# Acid−Base Properties of the Ground and Excited States of Ruthenium(II) Bis(2,2′-bipyridine) 3-Carboxyl-2,2′-bipyridine

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Acid−base properties for ruthenium(II) bis(2,2′-bipyridine) 3-carboxyl-2,2′-bipyridine reveal a ground state $pK_a$ of $0.82 \pm 0.07$ and an excited state $pK_a^*$ of $2.31 \pm 0.05$, a 1.5 pH unit increase from the ground state. The excited state $pK_a^*$ is temperature independent while the ground state $pK_a^0$ increases with temperature and has $\Delta H^0$ and $\Delta S^0$ values of $-990 \pm 149$ cm$^{-1}$ and $-4.57 \pm 0.48$ cm$^{-1}$ K$^{-1}$, respectively. The acidic form of the complex emits at lower energy than the basic form at both 296 and 77 K. The emission energy maxima are solvent dependent and decrease in energy when the solvent changes from 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ to water and when the pH decreases. Changes in excited state lifetimes with emission energy follow the energy gap law with an intercept of $49 \pm 1$ and a slope of $(2.11 \pm 0.09) \times 10^{-3}$. Emission quantum yields for protonated and deprotonated species in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ are $0.023 \pm 0.001$ and $0.110 \pm 0.002$, respectively. The temperature dependence of the emission lifetimes gives energy barriers of 270 cm$^{-1}$ for the complex in aqueous solution at pH $-0.5$, and 990 cm$^{-1}$ in aqueous solution at pH 4.5, and 1920 cm$^{-1}$ in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$.

## Introduction

The acid−base properties of transition metal complexes containing ligands with attached carboxylic acid groups or heterocyclic ligands with remote nitrogen donor atoms can provide important information about the nature of excited states. In general, an increase in acidity of the excited state with respect to the ground state suggests a ligand-to-metal charge transfer mechanism whereas a decrease in the acidity of the excited state suggests a metal-to-ligand charge transfer mechanism. In either case, the ligand containing the acid−base functional group is directly involved in charge separation. This behavior provides the opportunity to adjust excited state properties by changing the pH of the solution.

The acid−base properties in the ground and excited states of ruthenium(II) complexes containing dicarboxybipyridine ligands have been reported.[1−8] Difficulties in characterizing the excited states of these complexes arose from more than one protonation reaction. In addition, the purity of the starting materials were in doubt due to difficulties in syntheses and separation of similar products. To eliminate these difficulties, a simpler compound, the ruthenium(II) bis(2,2′-bipyridine) 3-carboxyl-2,2′-bipyridine cation, [Ru(bpy)$_2$(bpyCOOH)]$^{2+}$, was synthesized by a ring opening procedure recently discovered in our laboratories.[9] Detailed physical and photophysical studies of the acid−base properties of this compound are reported in this paper. Ground state $pK_a^0$ and excited state $pK_a^*$ values were determined as a

function of temperature by photospectrometric and fluorescence titrations, respectively. In addition, the photophysical properties of the acidic and basic forms of the title compound in aqueous solution are compared to their properties in a nonaqueous environment.

## Experimental Section

**Materials**. The preparation, purification, and characterization of Ru(bpy)$_2$Cl$_2$·2H$_2$O and 4,5-diazafluorenone were described previously.[9] Methylene chloride was optima grade and purchased from Fisher Scientific. 2-Methyltetrahydrofuran (2-MeTHF) was 99% purity and purchased from Aldrich Chemical Co., Inc. Concentrated HCl, NaOH, and NaCl were ACS reagent grade and purchased from Fisher Scientific.

**Preparation of [Ru(bpy)$_2$(bpyCOOH)](PF$_6$)$_2$.** Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.13 g, 0.25 mmol) and 4,5 diazafluorenone (0.46 g, 0.25 mmol) were refluxed in 10 mL of ethanol for about 5 h. The solution was filtered while still hot to remove solid impurities. The filtrate was evaporated to dryness by rotary evaporation, and then 5 mL of 4 M NaOH was added to the solid. The resulting solution was adjusted to pH 0.65 by adding concentrated HCl and then a saturated aqueous solution of NH$_4$Cl was added dropwise until precipitation was complete. Sequentially, the solution was evaporated to dryness by rotary evaporation. Then the solid was redissolved in acetonitrile to remove NaCl, and then the solution was evaporated to dryness again. Next the solid was dissolved in water and loaded onto a cation exchange chromatographpy column (Sephadex SP-C25, pharmacia 40−120 $\mu$m) and the complex was eluted with an aqueous solution of HCl. The fraction obtained with 0.2 M HCl which contained the desired complex was evaporated to dryness by rotary evaporation and then dissolved in a minimum amount of water. It was precipitated by adding a saturated aqueous solution of NH$_4$PF$_6$ dropwise until precipitation was complete. Yield = 0.14 g (60%). Anal. Calcd for [Ru(bpy)$_2$(bpyCOOH)](PF$_6$)$_2$: C, 41.20; H, 2.68; N, 9.30. Found: C, 41.00; H, 2.62; N, 9.10. UV−vis spectra measured in CH$_3$CN at 296 K: 450 nm ($1.32 \times 10^4$ M$^{-1}$ cm$^{-1}$); 287 nm ($7.02 \times 10^4$ M$^{-1}$ cm$^{-1}$); 254 nm ($1.80 \times 10^4$ M$^{-1}$ cm$^{-1}$); 243 nm ($1.92 \times 10^4$ M$^{-1}$ cm$^{-1}$). Cyclic voltammograms measured in CH$_3$CN with Ag/AgCl (SSCE) as reference electrode: 1.32 V (82); $-1.37$ V (80); $-1.56$ V (108); $-1.84$ V (irreversible).

**Physical Measurements.** UV−visible spectra were recorded with a double beam CARY 14 instrument modified with an OLIS automation package, and corrected emission spectra were obtained with a Spex 212 Fluorolog spectrofluorometer.

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The ground state p$K_a^0$ was determined by spectrometric titration, and the excited state p$K_a^*$ was measured by fluorescence titration. Aqueous solutions of different pH's, but a constant ionic strength of 0.1 M, were prepared by adding HCl and 0.1 M NaCl to solutions, and their pH values were determined at 296 K with a glass electrode calibrated with standard buffers.

Emission spectra and emission lifetimes for the complex were measured in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ and in aqueous solutions at different pH values. The samples were excited at two isosbestic points (412 and 474 nm) and the emission spectra were measured from 500 to 775 nm. The acidic form, [Ru(bpy)$_2$(bpyCOOH)]$^{2+}$, was prepared by dissolving the complex in 12 M HCl, extracting it into CH$_2$Cl$_2$ and then adjusting the solution to 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ by addition of the appropriate quantity of 2-MeTHF. In aqueous solution, it was prepared by dissolving the complex in water followed by adjusting the pH to less than 1. The basic form, [Ru(bpy)$_2$(bpyCOO)]$^+$, was prepared by dissolving the complex in 0.1 M NaOH, extracting it into CH$_2$Cl$_2$ and then adjusting the solution to 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ by addition of the appropriate quantity of 2-MeTHF. In aqueous solution, it was prepared by dissolving the complex in water followed by adjusting the pH to greater than 5. A sample of [Ru(bpy)$_2$(bpyCOOH)]$^{2+}$ was also prepared by directly dissolving it in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$. The samples in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ were degassed by three freeze−pump−thaw cycles. Aqueous solutions were deaired by purging with Ar for 20 min prior to emission measurements. The emission lifetimes of the aqueous samples were measured over the 283 to 343 K temperature range and those in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ were measured from 77 to 360 K.

Emission quantum yields for samples in their acidic and basic forms were measured at 296 K. The freeze−pump−thaw cycle was repeated until three successive measurements were constant. Rhodamine-B ($\phi_r$ = 0.71[10]) was used as a standard and eq 1 was used to calculate the

$$\phi_s = \phi_r \frac{A_r}{A_s} \frac{I_s}{I_r} \quad (1)$$

emission quantum yields. In eq 1, $\phi_s$ is the quantum yield of the sample, $\phi_r$ is the quantum yield of the reference Rhodamine B, $A_s$ and $A_r$ are absorbances of the sample and the reference at 474 nm respectively, and $I_s$ and $I_r$ are integrated areas under the emission spectra of interest.

Excited state emission lifetimes were measured by exciting the samples with an OPOTEK optical parametric oscillator pumped by a frequency tripled Nd:YAG laser (Continuum Surlite, run at <1.5 mJ/ 10 ns pulse). Spectra regions were isolated with a Hamamatsu R955 PMT in a cooled housing (15 °C, Amherst) coupled to an Acton SpectraPro 275 monochromator. Transients were recorded with a LeCroy 9359A digital oscilloscope (1 Gs/s). Oscilloscope control and data curve fitting were accomplished with a program developed in-house. Emission lifetimes from 90 to 270 K were measured using a Cryo Industries EVT cryostat controlled by a Lakeshore 805 temperature controller. The cryostat was modified in house by adding a larger copper thermal mass, and then calibrated with an auxiliary thermocouple using ice water as the reference junction. This resulted in a temperature accuracy of ±1.6 K over the 90−270 K range. For temperatures above 270 K, the samples were equilibrated outside the dewer in a Fisher Isotemp bath, and temperature was controlled during measurements by circulating constant temperature water through the sample cell holder. Emission lifetimes as a function of temperature were fit to eq 2 using the program ORIGIN. In eq 2, $k_0$ is the sum of radiative and

$$\tau^{-1} = k_0 + Ae^{-\Delta E/RT} \quad (2)$$

nonradiative rate constants and set equal to the observed emission decay rate constant at 77 K. The parameters $A$ and $\Delta E$ are related to the thermal deactivation process of the emitting state.

## Results

**UV−Visible Spectra and the Ground State p$K_a^0$.** The UV−vis absorption spectra for [Ru(bpy)$_2$(bpyCOOH)]$^{2+}$ in aqueous solution as a function of pH are shown in Figure 1A.
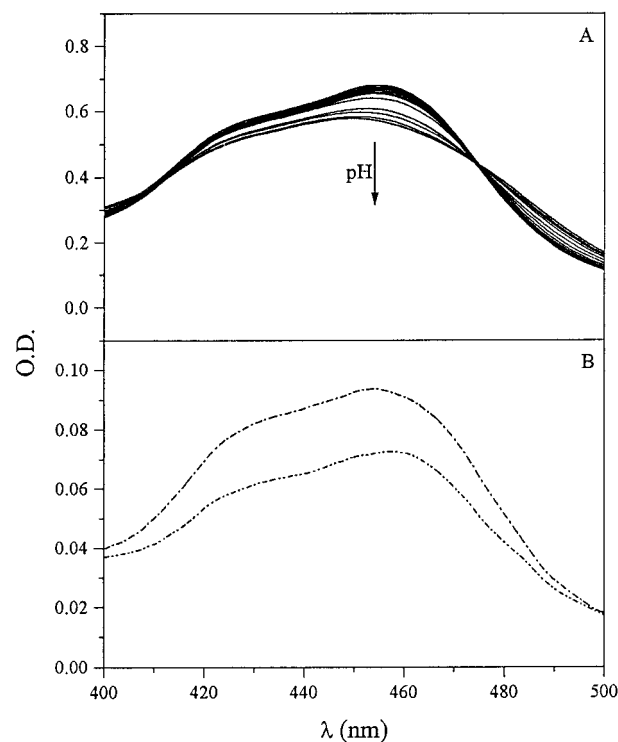
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**Figure 1.** UV−vis absorption spectra of [Ru(bpy)$_2$(bpyCOOH)]$^{2+}$ at different pHs. A: pH effects on the MLCT band for [Ru(bpy)$_2$-(bpyCOOH)]$^{2+}$ in aqueous solutions. pH decreases in the order of 4.78, 4.50, 4.25, 4.00, 3.75, 3.50, 3.25, 3.00, 2.50, 2.00, 1.75, 1.50, 1.25, 1.00, 0.60, 0.30, 0.00, −0.25, and −0.50. B: MLCT bands for [Ru-(bpy)$_2$(bpyCOOH)]$^{2+}$ (− · ·) and [Ru(bpy)$_2$(bpyCOO)]$^+$ (− · −) in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ pretreated with 12 M HCl and 0.1 M NaOH, respectively. The concentrations for the two samples were different and the optical densities should not be compared directly.

The absorption bands near 450 nm were assigned to metal-to-ligand charge transfer transitions by analogy to the parent compound [Ru(bpy)$_3$]$^{2+}$. As the pH decreased, the absorbance of the MLCT band decreased and broadened. As the pH increased, the energy maximum of the MLCT band near 450 nm became sharper and red-shifted. The spectra in Figure 1A show two isosbestic points at 412 nm and 474 nm. A plot (Figure 2A) of the absorption changes at 460 and 500 nm as a function of pH at 296 K shows clean titration curves with an inflection point (p$K_a^0$) at 0.82 ± 0.07. Equation 3 illustrates the chemical process.

$$[Ru(bpy)_2(bpyCOOH)]^{2+} + H_2O \rightleftharpoons$$
$$[Ru(bpy)_2(bpyCOO)]^+ + H_3O^+ \quad (3)$$
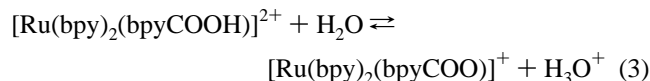
$$pK_a^0 = 0.82 \pm 0.07 \text{ at } 296 \text{ K}$$

Absorption bands at 450 nm for samples dissolved in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$, pretreated by 0.1 M NaOH and 12 M HCl, are shown in Figure 1B. The observed absorption bands were similar for the acidic and basic forms of the complex in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ and the basic form of the complex in aqueous solution at pH 5.0. However, as shown in Figure 1A, the absorption spectrum of the species in the solution of pH −0.5 differed from the others. Absorption spectra maxima in aqueous solutions between pH −0.5 and 5.0 varied between the one observed at pH −0.5 and the one observed at pH 5.0.

**Emission Properties**. Emission spectra of the acidic and basic forms of [Ru(bpy)$_2$(bpyCOOH)]$^{2+}$ at 77 and 296 K in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ are shown in Figure 3. At 77 K, the emission spectra showed structural features with vibronic progressions of *ca.* 1300 cm$^{-1}$, whereas a single broad band
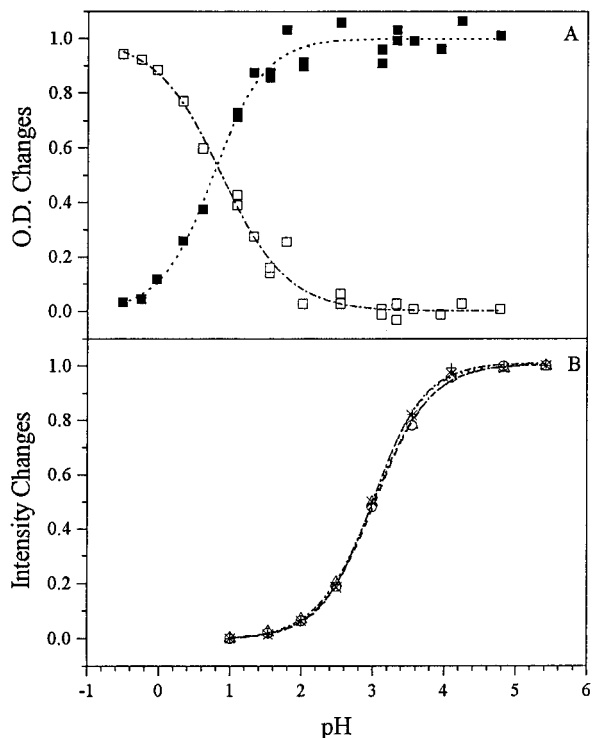
**Figure 2.** Titration curves. A: Optical density changes at 460 (■) and 500 nm (□) as a function of pH at 296 K. Data were taken from Figure 1. B: Emission intensity changes as a function of pH at 296 K: excited at 412 nm and observed at 617 nm (△) and 645 nm (○), respectively; excited at 474 nm and observed at 617 nm (+) and 645 nm (×), respectively.
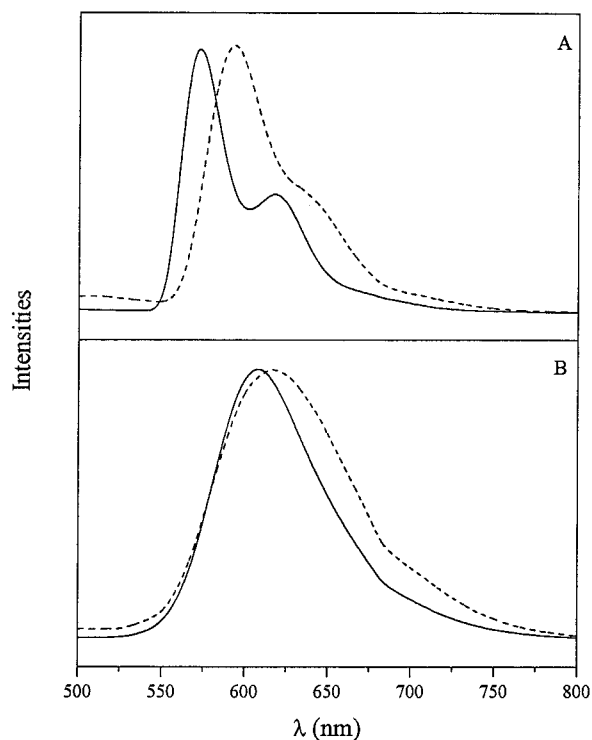


**Figure 4.** Emission spectra of $[Ru(bpy)_2(bpyCOOH)]^{2+}$ in aqueous solutions, excited at 474 nm. A: Emission spectra as a function of pH at 296 K. The emission intensity decreases as pH decreases in the order of 5.42, 4.83, 4.10, 3.55, 2.99, 2.49, 2.00, 1.53, and 1.00. B: Emission spectra as a function of temperature at pH 5.42 (—) and pH 1.00 (− − −), respectively. For the sample at pH 5.42 the emission intensity decreases as temperature increases in the order 283, 293, 303, 313, 323, 333, and 343 K. For the sample at pH 1.00 the emission intensity shows randomly minor variation as temperature changes in the above order.



**Figure 3.** Emission spectra of $[Ru(bpy)_2(bpyCOOH)]^{2+}$ (− − −) and $[Ru(bpy)_2(bpyCOO)]^+$ (—) in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ pretreated with 12 M HCl and 0.1 M NaOH, respectively: (A) 77 K; (B) 296 K. Emission spectra displayed are relative to the maximum intensities.

was observed at 296 K. In 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$, emission maxima shifted 620 cm$^{-1}$ between the acidic and basic forms at 77 K, but only 260 cm$^{-1}$ at 296 K. For the same form of the complex, the emission energy of the basic component red-shifted 1010 cm$^{-1}$ from 572 nm at 77 K to 607
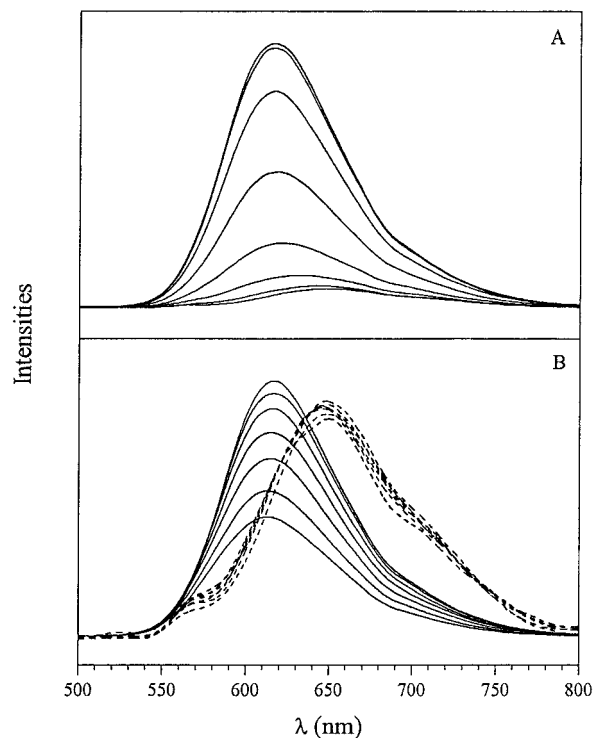
nm at 296 K; the emission energy of the acidic component also red-shifted, but only 650 cm$^{-1}$ from 593 nm at 77 K to 617 nm at 296 K. In aqueous solutions at 296 K, the emission energy maxima red-shifted 710 cm$^{-1}$ from 617 nm for $[Ru(bpy)_2$-$(bpyCOO)]^+$ to 645 nm for $[Ru(bpy)_2(bpyCOOH)]^{2+}$. When solvents were changed, the emitting state of the basic form at 296 K shifted 260 cm$^{-1}$, while that for acidic species shifted 710 cm$^{-1}$.

The luminescence intensities of aqueous solutions containing $[Ru(bpy)_2(bpyCOOH)]^{2+}$ were pH dependent. The emission intensity at 617 nm in solution of pH 5.42 at 296 K decreased as the pH decreased, while a new emission band of lower intensity appeared around 645 nm (Figure 4A). The luminescence peaks at 617 and 645 nm were assigned to the excited states of the deprotonated and protonated species, respectively. The emission intensity for the acidic species was weak compared to that of the basic species. At pH above 4.5, the emission maxima and intensities were independent of pH. As pH decreased below pH 4.5, the emission intensities first decreased gradually, and then a sudden decrease occurred as the pH decreased from 4 to 2. As pH continued to decrease, the emission intensity decreased slowly, and at a pH below 1 the emission maxima and intensities were again independent of pH.

Plots of luminescence intensities for aqueous solutions of Ru(bpy)$_2$(bpyCOO)]$^+$ at pH 5.42 and $[Ru(bpy)_2(bpyCOOH)]^{2+}$ at pH 1.00 as a function of temperature are shown in Figure 4B. For the sample at pH 5.42, the emission energy maximum blue-shifted slightly and the emission intensities decreased as the temperature increased from 283 to 343 K. Emission maxima and intensities for the sample at pH 1.00 showed less temperature dependence.

**Table 1.** Protonation Rate Constants ($k_H$) and Stern−Volmer Constants ($K_{SV}$) Determined from $I_0/I$ vs [H$^+$] Plots at Different Temperatures

| temp (K) | $K_{SV}$ (M) | $\tau_H$ (ns) | $\tau$ (ns) | $k_H$ ($10^9$ M·s$^{-1}$) |
|---|---|---|---|---|
| 283 | 909 ± 37 | 80 ± 2 | 488 ± 10 | 1.9 ± 0.1 |
| 293 | 954 ± 12 | 70 ± 4 | 442 ± 8 | 2.2 ± 0.1 |
| 303 | 919 ± 11 | 81 ± 3 | 412 ± 7 | 2.2 ± 0.1 |
| 313 | 891 ± 9 | 75 ± 3 | 366 ± 5 | 2.4 ± 0.1 |
| 323 | 776 ± 8 | 68 ± 4 | 361 ± 8 | 2.2 ± 0.1 |
| 333 | 605 ± 25 | 59 ± 2 | 258 ± 5 | 2.3 ± 0.1 |
| 343 | 543 ± 20 | 65 ± 3 | 212 ± 5 | 2.6 ± 0.2 |

A possible mechanism for the pH-dependent luminescence is proton-induced quenching.[5] At pH above 2.5, Stern−Volmer plots of the luminescence intensities vs [H$^+$] followed a linear relationship for samples at different temperatures. The Stern−Volmer analyses were carried out using eq 4,[11] where $I_0$ was

$$I_0/I = 1 + K_{SV}[\text{H}^+] \tag{4}$$

the luminescence intensity at pH 5.42, $I$ was the luminescence intensity at different pHs, and $K_{SV}$ was the Stern−Volmer constant with $K_{SV} = k_H\tau$. The $K_{SV}$'s and the quenching rate constants or protonation rate constants, $k_H$, were determined from linear Stern−Volmer plots at different temperatures and are listed in Table 1.

For samples at a pH above 2.5, the complex existed primarily in its deprotonated form (Figure 2A). The emission spectra at pH 2.5 showed a shifted emission maximum from 617 to 620 nm, suggesting that proton transfer occurred within the lifetime of the excited state. As shown in Table 1, the protonation process of excited state species approached the diffusion-controlled limit and was nearly independent of temperature.

**Emission Quantum Yields and Lifetimes**. Emission quantum yields for [Ru(bpy)$_2$(bpyCOOH)]$^{2+}$ and [Ru(bpy)$_2$(bpyCOO)]$^+$ in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ at 296 K, pretreated by 12 M HCl and 0.1 M NaOH, were 0.0023 ± 0.001 and 0.110 ± 0.002, respectively. These are similar to the ones reported for the acidic form ($\phi = 0.006$) and basic form ($\phi = 0.039$) of [Ru(bpy)$_2$(4,4′-(HOOC)$_2$bpy)]$^{2+}$ in water.[2]

Emission lifetimes for the compound in water are included in Table 1. At 77 K in a glassy matrix of 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$, emission lifetimes were 4.12 ± 0.15, 5.10 ± 0.08, and 4.39 ± 0.08 μs for the compounds with the following pretreatment: 12 HCl, no treatment, and 0.1 M NaOH, respectively. The emission lifetimes at 296 K for the compound dissolved in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ increased in the order 330 ± 20 ns < 440 ± 10 ns < 480 ± 10 ns with the following pretreatment: 12 HCl, no treatment, and 0.1 M NaOH, respectively. The emission lifetime for the compound in aqueous solution at pH 4.52 was similar to those measured in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ at 296 K. At 296 K, the emission lifetime measured in aqueous solution at pH 1.00 was 80 ± 10 ns compared to 380 ± 10 ns at pH 4.52.

The dependence of emission lifetimes on temperature for both the acidic and basic forms of the complex in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ showed that emission lifetimes remained nearly constant until the glass-to-fluid transition at 120 K where the emission lifetimes decreased rapidly until the matrix became fluid at 140 K. The emission lifetimes then slowly decreased with temperature to 280 K. A marked increase in the temperature dependence of emission lifetimes occurred after reaching this temperature (Figure 5).

Emission lifetimes in aqueous solutions at pH 5.42 and pH 1.00 were also determined as a function of temperature and are

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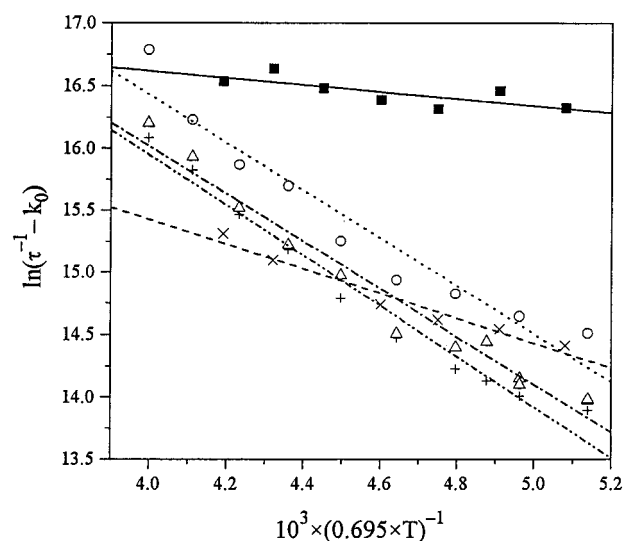


**Figure 5.** Plots of ln($\tau^{-1} - k_0$) vs $(0.695T)^{-1}$ (273−343 K), measured in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$: (○) pretreated with 12 M HCl; (△) pretreated with 0.1 M NaOH; (+) no pretreatment. Plots of ln($\tau^{-1} - k_0$) vs $(0.695T)^{-1}$, measured in H$_2$O: (×) at pH 5.42; (■) at pH 1.00. $k_0 = 2 \times 10^5$ s$^{-1}$.

**Table 2.** Photophysical Properties for [Ru(bpy)$_2$(bpyCOOH)]$^{2+}$ in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ and H$_2$O at Temperatures above 280K$^a$

| | $k_1$ ($10^9$ s$^{-1}$) | $\Delta E_1$ ($10^3$ cm$^{-1}$) |
|---|---|---|
| A | 29.3 | 1.92 ± 0.20 |
| B | 29.3 | 2.03 ± 0.12 |
| C | 19.6 | 1.92 ± 0.11 |
| D | 0.0486 | 0.27 ± 0.11 |
| E | 0.266 | 0.99 ± 0.10 |

$^a$ $k_0 = 2 \times 10^5$ s$^{-1}$. Samples A, B, and C were dissolved in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$ with pretreatment of 12 M HCl, no treatment, and 0.1 M NaOH, respectively. Samples D and E were dissolved in aqueous solutions of pH 1.00 and pH 5.42, respectively.

shown in Figure 5. The temperature dependence of the acidic form in water is weak compared to the results observed in 4:1 (v/v) 2-Me-THF−CH$_2$Cl$_2$.

Emission lifetimes as a function of temperature above 280 K were analyzed by eq 2 and the results are given in Table 2. The activation energy for acidic and basic species were similar (1920 cm$^{-1}$) in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$, but lower for both forms in aqueous solution. The activation energy for a sample at pH 5.42 was 990 ± 100 cm$^{-1}$. At pH 1.00, the activation energy was only 270 ± 110 cm$^{-1}$.

**Excited State p$K_a$\*.** Plots of emission intensity as a function of pH at 296 K are illustrated in Figure 2B. Inflection points derived from the plots of emission intensity and emission lifetime as functions of pH at different temperatures were determined and are given in Table 3. The inflection points, pH$_i$, derived from the emission titration curves were corrected for differences in the excited state lifetimes of the deprotonated ($\tau$) and protonated ($\tau_H$) species according to eq 5.[6] The p$K_a$\*'s

$$\text{p}K_a^* = \text{p}H_i + \log\left(\frac{\tau_H}{\tau}\right) \tag{5}$$

derived from eq 5 are also included in Table 3. The excited state p$K_a$\* at 296 K was 2.31 ± 0.05 and remained nearly constant over the temperature range 283−343 K. Compared to the ground state p$K_a^0$ of 0.82 ± 0.07 at 296 K, [Ru(bpy)$_2$(bpyCOO)]$^{+*}$ is a much stronger base than [Ru(bpy)$_2$(bpyCOO)]$^+$.

Excited state p$K_a$\* values were determined in the absence of buffer solutions due to the fact that organic buffer solutions were reported to quench excited states.[6,11] The light source

**Table 3.** Temperature Effects on the Measured Excited State $pK_a^*$'s and the Calculated Ground State $pK_a^0$'s from Equation 6[a]

| | $pH_i$ | $pK_a^* =$ $pH_i + \log(\tau_H/\tau)$ | $pK_a^0 = pK_a^* -$ $(\nu - \nu_H)(1.6T)^{-1}$ |
|---|---|---|---|
| $I$ vs pH, 283 K | $3.03 \pm 0.04$ | $2.24 \pm 0.04$ | 0.69 |
| $I$ vs pH, 293 K | $3.00 \pm 0.02$ | $2.20 \pm 0.05$ | 0.70 |
| $I$ vs pH, 296 K | $3.00 \pm 0.02$ | $2.31 \pm 0.05$ | 0.82 |
| $I$ vs pH, 303 K | $3.01 \pm 0.03$ | $2.30 \pm 0.05$ | 0.85 |
| $I$ vs pH, 313 K | $3.00 \pm 0.02$ | $2.31 \pm 0.04$ | 0.91 |
| $I$ vs pH, 323 K | $2.98 \pm 0.01$ | $2.26 \pm 0.05$ | 0.90 |
| $I$ vs pH, 333 K | $2.93 \pm 0.02$ | $2.26 \pm 0.04$ | 0.94 |
| $I$ vs pH, 343 K | $2.90 \pm 0.03$ | $2.39 \pm 0.06$ | 1.11 |
| $\tau$ vs pH, 283 K | $3.01 \pm 0.13$ | | |
| $\tau$ vs pH, 293 K | $3.06 \pm 0.07$ | | |
| $\tau$ vs pH, 296 K | $3.10 \pm 0.03$ | | |
| $\tau$ vs pH, 303 K | $3.18 \pm 0.08$ | | |
| $\tau$ vs pH, 313 K | $2.95 \pm 0.05$ | | |
| $\tau$ vs pH, 323 K | $3.12 \pm 0.15$ | | |
| $\tau$ vs pH, 333 K | $3.07 \pm 0.11$ | | |
| $\tau$ vs pH, 343 K | $2.96 \pm 0.23$ | | |

[a] Samples were excited at 474 nm, and emission was observed at 617 nm.

intensity at 450 nm was $1.9 \times 10^{-9}$ einsteins·s$^{-1}$. For a sample with an absorbance less than 0.1, the rate of populating the excited state equals $I_0(1 - 10^{-\epsilon cl})$. Thus, the concentration of the excited state species is expected to be small, and therefore, the change in the distribution of excited state species at equilibrium will not alter the [H$^+$] significantly.

## Discussion

**Ground State $pK_a^0$ and Excited State $pK_a^*$.** The increased $pK_a^*$ values relative to $pK_a^0$ indicate an electron has transferred from the ruthenium center to the carboxyl bipyridine ligand upon optical excitation. The increase in electron density on the carboxyl bipyridine ligand increases its basicity and, therefore, the increased excited state $pK_a^*$ value. This increase is also noted by excited state Stern–Volmer, proton quenching behavior where quenching is linearly dependent on [H$^+$].

Ground state $pK_a^0$ and excited state $pK_a^*$ have been related thermodynamically by a Förster cycle.[12] The thermodynamic cycle treats both the ground state and excited state species in thermal equilibrium. Excitation at either isosbestic point, where both the acidic form and basic form have the same extinction coefficient, promotes ground state species to their singlet excited states which undergo intersystem crossing resulting in formation of their corresponding triplet excited states. Due to fast protonation, an equilibrium between acidic and basic excited state species can then be established. Evidence for emission due to proton transfer between excited states is shown in Figure 4A where the emission energy maximum was located between the one for emission from [Ru(bpy)$_2$(bpyCOO)]$^{+*}$ and the one for emission from [Ru(bpy)$_2$(bpyCOOH)]$^{2+*}$.

The Förster treatment results in eq 6[6,12,13] which describes the relationship between ground state and excited state $pK_a$'s

$$pK_a^* = pK_a^0 + \frac{\nu - \nu_H}{1.6T} \quad (6)$$

based on pure 0–0 transitions in wavenumbers for the basic and acidic species, respectively.

In reality, these values are often difficult or even impossible to obtain. A good approximation is to use the emission maxima for $\nu$ and $\nu_H$ since protonation equilibrium is almost certainly

(12) Donckt, E. V. In *Progress in Reaction Kinetics 5*; Porter, G., Ed.; Pergamon Press: Oxford, England, 1970.
(13) Seefeld, K.-P.; Möbius, D.; Kuhn, H. *Helv. Chem. Acta* **1977**, *60*, 2608.

established between the $^3$MLCT states. Therefore, the energies of the emission maxima in wavenumbers were used in eq 6.

At 296 K, the ground state $pK_a^0$ was 0.82 and the emission energy maxima for acidic and basic forms were $\nu_H = 15.5 \times 10^3$ cm$^{-1}$ and $\nu = 16.2 \times 10^3$ cm$^{-1}$, respectively. The predicted excited state $pK_a^*$ was 2.31, which agreed well with the value measured by fluorescence titration. The good agreement between the measured $pK_a^*$ from fluorescence titration and the predicted $pK_a^*$ from eq 6 provides a reliable method to evaluate the $pK_a$ values for the ground state, and *vice versa*, $pK_a^*$ from ground state $pK_a$ values.

Less pronounced changes of absorption spectra (Figure 1A) make it difficult to obtain an accurate $pK_a^0$ from the absorption titration curve. The well-established relationship between $pK_a^0$ and $pK_a^*$ was justified by comparing the measured and calculated values at 296 K, which made it possible to obtain accurate ground state $pK_a^0$'s at different temperatures from the excited state $pK_a^*$'s by eq 6. The calculated ground state $pK_a^0$'s from the measured $pK_a^*$ values at various temperatures are listed in Table 3. While the excited-state $pK_a^*$'s remain nearly temperature independent, the ground-state $pK_a$'s increased with temperature. According to this information, [Ru(bpy)$_2$-(bpyCOO)]$^+$ becomes more basic as the temperature increases. From a plot of $pK_a^0$ vs $T^{-1}$, $\Delta H^0$ and $\Delta S^0$ for the ground state equilibrium were determined to be $-990 \pm 149$ cm$^{-1}$ and $-4.57 \pm 0.48$ cm$^{-1}$ T$^{-1}$, respectively. The temperature independence of the excited state $pK_a^*$'s are readily explained by the diffusion-controlled quenching of the excited states. As the protonation of excited state reaches its limit, further variation in temperature will not significantly alter the quenching process.

**Absorption and Emission Properties**. Optical transitions associated with the acidic and basic forms of the complex occurred at similar energies and showed similar MLCT profiles (Figure 1B) in nonaqueous media, but not in water (Figure 1A). As the pH of the solution decreased from +4.78 to −0.5, the assigned MLCT band located at 449 nm blue shifted by 6 nm to 455 nm with a small decrease in intensity. These observations suggest that the optical transition occurs from Ru(II) to the coordinated 3-carboxylbipyridine ligand. In mixed-ligand complexes like this monoacid compound, the electron transition upon optical absorption will occur between the metal center and the ligand which is the most easily reducible. The electron-withdrawing character of the carboxyl group will shift the reduction potential of the ligand positively relative to the reduction potential of the unsubstituted bipyridine ligand. Hence, the 3-carboxyl-2,2′-bipyridine is the most easily reduced ligand in accord with the optical assignment.

The shift of the MLCT band due to protonation in aqueous solutions most likely is due to hydrogen bonding since a similar shift was not found in nonaqueous media. Upon protonation in water, the net electron density on the carboxyl ligand decreases. This decrease in electron density on the carboxyl ligand enhances the electron transition process from the metal center to the ligand, bpyCOOH.

Changes in the medium also caused the emission energies, excited state lifetimes, and emission quantum yields to vary. These changes can be accounted for by the energy gap law which relates the nonradiative rate constant ($k_{nr}$) to the emission energy ($E_{em}$) by eq 7, where $k_{nr} = k_{obs} - k_r$ in s$^{-1}$, $C$ is the

$$k_{nr} \propto e^{-CE_{em}} \quad (7)$$

slope in cm, and $E_{em}$ is the energy in cm$^{-1}$ at the emission maximum. The radiative rate constant is related to the emission quantum yield by $k_r = \eta\phi_{em}k_{obs}$, where $\eta$ is the intersystem crossing quantum yield from the singlet state to the triplet state and is assumed to be 1 as found for [Ru(bpy)$_3$]$^{2+}$. A plot of
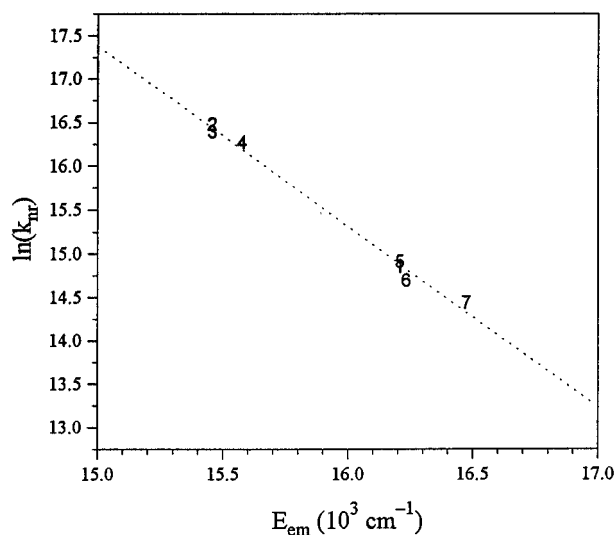
**Figure 6.** Plot of ln($k_{nr}$) vs $E_{em}$ at 296 K: (1) sample dissolved in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$, pretreated by 12 M HCl; (2) sample in H$_2$O at pH 0.26; (3) sample in H$_2$O at pH 0.88; (4) sample in H$_2$O at pH 1.65; (5) sample in H$_2$O at pH 3.56; (6) sample in H$_2$O at pH 4.50; (7) sample dissolved in 4:1 (v/v) 2-MeTHF−CH$_2$Cl$_2$, pretreated by 0.1 M NaOH.

the nonradiative rate constants for samples dissolved in both water and the mixed organic solvents at 296 K vs the emission energies is shown in Figure 6. From the plot, values of 49 ± 1 and (2.11 ± 0.09) × 10$^{-3}$ were derived for the intercept and the slope. These values are comparable with the literature values[14] of 40.21 and 1.46 × 10$^{-3}$ for [Re(bpy)(CO)$_3$L]$^+$, 31.52 and 1.26 × 10$^{-3}$ for [Rh(NH$_3$)$_5$L]$^{3+}$, 48.30 and 1.45 × 10$^{-3}$ for 6-hydroxy-9-phenylfluoron, and 63.01 and 2.38 × 10$^{-3}$ for fluorescein. This linear relationship between the emission energy maximum and the emission lifetime carries over to the emission quantum yields as well. According to the relationship $k_r = \eta\phi_{em}k_{obs}$, the emission quantum yield will vary directly with the emission lifetime under conditions where $\eta$ is constant and $k_{obs} \gg k_r$.

As shown earlier, excited state p$K_a$*'s were independent of temperature over the range 283−343 K. Thus the relative concentrations of both the basic and acidic species remain unchanged as the temperature varied from 283 to 343 K. Therefore, the observed temperature dependence of emission lifetimes are attributed to the temperature dependence of emission itself rather than excited state acid−base behavior.

The dependence of emission lifetime on temperature can be interpreted on the basis of the Crosby−Meyer model[15,16] shown in Figure 7. According to this model, at temperatures near and above room temperature, complexes having activation energies above 1000 cm$^{-1}$ undergo an additional decay pathway by thermally populating a dd state. Low activation and weak temperature dependence have been attributed to deactivation of a fourth state having more singlet character than the triplet states or to changes in the local matrix of the chromophores. In the systems studied here, with the exception of the protonated complex in water at low pH, the temperature dependence can be attributed to enhanced deactivation via the dd state. The effect of hydrogen bonding on the acidic form of the complex in water apparently either opens a decay pathway at energies
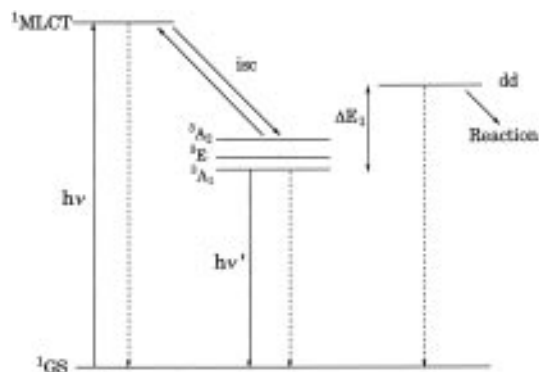
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(15) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.
(16) (a) Hager, G. D.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7031. (b) Hager, G. D.; Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7037. (c) Hipps, K. W.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7042.



**Figure 7.** Energy state diagram based on the Crosby−Meyer model.

just above the emitting state or it increases the energy of the dd state so it no longer is thermally accessible.

## Conclusions

The acid−base behavior of the complex [Ru(bpy)$_2$-(bpyCOOH)]$^{2+}$ in its ground state and excited state can be contrasted with the problems of ambiguity associated with previous reports on related studies of systems containing more than one carboxyl group, e.g. [(4,4′-(COOH)$_2$bpy)Ru(bpy)$_2$]$^{2+}$. [Ru(bpy)$_2$(bpyCOOH)]$^{2+}$ has a ground state p$K_a$ of 0.82 ± 0.07 and an excited state p$K_a$* of 2.31 ± 0.05, an increase of 1.5 pH unit. These can be compared to p$K_a$ and p$K_a$* values of 2.7 and 4.3, an increase of 1.6 pH unit, reported for [(4,4′-(COOH)$_2$-bpy)Ru(bpy)$_2$]$^{2+}$.[4,5] While the difference between the ground state and excited state p$K_a$ values for both compounds is approximately the same, the difference in ground state p$K_a$'s was approximately 2. The large difference may result from hydrogen bonding interaction that can occur between one of the oxygen atoms bonded to the carbonyl carbon atom in the 3 position with the hydrogen atom attached to the 3′ carbon atom. According to molecular modeling calculations, this distance falls in the 0.8 to 0.9 Å range, certainly within the hydrogen-bonding domain. This interaction would decrease the electron density on the carboxyl group increasing the acidity observed in [(3-(COOH)bpy)Ru(bpy)$_2$]$^{2+}$.

The excited state p$K_a$* is found to be temperature independent while the calculated ground state p$K_a^0$ is temperature dependent. The temperature independence of p$K_a$* may result from the diffusion controlled protonation reaction between the excited states.

Recently Fernando *et al.*[8] observed small increases in emission lifetimes with temperature for the ruthenium(II) bis-(2,2′-bipyridine) 3,5-dicarboxyl-2,2′-bipyridine complex. The increase in emission lifetime with temperature was observed in both water and methanol solvents. We did not observe such phenomena for our system in either mixed organic or water solvents for both the deprotonated and protonated species. We would note, however, that [(3,5-(COOH)$_2$bpy)Ru(bpy)$_2$]$^{2+}$ contains two non equivalent carboxyl groups, one in the 3 position and the other in the 5 position. The one in the 3 position would most likely behave in a manner similar to [(3-(COOH)bpy)Ru(bpy)$_2$]$^{2+}$ and the one in the 5 position similar to [(4,4′-(COOH)$_2$bpy)Ru(bpy)$_2$]$^{2+}$. The difference expected in the p$K_a$ values for [(3,5-(COOH)$_2$bpy)Ru(bpy)$_2$]$^{2+}$ was observed in the ground state, but not in the excited state.[8b]