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Dinitrogen Formation by Oxidative Intramolecular N---N Coupling in *cis,cis*-$[(bpy)_2(NH_3)RuORu(NH_3)(bpy)_2]^{4+}$

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The ^{15}N-labeled diammine(μ-oxo)ruthenium complex *cis*,*cis*-$[(bpy)_2(H_3{}^{15}N)Ru^{III}ORu^{III}({}^{15}NH_3)(bpy)_2]^{4+}$ ((**2**-$^{15}N)^{4+}$) was synthesized from *cis*,*cis*-$[(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$ by using $({}^{15}NH_4)_2SO_4$ and isolated as its perchlorate salt in 17% yield. A 1:1 mixture of (**2**-$^{15}N)^{4+}$ and nonlabeled *cis*,*cis*-$[(bpy)_2(H_3{}^{14}N)Ru^{III}ORu^{III}({}^{14}NH_3)(bpy)_2]^{4+}$ were electrochemically oxidized in aqueous solution. The gaseous products $^{14}N_2$ and $^{15}N_2$ were formed in equimolar amounts with only a small amount of $^{14}N^{15}N$ detected. This demonstrates that dinitrogen formation by oxidation of the diammine complex proceeds by intramolecular N---N coupling.

Introduction

The oxo-bridged ruthenium complex *cis*,*cis*-$[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$ ((**1**)$^{4+}$, bpy = 2, 2′-bipyridine) exhibits a remarkable catalytic capability toward oxygen evolution upon chemical or electrochemical oxidation. pH-dependent electrochemical and spectroscopic studies have provided evidence for a series of sequential oxidation steps accompanied by proton loss, ultimately to give $[(bpy)_2(O)Ru^{V}ORu^{V}(O)(bpy)_2]^{4+}$.[1−7] The results of kinetic and mechanistic studies on the oxygen evolution have been reported.[1−3,7] However, the details of how dioxygen is evolved — by inter- or intramolecular O---O coupling of oxo ligands or by oxo−aqua coupling with solvent water — are still not established with certainty. The results of ^{18}O isotope-labeling studies are ambiguous on this point because of substitution and exchange reactions that occur past the O_2-evolving step.[1e,3,8,19] There is no unequivocal evidence that

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(1) (a) Gersten, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029−4030. (b) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855−3864. (c) Doppelt, R.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 2027−2034. (d) Raven, S. J.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4478−4483. (e) Geselowiz, D.; Meyer, T. J. *Inorg. Chem.* **1990**, *29*, 3894−3896. (f) Chronister, C. W.; Binstead, R. A.; Ni, J. F.; Meyer, T. J. *Inorg. Chem.* **1997**, *36*, 3814−3815. (g) Schoonover, J. R.; Ni, J. F.; Roecker, L.; Whiter, P. S.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 5885−5892. (h) Bartolotti, L. J.; Pedersen, L. G.; Meyer, T. J. *Int. J. Quantum Chem.* **2001**, *83*, 143−149. (i) Yamada, H.; Hurst, J. K. *J. Am. Chem. Soc.* **2000**, *122*, 5303−5311. (j) Binstead, R. A.; Chronister, C. W.; Ni, J.; Hartshorn, C. M.; Meyer, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 8464−8473.

(2) Petach, H. H.; Elliott, M. C. *J. Electrochem. Soc.* **1992**, *139*, 2217−2221.

(3) Hurst, J. K.; Zhou, J.; Lei, Y. *Inorg. Chem.* **1992**, *31*, 1010−1017.

(4) Ramaraj, R.; Kira, A.; Kaneko, M. *J. Electroanal. Chem.* **1993**, *348*, 367−376.

(5) Lai, Y. K.; Wong, K. Y. *J. Electroanal. Chem.* **1995**, *380*, 193−200.

(6) (a) Rotzinger, F. P.; Munavalli, S.; Comte, P.; Hurst, J. K.; Grätzel, M.; Pern, F. J.; Frank, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 6619−6626. (b) Comte, P.; Nazeeruddin, M. K.; Rotzinger, F. P.; Frank, A. J.; Grätzel, M. *J. Mol. Catal.* **1989**, *52*, 63−84.

(7) (a) Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221C−228C. (b) Ruttinger, W.; Dismukes, G. C. *Chem. Rev.* **1997**, *97*, 1−24.

(8) Arakawa, R.; Kubota, N.; Fukuo, T.; Ishitani, O.; Ando, E. *Inorg. Chem.* **2002**, *41*, 3749−3754.

(9) Ishitani, O.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 2167−2168.

(10) Britton, H. T. S.; Robinson, R. A. *J. Chem. Soc.* **1931**, *458*, 1456.

(11) In *Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1992; pp 11−30.

(12) The collection of the loss of the complex from the central compartment was estimated using the following equation:

$$N_{\text{collect}} = N_0 \times \frac{C_{\text{obs}}}{nFN_0} = \frac{C_{\text{obs}}}{nF}$$

Here N_{collect} is the collected amount of the complex, N_0 is the amount of the complex used, F is the Faraday constant, C_{obs} is the flowed quantity of electricity, and n is the number of electrons flowing into one molecule of the complex; in this case $n = 7$ was used because the 6-electron-oxidized product $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{3+}$ (blue color) is oxidized to the $Ru^{IV}ORu^{III}$ form (red color) at this potential (eq 2).[1b]

(13) Coia, G. M.; Demadis, K. D.; Meyer, T. J. *Inorg. Chem.* **2000**, *39*, 2212−2223.

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oxidative intramolecular coupling can occur in this or other oxo-bridged ruthenium dimers.

Previously, we reported that the diammine complex *cis,cis*-$[(bpy)_2(H_3N)Ru^{III}ORu^{III}(NH_3)(bpy)_2]^{4+}$, which is stable to substitution in aqueous solution over a wide range of pH values, undergoes a net 7-electron oxidation with quantitative evolution of dinitrogen at pH $<$ 8, eqs 1 and 2.[9]

$$\mathit{cis,cis}\text{-}[(bpy)_2(NH_3)Ru^{III}ORu^{III}(NH_3)(bpy)_2]^{4+} + 2H_2O \xrightarrow{-6e^-,\ -6H^+} \mathit{cis,cis}\text{-}[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+} + N_2 \quad (1)$$

$$\mathit{cis,cis}\text{-}[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+} \xrightarrow{-e^-,\ -H^+} \mathit{cis,cis}\text{-}[(bpy)_2(HO)Ru^{IV}ORu^{III}(OH_2)(bpy)_2]^{4+} \quad (2)$$

In this paper, we have used the ^{15}N-labeled diammine complex to demonstrate that dinitrogen evolution proceeds by intramolecular N---N coupling.

Experimental Section

The diaqua complex *cis,cis*-$[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2](ClO_4)_4$ was synthesized according to the literature.[1b] ^{15}N-enriched $(NH_4)_2SO_4$ (98% ^{15}N) was purchased from Aldrich Co.

***cis,cis*-$[(bpy)_2(H_3{}^{14}N)Ru^{III}ORu^{III}({}^{14}NH_3)(bpy)_2](ClO_4)_4$ ((2-^{14}N)$(ClO_4)_4$).** An aqueous solution of 0.1 M Na_3PO_4 (20 mL) containing 0.47 mmol of *cis,cis*-$[(bpy)_2(H_2O)RuORu(OH_2)(bpy)_2](ClO_4)_4$ and 7.57 mmol of $(NH_4)_2SO_4$ was heated on a steam bath for 1 h. The solution was cooled to room temperature, and a saturated aqueous solution of $NaClO_4$ was added. The solution was kept at room temperature overnight, and a precipitate was collected on a frit. The solid was purified by column chromatography on a CM-Sephadex C-25 column by using a Britton−Robinson buffer (pH 7.24)−acetonitrile mixture (1:1 v/v) as eluent.[10] The perchlorate salt of *cis,cis*-$[(bpy)_2(H_3{}^{14}N)Ru^{III}ORu^{III}({}^{14}NH_3)(bpy)_2]^{4+}$ was precipitated by concentrating the eluted solution to half the original volume and adding of concentrated aqueous $NaClO_4$. The dark-blue microcrystals were collected on a frit and dried under vacuo for 1 night. [*Caution! Perchlorate salts can be explosive.*] The yield was 17%. ESI-MS [*m/z*; found (calcd)]: 325.0 (325.7), $[(\mathbf{2}\text{-}{}^{14}N)^{4+} + ClO_4]^{3+}$; 538.3 (538), $[(\mathbf{2}\text{-}{}^{14}N)^{4+} + 2ClO_4]^{2+}$; 1175.4 (1175), $[(\mathbf{2}\text{-}{}^{14}N)^{4+} + 3ClO_4^-]^+$.[8]

(2-^{15}N)$(ClO_4)_4$. The analogous ^{15}N-containing salt (**2**-^{15}N)$(ClO_4)_4$ was synthesized in a similar manner by using $({}^{15}NH_4)_2SO_4$. The yield was 17%. ESI-MS [*m/z*; found (calcd)]: 325.9 (326.3), $[(\mathbf{2}\text{-}{}^{15}N)^{4+} + ClO_4]^{3+}$; 538.7 (539), $[(\mathbf{2}\text{-}{}^{15}N)^{4+} + 2ClO_4]^{2+}$; 1177.5 (1177), $[(\mathbf{2}\text{-}{}^{15}N)^{4+} + 3ClO_4]^+$.

Measurements. Electrochemical experiments were carried out by using a GH Instruments CHI620 electrochemical analyzer. Cyclic voltammograms were obtained by using a glassy-carbon working electrode (3 mm OD), a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) in a three-compartment cell. Mass numbers of N_2 produced were determined by using a JMS-AMII15 mass spectrometer with a molecular sieve 5A column and helium as carrier gas.

Table 1. Percentage Ratios of $^{14}N_2$, $^{14}N^{15}N$, and $^{15}N_2$ Evolved by Electrochemical Oxidation of *cis,cis*-$[(bpy)_2(NH_3)RuORu(NH_3)(bpy)_2]^{4+}$ as (**2**-^{14}N)$^{4+}$, (**2**-^{15}N)$^{4+}$, or a Mixture of the Two Compared with Calculated Values in Parentheses[a]

complex	production ratio of N_2/%		
	$^{14}N_2$	$^{14}N^{15}N$	$^{15}N_2$
1:1 (**2**-^{14}N)$^{4+}$	48.4 (49.6)	3.7 (2.3)	47.9 (48.0)
+ (**2**-^{15}N)$^{4+}$	47.5 (49.6)	4.7 (2.3)	47.8 (48.0)
(**2**-^{14}N)$^{4+}$	98.1 (99.3)	1.7 (0.7)	0.2 (0.1)
	96.7 (99.3)	3.1 (0.7)	0.2 (0.1)
(**2**-^{15}N)$^{4+}$	0 (0)	6.1 (3.9)	93.9 (96.0)

[a] The experimental values were corrected for air leakage by using eq 3. Calculated values in parentheses assume 100% intramolecular coupling.

Electrolysis. A three-compartment cell was used for bulk electrolysis of the complexes. The central gastight compartment had both a gas-sampling port with a rubber septum and a ground-glass joint for attachment of a carbon mesh working electrode (Duocel 45 PPI, 2 × 3 × 0.5 cm) held by an attached Pt wire. It was separated from the other compartments with glass frits. The solution in the Pt-counter-electrode compartment was bubbled with Ar during the electrolysis. A reference electrode (SCE) was introduced into the remaining compartment through a rubber septum, and both it and the working-electrode compartment were protected from air by Ar bubbling. A phosphate buffer solution (0.1 M, pH 7) was introduced into the three compartments, and 20 mg of the complex(es) was added to the central compartment. Before electrolysis, the solutions in all three compartments were bubbled with Ar for 1 h and then 0.1 mL of the headspace gas in the central compartment was analyzed by GC-MS. Electrolyses were conducted at 1.08 V vs SCE for 40 min with stirring of the solution in the central compartment. The current decreased less than 5% of the initial value, and the color of the solution became red.

After electrolysis 0.1 mL of the headspace gas in the central compartment was introduced into the GC-MS apparatus by using a gastight syringe. Increase of the peak at $m/z = 32$ (O_2), that is, contamination by air during the procedure, was less than 3%, and the product distribution was corrected by using

$$I_x = I_x{}^{a} - I_x{}^{b} - \frac{78.09}{20.95}(I_{32}{}^{a} - I_{32}{}^{b})\,\frac{I_x{}^{b}}{I_{total}{}^{b}} \qquad (3)$$

In eq 3, I_x is the collected peak height at $m/z = x$, $I_x{}^b$ and $I_x{}^a$ are the observed peak heights at $m/z = x$ before and after electrolysis, respectively, $I_{total}{}^b$ is the sum of the peak heights at $m/z = 28$, 29, and 30 before electrolysis, and 78.09 and 20.95 are the contents of N_2 and O_2 in the air, respectively.

Calculation of the Product Ratio of the Dinitrogen Produced. Calculated isotopic ratios of the dinitrogen produced by assuming intramolecular N---N coupling were based on the natural ^{15}N content of 0.37%[11] and the $^{15}NH_3$ content of 98% in (**2**-^{15}N)$^{4+}$, which is the content of the ^{15}N-enriched $(NH_4)_2SO_4$ used in the synthesis of (**2**-^{15}N)$^{4+}$. Experimental and calculated ratios are listed in Table 1.

Results and Discussion

We have already reported that cyclic voltammograms of (**2**-^{14}N)$^{4+}$ at pH 7 show an irreversible wave at $E_p = +1.0$ V vs SCE and that electrolysis past this potential results in the 7-electron oxidation of (**2**-^{14}N)$^{4+}$ to produce dinitrogen and $[(bpy)_2(HO)Ru^{IV}ORu^{III}(H_2O)(bpy)_2]^{4+}$.[9]

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(14) Demadis, K. D.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1997**, *36*, 5678−5679.

(15) Huynh, M. H. V.; White, P. S.; John, K. D.; Meyer, T. J. *Angew. Chem. Int. Ed.* **2001**, *40*, 4049−4051.

(16) Collman, J. P.; Wagenknecht, P. S.; Lewis, N. S. *J. Am. Chem. Soc.* **1992**, *114*, 5665−5673.

(17) (a) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25−41. (2) Mayer, J. M. *Comments Inorg. Chem.* **1988**, *8*, 125−135.

(18) Yamada, H.; Koike, T.; Hurst, J. K. *J. Am. Chem. Soc.* **2001**, *123*, 12775−12780.

Cyclic voltammograms and oxidized products were the same for $(\mathbf{2}\text{-}^{14}N)^{4+}$, $(\mathbf{2}\text{-}^{15}N)^{4+}$, and a 1:1 mixture of $(\mathbf{2}\text{-}^{15}N)^{4+}$ and $(\mathbf{2}\text{-}^{14}N)^{4+}$. For each gas sample, the ratios of $^{15}N_2$, $^{14}N^{15}N$, and $^{14}N_2$ were determined on the basis of mass spectral peak heights at 28, 29, and 30 amu in GC-MS traces. No significant differences between the samples and background were noted at other mass numbers.

In the apparatus used, air leakage was <3% of the gas volume, but the yield of dinitrogen was only 46−61% because of loss of the solution containing the complex(es), which slowly passed into the side compartments due to an increase in pressure in the central compartment by the gas produced, and trapped gas bubbles on the carbon mesh electrode. A yield of 90% was obtained by using a coarser carbon-mesh electrode (30 PPI), delaying the gas analysis for several hours after the electrolysis, and correcting for the loss of solution,[12] but air leakage increased.

Experimental and calculated ratios of 28, 29, and 30 by GC-MS expressed as percentages are listed in Table 1. As noted above, the calculated values assume intramolecular coupling. The results obtained for a 1:1 mixture of $(\mathbf{2}\text{-}^{15}N)^{4+}$ and $(\mathbf{2}\text{-}^{14}N)^{4+}$ (entries 1 and 2) demonstrate dominant intramolecular coupling. In these experiments, $^{14}N_2$ and $^{15}N_2$ were produced in a 1:1 ratio with only small amounts of $^{14}N^{15}N$ detected. The latter would have been the major product if intermolecular coupling were dominant.

The similar ratios obtained in two separate experiments demonstrate that the reproducibility is high. The relatively high precision of the results is also demonstrated by the agreement between the amount of $^{15}N_2$ or $^{14}N_2$ produced upon oxidation of $(\mathbf{2}\text{-}^{15}N)^{4+}$ or $(\mathbf{2}\text{-}^{14}N)^{4+}$ and the calculated values assuming intramolecular N---N coupling.

Mechanism of Intramolecular N---N Coupling. Past the one-electron oxidation of $(\mathbf{2})^{4+}$ to the $Ru^{IV}{-}O{-}Ru^{III}$ form, $[(bpy)_2(NH_3)Ru^{IV}ORu^{III}(NH_3)(bpy)_2]^{5+}$ (eq 4), a further five-electron oxidation occurs, eq 5, but there is no further information about intermediates by cyclic voltammetry.[9]

$$cis,cis\text{-}[(bpy)_2(NH_3)Ru^{III}ORu^{III}(NH_3)(bpy)_2]^{4+} \xrightarrow{-e^-} cis,cis\text{-}[(bpy)_2(NH_2)Ru^{IV}ORu^{III}(NH_3)(bpy)_2]^{5+} \quad (4)$$

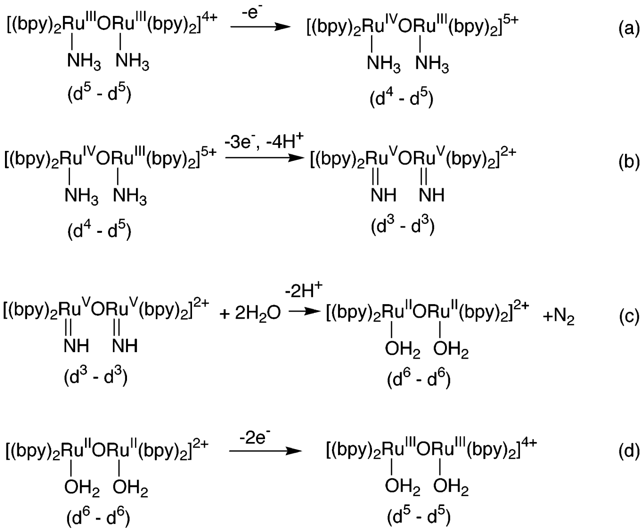
$$cis,cis\text{-}[(bpy)_2(NH_3)Ru^{IV}ORu^{III}(NH_3)(bpy)_2]^{5+} + 2H_2O \xrightarrow{-5e^-,\ -6H^+} cis,cis\text{-}[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+} + N_2 \quad (5)$$

The labeling results from a 1:1 mixture of $(\mathbf{2}\text{-}^{15}N)^{4+}$ and $(\mathbf{2}\text{-}^{14}N)^{4+}$ establish clearly that intramolecular N---N coupling dominates in the N_2 evolution mechanism. Insight that may be of relevance to this mechanism has been obtained from electrochemical measurements on related polypyridyl−ammine and −nitrido mononuclear complexes. For example, oxidation of $[Os^{III}(tpy)(Cl)_2(NH_3)]^+$ (tpy = 2,2′;6′2″-terpyridine) to Os^{IV} occurs with proton loss to give the amido complex $[Os^{IV}(tpy)(Cl)_2(NH_2)]^+$ as an intermediate. It is unstable with respect to disproportionation into $[Os^{III}(tpy)(Cl)_2(NH_3)]^+$ and $[Os^{VI}(tpy)(Cl)_2(N)]^+$.[13] Reduction of the nitrido complex in CH_3CN occurs by one electron to give Os^V, which undergoes rapid intermolecular N---N coupling to give the corresponding μ-N_2 complex (eqs 6 and 7).[14] Reduction of *mer*-$[Os^{VI}(bpy)(Cl)_3(N)]$ in strongly acidic solution gives *mer*-$[Os^V(bpy)(Cl)_3(NH)]$, which is also unstable with respect to disproportionation.[15] In the oxidation of *cis*-$[Os(bpy)_2(NH_3)Cl]^{2+}$, intermolecular N---N coupling is in competition with hydration of the N atom in Os^{IV} followed by oxidation to give the nitrosyl, *cis*-$[Os(bpy)_2(Cl)(NO)]^{2+}$.[13]

$$[Os^{VI}(tpy)(Cl)_2(N)]^+ + e^- \rightarrow [Os^V(tpy)(Cl)_2(N)] \quad (6)$$

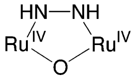
$$[Os^V(tpy)(Cl)_2(N)] \rightarrow 1/2[(Cl)_2(tpy)Os^{II}(NN)Os^{II}(tpy)(Cl)_2] \quad (7)$$

Scheme 1

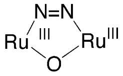


Given the related Os chemistry and the known pattern of redox events in the oxidation of $(\mathbf{1})^{4+}$ to $[(bpy)_2(O)Ru^VORu^V(O)(bpy)_2]^{4+}$, it is reasonable to propose that oxidation past the $Ru^{IV}{-}O{-}Ru^{III}$ stage (eq 4) occurs by a series of sequential electron−proton loss steps. This sequence presumably involves intermediates such as $[(bpy)_2(NH_2)Ru^{IV}ORu^{IV}(NH_2)(bpy)_2]^{4+}$, $[(bpy)_2(NH)Ru^VORu^{IV}(NH_2)(bpy)_2]^{4+}$, $[(bpy)_2(NH)Ru^VORu^V(NH)(bpy)_2]^{4+}$, and possibly even $[(bpy)_2(N)Ru^{VI}ORu^{VI}(N)(bpy)_2]^{4+}$. For $(\mathbf{1})^{4+}$, energy-minimized calculations have revealed the stepwise structural changes that occur on sequential oxidation to $[(bpy)_2(O)Ru^VORu^V(O)(bpy)_2]^{4+}$.[1h] Complete oxidation to Ru^VORu^V leads to a nearly linear Ru−O−Ru bridge and a shortening of the Ru−O terminal bonds consistent with Ru−oxo formation. Related structural changes presumably occur in the sequential oxidation of $(\mathbf{2})^{4+}$. For $(\mathbf{2})^{4+}$, the intermediates that appear past $(\mathbf{2})^{5+}$ undergo oxidation at potentials more negative than the $Ru^{IV}ORu^{III}/Ru^{IV}ORu^{IV}$ couple. This is shown by the appearance of a single, multielectron, irreversible, pH-dependent wave of oxidation of $Ru^{IV}ORu^{III}$. The higher oxidation state intermediates do not build up in solution.[9]

The actual N---N coupling mechanism is unknown, but given the precedence offered by the related Os chemistry, a reasonable sequence is shown in Scheme 1. It involves a series of sequential oxidations followed by N---N coupling, loss of N_2, and aquation. The coupling and loss of N_2 in reaction c may involve μ-hydrazido$-\mu$-oxo,



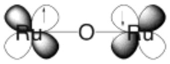
and/or μ-diazeno$-\mu$-oxo,



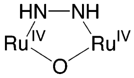
intermediates.[16] Other schemes could be written involving further oxidation to $[(bpy)_2(N)Ru^{VI}ORu^{VI}(N)(bpy)_2]^{4+}$ with direct N_2 release and formation of $(\mathbf{1})^{4+}$. The final $Ru^{IV}ORu^{III}$ product arises from the one-electron oxidation of $(\mathbf{1})^{4+}$ at the potential used in the electrolysis, eq 2.

In an orbital sense, a reasonable bonding scheme for the putative $Ru^{V}ORu^{V}$ intermediate can be constructed on the basis of an earlier scheme for the analogous $Ru^{V}ORu^{V}$ μ-oxo complex.[1d] If the z axis is defined to lie along the Ru$-$O$-$Ru bond, linear combinations of the in-plane d_{xz} orbitals at the d^3 Ru^{V} sites with a filled p(O) bridge orbital result in formation of bonding, nonbonding, and antibonding bridge-based levels. The multibonded Ru═NH interactions can then be constructed by linear combinations of d_{yz} at the separate Ru ions and p_z on the terminal imido ligands.[17] This imparts considerable antibonding character to d_{yz} (d_{yz}*). The electron occupation at each d^3 Ru^{III} sites is then $d_{xy}{}^2d_{yz}{}^{*1}$.

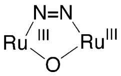
The results of a recent density functional calculation reveal considerable O-atom character at the terminal O atoms in $[(bpy)_2(O)Ru^{V}ORu^{V}(O)(bpy)_2]^{4+}$ with considerable $d\pi$---p(O) mixing.[1h] A similar buildup of radical character at the N atoms in $[(bpy)_2(NH)Ru^{V}ORu^{V}(NH)(bpy)_2]^{4+}$ would provide an electronic basis for the initiation of N---N coupling by a $d_{yz}{}^*$---$d_{yz}{}^*$ interaction shown as



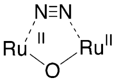
Further changes in electronic distribution and hybridization would lead to the discrete μ-hydrazido$-\mu$-oxo intermediate,



Additional electron transfer and proton loss would give



and then



(ref 16). This bookkeeping is important since microscopic reverse of this sequence could provide a viable sequence for dinitrogen reduction to NH_3.

The existence of N---N coupling in the oxidation of $(\mathbf{2})^{4+}$ offers a precedence for invoking the possible intervention of a related pathway in the catalytic oxidation of H_2O by $(\mathbf{1})^{4+}$. The results of ^{18}O-labeling studies with $H_2{}^{18}O$ bound in the $Ru^{IV}ORu^{III}$ form of $(\mathbf{1})^{4+}$ in $H_2{}^{16}O$ water show that a distribution of $^{18}O_2$, $^{18}O^{16}O$, and $^{16}O_2$ isotopic products is produced.[1e,3] If intramolecular O---O coupling were the only pathway for O_2 evolution, oxo-water O exchange in Ru^{V}-ORu^{V} would have to be invoked or mechanisms that involve both facile water exchange and electron-transfer exchange between oxidation states in the lower oxidation states.[8,15,18]

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