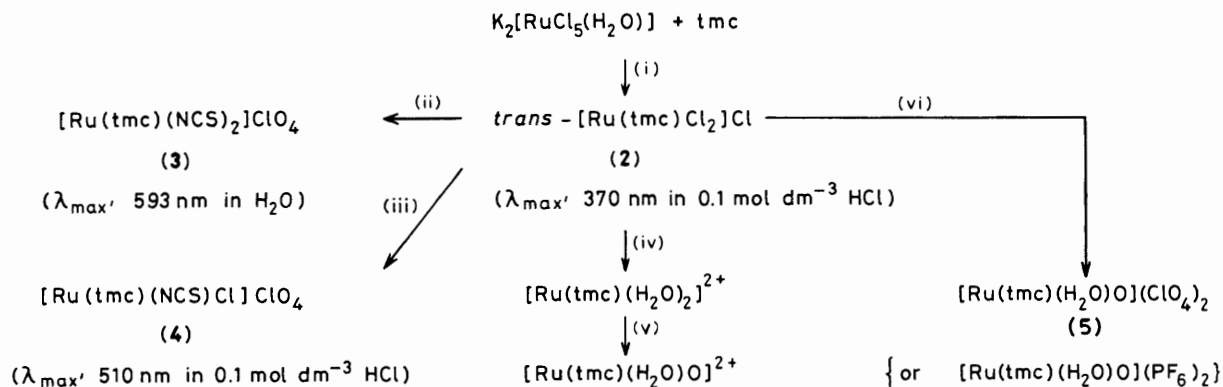


Figure 1. The c.v. of $[\text{Ru}(\text{tmc})(\text{NCS})\text{Cl}]^+$ in (*p*-TSA) (0.2 mol dm^{-3}) and at 200 mV s^{-1} scan rate.



Scheme 1. Reagents and conditions: (i) EtOH, reflux; (ii) excess of NaNCS, H_2O , boil, NaClO_4 ; (iii) calculated quantity of NaNCS, EtOH, boil, NaClO_4 ; (iv) electrochemical reduction in *p*-TSA (0.2 mol dm^{-3}) at -0.20 V vs. s.c.e.; (v) electrochemical oxidation at $0.6\text{--}0.7\text{ V}$ vs. s.c.e.; (vi) $30\% \text{ H}_2\text{O}_2$, NaClO_4 or KPF_6 .

0.63 V vs. s.c.e. This couple can be assigned as a Ru^{IV}/Ru^{III} couple. The absence of the first anodic peak indicates a rapid aquation of [Ru^{II}(tmc)(NCS)Cl] to [Ru(tmc)(NCS)(H₂O)]^{††} which gives rise to a reversible Ru^{III}/Ru^{II} couple at 0.17 V vs. s.c.e. This [Ru(tmc)(NCS)(H₂O)]^{2+.1+} couple has been shown to be the pre-requisite for the formation of the subsequent Ru^{IV}/Ru^{III} couple at 0.63 V by the observation that the addition of excess of chloride suppressed these two couples, more markedly for the latter.

† Independent kinetic studies showed that thiocyanate in ruthenium complexes is very inert to substitution.

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