Synthesis, Electrochemistry, and Reactivities of *trans*-$[Ru^{VI}(L)O_2]^{2+}$ (L = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)propylenediamine

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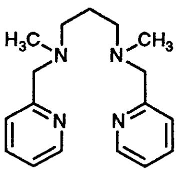
The synthesis and characterization of the ligand *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-propylenediamine (L) and the complex *trans*-$[Ru^{VI}(L)O_2]^{2+}$ are described. The complex has been characterized by u.v.–visible [$d_{xy} \longrightarrow d_{\pi^*}$ ($d_{\pi^*} = d_{xz},d_{yz}$) at 380—420 nm] and i.r. [$\nu_{asym}(RuO_2)$ at 860 cm^{-1}] spectroscopy. At pH 1.0 it exhibits three reversible couples Ru^{VI}–Ru^{IV}, Ru^{IV}–Ru^{III}, and Ru^{III}–Ru^{II} at potentials of 0.89, 0.60, and 0.28 V respectively *vs.* saturated calomel electrode. The Ru^{VI}–Ru^{IV} couple splits into two reversible one-electron couples Ru^{VI}–Ru^{V} and Ru^{V}–Ru^{IV} in alkaline solutions (pH $>$ 9). The complex is a powerful oxidant, capable of oxidizing toluene to benzaldehyde, alcohols to aldehydes/ketones, tetrahydrofuran to γ-butyrolactone, and norbornene to *exo*-2,3-epoxynorbornane in high yields at room temperature. Oxidation of *cis*- and *trans*-stilbenes gave benzaldehyde and *trans*-stilbene oxides.

Recent works from various groups have demonstrated the rich oxidation chemistry of high-valent ruthenium oxo complexes.[1–4] Our work in this area has focused on *trans*-dioxoruthenium(VI) complexes containing nitrogen-donor ligands such as π-aromatic di-imines and tetra-azamacrocycles.[1a–e] It has been found that replacement of a tertiary nitrogen atom by a pyridyl unit in the tetra-azamacrocyclic ligands will enhance the redox potential and reactivities of the ruthenium oxo oxidant. For example, the $E°$ of *trans*-dioxo[*meso*-2,3,7,11,12-pentamethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene]ruthenium(VI) is about 100 mV higher than that for *trans*-dioxo(1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)ruthenium(VI).[1e] As part of our program systematically to vary the $E°$ of ruthenium oxo oxidants in order to study the driving force in organic oxidation, the ligand *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)propylenediamine (L) which possesses two pyridine functional groups was synthesized. Herein are described the synthesis, electrochemistry, and reactivities of *trans*-$[Ru^{VI}(L)O_2]^{2+}$.



L

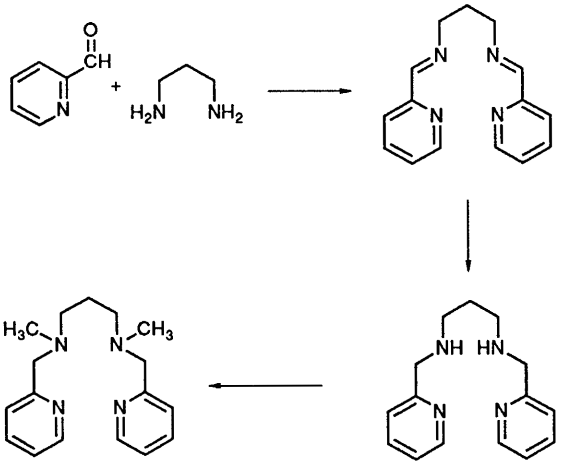
Experimental

Physical Measurements.—Elemental analyses of the new complexes were performed by Butterworth Laboratories. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer model 577 (4 000—200 cm^{-1}) spectrophotometer. Cyclic voltammograms were obtained with a Princeton Applied Research (PAR) instruments model 175 Universal Programmer and model 173 potentiostat-galvanostat. The working electrodes were pyrolytic graphite and glassy carbon. Constant-potential coulometry was performed using a PAR model 377A coulometric cell system. The solution was stirred with a synchronous stirring motor and under a nitrogen atmosphere during electrolysis. The quantity of electricity passed was measured by a PAR model 179 digital coulometer.

Stoicheiometric Oxidation.—Stoicheiometric oxidation of organic substrates by *trans*-$[Ru^{VI}(L)O_2][ClO_4]_2$ was performed by dissolving the ruthenium complex (20 mg) in acetonitrile (1 cm^3) containing the organic substrate (0.1 g). The reaction mixture was stirred with a magnetic stirrer at room temperature and under a nitrogen atmosphere. A control experiment in the absence of the oxidant was performed for each reaction. The products were analyzed by gas chromatography, ^{1}H n.m.r., mass, and u.v.–visible spectroscopy. Gas chromatographic analyses were conducted using a Varian model 940 gas chromatograph equipped with a flame ionization detector and a Shimadzu C-R3A electronic integrator, the details of which had been described previously.[1f] *cis*-Stilbene and *trans*-stilbene oxides were analyzed by ^{1}H n.m.r. spectroscopy. At the end of the stoicheiometric reaction the solution was evaporated. After addition of 1,1-diphenylethylene (5 μl) the solution was extracted with n-hexane at least five times. The combined extracts were rotary evaporated to dryness and redissolved in $CDCl_3$ (0.3 cm^3) for ^{1}H n.m.r. analysis.

Materials.—The salt $K_2[RuCl_5(H_2O)]$ was purchased from Johnson Matthey plc. All organic substrates for stoicheiometric oxidation were A.R. grade and purified by standard methods.

N,N'-*Dimethyl*-N,N'-*bis*(2-*pyridylmethyl*)*propylenediamine*. An ethanolic solution of pyridine-2-carbaldehyde (30 g in 50 cm^3) was mixed with anhydrous propylenediamine (8.5 g). After stirring for 30 min at room temperature the solution was rotary evaporated at about 60 °C to give *N,N'*-bis(2-pyridylmethylene)-propylenedi-imine, which is a yellowish oil. Reduction of the imine was carried out using $NaBH_4$ in hot methanol. To a well stirred, hot solution of imine (10 g) and disodium tetraborate (5 g) in dry methanol (1 000 cm^3) was slowly added $NaBH_4$ (15 g) over an hour. After the reaction the solution was concentrated to about 100 cm^3 and excess of water (*ca.* 500 cm^3) was added. Extraction was carried out by chloroform (3 × 100 cm^3). The organic extract was dried with sodium sulphate and rotary evaporated to give the oily *N,N'*-bis(2-pyridylmethyl)-propylenediamine (yield varied from 60 to 80%).



Scheme 1.

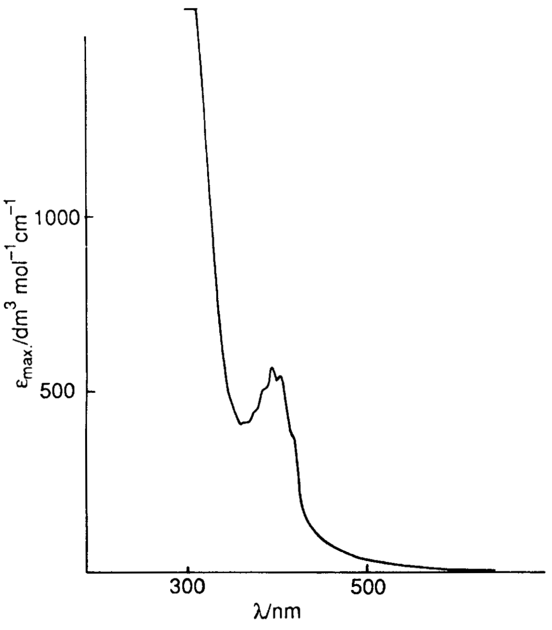


Figure 1. U.v.-visible spectrum of *trans*-$[Ru^{VI}(L)O_2]^{2+}$ in 0.1 mol dm^{-3} CF_3CO_2H

Ligand L was obtained by methylation of *N*,*N'*-bis(2-pyridylmethyl)propylenediamine using formic acid–formaldehyde. A mixture of the secondary amine (5 g), formic acid (25 cm^3, 98—100%), and formaldehyde (25 cm^3, 37—41%) was refluxed at 90 °C with stirring for 24 h. The solution was cooled in an ice-bath. A saturated solution of sodium hydroxide was added with stirring until the solution became alkaline (pH 12). The resulting solution was extracted with chloroform. The organic extract was dried over anhydrous sodium sulphate and evaporated under vacuum to give a thick oil. Purification was carried out by distillation under reduced pressure [light yellow oil, b.p. *ca.* 150 °C at 0.1 mmHg (*ca.* 13.3 Pa) yield 60%]. I.r.: no absorption at 3 000—3 500 cm^{-1} assignable to ν(N–H). Mass spectrum: parent molecular ion at *m*/*z* 284. ^1H N.m.r. ($CDCl_3$, $SiMe_4$): δ 8.52 (d, 2 H), 7.06—7.73 (m, 6 H), 3.64 (s, 4 H), 2.49 (t, 4 H), 2.24 (s, 6 H), and 1.6—1.9 (m, 2 H).

trans-$[Ru^{III}(L)Cl_2]ClO_4$. An ethanolic solution of L (0.43 g in 200 cm^3) was added dropwise to a vigorously stirred ethanolic suspension of $K_2[RuCl_5(H_2O)]$ (0.5 g in 200 cm^3) under reflux. The addition took 3 h for completion and the suspension was then refluxed for 1 d. The yellowish brown solution obtained was filtered and evaporated to dryness. The yellow solid was dissolved in hot hydrochloric acid (2 mol dm^{-3}, 10 cm^3) and the product *trans*-$[Ru^{III}(L)Cl_2]ClO_4$ was precipitated upon addition of $NaClO_4$. A pure sample was obtained by recrystallization from hot hydrochloric acid (2 mol dm^{-3}, 60 °C), yield 0.35 g (70%) {Found: C, 36.8; H, 4.5; Cl, 19.1; N, 10.0. Calc. for $[Ru(L)Cl_2]ClO_4$: C, 36.7; H, 4.3; Cl, 19.2; N, 10.1%}. U.v.-visible spectrum (water): $\lambda_{max.}$ ($\varepsilon_{max.}$) 385 (2 500) and 245 nm (3 600 dm^3 mol^{-1} cm^{-1}).

CAUTION: Perchlorate salts are potentially explosive and should be handled in small quantity.

trans-$[Ru^{VI}(L)O_2][ClO_4]_2$ (**1**). A mixture of *trans*-$[Ru^{III}(L)Cl_2]ClO_4$ (0.35 g) and silver trifluoromethanesulphonate (0.55 g) in deionized water (25 cm^3) was heated to about 80 °C with stirring for 0.5 h. When all the complex had dissolved the solution was greenish yellow. It was filtered to remove the insoluble silver chloride and the greenish yellow filtrate was cooled in an ice-bath. A soluton of $[NH_4]_2[Ce(NO_3)_6]$ was slowly added to the filtrate. Upon addition of excess of $NaClO_4$, yellow solid *trans*-$[Ru^{VI}(L)O_2][ClO_4]_2$ was precipitated. It was filtered off and recrystallized from hot $HClO_4$ (0.1 mol dm^{-3}, 60 °C), yield 0.2 g (55%) {Found: C, 33.2; H, 3.9; Cl, 11.6; N, 9.0. Calc. for $[Ru(L)O_2][ClO_4]_2$: C, 33.1; H, 3.9; Cl, 11.6; N, 9.1%}. U.v.-visible spectrum in water: $\lambda_{max.}$ ($\varepsilon_{max.}$): 395 (540), 340 (2 500), and 250 nm (8 300 dm^3 mol^{-1} cm^{-1}).

trans-$[Ru^{IV}(L)O(H_2O)]^{2+}$. This complex was prepared *in situ* by constant-potential reduction of *trans*-$[Ru^{VI}(L)O_2]^{2+}$ at 0.7 V *vs.* a saturated calomel electrode (s.c.e.) in 0.1 mol dm^{-3} CF_3CO_2H. U.v.-visible spectrum in 0.1 mol dm^{-3} CF_3CO_2H: $\lambda_{max.}$ ($\varepsilon_{max.}$): 420 (210), 290 (1 940), and 260 nm (4 040 dm^3 mol^{-1} cm^{-1}).

Results and Discussion

Previous work established that *trans*-dioxoruthenium(VI) complexes can be obtained with tetra-azamacrocyclic ligands.[1a,b,e] However, it would be difficult systematically to tune the reactivities and properties of the ruthenium oxo oxidants through variation of the structure of the macrocycles since macrocyclic ligands are usually synthesized by tedious and multi-step synthetic routes. In this work the ligand L is a noncyclic tetradentate amine and can easily be synthesized by condensation of 2-pyridinecarbaldehyde with the chelating diamine, followed by reduction and methylation (Scheme 1). The reactions in Scheme 1 are general. Thus it is not difficult to envisage that a whole class of linear-chain tetradentate amines can easily be synthesized by using different chelating diamines in the condensation reaction.

Insertion of ruthenium into the ligand L follows the well established synthetic procedure for dichloro(tetra-amine)ruthenium(III).[5] As for the synthesis of *trans*-$[Ru^{VI}(L')O_2]^{2+}$ (L' = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane),[1a] the reaction of $[Ru^{III}(L)Cl_2]^+$ with Ag^I gave *trans*-$[Ru^{III}(L)(OH)(H_2O)]^{2+}$ which was oxidized by Ce^{IV} to *trans*-$[Ru^{VI}(L)O_2]^{2+}$ (**1**). Assignment of a *trans* configuration to the ruthenium(VI) oxo complex is based on its electrochemistry, i.r. and u.v.-visible spectroscopy. Its u.v.-visible spectrum in water (Figure 1) shows a vibronically structured band at 380—420 nm, due to the characteristic $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{\pi^*})^1$ ($d_{\pi^*} = d_{xz}$, d_{yz}) transition of *trans*-dioxo(tetra-amine)ruthenium(VI).[1a–c] The i.r. spectrum exhibits the characteristic intense $\nu_{asym.}(RuO_2)$ stretch at 860 cm^{-1}, which is absent for *trans*-$[Ru^{III}(L)Cl_2]^+$. A direct comparison between *trans*-$[Ru^{VI}(L')O_2]^{2+}$,[1a] *trans*-$[Ru^{VI}(L'')O_2]^{2+}$ [L'' = meso-2,3,7,11,12-pentamethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene],[1e] (**1**), and *trans*-$[Ru^{VI}(bipy)_2O_2]^{2+}$ (bipy = 2,2'-bipyridine)[1b] reveals that the change of nitrogen donor from

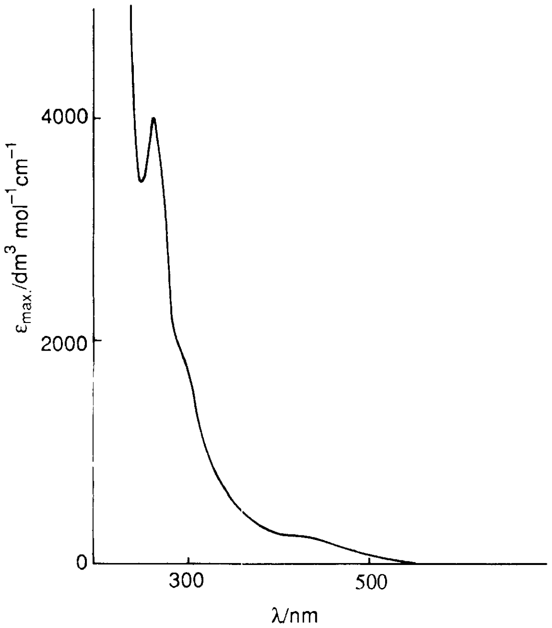


Figure 2. U.v.–visible spectrum of *trans*-$[\mathrm{Ru^{IV}(L)O(H_2O)}]^{2+}$ in 0.1 mol dm^{-3} $\mathrm{CF_3CO_2H}$

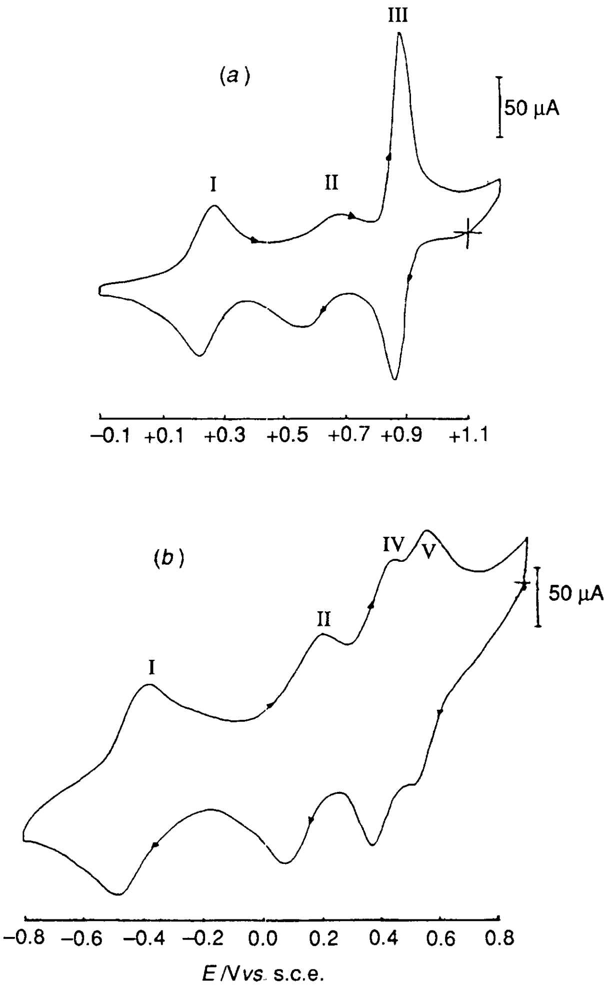


Figure 3. Cyclic voltammogram of *trans*-$[\mathrm{Ru^{VI}(L)O_2}]^{2+}$ at pH 1 (*a*) and 10.4 (*b*). Working electrode: edge-plane pyrolytic graphite. Scan rate: 50 mV s^{-1}

σ-saturated to π-aromatic type has virtually no effect on the $\nu_{\mathrm{asym.}}(\mathrm{RuO_2})$ stretching frequency, indicating that the Ru=O bond strengths in these systems are similar.

The complex *trans*-$[\mathrm{Ru^{IV}(L)O(H_2O)}]^{2+}$ was obtained by constant-potential reduction of complex (**1**) at 0.7 V *vs.* s.c.e. in 0.1 mol dm^{-3} $\mathrm{CF_3CO_2H}$. Its u.v.–visible spectrum is shown in Figure 2. Similarly to other *trans*-aquaoxoruthenium(IV) complexes,[1c,f] the weak absorption band at 420 nm is likely due to the low-energy $d_{xy} \longrightarrow d_{\pi^*}$ transition. The $p_{\pi}(\mathrm{O}) \longrightarrow d_{\pi^*}$ $(d_{\pi^*} = d_{xz}, d_{yz})$ charge-transfer transition, likely located at 260—300 nm is masked by the intraligand $\pi \longrightarrow \pi^*$ transition(s).

Electrochemistry.—The electrochemistry of complex (**1**) is similar to those of dicationic *trans*-dioxoruthenium(VI) complexes such as *trans*-$[\mathrm{Ru^{VI}(L')O_2}]^{2+}$ (refs. 1*a* and 6) and *trans*-$[\mathrm{Ru^{VI}(bipy)_2O_2}]^{2+}$.[1b] Its cyclic voltammogram in 0.1 mol dm^{-3} $\mathrm{CF_3CO_2H{-}CF_3CO_2Na}$ with edge-plane pyrolytic graphite as a working electrode [Figure 3(*a*)] shows three reversible/quasi-reversible couples I, II, and III with potentials at 0.28, 0.60, and 0.89 V *vs.* s.c.e. respectively. Controlled-potential reduction of *trans*-$[\mathrm{Ru^{VI}(L)O_2}]^{2+}$ established $n = 1$ for couples I and II and $n = 2$ for couple III. Thus the three couples are assigned as $\mathrm{Ru^{III}{-}Ru^{II}}$, $\mathrm{Ru^{IV}{-}Ru^{III}}$, and $\mathrm{Ru^{VI}{-}Ru^{IV}}$ respectively.

Couple III

$$\textit{trans}\text{-}[\mathrm{Ru^{VI}(L)O_2}]^{2+} + 2\,\mathrm{H^+} + 2\,e^- \longrightarrow \textit{trans}\text{-}[\mathrm{Ru^{IV}(L)O(H_2O)}]^{2+} \tag{1}$$

Couple II

$$\textit{trans}\text{-}[\mathrm{Ru^{IV}(L)O(H_2O)}]^{2+} + \mathrm{H^+} + e^- \longrightarrow \textit{trans}\text{-}[\mathrm{Ru^{III}(L)(OH)(H_2O)}]^{2+} \tag{2}$$

Couple I

$$\textit{trans}\text{-}[\mathrm{Ru^{III}(L)(OH)(H_2O)}]^{2+} + \mathrm{H^+} + e^- \longrightarrow \textit{trans}\text{-}[\mathrm{Ru^{II}(L)(H_2O)_2}]^{2+} \tag{3}$$

Scheme 2.

For couple I the peak-to-peak separation ($\Delta E_{\mathrm{p}} \approx 60$ mV) and current ratio ($i_{\mathrm{p_a}}/i_{\mathrm{p_c}} = 1$) show little dependence on scan rate and electrode surface. The reversibilities of couples II and III are strongly affected by the scan rate and nature of the electrode surface. Quasi-reversible couples are observed only with an edge-plane pyrolytic graphite electrode and with scan rates between 20 and 100 mV s^{-1}.

The E° values of couples I—III shift cathodically with increase in pH, as shown by the plots in Figure 4 and the data in Table 1. As expected, the E° of couple III shifts −60 mV per pH unit from pH 1 to 6. When the pH is greater than 8 couple III splits into two quasi-reversible one-electron couples IV and V [Figure 3(*b*)]. Couple V is pH independent while the E° of couple IV shifts −60 mV per pH unit. The corresponding electrode reactions are in Scheme 3.

Couple IV

$$\textit{trans}\text{-}[\mathrm{Ru^{V}(L)O_2}]^{+} + \mathrm{H^+} + e^- \longrightarrow \textit{trans}\text{-}[\mathrm{Ru^{IV}(L)(O)(OH)}]^{+} \tag{4}$$

Couple V

$$\textit{trans}\text{-}[\mathrm{Ru^{VI}(L)O_2}]^{2+} + e^- \longrightarrow \textit{trans}\text{-}[\mathrm{Ru^{V}(L)O_2}]^{+} \tag{5}$$

Scheme 3.

The direct two-electron reduction of *trans*-$[\mathrm{Ru^{VI}(L)O_2}]^{2+}$ to *trans*-$[\mathrm{Ru^{IV}(L)O(H_2O)}]^{2+}$ is in accordance with previous work that dioxoruthenium(V) disproportionates in acidic media

$$\textit{trans}\text{-}[\mathrm{Ru^{V}(L)O_2}]^{+} + \textit{trans}\text{-}[\mathrm{Ru^{V}(L)O(OH)}]^{2+} \longrightarrow \textit{trans}\text{-}[\mathrm{Ru^{IV}(L)O(OH)}]^{+} + \textit{trans}\text{-}[\mathrm{Ru^{VI}(L)O_2}]^{2+} \tag{6}$$

Table 1. Summary of E° (in V *vs.* s.c.e.) for various redox couples of *trans*-$[Ru^{VI}(L)O_2]^{2+}$ at different pH and 25 °C

	Couple				
pH	I (Ru^{III}–Ru^{II})	II (Ru^{IV}–Ru^{III})	IV (Ru^{V}–Ru^{IV})	III (Ru^{VI}–Ru^{IV})	V (Ru^{VI}–Ru^{V})
1.10	0.28	0.60		0.89	
1.81	0.24	0.57		0.85	
2.21	0.22	0.55		0.83	
2.56	0.19	0.53		0.80	
3.29	0.13	0.52		0.76	
4.10	0.08	0.47		0.72	
4.50	0.06	0.44		0.68	
5.02	0.03	0.42		0.65	
5.72	−0.03	0.38		0.62	
6.37	−0.07	0.35		0.58	
6.80	−0.11	0.33		0.57	
7.24	−0.16	0.30		0.55	
7.96	−0.25	0.25		0.51	
8.69	−0.31	0.22		0.50	
9.15	−0.35	0.20		0.49	
9.62	−0.40	0.18			
10.40	−0.44	0.15	0.41		0.53
11.20	−0.52	0.11	0.38		0.52
11.58	−0.58	0.06	0.33		0.53
11.98	−0.61	0.02	0.29		0.52

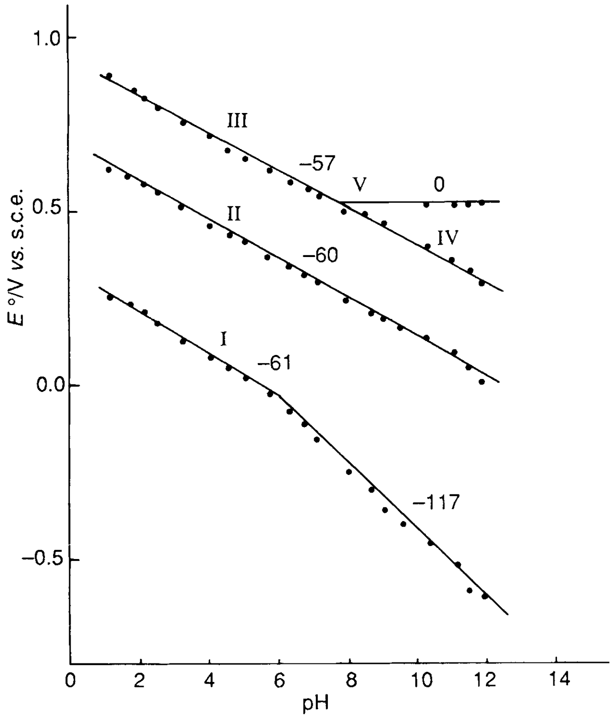


Figure 4. Plots of E° *versus* pH for the redox couples of *trans*-$[Ru^{VI}(L)O_2]^{2+}$. Arabic numbers are values of slopes in mV per pH unit

[equation (6)].[6,7] The disproportionation equilibrium constant K_{disp} is given by $[Ru^{IV}(L)O(OH)][Ru^{VI}(L)O_2]/[Ru^{V}(L)O_2]$-$[Ru^{V}(L)O(OH)]$. It can be estimated using E° for couples III—V at pH 1.0, *i.e.* $\Delta E_{disp} = E^\circ(Ru^{VI}–Ru^{V}) - E^\circ(Ru^{V}–Ru^{IV})$ where $E^\circ(Ru^{V}–Ru^{IV}) = 2E^\circ(Ru^{VI}–Ru^{IV}) - E^\circ(Ru^{VI}–Ru^{V})$, $\Delta G^\ominus{}_{disp} = -nF\Delta E_{disp}$, and $K_{disp} = \exp(-\Delta G^\ominus{}_{disp}/RT)$. The value was found to be 1.5×10^{12}; a similar value has been found for *trans*-$[Ru^{V}(L')O_2]^+$.[7]

For couple I and at pH 1—5.8, the E° shifts by −61 mV per pH unit corresponding to the electrode reaction (3). When the pH is greater than 5.8 the E° shifts by −117 mV per pH unit indicating that the electrode reaction is a one-electron two-proton transfer process (7). The breakpoint of the plot for

$$trans\text{-}[Ru^{III}(L)(OH)_2]^+ + 2H^+ + e^- \longrightarrow trans\text{-}[Ru^{II}(L)(H_2O)_2]^{2+} \quad (7)$$

couple I occurs at pH 5.8, which is the pK_a for *trans*-$[Ru^{III}(L)(OH)(H_2O)]^{2+}$.

For couple II a single straight line with a slope of −60 mV per pH unit is obtained between pH 1 and 12. This suggests that the pK_a values for *trans*-$[Ru^{III}(L)(OH)(H_2O)]^{2+}$ and *trans*-$[Ru^{IV}(L)O(H_2O)]^{2+}$ are similar. Near coincidence of pK_a values for *trans*-aquaoxoruthenium(IV) and *trans*-aquahydroxoruthenium(III) has recently been reported.[1f] Thus the electrode reactions are (2) at pH < 5.8 and (8) at pH > 5.8.

$$trans\text{-}[Ru^{IV}(L)O(OH)]^+ + H^+ + e^- \longrightarrow trans\text{-}[Ru^{III}(L)(OH)_2]^+ \quad (8)$$

A direct comparison between various *trans*-dioxo(tetraamine)ruthenium(VI) complexes reveals that replacement of a tertiary nitrogen donor by a pyridyl unit results in a systematic increase in the E° of the Ru^{VI}–Ru^{IV} and Ru^{IV}–Ru^{III} couples (Table 2). For example, the E° of the Ru^{VI}–Ru^{IV} couple of *trans*-$[Ru^{VI}(L)O_2]^{2+}$ is 130 mV higher than that for *trans*-$[Ru^{VI}(L'')O_2]^{2+}$.[1e] However, the equatorial amine ligand has virtually no effect on the pH dependence of the E° of *trans*-dioxoruthenium(VI). For example, the pH at which the Ru^{VI}–Ru^{IV} couple splits into Ru^{VI}–Ru^{V} and Ru^{V}–Ru^{IV} is around 9 for *trans*-$[Ru^{VI}(L')O_2]^{2+}$, *trans*-$[Ru^{VI}(L)O_2]^{2+}$, and *trans*-$[Ru^{VI}(bipy)O_2]^{2+}$.

Stoicheiometric Oxidation.—The oxidation of organic substrates by *trans*-$[Ru^{VI}(L')O_2]^{2+}$ and *trans*-$[Ru^{VI}(L'')O_2]^{2+}$ has been studied before, showing that incorporation of a pyridine functional group into the tetra-azamacrocycle enhances the reactivities of the ruthenyl complex. The present complex (**1**) has two pyridyl donors in the equatorial amine ligand. It has a

Table 2. Formal potentials (E°/V *vs.* s.c.e.) of redox couples for some *trans*-ruthenium(VI) dioxo complexes in 0.1 mol dm^{-3} CF_3CO_2H–CF_3CO_2Na (pH 1)

Complex	Couple I (Ru^{III}–Ru^{II})	 II (Ru^{IV}–Ru^{III})	 III (Ru^{VI}–Ru^{IV})
trans-$[Ru(L')O_2]^{2+}$	0.15	0.36	0.66
trans-$[Ru(L'')O_2]^{2+}$	0.07	0.52	0.76
trans-$[Ru(L)O_2]^{2+}$	0.28	0.60	0.89
trans-$[Ru(bipy)_2O_2]^{2+}$	0.44	0.88	1.01

Table 3. Results of stoicheiometric oxidation of organic substrates by *trans*-$[Ru^{VI}(L)O_2]^{2+}$ in CH_3CN at 25 °C. Reaction time, 1 h

Substrate	Product	Yield (%)*
Styrene	Styrene oxide	56
	Benzaldehyde	39
cis-Stilbene	*trans*-Stilbene oxide	18
	Benzaldehyde	11
trans-Stilbene	*trans*-Stilbene oxide	27
	Benzaldehyde	20
Cyclohexene	2-Cyclohexenone	93
Norborn-2-ene	*exo*-2,3-Epoxynorbornane	85
Cyclo-octene	Cyclo-octene oxide	50
Ethylbenaene	Acetophenone	89
Toluene	Benzaldehyde	91
Tetrahydrofuran	γ-Butyrolactone	98
Cyclobutanol	Cyclobutanone	95
Cyclohexanol	Cyclohexanone	98
Benzyl alcohol	Benzaldehyde	90

* Based on amount of complex used.

much higher redox potential and has been found to be an active oxidant. Table 3 summarizes the results of stoicheiometric oxidation of a wide variety of organic substrates by (**1**) in acetonitrile at room temperature. Controlled experiments showed negligible oxidation took place in the absence of the oxidant.

For the C–H bond oxidation and C=C bond epoxidation, the ruthenium product in each case has virtually the same optical spectrum as that of *trans*-$[Ru^{IV}(L)O(H_2O)]^{2+}$, indicating that the reactions are accompanied by the reduction of *trans*-dioxoruthenium(VI) to *trans*-aquaoxoruthenium(IV). This also suggests that *trans*-$[Ru^{IV}(L)O(H_2O)]^{2+}$ is not an active oxidant and could not oxidize the organic substrates under the reaction conditions employed for (**1**). This is in accordance with the much lower E° of Ru^{IV} than that of Ru^{VI}. As for *trans*-$[Ru^{VI}(L')O_2]^{2+}$ (ref. 1*c*) and *trans*-$[Ru^{VI}(L'')(O)_2]^{2+}$.[1e] (**1**) can rapidly oxidize alcohols to the corresponding aldehyde and ketone quantitatively; the reactions are usually complete in less than 1 h. Since oxidation of cyclobutanol gave cyclobutanone quantitatively, the ruthenium(VI) complex behaved as an overall two-electron oxidant. For the reactions with alkenes, both epoxidation and oxidative cleavage of the C=C double bond were observed. The reaction with norborn-2-ene gave *exo*-2,3-epoxynorbornane in nearly quantitative yield. In the reaction with *cis*-stilbene only *trans*-stilbene oxide and benzaldehyde were found. According to Castellino and Bruice,[8] this finding would indicate a redox pathway for the reaction between the Ru=O and C=C bonds. A direct comparison between complex (**1**) and *trans*-$[Ru^{VI}(L'')O_2]^{2+}$ reveals that the former is a much more active oxidant for C–H bond oxidation. For example, oxidation of toluene and ethylbenzene were found to give very high yields of the corresponding oxidized products, in contrast to the results for *trans*-$[Ru^{VI}(L'')O_2]^{2+}$.[1e]

Conclusion

The redox chemistry of *trans*-$[Ru^{VI}(L)O_2]^{2+}$ is very similar to that of other *trans*-dioxoruthenium(VI) complexes of tetra-azamacrocyclic ligands. However, the present complex has been found to be an active oxidant, which is capable of oxidizing tetrahydrofuran and aromatic hydrocarbons under mild conditions. The replacement of a tertiary nitrogen donor by a pyridine functional group increases both the redox potential and the reactivity of the ruthenium oxo oxidant.

Acknowledgements

We acknowledge support from the University of Hong Kong and the University and Polytechnic Granting Committee.

References

1 (*a*) C. M. Che, K. Y. Wong, and C. K. Poon, *Inorg. Chem.*, 1985, **24**, 1797; (*b*) C. M. Che, K. Y. Wong, W. H. Leung, and C. K. Poon, *ibid.*, 1986, **25**, 345; (*c*) C. M. Che, T. F. Lai, and K. Y. Wong, *ibid.*, 1987, **26**, 2289; (*d*) C. M. Che and W. H. Leung, *J. Chem. Soc., Chem. Commun.*, 1987, 1376; (*e*) C. M. Che, W. T. Tang, W. O. Lee, W. T. Wong, and T. F. Lai, *J. Chem. Soc., Dalton Trans.*, 1989, 2011; (*f*) C. M. Che, W. T. Tang, W. T. Wong, and T. F. Lai, *J. Am. Chem. Soc.*, 1989, **111**, 9048; (*g*) W. H. Leung and C. M. Che, *ibid.*, p. 8812.

2 B. A. Moyer and T. J. Meyer, *J. Am. Chem. Soc.*, 1978, **100**, 3601; B. A. Moyer, M. S. Thompson, and T. J. Meyer, *ibid.*, 1980, **102**, 2310; M. S. Thompson and T. J. Meyer, *ibid.*, 1982, **104**, 4106; T. J. Meyer, *J. Electrochem. Soc.*, 1984, **131**, 221C; L. Roecker and T. J. Meyer, *J. Am. Chem. Soc.*, 1986, **108**, 4066; J. C. Dobson, W. K. Seok, and T. J. Meyer, *Inorg. Chem.*, 1986, **25**, 1513; W. K. Seok and T. J. Meyer, *J. Am. Chem. Soc.*, 1988, **110**, 7358; J. C. Dobson and T. J. Meyer, *Inorg. Chem.*, 1988, **27**, 3283.

3 A. M. El-Hendawy, W. P. Griffith, B. Piggott, and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1988, 1983; W. P. Griffiths, S. V. Ley, G. P. Whitcombe, and A. D. White, *J. Chem. Soc., Chem. Commun.*, 1987, 1625; A. C. Dengel, W. P. Griffith, C. A. O'Mahoney, and D. J. Williams, *ibid.*, 1989, 1720.

4 T. C. Lau and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 1987, 798; M. E. Marmion and K. J. Takeuchi, *J. Am. Chem. Soc.*, 1988, **110**, 1472; C. L. Bailey and R. S. Drago, *J. Chem. Soc., Chem. Commun.*, 1987, 179; J. T. Groves and R. Quinn, *Inorg. Chem.*, 1984, **23**, 3844; *J. Am. Chem. Soc.*, 1985, **107**, 5790.

5 C. K. Poon and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1981, 495; C. M. Che, S. S. Kwong, and C. K. Poon, *Inorg. Chem.*, 1985, **24**, 1601.

6 C. M. Che, K. Y. Wong, and F. C. Anson, *J. Electroanal. Chem., Interfacial Electrochem.*, 1987, **226**, 211.

7 C. M. Che, K. Lau, T. C. Lau, and C. K. Poon, *J. Am. Chem. Soc.*, 1990, **112**, 5176; K. Lau, Ph.D. Thesis, University of Hong Kong, 1988.

8 A. J. Castellino and T. C. Bruice, *J. Am. Chem. Soc.*, 1988, **110**, 158.

Received 8*th February* 1990; *Paper* 0/00581I