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Acid−Base and Electrochemical Properties of the MLCT Excited States and One-Electron-Reduced Forms of Ruthenium(II) Complexes Containing 2-(2′-Pyridyl)pyrimidine and 2,2′-Bipyridine in Aqueous Solution

Fiorella Casalboni,[1a] Quinto G. Mulazzani,*,[1a] Catherine D. Clark,[1b] Morton Z. Hoffman,*,[1b] Peter L. Orizondo,[1c] Marc W. Perkovic,[1c] and D. Paul Rillema*,[1c]

Istituto di Fotochimica e Radiazioni d'Alta Energia del CNR, Via P. Gobetti 101, 40129 Bologna, Italy, Department of Chemistry, Boston University, Boston, Massachusetts 02215, and Department of Chemistry, Wichita State University, Wichita, Kansas 67260

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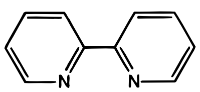
The acid−base and electrochemical properties of the MLCT excited states and the one-electron-reduced forms of the three $\mathrm{Ru(bpy)_{3-\mathit{p}}(pypm)_{\mathit{p}}^{2+}}$ complexes, where bpy = 2,2′-bipyridine, pypm = 2-(2′-pyridyl)pyrimidine, and $p = 1-3$, have been examined in aqueous solution; a determination has been made of the ground- and excited-state electrochemical potentials, the values of the $\mathrm{p}K_a$ and deprotonation rate constants of the conjugate acids of the excited states and the one-electron-reduced complexes, and the kinetics of the second-order decays of the reduced species. Comparison is made with the behavior of the analogous 10 complexes of the form $\mathrm{Ru(bpy)_{3-\mathit{m}-\mathit{z}}(bpm)_{\mathit{m}}(bpz)_{\mathit{z}}^{2+}}$, where bpm = 2,2′-bipyrimidine, bpz = 2,2′-bipyrazine, m and $z = 0-3$, and $m + z \leq 3$, which have been studied in detail before.

Introduction

Among the most well-characterized Ru(II) photosensitizers are those with symmetric diimine ligands such as 2,2′-bipyridine (bpy) and its analogues. Recently, attention has been given to complexes that possess asymmetric diimine ligands in order to fine-tune further the properties of their excited states.[2] One such ligand is 2-(2′-pyridyl)pyrimidine (pypm); ground and excited states of Ru(II) complexes that possess this ligand have been characterized in organic solvents.[3] Because pypm has a N heteroatom on the periphery of the ligand, the excited states and one-electron-reduced forms of its complexes would be expected to undergo protonation in aqueous solution. In this way, pypm is analogous to other ligands, such as 2,2′-bipyrazine (bpz) and 2,2′-bipyrimidine (bpm); the photophysics, photochemistry, electrochemistry, and radiation chemistry of their Ru(II) complexes ($\mathrm{RuL^{2+}}$) and one-electron-reduced protonated ($\mathrm{RuLH^{2+}}$) and -deprotonated ($\mathrm{RuL^{+}}$) forms have been very well studied in fluid solution.[4−15]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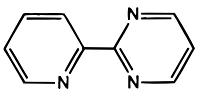
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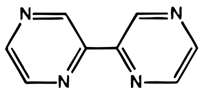
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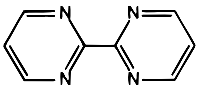
bpm

In addition to being asymmetric, pypm is structurally intermediate between bpy and bpm. As a result, the reduction potentials of the pypm complexes in $\mathrm{CH_3CN}$ are in the gap of ∼0.4 V between those of $\mathrm{Ru(bpy)_3^{2+}}$ and $\mathrm{Ru(bpy)_2(bpm)^{2+}}$.[3] The electron-transfer properties of the excited states ($\mathrm{{}^*RuL^{2+}}$) and the one-electron-reduced forms of the pypm complexes would, likewise, be expected to be intermediate between those of $\mathrm{Ru(bpy)_3^{2+}}$ and those of the bpz and bpm species. In addition, the acid−base properties of $\mathrm{{}^*RuL^{2+}}$ and $\mathrm{RuL^{+}}$ in aqueous solution, which would be expected to correlate with the ground-state reduction potentials in the way that their bpy, bpz, and bpm analogues do,[10] permit pH control of the redox properties of the photosensitizer system; the reduced forms of some of these complexes are sufficiently stable in the absence of air to undergo protonation, disproportionation, and cyclic reoxidation back to the ground state.[10]

In this study, we have examined the acid−base and electrochemical properties of the excited states and the one-electron-reduced forms of the three $\mathrm{Ru(bpy)_{3-\mathit{p}}(pypm)_{\mathit{p}}^{2+}}$ complexes, where bpy = 2,2′-bipyridine, pypm = 2-(2′-pyridyl)pyrimidine, and $p = 1-3$, in aqueous solution. Comparison is made with

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the behavior of the 10 complexes of the form $Ru(bpy)_{3-m-z}(bpm)_m(bpz)_z{}^{2+}$, where m and $z = 0-3$ and $m + z \leq 3$.

Experimental Section

Materials. $Ru(bpy)_2(pypm)^{2+}$, $Ru(pypm)_2(bpy)^{2+}$, and $Ru(pypm)_3{}^{2+}$ as the $PF_6{}^-$ salts were synthesized as previously described;[3] for convenience, these complexes will be referred to as yyp, ppy, and ppp, respectively, in the tables and figures. The complexes of bpy, bpz, and bpm, which were available from our previous investigations, will be abbreviated bpy = y, bpz = z, and bpm = m; thus, $Ru(bpy)_3{}^{2+}$ will be designated yyy, $Ru(bpm)_2(bpz)^{2+}$ as mmz, *etc*. Other solutes were of the purest grade available and were used as received. Solutions were prepared from doubly distilled water that had been passed through a Millipore purification train. The pH of the aqueous solutions was adjusted with $HClO_4$, NaOH, or phosphate buffers.

Electrochemistry. Reversible one-electron potentials were obtained from cyclic voltammetry measurements performed with an EG&G 273A potentiostat controlled by the EG&G M270A (version 4.0) software package. Experiments were performed at a scan rate of 0.2 V/s on Ar-purged aqueous solutions, containing 0.1 M tetraethylammonium perchlorate (TEAP; GFS electrochemical grade) and 2 mM complex. A glassy carbon working electrode, Ag/AgCl reference electrode, and Pt counter electrode were used; all electrodes were supplied by EG&G or Cypress Instruments and were polished, as appropriate, with Raybrite gem polish (Raytech) prior to use.

Steady-State emission. Emission spectra were measured at ambient temperature (25 °C) on Ar-purged solutions with the use of a SLM phase-shift spectrofluorimeter ($\lambda_{ex} = 450$ nm); the corrections of the emission spectra for phototube response were made by the program supplied with the instrument.

Pulsed-Laser Flash Photolysis. Transient emission measurements were made with a Nd:YAG pulsed laser ($\lambda_{ex} = 532$ nm; 100 mJ/pulse) and a red filter in front of the monochromator slit; details of the apparatus have been described before.[16] The output voltage of the photomultiplier (Hamamatsu R928) was controlled to produce a linear reponse, and the data were averaged for 20 shots. All solutions (Ar-purged or air-equilibrated) were contained in 1- × 1-cm or 2- × 1-cm cells; in the latter case they were excited along the shorter path and interrogated along the longer one. The temperature of the solutions was controlled at 25.0 (±0.1) °C with a thermostated circulating water bath. Excited-state lifetimes (τ) were determined on Ar-purged solutions that contained ~10 μM complex ($\lambda_{mon} = 630$ nm). Measurements of the first-order rate constant of excited-state decay ($1/\tau$) were repeated at least three times on different days; good agreement (±5%) was obtained.

Pulse Radiolysis. Pulse radiolyses with optical absorption detection were performed with the 12-MeV linear accelerator at FRAE-CNR, Bologna.[17] The pulsed irradiations were carried out at room temperature on samples contained in Spectrosil cells of 1- or 2-cm path length. The solutions were protected from the analyzing light by means of a shutter and appropriate UV cutoff filters. The radiation dose per pulse was monitored by means of a charge collector behind the irradiation cell, which was calibrated as previously described.[18] The determination of the rate of protonation of RuL^+ was performed in solutions of 0.65–0.80 mM ionic strength; $[H^+]$ was varied between 50 and 200 μM with $HClO_4$. Solutions, containing 0.5 M *tert*-butyl alcohol as a scavenger for $^{\bullet}OH$ radicals, were degassed using standard vacuum line techniques.

Generation of $CO_2{}^{\bullet-}$ radicals. The radiolysis of N_2O-saturated (25 mM) aqueous solutions containing $HCO_2{}^-$ produces $e_{aq}{}^-$, $^{\bullet}OH$ radicals, and $H^{\bullet}$ atoms with G values (G = number of species formed per 100 eV of energy absorbed by the solution) of 2.6, 2.7, and 0.6, respectively.[19] These initially formed species are rapidly converted to $CO_2{}^{\bullet-}$ by the reaction of $e_{aq}{}^-$ with N_2O to form $^{\bullet}OH$ and the reactions of $^{\bullet}OH$ and $H^{\bullet}$ with $HCO_2{}^-$. $CO_2{}^{\bullet-}$ is a strong reducing agent ($E°(CO_2/CO_2{}^{\bullet-}) = -1.90$ V;[20] it undergoes protonation only in very acidic solution ($pK_a = -0.2$).[22]

Table 1. Values of λ_{max} and τ_0 at 25 °C for Ar-Purged Aqueous Solutions

complex	λ_{max}, nm[a]	τ_0, μs
ppp	630	0.18
ppy	647	0.14
yyp	661	0.086
yyy	617	0.58

[a] From corrected spectra; $\lambda_{ex} = 450$ nm.

Results

Photophysics. Values of the emission maxima (λ_{max}) and excited-state lifetimes in neutral and alkaline solution (τ_0) in comparison to those of $Ru(bpy)_3{}^{2+}$ are given in Table 1.

Electrochemical Potentials. The measured values of $E°(Ru^{3+/2+})$ and $E°(Ru^{2+/+})$ are given in Table 2; no significant variation in the reduction potentials was observed across the pH range 1–13. Approximate values of the potentials of the excited states (Table 2) can be obtained from $E°$ of the ground states and the excitation energies for the transition between the ground- and excited-state zeroth vibrational energy levels (E_{00}): $E°(Ru^{3+/*2+}) = E°(Ru^{3+/2+}) - E_{00}$ and $E°(Ru^{*2+/+}) = E°(Ru^{2+/+}) + E_{00}$. Values of E_{00} may be approximated by the energy of the maximum of the emission, E_{em}, at ambient temperatures.[22]

Acid–Base Behavior of the Excited States. Values of τ and the emission intensities (I) of the pypm complexes decrease sharply as the pH is decreased in Ar-purged solution; Figure 1 shows the pH dependence of τ/τ_0. The variation of I in air-saturated solutions as a function of pH parallels that behavior; previous studies showed that the presence of air has no effect on the shapes of the curves for the bpz and bpm complexes.[11] From the midpoint of these "titration curves", the apparent excited-state pK_a ($pK_a{}^*(app)$) can be estimated to within ±0.2 units; values are given in Table 3. No new emission from the complexes at pH ~ 0 was observed.

One-Electron-Reduced Species. In the pulse radiolysis experiments, the reaction of $CO_2{}^{\bullet-}$ with RuL^{2+} results in spectral changes that are attributed to the loss of the substrate and the formation of RuL^+. From these changes as a function of time at selected wavelengths, the observed pseudo-first-order rate constants were obtained at different values of $[RuL^{2+}]$, from which were evaluated the rate constants for the reaction: $k = 4.5 \times 10^8$, 5.8×10^8, and 7.3×10^8 M^{-1} s^{-1} for yyp, ppy, and ppp, respectively.

As had been observed with complexes containing bpz and bpm,[4,7,10] the spectral changes are also a function of pH, reaching limits in acidic and basic solution. Figure 2 shows the observed difference spectra for the reduction of ppp; the difference spectra for the reduction of yyp and ppy are given in the Supporting Information. By monitoring of the spectral changes as a function of pH, "titration curves" were obtained, from which were determined the pK_a values of $RuLH^{2+}$ (Table 3); the inset of Figure 2 shows the curve for ppp.

The decays of RuL^+ and $RuLH^{2+}$ occurred via pH-dependent second-order kinetics across the entire pH range investigated; the observed rate constants are given in the Supporting Information.

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Table 2. Electrochemical Potentials (*vs* NHE) for Ground and Excited States of Ru(II)−pypm Complexes in Aqueous Solution at 25 °C

complex	E_{em}, eV	$E°(Ru^{3+/2+})$, V	$E°(Ru^{3+/*2+})$, V	$E°(Ru^{2+/+})$, V	$E°(Ru^{*2+/+})$, V	$E_3°(RuL^{2+},H^+/RuLH^{2+})$, V
yyp	1.88	1.38	−0.50	−1.01	0.87	−0.71
ppy	1.92	1.42	−0.50	−0.96	0.96	−0.69
ppp	1.97	1.54	−0.43	−0.95	1.02	−0.70

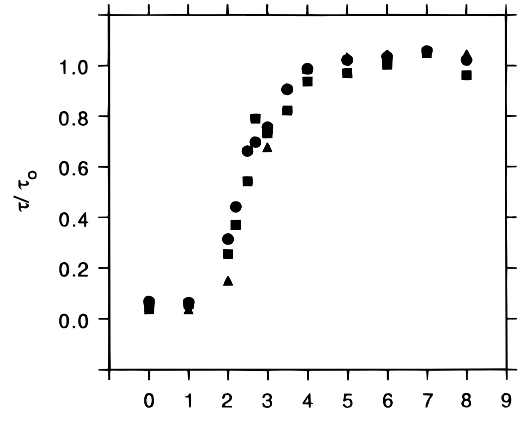

Figure 1. pH dependence of τ/τ_0 for $Ru(bpy)_2(pypm)^{2+}$ (●), $Ru(pypm)_2(bpy)^{2+}$ (■), and $Ru(pypm)_3^{2+}$ (▲) in Ar-purged aqueous solution at 25 °C.

Table 3. Acid−Base Properties of the Excited States and One-Electron-Reduced Forms at 25 °C

complex	pK_a^*(app)	pK_a^*	k_{-H}^*, s^{-1}	$pK_a(RuLH^{2+})$	k_{-H}, s^{-1}
yyp	2.4^{a}	3.3^{b}	3.6×10^6	8.1	1.0×10^2
ppy	2.8^{a}	2.7^{b}	1.4×10^7	7.5	4.1×10^2
ppp	2.7^{a}	2.4^{b}	2.8×10^7	7.2	8.2×10^2
yyz	2.8^{c}	$4.4^{b,c}$	$2.8 \times 10^{5\ c}$	9.2^{d}	8.2
zzy	3.4^{c}	$3.2^{b,c}$	$4.5 \times 10^{6\ c}$	8.0^{d}	1.3×10^2
zzz	3.3^{c}	$2.3^{c,e}$	$3.9 \times 10^{7\ c}$	7.1^{d}	1.0×10^3
yym	1.9^{c}	$2.4^{b,c}$	$8.6 \times 10^{6\ c}$	7.2^{d}	8.2×10^2
mmy	2.3^{c}	$2.1^{b,c}$	$5.6 \times 10^{7\ c}$	6.9^{d}	1.6×10^3
mmm	2.4^{c}	$1.5^{b,c}$	$2.2 \times 10^{8\ c}$	6.3^{d}	6.5×10^3
zzm	3.4^{c}	$2.4^{c,e}$	$2.7 \times 10^{7\ c}$	7.2^{d}	8.2×10^2
mmz	3.5^{c}	$2.9^{b,c}$	$8.6 \times 10^{6\ c}$	7.7^{d}	2.6×10^2
yzm	3.1^{c}	$4.0^{b,c}$	$7.1 \times 10^{5\ c}$	8.8^{d}	21

[a] Average of results from lifetime and luminescence intensity measurements (this work). [b] Calculated from $pK_a^* = pK_a(RuLH^{2+}) - 4.8$. [c] Reference 11. [d] Reference 10. [e] Determined from k_q for quenching of $*RuL^2$ by H^+, k_H^*, and τ_0' (ref 11).

Permanent spectral changes resulted from successive radiolysis pulses. As Figure 3 shows for $Ru(bpy)_2(pypm)^{2+}$, an absorption maximum grows in at 350 nm, the absorption increases at $\lambda > 450$ nm and decreases in the 310-nm and 390−450-nm regions, and three well-defined isosbestic points at 325, 390, and 450 nm are observed. The spectrum of the irradiated solution does not change when the sample is exposed to air.

When degassed solutions containing ~0.2 mM zzz, mmm, ppp, or yyz in 0.5 M *tert*-butyl alcohol and 0.05−0.2 mM $HClO_4$ were pulse irradiated with a dose of ~20 Gy, the rapid decay of e_{aq}^-, monitored at 720 nm, parallels the formation of RuL^+. Inasmuch as the pK_a values of the $RuLH^{2+}$ species of the four complexes are at least 2 units higher than the solution pH used, RuL^+ initially formed undergoes protonation that can be followed at wavelengths where the spectra of RuL^+ and $RuLH^{2+}$ are different. For the four complexes over the range of $[H^+]$ studied, the rate constant of protonation (k_H) is 1.3 (±0.2) × 10^{10} M^{-1} s^{-1}.

Discussion

Reaction of RuL^{2+} with $CO_2^{\bullet-}$ Radicals. In an earlier study, the values of k for reaction 1, involving the 10 $Ru(bpy)_{3-m-z}(bpm)_m(bpz)_z^{2+}$ complexes, were determined as a function of the driving force of the reaction.[9,10] Although the data were fitted satisfactorily to the Marcus theory, the large gap of ~400 mV made the extrapolation long and uncertain. The three pypm complexes of this study fit right into the middle of the gap and so serve as a useful probe of the efficacy of the treatment.

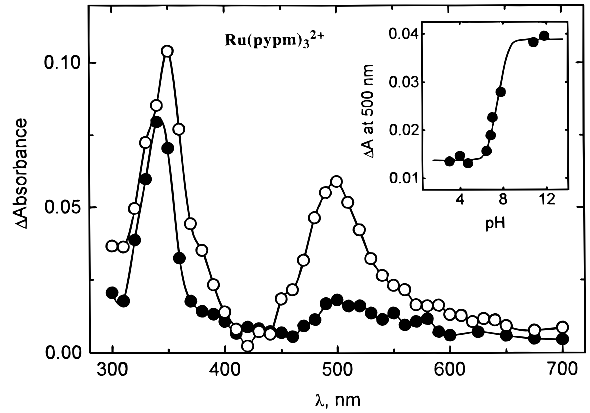

Figure 2. Observed transient difference spectra for the reaction of $CO_2^{\bullet-}$ with 55 μM $Ru(pypm)_3^{2+}$ upon the pulse irradiation of N_2O-saturated solutions containing 0.1 M HCO_2^-: optical path = 2 cm; dose per pulse = 10 Gy; pH 5 (●), pH 12 (○). Inset: Effect of pH on ΔA for solutions containing 0.1 mM $Ru(pypm)_3^{2+}$; $\lambda_{mon} = 500$ nm, optical path = 2 cm, and dose per pulse = 9.6 Gy.

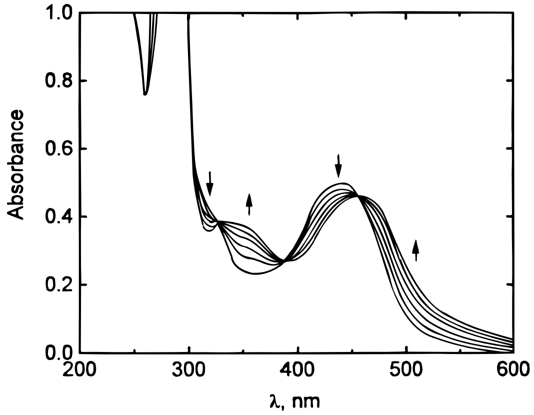

Figure 3. Permanent spectral changes upon the delivery of successive radiation pulses to a degassed solution of 54 μM $Ru(bpy)_2(pypm)^{2+}$ and 0.1 M HCO_2^- at pH 12; dose per pulse ~ 10 Gy. The spectra, except for the first one, were obtained after five pulses.

$$RuL^{2+} + CO_2^{\bullet-} \rightarrow RuL^+ + CO_2 \qquad (1)$$

The driving force of reaction 1 is given by eq 2, where w_r and w_p are the electrostatic work terms involved in the approach of the reactants and the diffusional separation of the products, respectively.[9,10] Inasmuch as one of the products is uncharged, $w_p = 0$. The value of w_r is approximately −2.1 kJ mol^{-1}, corresponding to −0.02 eV. Table 2 gives $E°(Ru^{2+/+})$; the values of $\Delta G°'$ for yyp, ppy, and ppp are −0.85, −0.90, and −0.91 V, respectively.

$$\Delta G°' = E°(CO_2/CO_2^{\bullet-}) - E°(Ru^{2+/+}) + w_p - w_r \qquad (2)$$

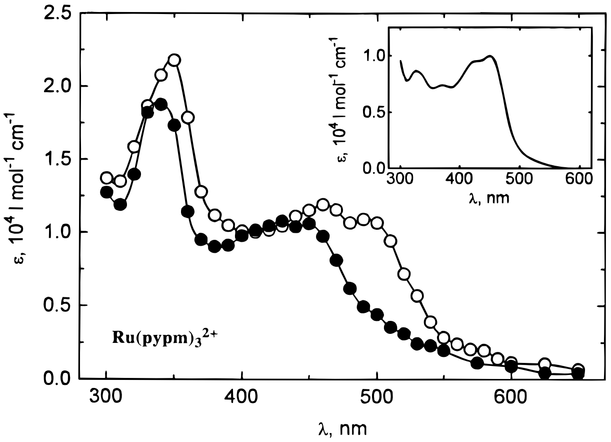

Figure 4. Absorption spectra of $Ru(pypm)_3{}^+$ (○) and $Ru(pypm)_2(pypmH)^{2+}$ (●). Inset: spectrum of $Ru(pypm)_3{}^{2+}$.

The plot of log k *vs* $\Delta G^{\circ\prime}$ for all 13 bpy, bpz, bpm, and pypm complexes, given in the Supporting Information, shows that the pypm complexes fall exactly on the previous fit, corroborating the model that was used earlier. The results reinforce the conclusions that were drawn then:[9,10] The intrinsic barrier ($\Delta G^{\ddagger}(0)$) of reaction 1 is 57 kJ mol^{-1}, and the self-exchange rate constant for the $CO_2/CO_2{}^{\bullet-}$ couple is 1.4×10^{-3} M^{-1} s^{-1}. As previously noted,[9,10] electron-transfer reactions of $CO_2{}^{\bullet-}$ require conditions of high driving force to overcome the very low self-exchange rate, despite the highly negative reduction potential of the $CO_2/CO_2{}^{\bullet-}$ couple.

Properties of the One-Electron-Reduced Species. From the observed difference spectra upon pulse radiolysis, a knowledge of the absorbed radiation dose, and the spectra of the ground-state complexes, the spectra of RuL^+ and $RuLH^{2+}$ can be evaluated. The assumption was made that $G(-RuL^{2+}) = G(CO_2{}^{\bullet-}) = G(e_{aq}{}^-) + G({}^{\bullet}OH) + G(H^{\bullet}) = 5.9$; corrections for the incomplete scavenging of $CO_2{}^{\bullet-}$ by RuL^{2+} were made when necessary. Figure 4 shows the absorption spectra of $Ru(pypm)_3{}^{2+}$, $Ru(pypm)_3{}^+$, and $Ru(pypm)_2(pypmH)^{2+}$; the spectra of the other pypm complexes and their one-electron-reduced forms and conjugate acids are given in the Supporting Information. The absorption spectra of RuL^+ exhibit characteristically intense bands in the 340- and 480-nm regions, which are assigned as overlapping ligand-localized transitions within the uniquely reduced ligand, and MLCT transitions between the metal center and the nonreduced ligands. In the protonated forms, both the ultraviolet and the visible bands are diminished in intensity and shifted to the blue. The spectra of the reduced pypm complexes are similar to their bpy-, bpz-, and bpm-containing analogues.[14] The spectral characteristics of the pypm complexes and their one-electron-reduced and protonated forms are given in the Supporting Information.

We have shown[10] that the pK_a values for $RuLH^{2+}$ complexes that possess bpz and bpm ligands correlate linearly with $E°(Ru^{2+/+})$; the interesting feature of the relationship is that the complexes for which bpz is the acceptor ligand lie on a distinctly different line than do the bpm-acceptor complexes. This result was taken as a further indication that protonation occurs on the uniquely reduced ligand, and that the added electron is localized on the ligand that is most easily reduced. Figure 5 shows the results for the pypm complexes overlaid with those of the others; clearly, the pypm-acceptor complexes lie on a different line.

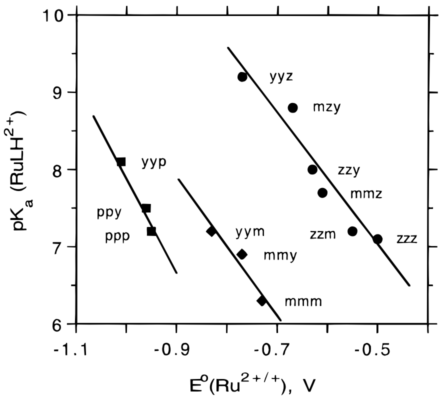

Figure 5. pK_a values for $RuLH^{2+}$ as a function of $E°(Ru^{2+/+})$. Abbreviations: y = bpy, z = bpz, m = bpm, and p = pypm.

The linear correlation between pK_a and $E°(Ru^{2+/+})$ exists for complexes with a specific acceptor ligand because reduction and protonation are, in effect, both charge-transfer processes; the easier it is for a complex to be reduced (*i.e.*, the less negative $E°(Ru^{2+/+})$), the harder it will be for it to be protonated (*i.e.*, the lower the pK_a of the conjugate acid), assuming, of course, that a site of protonation exists. The fact that the systems with pypm, bpm, and bpz acceptor ligands are on different lines is attributed to their different σ-donor strengths; strong σ-donating ligands (bpz < bpm)[23] shift charge from themselves into the metal center, making them more easily reduced. In this regard, the σ-donor strength of pypm must be greater than that of bpm; Tazuke *et al.*[22] reached the same conclusion in their study of the dependence of τ_0 of $*Ru(pypm)_3{}^{2+}$ and $*Ru(bpm)_3{}^{2+}$ on temperature in CH_3CN.

From a knowledge of $E°(Ru^{2+/+})$ and the pK_a of $RuLH^{2+}$ it is possible to calculate values of $E_{pH}°(RuL^{2+},H^+/RuLH^{2+})$ by the use of eq 3 at a pH of interest in the range where the reduced form is protonated. In order to compare the results for the pypm complexes with those of the others in the earlier report,[10] pH 3 was chosen for the calculation; the results are given in Table 2. The data show that the RuL^+ species are very good reducing agents, but that the protonated forms are poorer reducing agents by ~0.3 V.

$$E_{pH}°(RuL^{2+},H^+/RuLH^{2+}) = E°(Ru^{2+/+}) + 0.059(pK_a - pH) \quad (3)$$

Under the assumption that k_H (1.3×10^{10} M^{-1} s^{-1}) is the same for all 12 complexes that have the same charges and shapes, the rate constants of deprotonation (k_{-H}) of $RuLH^{2+}$ can be calculated from the pK_a values (Table 3).

The one-electron-reduced forms decay via pH-dependent second-order kinetics. The pH dependence is clearly due to the acid−base properties of those species; the second-order kinetics indicates that the reaction occurs via a bimolecular process, most likely electron-transfer disproportionation. The values of the rate constants (see Supporting Information), especially for $Ru(bpy)_2(pypm)^+$, for which more extensive data are available, show a low-pH plateau, a maximum around pH 7, and diminishing values in more alkaline solution. This behavior is very reminiscent of the disproportionation decay of $O_2{}^{\bullet-}$ (pK_a 4.8),[24] suggesting that the RuL^+ and $RuLH^{2+}$ species react with each other via disproportionation, but with different rate constants due to the different driving forces of the electron-transfer reactions. Reactions 4−7 summarize the overall

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(23) Crutchley, R. J.; Kress, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1983**, *105*, 1170.

(24) Bielski, B. H. J.; Cabelli, D. E.; Arudi, R. L.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1985**, *14*, 1041.

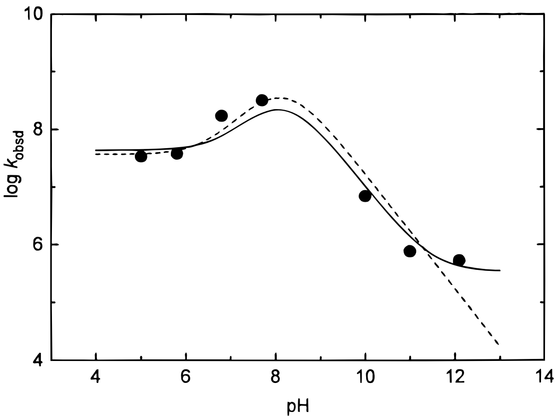


Figure 6. Fit of eq 8 for $Ru(bpy)_2(pypm)^{2+}$ (—); fit if the contribution of reaction 7 were negligible (– – –).

mechanism. $RuLH_2^{2+}$ represents the final product in which one of the rings of the reduced ligand has been hydrogenated. Figure 3 shows the growing in of the spectrum of this final product;[25] estimates of the values of ϵ are given in the Supporting Information.

$$RuLH^{2+} \overset{K_a}{\rightleftharpoons} RuL^{+} + H^{+} \qquad (4)$$

$$RuLH^{2+} + RuLH^{2+} \rightarrow RuL^{2+} + RuLH_2^{\;2+} \qquad (5)$$

$$RuLH^{2+} + RuL^{+} + H_2O \rightarrow RuL^{2+} + RuLH_2^{\;2+} + OH^{-} \qquad (6)$$

$$RuL^{+} + RuL^{+} + 2H_2O \rightarrow RuL^{2+} + RuLH_2^{\;2+} + 2OH^{-} \qquad (7)$$

The values of k_{obsd} as a function of pH are related to K_a and the rate constants for reactions 5–7 by eq 8.

$$k_{obsd} = \frac{2\left\{k_5 + \frac{k_6 K_a}{[H^+]} + k_7\left(\frac{K_a}{[H^+]}\right)^2\right\}}{\left(1 + \frac{K_a}{[H^+]}\right)^2} \qquad (8)$$

A very reasonable fit of the data, which is shown in Figure 6, was obtained with eq 8 for $Ru(bpy)_2(pypm)^+$; values of k_5, k_6, and k_7 of 2 × 10^7, 4 × 10^8, and 2 × 10^5 M^{-1} s^{-1}, respectively, are obtained. If k_7 for $Ru(bpy)_2(pypm)^+$ is assumed to be negligibly small, which appears to be the case for $Ru(bpz)_3^{\;+}$ in highly alkaline solution, where it is stable for many hours in the absence of air,[10] the values of k_5 and k_6 become 2 × 10^7 and 7 × 10^8 M^{-1} s^{-1}, respectively. We conclude that k_7 for yym has a value $<10^5$ M^{-1} s^{-1}.

Protonation of the Excited States. The variations of τ and the emission intensity with pH for the pypm complexes are very similar to those seen previously for the bpz and bpm complexes;[11] the values of pK_a*(app), given in Table 3, were treated according to the following scheme. Because emission was seen from $Ru(bpz)_3^{2+}$, $Ru(bpz)_2(bpm)^{2+}$, and $Ru(bpm)_2(bpz)^{2+}$ at pH 0.3, the lifetimes (τ_0') of the protonated forms of the excited states (*$RuLH^{3+}$) could be measured. Inasmuch as $pK_a^* = pK_a^*(app) + \log(\tau_0'/\tau_0)$, the thermodynamic values of the excited-state acid–base equilibrium constants ($K_a^* = k_{-H}^*/k_H^*$) were easily evaluated.

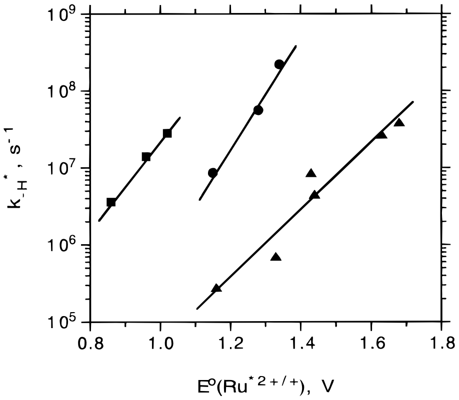
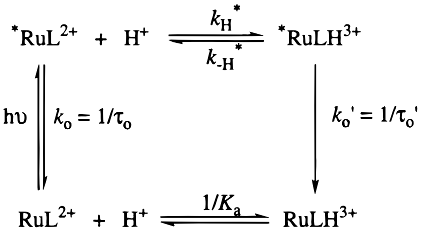


Figure 7. Plot of log k_{-H}^* *vs* $E°(Ru^{*2+/+})$ for complexes with pypm (■), bpm (●), and bpz (▲) electron-acceptor ligands.



We found[11] that the pK_a values for the protonated one-electron-reduced forms of the bpy, bpz, and bpm complexes were related to the pK_a* of the luminescent protonated excited states: $pK_a - pK_a^* = 4.8$; *$RuLH^{3+}$ is a stronger acid than is $RuLH^{2+}$, as expected from the similarity of the orbital nature of the ligand-localized electron and the ionic charges. By extension, the values of the pK_a* for the nonluminescent protonated excited states were calculated with the same relationship. For the pypm complexes here, which do not luminesce from the protonated excited states, this relationship gives the values in Table 3, which are about 1 unit larger than for the corresponding bpm complexes.[11] If k_H* is taken as the diffusional rate constant (7.1 × 10^9 M^{-1} s^{-1}), as was done previously,[11] k_{-H}* can be calculated (Table 3). A plot of log k_{-H}* *vs* $E°(Ru^{*2+/+})$ is linear with the complexes with the pypm-, bpz-, and bpm-acceptor ligands lying on different lines (Figure 7), consistent with the ligand localization of the MLCT excited states. An analogous plot of log k_{-H} *vs* $E°(Ru^{2+/+})$ (Supporting Information) shows the same linear correlation for the complexes that are protonated on their uniquely reduced ligands.

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(25) Because the total radiation dose delivered to the system was fairly high (~250 Gy), corresponding to the production of ~150 μM of reducing species, we cannot rule out the possibility that products more highly reduced and hydrogenated than $RuLH_2^{2+}$ (*e.g.*, $RuLH_4^{2+}$) are also formed.

Supporting Information Available: Table listing spectral characteristics of the pypm complexes and their one-electron reduced, protonated, and hydrogenated forms, table listing observed rate constants for the decay of the reduced species, observed transient difference spectra for the reaction of $CO_2^{\bullet-}$ with yyp and ppy, plot of log k *vs* $\Delta G^{\circ\prime}$ for the reaction of $CO_2^{\bullet-}$ with the complexes, absorption spectra of the reduced forms of yyp and ppy, and plot of log k_{-H} *vs* $E^{\circ}(Ru^{2+/+})$ for the complexes (9 pages). Ordering information is given on any current masthead page.

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