# A Ruthenium(IV) Oxo Complex that contains a Tertiary Diamine Ligand

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The complex $[Ru(terpy)(tmen)(OH_2)]^{2+}$ (terpy = 2,2′:6′2″-terpyridine, tmen = *N,N,N′,N′*-tetramethylethylenediamine) and its corresponding oxo complex have been prepared. Their spectral properties and redox properties in aqueous solution were investigated. Evidence for two one-electron redox processes has been obtained for the $Ru^{IV}$–$Ru^{III}$ and $Ru^{III}$–$Ru^{II}$ couples.
The reactions of the new ruthenium(IV) oxo species with olefins have been found to proceed with second-order kinetics, rate = $k_2[Ru^{IV}][olefin]$ where $k_2 = (3.3 \pm 0.3) \times 10^{-3}$ and $(2.0 \pm 0.2) \times 10^{-2}$ $dm^3 mol^{-1} s^{-1}$ at 25 °C for norbornene and styrene respectively.

There is a current interest in the syntheses and reactivities of ruthenium oxo complexes in the oxidation states IV, V, and VI.[1-5] Notably, the oxidation chemistry of ruthenium(IV) oxo complexes containing polypyridine ligands, such as $[Ru(terpy)(bipy)O]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine, bipy = 2,2′-bipyridine) and $[Ru(bipy)_2(py)O]^{2+}$ (py = pyridine), has been extensively studied by Meyer and co-workers.[1] We have attempted to vary the structures of these complexes by replacing a bipy ligand with a tertiary diamine ligand such as tmen (tmen = *N,N,N′,N′*-tetramethylethylenediamine). Due to the better σ-donating properties and increased bulkiness of tertiary diamines relative to those of 2,2′-bipyridine, we anticipate that oxoruthenium(IV) complexes which utilize a tertiary diamine ligand should display quite different reactivities from those of the analogous bipyridine complexes. In addition, a great deal of interest has been shown in the use of $C_2$-symmetric chiral diamines in asymmetric oxidation of olefins.[6] We are thus interested in developing synthetic pathways for ruthenium oxo species containing chelating diamines in order to explore the possibility of asymmetric epoxidation of olefins using these systems.

We report here the synthesis and reactivity of $[Ru(terpy)(tmen)O][ClO_4]_2$.

## Experimental

*Materials.*—$[Ru(terpy)Cl_3]\cdot 3H_2O$ was prepared according to the literature.[7] All reagents were AR grade and were used without further purification, except the acetonitrile used in kinetics was distilled over potassium permanganate and then calcium hydride.

*Preparations.*—$[Ru(terpy)(tmen)Cl]ClO_4$. The complex $[Ru(terpy)Cl_3]\cdot 3H_2O$ (0.4 g) and tmen (4 $cm^3$) in ethylene glycol (4 $cm^3$) were heated at reflux for 4 h. After cooling, ethanol (5 $cm^3$) was added, followed by a saturated aqueous solution of $NaClO_4$ (10 $cm^3$). The resulting dark purple microcrystalline solid was filtered off, washed with ice-cold water, then diethyl ether, and dried *in vacuo*. Yield: 0.4 g (70%). The hexafluorophosphate salt was similarly prepared by using $NH_4PF_6$ instead of $NaClO_4$. Elemental analyses indicated that the perchlorate salt was always contaminated with some $NaClO_4$ (Found: C, 39.2; H, 4.35; Cl, 13.3; N, 11.1. Calc. for $C_{21}H_{27}Cl_{2.5}N_5O_6Na_{0.5}Ru$: C, 39.0; H, 4.20; Cl, 13.7; N, 10.8%). U.v.–visible spectrum in $CH_2Cl_2$: $\lambda_{max.}$/nm ($\varepsilon_{max.}$/$dm^3 mol^{-1} cm^{-1}$): 561 (sh) (3 310), 520 (sh) (3 200), 380 (3 480), 325 (18 900), and 282 (15 400).

$[Ru(terpy)(tmen)(H_2O)][PF_6]_2\cdot H_2O$ (**1**). $[Ru(terpy)(tmen)Cl]PF_6$ (0.3 g) and silver toluene-*p*-sulphonate (0.15 g) in acetone–water (3:1) (20 $cm^3$) were heated at reflux for 30 min. Silver chloride was filtered off, the solution volume was reduced to *ca.* 5 $cm^3$, and solid $NH_4PF_6$ was added (*ca.* 2 g). The reddish purple microcrystalline product was filtered off, washed with a little ice-cold water, and dried *in vacuo*. Yield: 60—70% (Found: C, 32.0; H, 3.75; N, 8.80. Calc. for $C_{21}H_{31}F_{12}N_5O_2P_2Ru$: C, 32.5; H, 4.00; N, 9.00%). U.v.–visible spectrum in water: $\lambda_{max.}$/nm ($\varepsilon_{max.}$/$dm^3 mol^{-1} cm^{-1}$): 523 (2 660), 460 (sh) (1 870), 322 (26 000), and 270 (17 000).

The perchlorate salt was prepared in a similar way from $[Ru(terpy)(tmen)Cl]ClO_4$ by using $NaClO_4$ instead of $NH_4PF_6$.

$[Ru(terpy)(tmen)O][ClO_4]_2\cdot H_2O$ (**2**). The complex $[Ru(terpy)(tmen)(OH_2)][ClO_4]_2$ (0.1 g) was dissolved in hot water (70—80 °C, 20 $cm^3$) and then added to a solution of $[NH_4]_2[Ce(NO_3)_6]$ (2g, 20 $cm^3$). After a few minutes, excess of $NaClO_4$ was added to precipitate a green-yellow solid which was filtered off, washed with ice-cold water, and dried *in vacuo*. Yield: 0.5 g (50%) (Found: C, 36.8; H, 3.90; N, 10.3. Calc. for $C_{21}H_{29}Cl_2N_5O_{10}Ru$: C, 36.9; H, 4.20; N, 10.2%). U.v.–visible spectrum: (in water) $\lambda_{max.}$/nm ($\varepsilon_{max.}$/$dm^3 mol^{-1} cm^{-1}$): 354 (sh) (5 700), 338 (7 300), and 289 (8 300); (in $CH_3CN$): 352 (8 000), 339 (9 870), and 278 (11 000).

*Measurements.*—U.v.–visible spectra were recorded on a Shimadzu UV-240 spectrophotometer, i.r. spectra of Nujol mulls on a Nicolet model 20 FXC FT-IR spectrophotometer. Cyclic voltammetry was conducted with a PAR model 175 universal programmer and model 173 potentiostat using an edge-plane pyrolytic graphite working electrode and a saturated calomel reference electrode (s.c.e.). Organic products were analysed on a Varian 2440 gas chromatograph equipped with a flame ionization detector. Kinetics were monitored spectrophotometrically under pseudo-first-order conditions.

## Results and Discussions

The synthesis of $[Ru(terpy)(tmen)(H_2O)]^{2+}$ (**1**) follows Meyer's procedure for the bipy analogue, using $[Ru(terpy)Cl_3]$ as the starting material. It shows visible absorption bands around 500 nm (Figure 1), which are the characteristic $d_\pi(Ru) \longrightarrow \pi^*$-(terpy) transitions of ruthenium(II) di-imine complexes. Spectrophotometric measurement established that the $pK_a$ value of the

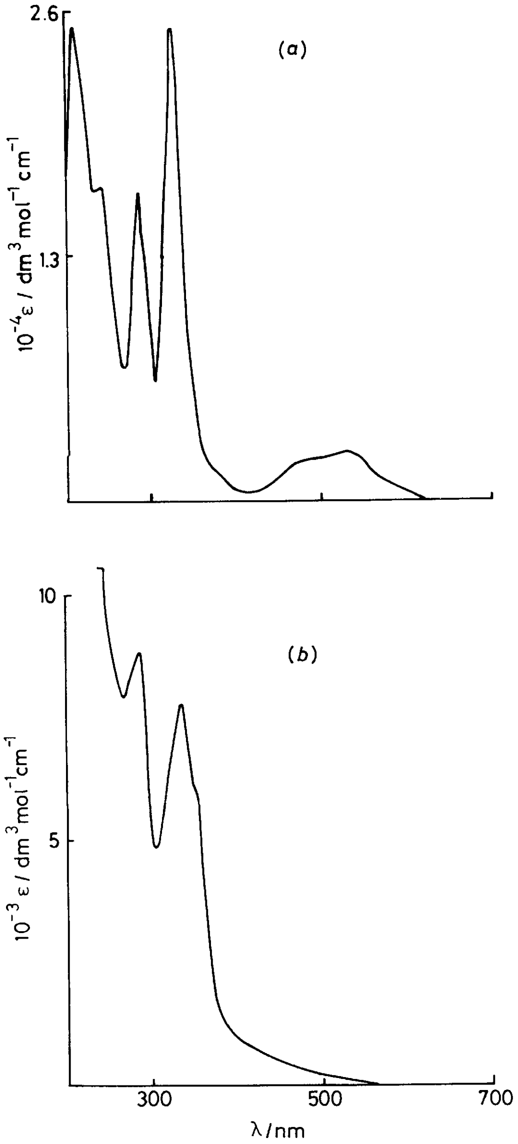

**Figure 1.** U.v.–visible spectra of (*a*) [Ru(terpy)(tmen)($H_2O$)][$ClO_4$]$_2$ and (*b*) [Ru(terpy)(tmen)O][$ClO_4$]$_2$ in water

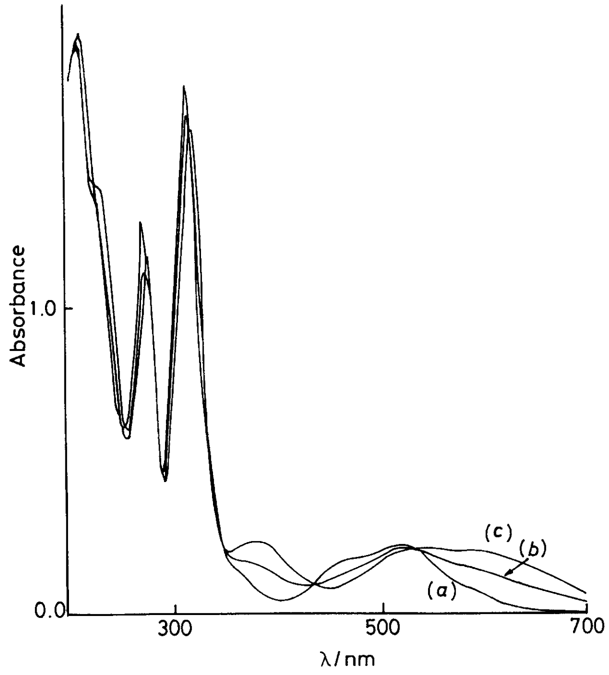

**Figure 2.** U.v.–visible spectra of [Ru(terpy)(tmen)($H_2O$)]$^{2+}$ at different pH 1.81 (*a*), 11.2 (*b*), and 12.0 (*c*)

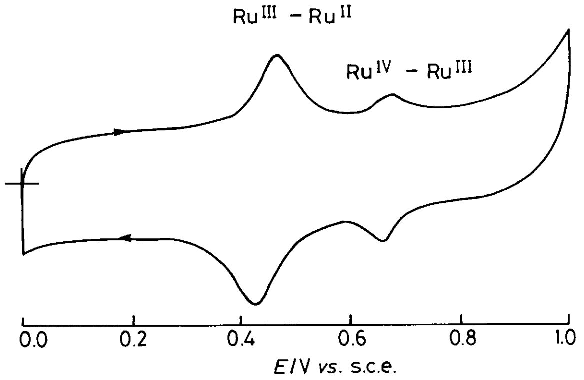

**Figure 3.** Cyclic voltammogram of [Ru(terpy)(tmen)($H_2O$)][$ClO_4$]$_2$ in aqueous solution buffered at pH 5.6 (0.2 mol dm$^{-3}$ acetic acid–0.2 mol dm$^{-3}$ sodium acetate) with an edge-plane pyrolytic graphite working electrode at scan rate 50 mV s$^{-1}$

co-ordinated water in complex (**1**) is 11.2 (Figure 2), which is higher than that for [Ru(terpy)(bipy)($H_2O$)]$^{2+}$ (p$K_a$ = 9.7).[1f] This is in accordance with the better σ-donating strength of tmen than bipy. Oxidation of (**1**) by Ce$^{IV}$ gave [Ru(terpy)(tmen)O]$^{2+}$ (**2**). As found for the bipy analogue, the optical spectrum of (**2**) in the visible region is featureless with the complete absence of the metal-to-ligand charge-transfer bands at 500 nm (Figure 1). The i.r. spectrum of [Ru(terpy)(tmen)O][$ClO_4$]$_2$ shows an absorption at 773 cm$^{-1}$ which is absent for the corresponding aquaruthenium(II) species; this peak is assigned to the Ru$^{IV}$=O stretch by comparison with reported ruthenium(IV) oxo compounds.[2a,3,7] Complex (**2**) is paramagnetic with a measured $\mu_{eff.}$ value of 2.8 $\mu_B$ at room temperature.

The electrochemistry of complex (**1**) or (**2**) is very similar to that for its bipy analogues, which exhibit a dependence on the nature of the electrode surface. With basal-plane pyrolytic graphite as the working electrode, the cyclic voltammograms of (**1**) and (**2**) in aqueous solutions are identical and consist of two waves: a reversible wave corresponding to the Ru$^{III}$–Ru$^{II}$ couple and a second, quasi-reversible wave, with a smaller measured current, corresponding to the Ru$^{IV}$–Ru$^{III}$ couple (Figure 3). At pH 5.6, these couples occur at 0.44 and 0.67 V *vs.* s.c.e., respectively; both couples shift 60 mV per pH unit over the range pH 1—7 (Figure 4), suggesting that the redox processes involve one-electron, one-proton transfers [equations (1) and (2)].

$$[\mathrm{Ru(terpy)(tmen)(OH)}]^{2+} + \mathrm{H}^+ + \mathrm{e} \longrightarrow [\mathrm{Ru(terpy)(tmen)(OH_2)}]^{2+} \quad (1)$$

$$[\mathrm{Ru(terpy)(tmen)O}]^{2+} + \mathrm{H}^+ + \mathrm{e} \longrightarrow [\mathrm{Ru(terpy)(tmen)(OH)}]^{2+} \quad (2)$$

The much smaller current for the Ru$^{IV}$–Ru$^{III}$ couple has previously been investigated by many workers,[8] and has been attributed to the deprotonation of the Ru–$H_2O$ group prior to oxidation of Ru$^{III}$ to Ru$^{IV}$. The $E^\circ$ value for [Ru(terpy)(tmen)O]$^{2+}$ is about 80 mV less than that for [Ru(terpy)(bipy)O]$^{2+}$ {at pH 7.0, $E^\circ$ (Ru$^{IV}$–Ru$^{III}$) for (**2**) and [Ru(terpy)(bipy)O]$^{2+}$ are

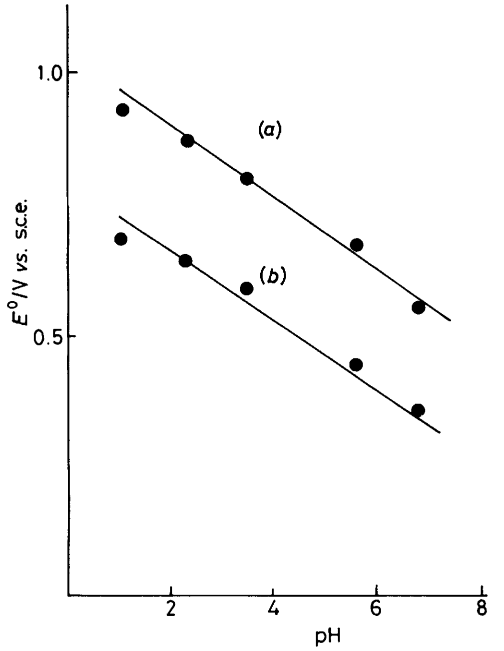

**Figure 4.** Plot of $E^0$ *versus* pH for the couples (*a*) $Ru^{IV}$–$Ru^{III}$ and (*b*) $Ru^{III}$–$Ru^{II}$

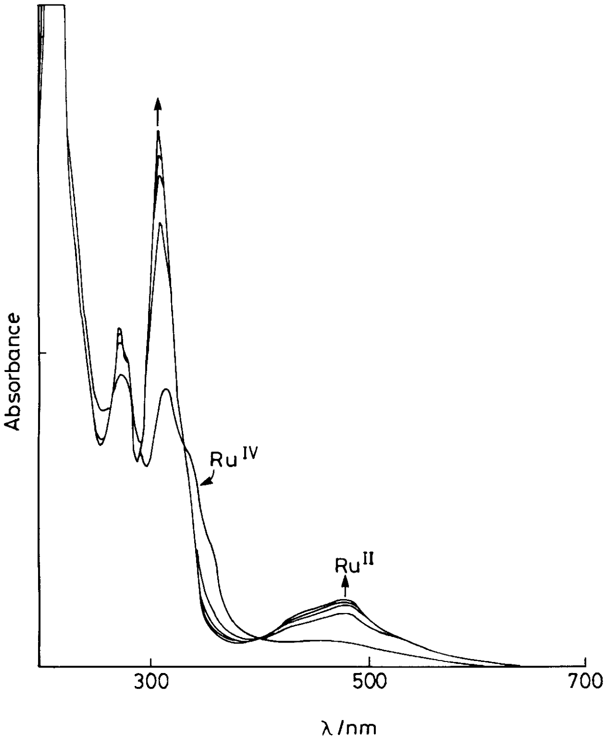

**Figure 5.** Spectral changes during the reaction of norbornene with [Ru(terpy)(tmen)O][$ClO_4$]$_2$ in $CH_3CN$

0.54 and 0.62 [1f] V *vs.* s.c.e. respectively}, illustrating once again that tertiary amine ligands are better than π-aromatic di-imines in the stabilization of high-valent ruthenium oxo complexes.

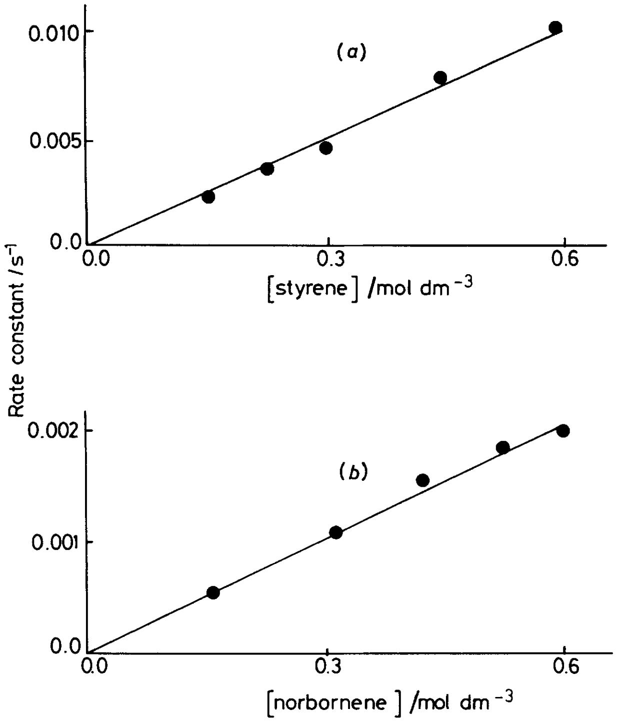

**Figure 6.** Plots of rate constants *versus* concentrations of olefins for the epoxidation of (*a*) styrene and (*b*) norbornene by [Ru(terpy)(tmen)O]$^{2+}$ in acetonitrile

*Reactivity.*—To test the efficiency of this new ruthenium(IV) oxo species towards olefin epoxidation, norbornene and styrene were chosen as substrates. In $CH_3CN$, spectrophotometric changes indicated clean conversion of [Ru(terpy)(tmen)O]$^{2+}$ into [Ru(terpy)(tmen)($CH_3CN$)]$^{2+}$,* with well defined isosbestic points (Figure 5). Norbornene oxide and styrene oxide (7% benzaldehyde as side product) were detected in 90 and 70% yield respectively, indicating the stoicheiometry for epoxidation to be as in equation (3). The epoxidation reaction proceeds with

$$[\mathrm{Ru(terpy)(tmen)O}]^{2+} + \text{olefin} \longrightarrow [\mathrm{Ru(terpy)(tmen)(CH_3CN)}]^{2+} + \text{epoxide} \quad (3)$$

second-order kinetics, with rate = $k_2[Ru^{IV}]$[olefin]. Figure 6 shows plots of rate constants *versus* concentrations of olefin, from which second-order rate constants ($k_2$) were deduced. The values are $(3.3 \pm 0.3) \times 10^{-3}$ and $(2.0 \pm 0.2) \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 25 °C for norbornene and styrene respectively. The complex [Ru(terpy)(tmen)O]$^{2+}$ is also capable of oxidizing alcohols to aldehydes or ketones. For example, benzyl alcohol and isopropyl alcohol were oxidized to benzaldehyde and acetone respectively. The reaction of (**2**) with isopropyl alcohol in $CH_3CN$ obeys the stoicheiometry (4). At 25 °C, the second-order rate constant for this oxidation was found to be $(4.3 \pm 0.4) \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$.

$$[\mathrm{Ru(terpy)(tmen)O}]^{2+} + \mathrm{(CH_3)_2CHOH} \longrightarrow [\mathrm{Ru(terpy)(tmen)(CH_3CN)}]^{2+} + \mathrm{(CH_3)_2C{=}O} \quad (4)$$

The present work indicates that the new ruthenium(IV) oxo species is a stable oxidant which can oxidize a variety of organic substrates, in a way similar to that of [Ru(terpy)(bipy)O]$^{2+}$, which has been subjected to extensive study by Meyer and co-workers.[1] The finding that a $Ru^{IV}$=O complex of tmen can epoxidize olefins is encouraging, and work is continuing

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* The complex [Ru(terpy)(tmen)($CH_3CN$)]$^{2+}$ could be obtained by dissolving [Ru(terpy)(tmen)($H_2O$)]$^{2+}$ in $CH_3CN$. U.v.–visible spectrum, $\lambda_{max.}$/nm ($\varepsilon_{max.}$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 522 (sh) (2 200), 478 (4 200), 312 (28 000), and 275 (18 000).

to synthesize ruthenium(IV) oxo species that contain chiral diamines for asymmetric epoxidation.

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