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Formation of Dinitrogen by Oxidation of $[(bpy)_2(NH_3)RuORu(NH_3)(bpy)_2]^{4+}$

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Coordinated ammonia in ruthenium and osmium polypyridyl complexes is oxidized to the nitrosyl which is in acid−base equilibrium with nitro (bpy is 2,2′-bipyridine; tpy is 2,2′,2″-terpyridine), e.g.[2,3]

$$M(tpy)(bpy)(NH_3)^{2+} \xrightarrow[+H_2O]{-6e^-,\ -5H^+} M(tpy)(bpy)(NO)^{3+} \tag{1}$$

$$M(tpy)(bpy)(NO)^{3+} + H_2O \rightleftharpoons M(tpy)(bpy)(NO_2)^{+} + 2H^{+} \tag{2}$$

$$M = Ru, Os$$

In μ-oxo complexes, the oxo bridge promotes electronic coupling and provides a short span between ions which influences reactivity.[4−6] The most striking example is $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$ (**1**), in which oxidation occurs by loss of 4 electrons and 4 protons to give O_2.[4,6] We report here that oxidation of $[(bpy)_2(NH_3)Ru^{III}ORu^{III}(NH_3)(bpy)_2]^{4+}$ (**2**) leads to dinitrogen.

In the synthesis of **2**, **1**[4b] (2.18 g) dissolved in 200 mL of 28% NH_4OH aqueous solution was heated on a steam bath for 30 min. Addition of saturated $NaClO_4$ and cooling in a refrigerator overnight gave 1.47 g of a dark blue solid which is a ∼1:4 mixture of the ClO_4^- salt of **2** and $[(bpy)_2NH_3)RuORu(OH)(bpy)_2](ClO_4)_3$.[7] [*Caution: Perchlorate salts can be explosive.*] The blue solid was collected by filtration and washed with five ∼100 mL portions of acetone to remove the ammine−hydroxo salt. Crystals of the ClO_4^- salt of **2** were grown by addition of 1 M $NaClO_4$ in water to the salt dissolved in 1 M NH_4OH.

The molecular structure of **2**[8] determined by X-ray crystallography of the ClO_4^- salt is shown in Figure 1. The configuration of the cation is Δ,Δ, but there are equal numbers of Λ,Λ and Δ,Δ isomers having the same steric configuration as **1** in the crystal because the cation sits on a 2-fold axis in the centrosymmetric space group *C*2/*c*.[4b] The Ru−O bond distance of the bridge, 1.8939(15) Å, is longer than in **1**, 1.869(0) Å, and the Ru−O−Ru angle of 158.2(4)° is smaller, 165.4(3)°. The N1(ammonia)−Ru−Ru−N1(ammonia) torsional angle is 28.45° compared to 65.7° for the O(water)−Ru−Ru−O(water) angle in **1**.[4b] The distance between the N atoms of the ammines is 4.816 Å. Similar to **1**, the ^{1}H-NMR spectrum of **2** in DMSO-d_6 is paramagnetically shifted with relatively sharp resonances appearing from −12.72 to 26.66 ppm.[4e] In the UV−visible spectrum in water, absorption maxima appear at 632 nm (ϵ = 37 300 M^{-1} cm^{-1}), 284 nm (ϵ = 50 600 M^{-1} cm^{-1}), and 248 nm (37 300 M^{-1} cm^{-1}).

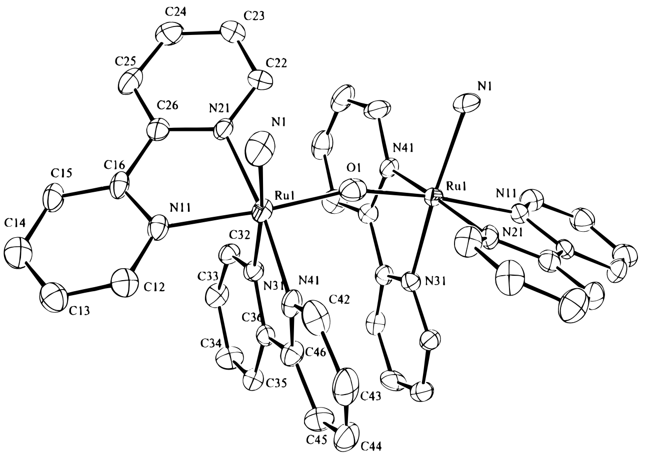

Figure 1. View of **2** in crystals of $[(bpy)_2(NH_3)RuORu(NH_3)(bpy)_2](ClO_4)_4$. Hydrogen atoms are omitted for clarity.

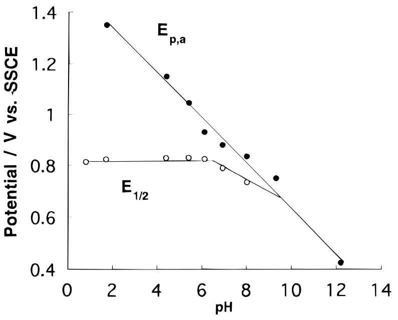

Figure 2. Potential vs pH diagrams for the reversible ($E_{1/2}$, ○) and irreversible ($E_{p,a}$, ●) waves of **2** in 0.1 M phosphate buffer solutions by cyclic voltammetric measurements at a scan rate of 100 mV/s.

In cyclic voltammograms of solutions containing **2** at pH 4.4 in 0.1 M NaH_2PO_4, a reversible, 1-electron wave appears at $E_{1/2}$ = +0.83 V and an irreversible wave at $E_{p,a}$ = +1.15 V vs SSCE. Their variations with pH are shown in Figure 2. The 1-electron couple, $[(bpy)_2(NH_3)RuORu(NH_3)(bpy)_2]^{5+/4+}$, is pH-

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(7) The ClO_4^- salt of the hydroxo ammine has been characterized by elemental analysis and X-ray structure determination (Ishitani, O. Work in progress).

(8) Crystals of $[(bpy)_2(NH_3)RuORu(NH_3)(bpy)_2](ClO_4)_4$ were monoclinic, of space group *C*2/*c*, with a = 21.617(4) Å, b = 11.998(3) Å, c = 17.999(5) Å, β = 94.469(20)°, V = 4654.0(20) Å^3, Z = 4, d_{calc} = 1.819 Mg m^{-3}, and μ = 0.95 mm^{-1}. Data were collected from a blue needle 0.18 × 0.18 × 0.35 mm, on a Rigaku diffractometer with Mo Kα radiation (λ = 0.710 73 Å) by using a $\theta/2\theta$ scan mode with θ_{max} = 45°, resulting in 2778 unique reflections of which 1877 were observed ($I > 2.5\sigma(I)$). No correction was made for absorption. R = 0.038 and R_w = 0.045. Attempts to refine the structure in *Cc* failed to improve the agreement factors, indicating *C*2/*C* as the correct choice of space group.

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independent below pH 6.5, but decreases by ~50 mV/pH unit from pH 6.5 to 8.0, consistent with eq 3, and $pK_{a1} \sim 6.5$ for loss of a proton from coordinated NH_3.[9] This wave falls under the irreversible multielectron−multiproton wave above pH 8.

$$\mathbf{2} \xrightarrow{-e^-} [(bpy)_2(NH_2)Ru^{IV}ORu^{III}(NH_3)(bpy)_2]^{4+} + H^+ \qquad (3)$$

Following a scan through this wave, new waves appear at $E_{1/2} = 1.05$ and 0.65 V characteristic of the $Ru^V{-}O{-}Ru^{IV}/Ru^{IV}{-}O{-}Ru^{III}$ and $Ru^{IV}{-}O{-}Ru^{III}/Ru^{III}{-}O{-}Ru^{III}$ couples of **1** at pH 4.4.[4b]

Controlled-potential electrolysis of **2** at pH 6.9 at a carbon mesh electrode, $E_{app} = 1.05$ V vs SSCE, for 1 h occurred with $n = 8.2$. The products were N_2[11] and a mixture of the $Ru^V{-}O{-}Ru^{IV}$ and $Ru^{IV}{-}O{-}Ru^{III}$ forms of **1**. The sum of these was formed in quantitative yield as shown by spectrophotometric and electrochemical analysis.[11] Of the total electron count, 6 electrons past **2** are used to oxidize ammonia to N_2. The remainder leads to the mixture of oxidation states of **1** and some O_2.

The variation of $E_{p,a}$ with pH for the irreversible wave is ~85 mV/pH unit (Figure 2). It may involve a net 5-electron oxidation accompanied by loss of 6 protons, eq 4. Oxidation

$$[(bpy)_2(NH_3)Ru^{IV}ORu^{III}(NH_3)(bpy)_2]^{5+} \xrightarrow[2H_2O]{-5e^-,\,-6H^+} N_2 + [(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+} \qquad (4)$$

of coordinated ammonia and release of N_2 would be followed by further oxidation and proton loss from **2** to give $[(bpy)_2(OH)Ru^{IV}ORu^{III}(H_2O)(bpy)_2]^{4+}$ and $[(bpy)_2(O)Ru^{V}ORu^{IV}(O)(bpy)_2]^{3+}$.[4b]

In related monomeric polypyridyl complexes, it has been found, or inferred, that oxidation of coordinated ammonia occurs by electron−proton loss and formation of nitrenes[13a]

$$Os^{II}(tpy)(bpy)(NH_3)^{2+} \xrightarrow[-2H^+]{-2e^-} Os^{IV}(tpy)(bpy)(NH)^{2+} \qquad (5)$$

or nitridos[12b]

$$Os^{III}(tpy)(Cl)_2(NH_3)^{+} \xrightarrow[-3H^+]{-3e^-} Os^{VI}(tpy)(Cl)_2(N)^{3+} \qquad (6)$$

Quantitative or near-quantitative formation of dinitrogen and oxidized forms of **1** in acidic solution following the oxidation suggest that related intermediates may play a role, perhaps as in

$$[(bpy)_2(NH_3)Ru^{IV}ORu^{III}(NH_3)(bpy)_2]^{5+} \xrightarrow[-4H^+]{-3e^-} \underset{\mathbf{3}}{[(bpy)_2(NH)Ru^{V}ORu^{V}(NH)(bpy)_2]^{4+}} \xrightarrow[-2H^+]{-2e^-} \underset{\mathbf{4}}{[(bpy)_2(N)Ru^{VI}ORu^{VI}(N)(bpy)_2]^{4+}} \qquad (7)$$

followed by N−N coupling.[14] It has been reported that oxidation of a face-to-face Ru porphyrin containing axially ligated NH_3 in an organic solvent with 1 equiv of *tert*-butyl hydroperoxide gives the corresponding μ-dinitrogen complex in 4% yield, the μ-diazene in 6% yield, and the μ-hydrazine in 17% yield.[15]

The appearance of intramolecular N−N coupling[14] is significant in its implications for the design of possible catalysts for N_2 reduction. In a more strongly reducing coordination environment having a related bridging structure, the reverse of eq 4 may occur through intermediates related to **3** and **4**.

The yield of **1** upon oxidation of **2** is quantitative below pH 8, decreases to 80% at pH 9.3, and decreases further to 55% at pH 12.2. $[(bpy)_2(NO_2)RuORu(NO_2)(bpy)_2]^{2+}$ appears as an additional product at high pH as shown by UV−visible and electrochemical measurements.[5] It is produced in 11% yield at pH 12.2. Two other, as yet unidentified, blue or green products were detected by ion exchange chromatography. At pH 12.2, the electrolysis (0.6 V, 1 h) occurred with $n = \sim 10$ and N_2 was obtained in ~50% yield.

Oxidation of related monomeric ammines is known to give nitrosyls, eq 1. These reactions also appear to occur through intermediates such as nitridos, e.g., $M(tpy)(bpy)(N)^{3+}$, followed by water attack at the N atom, further oxidation, and proton loss.[3] A related chemistry exists for **2**, as evidenced by the appearance of $[(bpy)_2(NO_2)RuORu(NO_2)(bpy)_2]^{2+}$ as a product above pH ~9. Presumably, if intermediates such as **3** or **4** form, there is a competition in the subsequent chemistry between N−N coupling and OH^- attack, with OH^- attack increasing in importance as the pH is raised.

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Supporting Information Available: A listing of spectral and elemental analysis data for **2** and tables of atomic coordinates, thermal parameters, and bond distances and angles for the ClO_4^- salt of **2** (7 pages). Ordering information is given on any current masthead page.

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(9) From the Nernst equation at room temperature, the reduction potential of a pH-dependent half cell reaction is $E = E_f - (n/m)(0.05916)$pH where E_f is the formal potential and *n* and *m* are the number of electrons and protons transferred for the half-reaction. See, for example, ref 4b.

(10) Because of strong electronic coupling across the μ-oxo bridge, the use of localized oxidation state labels such as $Ru^{III}{-}O{-}Ru^{IV}$ may be inappropriate.

(11) The relative amounts of $Ru^V{-}O{-}Ru^{IV}$ and $Ru^{IV}{-}O{-}Ru^{III}$ vary with time because of slow water oxidation by $Ru^V{-}O{-}Ru^{IV}$ to give O_2 and $Ru^{IV}{-}O{-}Ru^{III}$.[4f,12] Quantitative spectrophotometric or electrochemical analysis was performed after electrochemical reduction to **1**. Dinitrogen gas, produced in the bulk electrolysis by using a gastight cell, was measured by gas chromatography with a molecular sieve 5A column. Because of the pressure buildup in the cell as N_2 was produced, yields of N_2 were less than stoichiometric. A yield as high as 87% was obtained in a series of three experiments.

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