

Acid-Base Behavior in the Ground and Excited States of Ruthenium(II) Complexes Containing Tetraamines or Dicarboxybipyridines as Protonatable Ligands

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A study of the influence of the protonating ligand and spectator ligand on the photophysical properties and on the acid-base reactions in the ground and MLCT excited states of polypyridyl complexes of Ru(II) with one or more protonatable ligands, $[\text{Ru}(\text{PL})_n(\text{LL})_{3-n}]$ (PL = dpp, bpym, 4,4'-dcbpy, 5,5'-dcbpy; LL = Me₂bpy, bpy, phen, 5-Cl-phen; $n = 1-3$), is presented. In all cases the Ru complexes are much stronger bases in the excited state than in the ground state. The effects are more pronounced in complexes with tetraamine ligands than in those with dicarboxybipyridines. In complexes with several protonatable ligands, the difference in the $\text{p}K_a$ between the ground and excited state ($\Delta\text{p}K_a$) is most pronounced for the first protonation step, confirming the validity of the localized electron model for the MLCT excited state.

Introduction

Synthesis and characterization of electrochemical and photochemical properties of various polypyridyl transition-metal complexes have been of prime focus in recent years in numerous research groups. Enormous success obtained in these studies¹⁻³ now allows a very detailed quantitative description of the excited-state manifolds and their dynamics. An intriguing feature of the photophysics is acid-base reactions in the excited state. Acid-base properties of coordinated ligands provide a direct measure of the interplay between the σ -donor strength and π -bonding properties in influencing $d\pi-\pi^*$ (metal-to-ligand charge transfer) interactions. Few studies in this area⁴⁻⁸ have unambiguously demonstrated that optical excitation of metal complexes alters significantly the acid-base equilibria involving protonatable polypyridyl ligands. In this work, we have made a systematic, quantitative study of this phenomenon, using several mixed-ligand polypyridyl complexes of Ru with one or more protonatable ligands as candidates. Two groups of protonatable ligands are examined: tetraamine ligands with two extra "protonatable" nitrogen centers such as 2,2'-bipyrimidine (bpym), 2,3-bis(2-pyridyl)pyrazine (dpp), and two isomeric dicarboxybipyridines (4,4'- and 5,5'-dcbpy). Interest in Ru complexes with tetraamine ligands such as bpym and dpp is growing rapidly in connection with "photochemistry of binuclear Ru complexes with bpym, dpp as bridging ligands".⁹ The spectroscopy and photochemistry of Ru complexes containing dicarboxybipyridines have been of particular interest in our laboratory, in connection with the development of efficient homogeneous water oxidation catalysts¹⁰ and in photoelectrochemical

Scheme I

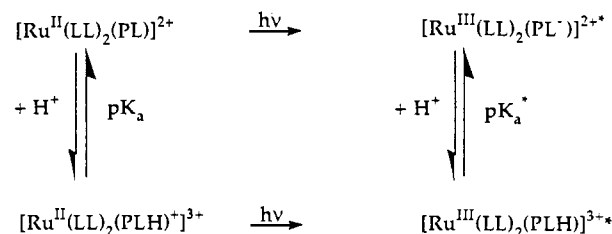


Table I. Ground-State Absorption Spectral Data for the Mixed-Ligand Complexes of Ru-Containing Tetraamine Ligands in Aqueous Solutions (pH 7.0)^a

complex	abs max, nm (rel intens)		
	M-PL CT	M-LL CT	$\pi-\pi^*(\text{PL}/\text{LL})$
Ru(dpp)(Me ₂ bpy) ₂	486 (1.0)	424 (1.10)	282 (5.69) 244 (2.67)
Ru(dpp)(bpy) ₂	478 (1.0)	422 (1.10)	282 (6.73) 242 (3.10)
Ru(dpp)(phen) ₂	474 (1.0)	428 (0.94)	305 sh 262 (5.70)
Ru(dpp)(5-Cl-phen) ₂	468 (1.0)	428 (0.98)	305 sh 265 (6.10)
Ru(dpp) ₃	456 (1.0)	428 sh	295 (3.16)
Ru(bpym)(bpy) ₂	480 sh	415 (1.0)	282 (4.54) 240 (3.11)

^a Shown are relative absorbances, normalized with respect to the MLCT bands.

sensitization of large band-gap semiconductors with visible light.¹¹ There have been a number of reports describing the absorption, emission, and redox properties of Ru complexes with these polypyridyl ligands [see, for example, dpp,¹² bpym,¹³ and dicarboxy-4,4'-bipyridine(4,4'-dcbpy)^{4,14}].

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Table II. Ground-State Absorption Data for the Mixed-Ligand Complexes of Ru-Containing dcbpy Ligands^a

complex	pH	abs max, nm (rel intens)					ref ^b
		M-PL	M-LL		$\pi-\pi^*$ (PL/LL)		
Ru(4,4'-dcbpy)(bpy) ₂	9.0	450 (1.0)	438 sh,	345	302	288	c
	0	485 (1.0)	420 sh,	364	310	288	c
Ru(4,4'-dcbpy) ₂ (bpy)	10.0	465 (1.0)	438 sh (0.87)	335 (0.72)	300 (3.36)	288 (3.22)	tw
	0.40	480 (1.0)	438 sh (0.81)	358 (0.82)	310 (3.11)	288 (2.39)	tw
Ru(4,4'-dcbpy) ₃	9.70	467 (1.0)	436 sh (0.80)	342 (0.79)	302 (2.69)		tw
	0.30	468 (1.0)	436 sh	352 (0.83)	306 (3.52)	244 (2.38)	tw
	CH ₃ CN	469 (1.0)	444 (0.8),	355	311		d
Ru(4,4'-dcbpy) ₂ (dpp)	10.0	459 (1.0)	438 sh	360 sh	298 (3.51)	262, 244 sh	tw
	1.0	461 (1.0)	438 sh		305 (3.26)	262, 244 sh	tw
Ru(5,5'-dcbpy) ₃	10.9	483 (1.0)	452 sh (0.92)	352 (0.78)	297 (10.54)	254 (4.07)	tw
	1.6	495 (1.0)	460 sh	352 (0.78)	305 (3.26)	254 (4.51)	tw
	CH ₃ CN	505 (1.0)	465				e

^a Shown are relative absorbances, normalized with respect to the MLCT bands. ^b tw = this work. ^c Reference 4d. ^d Reference 14i. ^e Reference 14c.

Current descriptions of the MLCT excited state of a Ru complex picture the complex in the excited state to be composed of Ru in the 3+ state and an electron located in one of the polypyridyl ligand L. In mixed-ligand complexes (of the type [RuL₂L']²⁺ for example), the electron is largely localized on that ligand which is more easily reduced. If this ligand happens to be protonatable (e.g. 2,2'-bipyrimidine, 4,4'-dicarboxybipyridine, ...), then the formation of the MLCT excited state causes significant changes in the acid-base equilibria of the complex (cf. Scheme I). Also, one can anticipate larger shifts in the pK_a of the ligand that receives primarily the electron and minor effects on the others.

However, there are indications in the literature that the coupling between various polypyridyl ligands through the metal center is indeed very severe. A consequence is that, even if the ligand that is largely associated with the formation of the MLCT excited state is not protonatable, the presence of protonatable sites in the other "spectator" ligands can cause significant acid-base effects in the MLCT excited-state luminescence. For example, in the [Ru(bpy)₂(4,7-(OH)₂phen)] and [Ru(bpy)₂(CN)₂] complexes, the emitting state, attributed largely as due to Ru-bpy charge transfer shows pH-dependent emission. Hence, a principal focus of this study is to examine in detail this spectator ligand effect on the excited-state acid-base reactions.

Experimental Section

Materials. Ligands. Except for 5,5'-dicarboxy-2,2'-bipyridine (5,5'-dcbpy) all other ligands [2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy), 5-chloro-1,10-phenanthroline (5-Cl-phen), 2,3-bis(2-pyridyl)pyrazine (dpp), 2,2'-bipyrimidine (bpym), 4,4'-dicarboxy-2,2'-bipyridine (4,4'-dcbpy)] were commercial samples from Alfa Inorganics and were used as supplied. Synthesis of the ligand 5,5'-dcbpy is described in our earlier work.^{10a}

Various Ru(II) tris chelates Ru(LL)₃²⁺ (LL = 4,4'-dcbpy, 5,5'-dcbpy, dpp, bpym) were synthesized from a reflux of RuCl₃ with a 3-fold quantity of the ligand LL, as described in the literature.¹³ Mixed-ligand complexes of the type [Ru(LL)₂(LL')]²⁺ were synthesized via a two-step procedure, involving initial synthesis of Ru(LL)₂(Cl)₂ and subsequent reaction of Ru(LL)₂(Cl)₂ with the ligand LL'. The complexes were subsequently purified on a neutral alumina column using CH₃CN as an eluent. Ru complexes containing one or more dicarboxybipyridine ligands can also be purified via selective precipitation of the complexes at their isoelectric point, which is in the narrow pH range 2.6–2.8. Wherever comparison can be made, measured absorption spectral and photophysical properties of the complexes are in good agreement with the literature.

Absorption spectral data on various ruthenium polypyridyl complexes examined in this work are reported in Tables I and II.

Methods. Steady-state luminescence spectra and yields were recorded and measured on a Hitachi Perkin-Elmer MPF 4F spectrofluorimeter equipped with a red-sensitive Hamamatsu R928 photomultiplier tube. Emission lifetimes were measured on a nanosecond laser flash photolysis set-up using 530-nm, 10-ns pulses from a pulsed, Q-switched Nd YAG-Glass laser system as the excitation source. Solutions were thoroughly degassed for at least 15 min with ultrapure N₂ before measurements. Absorption spectra were recorded on a Cary 214 absorption spectrophotometer. H₀ values for various concentrations of concentrated H₂SO₄ are taken from ref 15. pH titrations to determine the ground-state pK_a values of carboxylate complexes were also made on a Metrohm Titrprocessor using either 1 N H₂SO₄ or 1 N NaOH as the titrant. Electrochemical measurements were made on a three-electrode cell using a PAR potentiostat in DMF solutions with glassy-carbon electrodes and tetrabutylammonium perchlorate as a support electrolyte. Redox potential data quoted are E_{1/2} values vs SCE. Estimated errors in reported values are as follows: absorption and emission maxima, ±2 nm (±5 nm for weak emitters); emission lifetime, ±10%; pK_a, pK_a^{*}, ±0.10; redox potentials, ±20 mV.

Results and Discussion

(I) Acid-Base Reactions in the Ground and Excited State of Ru Complexes with Tetraimine Ligands (bpym, dpp, ...). (A) **Absorption and Emission Spectra of the Ru Complexes in Solution.** In this work we examine a graded series of mixed-ligand Ru complexes with different spectator ligands, [Ru(PL)(LL)₂] (LL = bpy, Me₂bpy, phen, 5-Cl-phen; PL = dpp, bpym). Table I presents data on the ground-state absorption properties of these complexes. The photophysics and redox chemistry of representative Ru complexes with dpp or bpym have been described earlier.^{12–14} Herein, we cite some principal features of their absorption and emission to facilitate discussion on their acid-base properties. In all of the mixed-ligand complexes, the MLCT absorption consists of two well-resolved bands. The high-energy one remains nearly constant at 424 ± 4 nm, and the low-energy band is located anywhere between 460 and 490 nm, being strongly dependent on the nature of the spectator ligand LL. The two bands are assigned respectively to the M-LL and M-PL charge-transfer absorptions, in accordance with the electrochemical measurements and pH dependence of absorption. Redox potential data presented in Table III show that the first reduction process occurs at the tetraimine ligand dpp or bpym. The $\pi-\pi^*$ absorptions are located at 295 (dpp), 282 (bpy, bpym), and 266 nm (phen).

Mixed-ligand complexes [Ru(PL)(LL)₂] with protonatable ligands (PL) such as dpp or bpym show moderate red emission in degassed solution at room temperature. Even though there are two potential candidates for luminescence (PL → Ru charge transfer or LL → Ru charge transfer), the emission in all cases is assigned as due to the PL → Ru CT following the earlier generalizations: In numerous mixed-ligand Ru complexes that have been examined, the emission invariably is from the MLCT

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Table III. Data for the Excited-State Acid-Base Equilibria in Ruthenium Polypyridyl Mixed-Ligand Complexes

complex	$E^{2+/+}$, V vs SCE	M-PL abs		pK_a	emission (basic form)		pK_a^*		ref ^a
		unprot	prot		λ_{max} , nm	τ , ns	obs	calc	
[Ru(dpp)(Me ₂ bpy) ₂] ²⁺	-1.02	486	573	-3.7	710	64	2.75	2.95	tw
[Ru(dpp)(bpy) ₂] ²⁺	-1.00	478	561	-3.8	690	127	2.85	2.75	tw
[Ru(dpp)(phen) ₂] ²⁺	-0.97	474	559	-4.0	663	202	3.05	2.70	tw
[Ru(dpp)(5-Cl-phen) ₂] ²⁺	-1.05	468			657	260	3.15		tw
Ru(dpp) ₃ ²⁺	-0.87	456	534	-4.8	625	270	3.50	1.75	tw
[Ru(bpym)(bpy) ₂] ²⁺	-0.92	480 sh	570 sh	-2.9	690	13	1.95		tw
[Ru(bpym) ₂ (bpy)] ²⁺	-0.88						2.2		b
Ru(bpym) ₃ ²⁺	-0.84			-1.0?	660	83	2.2		c
[Ru(bpz) ₂ (bpy)] ²⁺	-0.72						3.5		b
Ru(bpz) ₃ ²⁺	-0.61			-2.2	595	900	2.0		d
Ru(TAP) ₃		436	500	-3.0	595	230	3.5	3.13	e
Ru(TAP) ₂ (bpy)		465	540	-2.6	640	620	4.0	3.71	e
Ru(TAP)(bpy) ₂		500	580	-2.0	720	130	3.1	3.76	e

^atw = this work. ^bReference 13f. ^cReference 13a. ^dReference 7. ^eReference 8.

Table IV. Ground-State pK_a and Absorption Spectral Data for Unprotonated and Protonated Forms of Free Ligands in Aqueous Solutions

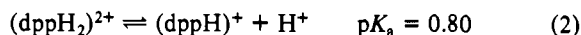
ligand ^a	pK_a		$E(L/L^-)$, V	abs max (A ⁻), nm	abs max (HA), nm	ref ^b
	1	2				
bpy	4.45	0.52	-2.18			
4,4'-dcbpy	4.20		-1.60	293 (1.0), 235 sh (1.20)	310 (1.00), 240 sh (0.96)	tw
	3.70	<2.0				c
5,5'-dcbpy	4.00		-1.28	295 (1.0), 244 sh (0.81)	305 (1.0), 244 sh (0.88)	tw
bpz	0.45	-1.35	-1.67	288 (1.0), 228 (0.80)		d
bpym	0.75	<0	-1.54	242 (1.0), 274 (0.13)	242 (1.0), 273 (0.70)	tw
dpp	2.90	0.80		282 (1.0), 240 (0.66)	285 (1.0), 235 (0.51)	tw

^abpy = 2,2'-bipyridine; 4,4'-dcbpy = 4,4'-dicarboxy-2,2'-bipyridine; 5,5'-dcbpy = 5,5'-dicarboxy-2,2'-bipyridine; bpz = 2,2'-bipyrazine; bpym = 2,2'-bipyrimidine; dpp = 2,3-bis(2-pyridyl)pyrazine. ^btw = this work. ^cReference 4c. ^dReference 7.

state lowest in energy. Complexed tetraimine ligands such as dpp or bpym are easily reduced as compared to substituted phen or bpy. MLCT energies as monitored by Ru^{2+/+} redox potentials (data shown in Table III) show that the electron in the excited state is localized on the PL ligand. Compared to the dpp complexes, the bpym complexes are weak emitters with short-lived excited states ($\tau \leq 100$ ns). To assess the extent of basicity shifts upon complexation, we determined first the pK_a of the free ligands in aqueous solution.

(B) Protonation Equilibria of Free Ligands in Aqueous Solution.

The ligand 2,3-bis(2-pyridyl)pyrazine (dpp) has its intraligand $\pi-\pi^*$ absorption bands located at 282 and 240 nm in neutral and alkaline solutions. Lowering of pH leads initially to a small red shift of the 282-nm band to ca. 286 nm with a small decrease in absorption intensity. The 240-nm band decreases significantly in intensity and blue shifts to 235 nm. Later the main band decreases in intensity and red shifts to 290 nm. The absorption spectral changes accompanying protonation are in many aspects similar to that of 2,2'-bipyrazine reported earlier.⁷ Quantitative analysis of the absorbance changes at selected wavelengths (282, 322 nm) within the pH range 0-10 led to identification of two pK_a values at 2.90 and 0.80 (eq 1 and 2). The ligand dpp has



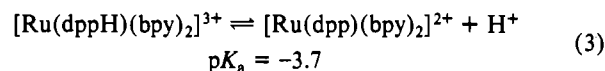
two pyrazinyl nitrogen and two pyridyl nitrogen centers available for protonation. Since the latter are readily protonated (pK_a values of 5.25 for pyridine and 4.45 and 1.80 for 2,2'-bipyridine vs values of 0.65 for pyrazine and 0.45 and -1.35 for 2,2'-bipyrazine), the observed pK_a values probably reflect protonation occurring at these pyridyl N-centers.

Free-ligand 2,2'-bipyrimidine has its principal $\pi-\pi^*$ absorption located at 242 nm with a shoulder at 274 nm. Lowering of pH leads to an increase in the absorption intensity of the low-energy shoulder. Quantitative analysis of the absorption spectral changes at 274 nm over the pH range -0.5 to 7.0 yielded a single pK_a at 0.75. A slightly smaller pK_a value of 0.75 as compared to 1.30 reported for pyrimidine is in accord with similar trends observed between the pairs py, bpy and pz, bpz. Table IV presents a

summary of the pK_a and absorption spectral data on the basic and monoprotated forms of various polypyridyl ligands in aqueous solution.

(C) Acid-Base Equilibria in the Ground State of Ru Complexes.

The extra N-centers in the Ru complexes with tetraimine ligands such as dpp, bpym, or bpz can undergo protonation equilibria. As has been shown earlier for Ru(bpz)₃²⁺,⁷ the process is accompanied by significant changes in the absorption and emission properties. Ru complexes with dpp as a protonatable ligand are very weak bases, exhibiting protonation behavior only in concentrated acid solutions. Figure 1 (top) presents absorption spectral changes that occur upon protonation of a typical dpp complex, [Ru(bpy)₂(dpp)]²⁺, in concentrated sulfuric acid solutions (H_0 increase from -0.05 to -7.34). Increase of solution acidity leads to distinct color changes of the solution from orange to pink and then to deep violet. The protonation is accompanied by a red shift of the M-PL charge-transfer band from 485 to 560 nm. Small spectral shifts, especially in the early stages, possibly due to medium sensitivity of M-PL charge-transfer bands and/or ion-pairing effects between the dicationic Ru complex and sulfate anions, mask observation of a clean isobestic point throughout the entire titration. However, quantitative analysis of the absorption growth at 561 nm does show a clean single titration with an inflection point (pK_a) at -3.7 (eq 3).



The absorption spectral changes that occur upon protonation of the bpym complexes are much less pronounced. In the bpym complexes, the M-PL charge-transfer band is rather weak and appears as a shoulder both in the unprotonated and monoprotated Ru complexes. Figure 1 (bottom) presents the titration curves for [Ru(dpp)₃]²⁺, [Ru(bpy)₂(dpp)]²⁺, and [Ru(bpy)₂(bpym)]²⁺.

In the graded series of Ru(LL)₂(dpp)]²⁺ complexes, both the pK_a and the absorption maxima of the monoprotated form are dependent on the nature of the spectator ligand LL. Table III presents a summary of the M-PL CT absorption maxima of the basic and protonated forms along with associated pK_a values for

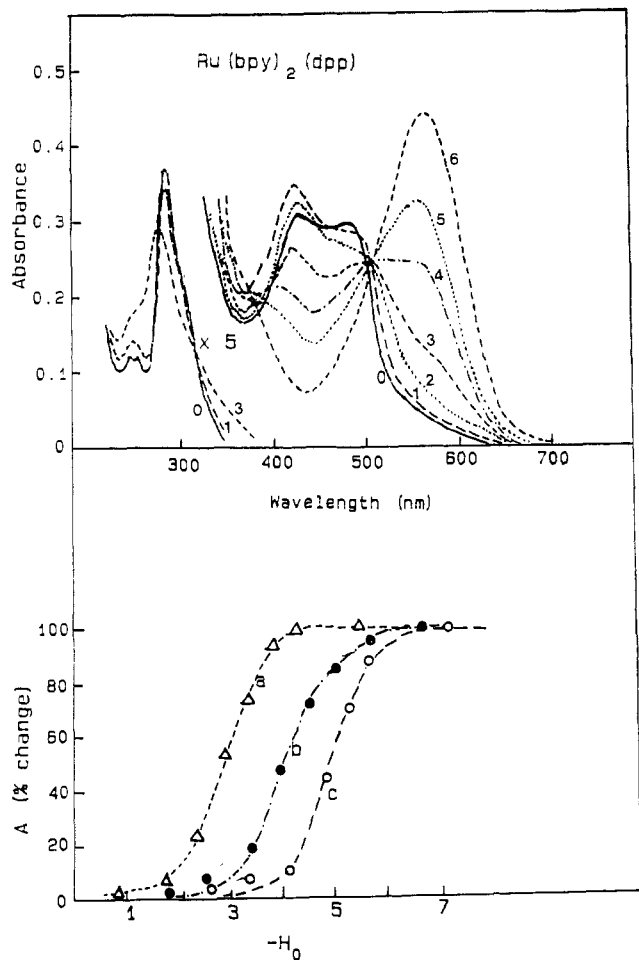


Figure 1. Top: Absorption spectral changes accompanying protonation of $[Ru(bpy)_2(dpp)]^{2+}$. H_0 values corresponding to various curves are 0.05 (0), -1.82 (1), -2.54 (2), -3.41 (3), -3.91 (4), -4.51 (5), and -7.34 (6). Bottom: Titration curve (% absorbance changes vs H_0). Curve a = $[Ru(bpy)_2(bpym)]^{2+}$ (570 nm), curve b = $[Ru(bpy)_2(dpp)]^{2+}$ (560 nm), and curve c = $[Ru(dpp)_3]^{2+}$ (534 nm).

various Ru-dpp and Ru-bpym complexes. The shift in the ground-state pK_a upon chelation of dpp in the Ru(II) complexes, $\Delta pK_a (=pK_{a(Ru)} - pK_{a(PL)})$ of over 6 pK_a units is very significant. Of the two possible protonation sites in the chelated Ru complex, pyridyl nitrogen and pyrazinyl nitrogen para to the ruthenium coordination, extremely low pK_a values suggest possible protonation occurring at the latter pyrazinyl nitrogen centers. For the bpym complex, the shift in pK_a upon complexation (ΔpK_a) is smaller as compared to those observed with dpp. On a relative basis, the mixed-ligand Ru complexes with bpym as protonatable ligand are more basic.

(D) Acid-Base Equilibria in the Excited State of Ru Complexes.

For all the complexes examined, above pH 7.0, the emission is pH independent. Unlike the absorption, the emission intensities of all the Ru complexes vary significantly in dilute acidic solutions. The emission intensity decreases rapidly in mildly acidic solutions, and no detectable emission is observed in acidic (pH 0) solutions. Figure 2 presents typical pH dependence of emission for two of the mixed-ligand dpp complexes $[Ru(bpy)_2(dpp)]^{2+}$ and $[Ru(Me_2bpy)_2(dpp)]^{2+}$.

Figure 3 presents typical emission intensity vs pH titration curves for a few Ru mixed-ligand complexes containing tetraimine ligands. The curves passing through the experimental points of Figure 3 are calculated intensity curves for the deprotonation process occurring according to eq 4. The calculations are based

$$[Ru(LL)_2(PLH)^+]^* \rightleftharpoons [Ru(LL)_2(PL)]^* + H^+ \quad pK_a^* \quad (4)$$

under the following assumptions: (a) a single titration point (pK_a) exists in the pH range 0-7; (b) the emission intensity of the basic form (pH ≥ 7) is normalized at 100%, and emission from the

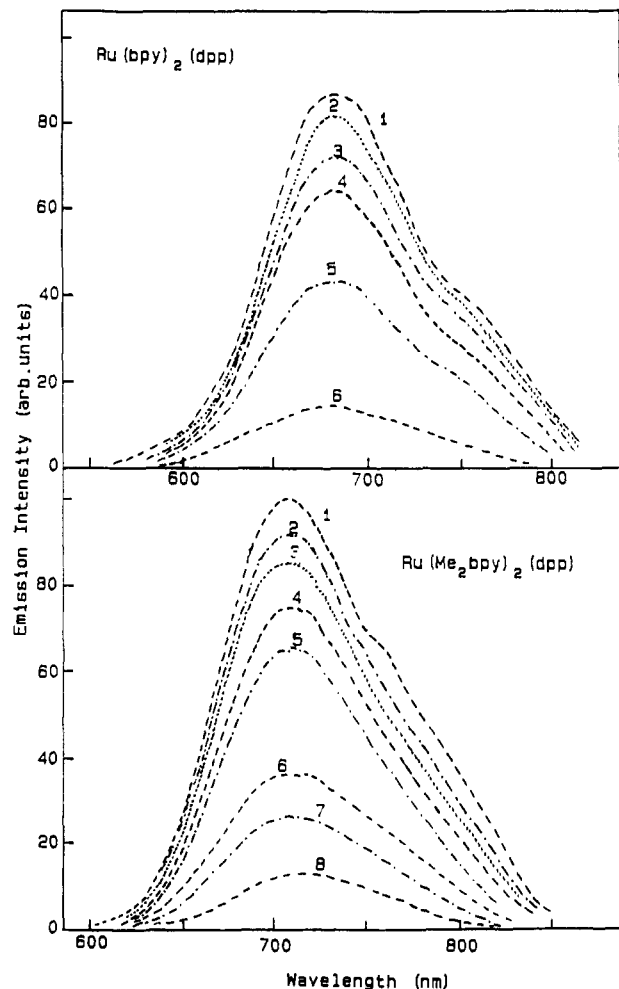


Figure 2. pH dependence of room-temperature emission for $[Ru(bpy)_2(dpp)]^{2+}$, pH = 5.65 (1), 4.58 (2), 3.57 (3), 3.30 (4), 2.88 (5), and 2.17 (6), and for $[Ru(Me_2bpy)_2(dpp)]^{2+}$, pH = 5.18 (1), 3.74 (2), 3.54 (3), 3.33 (4), 2.97 (5), 2.48 (6), 2.33 (7), and 2.02 (8).

protonated form is negligible at the wavelength of monitoring and analysis. In the pH range examined (0-10), it can be noted that the variation in the emission intensity can be quantitatively accounted by a single inflection point (pK_a^*).

In principle, the inflection point, denoted as pK_a^* , derived from emission titration curves, needs to be corrected for the differences in the excited-state lifetime of the unprotonated (τ') and protonated forms (τ) according to eq 5.

$$pK_a^* = pK_a^* - \log(\tau/\tau') \quad (5)$$

emission in acidic solutions corresponding to the monoprotonated form of the complexes does not permit evaluation of absolute pK_a^* values. Table III presents a collection of data on the emission maxima and excited-state lifetimes for the basic forms and derived pK_a^* values for all the complexes examined.

Several empirical methods based on Forster's cycle have been described in the literature for the calculation of the excited-state pK_a values (pK_a^*) from the absorption and emission spectral data and their titration curves.¹⁶ In the absence of authentic emission from the protonated form of the Ru complexes, we have used the Forster equation (eq 6) on the basis of the absorption of the basic

$$pK_a^* = pK_a + 0.00209(\nu_B - \nu_{BH^+}) \quad (6)$$

and protonated forms and ground-state pK_a values. In eq 6 ν_B and ν_{BH^+} denote wavenumbers of the absorption maxima of the basic and acidic forms. pK_a^* values calculated according to eq 6, shown in Table III, are in reasonable agreement with the

(16) (a) Weller, A. *Prog. React. Kinet.* **1961**, *1*, 189. (b) Ireland, I. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131.

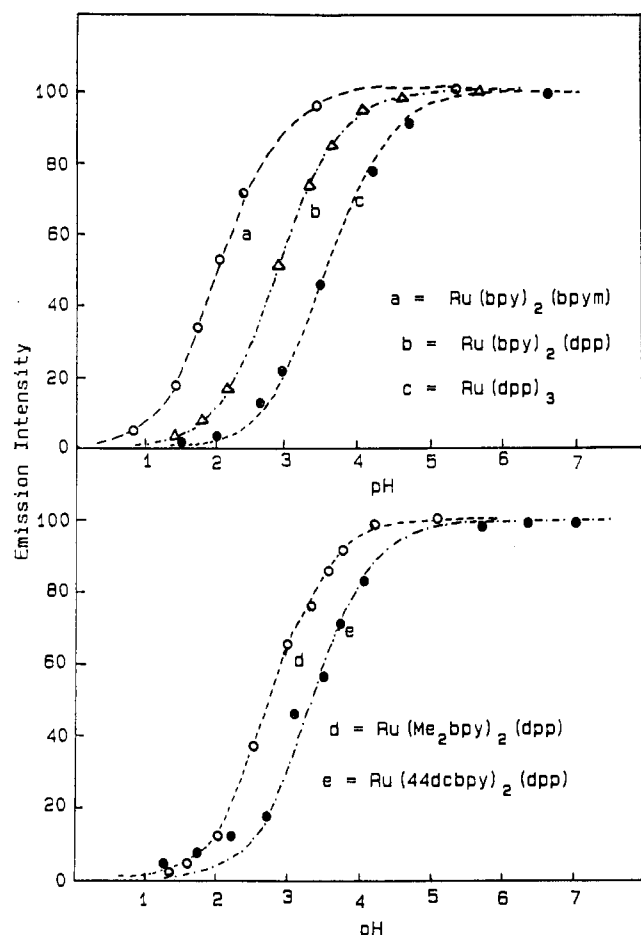


Figure 3. Titration curves for emission intensity variation with pH for different mixed-ligand complexes: (a) $[\text{Ru}(\text{bpy})_2(\text{bpym})]^{2+}$ (690 nm); (b) $[\text{Ru}(\text{bpy})_2(\text{dpp})]^{2+}$ (690 nm); (c) $[\text{Ru}(\text{dpp})_3]^{2+}$ (625 nm); (d) $[\text{Ru}(\text{Me}_2\text{bpy})_2(\text{dpp})]^{2+}$ (710 nm); (e) $[\text{Ru}(4,4'\text{-dcbpy})_2(\text{dpp})]^{2+}$ (665 nm). The dashed curves passing through the points are calculated curves for a single $\text{p}K_a$ titration (see text).

apparent $\text{p}K_a^*$ values ($\text{p}K_a^{* \text{app}}$) determined from the emission titration curves. Given the limitations of such calculations, the agreement is satisfactory. Recently, Kirsch de Mesmaeker et al. have described acid-base equilibria in the ground and excited state of a series of ruthenium tetraimine complexes $\text{Ru}(\text{TAP})_n(\text{bpy})_{3-n}$ ($n = 1-3$; TAP = tetraazaphenanthrene).⁸ Estimates of excited-state $\text{p}K_a$ ($\text{p}K_a^*$) values, calculated by using an analogous equation that uses the emission maxima, showed poor agreement with apparent $\text{p}K_a^*$ ($\text{p}K_a^{* \text{app}}$) values derived from emission titration curves. We have used their reported absorption maxima of unprotonated and monoprotonated forms of these complexes to calculate $\text{p}K_a^*$ values by using eq 6. Table III also presents a comparison of such calculated $\text{p}K_a^*$ values with measured $\text{p}K_a^*$ values. The agreement is much better as in the case of dpp complexes described above. Presumably, the large errors in the measurement of true onset for weak emission in the red/near-IR region coupled with the irreversible nature of the protonation in the excited state are responsible for the poor agreement in the emission spectral data-based calculations.

A possible mechanism for the pH-dependent luminescence of these polypyridyl complexes is proton-induced quenching. Several cases of quenching of luminescence of organic molecules in acidic solutions have been interpreted earlier by such proton-induced quenching mechanisms. Quenching occurs possibly by promoting nonradiative pathways. It is interesting to note that the uncorrected $\text{p}K_a^*$ values of the tetraimine complexes correlate well with the excited-state lifetime of the basic form of these complexes (cf. Table III). The implications are that "what is being observed in emission titration is actually a kinetically controlled event involving diffusion-limited proton movement and protonation of the excited state where the $\text{p}K_a^*$ is certainly higher than that of the ground

state". (We thank the reviewer for pointing out this mechanistic interpretation.)

In the excited state, the dpp and bpym complexes are considerably more basic ($\Delta\text{p}K_a > 5$ pH units). Such pronounced shifts are in agreement with a localized electron description of MLCT excited state and the scheme cited in the introductory paragraphs—a significant increase in basicity to be observed upon optical excitation for the easily reduced ligand. Of the two N-centers in the chelated dpp, protonation presumably occurs at the pyrazinyl nitrogen center para to the coordinated Ru. The charge-density changes are likely to be more pronounced on the pyrazinyl ring directly involved in coordination as compared to the remote pyridyl ring.¹⁷ In $\text{Ru}(\text{dpp})_3^{2+}$, upon optical excitation, two of the other dpp ligands should behave marginally perturbed from the ground-state basicity. Lever et al. in their studies of the excited-state protonation of $\text{Ru}(\text{bpz})_3^{2+}$, found $\Delta\text{p}K_a^*$ for the first protonation step significantly larger as compared to others [$\Delta\text{p}K_a^*(1) = 4.2$ vs $\Delta\text{p}K_a^*(2) = 0.6$]. Along with the TAP series of complexes reported recently, dpp complexes have the highest $\Delta\text{p}K_a^*$ values reported for any ruthenium(II) polypyridyl complexes.

Data presented in Table III on complexes with dpp and bpym reveal several interesting "spectator ligand (LL)" effects on the PL \rightarrow Ru luminescence. Along the spectator ligand series Me_2bpy , bpy, phen and 5-Cl-phen one can note the following: (a) the potential for the ligand-based reduction $\text{Ru}^{2+/+}$ decreases by ca. 150 mV; (b) the absorption maxima of the unprotonated and monoprotonated forms and the emission maxima of unprotonated forms all blue shift with increasing excited-state lifetime and emission intensity; (c) the uncorrected $\text{p}K_a^*$ value for the PL \rightarrow Ru CT emission increases. It is interesting that the emission properties are so sensitive to such "fine tuning" of the excited-state energies.

For the Ru(II) complexes with typical MLCT interactions, the redox potentials for one-electron reduction show linear correlation with the energy of the LUMO of the ligand and hence with the M-L CT bands. In such cases, electron-donating groups cause hypsochromic shifts. The direction of the spectral shifts and the linear variation of the $E_{1/2}(\text{L}/\text{L}^-)$ with $\nu_{\text{M-PL CT}}$ (plot not shown) for various dpp complexes are consistent with CT assignment of the low-energy band in these complexes. Substantial decrease in the basicity of the ligand dpp upon complexation [$\Delta\text{p}K_a = \text{p}K_a(\text{Ru}) - \text{p}K_a(\text{PL})$] suggests extensive back-donation of electron density. In such cases, replacement of a spectator ligand by another with better π -acceptor properties is expected to increase the basicity of the coordinated ligand, as this spectator ligand will compete effectively for the π -electron density. The direction and the magnitude of the basicity shifts in the series of dpp complexes are in accord with such expectations.

(II) Acid-Base Reactions in the Ground and Excited States of Ru Complexes with "Dicarboxybipyridines" as Protonatable Ligands. The acid-base behavior in the ground and excited states has been examined for several complexes of the series $[\text{Ru}(\text{bpy})_n(\text{dcbpy})_{3-n}]$ [bpy = 2,2'-bipyridine, dcbpy = 4,4'-dicarboxy-2,2'-bipyridine (4,4'-dcbpy) or 5,5'-dicarboxy-2,2'-bipyridine (5,5'-dcbpy); $n = 1-3$]. Analyses of the absorption and emission spectra and emission lifetimes were made over a large pH range 0-12.

(A) Acid-Base Properties of the Free Ligands in Solution. (i) Protonation of 4,4'-Dicarboxy-2,2'-bipyridine (4,4'-dcbpy). In neutral or alkaline solutions, the 4,4'-dcbpy ligand is fully deprotonated and is present as a dianion. The $\pi-\pi^*$ absorption bands are located at 293 and 235 nm. Lowering of pH leads to a distinct red shift of these bands (to 310 and 240 nm, respectively) up to

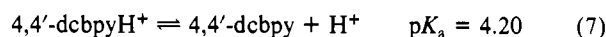
(17) It is also likely that pyridyl N-centers protonate first, but due to the remote nature of this site, the protonation process is not accompanied by distinct spectral changes. If such is the case, then the following discussions on $\Delta\text{p}K_a$ values need to be considered on reserve. An alternate way of monitoring protonation is via conventional acid-base titration. Unfortunately, no $\text{p}K_a$ is detected up to pH 1.0 and the method does not work in more acidic solutions. We thank Prof. C. M. Elliott for enlightening discussions on this point.

Table V. Data for the Ground- and Excited-State Acid-Base Equilibria in Ruthenium Polypyridyl Complexes Containing dcbpy Ligands

complex	p <i>K</i> _a		p <i>K</i> _a [*]		emission (pH >7.0)		emission (pH 0)		ref ^a
	1	2	1	2	λ _{max} , nm	τ, ns	λ _{max} , nm	τ, ns	
Ru(4,4'-dcbpy) ₃	2.20	1.70	4.60	1.75	618 (625)	700	618 (625)	755	tw, b
Ru(4,4'-dcbpy) ₂ (bpy)	2.50	1.80	4.40	1.75	625	664	660	446	tw, b
Ru(4,4'-dcbpy)(bpy) ₂	2.85	1.75	4.25		638	395	670	320	b, c
					659	636	686	299	d
Ru(4,4'-dcbpy) ₂ (dpp)			3.30		670	174	640	220?	tw
Ru(5,5'-dcbpy) ₃	2.80		3.80	1.80	665	37	695		tw

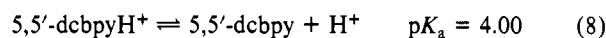
^aTw = this work. ^bReference 4d. ^cReference 4b. ^dReference 4a.

pH 3.0. Quantitative analysis of the absorption spectral changes at selected wavelengths, e.g. 322 nm, led to identification of the first p*K*_a to be at 4.20, corresponding to eq 7 (clean isosbestic points



are obtained at 264 and 300 nm). Precipitation of the neutral ligand from the aqueous solution occurs at pH <2.8, and this did not permit determination of the second p*K*_a. Though the spectral changes observed upon protonation are similar to those described earlier by Shimidzu et al.,^{4c} the first p*K*_a value determined in this work is somewhat higher than the value of 3.7 reported. The origin of the discrepancy is not clear.

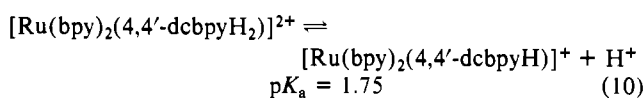
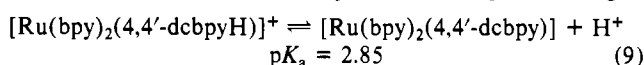
(ii) **Protonation of 5,5'-Dicarboxy-2,2'-bipyridine (5,5'-dcbpy).** Absorption spectral changes accompanying protonation of 5,5'-dcbpy is very similar to that of 4,4'-dcbpy but much less pronounced. Upon protonation, π-π* band red shifts from 295 to 305 nm. The measured first p*K*_a at 322 nm is 4.00, slightly smaller than that of 4,4'-dcbpy (eq 8). Precipitation of the ligand from



the solution at pH <2.5 again does not permit determination of the second p*K*_a. The lower p*K*_a of the 5,5'-dcbpy is consistent with the increased basicity of this ligand. Table IV provides a summary of the absorption spectral data for the basic and monoprotonated form of the dcbpy ligands along with associated p*K*_a values.

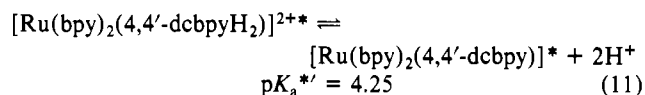
(B) **pH Dependence in the Series [Ru(bpy)_n(4,4'-dcbpy)_{3-n}].** The pH dependence of the series [Ru(bpy)_n(4,4'-dcbpy)_{3-n}] has been the subject of some earlier investigations. Foreman, in his doctoral dissertation,^{4d} has described qualitatively the pH-dependent changes in the absorption and emission spectra for all the three members of the series (n = 0–2). No attempt however was made to quantitatively analyze the data to deduce p*K*_a values in the ground and excited states. We have reinvestigated the photo-physics and pH dependence of absorption and emission for the entire series of complexes. Table II presents absorption spectral data for the basic form of various dicarboxybipyridine complexes examined in this work.

(i) **Case with a Single 4,4'-dcbpy Ligand, [Ru(bpy)₂(4,4'-dcbpy)].** The simplest case with a single 4,4'-dcbpy ligand, [Ru(bpy)₂(4,4'-dcbpy)], has been analyzed quantitatively by Wrighton, Sasse, and co-workers.^{4a-d} The situation is most favorable with maximal changes observed in the spectral shifts and intensity changes in the absorption and emission. Protonation of the dicarboxybipyridine ligand leads to a significant perturbation in the absorption spectrum: upon lowering of pH, the MLCT band located at 450 nm red shifts by ca. 35 nm to 485 nm with a small increase in intensity. The π-π* transition of the dcbpy ligand located at 302 nm also red shifts to 310 nm. Quantitative analysis of the spectral changes yield two closely lying p*K*_a values for the ground state as 1.75 and 2.85 (eq 9 and 10). Upon lowering of



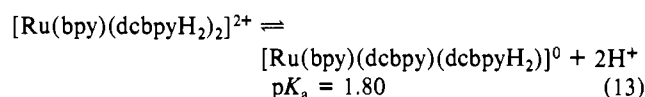
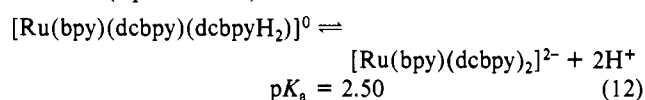
pH, the emission spectrum with a maximum at 638 nm in neutral/alkaline pH decreases monotonically and red shifts to a maximum at 670 nm. The emission intensity of the diacid form

is very weak (ca. 1%) as compared to that of the deprotonated complex. Analysis of the emission intensity variation yields a single inflection point with a p*K*_a^{*} = 4.25 (eq 11). Table V presents

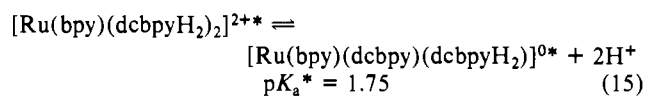
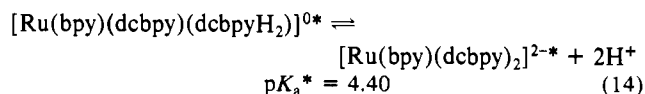


a summary of the emission data for different dicarboxybipyridine complexes at two selected pH values 7 and 0.

(ii) **Case with Two 4,4'-dcbpy Ligands, [Ru(bpy)(4,4'-dcbpy)₂].** In complexes with two or more dcbpy ligands, analysis of the pH-dependent spectral changes becomes more complex. To resolve the overlapping emission and absorption spectra, we have resorted to theoretical fitting of the experimental titration curves (intensity changes vs pH) as explained below. Upon lowering of the pH, the absorption spectrum of the complex also shows moderate changes. The MLCT absorption band with a maximum at 465 nm (at pH ≥7.0) red shifts by ca. 15 nm to 480 nm. The π-π* absorption of the dcbpy ligand also red shifts from 302 to 310 nm. Quantitative analysis of the absorption intensity changes at several wavelengths yielded two ground-state p*K*_a values of 2.50 and 1.80 (eq 12 and 13).



In neutral or alkaline solutions (pH ≥7.0), the emission spectrum has a maximum at 625 nm. Lowering of pH leads to a gradual red shift to 665 nm up to pH ≈2.5 (intensity minimal). Upon further lowering of pH, the emission slightly blue shifts with an increase in emission intensity (emission maximum at ca 660 nm at pH ≈0). Figure 4 (curve a) shows the variation in the emission intensity at 625 nm as a function of pH. At λ = 625 nm, the emission intensity at pH ≈0 is 40% of that at pH ≈7.0 (curve b), in good agreement with the earlier observation of Foreman. As shown in the figure, the variation in the emission intensity over the entire pH range 0–10 can be fitted reasonably well with two titration curves with p*K*_a^{*} = 4.40 and 1.75 (eq 14 and 15), the former based on the emission intensity changes at



625 nm in the pH range 7.0–4.0 and the latter based on emission intensity changes at 660 nm in the pH range 0.0–3.0. [Such a two-p*K*_a^{*} fit analysis, of course, assumes existence of "pure" (or predominant) emission from one form of the excited chromophore at the wavelengths of analysis. Clearly, the emission in the intermediate pH range 2.0–4.0 is *mixed*.] If the emission intensity values at the two-plateau region are used (pH ≥7.0 and pH 0–1.0) as those corresponding to pure forms of excited [Ru(bpy)(dcbpy)₂]²⁻ and [Ru(bpy)(dcbpyH₂)₂]²⁺, emission intensity of each

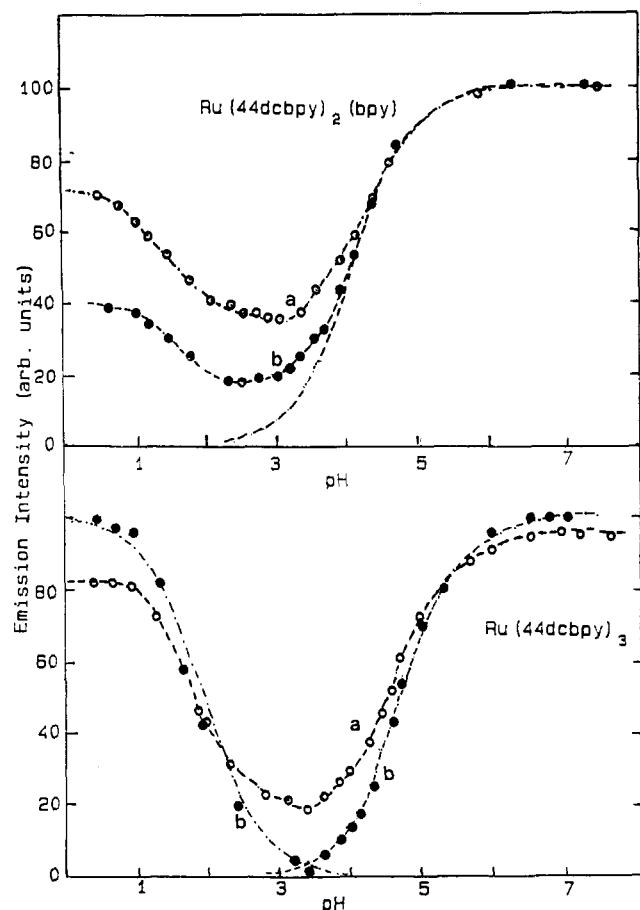
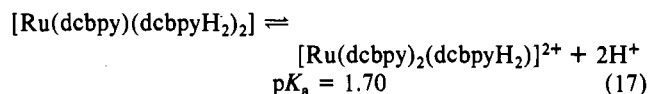
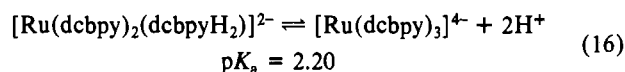


Figure 4. Top: Variation in the emission intensity with pH for $[Ru(4,4'-dcbpy)_2(bpy)]^{2-}$ at 660 (curve a) and 625 nm (curve b). Bottom: Variation in the total emission intensity with pH for $[Ru(4,4'-dcbpy)_3]^+$ at 620 nm in degassed aqueous solution (curve a) and deconvolution of the emission intensity at 620 nm into two titration curves with inflection points at 4.65 and 1.75 (curve b) (see text).

form can be computed over the entire pH range. The observed total emission intensities in the intermediate pH ranges are in good agreement with such estimates, confirming validity of such an analysis. The pK_a^* values deduced for the protonation of the first dcbpy ligand (4.40) is in the range determined for the protonation of dcbpy in the complex $[Ru(bpy)_2(dcbpy)]$, $pK_a^* = 4.25$.

(iii) **Case with Three Protonatable dcbpy Ligands, $[Ru(dcbpy)_3]^+$.** For the $(dcbpy)_3$ complex, over the pH range 0–10 examined, the absorption spectral changes are too small to allow meaningful measurements of protonation equilibria. Hence, we resorted to monitoring of the protonation changes by conventional pH titration on an automated pH titroprocessor. By this technique, we could detect two ground-state deprotonations at pH 2.20 and 1.70 (eq 16 and 17).



Over the pH range 0–10.00, the emission from $[Ru(4,4'-dcbpy)_3]^+$ shows more pronounced variation in intensity and emission maxima. As shown in Figure 5, if we start at pH 7.0, lowering of pH leads to a decreased emission intensity and small red shifts up to pH of about 3.40. Further lowering of pH leads to enhanced emission intensity and small blue shifts. The emission maximum at pH 0 is very similar to that observed at pH ≥ 7 with a regaining of >90% intensity. Figure 4 also presents the emission intensity variation monitored at $\lambda = 620$ nm as a function of pH. A two- pK_a^* analysis similar to that carried out on the complex (fit shown in the lower part of Figure 4) leads to identification

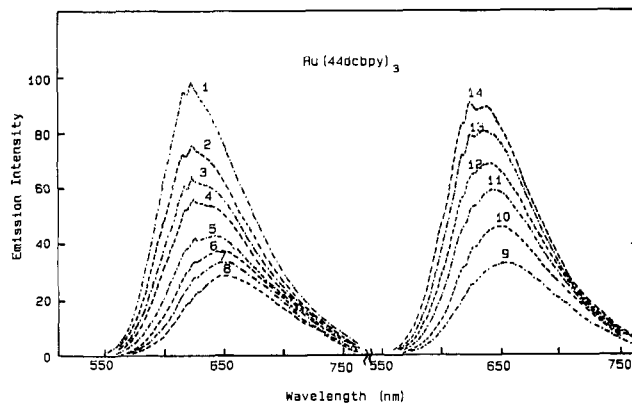
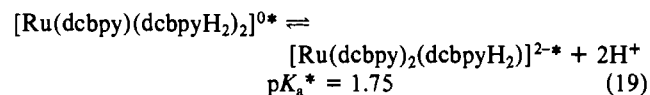
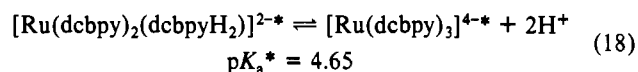


Figure 5. pH dependence of emission spectra for $[Ru(4,4'-dcbpy)_3]^+$ in degassed aqueous solution. pH values of the solutions corresponding to various curves are 7.10 (1), 5.02 (2), 4.71 (3), 4.60 (4), 4.27 (5), 4.00 (6), 3.60 (7), 3.40 (8), 3.22 (9), 2.34 (10), 1.88 (11), 1.59 (12), 1.27 (13), and 0.96 (14).

of two excited-state pK_a^* values of 4.60 and 1.75 corresponding to eq 18 and 19.



It was mentioned earlier that in the currently accepted model for the MLCT excited state, the electron upon optical excitation resides primarily on the ligand easily reduced. This implies then that, in mixed-ligand complexes with one or more dcbpy ligands, the dcbpy ligand that receives the electron in the excited state should show protonation behavior quite different from that of the others. The pK_a of the spectator dcbpy ligands should be altered only marginally in the excited state as the electron density on these ligands does not vary much. It can be noted that, of the two pK_a values that can be discerned within the pH range 0–10 examined, the first one shows significant difference upon excitation and the second pK_a values are very similar in the ground and excited states. For the $[Ru(4,4'-dcbpy)_3]^+$ complex, $\Delta pK_a^*(1) = 2.4$ as compared to $\Delta pK_a^*(2) \approx 0.05$. Thus, the pK_a values in the ground and excited states of Ru complexes with multiple protonatable ligands can also serve to characterize the nature of charge distribution in the excited state.

It is interesting to compare the shift in the ground-state pK_a values upon replacement of dcbpy ligand by bpy in the $4,4'$ -dcbpy complexes and also upon formation of the MLCT excited state. The ground-state pK_a values increase by ca. 0.3 pK_a units for each replacement of $4,4'$ -dcbpy by unsubstituted bpy. The excited-state pK_a (pK_a^*) values for the first protonation however decrease by ca. 0.25 units for each replacement of dcbpy by bpy. Hence, the difference between the first ground- and excited-state pK_a (ΔpK_a) decreases from 2.4 for the $[Ru(4,4'-dcbpy)_3]^+$ complex to 1.9 in the $[Ru(dcbpy)_2(bpy)]$ and to 1.4 in the $[Ru(dcbpy)(bpy)_2]$ complex. One possible explanation for this gradual increase in the ΔpK_a values with the number of dcbpy ligands is electrostatic in origin. The global charges on the Ru complexes with one, two, and three dcbpy ligands are 0, -2, and -4, respectively.

(C) **Acid-Base Equilibria in the Ground and Excited States of $Ru(5,5'$ -dcbpy)₃.** Ru(II) complexes with the isomeric 5,5'-dicarboxy-2,2'-bipyridine ($5,5'$ -dcbpy) provide an interesting comparison to the analogous $[Ru(4,4'-dcbpy)_3]^+$ complex. Spectral and redox properties of the complexes with $5,5'$ -dcbpy ligand are quite different from those with $4,4'$ -dcbpy.¹⁸ On a relative basis, the

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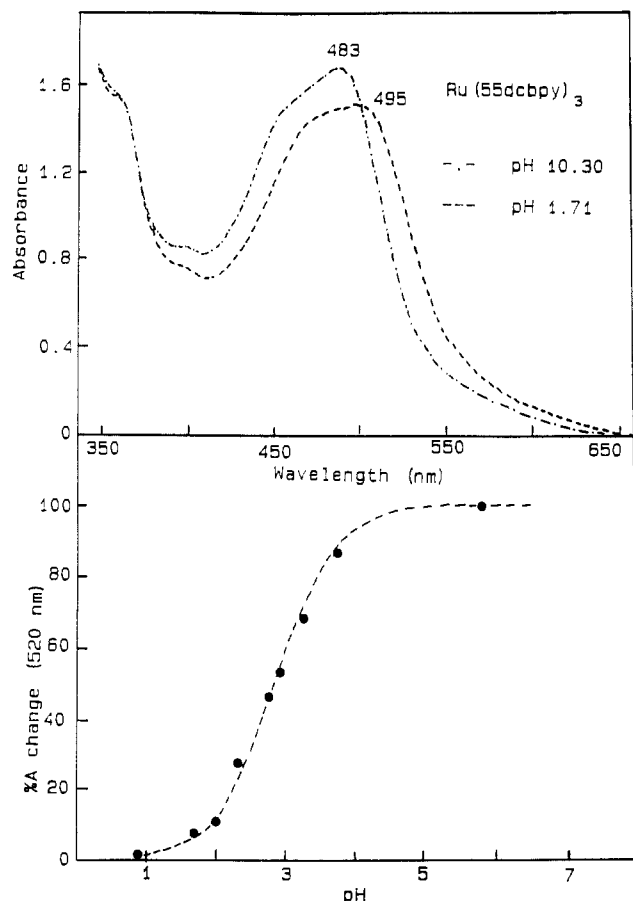
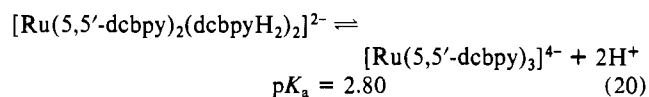


Figure 6. Top: Absorption spectra of fully deprotonated (pH 10.30) and diprotonated forms (pH 1.71) of $[\text{Ru}(5,5'\text{-dcbpy})_3]^{4-}$. Bottom: Titration curve for absorbance changes at 520 nm for $[\text{Ru}(5,5'\text{-dcbpy})_3]^{4-}$ in aqueous solution.

former ligand is relatively less basic and its Ru(II) complexes are easily reduced.^{14c}

Compared to that of the tris(4,4'-dicarboxy-2,2'-bipyridine) complex, the emission from the tris(5,5'-dicarboxy-2,2'-bipyridine) complex is rather weak and short-lived. Over the pH range 10.0–5.0, the absorption spectrum of $[\text{Ru}(5,5'\text{-dcbpy})_3]^{4-}$ is pH independent. Below pH 5.0, lowering of pH leads to significant spectral changes. Figure 6 (top) presents a comparison of the absorption spectra of the fully deprotonated and protonated forms of the complex. The MLCT absorption maximum located at 483 nm red shifts to 495 nm with a small decrease in absorption intensity. Quantitative analysis of the absorbance changes at selected wavelengths (for example, Figure 7 (bottom) shows such a fit for analysis at 520 nm) along the lines outlined earlier for the 4,4'-dcbpy derivatives led to identification of a single $\text{p}K_a$ at 2.80 (eq 20).



The variations in the emission spectra of $[\text{Ru}(5,5'\text{-dcbpy})_3]^{4-}$ are similar in some aspects to that of $[\text{Ru}(4,4'\text{-dcbpy})_3]^{4-}$ outlined earlier. Figure 7 presents the dependence of the emission spectra and intensity as a function of pH. The fully ionized form, present at $\text{pH} \geq 7.0$, has its emission maximum located at 665 nm. The emission is red-shifted by ca. 50 nm, very weak and short-lived as compared to that of the 4,4'-dcbpy complex. Lowering of pH leads to a decrease in intensity up to pH 2.80 that then increases marginally thereafter. As compared to the analogous 4,4'-dcbpy complex, the recovery of the emission in acidic solutions is much lower (ca. 25%) and emission intensity levels off at $\text{pH} \leq 0.8$. Figure 7 (insert) presents an analysis of the emission intensity variation as a function of pH. Fitting of the total emission intensity

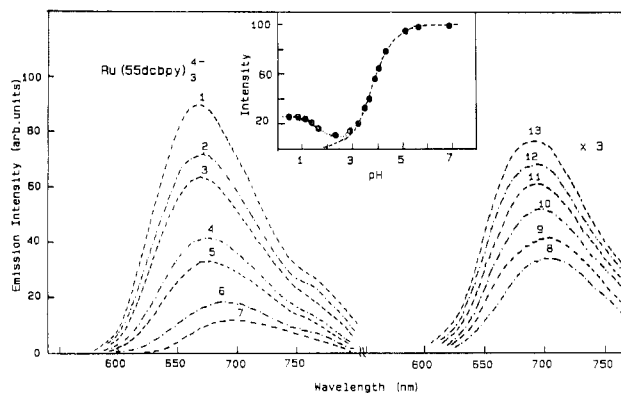
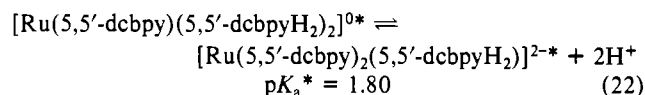
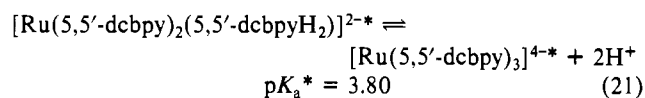


Figure 7. pH dependence of emission spectra of $[\text{Ru}(5,5'\text{-dcbpy})_3]^{4-}$ in degassed aqueous solution. pH values of the solutions corresponding to various curves are 5.72 (1), 4.34 (2), 4.04 (3), 3.90 (4), 3.63 (5), 3.48 (6), 3.19 (7), 2.87 (8), 2.31 (9), 1.60 (10), 1.35 (11), 1.11 (12), and 0.85 (13). Insert: Titration curves for emission intensity variation with pH for $[\text{Ru}(5,5'\text{-dcbpy})_3]^{4-}$ monitored at 695 nm in degassed aqueous solution. The dashed curve passing through the points is calculated for single $\text{p}K_a$ titration (see text).

curve to a two distinct $\text{p}K_a^*$ model (on lines similar to that outlined earlier for the 4,4'-dcbpy complex) yielded two inflection points ($\text{p}K_a^*$ values) at 3.80 and 1.80 corresponding to eq 21 and 22.



Comparison of similar data for the 4,4'-dcbpy complex shows that the shift in the first $\text{p}K_a$ upon formation of the MLCT excited state is much less pronounced ($\Delta\text{p}K_a = 1.00$ for the (5,5'-dcbpy)₃ complex as compared to > 2.0 for the (4,4'-dcbpy)₃ complex). The second $\text{p}K_a^*$ values for the two isomeric complexes however are very similar.

Table V presents a summary of the absorption and emission properties measured in this work for various dcbpy complexes in the unprotonated and protonated forms. The differences in the emission lifetimes between these basic and acidic forms in the dicarboxybipyridine chelates are quite significant. The emission lifetime ratios between the unprotonated and protonated forms are consistent with the emission intensity ratios measured in the steady-state luminescence measurements. In complexes with several ionizable carboxyl groups, one would expect several more protonation equilibria than the minimal picture presented above. In our assignments of the protonation equilibria in the ground state, we have been guided by three sets of observations that shed light on the nature of the species present at a given pH: (i) pH titrations on a titroprocessor; (ii) dilution conductivities of complexes as prepared by using neutral carboxybipyridine ligands in aprotic solvents and as precipitated at several pH values in aqueous solution; (iii) existence of isoelectric points invariably in a narrow pH range of 2.2–2.5 where the neutral complex precipitates out of aqueous solution.

A final point on the photophysics of the Ru complexes containing dcbpy ligands concerns the effect of esterification of the dcbpy ligands on the excited-state lifetime and emission intensities. We have confirmed the observations of Foreman and others that esterification leads to a pronounced increase in the MLCT excited-state lifetime and correspondingly increased emission intensities. It is surprising that the dcbpy complexes with very similar global and local charges have different emission lifetimes and intensities (both bpy-COOH and bpy-COOEt are electrically neutral). Possible reasons for the effect are proton-induced quenching, H-bonding, ...

(D) Excited-State Absorption Spectra of Unprotonated and Protonated Forms of the Ru Complexes. As in the case of ex-

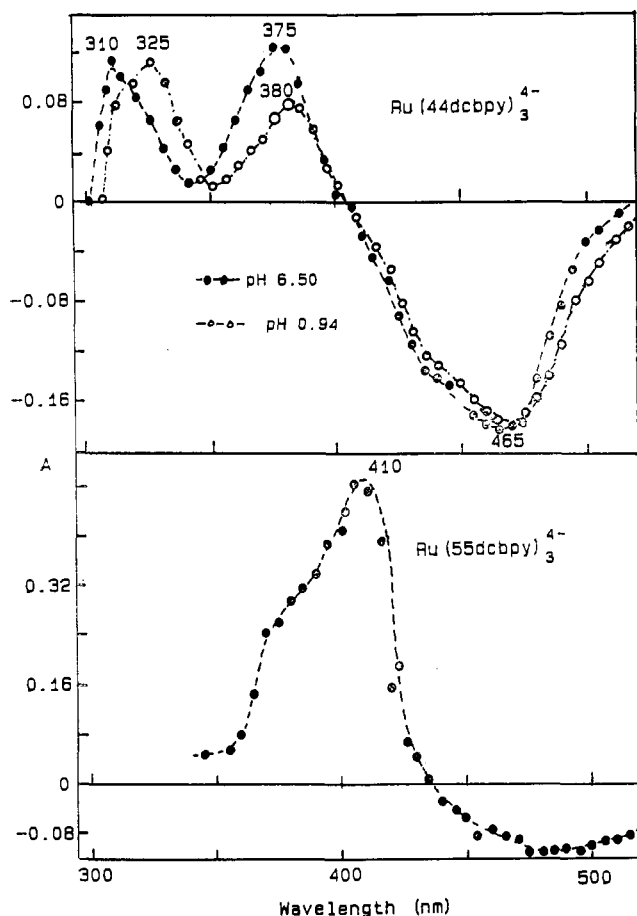


Figure 8. Top: Transient difference absorption spectra corresponding to the MLCT excited state of $[\text{Ru}(4,4'\text{-dcbpy})_3]^{4-}$ recorded at 50 ns after laser pulse excitation (530 nm) [pH 6.50 (●); pH 0.94 (○)]. Bottom: Transient difference absorption spectra corresponding to the MLCT excited state of $[\text{Ru}(5,5'\text{-dcbpy})_3]^{4-}$ recorded at 50 ns after laser pulse excitation (530 nm).

cited-state Raman spectra, absorption spectra of the excited state are direct indicators of charge distribution in the excited state. Existence of long-lived excited states for the protonated forms of the dicarboxybipyridine complexes allows a direct comparison of the absorption spectra in the unprotonated and protonated forms. Figure 8 presents transient difference spectra of the $\text{Ru}(4,4'\text{-dcbpy})_3^{4-}$ and of $\text{Ru}(5,5'\text{-dcbpy})_3^{4-}$ in aqueous solution at two different pH values. In the case of the $4,4'\text{-dcbpy}$ derivative, the absorption spectrum in neutral aqueous solution is very similar to that of $\text{Ru}(\text{bpy})_3^{2+}$. The reduced dcbpy ligand absorption,

located at 375 nm, slightly red shifts to 380 nm upon protonation in the excited state. For the $\text{tris}(5,5'\text{-dicarboxy-2,2'}\text{-bipyridine})$ complex, the distinct feature to note is the unusually intense absorption at 410 nm, characteristic of the reduced ligand. Similar intense absorption with a maximum at 410 nm has also been observed in the electrochemical reduction of the $\text{tris}(5,5'\text{-dicarboxy-2,2'}\text{-bipyridine})$ complex in the spectroelectrochemical investigations of DeArmond et al.¹⁷ Studies of absorption spectra of reduction products of $4,4'\text{-dcbpy}$ and $5,5'\text{-dcbpy}$ derivatives do indicate localized nature of the redox orbitals in the latter complex. One possible explanation of this unusually intense reduced ligand band observed in the MLCT excited state of the $5,5'\text{-dcbpy}$ complex—as compared to the analogous band in the $4,4'\text{-dcbpy}$ complex—is that the electron localization is nearly quantitative in the excited state of the former complex and is only partial in others (possibly due to extensive π -back-bonding).

Concluding Remarks

An examination of the photophysical and acid-base properties of a series of ruthenium polypyridyl complexes with tetraamines or carboxybipyridines as protonatable ligands has allowed a quantitative measure of effects of the spectator and protonatable ligands on the MLCT excited-state photophysics. In the tetraamine complexes, the intraligand interactions through the metal center as revealed in the shifts in the protonation behavior in the ground and excited states are very pronounced.

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Registry No. bpy, 366-18-7; $4,4'\text{-dcbpy}$, 122968-21-2; $5,5'\text{-dcbpy}$, 122968-22-3; bpym, 34671-83-5; dpp, 25005-96-3; $4,4'\text{-dcbpyH}_2$, 6813-38-3; $5,5'\text{-dcbpyH}_2$, 1802-30-8; bpymH, 122968-23-4; dppH, 122968-24-5; $[\text{Ru}(\text{dpp})(\text{Me}_2\text{bpy})_2]^{2+}$, 122968-25-6; $[\text{Ru}(\text{dpp})(\text{bpy})_2]^{2+}$, 88635-47-6; $[\text{Ru}(\text{dpp})(\text{phen})_2]^{2+}$, 122968-26-7; $[\text{Ru}(\text{dpp})(5\text{-Cl-phen})_2]^{2+}$, 122968-27-8; $[\text{Ru}(\text{dpp})_3]^{2+}$, 122968-28-9; $[\text{Ru}(\text{bpym})(\text{bpy})_2]^{2+}$, 65013-22-1; $\text{Ru}(\text{Me}_2\text{bpy})_2\text{Cl}_2$, 68510-55-4; $\text{Ru}(4,4'\text{-dcbpy})_2(\text{bpy})$, 122968-29-0; $\text{Ru}(4,4'\text{-dcbpy})_3$, 78338-26-8; $\text{Ru}(4,4'\text{-dcbpy})_2(\text{dpp})$, 123001-88-7; $\text{Ru}(5,5'\text{-dcbpy})_3$, 122968-30-3; $[\text{Ru}(\text{dpp})(\text{Me}_2\text{bpy})_2]^+$, 123001-89-8; $[\text{Ru}(\text{dpp})(\text{bpy})_2]^+$, 107495-12-5; $[\text{Ru}(\text{dpp})(\text{phen})_2]^+$, 122968-31-4; $[\text{Ru}(\text{dpp})(5\text{-Cl-phen})_2]^+$, 123001-90-1; $[\text{Ru}(\text{dpp})_3]^+$, 122968-32-5; $[\text{Ru}(\text{bpym})(\text{bpy})_2]^+$, 122968-33-6; $[\text{Ru}(\text{dppH})(\text{Me}_2\text{bpy})_2]^{3+}$, 122968-34-7; $[\text{Ru}(\text{dppH})(\text{bpy})_2]^{3+}$, 122968-35-8; $[\text{Ru}(\text{dppH})(\text{phen})_2]^{3+}$, 123001-91-2; $[\text{Ru}(\text{dppH})(\text{dpp})_2]^{3+}$, 122968-36-9; $[\text{Ru}(\text{dpymH})(\text{bpy})_2]^{3+}$, 122968-37-0; $\text{Ru}(\text{bpy})(\text{dcbpy})(\text{dcbpyH}_2)$, 122968-38-1; $[\text{Ru}(5,5'\text{-dcbpy})_2(5,5'\text{-dcbpyH}_2)]^{2-}$, 122968-39-2; $\text{Ru}(\text{bpy})_2\text{Cl}_2$, 15746-57-3; $\text{Ru}(\text{phen})_2\text{Cl}_2$, 85718-09-8; $\text{Ru}(5\text{-Cl-phen})_2\text{Cl}_2$, 123001-92-3; $\text{Ru}(4,4'\text{-dcbpyH}_2)_2\text{Cl}_2$, 123049-50-3; $\text{Ru}(4,4'\text{-dcbpyH}_2)_2(\text{bpy})$, 122968-40-5; $\text{Ru}(4,4'\text{-dcbpyH}_2)_3$, 99837-92-0; $\text{Ru}(4,4'\text{-dcbpyH}_2)_2(\text{dpp})$, 122968-41-6; $\text{Ru}(5,5'\text{-dcbpyH}_2)_3$, 115824-15-2.