Electrochemical Evidence for a Two-Electron Reduction Process in a (μ-Oxo)bis(μ-acetato)diruthenium(III) Complex Containing Terminal 1-Methylimidazole Ligands

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The respiratory protein hemerythrin (Hr) cycles between the diferrous deoxyHr and the diferric oxyHr forms. The process that involves a one-step two-electron transfer resulting from the binding of a dioxygen molecule is extremely rapid and reversible.[1] A similar redox process is unknown[2-5] among the synthetic model 3d-5d transition-metal complexes with a (μ-oxo)bis(μ-carboxylato)dimetal core. This report on a new diruthenium(III) complex, $[\{(1\text{-MeIm})_3\text{Ru}\}_2(\mu\text{-O})(\mu\text{-O}_2\text{CMe})_2](\text{ClO}_4)_2$ (**1**), provides the first electrochemical evidence for a quasireversible two-electron reduction process involving the tribridged core (1-MeIm = 1-methylimidazole).

Complex **1** was prepared by reacting $\text{Ru}_2\text{Cl}(\mu\text{-O}_2\text{CMe})_4$[5] (1 mmol) with 1-MeIm (8 mmol) in methanol (25 mL) at 25 °C and was isolated as a perchlorate salt.[6] The molecular structure of **1** has been determined by X-ray crystallography.[7,8] The complex cation, shown in Figure 1, has a $[\text{Ru}_2(\mu\text{-O})(\mu\text{-O}_2\text{CMe})_2]^{2+}$ core and six terminal 1-MeIm ligands. The redox properties of **1** have been studied by cyclic voltammetry.[6] The complex in 0.1 M $\text{Bu}^n{}_4\text{NClO}_4$–MeCN shows three responses near +1.5, +0.4, and −1.1 V vs SCE (Figure 2). The voltammogram appearing at 0.36 V corresponds to a reversible one-electron oxidation of the diruthenium(III) unit as evidenced from the ΔE_p value of 60 mV, the i_{pc}/i_{pa} ratio of unity (v = 10–100 mV s^{-1}), and a n value of 1.0 from coulometric oxidation. The quasireversible voltammetric response at 1.52 V with $i_{pc} \approx i_{pa}$ (ΔE_p = 70–80 mV at v = 10–100 mV s^{-1}) is assignable to the $\text{Ru}^{\text{III}}\text{Ru}^{\text{IV}}$

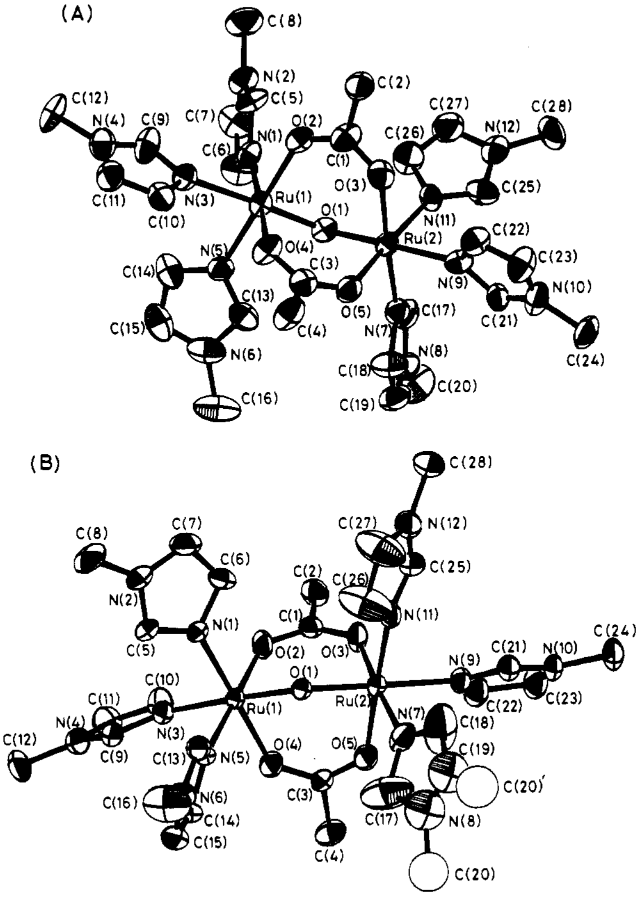

Figure 1. ORTEP diagrams of the complex cations in **1** (A) and **2** (B) along with atom numbering schemes. Selected bond distances (Å) and angles (deg) are as follows: Ru(1)···Ru(2) = 3.266(1), Ru(1)–O(1) = 1.861(7), Ru(2)–O(1) = 1.868(7), Ru(1)–N(1) = 2.041(10), Ru(1)–N(3) = 2.156(9), Ru(1)–N(5) = 2.081(9), Ru(2)–N(7) = 2.055(10), Ru(2)–N(9) = 2.116(9), Ru(2)–N(11) = 2.089(10), and Ru(1)–O(1)–Ru(2) = 122.3(4) for complex **1** and Ru(1)···Ru(2) = 3.326(1), Ru(1)–O(1) = 1.801(4), Ru(1)–N(1) = 2.041(5), Ru(1)–N(3) = 2.090(5), Ru(1)–N(5) = 2.046(5), Ru(2)–O(1) = 1.820(3), Ru(2)–N(7) = 2.033(7), Ru(2)–N(9) = 2.085(4), Ru(2)–N(11) = 2.028(5), and Ru(1)–O(1)–Ru(2) = 133.4(2) for complex **2**.

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(6) Preparative yield: ca. 70%. Anal. Calcd for $\text{C}_{28}\text{H}_{42}\text{N}_{12}\text{O}_{13}\text{Cl}_2\text{Ru}_2$: C, 32.49; H, 4.06; N, 16.25. Found: C, 32.66; H, 3.97; N, 16.53. Λ_M(MeCN) = 300 mho cm^2 mol^{-1} (1:2 electrolyte). λ_{max}, nm (ϵ, M^{-1} cm^{-1}) in MeCN: 565 (7200), 327 sh (4450). ^{1}H NMR in CDCl_3 (δ, ppm): 1.49 (s, 6H, *Me*CO_2^-); 3.80 (s, 12H, cis-oxo 1-*Me*Im); 4.29 (s, 6H, trans-oxo 1-*Me*Im); 5.67 (s), 6.62 (s), 7.58 (s) (3 × 4H, cis-oxo 1-Me*Im*); 7.78 (s), 7.91 (s), 8.61 (s) (3 × 2H, trans-oxo 1-Me*Im*). CV experiments were done on a PAR Model 174A polarographic analyzer connected with a Houston Instruments Omnigraphic X-Y recorder using a three-electrode set up with platinum-button working, platinum-wire auxiliary, and saturated calomel reference electrodes. Measurements were done in 0.1 M $\text{Bu}^n{}_4\text{NClO}_4$–MeCN at 15 °C and the data are uncorrected for junctional potentials. Under these same experimental conditions, the ferrocenium/ferrocene couple has an $E_{1/2}$ value of +0.41 V vs SCE. Coulometric measurements were made on a PAR Model 173 potentiostat fitted with a digital coulometer.

(7) Crystal data for **1**: orthorhombic, $P2_12_12_1$, a = 7.659(3) Å, b = 22.366(3) Å, c = 23.688(2) Å, V = 4058(1) Å^3, Z = 4, d_{calcd} = 1.68 g/cm^3, μ(Mo Kα) = 9.34 cm^{-1}. An Enraf-Nonius CAD-4 diffractometer was used to collect 2722 data with $I > 1.5\sigma(I)$. An empirical absorption correction[8a] was made on the data. The positions of two independent ruthenium atoms in the crystallographic asymmetric unit were derived from the Patterson map and refined by least-squares methods.[8c] The residuals are R = 0.051 and R_w = 0.051 (g = 0.000 548).

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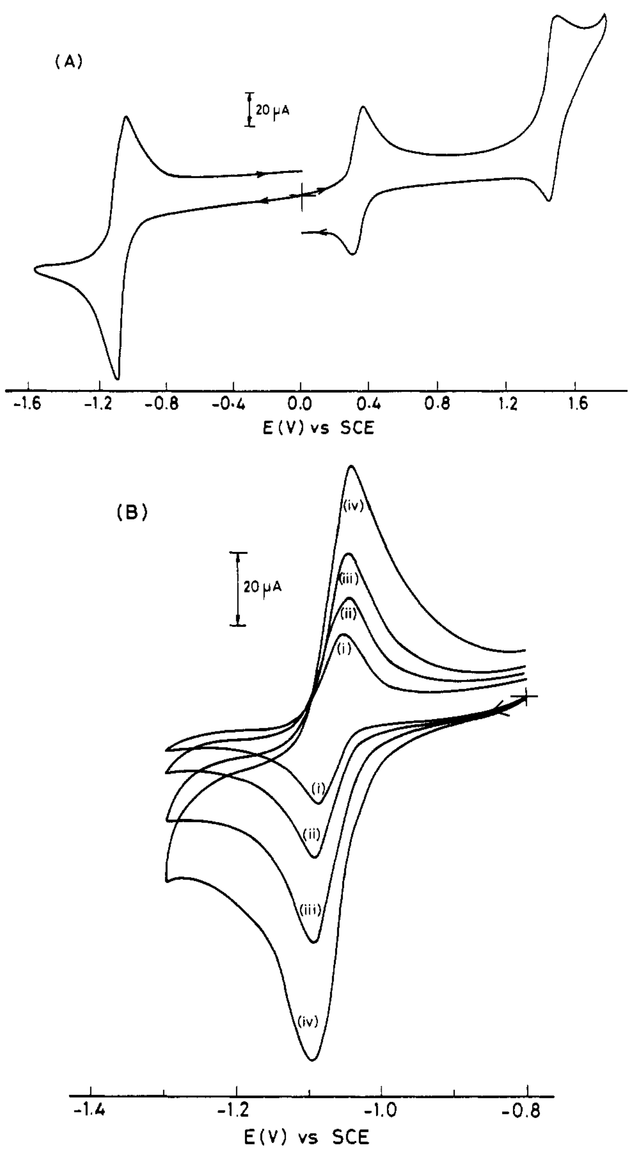

Figure 2. (A) Cyclic voltammograms of **1** at 50 mV s^{-1} (B) cyclic voltammograms for the $Ru_2(III,III) \rightleftharpoons Ru_2(II,II)$ couple at various scan rates [(i) 5, (ii) 10, (iii) 20, and (iv) 50 mV s^{-1}) in MeCN–0.1 M $Bu^n_4NClO_4$.

$\rightleftharpoons$ Ru$^{IV}_2$ couple (i_{pc} and i_{pa} are the cathodic and anodic peak currents). The one-electron-oxidized product of **1** has been isolated and structurally characterized.[9] It is interesting that the redox couple has excellent Nernstian behavior, even though the Ru–Ru and Ru–O$_{oxo}$ distances and the Ru-O-Ru angle in the $[Ru_2(\mu\text{-}O)]^{n+}$ (n = 4,5) units are different from each other (Figure 1).

The significant aspect of the present study is the observation of a one-step two-electron-transfer process occurring at −1.07 V vs SCE. The peak to peak separation (ΔE_p) of 30–50 mV at different scan rates v = 5–100 mV s^{-1}, the i_{pc}/i_{pa} ratio of unity at various scan rates, and a n value of 2.09 from coulometric reduction of **1** at −1.3 V suggest the quasireversible nature of the Ru$^{III}_2$ $\rightleftharpoons$ Ru$^{II}_2$ couple. The electrochemical behavior of **1** is unprecedented in the chemistry of synthetic model complexes with a (μ-oxo)bis(μ-carboxylato)dimetal core, and it even differs considerably from that reported[4a] for a structurally similar complex, $[\{(py)_3Ru\}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2](PF_6)_2$, for which two one-electron reductions occur at −0.85 and −1.4 V. Complex **1** is unique in displaying its ability to retain the $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2]^{n+}$ (n = 0–4) core structures on addition or removal of two electrons in the potential range +2.0 to −1.5 V vs SCE. Complex **1** in MeCN, on treatment with dry HCl in the electrochemical cell, converts to the μ-hydroxo complex $[\{(1\text{-}MeIm)_3Ru\}_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)_2]^{3+}$, which exhibits electron-transfer processes at +0.44 and −0.83 V vs SCE. The hydroxo complex as hexafluorophosphate salt was prepared in quantitative yield by reacting **1** with 2 M HCl in MeOH–H$_2$O in the presence of NH_4PF_6. Protonation experiments monitored by visible spectroscopy showed a quantitative conversion of $[Ru_2(\mu\text{-}O)]^{4+}$ to $[Ru_2(\mu\text{-}OH)]^{5+}$ core on addition of 1 equiv of HClO$_4$ to the MeCN solution of **1** [λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 500 (3600), 300 (8800) in MeCN]. The protonation process is reversible. The variable-pH visible spectral and electrochemical measurements gave a pK_a value of 2.45 for **1**. Further studies aimed toward understanding the role of imidazole bases and histidine terminal ligands on the two-electron-transfer process are in progress.

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Supplementary Material Available: Tables of crystallographic data, atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **1** and **2** (23 pages). Ordering information is given on any current masthead page.

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(9) The complex $[\{(1\text{-}MeIm)_3Ru\}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2](ClO_4)_3$ (**2**) was prepared in quantitative yield by reacting **1** with $Na_2S_2O_8$ in an aqueous medium in the presence of NaClO$_4$. λ_{max}, nm (ϵ, M^{-1} cm^{-1}) in MeCN: 498 (10 600), 308 (10 500). The one-electron paramagnetic complex exhibits rhombic EPR spectrum giving g_1 = 2.12, g_2 = 1.86, and g_3 = 1.39 in MeCN glass at 77 K. Crystals of **2**. 1.5 H$_2$O are triclinic, $P\bar{1}$, with a = 11.969(3) Å, b = 12.090(6) Å, c = 17.421(3) Å, α = 108.93(2)°, β = 84.42(2)°, γ = 105.97(2)°, V = 2292(1) Å^3, Z = 2, d_{calcd} = 1.67 g/cm^3, and μ(Mo Kα) = 9.01 cm^{-1}. Structure solution methods were similar to those for **1**. Residuals are R = 0.060 and R_w = 0.075 (g = 0.004 342) for 6767 data with $I > 3\sigma(I)$. One 1-MeIm ligand in the structure has a 1:1 orientational disorder. The atoms C(20) and C(20)′ were refined with a site occupancy factor of 0.5.