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A *cis*-Dioxoruthenium(v₁) Complex as Active Oxidant of Chloride and Organic Substrates; Preparation, Characterization, and Reactivity of *cis*-[Ru^{v₁}(6,6'-Cl₂bpy)₂O₂]²⁺ (6,6'-Cl₂bpy = 6,6'-dichloro-2,2'-bipyridine)

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Oxidation of *cis*-[Ru^{II}(6,6'-Cl₂bpy)₂(OH₂)₂]²⁺ with Ce^{IV} gave *cis*-[Ru^{VI}(6,6'-Cl₂bpy)₂O₂]²⁺, isolated as the diamagnetic ClO₄⁻⁻ salt, which rapidly oxidizes Cl⁻⁻ (to Cl₂) and a wide variety of organic substrates (tetrahydrofuran to butyrolactone and cyclohexane to cyclohexanone).

The chemistry of *cis*-dioxoruthenium(vi) complexes remains little explored despite their potential uses in oxidative reactions.1-4 Several reports2-4 describe the electrochemical generation of $cis-[Ru^{VI}(B)_2O_2]^{2+}$ cis-[Ru¹¹from $(B)_2(OH_2)_2]^{2+}$ [B = 2,2'-bipyridine (bpy) or 2,9-dimethyl-1,10-phenanthroline (dmp)]; however, the electrochemistry of these metal complexes is usually complex because the nature of the electrode surface generally affects the reversibility of the Ru=O/Ru-OH2 couple.5-7 Difficulties have been encountered in the isolation of $cis [Ru^{VI}(B)_2O_2]^{2+}$ from cis-[Ru^{II}(B)₂(OH₂)₂]^{2+,2} Formation of an unidentified green species, and isomerization leading to the more stable transdioxoruthenium(vi) system, were observed. We expected that these problems could be minimized by the steric effects of substituents at the ortho-positions of 2,2'-bipyridine.1 We regarded 6,6'-dichloro-2,2'-bipyridine⁸ as a good ligand system for cis-dioxoruthenium(vI) complexes: compared with dmp, it has the additional advantage that its ortho-substituents are inert towards oxidation. Here we describe the preparation, characterization, and reactivity of cis-[Ru^{VI}(6,6'- $Cl_2bpy)_2O_2$ [ClO₄]₂.

Scheme 1 outlines the synthesis of cis-[Ru^{II}(6,6'-Cl₂bpy)₂(OH₂)₂][ClO₄]₂ (1) and cis-[Ru^{VI}(6,6'-

 $Cl_2bpy)_2O_2$ [ClO₄]₂ (2).† As expected for an Ru^{IL}-2,2'-bipyridine system,⁹ the optical spectrum of (1) in water displays intense $d_{\pi}(Ru) \rightarrow \pi^*(6,6'-Cl_2bpy)$ charge-transfer transition at 495 nm [λ /nm (log ϵ) 495(3.92), 309(4.58), 260(3.93), and 248(4.01)]. The complex (2) is a yellowish-green solid and, as expected for a d²-cis-dioxometal system, it is diamagnetic (μ_{eff}) = 0; solid sample, Gouy method) and exhibits two i.r. v(Ru=O) bands, at 840 cm⁻¹ and ca. 790 cm⁻¹. The 90 MHz ¹H n.m.r. spectra of (1) and (2) are similar but the latter is not well resolved because of instability and low solubility. The spectrum of (1) shows the non-equivalence of the aromatic protons and the cis-configuration of the metal complex. The complex (2) is moderately stable in dry MeCN but slowly decomposes in water. Its optical spectrum in MeCN shows intense $\pi \rightarrow \pi^*$ transitions at 238, 292 and 301 nm, a shoulder at 340 nm, and a weak absorption band at 448 nm. The cyclic voltammograms of (1) and (2) in 0.1 M-CF₃Co₂H are the same, further suggesting the cis-configuration of 6,6'-Cl₂bpy ligand in (2), as in (1). At pH 1.1, two quasi-reversible couples [I and II in Figure 1(a)] at 0.93 and 1.17 V (vs. s.c.e.) are found.

[†] Satisfactory elemental analyses were obtained.

$$\begin{array}{c} \operatorname{RuCl}_3 + 6,6'-\operatorname{Cl}_2 bpy \xrightarrow{1} cis\operatorname{-}[\operatorname{RuII}(6,6'-\operatorname{Cl}_2 bpy)_2 \operatorname{Cl}_2] \\ & \downarrow ii \\ cis\operatorname{-}[\operatorname{RuII}(6,6'-\operatorname{Cl}_2 bpy)_2 (\operatorname{OH}_2)_2]^{2+} \\ & \downarrow iii \\ cis\operatorname{-}[\operatorname{RuVI}(6,6'-\operatorname{Cl}_2 bpy)_2 \operatorname{O}_2][\operatorname{ClO}_4]_2 \end{array}$$

Scheme 1. Reagents: i, reflux in ethylene glycol for 4 h under N₂; ii, digestion with silver(1) toluene-*p*-sulphonate in water at 70 °C; iii, oxidation with $[NH_4]_2[Ce(NO_3)_6]$ in the presence of NaClO₄.

Table 1. Oxidation of chloride^a and organic substrates^b by *cis*- $[Ru^{VI}(6,6'-Cl_2bpy)_2O_2][CIO_4]_2$

Substrate	Product (Yield) ^c
Toluene Tetrahydrofuran Cyclobeyane	Benzaldehyde (31%) Butyrolacetone (41%) Cyclobexanone (57%)
Styrene	Benzaldehyde (32%) Styrene oxide (44%)
Norbornene Hydrochloric acid (1 м)	exo-2,3-Epoxynorbornane (12%) Chlorine (80%)

^a Ru complex (2 mg) stirred in 1 M-HCl for 15 min at room temperature. ^b Ru complex (30 mg) and substrate [liquid (0.4 ml); solid (0.1 g)] in dry MeCN stirred at 25 °C for $1\frac{1}{2}$ h. ^c Based on the amount of metal complex used.



Figure 1. Cyclic voltammogram of *cis*-[Ru^{II}(6,6'-Cl₂bpy)₂(OH₂)₂]-[ClO₄]₂ at (a) pH 1.1 or (b) pH 2.4; working electrode, edge plane pyrolytic graphite; scan rate 100 mV s⁻¹. s.c.e. = standard calomel electrode.

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The couple I (ΔE_p 60—70 mV for 50—200 mV s⁻¹) is a simple one-electron oxidation of Ru^{II} to Ru^{III} ($n = 1.0 \pm 0.1$ by coulometry), cis-[Ru^{III}(6,6'-Cl₂bpy)₂(OH₂)]²⁺ + H⁺ + e⁻ \rightarrow cis-[Ru^{II}(6,6'-Cl₂bpy)₂(OH₂)₂]²⁺. As expected for a oneelectron one-proton transfer process, its $E_{\frac{1}{2}}$ value shifts by -60 mV per unit increase in pH (pH 1-5). Controlled potential electrolysis (at 1.2 V vs. s.c.e.) of cis-[RuIII(6,6'- $Cl_2bpy)_2(OH)(OH_2)]^{2+}$ which was generated by electrochemical oxidation of (1) at 1.0 V (vs. s.c.e.) established n = 3.2 for the couple II; however, the cyclic voltammogram of the solution after electrolysis showed that decomposition of the metal complex had occurred. Rotating disc experiments $(0.1 \text{ m-CF}_3\text{CO}_2\text{H}, \text{ edge-plane pyrolytic graphite, } 5 \text{ mV s}^{-1})$ showed that the couple II has a non-linear Levich plot $(i_1 vs.)$ w_{i}) and a larger limiting plateau current (i_{i}) than for the couple I. These results suggest that the couple II is multi-electron transfer in nature, and that the electrode reaction is not a simple electron transfer process.¹⁰ At pH 2.4, the couple II splits into two reversible waves, III and IV [Figure 1(b)], that become ill-defined and irreversible as the pH of the solution increases (pH >3); however the anodic peak potential (E_{pa}) of the couple IV appears to be the same at pH 2.6–6. These electrode reactions arising from the oxidation of cis- $[Ru^{III}(6,6'-Cl_2bpy)(OH)(OH_2)]^{2+}$ are complex and further work is in progress to understand the mechanism of oxidation of (1) to (2).

The complex (2) proves to be a powerful oxidant. The results of its reactions with chloride and organic substrates are summarized in Table 1. Stirring (2) in 1 M-HCl for 15 min produced Cl₂ in over 80% yield, thereby supporting previous claims that the *cis*-dioxoruthenium(vI) system is a powerful oxidant for chloride.¹¹ More importantly, it can oxidize unactivated C-H and C=C bonds. The ease of conversion of tetrahydrofuran to butyrolactone and of cyclohexane to cyclohexanone by (2) in aprotic medium suggests its potential use in organic synthesis.

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