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Properties of the Oxo/Aquo System $(bpy)_2(py)RuO^{2+}/(bpy)_2(py)Ru(OH_2)^{2+}$

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The complex $Ru(bpy)_2(py)H_2O^{2+}$ (bpy is 2,2′-bipyridine; py is pyridine) has been prepared and found to undergo two reversible one-electron oxidations both by electrochemical means and by redox titrations using Ce(IV). The one-electron oxidation product, $Ru(bpy)_2(py)H_2O^{3+}$, has strongly enchanced properties as an acid, $pK_a = 0.85 \pm 0.03$ at 25.0 °C, $I = 1.0$ M, compared to the Ru(II) complex, $pK_a = 10.79 \pm 0.01$. The hydroxy complex, $Ru(bpy)_2(py)OH^{2+}$, has also been isolated and characterized as its perchlorate salt. The two-electron product, $Ru(bpy)_2(py)O^{2+}$, was shown to be a Ru(IV)–oxo complex by the results of a series of experiments including elemental analysis, solution conductivity, magnetism, and ^{18}O labeling. Given the acid–base properties of the complexes, redox potentials for the Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples have the expected pH dependences, and at pH 7 the potentials are (vs. the SCE) $(bpy)_2(py)RuO^{2+} \overset{0.53\ \mathrm{V}}{\overline{\hspace{2em}}} (bpy)_2(py)RuOH^{2+} \overset{0.42\ \mathrm{V}}{\overline{\hspace{2em}}} (bpy)_2(py)RuOH_2^{2+}$. Our ability to isolate a stable Ru(IV)–oxo complex and the general redox characteristics of the system are discussed in the context of the oxidation of water, the reduction of oxygen, and the competitive formation of oxo-bridged dimers.

Introduction

It has long been suggested that the irreversible oxidation of certain transition-metal complexes by O_2 takes place via dinuclear, O_2-bridged intermediates which subsequently undergo O–O bond rupture to give terminal oxo complexes as the immediate products.[1,2] The evidence for such processes (note eq 1) is, however, for the most part indirect, and consequently, the chemical events related to the breaking of the O–O bond are not well understood. Since oxo complexes are known to be highly reactive oxidizing agents in organic chemistry,[3] catalytic schemes based in part on steps like eq 1 are very attractive and have been invoked in proposed mechanisms in both chemical and biological oxidative cycles using O_2.[2] The microscopic reverse of eq 1 is equally important in providing a possible pathway for the oxidation of water, a key reaction in photosynthesis,[4] and a primary concern in the development of photochemical methods for splitting H_2O into H_2 and O_2.[5]

$$2M + O_2 \rightleftharpoons M{-}O{-}O{-}M \rightleftharpoons 2M{=}O \qquad (1)$$

Although terminal oxo complexes may play a central role in the transition-metal chemistry associated with both the oxidation of H_2O and reduction of O_2, the redox chemistry of terminal oxo complexes is not particularly well developed. This is especially true with regard to their formation in solution, their electron-transfer properties, and their potential role as redox catalysts.

In an earlier communication,[6a] we reported that a net 2e oxidation of the aquo complex $(bpy)_2(py)Ru(OH_2)^{2+}$ (bpy is 2,2′-bipyridine) resulted in the reversible formation of the ruthenyl complex $(bpy)_2(py)RuO^{2+}$. In the net reaction, the loss of two protons from the aquo ligand apparently stabilizes the metal in the 4+ oxidation state:

$$(bpy)_2(py)Ru(OH_2)^{2+} \rightarrow (bpy)_2(py)RuO^{2+} + 2H^+ + 2e^- \qquad (2)$$

That this is so is suggested by the fact that in related complexes like $Ru(bpy)_2Cl_2^+$, where oxidation to the 4+ state does not involve proton gain or loss, Ru(IV)/Ru(III) potentials occur at significantly higher redox potentials.[7]

From the perspective of the H_2O-oxidation/O_2-reduction problem, the chemistry of $(bpy)_2(py)RuO^{2+}$ is significant because it demonstrates the existence of a facile, reversible oxo–aquo ligand transformation in which the metal spans three oxidation states without any apparent disruption of the remainder of the coordination sphere. With the exception of the vanadyl ion in vanadium chemistry, terminal oxo complexes in the 4+ oxidation state exist only rarely as stable, isolable entities. Their nonexistence is due most notably to formation of oxo-bridged dimers.[7]

We have found no evidence that $(bpy)_2(py)RuO^{2+}$ can undergo the reverse of eq 1 to initiate a bimolecular 4e process to liberate O_2, but the complex has been shown to undergo oxygen transfer in the net 2e oxidation of PPh_3 to $OPPh_3$.[6] The multiple electron–atom transfer capability of the system is also probably responsible for the facile catalytic reduction of NO_3^- by $(bpy)_2(py)Ru(OH_2)^{2+}$ [8] and for a similar series of reactions observed for aquo complexes of Ru(II).[9] Not surprisingly, $(bpy)_2(py)RuO^{2+}$ and the related oxo complex $(terpy)(bpy)RuO^{2+}$ (terpy is 2,2′,2″-terpyridine) readily oxidize selected organic compounds in reactions that can be made fully catalytic when electrochemically driven.[10] In this paper, we report the details of our characterization of the compound $[(bpy)_2(py)RuO](ClO_4)_2$ as well as relevant aspects of the underlying Ru(II) and Ru(III) chemistry from which it is derived.

Experimental Section

Materials. For the conductivity experiments, water of high purity (deionized and distilled) was obtained from Dr. R. P. Buck of The University of North Carolina. Otherwise, deionized water was distilled once from $KMnO_4$. Nitrogen was purified by bubbling through an alkaline dithionite reducing solution[11] or by passing through a column

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of BTS R3-11 catalyst (BASF). Ce(IV) solutions in 1 M $HClO_4$ were prepared with recrystallized[12] or reagent grade $(NH_4)_2[Ce(NO_3)_6]$ (G. F. Smith Chemical Co.) and standardized spectrophotometrically at 320 nm with use of $\epsilon = 1230$.[13a] KCl (Ventron), Na_2SO_4, and KN_3 were recrystallized at least once from H_2O and dried in a vacuum oven. $LiClO_4$ (anhydrous, G. F. Smith Chemical Co.) required five recrystallizations from H_2O followed by drying in vacuo at 120 °C to remove impurities that reduced solutions of $(bpy)_2(py)RuO^{2+}$. All other reagents, solvents, acids, and bases were of reagent quality and were used without further purification.

Measurements. UV–vis spectra were obtained with the use of either Bausch and Lomb Spectronic 210 UV or Cary 14 spectrophotometers. Beer's law was verified with at least three dilutions of a stock solution for extinction coefficient measurements. IR spectra were obtained on a Beckman IR4250 spectrometer as either Nujol mulls or evaporated thin films (from CH_3CN) on NaCl plates. Elemental analyses were obtained from Integral Microanalytical Labs, Raleigh, N.C.

An Industrial Instruments Model RC-16B2 conductivity bridge was employed in the conductivity measurements using Pt electrodes (approximately 1 cm square and 1 cm apart) coated with Pt black.[14a] The cell design consisted of a vertical cylindrical tube (2.5-cm diameter) in which a removable electrode assembly was secured by a ground-glass joint at the top. A second ground-glass joint permitted access to the cell compartment. With the use of 0.01000 M KCl with a known specific conductance of 0.001 413 Ω^{-1} cm^{-1}, the cell constant was found to be 0.307 cm^{-1}.[15] Conductivity experiments were run basically as outlined by Feltham and Hayter[16] by delivering accurate volumes of a stock solution of electrolyte via a Radiometer Autoburette ABU11 to a known volume of H_2O in the conductivity cell thermostated at 25.0 ± 0.2 °C under deoxygenated N_2. UV–vis spectra showed that, over the course of the experiment, only slight reduction of $(bpy)_2(py)RuO^{2+}$ occurred.

Room-temperature (22 °C) magnetic susceptibility measurements were made by the Faraday technique[17] employing an approximately 5000-G permanent magnet and a Khan Gram Model G electrobalance located at Duke University under the supervision of Dr. Richard A. Palmer. The experimental susceptibility ($\chi_m = 16.44 \times 10^{-6}$ cgsu emu/g at 20 °C)[18] and tables of diamagnetic susceptibilities[17] were used to calculate μ_{eff} from $\mu_{eff} = 2.828(\chi_m T)^{1/2}$ where T is the absolute temperature and χ_m is the molar susceptibility.

p*K*a Measurements. The pK_a of $(bpy)_2(py)Ru(OH_2)^{2+}$ at 25.0 °C was determined spectrophotometrically with the use of extinction coefficients for $(bpy)_2(py)Ru(OH_2)^{2+}$ (at pH ~7) and its conjugate base (at pH ~13) at two different wavelengths (469 and 505 nm) to calculate the respective concentrations of the two forms in seven different solutions at intermediate pH values. pH measurements were obtained with use of separate glass and saturated calomel electrodes with a Radiometer 26 pH meter calibrated relative to standard[19a] borate (pH 9.18) and phosphate (pH 7.41) buffer solutions supplied by Fisher Scientific Co. A borax buffer was used to stabilize solutions at pH ≤10.5, and all solutions were protected from the atmosphere under a blanket of N_2. Constant ionic strength was maintained at 1.0 M throughout the experiment with Na_2SO_4 (0.3333 M). The resulting activity and junction potential effects were circumvented by using a calibration curve determined from titration data such that measured pH values could be correlated directly with OH^- concentration. In the range pH 10.6–12.4, the calibration curve was linear as expected[19b] and obeyed the relation $pOH = 0.94pH_{measd} + 13.06$, where pH_{measd} was the meter reading, $pOH = -\log [OH^-]$, and $[OH^-]$ is the actual hydroxide concentration.

The pK_a of $(bpy)_2(py)Ru(OH_2)^{3+}$ at 25.0 ± 0.2 °C was also determined spectrophotometrically by using eight solutions in which the $HClO_4$ concentration was varied from 0.04 to 1.0 M. $LiClO_4$ was used to hold the ionic strength constant at 1.0 M. Due to the low solubility of the complexes in this medium, the total concentration of Ru(III), $(bpy)_2(py)Ru(OH_2)^{3+}$, and $(bpy)_2(py)Ru(OH)^{2+}$ was kept low (3.7×10^{-5} M), and 5-cm cells were required to obtain useful spectrophotometric data. Formation of Ru(III) was accomplished in situ by mixing solutions of $(bpy)_2(py)Ru(OH_2)^{2+}$ and $(bpy)_2(py)RuO^{2+}$ in a ratio of approximately 1:2. The excess of Ru(IV) was needed to suppress the slight disproportionation of the conjugate base $(bpy)_2(py)Ru(OH)^{2+}$. Extinction coefficient data for $(bpy)_2(py)Ru(OH)^{2+}$ were readily obtained in this fashion from a solution at neutral pH after correcting for Ru(IV), but the extinction coefficients for $(bpy)_2(py)Ru(OH_2)^{3+}$ could not be obtained directly since the very low pK_a (0.85) would require unreasonably high $HClO_4$ concentrations. Instead, an iterative calculation to obtain both the extinction coefficient and K_a was carried out on the UNC IBM 360/375 computer facility on the basis of the relation in eq 3 where

$$A_\lambda - A_{Ru(IV)} = 5\epsilon_{CA}[Ru(III)]_0 - [Ru(III)]_0\frac{K_a}{[H^+] + K_a} + 5\epsilon_{CB}[Ru(III)]_0\frac{K_a}{[H^+] + K_a} \quad (3)^{20}$$

A_λ is the absorbance of a solution in a 5-cm cell at wavelength λ, ϵ_{CA} and ϵ_{CB} are the extinction coefficients at wavelength λ for the conjugate acid and base, respectively. A method of successive approximations was carried out on the basis of eq 3 by choosing ϵ_{CA} according to the most acidic solution and then calculating K_a. The value of K_a so obtained was then used to compute a better value of ϵ_{CA}. After ten such cycles, convergence was achieved to give a self-consistent result to within ±0.03 pK_a unit (standard deviation). The reported result is the average of six calculations using data at various wavelengths from 360 to 410 nm.

Redox Titrations. Spectrophotometric redox titrations were in general carried out by adding a volume of Ce(IV) in 1 M $HClO_4$ via buret to solutions of $(bpy)_2(py)Ru(OH_2)^{2+}$. Due to instability problems at low concentrations, especially in the presence of electrolytes, it was difficult to use $(bpy)_2(py)RuO^{2+}$ as an exact stoichiometric reagent in solution, and at $[H^+] < 0.5$ M, Ce(IV) did not behave stoichiometrically and gave irreproducible results. The spectrophotometric titrations were reproducible to within ±5%.

One of the Ce(IV) spectrophotometric titrations in 0.96 M $HClO_4$ was also followed potentiometrically at 25.0 °C under N_2 by using a PAR Model 173 potentiostat/galvanostat to measure electrometrically the potential at a Pt flag electrode vs. the SCE (saturated calomel electrode). While both waves in the titration due to Ru(III)/Ru(II) and Ru(IV)/Ru(III) couples were in themselves purely Nernstian, the modified expressions eq 4 and 5 were actually used

$$E_{measd}(\text{wave 1}) = E^{\circ\prime}_{III/II} - 0.05916 \log \frac{[H^+]}{[H^+] + K_a} - 0.05919 \log \frac{1 - R}{R} \quad (4)$$

$$E_{measd}(\text{wave 2}) = E^{\circ\prime}_{IV/III} + 0.1183 \log [H^+] - 0.05916 \log \frac{[H^+]}{[H^+] + K_a} - 0.05916 \log \frac{2 - R}{R - 1} \quad (5)$$

to derive values for the formal reduction potentials for the Ru(III)/Ru(II) and Ru(IV)/Ru(III) couples.[20] In eq 4 and 5, R is the Ce:Ru mole ratio and K_a is the concentration proton dissociation constant found for $(bpy)_2(py)Ru(OH_2)^{3+}$. $E^{\circ\prime}_{III/II}$ and $E^{\circ\prime}_{IV/III}$ are the potentials for the two couples at $[H^+] = 1.0$ M, but they are not strictly reduction potentials because they were calculated with use of concentrations and thus contain an additive term related to the ratio of activity coefficients. Since the difference $E^{\circ\prime}_{IV/III} - E^{\circ\prime}_{III/II}$ is 0.21 V, no correction was necessary to account for the effect of eq 6 in the calculations at values of R not close to any inflection points.

$$Ru(II) + Ru(IV) \rightleftharpoons 2Ru(III) \quad (6)$$

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The potentiometric behavior of the Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples with respect to pH was measured with use of a Radiometer PHM62 pH meter for both pH measurements (glass vs. SCE electrodes) and static potentials (Pt gauze or flag vs. SCE) at 25.0 ± 0.2 °C. Stock solutions of $(bpy)_2(py)RuO^{2+}$ and $(bpy)_2(py)Ru(OH_2)^{2+}$ both made up to be 1.12×10^{-3} M were mixed and diluted to 10 mL in the following ratios: 4 mL of Ru(IV):1 mL of Ru(II), 3 mL of Ru(IV):3 mL of Ru(II), and 1 mL of Ru(IV):4 mL of Ru(II). Na_2SO_4 was used to hold the ionic strength constant at 1.0 M (0.333 M Na_2SO_4). The procedure involved adding volumetrically negligible amounts of H_2SO_4 to these solutions to lower the pH as both pH and the potential were monitored. Under a steady stream of N_2 purified by bubbling through alkaline dithionite, the pH and static potentials were adequately stable at pH 6–8 without buffer and were very stable at lower pH values. The respective least-squares fits of the data in Na_2SO_4 media expressed in millivolts vs. SCE are given by $E_{measd} = -57.2\text{pH} + 959$, $-57.4\text{pH} + 887$, and $-57.6\text{pH} + 823$ for the 4:1, 1:1, and 1:1 Ru(IV):Ru(II) solutions.

Electrochemical Measurements. Electrochemical experiments were conducted at room temperature under N_2 with use of a PAR Model 175 universal programmer and a PAR Model 173 potentiostat/galvanostat. Cyclic voltammetric work was conducted either in three-compartment fritted cells or in one-compartment arrangements using a vial covered with a serum cap. Au-disk, Au-wire, and glassy-carbon-disk working electrodes were employed vs. the SCE (saturated calomel electrode) or the SSCE (saturated sodium chloride calomel electrode), and no attempt was made to optimize placement of the electrodes. Before each experiment, the Au electrodes were pretreated by cycling past the anodic and cathodic limits in 1 M H_2SO_4.[14c] Pt-gauze electrodes were used as the working electrode in exhaustive electrolysis experiments which were judged essentially complete when the current had dropped to approximately 1% of the initial current. $HClO_4$, $HClO_4/LiClO_4$, H_2SO_4, CF_3COOH, or buffered Na_2SO_4 solutions were used as electrolytes although the low solubility of the complexes in perchlorate media was troublesome.

Measurements of dissolved O_2 in alkaline solutions were obtained by using a YSI 5750 probe. For acidic solutions, syringe/serum cap techniques were used to sample the atmosphere above the solution. Separation and analysis of the gaseous components were done on a 2-ft GC column of activated alumina with the carrier gas cooled in a dry ice/isopropyl alcohol bath.

Preparations. The starting materials $[Ru(bpy)_2(py)(NO)](PF_6)_3$[21] and $(bpy)_2RuCl_2\cdot 2H_2O$[22,23a] were prepared as previously described. Both $[(bpy)_2(py)Ru(OH_2)](PF_6)_2\cdot H_2O$ and $[(bpy)_2(py)RuCl](PF_6)\cdot H_2O$ were prepared according to the outlines given below, and alternate photochemical preparations are now available.[24]

$[(bpy)_2(py)Ru(OH_2)](PF_6)_2\cdot H_2O$. In a typical preparation, 1.29 g (1.35 mmol) of $[Ru(bpy)_2(py)(NO)](PF_6)_3$ was dissolved in 50 mL of acetone (dried over $MgSO_4$) in a three-neck flask. The solution was purged with N_2 and protected from light, and a solution of 0.419 g (1.34 mmol) of KN_3 in 10 mL of warm methanol (dried over $CaSO_4$) was added dropwise. After 1 h of stirring, several milliliters of H_2O was added and the solution evaporated to dryness. The residue was redissolved in a minimum amount of acetone (5 mL), and the solution was added to 35 mL of H_2O from which a red-orange precipitate formed. After the volume was reduced, the product was filtered and then stirred with several 3-mL portions of H_2O to ensure complete removal of KPF_6. The product was vacuum dried to give a yield of 0.990 g (90%). Anal. Calcd for $[(bpy)_2(py)Ru(OH_2)](PF_6)_2\cdot H_2O$: C, 36.69; H, 3.08; N, 8.56. Found: C, 36.43; H, 3.33; N, 8.42.

$[(bpy)_2(py)RuCl](PF_6)\cdot H_2O$. An alternate, more direct route to this previously prepared complex[25] was devised to avoid time-consuming intermediate steps. An alternate photochemical preparation is also available.[24] A 3.00-g sample of $(bpy)_2RuCl_2\cdot 2H_2O$ was dissolved in approximately 70 mL of hot H_2O under a stream of N_2 gas (necessary to prevent air oxidation). To the solution was added a small volume of aqueous pyridine sufficient to give 1.3 stoichiometric equiv of pyridine with respect to complex, and the resulting solution was heated at reflux for 1 h. Systematic variations of the py:Ru ratio showed that, at a ratio of 1.5 a chromatographic band due to $[Ru(bpy)_2(py)_2](PF_6)_2$ appeared in the product as found spectrophotometrically (λ_{max} = 452 nm in H_2O or 450 nm in CH_3CN)[26] but that, at ratios of less than 1.3, significant amounts of starting complex, $(bpy)_2RuCl_2\cdot 2H_2O$, were separated from the product mixture. After the solution cooled, several grams of NaCl and 2–3 drops of saturated NH_4PF_6 solution were added to the reaction mixture followed by extraction with methylene chloride. The deep red methylene chloride layer was removed, several more drops of NH_4PF_6 solution were added, while care was taken not to cause precipitation of PF_6^- salts of the complexes present, and the extraction was repeated. This procedure was carried out six to seven more times until the methylene chloride layer became noticeably orange. The combined methylene chloride extracts were then evaporated to dryness. A yield of 3.34 g of crude product was obtained, half of which could be conveniently purified by adsorbing the complex onto a 4 in. length by $1^1/_2$ in. diameter activated alumina column from a methylene chloride solution and eluting with 1–2% isopropyl alcohol in methylene chloride. After the leading band only was collected, a combined yield of 2.26 g (57%) was obtained after evaporation and drying in vacuo.

$[(bpy)_2(py)Ru(OH_2)](ClO_4)_2\cdot H_2O$. In a procedure found to give very pure product, 0.500 g of $[(bpy)_2(py)RuCl](PF_6)\cdot H_2O$ was dissolved in 250 mL of methanol, the solution was added to 250 mL of H_2O, and the resulting solution was put onto a column of Sephadex SP-C25-120 cation exchanger in the Na^+ form. H_2O was passed through the column until $AgNO_3$ no longer precipitated Cl^- from the eluant, and then 0.1 M $NaClO_4$ was used to elute the complex. Depending on the purity of starting material and its handling, other products were sometimes present but were conveniently separated as other bands on the cation exchanger. Only the eluant with λ_{max} = 470 nm was collected, whereupon the volume was reduced at 20–30 °C under vacuum to 100-mL final volume. Rotary evaporation of the ClO_4^- salt at higher temperatures frequently caused decomposition of the complex. The bright orange precipitate was then filtered and carefully washed with six or seven $^1/_2$-mL portions of H_2O to completely remove $NaClO_4$. Yields varied but averaged 70% of the theoretical after drying in vacuo. Anal. Calcd for $[(bpy)_2(py)Ru(OH_2)](ClO_4)_2\cdot H_2O$: C, 41.28; H, 3.46; N, 9.63. Found: C, 41.64; H, 3.32; N, 9.29.

$[(bpy)_2(py)Ru(OH)](ClO_4)_2$. A 0.0606-g sample of $[(bpy)_2(py)Ru(OH_2)](ClO_4)_2\cdot H_2O$ was dissolved in approximately 20 mL of 0.05 M $NaClO_4$ with sufficient Na_2HPO_4 and KH_2PO_4 added to stabilize the pH throughout the preparation. The solution was placed in a three-compartment electrochemical cell and oxidized at +0.80 V with a Pt-gauze electrode vs. the SCE until an integrated current of 1.0 electrochemical equiv was obtained. Continued electrolysis would give Ru(IV). A few drops of saturated $NaClO_4$ solution were then added to aid in the precipitation of the product which was filtered and washed with six $^1/_2$-mL aliquots of H_2O. The greenish yellow product was dried in vacuo, giving a yield of 0.030 g (56% theoretical). Anal. Calcd for $[(bpy)_2(py)Ru(OH)](ClO_4)_2$: C, 42.39; H, 3.13; N, 9.89. Found: C, 42.07; H, 3.00; N, 9.78.

$[(bpy)_2(py)RuO](ClO_4)_2$. A 0.200-g sample of $[(bpy)_2(py)Ru(OH_2)](ClO_4)_2\cdot H_2O$ was dissolved in ~200 mL of H_2O and 2–3 mL of 60% $HClO_4$ added. A standardized solution of Ce(IV) in 1 M $HClO_4$ was added in the volume necessary to provide a 2.0:2.05 Ce:Ru stoichiometry. After several minutes of stirring, 10–20 mL of 60% $HClO_4$ was slowly added, causing the precipitation of a light green powder which was then filtered and washed with four or five $^1/_2$-mL portions of H_2O until the pH of the filtrate was neutral. The yield was 0.174 g (89%) after drying in vacuo. Anal. Calcd for $[(bpy)_2(py)RuO](ClO_4)_2$: C, 42.44; H, 2.99; N, 9.90. Found: C, 42.17; H, 2.74; N, 9.85.

^{18}O Labeling. A 0.019-g sample of $[(bpy)_2(py)Ru(OH_2)](ClO_4)_2\cdot H_2O$ was suspended in 1.0 mL of $H_2{}^{18}O$ (90.43% ^{18}O, 3.21% ^{17}O, 6.36% ^{16}O) obtained from Mound Laboratories, Miamisburg, Ohio, and stirred for approximately 24 h in the absence of light. A volume of 0.10 mL of 70% $HClO_4$ was then added followed by 2.00 stoichiometric equiv of solid $(NH_4)_2Ce(NO_3)_6$, which had previously been analyzed spectrophotometrically[13a] to determine the effective molecular weight of Ce(IV). After the mixture was stirred overnight, the light green suspended material was filtered and washed quickly

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(23) (a) Dwyer, F. P.; Goodwin, H. A.; Gyarfas, E. C. *Aust. J. Chem.* **1963**, *16*, 544. (b) *Ibid.* **1963**, *16*, 42.
(24) Durham, B.; Walsh, J. L.; Carter, C. L.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 860.
(25) Adeyemi, S. A.; Miller, F. J.; Meyer, T. J. *Inorg. Chem.* **1972**, *11*, 994.
(26) Braddock, J. N.; Meyer, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 3158.

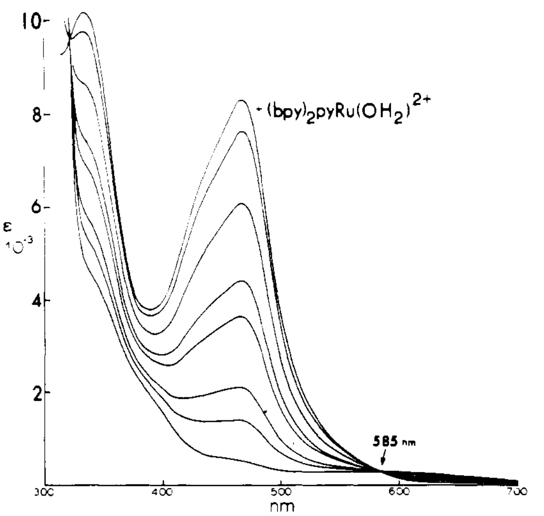

Figure 1. Spectrophotometric titration of $(bpy)_2(py)Ru(OH_2)^{2+}$ by Ce(IV). The solutions contained initially 9.84×10^{-5} M Ru(II) and the following stoichiometric equivalents of Ce(IV): 0.00 (top spectrum), 0.10, 0.30, 0.50, 0.60, 0.80, 0.90, and 0.99. Conditions: room temperature, in 0.962 M $HClO_4$/0.038 M $NaClO_4$.

five times with a few drops of ordinary distilled H_2O until the rinse was neutral. The solid was then dried in vacuo. IR analysis (Nujol mulls, NaCl plates) permitted the estimation of the ^{16}O content of the oxo ligand. The estimation was made by comparing the ratios of the peak heights of the 792-cm^{-1} $\nu_{Ru=^{16}O}$ absorption to those of two organic ligand peaks at 766 and 1610 cm^{-1}. The assumption was made that the intensity of the 766- and 1610-cm^{-1} peaks are unaffected by the isotopic content of the oxo ligand. The results showed that 26 ± 5% of the oxo ligands contained the ^{16}O isotope and, further, that the ^{16}O content increased to 42 ± 6% after storage in a vial at room temperature for 3–4 months.

Results and Discussion

Synthesis. The synthetic chemistry of bpy, phen (1,10-phenanthroline), and terpy (2,2′,2″-terpyridine) complexes of Ru(II) was initially developed by Dwyer and co-workers.[23] By aquation of a pyridine ligand in refluxing aqueous solution, they prepared salts of both $(terpy)(bpy)Ru(OH_2)^{2+}$ and $(phen)_2(py)Ru(OH_2)^{2+}$. More recently, ligands more labile than pyridine (especially solvento ligands) have greatly facilitated the systematic preparation of many related complexes.[27] Aquation of solvento ligands was found to be a convenient synthetic route to $(bpy)_2(py)Ru(OH_2)^{2+}$ (eq 7).

$$\begin{tikzcd} \mathrm{(bpy)_2(py)RuNO^{3+}} + \mathrm{N_3^-} \arrow[r, "\mathrm{S}"] & \mathrm{(bpy)_2(py)RuS^{2+}} + \mathrm{N_2} + \mathrm{N_2O} \arrow[d, "{+\mathrm{H_2O}, -\mathrm{S}\ (\mathrm{S} = \mathrm{CH_3OH/CH_3C(O)CH_3})}"] \\ & \mathrm{(bpy)_2(py)Ru(OH_2)^{2+}} \end{tikzcd} \qquad (7)$$

Davies and Mullins[28] reported that $(terpy)(bpy)RuCl^+$ undergoes rapid and essentially complete aquation in aqueous solution, and their observation was made the basis for an alternate route to $(bpy)_2(py)Ru(OH_2)^{2+}$ involving fewer synthetic intermediates (eq 8). The aquo ligand is itself

$$(bpy)_2(py)RuCl^+ \xrightarrow{H_2O} (bpy)_2(py)Ru(OH_2)^{2+} + Cl^- \qquad (8)$$

weakly bound and can be easily displaced by other potential ligands in solution.[28] It is likely[28] that $(bpy)_2(py)Ru(OH_2)^{2+}$ and related aquo complexes were in situ intermediates in many of Dwyer's original preparations.[23] The PF_6^- salt of $(bpy)_2(py)Ru(OH_2)^{2+}$ was in fact isolated from the photolysis of $(bpy)_2Ru(py)_2^{2+}$ in CH_2Cl_2, where the trace water content of the solvent is apparently sufficient to give a completely substituted complex.[24] Structurally, $(bpy)_2(py)Ru(OH_2)^{2+}$ is presumed to be in the cis configuration due to steric crowding associated with the trans geometry in bis(bpy) and bis(phen) complexes as a class.[29,30]

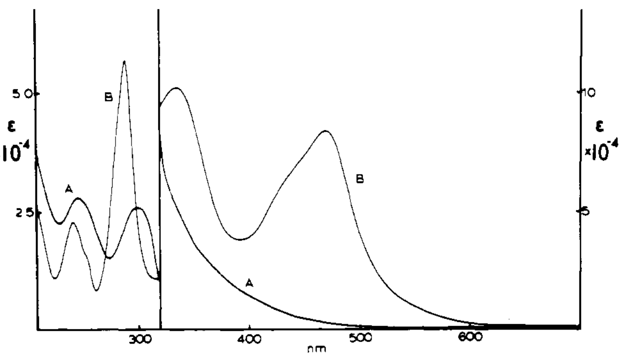

Figure 2. Electronic spectra of (A) $[(bpy)_2(py)RuO](ClO_4)_2$ in H_2O and (B) $[(bpy)_2(py)Ru(OH_2)](PF_6)_2{\cdot}H_2O$ in 1 M $HClO_4$; concentration of each complex 1.08×10^{-4} M; 0.1-cm cells for the UV and 1-cm cells for the visible part of the spectrum.

Table I. Electronic Spectral Data in Aqueous Solution

complex	λ_{max}, nm $(\epsilon)^a$
$(bpy)_2(py)Ru(OH_2)^{2+\,b}$	470 (8400), 335 (10 500), 290 (57 000), 243 (24 000)
$(bpy)_2(py)Ru(OH)^{+\,c}$	505 (8000), 363 (10 400)
$(bpy)_2(py)RuO^{2+\,d}$	300 (23 000), 248 (26 000)
$(bpy)_2(py)Ru(OH)^{2+\,d}$	364 (4700,^{e} 4900^f), 312 (20 000^e), 291 (23 000^e), 255 (25 000^e)
$(bpy)_2(py)Ru(OH_2)^{3+\,b}$	587 (250,^{e} 290^{f,g}), 312 (24 000^e), 302 (25 000^e), 246 (27 000^e)

[a] Molar extinction coefficients (±5%) are given in parentheses. [b] In 1 M $HClO_4$. [c] In 0.25 M NaOH/0.22 M Na_2SO_4; π(bpy) → π*(bpy) transitions not included. [d] In H_2O. [e] Apparent ε values: not corrected for equilibrium effects. [f] Corrected for partial disproportionation to Ru(II) and Ru(IV). [g] Corrected for partial proton dissociation.

Spectrophotometric Titrations with Ce(IV). An investigation of the redox properties of $(bpy)_2(py)Ru(OH_2)^{2+}$ began with a Ce(IV) titration in 1 M $HClO_4$, shown in Figure 1. The electronic spectrum of $(bpy)_2(py)Ru(OH_2)^{2+}$ in aqueous solution (see also Figure 2) is similar to spectra of related bipyridine–Ru(II) complexes in that the typical dπ(Ru) → π*(bpy) and π(bpy) → π*(bpy) transitions are present (see Table I).[33a] With the addition of Ce(IV), the visible absorption peak at 470 nm decreases in intensity with the occurrence of isosbestic points at 322 and 585 nm. A mole ratio plot given in Figure 3 for the reaction shows a linear decrease in absorbance at 390 nm (true at other wavelengths as well) with a break in slope at a Ce:Ru mole ratio of 1.0. At this point, the visible spectrum, characterized by only one weak band centered at 587 nm (apparent extinction coefficient 250), is consistent with the presence of the Ru(III) ion, $(bpy)_2(py)Ru(OH_2)^{3+}$. Similar bands have been observed in a variety of bis(bipyridine)–Ru(III) complexes and have been assigned

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(27) Adeyemi, S. A.; Johnson, E. C.; Miller, F. J.; Meyer, T. J. *Inorg. Chem.* **1973**, *12*, 2371. Sullivan, B. P.; Salmon, D. J.; Meyer, T. J.; Peedin, J. *Inorg. Chem.* **1979**, *18*, 3369. Connor, J. A.; Meyer, T. J.; Sullivan, B. P. *Ibid.* **1979**, *18*, 1388.

(28) Davies, N. R.; Mullins, T. L. *Aust. J. Chem.* **1968**, *21*, 915.

(29) McKenzie, E. D. *Coord. Chem. Rev.* **1971**, *6*, 189.

(30) The trans configuration has now been confirmed by X-ray diffraction for *trans*-$[(bpy)_2Ru(OH_2)(OH)](ClO_4)_2$.[31] On the basis of IR spectra, *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$ and *trans*-$[Ru(bpy)(phen)(py)_2](ClO_4)_2$ have also been claimed.[32]

(31) Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.

(32) Krause, R. A. *Inorg. Chim. Acta* **1977**, *22*, 209.

(33) (a) Bryant, G. M.; Fergusson, J. E.; Powell, H. K. J. *Aust. J. Chem.* **1971**, *24*, 257. (b) *Ibid.* **1971**, *24*, 275.

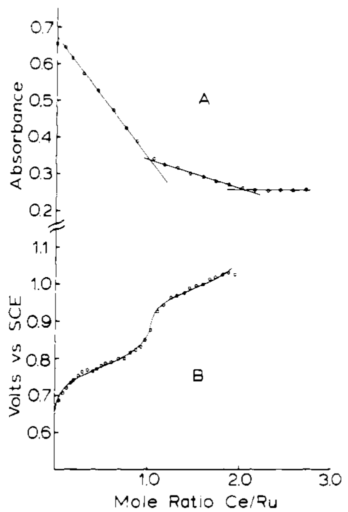
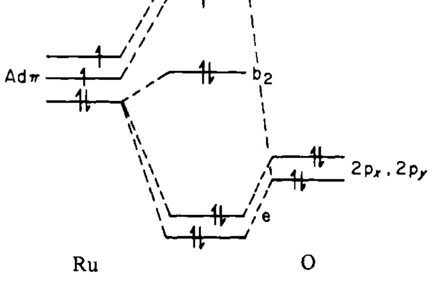


Figure 3. Titration of $[(bpy)_2(py)Ru(OH_2)](PF_6)_2 \cdot H_2O$ by Ce(IV) in 0.962 M $HClO_4$/0.038 M $NaClO_4$ at 25.0 (±0.2) °C under N_2. Standardized 1.00×10^{-3} M Ce(IV) was added via buret to 20 mL of 1.78×10^{-4} M Ru(II). A: mole ratio plot of spectrophotometric data (1-cm cells) at 390 nm corrected for the increase in volume. B: potentials measured at a Pt flag electrode vs. SCE (circles) and the Nernstian response (solid line).

to a $\pi(bpy) \rightarrow d\pi(Ru)$ transition.[33b]

The mole ratio plot (Figure 3) also shows that continued addition of Ce(IV) causes a further linear decrease in absorbance until an apparent end point at Ce:Ru = 2.0 is observed. No new significant absorptions ($\epsilon > 100$) in the visible spectrum are evident at this mole ratio, and a band at 590 nm characteristic of Ru(III) is absent. At Ce:Ru mole ratios greater than 2.0, another reaction occurs, but in contrast to the first two steps, which proceed quite rapidly, the spectral changes associated with the reaction take place slowly after an initial induction period. On standing for 6–40 h, solutions initially containing more than approximately 2.5 equiv of Ce(IV) give rise to a new charge-transfer band at 426 nm, which finally levels off in intensity at approximately 8 equiv of Ce(IV) (apparent extinction coefficient 10000). Owing to the seemingly high stoichiometry of Ce(IV) required for completion of the color change, the chemistry involved seems to be oxidation of the organic ligands. This possibility is currently under investigation.

Isolation and Characterization of $[(bpy)_2(py)RuO](ClO_4)_2$. On a preparative scale, the 2-equiv oxidation product of $(bpy)_2(py)Ru(OH_2)^{2+}$, with Ce(IV) in dilute $HClO_4$ as oxidant, was isolated as a pale green solid by adding an excess of 60% $HClO_4$ to the solution. Elemental analysis of the solid supports the formulation $[(bpy)_2(py)RuO](ClO_4)_2$, and the room-temperature magnetic moment, μ_{eff}, was found to be 2.94 μ_B, close to the spin-only value (2.83 μ_B) for two unpaired spins. With the assumption of an approximate C_{4v} symmetry, the $d\pi$ levels should be split into an e* set, which is destabilized due to $p(O) \rightarrow d\pi(Ru)$ mixing, and a b_2 level as shown here schematically:



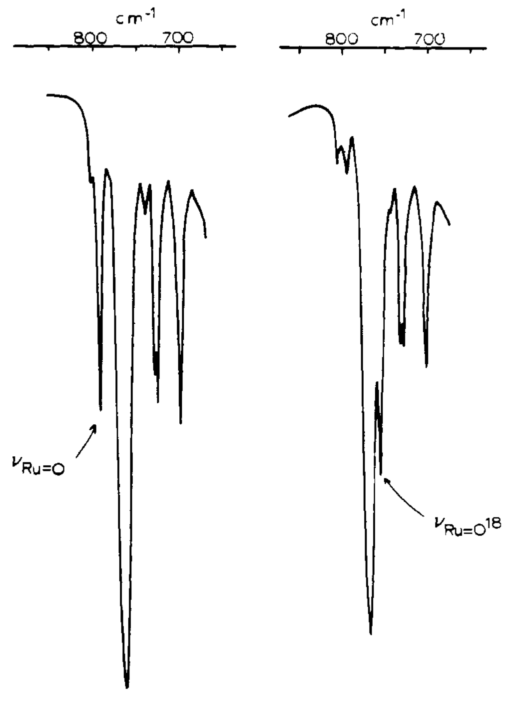


Figure 4. Infrared labeling study of $[(bpy)_2(py)RuO](ClO_4)_2$. The ruthenium–oxo stretch at 792 cm^{-1} (mull, NaCl plates) shifts to 752 cm^{-1} upon ^{18}O labeling.

With the assumption of a relatively strong field from the oxo ligand, crystal field arguments for C_{4v} symmetry yield the same result. Given the actual symmetry of the complex, two unpaired spins are expected if the degeneracies of the e sets are lifted only slightly. The light green color of the complex both in solution and in the solid state is due to a weak absorption at 670 nm (apparent extinction coefficient 50 per Ru) which is possibly a persistent oxo-bridged Ru(III) impurity having a very large extinction coefficient.[7] Otherwise, the electronic spectra (Figure 2) from 210 to 1600 nm with H_2O or CH_3CN as solvents are characterized only by the bpy and py intraligand bands in the UV (see Table I). No significant changes in the spectrum occur in the pH interval 0–7.

Consistent with the analytical data, infrared spectra of dry samples of $[(bpy)_2(py)RuO](ClO_4)_2$ do not show the prominent O–H stretching bands which are evident in the salts $[(bpy)_2(py)Ru(OH_2)](ClO_4)_2 \cdot H_2O$ and $[(bpy)_2(py)Ru(OH_2)](PF_6)_2 \cdot H_2O$. Conspicuously absent in the Ru(II) spectra, however, is a sharp, intense peak at 792 cm^{-1} which occurs for $[(bpy)_2(py)RuO](ClO_4)_2$ (mull). On the basis of the shift of this peak to 752 cm^{-1} upon labeling with ^{18}O, the peak is assignable to the Ru=O stretch (Figure 4). The expected shift is exactly that predicted by a simple Hook's law approximation.[34] Other terminal oxo stretching frequencies for a variety of oxidation states of ruthenium occur in the region 785–890 cm^{-1}, although this appears to be the first characterized example of a terminal oxo ligand in a Ru(IV) complex.[35,36] Except for the differences noted, the infrared spectra of $[(bpy)_2(py)RuO](ClO_4)_2$ and $[(bpy)_2(py)Ru(OH_2)](ClO_4)_2 \cdot H_2O$ in the range 4000–600 cm^{-1} appear quite similar, which supports the conclusion that the $(bpy)_2(py)Ru$ unit remains intact in the oxidation process and also that no net chemistry has occurred at the ligands such as "covalent

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(34) Conley, R. T. "Infrared Spectroscopy", 2nd ed.; Allyn and Bacon: Boston, 1972; p 18.

(35) Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459.

(36) (a) Griffith, W. P.; Rossetti, R. *J. Chem. Soc., Chem. Commun.* **1972**, 1449. (b) Griffith, W. P.; Pawson, D. *Ibid.* **1973**, 1315. (c) Griffith, W. P. "The Chemistry of the Rarer Platinum Metals"; Interscience: New York, 1967.

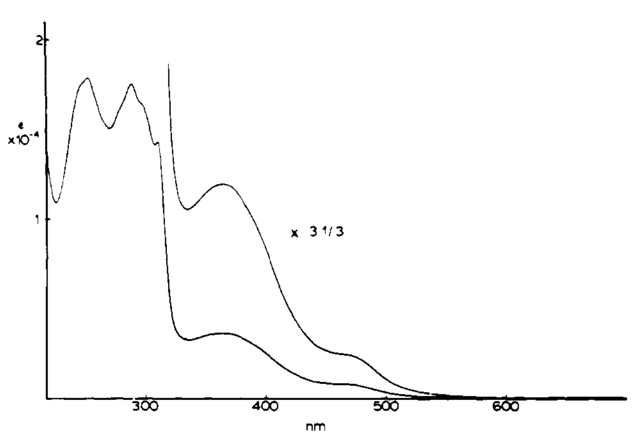

Figure 5. Electronic spectrum of $(bpy)_2(py)Ru(OH)^{2+}$ in H_2O. The peak at 470 nm is due to a small equilibrium concentration of $(bpy)_2(py)Ru(OH_2)^{2+}$ present because of disproportionation.

hydrate" formation.[37,38] Such chemistry may well play an important role under conditions different from those described here.

According to Feltham and Hayter,[16] a simple conductivity experiment can be used to assign a charge type to a particular electrolyte in solution. This is a clear aid in distinguishing charged monomeric species from possible dimeric or polymeric formulations where elemental analysis results are ambiguous. Experimentally, salts of the same charge type yield similar slopes (±10) when the equivalent conductance is plotted vs. the square root of the equivalent concentration, particularly when either the cation or anion is kept constant throughout the series. Thus, when the procedure was carried out on the 1:2 salts, $[(phen)_3Fe](ClO_4)_2$, $[(bpy)_2(py)Ru(OH_2)](ClO_4)_2\cdot H_2O$, and $[(bpy)_2(py)RuO](ClO_4)_2$, in water, the slopes were found to fall in a narrow range: $\Lambda_e = -176C_e^{1/2} + 94.3$, $-157C_e^{1/2} + 101.3$, and $-167C_e^{1/2} + 104.1$, respectively.[20] The results are consistent with the existence of monomeric $(bpy)_2(py)RuO^{2+}$ ions in aqueous solution.

Formation and Isolation of $[(bpy)_2(py)Ru(OH)](ClO_4)_2$. The hydroxide complex was isolated as the perchlorate salt, $[(bpy)_2(py)Ru(OH)](ClO_4)_2$, following electrochemical oxidation of $[(bpy)_2(py)Ru(OH_2)](ClO_4)_2\cdot H_2O$. The oxidation was carried out at +0.80 V vs. SCE in neutral aqueous solution (phosphate buffer) and the electrolysis was stopped at $n = 1.0$. After addition of excess $NaClO_4$, the $[(bpy)_2(py)Ru(OH)](ClO_4)_2$ salt precipitated from the solution. The spectrum of the complex in 1 M $HClO_4$ is essentially identical with the spectrum obtained by oxidation of $(bpy)_2(py)Ru(OH_2)^{2+}$ with 1 equiv of Ce(IV) (Figure 1). However, the spectrum is pH dependent (Figures 1 and 5) which is consistent with reversible proton loss

$$(bpy)_2(py)Ru(OH_2)^{3+} \rightleftharpoons (bpy)_2(py)Ru(OH)^{2+} + H^+ \quad (9)$$

and expected for a 3+ transition-metal aquo complex.[39] Given the acid–base chemistry, the net reaction in neutral solution when $Ru(bpy)_2(py)H_2O^{2+}$ is oxidized is

$$(bpy)_2(py)Ru(OH_2)^{2+} \rightarrow (bpy)_2(py)Ru(OH)^{2+} + H^+ + e^- \quad (10)$$

An analysis of the potentiometric results in Figure 3, which are summarized later in Scheme I, indicates that in solutions of Ru(III) at pH >0, there should be small but significant equilibrium amounts of $(bpy)_2(py)RuO^{2+}$ and $(bpy)_2(py)Ru(OH_2)^{2+}$ due to the disproportionation reaction

$$2(bpy)_2(py)Ru(OH)^{2+} \rightleftharpoons (bpy)_2(py)RuO^{2+} + (bpy)_2(py)Ru(OH_2)^{2+} \quad (11)$$

$$\Delta G^{\circ\prime} = +0.11 \text{ V}$$

In neutral and slightly acidic solution where $(bpy)_2(py)Ru(OH)^{2+}$ is the predominant form of Ru(III), the disproportionation is evident spectrally, giving rise to the 470-nm peak due to $(bpy)_2(py)Ru(OH_2)^{2+}$ and complicating the $\pi(bpy) \rightarrow \pi^*(bpy)$ region in the UV (Figure 5). Extinction coefficients listed in Table I for the Ru(III) complexes were taken from the spectra in Figures 1 and 5 and are in reasonable agreement (±10%) with the extinction coefficients that were calculated from spectrophotometric titrations at other points in this work.

Reduction of $(bpy)_2(py)RuO^{2+}$ by $(bpy)_2(py)Ru(OH_2)^{2+}$. A convenient method for the preparation of the Ru(III) complexes in situ is to mix stoichiometric amounts of $(bpy)_2(py)RuO^{2+}$ and $(bpy)_2(py)Ru(OH_2)^{2+}$ in aqueous solution. A spectrophotometric titration[20] showed that the reaction proceeds very rapidly in 1 M $HClO_4$ according to the stoichiometry

$$(bpy)_2(py)RuO^{2+} + (bpy)_2(py)Ru(OH_2)^{2+} + 2H^+ \xrightarrow{1\text{ M }HClO_4} 2(bpy)_2(py)Ru(OH_2)^{3+} \quad (12)$$

The spectrum of the product solution in 1 M $HClO_4$ was identical with the spectrum shown in Figure 1, and when the reaction was carried out in 0.0021 M $HClO_4$ (also very rapid), the spectrum of Figure 5 was obtained. Above pH 2, the reaction (eq 13) occurs under more nearly equilibrium conditions ($\Delta G^{\circ\prime} = -0.11$ V), and consequently, the spectrophotometric titration yielded a less well-defined end point.

$$(bpy)_2(py)RuO^{2+} + (bpy)_2(py)Ru(OH_2)^{2+} \rightleftharpoons 2(bpy)_2(py)Ru(OH)^{2+} \quad (13)$$

Acid–Base Properties of $(bpy)_2(py)Ry(OH_2)^{2+}$ and $(bpy)_2(py)Ru(OH_2)^{3+}$. The concentration pK_a of $(bpy)_2(py)Ru(OH_2)^{3+}$ as expressed by eq 14 was determined spectrophotometrically at 25 °C, with the ionic strength held constant at 1.0 M with appropriate ratios of $HClO_4$ and $LiClO_4$.

$$pK_a = -\log \frac{[H^+][(bpy)_2(py)Ru(OH)^{2+}]}{[(bpy)_2(py)Ru(OH_2)^{3+}]} \quad (14)$$

Since $(bpy)_2(py)Ru(OH_2)^{3+}$ is a comparatively strong acid, buffer solutions were not required and the hydrogen ion concentration could be varied directly with $HClO_4$. Ru(III) was formed in situ by mixing $(bpy)_2(py)Ru(OH_2)^{2+}$ and $(bpy)_2(py)RuO^{2+}$, and data were taken in the region about 364 nm where $(bpy)_2(py)Ru(OH)^{2+}$ has a charge-transfer band (Figure 5). Compared to other tervalent-metal aquo complexes,[39] including $(NH_3)_5Ru(OH_2)^{3+}$ ($pK_a = 4.1$),[40] the observed value, 0.85 ± 0.03, is a remarkably low pK_a, probably reflective both of the oxidizing nature of $(bpy)_2(py)Ru(OH_2)^{3+}$ and of efficient p(hydroxo) → $d\pi$(Ru) π-type interactions in $(bpy)_2(py)Ru(OH)^{2+}$.

By contrast, $(bpy)_2(py)Ru(OH_2)^{2+}$ is only a very weak acid as shown in a similar spectrophotometric experiment. As the pH is varied between 10 and 12, the 470-nm metal–ligand charge-transfer bands for $(bpy)_2(py)Ru(OH_2)^{2+}$ are red shifted to 505 and 363 nm, respectively. Similar spectral shifts have been observed previously[28] for reversible proton dissociation from $(terpy)(bpy)Ru(OH_2)^{2+}$ with $pK_a \approx 10.0$. Rationalization of the red shifts can be made on the basis of destabilization of the $d\pi$(Ru) levels by $p(OH^-) \rightarrow d\pi$(Ru) donation

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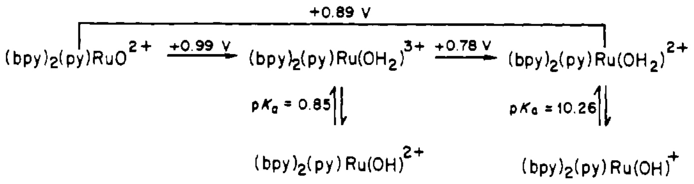
(37) Gillard, R. D. *Coord. Chem. Rev.* **1975**, *16*, 67.

(38) Gillard, R. D.; Hughes, C. T. *J. Chem. Soc., Chem. Commun.* **1977**, 776.

(39) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; New York, 1967; p 32. Baes, C. F., Jr.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley-Interscience: New York, 1976.

(40) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98* 689.

Scheme I[a]



[a] 1 M H^+, vs. SCE.

which decreases the energy gap between the $d\pi$(Ru) and π^*(bpy) levels.

With use of absorbance data at 470 and 505 nm, the "mixed" pK_a[19b] for $(bpy)_2(py)Ru(OH_2)^{2+}$, expressed by eq 15,

$$pK_a = -\log \frac{(a_{H^+}{}^{measd})[(bpy)_2(py)Ru(OH)^+]}{[(bpy)_2(py)Ru(OH_2)^{2+}]} \quad (15)$$

was found to be 10.70 ± 0.01 at 25 °C and 1.0 M ionic strength (0.333 M Na_2SO_4). In eq 15 $a_{H^+}{}^{measd}$ is the relative proton activity measured on the pH meter in this medium, and the other quantities represent concentrations. Although its physical meaning is dubious, the mixed pK_a is probably most suited for comparison to other values in the literature which are reported this way. Of more value is the concentration pK_b, 2.92 ± 0.04, as determined from a calibration of the pH meter in terms of actual OH^- concentraton:

$$pK_b = -\log \frac{[OH^-][(bpy)_2(py)Ru(OH_2)^{2+}]}{[(bpy)_2(py)Ru(OH)^+]} \quad (16)$$

According to data presented by Akerlof,[41] the concentration product, $[H^+][OH^-]$, under the conditions of the experiment is 6.66×10^{-14}, and it follows that the concentration pK_a is 10.26 ± 0.04. The value, 10.79, for the mixed pK_a of $(bpy)_2(py)Ru(OH_2)^{2+}$ is about 2 orders of magnitude lower than the values 12.3[42] and 13.1[40] reported for $(NH_3)_5Ru(OH_2)^{2+}$, which is consistent with the π-acceptor nature and weaker σ donation of the bpy and py ligands.

Redox Potentials of the Ru(IV)/Ru(III) and Ru(III)/Ru(II) Couples. The formal reduction potentials at 25 °C for the Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples in 0.962 M $HClO_4$ (adjusted to 1.0 M ionic strength with $NaClO_4$) were determined by a potentiometric titration using Ce(IV) as the oxidant. As shown in Figure 3, an inflection point occurs at a Ce:Ru mole ratio of 1.0, corresponding to complete conversion to Ru(III), chiefly in the undissociated form, $(bpy)_2(py)Ru(OH_2)^{3+}$. Continued addition of Ce(IV) produces $(bpy)_2(py)RuO^{2+}$ as observed in the spectrophotometric titrations. Potentials measured at or above a mole ratio of 2.0, however, did not come to a stable value in a reasonable length of time but instead slowly decreased so that a discrete end point was not observed, possibly the result of further uncharacterized reactions with Ce(IV) or surface oxidation of the Pt electrode.[14d,43] The data at less than a mole ratio of 2.0 fit the Nernst equation well for two well-separated consecutive waves. After correction to $[H^+] = 1$ M and allowance for partial dissociation of $(bpy)_2(py)Ru(OH_2)^{3+}$, which involves a minor correction, the standard reduction potentials (vs. SCE) for the Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples in eq 17 and 18 are approximately[44] +0.99 and +0.78 V, respectively.

$$(bpy)_2(py)RuO^{2+} + 2H^+ + e \rightarrow (bpy)_2(py)Ru(OH_2)^{3+} \quad (17)$$

$$(bpy)_2(py)Ru(OH_2)^{3+} + e \rightarrow (bpy)_2(py)Ru(OH_2)^{2+} \quad (18)$$

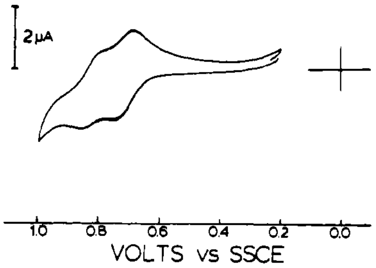
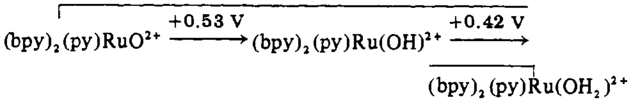


Figure 6. Cyclic voltammogram of $(bpy)_2(py)Ru(OH_2)^{2+}$. Conditions: room temperature, Au wire electrode, SSCE reference electrode, 20 mV/s sweep rate, 0.1 M $LiClO_4$, 0.01 M $HClO_4$.

Scheme II[a]



[a] pH 7.

The Latimer diagram[45] shown in Scheme I summarizes the aqueous acid–base and redox chemistry described so far; the potentials vs. SCE are for 1 M $HClO_4$.

In the interval 2 < pH < 9, where $(bpy)_2(py)Ru(OH_2)^{3+}$ is completely dissociated into the hydroxy complex, eq 17 and 18 no longer apply, and the Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples become

$$(bpy)_2(py)RuO^{2+} + H^+ + e \rightarrow (bpy)_2(py)Ru(OH)^{2+} \quad (19)$$

$$(bpy)_2(py)Ru(OH)^{2+} + H^+ + e \rightarrow (bpy)_2(py)Ru(OH_2)^{2+} \quad (20)$$

With use of the information in Scheme I, the reduction potentials vs. SCE for the couples in eq 19 and 20 would be +0.53 and +0.42 V, respectively, at pH 7 as shown in Scheme II.

While it is apparent that $(bpy)_2(py)Ru(OH_2)^{3+}$ is stable with respect to disproportionation, appreciable concentrations of $(bpy)_2(py)RuO^{2+}$ and $(bpy)_2(py)Ru(OH_2)^{2+}$ will exist in solutions of $(bpy)_2(py)Ru(OH)^{2+}$. As shown in a potentiometric experiment, the measured potentials vs. the SCE for the Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples decrease approximately 59 mV/pH unit over the interval 2 < pH < 8.[20]

Electrochemistry. Electrochemical studies corroborate the description of the redox chemistry outlined in Scheme I but also reveal some curious features. A cyclic voltammogram of $(bpy)_2(py)Ru(OH_2)^{2+}$ in aqueous perchlorate solution (pH approximately 2) is shown in Figure 6. Two waves are visible, and exhaustive electrolysis past the second wave gave $n = 2.0$. If the electrolysis is deliberately stopped at $n = 1.0$, $[(bpy)_2(py)Ru(OH)](ClO_4)_2$ can be isolated, as mentioned previously. Solutions containing $(bpy)_2(py)RuO^{2+}$ give cyclic

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[41] Akerlof, G. *J. Am. Chem. Soc.* **1926**, *48*, 1160.

[42] Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460.

[43] Adams, R. N. "Electrochemistry at Solid Electrodes"; Marcel Dekker: New York, 1969; Chapter 2.

[44] The potentials are uncorrected for activity effects. Junction potentials in the experiment are negligible on this level of precision.[13b]

[45] Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice Hall: Englewood Cliffs, N.J., 1952.

Scheme III

$$2(bpy)_2(py)Ru(OH_2)^{2+} \rightarrow 2(bpy)_2(py)Ru(OH)^{2+} + 2H^+ + 2e^-$$

$$2(bpy)_2(py)Ru(OH)^{2+} \rightleftharpoons (bpy)_2(py)Ru(OH_2)^{2+} + (bpy)_2(py)RuO^{2+} \quad (21)$$

voltammograms similar to that for $(bpy)_2(py)Ru(OH_2)^{2+}$, and an exhaustive electrolysis at +0.60 V vs. the SCE in 0.1 M CF_3COOH (in which it is reasonably soluble) showed that $(bpy)_2(py)Ru(OH_2)^{2+}$ forms quantitatively ($n = 2$) as shown spectrophotometrically. For $(bpy)_2(py)Ru(OH_2)^{2+}$ in 1 M $HClO_4$ ($E_{1/2} = +0.79$ V) or 1 M H_2SO_4 ($E_{1/2} = +0.78$ V), only the Ru(III)/Ru(II) wave occurs within the solvent limits, at a gold electrode. The Ru(IV)/Ru(III) wave is apparently lost in the solvent background.

The Ru(III)/Ru(II) wave appears nearly reversible electrochemically ($\Delta E_p = 60$–70 mV, $i_{p,a} \approx i_{p,c}$), and the expected linear dependence of the anodic peak height vs. the square root of the sweep rate was observed.[46] In good agreement with the potentiometric results, the Ru(III)/Ru(II) wave (500 mV/s sweep rate, ambient temperature) shifts with a change in pH in the interval $2 < pH < 7$ according to the relation $E_{1/2} = -0.0565pH + 0.84$, where $E_{1/2}$ is the half-wave potential in buffered sulfate media.

The Ru(IV)/Ru(III) wave also appears roughly reversible and exhibits a similar $E_{1/2}$ vs. pH dependence. Unlike the Ru(III)/Ru(II) wave, however, the peak height of the Ru(IV)/Ru(III) wave is strongly sweep-rate dependent, disappearing altogether as the sweep rate is increased to 200 mV/s in $LiClO_4$ media. As the peak disappeared, there was no obvious change in ΔE_p or $E_{1/2}$. In Na_2SO_4 media, the current is much lower at a given sweep rate and the wave is just discernible at 20 mV/s sweep rate. Qualitatively at least, no change in the peak-height vs. sweep-rate behavior was observed in the range $2 < pH < 7$, and no changes in the properties of the wave behavior were noted when a glassy-carbon electrode was used instead of gold.

The peak height vs. sweep rate behavior of the Ru(IV)/Ru(III) wave is diagnostic of a chemical step which precedes the electron-transfer step.[46] A mechanism that may explain the electrochemistry is formation of Ru(IV) via disproportionation of Ru(III) (Scheme III).

The kinetics of the reverse of eq 21 have been studied,[20,47] and the rate is independent of pH in the range $2 < pH < 9$. By the principle of microscopic reversibility, the disproportionation of Ru(III) would therefore be expected to provide a pH-independent pathway for Ru(IV) formation which is consistent with the electrochemical observations. It is not clear, however, what wave shape would be expected for the proposed mechanism, but initial results suggest that chemical reduction of $(bpy)_2(py)RuO^{2+}$ with certain outer-sphere reductants does occur via the microscopic reverse of Scheme III as the rate-determining step.[20,47]

Decomposition Pathways and the Possibility of Oxidation of Water. In the range $0 < pH < 8$, Scheme I has been shown to account adequately for the observed aqueous solution chemistry of $(bpy)_2(py)Ru(OH_2)^{2+}$ and its one- and two-electron *oxidation* products. All species appear to be reasonably stable at least on a normal experimental time scale in this pH interval at 25 °C. Oxidation of $(bpy)_2(py)Ru(OH_2)^{2+}$ by HNO_3 (and similarly by $HClO_4$) can be understood by reference to the redox potentials in Scheme I and potentials for the HNO_3/HNO_2 couple as discussed in a previous paper.[8]

Scheme I predicts that over the pH interval studied ($0 < pH < 8$), O_2 is thermodynamically capable of oxidizing $(bpy)_2(py)Ru(OH_2)^{2+}$ to $(bpy)_2(py)RuO^{2+}$. No evidence for the air oxidation of $(bpy)_2(py)Ru(OH_2)^{2+}$ was observed, however, and solutions could be routinely handled at any pH without precautions to exclude air. On the other hand, Scheme I would predict that in strongly acidic solution, the Ru(IV)/Ru(III) couple would have sufficient potential to oxidize H_2O to O_2. A reaction was found to occur in 5–10 M H_2SO_4, involving the apparent formation of Ru(III) from $(bpy)_2(py)RuO^{2+}$ as indicated spectrophotometrically by the initial appearance of a weak absorption at approximately 610 nm which gradually shifted to 555 nm. No O_2 was detected by GC, however, and the reaction was not characterized further.

In basic solution, there is another possibility of oxidation of H_2O (as OH^-) via the Ru(III)/Ru(II) or Ru(IV)/Ru(II) couples. While it is true that solutions of either $(bpy)_2(py)RuO^{2+}$ or $(bpy)_2(py)Ru(OH)^{2+}$ turn pink in 0.1 or 1.0 M NaOH due to the appearance of $(bpy)_2(py)Ru(OH)^+$, which can be seen spectrophotometrically, experiments with a dissolved oxygen probe indicate that O_2 is not liberated. The reaction was not examined in detail, but spectrophotometric experiments suggest that nearly all of the complex ends up as $(bpy)_2(py)Ru(OH)^+$, roughly 85% for $(bpy)_2(py)RuO^{2+}$ and 95% for $(bpy)_2(py)Ru(OH)^{2+}$.

Chemical oxidation of $(bpy)_2(py)Ru(OH)^+$, using $KMnO_4$ in 0.1 M NaOH, showed that a large number of oxidizing equivalents per mole of ruthenium (approximately 14, assuming 3 equiv/mol of $KMnO_4$) are required to remove completely the $(bpy)_2(py)Ru(OH)^+$ peak at 505 nm. These results point to a complicated and extensive chemistry involving oxidation of the organic ligand. Sutin[48] and Gillard[37,38] have presented evidence that bpy and phen ligands are susceptible to attack by OH^- ion, particularly when the metal is in an oxidized form. Just as in quinone chemistry,[49] nucleophilic attack by OH^- ion may render the phen or bpy ligand susceptible to further oxidation reactions.

Interestingly, solutions of $(bpy)_2(py)Ru(OH)^{2+}$ are fairly stable with respect to formation of μ-oxo species such as $(bpy)_2(OH_2)RuORu(OH_2)(bpy)_2^{4+}$ [35] which are common side products in the preparation of many poly(pyridine) complexes of ruthenium. Given the propensity of Fe(III)[50] and Ru(III)[35,9b] complexes toward oxo-bridged formation, it is a subtle yet important aspect of this work that μ-oxo formation is inhibited in the $(bpy)_2(py)Ru(OH_2)^{2+}$ system. Formation of oxo-bridged Ru(III) complexes is not well understood kinetically, but competition between outer-sphere electron transfer and substitution reactions would appear to be an important consideration. Vanadyl ion, VO^{2+}, is known to form an oxo-bridged dimer with $(NH_3)_5Ru(OH_2)^{2+}$ by what is, at least initially, a substitution step:[51]

$$(H_2O)_5VO^{2+} + (NH_3)_5Ru(OH_2)^{2+} \xrightarrow{k_0} (H_2O)_5VORu(NH_3)_5^{4+} + H_2O \quad (22)$$

Outer-sphere electron transfer is not expected to occur in this case on thermodynamic grounds. If steps like eq 22 are important in the solution chemistry of related ruthenium complexes, the oxo-bridging step in eq 23 must compete with other electron-transfer pathways[20,47] as noted in eq 24 ($2 < pH < 9$). It has been found that k_2 is 5.2×10^5 M^{-1} s^{-1} in 0.333 M Na_2SO_4 at 25 °C,[20,47] which probably greatly exceeds the

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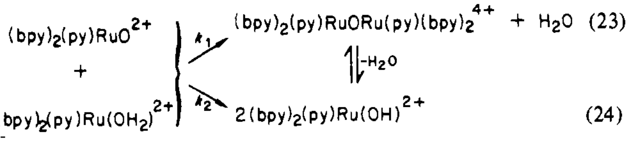

rate constant k_1 for the competing substitution step.

In fact, if the oxo-bridging reaction is very favorable thermodynamically, solutions of $(bpy)_2(py)Ru(OH)^{2+}$ would be expected to form oxo-bridged dimers eventually. Upon heating or standing for days at room temperature, aqueous solutions of $(bpy)_2(py)(OH)^{2+}$ turn green with the appearance of an intense charge-transfer band at 645 nm,[8,10,20] a feature characteristic of other μ-oxo Ru(III) dimers which have λ_{max} values in the range 600–700 nm.[7,35] The reaction appears to involve the initial loss of a pyridine ligand to give a dimer like $(bpy)_2(H_2O)RuORu(py)(bpy)_2{}^{4+}$. Formation of the analogous dimer containing two pyridine ligands may well be inhibited on steric grounds.[52]

Conclusions

The net 2e oxidation of the complex $(bpy)_2(py)Ru(OH_2)^{2+}$ has led to reversible formation of the first readily isolable, terminal oxo Ru(IV) complex $(bpy)_2(py)RuO^{2+}$. In the Ru(IV) state, the high formal charge created at the metal is balanced by the loss of two protons from the aquo ligand to give an oxo ligand. Considering the widespread occurrence of the oxo ligand in the higher oxidation states of ruthenium and in transition metals generally,[36] the "ruthenyl" complex $(bpy)_2(py)RuO^{2+}$ is not at all out of place, but it is an unusual example where a terminal oxo ligand arises simply and reversibly from an aquo ligand with an absence of interfering side reactions.

The Ru(IV) oxidation state is not a common one compared with the large number of Ru(II) and Ru(III) complexes that can be isolated, but a number of well-characterized examples are known, including RuO_2,[36a] $[RuX_6]^{2-}$ ($X = F^-$, Cl^-, Br^-),[36a,53] $[Ru(Et_2PhPN)(Et_2PhP)_2Cl_3]$,[54] and $[Ru(Et_2NCS_2)_3Cl]$.[55] On the other hand, the aqueous solution chemistry of Ru(IV) appears to be quite extensive (and complex), and knowledge of $(bpy)_2(py)RuO^{2+}$ may be of value in interpreting the solution chemistry in cases where other "ruthenyl" species may be present as kinetic intermediates or as components of complex mixtures.[9,36a,56]

Since transition-metal "yl" compounds in the 4+ oxidation state are rather elusive and as discussed earlier they may be important intermediates in a number of important reactions, the $(bpy)_2(py)Ru(OH_2)^{2+}/(bpy)_2(py)RuO^{2+}$ system was characterized in some detail. Noteworthy is the fact that the system appears to be well-defined over a broad pH range ($0 < pH < 8$), and its thermodynamic redox properties are described by Scheme I. The absence of complications from oxo bridging is important when comparisons are made to related first-row transition-metal systems, but it is probably true in the ruthenium case that the inevitable is only delayed here because of kinetic and steric problems. A last point to note is that the Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples are chemically reversible and relatively low in potential as oxidants at least within the context of related poly(pyridine) complexes of ruthenium.

Although no aspect of this work has led directly to the oxidation of H_2O to O_2 or to the reverse reaction, some key elements of the problem have been shown to exist in the ruthenium system: (1) the existence of Ru(IV) terminal oxo species, (2) the direct connection between aquo and terminal oxo ligands, and (3) inhibition of μ-oxo Ru(III) dimer formation. In addition, the results of experiments which are described in detail elsewhere[6–8] implicate $(bpy)_2(py)RuO^{2+}$ as an oxygen atom transfer reagent and show that the oxo ligand is a highly "activated" redox site.

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Registry No. $(bpy)_2(py)Ru(OH_2)^{2+}$, 70702-30-6; $(bpy)_2(py)Ru(OH)^+$, 75495-06-6; $(bpy)_2(py)RuO^{2+}$, 67202-43-1; $(bpy)_2(py)Ru(OH)^{2+}$, 75495-07-7; $(bpy)_2(py)Ru(OH_2)^{3+}$, 75495-08-8; $[(bpy)_2(py)Ru(OH_2)](PF_6)_2$, 75495-09-9; $[(bpy)_2(py)RuO](ClO_4)_2$, 67202-44-2; $[(bpy)_2(py)Ru(OH_2)](ClO_4)_2$, 70702-31-7; $[(bpy)_2(py)Ru(OH)](ClO_4)_2$, 75495-10-2; $[(bpy)_2(py)RuCl](PF_6)$, 62387-78-4; $[Ru(bpy)_2(py)(NO)](PF_6)_3$, 29241-00-7; $(bpy)_2RuCl_2$, 15746-57-3; Ce^{4+}, 16065-90-0.

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(52) The complex $(terpy)(bpy)Ru(OH)^{2+}$ also undergoes oxo bridging slowly. Significantly, both $(terpy)(bpy)RuO^{2+}$ and $(bpy)_2(py)RuO^{2+}$ undergo oxo-bridge formation more rapidly in solution than do their Ru(III) counterparts. Other, as yet uncharacterized, pathways may therefore be important in the oxo-bridging reactions. Predictably, higher temperature, higher ionic strengths, and higher concentrations of complex are conditions which tend to accelerate oxo-bridge formation.[38]

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