Notes

High-valent Ruthenium Oxo Complexes of *NNN'N'*-Tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine (L^1). *X*-Ray Crystal Structure Determination of *cis*-[Ru^{III}(L^1)Cl$_2$]ClO$_4$†

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The reaction of $K_2[RuCl_5(H_2O)]$ with *NNN'N'*-tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine (L^1) in ethanol yielded *cis*-[Ru^{III}(L^1)Cl$_2$]$^+$, which was isolated as the ClO_4^- salt. The optical spectrum of *cis*-[Ru^{III}(L^1)Cl$_2$]ClO$_4$ in acetonitrile displays one intense band at 375 nm attributed to a $p_\pi(Cl) \longrightarrow d_\pi^*(Ru)$ transition. *cis*-[Ru^{III}(L^1)Cl$_2$]ClO$_4$ has been characterized by *X*-ray crystallography: space group $P2_1/c$, $a = 11.716(5)$, $b = 13.089(4)$, $c = 12.981(5)$ Å, $\beta = 94.28(2)°$, $Z = 4$, and $R = 0.076$ for 1 913 observed Mo-K_α data. The co-ordination geometry around the metal ion is distorted octahedral with *cis* arrangement of the two chloride ligands. The average Ru–N and Ru–Cl bond distances are 2.17(1) and 2.345(4) Å, respectively. Treatment of *cis*-[Ru^{III}(L^1)Cl$_2$]ClO$_4$ with silver(I) *p*-toluenesulphonate in hot water and then H_2O_2 gave [Ru^{VI}(L^1)(O)$_2$]$^{2+}$ isolated as the ClO_4^- salt. [Ru^{VI}(L^1)(O)$_2$][ClO$_4$]$_2$ is diamagnetic ($\mu_{eff.} = 0$) and has an intense i.r. band at *ca.* 850 cm^{-1} attributed to ν_{asym}(Ru=O) stretching. The $E_{\frac{1}{2}}$ value of the [Ru^{VI}(L^1)(O)$_2$]$^{2+}$/[Ru^{IV}(L^1)(O)(H$_2$O)]$^{2+}$ couple in 0.1 mol dm^{-3} CF_3CO_2H is 0.79 V *vs.* a saturated calomel electrode. The reaction of [Ru^{VI}(L^1)(O)$_2$][ClO$_4$]$_2$ with styrene produced benzaldehyde.

Relatively few studies have been reported on the chemistry of d^2 *cis*-dioxo-ruthenium(VI) and -osmium(VI) complexes despite the fact that they are potentially strong oxidants.[1–5] Meyer and co-workers[2] recently claimed the electrochemical generation of *cis*-[Ru^{VI}(bipy)$_2$(O)$_2$]$^{2+}$ (bipy = 2,2'-bipyridyl) from *cis*-[Ru^{II}(bipy)$_2$(H$_2$O)$_2$]$^{2+}$; however, the identification of the Ru$^{VI/V}$ couple is ambiguous owing to the complexity of Ru–bipy electrochemistry. [However, well defined Ru$^{VI/V}$, Ru$^{V/IV}$, and Ru$^{IV/III}$ couples have been observed using edge-plane pyrolytic graphite electrodes.[6]] Recently we have shown that stable high-valent Ru=O complexes can be obtained by employing quadridentate tertiary amine ligands.[7] The ligand *NNN'N'*-tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine (L^1), which would give too small a central cavity if the four N lone pairs were arranged about it equatorially, is expected to co-ordinate ruthenium in a *cis* fashion.[8] We describe here the chemistry, structure, and spectroscopic properties of *cis*-[Ru(L^1)Cl$_2$]ClO$_4$ and its high-valent oxo derivative.

Experimental

$K_2[RuCl_5(H_2O)]$ is purchased from Johnson Matthey. All reagents and solvents used were of analytical grade. Acetonitrile was twice redistilled over CaH_2 before use.

Preparation of Ligand L^1.—A mixture of triethylenetetramine (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 then cooled in an ice-bath. A saturated solution of sodium hydroxide was added with stirring until the solution became alkaline (pH 12). This was then extracted with chloroform; the organic extract was collected and dried over anhydrous Na_2SO_4. The organic solvent was rotatory evaporated to give a thick oil, which was purified by distillation at reduced pressure (*ca.* 80 °C at 0.1 mmHg). Yield *ca.* 70% (Found: C, 62.3; H, 13.2; N, 24.1. Calc. for $C_{12}H_{30}N_4$: C, 62.6; H, 13.0; N, 24.3%). ^{1}H N.m.r. (CDCl$_3$); δ 2.6—2.4 (m, 12 H), 2.26, 2.23 (d, 18 H). I.r.: no ν(N–H) stretch observed in the 3 000—3 500 cm^{-1} region. Mass spectrum: m/z 230 $[M]^+$.

cis-[Ru^{III}(L^1)Cl$_2$]ClO$_4$.—An ethanolic solution of L^1 (0.5 g in 230 cm^3) was added dropwise to an ethanolic suspension of $K_2[RuCl_5(H_2O)]$ (0.5 g in 200 cm^3) under conditions of reflux and vigorous stirring. The addition process took 3—4 h for completion and the solution mixture was further refluxed for 24 h. After completion, a few drops of concentrated HCl were added and the solution filtered hot; it was then rotatory evaporated to dryness. The yellowish brown residue was dissolved in 2 mol dm^{-3} HCl, and excess NaClO$_4$ was added. Yellow *cis*-[Ru^{III}(L^1)Cl$_2$]ClO$_4$ precipitated on cooling to *ca.* 10 °C. The crude product could be recrystallized from 1 mol dm^{-3} HCl or MeCN–Et$_2$O. Yield 30—40% (Found: C, 28.7; H, 6.1; Cl, 21.0; N, 11.2. Calc. for $C_{12}H_{30}Cl_3N_4O_4Ru$: C, 28.7; H, 6.0; Cl, 21.2; N, 11.2%). U.v.–visible spectrum (CH$_3$CN): $\lambda_{max.}$ 375 nm ($\varepsilon_{max.}$ 2 040 dm^3 mol^{-1} cm^{-1}), 275 (2 870).

[Ru^{VI}(L^1)(O)$_2$][ClO$_4$]$_2$.—*cis*-[Ru^{III}(L^1)Cl$_2$]ClO$_4$ (0.5 g) and excess silver(I) *p*-toluenesulphonate were digested in water (25 cm^3) at 80—90 °C for 30 min until all the AgCl had precipitated. The hot solution was filtered to remove this insoluble precipitate, and H_2O_2 (30%, 2—3 cm^3) was added dropwise with the solution maintained at *ca.* 50 °C. After effervescence had ceased, excess NaClO$_4$ was added. On standing, green crystals of [Ru^{VI}(L^1)(O)$_2$][ClO$_4$]$_2$ were deposited. Yield *ca.*

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† Dichloro(*NNN'N'*-tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine)ruthenium(III) perchlorate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, Issue 1, 1988, p. xvii—xx.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

60%. The crude product could be recrystallized from 0.1 mol dm^{-3} CF_3CO_2H or 0.1 mol dm^{-3} $HClO_4$ (Found: C, 29.0; H, 6.2; Cl, 14.2; N, 11.3. Calc. for $C_{12}H_{30}Cl_2N_4O_6Ru$: C, 28.9; H, 6.0; Cl, 14.3; N, 11.2%). U.v. in 0.1 mol dm^{-3} CF_3CO_2H: $\lambda_{max.}$ 304 ($\varepsilon_{max.}$ 1 420 dm^3 mol^{-1} cm^{-1}), 277 (5 710). I.r. (Nujol mull): ν_{asym}(Ru=O) 850 cm^{-1}. $\mu_{eff.}$ = 0 (Gouy method, crystalline sample).

Physical Measurements.—Proton n.m.r. spectra were run on a JEOL model (90 MHz) FX90Q spectrometer. U.v.–visible spectra were measured with a Beckman Acta CIII spectrophotometer. I.r. spectra were obtained as Nujol mulls on a Perkin-Elmer 577 spectrophotometer (4 000—200 cm^{-1}).

Cyclic voltammetric measurements were performed using a PAR universal programmer (model 175), potentiostat (model 173), and digital coulometer (model 179). Formal potentials were taken from the mean value of the cathodic and anodic peak potentials at 25 °C at a scan rate of 100 mV s^{-1}. Pyrolytic graphite was used as the working electrode. All measurements were made against Ag–$AgNO_3$ (0.1 mol dm^{-3} in CH_3CN) or saturated calomel electrode (s.c.e.).

X-Ray Structural Studies.—*Crystal data.* $C_{12}H_{30}Cl_3N_4O_4$-Ru, M = 501.82, monoclinic, space group $P2_1/c$, a = 11.716(5), b = 13.089(4), c = 12.981(5) Å, β = 94.28(2)°, U = 1 985(1) Å^3, D_m = 1.675, D_c (Z = 4) = 1.679 g cm^{-3}, Mo-K_α (graphite-monochromatized) radiation, λ = 0.710 69 Å, μ = 12.05 cm^{-1}, T = 295 K, crystal size 0.26 × 0.22 × 0.22 mm, empirical absorption correction (μr = 0.14, transmission factors 0.642—0.715), 2 154 unique reflections ($2\theta_{max.}$ = 46°), 1 913 observed [$|F_o| > 3\sigma(|F_o|)$], R = 0.076, R' = 0.100, S = 2.802 for 235 variables with $w = [\sigma^2(|F_o|) + 0.0006|F_o|^2]^{-1}$. The structure was solved by the heavy-atom method and refined using the SHELXTL[9] system on a Data General Nova 3/12 minicomputer. All non-H atoms were varied anisotropically. The methylene H atoms were allowed to ride on their respective parent C atoms and the methyl groups were treated as rigid groups (C–H bond fixed at 0.96 Å; isotropic thermal parameters assigned to H atoms).

The final atomic co-ordinates are given in Table 1, and bond distances and angles in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Table 1. Atomic co-ordinates (× 10^5 for Ru; × 10^4 for other atoms) for *cis*-$[Ru(L^1)Cl_2]ClO_4$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	24 196(9)	4 678(8)	30 989(8)	C(1)	2 046(20)	165(16)	5 437(14)
Cl(1)	811(4)	1 386(3)	3 544(4)	C(2)	3 199(15)	−1 095(14)	4 764(12)
Cl(2)	3 807(4)	1 398(3)	4 101(4)	C(3)	1 203(16)	−1 062(13)	4 296(13)
Cl(3)	2 657(3)	5 862(3)	3 597(3)	C(4)	1 211(19)	−1 544(18)	3 163(17)
O(1)	2 755(15)	4 788(10)	3 582(12)	C(5)	198(15)	−548(15)	1 993(17)
O(2)	2 639(18)	6 184(13)	2 546(12)	C(6)	2 011(16)	−1 264(13)	1 610(16)
O(3)	1 670(11)	6 151(10)	4 000(11)	C(7)	3 289(13)	−1 329(12)	1 960(15)
O(4)	3 584(12)	6 311(10)	4 135(13)	C(8)	4 836(14)	−450(14)	2 807(17)
N(1)	2 252(11)	−463(9)	4 501(8)	C(9)	3 859(19)	316(21)	1 232(18)
N(2)	1 383(11)	−703(10)	2 346(10)	C(10)	3 706(19)	1 430(15)	1 500(26)
N(3)	3 703(11)	−393(11)	2 331(11)	C(11)	2 554(18)	2 638(11)	2 184(17)
N(4)	2 584(12)	1 567(11)	1 890(12)	C(12)	1 630(20)	1 475(16)	990(15)

Table 2. Bond lengths (Å) and angles (°) in *cis*-$[Ru(L^1)Cl_2]ClO_4$

(*a*) Cation

Ru–Cl(1)	2.343(4)	Ru–Cl(2)	2.346(4)	N(2)–C(5)	1.44(2)	N(2)–C(6)	1.45(2)
Ru–N(1)	2.21(1)	Ru–N(2)	2.15(1)	N(3)–C(7)	1.39(2)	N(3)–C(8)	1.42(2)
Ru–N(3)	2.18(1)	Ru–N(4)	2.15(1)	N(3)–C(9)	1.72(3)	N(4)–C(10)	1.45(3)
N(1)–C(1)	1.50(2)	N(1)–C(2)	1.41(2)	N(4)–C(11)	1.45(2)	N(4)–C(12)	1.56(2)
N(1)–C(3)	1.47(2)	N(2)–C(4)	1.56(3)	C(3)–C(4)	1.61(3)	C(6)–C(7)	1.53(2)
				C(9)–C(10)	1.51(2)		
Cl(1)–Ru–Cl(2)	97.7(2)	Cl(1)–Ru–N(1)	87.6(4)	Ru–N(2)–C(5)	123(1)	C(4)–N(2)–C(5)	98(1)
Cl(2)–Ru–N(1)	86.0(3)	Cl(1)–Ru–N(2)	92.3(4)	Ru–N(2)–C(6)	111(1)	C(4)–N(2)–C(6)	101(1)
Cl(2)–Ru–N(2)	165.6(4)	N(1)–Ru–N(2)	84.2(5)	C(5)–N(2)–C(6)	123(1)	Ru–N(3)–C(7)	112(1)
Cl(1)–Ru–N(3)	166.6(4)	Cl(2)–Ru–N(3)	92.8(4)	Ru–N(3)–C(8)	119(1)	C(7)–N(3)–C(8)	113(1)
N(1)–Ru–N(3)	101.5(4)	N(2)–Ru–N(3)	79.0(5)	Ru–N(3)–C(9)	103(1)	C(7)–N(3)–C(9)	104(1)
Cl(1)–Ru–N(4)	87.4(4)	Cl(2)–Ru–N(4)	87.8(4)	C(8)–N(3)–C(9)	104(1)	Ru–N(4)–C(10)	108(1)
N(1)–Ru–N(4)	171.4(5)	N(2)–Ru–N(4)	103.0(5)	Ru–N(4)–C(11)	117(1)	C(10)–N(4)–C(11)	105(1)
N(3)–Ru–N(4)	84.8(5)	Ru–N(1)–C(1)	113(1)	Ru–N(4)–C(12)	113(1)	C(10)–N(4)–C(12)	110(2)
Ru–N(1)–C(2)	114(1)	C(1)–N(1)–C(2)	107(1)	C(11)–N(4)–C(12)	104(1)	N(1)–C(3)–C(4)	109(1)
Ru–N(1)–C(3)	106(1)	C(1)–N(1)–C(3)	105(1)	N(2)–C(4)–C(3)	110(2)	N(2)–C(6)–C(7)	111(1)
C(2)–N(1)–C(3)	112(1)	Ru–N(2)–C(4)	107(1)	N(3)–C(7)–C(6)	111(1)	N(3)–C(9)–C(10)	108(2)
				N(4)–C(10)–C(9)	109(2)		

(*b*) Anion

Cl(1)–O(1)	1.41(1)	Cl(3)–O(2)	1.43(2)	O(1)–Cl(3)–O(2)	106(1)	O(1)–Cl(3)–O(3)	111(1)
Cl(3)–O(3)	1.36(1)	Cl(3)–O(4)	1.39(1)	O(1)–Cl(3)–O(4)	112(1)	O(2)–Cl(3)–O(3)	110(1)
				O(2)–Cl(3)–O(4)	108(1)	O(3)–Cl(3)–O(4)	110(1)

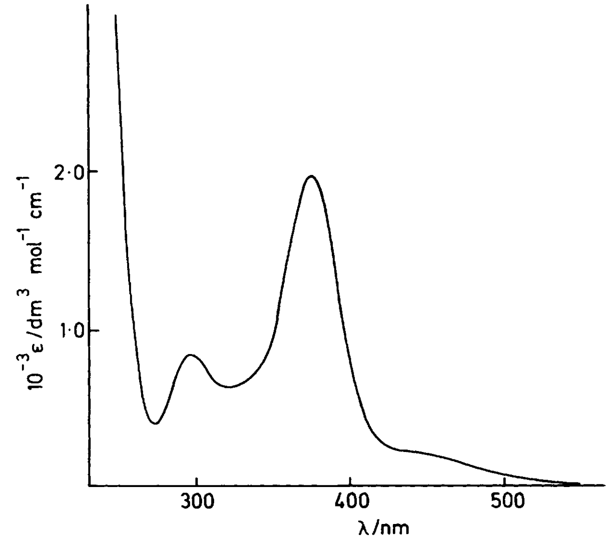

Figure 1. U.v.-visible spectrum of *cis*-$[Ru^{III}(L^1)Cl_2]ClO_4$ in acetonitrile

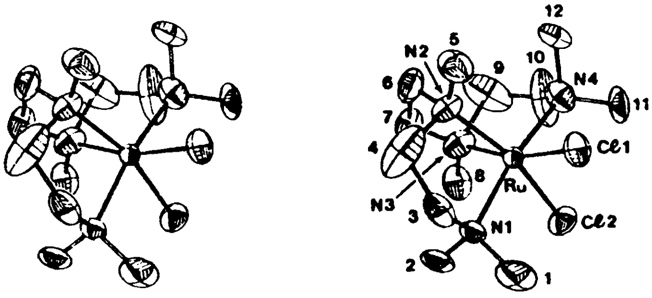

Figure 2. Perspective view of the *cis*-$[Ru(L^1)Cl_2]^+$ cation (35% probability ellipsoids), which has approximate C_{2v} molecular symmetry

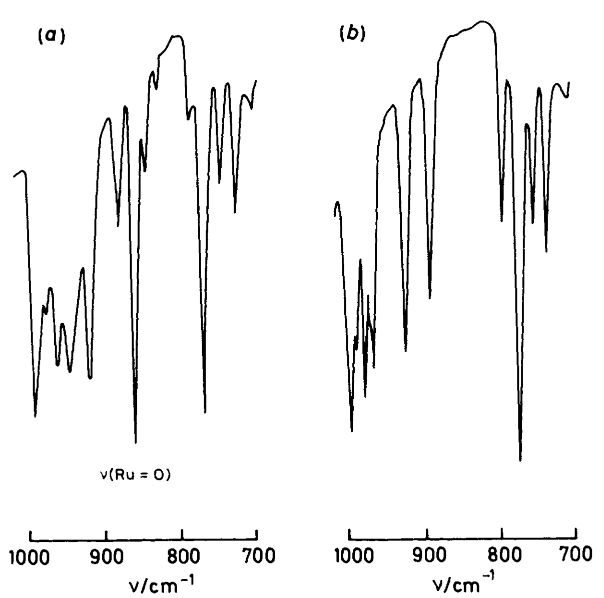

Figure 3. I.r. spectra of (*a*) $[Ru^{IV}(L^1)(O)_2][ClO_4]_2$ and (*b*) *cis*-$[Ru^{III}(L^1)Cl_2]ClO_4$ in the 1 000—750 cm^{-1} region

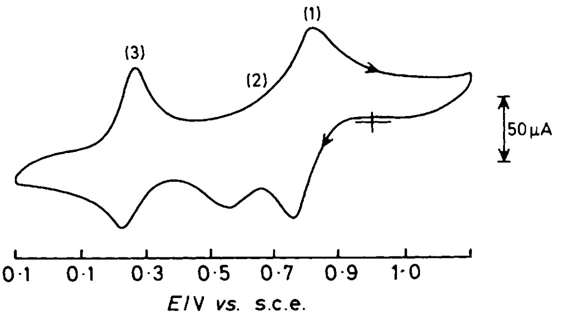

Figure 4. Cyclic voltammogram of $[Ru^{VI}(L^1)(O)_2][ClO_4]_2$ in 0.1 mol dm^{-3} CF_3CO_2H with pyrolytic graphite (basal plane) as the working electrode; see equations (1)—(3). Scan rate, 50 mV s^{-1}

Results and Discussion

As with the macrocyclic tertiary amines, the ligand L^1 was obtained by N-methylation of triethylenetetramine with HCHO–HCOOH.[10] Previous studies showed that an extensive series of *trans*-$[Ru^{III}(L)Cl_2]^+$ complexes (L = two bidentate amines or one quadridentate amine) could be obtained by the reaction of $K_2[RuCl_5(H_2O)]$ with L in refluxing ethanol.[11,12] In the present case with L^1 only the *cis* isomer was obtained, as the central cavity resulting from an equatorial arrangement of the four N lone pairs would be too small to accommodate the Ru^{III} atom. Figure 1 shows the optical spectrum of *cis*-$[Ru^{III}(L^1)Cl_2]ClO_4$ in acetonitrile, an intriguing feature being the occurrence of one intense band at 375 nm corresponding to a $p_\pi(Cl) \longrightarrow d_\pi{}^*(Ru)$ ligand-to-metal charge-transfer (l.m.c.t.) transition.[12,13] Verdonck and Vanquickenborne[14] have suggested that the *cis* and *trans* isomers of $[Ru(L)Cl_2]^+$ may be distinguished by their optical spectra: the *trans* complexes are characterized by one intense $p_\pi(Cl) \longrightarrow d_\pi{}^*(Ru)$ absorption band, whereas two equal intensity l.m.c.t. absorptions are expected for the *cis* isomers. Apart from the weak shoulder at 450 nm, Figure 1 resembles the optical spectrum of *trans*-$[Ru^{III}(L^2)Cl_2]^+$ (L^2 = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)[11c] rather than that of *cis*-$[Ru^{III}(H_2NCH_2CH_2NH_2)_2Cl_2]^+$ [15] or *cis*-$[Ru^{III}(NH_3)_4Cl_2]^+$.[16]

The *X*-ray structure of the *cis*-$[Ru^{III}(L^1)Cl_2]^+$ cation (Figure 2) features the first example of a dichloro(tertiary tetra-amine)ruthenium(III) complex in the *cis* configuration. The co-ordination geometry about the metal ion is distorted octahedral with two chloride ligands *cis* to each other. Because of the steric interaction of the N–CH_3 groups, the N(1)–Ru–N(4), Cl(2)–Ru–N(2), and Cl(1)–Ru–N(3) axes are bent, the corresponding angles being 171.4(5), 165.6(4), and 166.6(4)° respectively. The average Ru–N and Ru–Cl bond distances of 2.17(1) and 2.345(4) Å, respectively, are comparable to those found in *cis*- and *trans*-$[Ru(L^3)Cl_2]^+$ (L^3 = 1,4,8,11-tetra-azacyclotetradecane)[12,17] and other ruthenium–amine systems.[7,18]

The co-ordinated chlorides in *cis*-$[Ru(L^1)Cl_2]^+$ were removed by heating the metal complex with silver(I) *p*-toluenesulphonate in water at *ca.* 80 °C. The resulting aqua complex, $[Ru(L^1)(OH)(H_2O)]^{2+}$, could be oxidized by H_2O_2 to a green substance analysed as $[Ru(L^1)(O)_2][ClO_4]_2$. It is diamagnetic, as expected for a d^2 dioxo metal complex, and has a single intense i.r. band at 850 cm^{-1} [Figure 3(*a*)], typical of ν_{asym}(Ru=O) stretching in a *trans*-dioxo(tetra-amine)ruthenium(VI) system.[7d,19,20] A *cis*-dioxo metal complex would be expected to have two i.r.-active M=O stretches.[1b,3] In the 1 000—900 cm^{-1} region which corresponds to the ligand stretching modes, the i.r. spectra of *cis*-$[Ru^{III}(L^1)Cl_2]ClO_4$ [Figure 3(*b*)] and $[Ru^{VI}(L^1)(O)_2][ClO_4]_2$ are similar but not superimposable. The geometry of $[Ru^{VI}(L^1)(O)_2][ClO_4]_2$ is also inferred from its electrochemistry. We[6] and Meyer and coworkers[2,3] have observed four well defined couples corresponding to $Ru^{VI/V}$, $Ru^{V/IV}$, $Ru^{IV/III}$, and $Ru^{III/II}$ in the cyclic voltammograms of *cis*-dioxo–ruthenium(VI) complexes such as *cis*-$[Ru^{VI}(bipy)_2(O)_2]^{2+}$ at pH 1—4. For the *trans*-dioxo–ruthenium(VI) system, only three well defined couples, $Ru^{VI/IV}$, $Ru^{IV/III}$, and $Ru^{III/II}$ were found (pH 1—6).[7d,19] Figure 4 shows the cyclic voltammogram of $[Ru^{VI}(L^1)(O)_2][ClO_4]_2$ in 0.1 mol dm^{-3} CF_3CO_2H with pyrolytic graphite (basal plane) as the working electrode; its shape is similar to those of *trans*-$[Ru^{VI}(bipy)_2(O)_2]^{2+}$ and *trans*-$[Ru^{VI}(L^2)(O)_2]^{2+}$, with three well defined couples at potentials of 0.79, 0.60, and 0.25 V *vs.* s.c.e corresponding to the electrode reactions (1)—(3). However,

$$[Ru^{VI}(L^1)(O)_2]^{2+} + 2H^+ + 2e^- \longrightarrow [Ru^{IV}(L^1)(O)(H_2O)]^{2+} \quad (1)$$

$$[Ru^{IV}(L^1)(O)(H_2O)]^{2+} + H^+ + e^- \longrightarrow [Ru^{III}(L^1)(OH)(H_2O)]^{2+} \quad (2)$$

$$[Ru^{III}(L^1)(OH)(H_2O)]^{2+} + H^+ + e^- \longrightarrow [Ru^{II}(L^1)(H_2O)_2]^{2+} \quad (3)$$

the $[Ru^{VI}(L^1)(O)_2]^{2+}$ complex was found to be unstable in solution at pH > 3, rendering the study of its electrochemistry difficult.

The electrochemical results together with the i.r. spectral data suggest that $[Ru^{VI}(L^1)(O)_2][ClO_4]_2$ is likely to have a *trans* configuration. Importantly, it is a more powerful oxidant than *trans*-$[Ru^{VI}(L^2)(O)_2][ClO_4]_2$; the formal potential of the $Ru^{VI/IV}$ couple for the former system is 130 mV higher than that for the latter (0.66 V *vs.* s.c.e. at pH 1).[7d] This could be ascribed to the straining effect of the ligand L^1 caused by forcing the four nitrogen atoms to lie in the equatorial plane. Whereas *trans*-$[Ru^{VI}(L^2)(O)_2][ClO_4]_2$ is inert towards styrene,[21] stirring $[Ru^{VI}(L^1)(O)_2][ClO_4]_2$ with styrene for 12 h at room temperature produced benzaldehyde (identified by gas chromatography) with a 40% yield (based on the amount of metal complex used).

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