

[BuPPh<sub>3</sub>]<sub>3</sub>Ln(NCS)<sub>6</sub> lattices develop no new features on irradiation. The only observable effect is a slight initial drop in the intensity of the main band on commencing irradiation, followed by no further change.

**Analysis of the Phenomena.** The photolysis of iron thiocyanate complexes in solution is well-known. Detailed studies have been undertaken<sup>17</sup> that indicate the production and consequent decay of thiocyanogen radicals (NCS) and the formation of ferrous iron. It is unlikely that a similar mechanism exists in crystals at cryogenic temperatures for the following reason. New bands appear at frequencies quite similar to those in the normal iron(III) complex, while if an iron(II) complex were the product of the photolysis, bands at considerably higher energies would be expected.<sup>11</sup>

It appears most probable that what occurs on irradiation is the dissociation of an NCS<sup>-</sup> group, leaving the Fe(NCS)<sub>5</sub><sup>2-</sup> chromophore. This new iron(III) complex is expected to have a spectrum like the old, since the two differ by only one ligand. The bands that appear at 17 020 cm<sup>-1</sup> in *a* and 16 060 cm<sup>-1</sup> in *b* in the Gd spectrum lie about 4000 cm<sup>-1</sup> below the principal bands of the nonirradiated complex and may be assigned to analogous transitions in the new complex. If the new band in *b* possesses a shoulder similar to that observed in the original spectrum, it would lie under the band due to the original complex.

The new band at 24 690 cm<sup>-1</sup> in *b* is completely polarized. Since it lies 8600 cm<sup>-1</sup> above the other new band, it is not likely to be a split component arising from the same ligand level; splittings of such large magnitude are not expected. If it were from the next lowest ligand level (probably t<sub>2u</sub>), it is not clear

why an analogous band was not observed in the spectrum of the initial complex. It probably represents a transition within some other species, the most likely one being the isolated NCS<sup>-</sup> group. A band found between 27 800 and 29 400 cm<sup>-1</sup> in the spectra of aqueous thiocyanates has been assigned to a  $\pi \rightarrow \pi^*$  transition on the NCS<sup>-</sup> ion, specifically  $^1\Sigma^+ \rightarrow ^3\Sigma^+$ .<sup>18</sup> Under spin-orbit coupling this becomes  $\Sigma^+ \rightarrow \Pi + \Sigma^-$ . Only the transition to the former states is allowed and then only in the *xy* polarization. This is consistent with our observations, since our *a* and *b* spectra seem best interpreted as *z* and *xy*, respectively. McDonald et al.<sup>18</sup> also note that their data are best interpreted if the equilibrium geometry of the  $^3\Sigma^+$  excited state is assumed to be bent.

An alternate explanation would have the photolysis give rise to angular rearrangements without dissociation, such that one or more FeNC angles change upon irradiation. The strong polarization of the spectra indicates that such changes must take place only in certain directions in the lattices containing Nd, Sm, or Gd. The appearance of unpolarized bands on irradiation in the yttrium lattice under severe conditions seems to correlate with the fact that there are fundamental differences in structure between the host lattices formed by the larger early lanthanide ions and the smaller trivalent yttrium cation. These issues will, we hope, be clarified in forthcoming papers.

**Acknowledgment.** P.J.M. is grateful to the Research Corp. for the funds to purchase the Displex cryogenic refrigerator. I.M.W. thanks the National Research Council of Canada for its generous support.

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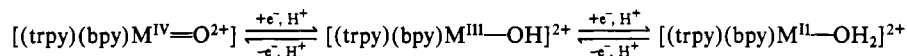
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## Redox and Spectral Properties of Monooxo Polypyridyl Complexes of Ruthenium and Osmium in Aqueous Media

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The complexes [(trpy)(bpy)M—OH<sub>2</sub>]<sup>2+</sup> (M = Ru, Os; trpy = 2,2',2''-terpyridine; bpy = 2,2'-bipyridine) have been prepared and their redox properties in aqueous solution investigated by using electrochemical techniques. Evidence for two one-electron redox processes has been obtained for M(IV/III) and M(III/II) couples and for an irreversible Os(IV/V) oxidation. In certain pH ranges the couples are proton dependent because of loss of both protons and electrons upon oxidation; e.g., at pH 7 the couples are



*E*<sub>1/2</sub> vs. pH studies over a broad pH range (0–13) can be interpreted in terms of simple acid–base chemistry on the basis of the Nernst equation. The *E*<sub>1/2</sub> vs. pH data are revealing in terms of the relative stabilities of the various oxidation states and of the use of pH variations to control redox potentials for these known redox catalysts. Comparisons between data for the equivalent Os and Ru complexes also give insight into shifts in p*K*<sub>a</sub> values in pH domains of oxidation-state stability and into the probable role of the M–O interaction in oxo and hydroxo complexes in determining the redox properties of these systems.

### Introduction

A number of mechanistic studies and catalytic redox applications involving the couples [(trpy)(bpy)Ru=O]<sup>2+</sup>/[(trpy)(bpy)Ru—OH<sub>2</sub>]<sup>2+</sup> or [(bpy)<sub>2</sub>(py)Ru=O]<sup>2+</sup>/[(bpy)<sub>2</sub>(py)Ru—OH<sub>2</sub>]<sup>2+</sup> (trpy = 2,2',2''-terpyridine; bpy = 2,2'-bipyridine; py = pyridine) and a variety of organic and inorganic substrates have recently appeared.<sup>1</sup> In order to characterize

the redox characteristics of monooxo complexes in further detail, we report here the results of a series of studies that were

(1) (a) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* 1980, 102, 2310–2. (b) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* 1981, 20, 436. (c) Moyer, B. A.; Sipe, B. K.; Meyer, T. J. *Ibid.* 1981, 20, 1475. (d) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* 1979, 101, 1326–8. (e) Meyer, T. J. *J. Electrochem. Soc.*, in press.

designed to explore (1) how the redox potentials for the monooxo complexes vary with changes in metal and in non-oxo ligands, (2) the variations in redox potential with pH for the M(IV/III) and M(III/II) (M = Ru, Os) couples, and (3) whether the variations in redox characteristics between  $[(\text{trpy})(\text{bpy})\text{Ru}=\text{O}]^{2+}$  and  $[(\text{trpy})(\text{bpy})\text{Os}=\text{O}]^{2+}$  could provide further insight into the behavior of metal-oxo complexes as redox catalysts.

### Experimental Section

**Materials.** The water used throughout was deionized and then distilled from alkaline potassium permanganate.  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  was obtained from Johnson Matthey, and  $(\text{NH}_4)_2\text{OsCl}_6$  was obtained from Englehard Industries. 2,2',2''-Terpyridine was obtained from G. F. Smith Co., and 2,2'-bipyridine was obtained from Aldrich Chemical Co. All solvents and other reagents were used without further purification.

**Measurements.** Routine UV-vis spectra were obtained in quartz cells by using a Bausch & Lomb Spectronic 210 UV 2000 spectrophotometer or a Varian 634 spectrophotometer. IR spectra were obtained in Nujol mulls with a Beckman IR 4250 spectrophotometer.

Spectrophotometric titrations were performed in a three-compartment electrochemical cell where the working electrode compartment was a 1-cm quartz cell. Potentiometric titrations were performed in a conventional three-compartment cell, water jacketed for temperature control. For both experiments, potentials were applied by using a PAR 173 galvanostat/potentiostat and the electrical equivalents associated with Coulombic experiments were measured with a PAR 179 digital coulometer. Cell potentials for the potentiometric titration experiments were measured with a Radiometer Copenhagen PH64 potentiometer. Constant cell temperatures were maintained with a Forma Scientific Model 2095 circulating bath.

Cyclic voltammetric experiments were conducted in a one-compartment cell equipped with a glassy-carbon or carbon-paste working electrode, a platinum-wire auxiliary electrode, and a saturated sodium calomel reference electrode. Cyclic voltammograms were obtained with a PAR 173 galvanostat/potentiostat connected to a Super Cycle wave generator<sup>2</sup> or a PAR 175 universal programmer. The pHs of the solutions used in electrochemical experiments were buffered at an ionic strength of 0.1 M by  $\text{HClO}_4$  and  $\text{NaClO}_4$  (pH 0–2),  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , and  $\text{Na}_3\text{PO}_4$  (pH 3–12), and  $\text{NaOH}$  (pH 13–14). At pH  $\sim 0$  and 14, the ionic strength was 1 M (1 M  $\text{HClO}_4$  and 1 M  $\text{NaOH}$ ).

**Preparations.**  $\text{Ru}(\text{trpy})\text{Cl}_3$ . A literature procedure was used to prepare this material.<sup>3</sup>

$[(\text{trpy})(\text{bpy})\text{RuCl}]\text{Cl}$ . A 2.00-g quantity of  $\text{Ru}(\text{trpy})\text{Cl}_3$  (4.54 mmol) and 0.71 g (4.54 mmol) of 2,2'-bipyridine were heated at reflux for 4 h in 400 mL of 75% EtOH/25%  $\text{H}_2\text{O}$  containing 0.2 g ( $\sim 25$  mmol) of LiCl and 1 mL of triethylamine as a reductant. The pot contents were filtered hot and their volume reduced to  $\sim 100$  mL with a rotary evaporator. The pot contents were then chilled in a refrigerator for 24 h. The solid was collected on a frit and washed with  $2 \times 10$  mL portions of chilled 3 M HCl. The solid was then washed with 30 mL of acetone and 200 mL of anhydrous ether and air-dried. Yield: 1.63 g (64%).

$[(\text{trpy})(\text{bpy})\text{RuCl}](\text{PF}_6)$ . A 0.50-g sample of  $[(\text{trpy})(\text{bpy})\text{RuCl}]\text{Cl}$  (0.89 mmol) was dissolved in 25 mL of absolute ethanol and precipitated as the  $\text{PF}_6^-$  salt by adding 2 mL of an  $\text{NH}_4\text{PF}_6$ -saturated ethanol solution. The solid was collected on a frit and washed with 25 mL of cold water. The solid collected was dissolved in a minimum ( $\sim 20$  mL) amount of boiling ethanol and the mixture filtered hot. The solution was placed in a freezer ( $\sim -20^\circ\text{C}$ ) for 48 h. The resulting black crystals were collected and washed with  $\sim 1$  mL of cold water. Yield: 0.31 g (52%). Anal. Calcd: C, 44.75; H, 2.86; N, 10.44. Found: C, 44.62; H, 3.17; N, 11.04.

$[(\text{trpy})(\text{bpy})\text{RuOH}_2](\text{ClO}_4)_2$ . A 1.63-g amount of  $[(\text{trpy})(\text{bpy})\text{RuCl}]\text{Cl}$  (2.91 mmol) and 1.21 g of  $\text{AgClO}_4$  (5.82 mmol) were heated together at reflux for 1 h in 200 mL of 75% acetone/25%  $\text{H}_2\text{O}$ .  $\text{AgCl}$  was filtered off, the solution volume reduced to 35 mL on a rotary evaporator, and the mixture chilled. Brown/black crystals of

$[(\text{trpy})(\text{bpy})\text{RuOH}_2](\text{ClO}_4)_2$  were collected on a frit, washed with  $\sim 1$  mL of cold water, and then air-dried. Yield: 1.85 g (90%). Anal. Calcd: C, 42.44; H, 2.99; N, 9.90. Found: C, 41.87; H, 2.69; N, 9.58.

$[(\text{trpy})(\text{bpy})\text{RuO}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ . A 50-mg sample of  $[(\text{trpy})(\text{bpy})\text{RuOH}_2](\text{ClO}_4)_2$  was dissolved in 25 mL of warm ( $\sim 50^\circ\text{C}$ ) water. Bromine gas was bubbled through the solution for 5 min, and during this time the solution changed color from deep orange to a light green. The bromine was removed from the solution with a dinitrogen gas purge, and the product was precipitated by the addition of 1 mL of  $\text{NaClO}_4$ -saturated water. The solid was collected on a frit, washed six times with a minimum amount of cold water, and air-dried. Yield: 32 mg (64%). Anal. Calcd: C, 40.37; H, 3.10; N, 9.42. Found: C, 40.09; H, 2.45; N, 9.32.

**4,4'-Dimethoxy-2,2'-bipyridine (4,4'-(MeO)<sub>2</sub>bpy)**. A literature procedure was used to prepare this material.<sup>4</sup>

$[(\text{trpy})(4,4'-(\text{MeO})_2\text{bpy})\text{RuCl}]\text{Cl}$ . The preparation was carried out by using the same procedure as for  $[(\text{trpy})(\text{bpy})\text{RuCl}]\text{Cl}$ , substituting 4,4'-dimethoxybipyridine for the bipyridine ligand. Yield: 62%.

$[(\text{trpy})(4,4'-(\text{MeO})_2\text{bpy})\text{RuOH}_2](\text{ClO}_4)_2$ . The same procedure as that for the preparation of  $[(\text{trpy})(\text{bpy})\text{RuOH}_2](\text{ClO}_4)_2$  was used, giving a yield of 80%. Anal. Calcd: C, 42.25; H, 3.28; N, 9.13. Found: C, 42.35; H, 3.47; N, 8.92.

$(\text{bpy})\text{RuCl}_4$ . A literature procedure was used to prepare this material.<sup>5</sup>

$(\text{bpy})(2,6\text{-pyridinedicarboxylato})\text{RuCl}$ . A 0.1-g sample of  $(\text{bpy})\text{RuCl}_4$  (0.25 mmol) and 0.042 g of 2,6-pyridinedicarboxylic acid (0.25 mmol) were added to 10 mL of a 50% water/50% ethanol solution. The mixture was heated at reflux for 6 h and then cooled to room temperature. Orange needles were collected from the red solution and washed with a small amount of water. Yield: 0.054 g (47%). Anal. Calcd: C, 44.60; H, 2.42; N, 9.18. Found: C, 44.38; H, 2.46; N, 9.25.

$[(\text{trpy})(\text{bpy})\text{OsCl}](\text{PF}_6)$ . A literature procedure was used to prepare this material.<sup>6</sup>

$[(\text{trpy})(\text{bpy})\text{OsOH}_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ . A 0.2-g quantity of  $[(\text{trpy})(\text{bpy})\text{OsCl}](\text{PF}_6)$  (0.26 mmol) was added to 3 mL of concentrated trifluoromethanesulfonic acid. The solution was heated at  $110^\circ\text{C}$  for 1 h under an argon atmosphere and then cooled to room temperature. Five milliliters of distilled water was then added to the solution along with zinc amalgam, and the mixture was stirred for 3 h. After the zinc amalgam was separated from the solution, the addition of 0.5 mL of saturated aqueous  $\text{NH}_4\text{PF}_6$  solution induced the precipitation of the aquo complex as the  $\text{PF}_6^-$  salt. Conversion of the aquo complex to the  $\text{ClO}_4^-$  salt and purification were achieved by column chromatography using Sephadex SP-120 as the column support and a  $\text{NaClO}_4$  aqueous solution as the eluant. By the use of a 0.1 M  $\text{NaClO}_4$  eluant, a brown band was recovered from the Sephadex column, and this brown solution was reduced in volume by rotary evaporation until a precipitate began to form. The solution was then cooled at  $5^\circ\text{C}$  for several hours, and a black product was recovered by filtration. Yield: 0.1 g (44%). Anal. Calcd: C, 34.56; H, 3.37; N, 8.06. Found: C, 34.19; H, 2.90; N, 7.88.

The aquo complex,  $[(\text{trpy})(\text{bpy})\text{OsOH}_2]^{2+}$ , was also prepared from the nitrosyl complex,  $[(\text{trpy})(\text{bpy})\text{OsNO}]^{3+}$ .<sup>7</sup> To a refluxing aqueous solution of the nitrosyl complex was slowly added 1 equiv of sodium azide over a 4-h period. The isolation and purification of the aquo complex were performed as outlined above.

### Results and Discussion

**Syntheses.** Synthetic procedures for the preparations of the cations  $[(\text{trpy})(\text{bpy})\text{RuCl}]^+$  and  $[(\text{trpy})(\text{bpy})\text{RuOH}_2]^{2+}$  (1) have been reported by Dwyer and co-workers.<sup>3</sup> The preparations reported here represent alternate procedures for obtaining the same complexes, and the procedures have proven to be successful on a routine basis.

The preparation of  $[(\text{trpy})(\text{bpy})\text{OsOH}_2](\text{ClO}_4)_2$  (2) proved to be much more involved than the synthesis of 1, the Ru analogue. Removal of the chloride ligand from  $[(\text{trpy})$

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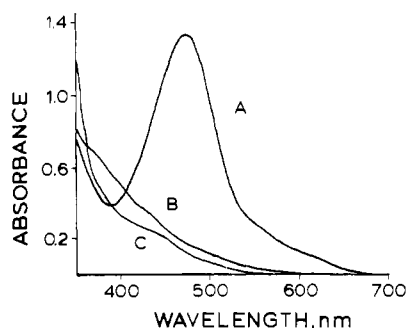
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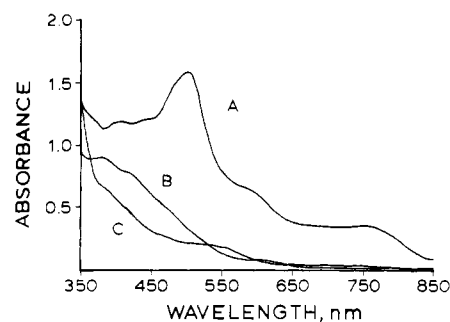


**Figure 1.** Visible spectra of  $1.4 \times 10^{-4}$  M aqueous solutions of (A)  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{II}}-\text{OH}_2]^{2+}$ , (B)  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}-\text{OH}]^{2+}$ , and (C)  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{IV}}=\text{O}]^{2+}$  (pH 6.8,  $I = 0.1$  M phosphate buffer;  $T = 23.0 (\pm 0.1)^\circ\text{C}$ ).

(bpy)OsCl)(PF<sub>6</sub>) (3) could not be accomplished by the addition of Ag<sup>+</sup>, as was the case with the Ru analogue. Addition of 1 equiv of Ag<sup>+</sup> to an aqueous solution of 3 resulted in the oxidation of the metal to Os(III).<sup>6</sup> The addition of a second equivalent of Ag<sup>+</sup> produced a complex mixture of products, including the oxo-bridged dimer  $[(\text{trpy})(\text{bpy})\text{Os}_2\text{O}^{4+}$  (4). In order to remove the chloride ligand from 3, the use of trifluoromethanesulfonic acid (TFMSH) as a substituting ligand was found to be successful.<sup>8</sup> When 3 is heated at reflux in concentrated TFMSH solution, the chloride ligand is lost as HCl gas, forming  $[(\text{trpy})(\text{bpy})\text{OsTFMS}]^{2+}$  (5). Compound 5 can then be readily aquated in aqueous solution to form  $[(\text{trpy})(\text{bpy})\text{OsOH}_2]^{3+}$ , which was reduced to  $[(\text{trpy})(\text{bpy})\text{OsOH}_2]^{2+}$  (2) by using zinc amalgam as the reductant. It should be noted that in the formation of 5 the oxo-bridged dimer 4, is also formed. However, the dimer in the solution containing 4 and 5 can be reduced to the monomer by reduction over zinc amalgam and the resulting reduced mixture purified by column chromatography. The difficulties encountered in this synthesis emphasize the high affinity of Os(II) for Cl<sup>-</sup> and its relative inertness toward substitution, in addition to the relative ease with which osmium oxo-bridged dimers are formed.

Another route to the preparation of 2 involves the addition of 1 equiv of azide ion (N<sub>3</sub><sup>-</sup>) to  $[(\text{trpy})(\text{bpy})\text{OsNO}]^{3+}$  (6) in aqueous solution. Unlike ruthenium nitrosyls, such as  $[(\text{bpy})_2(\text{py})\text{RuNO}]^{3+}$ , which react rapidly with azide ion to yield the solvento complex,<sup>9</sup> the osmium nitrosyl complex, 6, required approximately 4 h in refluxing aqueous solution before reaction was complete. Because of the slowness of the reaction, azide ion must be added slowly to the nitrosyl complex in order to prevent the formation of the azido complex  $[(\text{trpy})(\text{bpy})\text{OsN}_3]^{+}$ .

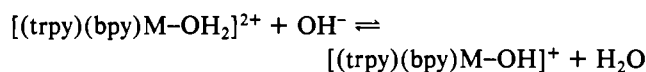
**Electronic Spectra and Spectrophotometric Titrations.** The absorption spectra of  $[(\text{trpy})(\text{bpy})\text{RuOH}_2]^{2+}$  (1) (Figure 1) and  $[(\text{trpy})(\text{bpy})\text{OsOH}_2]^{2+}$  (2) (Figure 2) in aqueous solution are similar in that the major visible spectral features for both—e.g., for 1  $\lambda_{\text{max}} = 477$  nm,  $\epsilon = 9600$  M<sup>-1</sup> cm<sup>-1</sup> and for 2  $\lambda_{\text{max}} = 499$  nm,  $\epsilon = 9200$  M<sup>-1</sup> cm<sup>-1</sup>—can be attributed to metal to ligand,  $d\pi(\text{M}) \rightarrow \pi^*(\text{polypyridyl})$  transitions. The spectrum of 2 displays more bands, due to the appearance of formally forbidden singlet-triplet transitions which gain significant intensity by spin-orbit coupling induced mixing of excited singlet and triplet states.<sup>10</sup> In addition, both spectra show several very intense bands in the UV region, assignable



**Figure 2.** Visible spectra of  $1.7 \times 10^{-4}$  M aqueous solutions of (A)  $[(\text{trpy})(\text{bpy})\text{Os}^{\text{II}}-\text{OH}_2]^{2+}$ , (B)  $[(\text{trpy})(\text{bpy})\text{Os}^{\text{III}}-\text{OH}]^{2+}$ , and (C)  $[(\text{trpy})(\text{bpy})\text{Os}^{\text{IV}}=\text{O}]^{2+}$  (pH 6.8,  $I = 0.1$  M phosphate buffer;  $T = 23.0 \pm (\pm 0.1)^\circ\text{C}$ ).

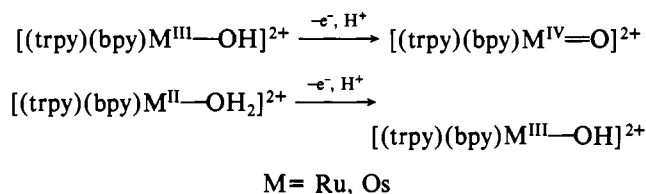
to ligand (polypyridyl)  $\pi \rightarrow \pi^*$  excitations.

As the pH of an aqueous solution of 1 is raised above 10, the band at 477 nm shifts to 508 nm with a small loss in intensity. The color change can be reversed by the addition of acid to the solution. The spectrum for 2 shows a pH dependence similar to that described for 1 in basic solution (pH > 8); the band at 499 nm shifts to 520 nm, with a loss in intensity. Once again, the color change can be reversed by the addition of acid to the solution. The origins of the spectral pH dependences for 1 and 2 lie in the equilibrium



At lower pH values, the aquo complexes are the dominant form while, at higher pH values, the hydroxo complexes are the predominant form. The red shift in  $\lambda_{\text{max}}$  at higher pH for both Ru and Os is due to a destabilization of the  $d\pi(\text{M})$  electrons by OH<sup>-</sup> relative to H<sub>2</sub>O, causing the  $d\pi(\text{M}) \rightarrow \pi^*(\text{bpy})$  transitions to occur at lower energy.

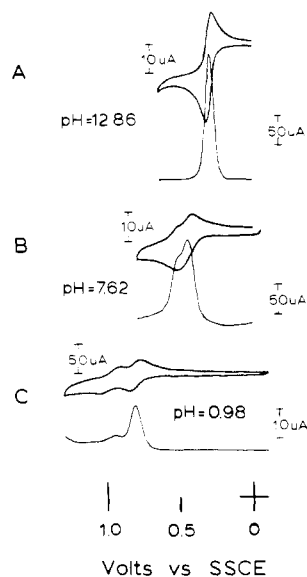
The spectra of the M(III) and M(IV) complexes in Figures 1 and 2 appear similar, with more bands appearing in the Os(III) spectrum than in the corresponding Ru spectrum. The spectra appearing in Figures 1 and 2 were generated at pH 6.8 by electrochemical oxidation.



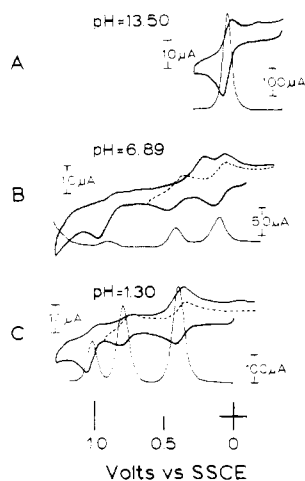
For the Ru complexes, isosbestic points were observed at 406 nm for the oxidation of  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{II}}-\text{OH}_2]^{2+}$  to  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}-\text{OH}]^{2+}$  and at 362 nm for the oxidation of  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}-\text{OH}]^{2+}$  to  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ . For the Os complexes, no isosbestic points were observed for the oxidation of  $[(\text{trpy})(\text{bpy})\text{Os}^{\text{II}}-\text{OH}_2]^{2+}$  to  $[(\text{trpy})(\text{bpy})\text{Os}^{\text{III}}-\text{OH}]^{2+}$ , but two well-defined isosbestic points at 528 nm and 362 nm were observed for the oxidation of  $[(\text{trpy})(\text{bpy})\text{Os}^{\text{III}}-\text{OH}]^{2+}$  to  $[(\text{trpy})(\text{bpy})\text{Os}^{\text{IV}}=\text{O}]^{2+}$ .

**Redox Properties.** A cyclic voltammogram of  $[(\text{trpy})(\text{bpy})\text{RuOH}_2]^{2+}$  (1) in an aqueous solution buffered at pH 7.62 shows two distinct reversible redox waves (Figure 3b). Similarly, a cyclic voltammogram of  $[(\text{trpy})(\text{bpy})\text{OsOH}_2]^{2+}$  (2) in aqueous solution buffered at pH 6.89 shows two distinct reversible redox waves and one irreversible oxidation wave (Figure 4b). For 1, the potentials for the two redox waves vary with the pH of the solution, resulting in the  $E_{1/2}$  vs. pH variations depicted in Figure 5. Within the  $10 > \text{pH} > 1.5$  region, the potentials for the Ru(IV/III) couple and the Ru(III/II) couple form two straight lines, with slopes very close

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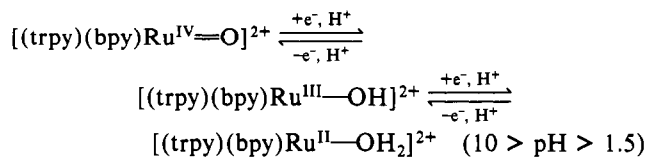


**Figure 3.** Cyclic voltammograms (scan rate 20 mV/s) and differential-pulse polarograms (scan rate 2 mV/s) of  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{II}}-\text{OH}_2]^{2+}$  in aqueous solution ( $I = 0.1 \text{ M}$ ;  $T = 23.0 (\pm 0.1) ^\circ\text{C}$ ; carbon-paste working electrode): (A) pH 12.86; (B) pH 7.62; (C) pH 0.98.

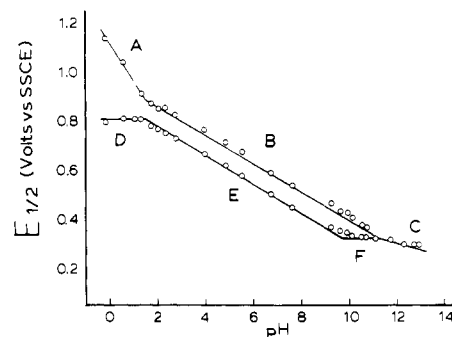


**Figure 4.** Cyclic voltammograms (scan rate 100 mV/s) and differential-pulse polarographs (scan rate 2 mV/s) of  $[(\text{trpy})(\text{bpy})\text{Os}^{\text{II}}-\text{OH}_2]^{2+}$  in aqueous solution ( $I = 0.1 \text{ M}$ ;  $T = 23.0 (\pm 0.1) ^\circ\text{C}$ ; glassy-carbon working electrode): (A) pH 13.50; (B) pH 6.89; (C) pH 1.30.

to the Nernstian prediction of  $-0.059 \text{ V/pH}$  unit, indicative of a one-electron oxidation accompanied by the dissociation of one proton.<sup>11</sup> Note that in this pH region, a separation ( $\Delta E_{1/2}$ ) of  $\sim 0.1 \text{ V}$  exists between the Ru(IV/III) and Ru(III/II) couples

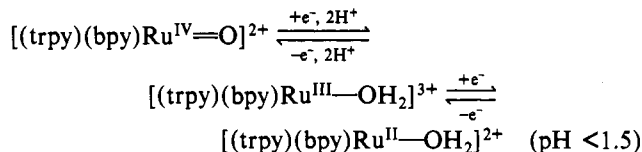


For  $\text{pH} < 1.5$ , the  $E_{1/2}$ -pH variation for the Ru(IV/III) couple

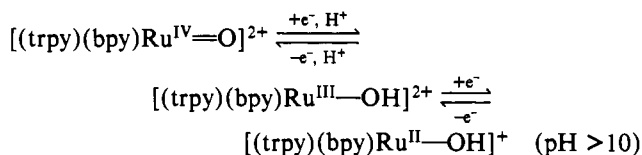


**Figure 5.** Plots of  $E_{1/2}$  (V vs. SSCE)<sup>18</sup> vs. pH for the Ru(IV/III) and Ru(III/II) redox couples of  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{II}}-\text{OH}_2]^{2+}$  in aqueous solution ( $I = 0.1 \text{ M}$ ;  $T = 23.0 (\pm 0.1) ^\circ\text{C}$ ; carbon-paste working electrode): (A)  $\text{Ru}^{\text{IV}}=\text{O}^{2+}/\text{Ru}^{\text{III}}-\text{OH}_2^{3+}$ ; (B)  $\text{Ru}^{\text{IV}}=\text{O}^{2+}/\text{Ru}^{\text{III}}-\text{OH}^{2+}$ ; (C)  $\text{Ru}^{\text{IV}}=\text{O}^{2+}/\text{Ru}^{\text{II}}-\text{OH}^+$ ; (D)  $\text{Ru}^{\text{III}}-\text{OH}_2^{3+}/\text{Ru}^{\text{II}}-\text{OH}_2^{2+}$ ; (E)  $\text{Ru}^{\text{III}}-\text{OH}^{2+}/\text{Ru}^{\text{II}}-\text{OH}_2^{2+}$ ; (F)  $\text{Ru}^{\text{III}}-\text{OH}^{2+}/\text{Ru}^{\text{II}}-\text{OH}^+$ .

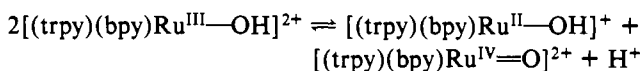
is linear but with a slope close to  $-0.118 \text{ V/pH}$  unit, indicative of a one-electron couple accompanied by the dissociation of two protons upon oxidation. In this same pH region, the variation in potential with pH for the Ru(III/II) couple is linear with zero slope, indicative of a one-electron couple with no protons lost upon oxidation. As the pH is decreased further, the separation between the two couples increases until it reaches a value of  $\sim 0.31 \text{ V}$  at pH 0. In strongly acidic solution the couples become



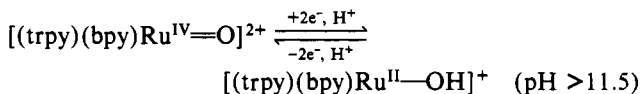
At  $\text{pH} > 10$ , the potentials for the Ru(IV/III) couple continue to vary linearly with pH, with a slope near  $-0.059 \text{ V/pH}$  unit, but the potentials for the Ru(III/II) couple become pH independent as a consequence of a loss of a proton from  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{II}}-\text{OH}_2]^{2+}$ . In this region, the couples become



Because of the different pH dependences for the two couples, the potentials for the Ru(IV/III) and Ru(III/II) couples cross at pH 11.5. At this pH,  $E_{1/2}$  values for the two couples are equal and  $\Delta E^{0'} \approx 0$  for the disproportionation of  $\text{Ru}^{\text{III}}$ .

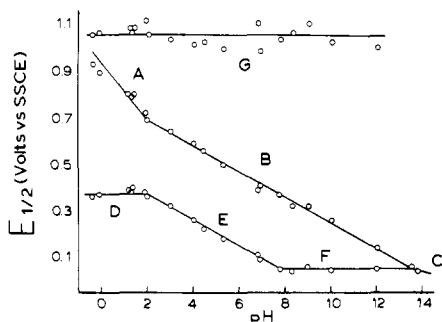


As a consequence, at  $\text{pH} > 11.5$ , Ru(III) is unstable with respect to disproportionation since the potentials for the Ru(IV/III) couple fall below the potential for the Ru(III/II) couple. This results in the observation of a single wave (Figure 3a) with the expected pH dependence of  $-0.030 \text{ V/pH}$  unit, consistent with a *two-electron*, one-proton couple:



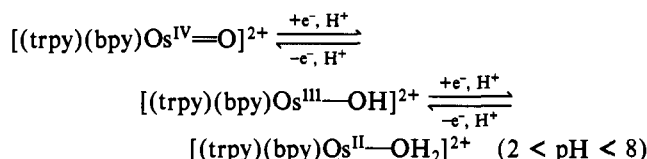
Variations in  $E_{1/2}$  with pH for the analogous Os(IV/III) and Os(III/II) couples are similar in form but different in detail, as shown in Figure 6. Within the range  $2 < \text{pH} < 8$ , the pH-potential variations for the Os(IV/III) and Os(III/II) couples are linear, having observed slopes very near

(11) By incorporation of the acid/base equilibrium constant,  $K_A$ , into the Nernst equation, the proton/electron dependence for the potentials of the oxo/aquo couples can be expressed as  $E_{1/2} \propto 0.059 (m/n)\text{pH}$  (where  $m$  = number of protons and  $n$  = number of electrons involved in the redox couple). Thus, for a one-electron reduction coupled with a one-proton acid/base equilibrium ( $n = 1$ ,  $m = 1$ ), the slope of a  $E_{1/2}$  vs. pH plot should be  $0.059 \text{ V/pH}$  unit.

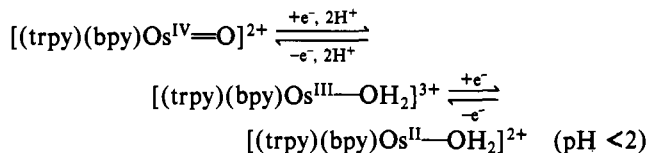


**Figure 6.** Plots of  $E_{1/2}$  (V vs. SSCE)<sup>18</sup> vs. pH for the Os(V/IV), Os(IV/III), and Os(III/II) redox couples of  $[(\text{trpy})(\text{bpy})\text{Os}^{\text{II}}\text{-OH}_2]^{2+}$  in aqueous solution ( $I = 0.1 \text{ M}$ ;  $T = 23.0 (\pm 0.1) \text{ }^\circ\text{C}$ ; glassy-carbon working electrode): (A)  $\text{Os}^{\text{IV}}=\text{O}^{2+}/\text{Os}^{\text{III}}\text{-OH}_2^{3+}$ ; (B)  $\text{Os}^{\text{IV}}=\text{O}^{2+}/\text{Os}^{\text{III}}\text{-OH}^{2+}$ ; (C)  $\text{Os}^{\text{IV}}=\text{O}^{2+}/\text{Os}^{\text{II}}\text{-OH}^+$ ; (D)  $\text{Os}^{\text{III}}\text{-OH}_2^{3+}/\text{Os}^{\text{II}}\text{-OH}_2^{2+}$ ; (E)  $\text{Os}^{\text{III}}\text{-OH}_2^{2+}/\text{Os}^{\text{II}}\text{-OH}_2^{2+}$ ; (F)  $\text{Os}^{\text{III}}\text{-OH}_2^{2+}/\text{Os}^{\text{II}}\text{-OH}^+$ ; (G)  $\text{Os}^{\text{V}}=\text{O}^{3+}/\text{Os}^{\text{IV}}=\text{O}^{2+}$ .

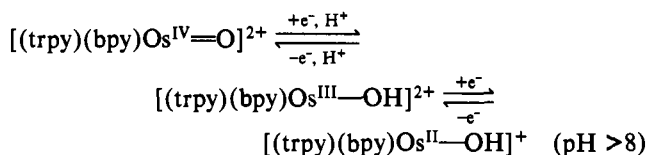
$-0.059 \text{ V/pH}$  unit and a separation ( $\Delta E_{1/2}$ ) of  $\sim 0.32 \text{ V}$  between the two couples



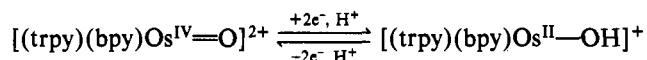
For  $\text{pH} < 2$ , the slope of the  $\text{pH}-E_{1/2}$  plot for the Os(IV/III) couple is near  $-0.118 \text{ V/pH}$  unit, while the Os(III/II) couple becomes pH independent. The change in the couples is triggered by loss of a proton from Os(III) and the couples become



With further decreases in pH, the separation between the two couples continues to increase, reaching  $\Delta E_{1/2} \approx 0.55 \text{ V}$  at pH 0. At  $\text{pH} > 8$ , the potentials for the Os(IV/III) couple continue to vary with a slope near  $-0.059 \text{ V/pH}$  unit, while the potentials for the Os(III/II) couple become pH independent because of loss of a proton from Os(II):

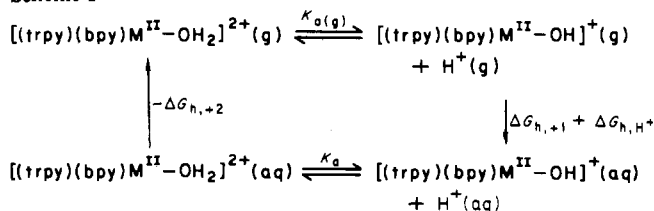


At pH 13.5, the  $E_{1/2}$ -pH plots for the two couples cross, Os(III) becomes unstable with respect to disproportionation, and the onset of a single two-electron, one-proton wave (Figure 4a) is observed:



An additional feature appears in the electrochemistry of the osmium complex, namely, the appearance of a chemically irreversible wave at  $+1.05 \text{ V}$  whose  $E_p$  value is independent of pH over the range pH 0–12. From coulometry experiments the instability following oxidation to Os(V),  $[(\text{trpy})(\text{bpy})\text{Os}^{\text{IV}}\text{O}]^{2+} - e^- \rightarrow [(\text{trpy})(\text{bpy})\text{Os}^{\text{V}}\text{O}]^{3+}$ , apparently arises through loss of bpy with a further one-electron oxidation to give  $[(\text{trpy})\text{Os}^{\text{VI}}(\text{O})_2(\text{OH})]^+$ . The chemical reversibility of the Os(V/IV) couple is scan rate dependent. At pH 1.0 the couple is nearly completely reversible at a scan rate of  $10 \text{ V/s}$ .

## Scheme I



The ligand loss chemistry is currently under investigation, but the instability of Os(V), once formed, is notable, as is the inaccessibility of the higher oxidation of Ru in the same potential range.

**Comparisons between Redox Properties: Acidities of the Aquo Ions.** Although the overall features of the  $E_{1/2}$  vs. pH profiles for Ru and Os are similar, the differences are notable. The separation between the two couples ( $\Delta E_{1/2}$ ) in the one-electron one-proton region is  $\sim 0.1 \text{ V}$  for Ru and  $\sim 0.32 \text{ V}$  for Os. The changes in slope for the Ru(III/II)  $E_{1/2}$  vs. pH plot occur at  $\text{pH} \approx 1.7$  and  $\text{pH} \approx 9.7$ , with the changes in the Os(III/II)  $E_{1/2}$  vs. pH plot occurring at  $\text{pH} \approx 2.0$  and at  $\text{pH} \approx 7.8$ . These breaks in the  $E_{1/2}$  vs. pH plots in the different pH regions are triggered by the loss of protons from  $[(\text{trpy})(\text{bpy})\text{M}^{\text{III}}\text{-OH}_2]^{3+}$  and  $[(\text{trpy})(\text{bpy})\text{M}^{\text{II}}\text{-OH}_2]^{2+}$ , respectively. For example, for  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}\text{-OH}_2]^{3+}$  at  $\text{pH} < 1.7$ , the dominant form of Ru(III) in solution is  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}\text{-OH}_2]^{3+}$ , while at  $\text{pH} > 1.7$  the dominant form is  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}\text{-OH}]^{2+}$ . This implies that at  $\text{pH} \approx 1.7$   $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}\text{-OH}_2]^{3+} \approx [(\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}\text{-OH}]^{2+}$ , which is the condition where  $\text{pH} \approx \text{p}K_{\text{a}}$ . Thus, from the pH values where breakpoints occur (Figures 5 and 6), the following  $\text{p}K_{\text{a}}$  values can be estimated: for  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{III}}\text{-OH}_2]^{3+}$ ,  $\text{p}K_{\text{a}} \approx 1.7$ ; for  $[(\text{trpy})(\text{bpy})\text{Ru}^{\text{II}}\text{-OH}_2]^{2+}$ ,  $\text{p}K_{\text{a}} \approx 9.7$ ; for  $[(\text{trpy})(\text{bpy})\text{Os}^{\text{III}}\text{-OH}_2]^{3+}$ ,  $\text{p}K_{\text{a}} \approx 2.0$ ; and for  $[(\text{trpy})(\text{bpy})\text{Os}^{\text{II}}\text{-OH}_2]^{2+}$ ,  $\text{p}K_{\text{a}} \approx 7.8$ .

It is notable that the  $\text{p}K_{\text{a}}$  for Os(II) is significantly lower than the  $\text{p}K_{\text{a}}$  for Ru(II). The point is considered in the thermodynamic cycle in Scheme I. Since the Ru and Os complexes have nearly identical structures, the hydration free energy terms in the scheme,  $\Delta G_{\text{h},+2}$  and  $\Delta G_{\text{h},+1}$ , are expected to be nearly the same. As a consequence, the free energy difference associated with the differences in the  $\text{p}K_{\text{a}}$  values,  $\Delta(\Delta G) = -RT \ln (K_{\text{a,Os}}/K_{\text{a,Ru}}) \approx -0.41 \text{ V}$ , is an approximate measure of the difference in the corresponding gas-phase acidities,  $K_{\text{a}}(\text{g})$ . The greater gas-phase acidity for  $\text{Os}^{\text{II}}$  indicates a higher relative affinity for  $\text{OH}^-$  over  $\text{H}_2\text{O}$  for  $\text{Os}^{\text{II}}$ , which may have its origin in greater covalency effects, arising from more extensive  $d\sigma^*(\text{Os})-\sigma(\text{OH}^-)$  mixing.

The  $\text{p}K_{\text{a}}$  values are nearly the same for the related M(III) complexes,  $[(\text{trpy})(\text{bpy})\text{M}^{\text{III}}\text{-OH}_2]^{3+}$ . If  $\sigma$ -covalency effects are also more important for Os(III) than for Ru(III), there may be a compensation associated with greater  $\pi(\text{OH}^-) \rightarrow d\pi(\text{M}(\text{III}))$  mixing for Ru(III). Although  $\pi \rightarrow d\pi$  overlap may be favored for Os over Ru, on the basis of a greater  $d\pi$ -orbital extension for Os, the Ru(III) site is more strongly oxidizing than Os(III) and thus the unmixed Ru(III)  $d\pi$  levels are nearer in energy to filled  $\pi(\text{OH}^-)$  levels, which would favor enhanced  $\pi \rightarrow d\pi$  mixing.

It is important to note that the potential separation between the Os(IV/III) and Os(III/II) couples ( $\Delta E_{1/2} = 0.32$  at pH 4) is greater than the separation for the analogous Ru couples ( $\Delta E_{1/2} = 0.09 \text{ V}$  at pH 4). It can be argued that the potential for the Os(III/II) couple is expected<sup>12</sup> to be  $\sim 0.4 \text{ V}$  lower than the analogous Ru(III/II) couple and that the increased  $\Delta E_{1/2}$  for Os has its origin in a relative destabilization of

(12) We have observed on numerous occasions that the potential difference ( $\Delta E_{1/2}$ ) between the Os(III/II) couple and the Ru(III/II) couple of analogous compounds is  $\sim 400 \text{ mV}$ .

Table I. Reduction Potentials at pH 7 vs. SSCE and  $pK_a$  Values (at 23 °C and  $I = 0.1$  M)

system	$E_{1/2}$ , V		$\sim pK_a$	
	Ru-(III/II)	Ru-(IV/III)	$M^{III}-OH_2^{3+}$	$M^{II}-OH_2^{2+}$
$[(trpy)(bpy)Ru-OH_2]^{2+}$	0.49	0.62	1.7	9.7
$[(bpy)_2(py)Ru-OH_2]^{2+}$	0.42 <sup>b</sup>	0.53 <sup>b</sup>	0.85 <sup>b</sup>	10.79 <sup>b</sup>
$[(trpy)(bpy)Os-OH_2]^{2+}$ <sup>a</sup>	0.09	0.41	2.0	7.8

<sup>a</sup> A pH-independent, chemically irreversible wave occurs at  $E_{p,a} = 1.05$  V. <sup>b</sup> At  $I = 1.0$  M; ref 16.

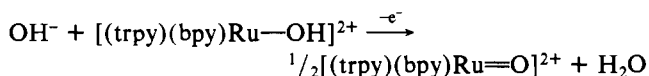
Os(IV) compared to Ru(IV). This theme will be developed in detail in a later paper.

We have also begun a systematic investigation of the effect of ligand variations on the potentials of the Ru(IV/III) and Ru(III/II) couples. In this context, the 4,4'-dimethoxy-2,2'-bipyridine analogue of  $[(trpy)(bpy)RuOH_2]^{2+}$  was synthesized and its electrochemistry in aqueous solution investigated. In the pH range 4.5–9.1, the  $E_{1/2}$  values for the Ru(III/II) couple of  $[(trpy)(4,4'-(MeO)_2-2,2'-bpy)RuOH_2]^{2+}$  decrease linearly with a slope of  $\sim -0.059$  V/pH unit. In this range, the potentials for the Ru(III/II) redox couple were 70 mV less than the potentials for the corresponding Ru(III/II) redox couples of **1**, reflecting the electron-donating effect of the methoxy substituents on the bipyridine ligand. The potentials for the Ru(IV/III) couple of **5** at pH 6.7 and pH 9.1 are essentially superimposable with the potentials for **1**. Clearly, a great deal of work remains to be done before the effects of ligand variation on the potentials of the Ru(IV/III) and Ru(III/II) couples can be understood and exploited in a systematic way.

#### Final Comments

For purposes of comparison, in Table I are given reduction potential and  $pK_a$  values based on the three systems  $[(trpy)(bpy)M-OH_2]^{2+}$  ( $M = Ru, Os$ ) and  $[(bpy)_2(py)Ru-OH_2]^{2+}$ .

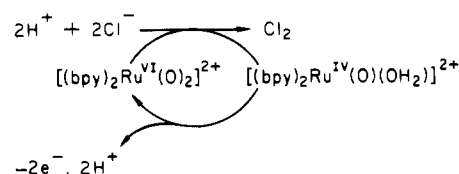
The comparisons between equivalent Ru and Os complexes of the type  $[(trpy)(bpy)M-OH_2]^{2+}$  lead to some useful conclusions concerning transition metal "yl" compounds in oxidation state IV. Overall, the  $E_{1/2}$  vs. pH profiles for Ru and Os are very similar, but differences do exist, which arise from differences in  $pK_a$  values for the M(III) or M(II) aquo complexes. In addition,  $\Delta E_{1/2}$  for the Os(IV/III) and Os(III/II) couples is considerably larger (320 mV) than for Ru (90 mV). These effects are of considerable importance in terms of the known and possible redox chemistries of the metal-oxo species. For example, the fact that the potentials for the Ru(IV/III) and Ru(III/II) redox couples are so close (90 mV) over the region  $2 < pH < 10$  means that the thermodynamic energy content associated with a two-electron process is nearly the same as for a one-electron process. In this pH range, the driving force for Ru(IV) as a two-electron oxidant is only 0.045 V less than the driving force as a one-electron oxidant. In fact, by pH 11.5, loss of a single electron from Ru(II) leads directly to the potential two-electron oxidant, Ru(IV), by disproportionation of Ru(III)



and Ru(IV) is a stronger two-electron oxidant than it is a one-electron oxidant. This is an important observation, for example, in the context of potential photoredox applications where excitation by a single photon and excited-state quenching could lead to a net two-electron redox reagent.

For Os, the potentials for the M(IV/III) and M(III/II) couples are much further separated over most of the pH range, with Os(IV) a considerably stronger oxidant than Os(III). As

#### Scheme II



a consequence, Os(IV) is a noticeably less strong two-electron than one-electron oxidant. In particular, for the pH range 2–8, where both the Os(IV/III) and Os(III/II) couples vary linearly with pH, Os(IV) is a stronger one-electron oxidant by 160 mV. Nonetheless, in more basic solutions the greater acidity of Os(II) compared to that of Ru(II) allows the Os(IV/III) potentials to cross, although at very high pH (pH 13.5) and in basic solutions Os(IV) becomes a better two-electron oxidant than one-electron oxidant in the thermodynamic sense.

The  $E_{1/2}$  vs. pH dependences of the redox couples may also allow for mechanistic control of reactions in either kinetic or thermodynamic terms. An example of the latter case was recently reported, involving the oxidation of  $Cl^-$  to  $Cl_2$  by the Ru(VI) monomer  $[(bpy)_2Ru^{VI}(O)_2]^{2+13}$  (Scheme II). At pH 2,  $\Delta G = 0$  for the reaction in Scheme II.<sup>14</sup> As the pH is raised, the oxidation of  $Cl^-$  to  $Cl_2$  by  $(bpy)_2Ru^{VI}(O)_2^{2+}$  is slowed and ultimately stops at high pH values, when the redox potential for the Ru(VI/IV) couple falls below the thermodynamic potential for oxidation of  $Cl^-$ . In fact, at high pH values,  $Cl_2$  (or HOCl) carries out the reverse process, the oxidation of Ru(IV) to Ru(VI). Thus, by careful pH control of the reaction solution, the oxidation potential of oxo compounds can be "fine-tuned" to maximize the efficiency of oxo compounds as oxidation catalysts.

Although not dwelt upon here, it should be noted that the proton gains and losses involved for the various redox couples can lead to kinetic electron-transfer difficulties, which have been documented for both chemical<sup>15</sup> and electrochemical<sup>16</sup> redox steps. As an example of such effects observed here, electrochemical responses for the Ru(IV/III) couple of  $[(trpy)(bpy)Ru^{IV}=O]^{2+}$  show marked pH effects. At pH < 1, the Ru(IV/III) couple becomes increasingly irreversible in the electrochemical sense as evidenced by an increasing and scan-rate-dependent splitting of the oxidative and reductive peak currents in cyclic voltammetry. The origin of these effects seems to lie, at least in part, in proton composition problems that are obviously severe for the Ru(IV/III) couple at low pH because of the requirement of a  $2H^+$  change. By electrochemical "activation" of the carbon electrode, the reversible nature of the Ru(IV/III) couple can sometimes be enhanced.<sup>17</sup>

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**Registry No.** **1**, 16389-43-8; **2**, 89463-51-4; **3**, 89576-34-1; **4**, 89463-52-5; **5**, 89463-53-6; **6**, 83006-34-2;  $[(trpy)(4,4'-(MeO)_2-$

- (13) Ellis, C. D.; Gilbert, J.; Murray, W. R., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4842.
- (14) At pH 2, the  $E_{1/2}$  for the Ru(VI/IV) couple (two-electrons) is equal to the  $E_{1/2}$  for the  $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$  couple.
- (15) (a) Binstead, R. A.; Moyer, B. A.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2897–9. (b) Gilbert, J. A.; Gersten, S. W.; Meyer, T. J. *Ibid.* **1982**, *104*, 6620.
- (16) Takeuchi, K. J.; Samuels, G. J.; Gersten, S. W.; Gilbert, J. A.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1407–9.
- (17) Cabaniss, G. E.; Diamantis, A. A.; Murphy, W. R., Jr.; Linton, R. W.; Meyer, T. J., submitted for publication.
- (18)  $E_{1/2}$  values were determined by using the equation  $E_{1/2} = \frac{1}{2}(E_{p,a} + E_{p,c})$ . For the Os(V/IV) couple and several of the Ru(IV/III) and Os(IV/III) couples in low pH solutions, the  $E_{p,a}$  values from differential-pulse-polarographic measurements were used.

2,2'-bpy)RuOH<sub>2</sub>]<sup>2+</sup>, 89486-25-9; Ru(trpy)Cl<sub>3</sub>, 72905-30-7; [(trpy)(bpy)RuCl]Cl, 89463-54-7; [(trpy)(bpy)RuCl](PF<sub>6</sub>), 83572-47-8; [(trpy)(bpy)RuO](ClO<sub>4</sub>)<sub>2</sub>, 89463-57-0; [(trpy)(4,4'-(MeO)<sub>2</sub>-2,2'-bpy)RuCl]Cl, 89463-58-1; (bpy)(2,6-pyridinedicarboxylato)RuCl,

89486-26-0; (bpy)RuCl<sub>4</sub>, 63338-26-1; [(trpy)(bpy)Ru<sup>III</sup>-OH]<sup>2+</sup>, 81971-63-3; [(trpy)(bpy)Os<sup>III</sup>-OH]<sup>2+</sup>, 89463-59-2; [(trpy)(bpy)-Os<sup>IV</sup>=O]<sup>2+</sup>, 89463-60-5; [(trpy)(bpy)Ru<sup>III</sup>-OH<sub>2</sub>]<sup>3+</sup>, 89463-61-6; [(trpy)(bpy)Os<sup>III</sup>-OH<sub>2</sub>]<sup>3+</sup>, 89463-62-7.

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## Influence of the Metal Centers on the pK<sub>a</sub> of the Pyrrole Hydrogen of Imidazole Complexes of (NH<sub>3</sub>)<sub>5</sub>M<sup>3+</sup>, M(III) = Co(III), Rh(III), Ir(III), Ru(III)

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The pK<sub>a</sub>'s at 298 K, μ = 0.10 (NaCl), and the temperature dependence (273–343 K) for the deprotonation of the pyrrole NH of several imidazoles coordinated to (NH<sub>3</sub>)<sub>5</sub>M<sup>3+</sup> moieties (M = Co<sup>III</sup>, Rh<sup>III</sup>, Ir<sup>III</sup>, Ru<sup>III</sup>) are reported. A greater importance of d<sup>n</sup> configuration over ion size is found. Data summarized for various systems are as follows (ligand, M (pK<sub>298</sub>, ΔH<sub>a</sub><sup>o</sup> in kcal/mol, ΔS<sub>a</sub><sup>o</sup> in eu): imidazole = imH, Co<sup>III</sup> (9.99, 14.0 ± 0.5, 1.3 ± 1.6), Rh<sup>III</sup> (9.97, 13.6 ± 0.3, 0.1 ± 1.3), Ir<sup>III</sup> (10.05, 13.4 ± 0.3, 1.2 ± 1.0), Ru<sup>III</sup> (8.9, 10.0 ± 0.8, 3.7 ± 1.2); 2-methylimidazole = 2-MeimH, Co<sup>III</sup> (10.67, 17.8 ± 0.7, 11.2 ± 2.4); 2,4(5)-dimethylimidazole = 2,5-Me<sub>2</sub>imH, Co<sup>III</sup> (11.04, 13.4 ± 0.5, 5.3 ± 1.6), Ru<sup>III</sup> (10.20, 13.2 ± 0.6, -2.1 ± 1.6). <sup>1</sup>H NMR spectra of low-spin d<sup>6</sup> complexes of imidazoles and ring-methylated imidazoles are discussed for Co<sup>III</sup>, Rh<sup>III</sup>, Ir<sup>III</sup>, and Ru<sup>III</sup>. C-2 and remote ring, C-5, substituents are shifted downfield relative to the free imidazole ligand in the order H<sup>+</sup> > Co<sup>III</sup> > Rh<sup>III</sup> > Ir<sup>III</sup>. The C-4 position is influenced competitively by σ-withdrawal ring substituents and TIP effects for Co<sup>III</sup>. Assignments of the remote isomer for (NH<sub>3</sub>)<sub>5</sub>M(2,5-Me<sub>2</sub>imH)<sup>3+</sup> (M = Co<sup>III</sup>, Ru<sup>III</sup>) are made from the <sup>1</sup>H NMR spectra of the Co<sup>III</sup> and Ru<sup>III</sup> complexes. The Ru<sup>III</sup> complexes of 2,5-Me<sub>2</sub>imH and the imidazolato form (2,5-Me<sub>2</sub>im<sup>-</sup>) both exhibit LMCT spectra. The imidazolato form has three bands at 655, 377, and 272 nm, proposed for Π<sub>1</sub> → Π<sub>d</sub>, Π<sub>2</sub> → Π<sub>d</sub>, and n → Π<sub>d</sub> transitions, where Π<sub>1</sub>, Π<sub>2</sub>, and n are the highest HOMO's of the imidazolato ring.

### Introduction

The inductive influence of a cationic metal center is responsible for many common, but important, chemical phenomena. For example, the hydrolysis and polymerization of simple aqua ions such as Fe(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> and the Lewis acid catalysis of ions such as H<sup>+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, and Al<sup>3+</sup> on ester hydrolysis and numerous other organic reactions come to mind. The Lewis acid influence operates predominantly through σ withdrawal on the coordinated ligand to promote nucleophilic reactions at positions adjacent to the coordinated atom. If the ligand is protonic as with H<sub>2</sub>O, H<sub>2</sub>S, imidazoles, pyrazoles, amines, and amides, the inductive effect alters the pK<sub>a</sub> of a site of deprotonation. If σ induction only operates to change the pK<sub>a</sub>, the influence should attenuate rapidly with bond distance or, for ions of constant charge, the acidity should decrease with size. We set out to examine the applicability of this simple model in terms of the influence of varying the metal center on the pK<sub>a</sub> of a coordinated imidazole ligand as a function of ionic potential and d<sup>n</sup> configuration. A study of this sort has relevance to biochemical systems and catalysis. In particular, the imidazolato ion, which is produced by deprotonation of imidazole or with amino acids via the side-chain residue of histidine, is of interest in regard to its function as the bridging ligand between Cu(II) and Zn(II) in bovine erythrocyte superoxide dismutase<sup>1</sup> and as a strong base for other enzymes. We recently reported on the affinity of imidazole and imidazolato as ligands toward the low-spin d<sup>5</sup> center (CN)<sub>5</sub>Fe<sup>2+</sup>.<sup>2</sup> It was shown for Fe(III) in the (CN)<sub>5</sub>FeL<sup>2-</sup> environment that the influence of the metal ion originates largely from changing the enthalpy of dissociation of the pyrrole N-H bond relative to that of the free ligand.<sup>2,3</sup>

The barrier is lowered by ca. 8.8 kcal/mol by coordination to (CN)<sub>5</sub>Fe<sup>2-</sup>. Harrowfield et al. have measured the pK<sub>a</sub> of (NH<sub>3</sub>)<sub>5</sub>Co(imH)<sup>3+</sup> at 25.0 °C as 10.02;<sup>4,5</sup> this is close to the value obtained for (CN)<sub>5</sub>Fe(imH)<sup>2-</sup> (10.93)<sup>2</sup> as well as for the complexes of imidazole with ferrimyoglobin (10.34),<sup>3</sup> cobalamin (10.25),<sup>6</sup> and methylmercuric ion (9.61).<sup>7</sup> It becomes difficult to evaluate the influence of the metal ion for such diverse species where solvation differences are likely for highly charged cations and anions compared with bulky hydrophobic molecules and organometallic ions. Therefore, special influences of particular metal centers become hidden. It is of interest to know if the results for (CN)<sub>5</sub>Fe(imH)<sup>2-</sup> are representative. Comparisons should be made among a related series of ions of the same charge in a constant spectator ligand set where attention could be placed on the chemical nature of the central metal ion. Solubilities and synthetic work suggested that comparisons among the (NH<sub>3</sub>)<sub>5</sub>ML<sup>3+</sup> complexes would be the best case. In addition the synthesis of this series has been expedited by the recent reports of Taube and Sargeson<sup>8</sup> concerning the use of trifluoromethanesulfonato (TFMS) complexes of (NH<sub>3</sub>)<sub>5</sub>M<sup>3+</sup>, M = Co(III), Rh(III), Ir(III), Ru(III), Os(III). The TFMS intermediate complexes are readily obtained from available [(NH<sub>3</sub>)<sub>5</sub>MCl]Cl<sub>2</sub> precursor compounds. With slight modifications to these literature procedures one can prepare the imidazole complexes of Co(III), Rh(III), Ir(III), and Ru(III) in order that chemical trends for this series of ions can be examined. The results of

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