A *cis*-Dioxoruthenium(VI) Complex as Active Oxidant of Chloride and Organic Substrates; Preparation, Characterization, and Reactivity of *cis*-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2O_2]^{2+}$ (6,6'-Cl_2bpy = 6,6'-dichloro-2,2'-bipyridine)

Chi-Ming Che* and Wai-Ho Leung

Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

Oxidation of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$ with Ce^{IV} gave *cis*-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2O_2]^{2+}$, isolated as the diamagnetic ClO_4^- salt, which rapidly oxidizes Cl^- (to Cl_2) 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 reports[2—4] describe the electrochemical generation of *cis*-$[Ru^{VI}(B)_2O_2]^{2+}$ from *cis*-$[Ru^{II}(B)_2(OH_2)_2]^{2+}$ [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–OH_2 couple.[5—7] Difficulties have been encountered in the isolation of *cis*-$[Ru^{VI}(B)_2O_2]^{2+}$ from *cis*-$[Ru^{II}(B)_2(OH_2)_2]^{2+}$.[2] Formation of an unidentified green species, and isomerization leading to the more stable *trans*-dioxoruthenium(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'-bipyridine[8] 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*-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2O_2][ClO_4]_2$.

Scheme 1 outlines the synthesis of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2][ClO_4]_2$ (**1**) and *cis*-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2O_2][ClO_4]_2$ (**2**).† As expected for an Ru^{II}–2,2'-bipyridine system,[9] the optical spectrum of (**1**) in water displays intense $d_\pi(Ru) \rightarrow \pi^*(6,6'\text{-}Cl_2bpy)$ 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 d^2-*cis*-dioxometal system, it is diamagnetic ($\mu_{eff.} = 0$; solid sample, Gouy method) and exhibits two i.r. ν(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-CF_3CO_2H are the same, further suggesting the *cis*-configuration of 6,6'-Cl_2bpy 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.

$$\mathrm{RuCl_3 + 6,6'\text{-}Cl_2bpy} \xrightarrow{\text{i}} \textit{cis}\text{-}\mathrm{[Ru^{II}(6,6'\text{-}Cl_2bpy)_2Cl_2]}$$
$$\downarrow \text{ii}$$
$$\textit{cis}\text{-}\mathrm{[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}}$$
$$\downarrow \text{iii}$$
$$\textit{cis}\text{-}\mathrm{[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2O_2][ClO_4]_2}$$

Scheme 1. *Reagents:* i, reflux in ethylene glycol for 4 h under N_2; ii, digestion with silver(I) toluene-*p*-sulphonate in water at 70 °C; iii, oxidation with $[NH_4]_2[Ce(NO_3)_6]$ in the presence of $NaClO_4$.

Table 1. Oxidation of chloride[a] and organic substrates[b] by *cis*-$[Ru^{VI}(6,6'\text{-}Cl_2bpy)_2O_2][ClO_4]_2$

Substrate	Product (Yield)[c]
Toluene	Benzaldehyde (31%)
Tetrahydrofuran	Butyrolacetone (41%)
Cyclohexane	Cyclohexanone (57%)
Styrene	Benzaldehyde (32%) Styrene oxide (44%)
Norbornene	*exo*-2,3-Epoxynorbornane (12%)
Hydrochloric acid (1 M)	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 1½ h. [c] Based on the amount of metal complex used.

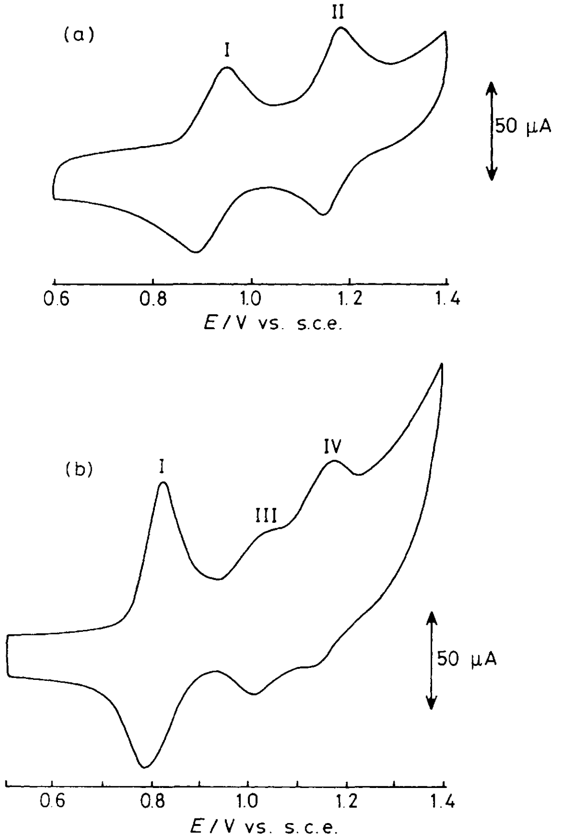

Figure 1. Cyclic voltammogram of *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]$-$[ClO_4]_2$ at (a) pH 1.1 or (b) pH 2.4; working electrode, edge plane pyrolytic graphite; scan rate 100 mV s^{-1}. s.c.e. = standard calomel electrode.

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*-$[Ru^{III}(6,6'\text{-}Cl_2bpy)_2(OH_2)]^{2+} + H^+ + e^- \rightarrow$ *cis*-$[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+}$. As expected for a one-electron 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*-$[Ru^{III}(6,6'\text{-}Cl_2bpy)_2(OH)(OH_2)]^{2+}$ 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 M-CF_3CO_2H, edge-plane pyrolytic graphite, 5 mV s^{-1}) showed that the couple II has a non-linear Levich plot (i_l *vs.* $w_{\frac{1}{2}}$) and a larger limiting plateau current (i_l) 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*-$[Ru^{III}(6,6'\text{-}Cl_2bpy)(OH)(OH_2)]^{2+}$ 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 Cl_2 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.

We acknowledge support from the Croucher Foundation and the Research and Conference Grants of the University of Hong Kong. Wai-Ho Leung is a Croucher Foundation Studentship holder.

Received, 7th April 1987; Com. 453

References

1 C. L. Bailey and R. S. Drago, *J. Chem. Soc., Chem. Commun.*, 1987, 179.
2 K. J. Takeuchi, G. J. Samuels, S. W. Gersten, J. A. Gilbert, and T. J. Meyer, *Inorg. Chem.*, 1983, **22**, 1407.
3 J. C. Dobson, K. J. Takeuchi, D. W. Pipes, D. A. Geselowitz, and T. J. Meyer, *Inorg. Chem.*, 1986, **25**, 2357.
4 J. D. Collin and J. P. Sauvage, *Inorg. Chem.*, 1986, **25**, 135.
5 C. M. Che; K. Y. Wong, and F. C. Anson, *J. Electroanal. Chem.*, in the press.
6 R. C. McHatton and F. C. Anson, *Inorg. Chem.*, 1984, **23**, 3935.
7 A. A. Dimantis, W. R. Murphy, Jr., and T. J. Meyer, *Inorg. Chem.*, 1984, **23**, 3230.
8 S. Ogawa and S. Shiraishi, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2527.
9 B. Durham, S. R. Wilson, D. J. Hodgson, and T. J. Meyer, *J. Am. Chem. Soc.*, 1980, **102**, 600.
10 Reversible proton assisted multi-electron redox couples have been reported previously: (a) C. M. Che and W. K. Cheng, *J. Am. Chem. Soc*, 1986, **108**, 4644; (b) D. W. Pipes and T. J. Meyer, *ibid.*, 1984, **106**, 7653.
11 C. D. Ellis, J. A. Gilbert, W. R. Murphy, Jr., and T. J. Meyer, *J. Am. Chem. Soc.*, 1983, **105**, 4842.