In contrast, however, the magnesium atom is considerably smaller than calcium or strontium and hence less polarizable. For CaMg the electronic transition energy is red shifted from the mean of Ca_2 and Mg_2 and the ω_e'' is greater than for either Mg_2 or Ca_2! Likewise, the SrMg transition is red shifted but no ground-state constants could be determined. Unfortunately, the most interesting property of these van der Waals molecules, the potential well depth, cannot be compared as only relatively crude estimates can be made from the matrix data.

The two homonuclear molecules Ca_2 and Mg_2 exhibited large gas to matrix shifts in ω_e'' of 17 and 40 cm^{-1}, respectively. The large shift for Mg_2 is probably matched by CaMg; if this suggestion is correct, gaseous CaMg is predicted to have $\omega_e'' \approx 55 \pm 5$ cm^{-1}.

Finally, the observation of vibrationally unrelaxed emission for CaMg is of interest, particularly in light of the large guest–host interaction evidenced by the intense multiphonon bands in the excitation spectrum. Similar, more extensive hot bands were seen for Mg_2[6] and Ca_2,[7,10] where the lifetime is known to be short[10] and less phonon interaction was observed.

V. Conclusions

Emission from the heteronuclear group 2A dimers CaMg, SrMg, and SrCa has been observed and assigned to the same $^1\Sigma^+ \rightarrow {}^1\Sigma^+$ transition previously observed in absorption studies. For CaMg and SrCa vibronically discrete spectra provided constants describing the van der Waals ground state. Excitation spectra were similar to the absorption spectra. Several comparisons with the corresponding homonuclear dimers were made and matrix effects were discussed. Unrelaxed emission was observed from CaMg which indicates an extremely short fluorescence lifetime for this molecule.

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Excited State Proton Transfer of Ruthenium(II) Complexes of 4,7-Dihydroxy-1,10-phenanthroline. Increased Acidity in the Excited State

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Abstract: Studies are reported for acid–base equilibria for aqueous solutions of ground and lowest excited states of complexes of the general formula $[L_2Ru(4,7\text{-dihydroxy-}1,10\text{-phenanthroline})]^{2+}$ (L = 2,2′-bipyridine, 1,10-phenanthroline, 4,4′-dimethyl-2,2′-bipyridine, and 3,4,7,8-tetramethyl-1,10-phenanthroline). Optical emission from both the fully protonated and fully deprotonated forms of the complexes allows the direct determination of the excited state equilibrium constant for the deprotonation–protonation associated with the two hydroxy groups on one of the ligands. The complexes are stronger acids in the excited state compared to the ground state. Data for L = 2,2′-bipyridine are representative: $pK_a = 10.1$ and $pK_a^* = 5.1$ for the two-proton ground and excited state equilibria, respectively. Optical spectral features are consistent with a more acidic excited state; absorption maxima and emission maxima red shift upon deprotonation of the complex from ~450 to ~500 nm and from ~650 to 735 nm, respectively. The data suggest that the deprotonated 4,7-dihydroxy-1,10-phenanthroline is a strong π donor and in the excited state the π-donor capability is more fully exploited and serves to stabilize the Ru → L charge transfer. Resonance structures associated with the aromatic heterocyclic hydroxy compound allow rationalization of the π-donor properties. Emission quantum yield and lifetime data for all of the complexes are reported at 298 and 77 K.

We recently added[1] excited state proton transfer to the growing list of bimolecular processes of electronic excited inorganic and organometallic complexes.[2-12] The study of acid–base chemistry *in the excited state* has proven to be valuable in the understanding of charge redistribution upon electronic excitation of organic molecules[13] and such should be useful in the study of inorganic and organometallic substances as well. In particular, we have set out to study such chemistry in complexes having lowest lying metal to ligand charge transfer (MLCT) states. In our first study[1] we found that the lowest excited state of Ru(2,2′-bipyridine)$_2$(4,4′-dicarboxylate-2,2′-bipyridine) is a stronger base than the ground state, consistent with the direction of the CT.

In this paper we wish to report on the ground and excited state acid–base chemistry of the four complexes $[(4,7\text{-dihydroxy-}1,10\text{-phenanthroline})RuL_2]^{2+}$ (L = 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 1,10-phenanthroline, and 3,4,7,8-tetramethyl-1,10-phenanthroline). We have found that both the protonated and deprotonated forms are emissive in aqueous solutions and have carried out spectroscopic studies which allow the evaluation of the ground and excited state acid dissociation constants, pK_a and pK_a^*, respectively.

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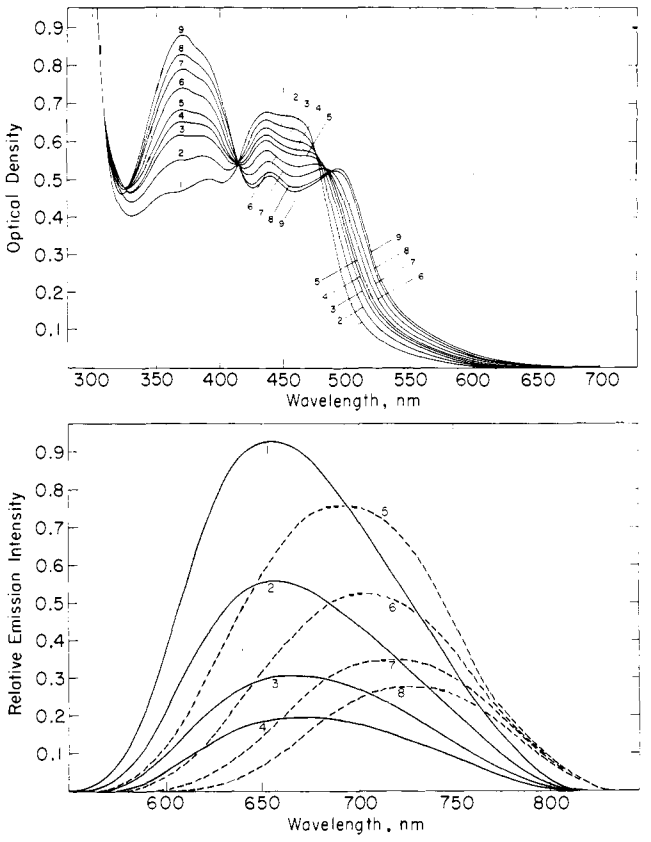
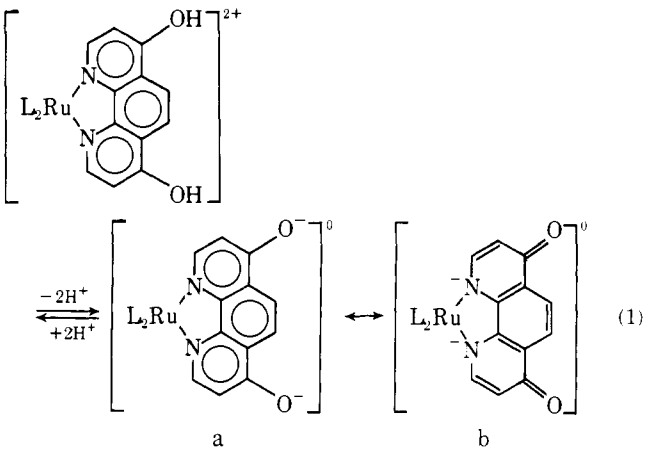


Figure 1. Absorption spectrum (top) of 5.2×10^{-5} M $[Ru(bpy)_2(4,7\text{-dihydroxy-1,10-phenanthroline})]^{2+}$ in aqueous solution at 298 K as a function of pH; curves 2, 3, 4, 5, 6, 7, and 8 correspond to pHs of 4.33, 4.70, 4.90, 5.10, 5.35, 5.65, and 5.85, respectively. Curve 1 is the spectrum at pH 0.5 or 3.0, and curve 9 is the spectrum at pH 7.25 and 13. Emission spectra (bottom) under the same conditions exciting at 415 nm; the dashed curves are recorded at 6× sensitivity. Curves 1, 2, 3, 4, 5, 6, 7, and 8 correspond to pHs of 0.5, 2.0, 2.5, 3.5, 4.5, 5.0, 6.0, and 13, respectively.

Results and Discussion

1. Ground State Acid Dissociation Constants. The spectral studies are consistent with an acid–base equilibrium represented as in eq 1 for the four complexes studied. First, consider



(1)

the optical absorption spectrum as a function of pH. There are substantial, but completely reversible, changes in the spectrum with variation in pH; Figures 1 and 3 are representative and Table I summarizes the absorption spectral features in acid and basic media for each of the four complexes. The spectrum at pH 1 represents that for the fully protonated and that at pH 13 for the fully deprotonated form. This follows from the facts that (1) the plot of change in the optical density, at any point

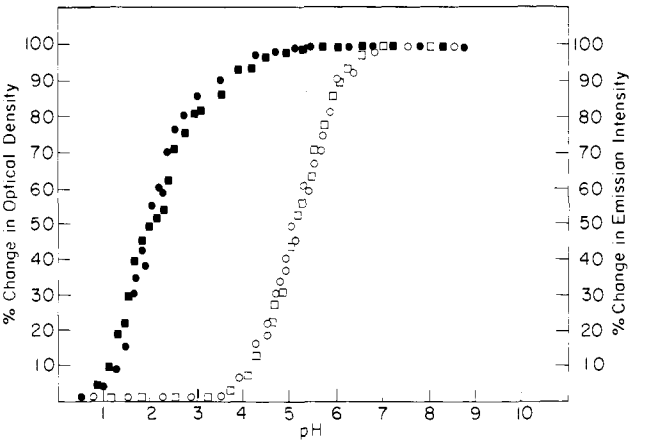


Figure 2. Plots of percent change in optical density against pH at 510 (□) or 365 nm (○) and emission intensity at 630 nm with excitation at either 415 (■) or 480 nm (●) for a 298 K, 5×10^{-5} M aqueous solution of $[Ru(bpy)_2(4,7\text{-dihydroxy-1,10-phenanthroline})]^{2+}$.

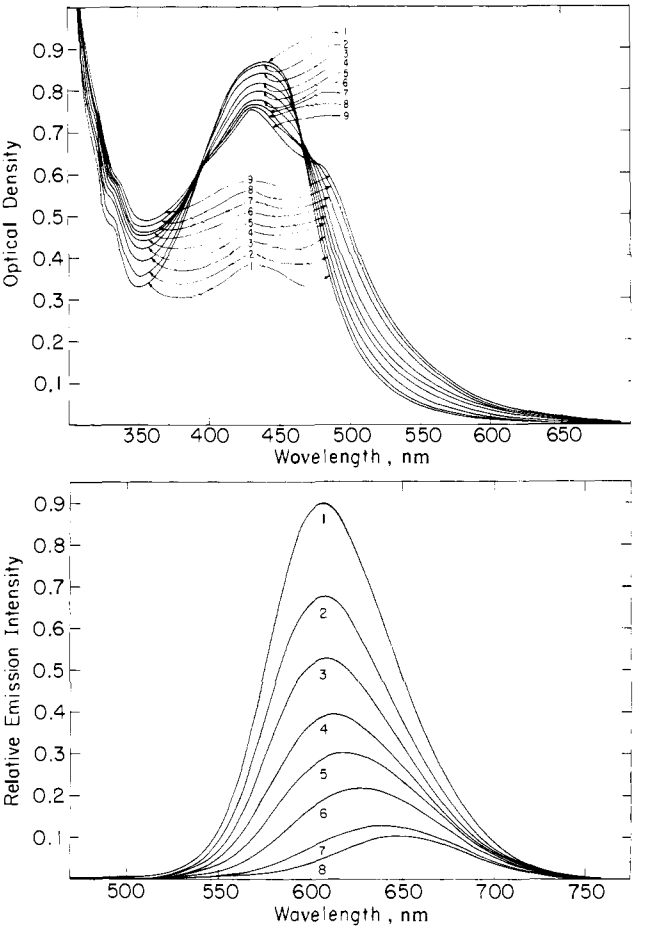


Figure 3. Absorption spectrum (top) of 4.7×10^{-5} M $[Ru(3,4,7,8\text{-tetramethyl-1,10-phenanthroline})_2(4,7\text{-dihydroxy-1,10-phenanthroline})]^{2+}$ in aqueous solution at 298 K as a function of pH; curves, 1, 2, 3, 4, 5, 6, 7, 8, and 9 are at pH 2.5, 3.0, 3.75, 4.25, 4.50, 4.85, 5.15, 5.50, and 13.0, respectively. Emission spectra (bottom) under the same conditions exciting at 395 nm. Curves 1, 2, 3, 4, 5, 6, 7, and 8 are at pH 1, 2, 2.5, 3.0, 4.5, 6.0, and 13.0, respectively.

where there is a change, against pH (Figures 2 and 4 are representative) shows no further optical density change above pH ≈7 or below pH ≈3, and (2) titration of the protonated form of the complex shows that the deprotonation consists of two (±0.05) protons per Ru. The titration shows only one end point, consistent with the plots of change in optical density vs. pH which show only one inflection point. These facts are in accord

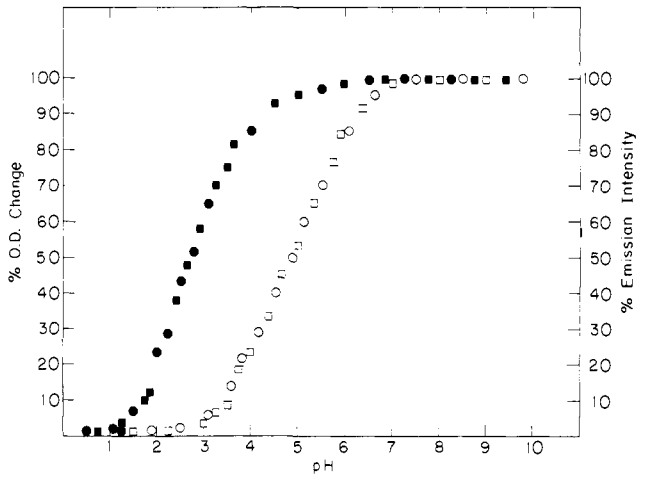


Figure 4. Plots of percent change in optical density against pH at 500 (□) or 350 nm (○) and emission intensity at 600 nm with excitation at either 395 (■) or 470 nm (●) for a 298 K, 5×10^{-5} M aqueous solution of [Ru(3,4,7,8-tetramethyl-1,10-phenanthroline)$_2$(4,7-dihydroxy-1,10-phenanthroline)]$^{2+}$.

with nearly the same value of $(pK_a)_1$ and $(pK_a)_2$, despite the fact that the spectral changes do not show precise preservation of isosbestic points. However, we will deal only with the overall dissociation constant $pK_a = (pK_a)_1 + (pK_a)_2$. By definition, pK_a is equal to 2pH at the inflection point of the plots of change in optical density vs. pH; cf. Figures 2 and 4. The values of pK_a for the four complexes studied are given in Table II.

2. Excited State Acid Dissociation Constants. Each of the four complexes and their deprotonated forms are emissive in aerated aqueous solution; emission quantum yields are independent of excitation wavelength for $\lambda > 300$ nm. The emission efficiency, energetic distribution, and lifetime are all pH sensitive. Representative emission spectral changes (exciting at a wavelength where there is little absorbance change) with variation in pH are given in Figures 1 and 3, and other emission data are summarized in Table III. Plots of emission intensity at a given wavelength against pH show one inflection point, e.g., Figures 2 and 4, and such data along with the emission lifetimes of protonated and deprotonated forms under the conditions of the experiment allow evaluation of pK_a^*, the overall two-proton excited state dissociation constant. The values of pK_a^* determined from the luminescence titrations are included in Table II. Also included in Table II are the calculated values of pK_a^* from the measured values of pK_a and the emission maxima.[13]

The data in Table II clearly show that the excited species are stronger acids than their ground-state counterparts. The change in the value of the overall dissociation constant is very substantial and much larger than the change previously reported[1] for Ru(2,2′-bipyridine)$_2$(4,4′-dicarboxylate-2,2′-bipyridine). Also, there is a fairly large discrepancy between the calculated values of pK_a^* and those calculated from the emission maxima. In part at least, this discrepancy must be a consequence of the fact that we have not used the 0–0 band position of the emission in the calculation; with the featureless emission there is no unequivocal way to assign its position from the room temperature spectrum.

3. Optical Spectral Assignments. In order to interpret the increased acidity of the complexes upon photoexcitation, it is necessary to assign the optical spectra. First, from the data in Table I we find a number of absorptions in the UV and visible range. Of paramount interest is the nature of the lowest excited state. The high-energy bands with molar absorptivities in the range of 60 000 L mol^{-1} cm^{-1} are attributable to intraligand $\pi \rightarrow \pi^*$ excitations of phenanthroline and bipyridine ligand systems. The lowest absorption maximum, in the range

Table I. Electronic Absorption Spectral Band Maxima for [L$_2$Ru(4,7-dihydroxy-1,10-phenanthroline)]$^{2+}$ Complexes[a]

L	solvent	band max, nm
2,2′-bipyridine	aqueous—pH 1	253 (70 550), 288 (65 280), 445 (12 900), 460 (12 600)
	aqueous—pH 13	258 (71 460), 292 (66 385), 370 (18 700), 450 (9700), 495 (10 000)
4,4′-dimethyl-2,2′-bipyridine	aqueous—pH 1	245 (62 275), 288 (61 800), 440 (13 550), 460 (13 550)
	aqueous—pH 13	248 (65 100), 292 (59 750), 375 (17 500), 445 (10 100), 500 (9720)
1,10-phenanthroline	aqeuous—pH 1	255 (76 800), 263 (78 800), 425 (16 700), 455 (15 000)
	aqueous—pH 13	252 (74 175), 268 (75 750), 385 (14 750), 428 (15 600), 490 (12 380)
3,4,7,8-tetramethyl-1,10-phenanthroline	aqueous—pH 1	255 (75 600), 270 (94 100), 425 (18 500), 450 (16 700)
	aqueous—pH 13	272 (89 800), 477 (13 750), 428 (15 600), 492 (13 200)

[a] All data were recorded at 298 K using 1.0-mm path length cells.

425–505 nm, with a molar absorptivity in the range of 10 000–20 000 L mol^{-1} cm^{-1}, is logically attributable to a Ru(II) → ligand CT absorption following the assignment of earlier workers for [Ru(bpy)$_3$]$^{2+}$ and related complexes and for species such as Ru(bpy)$_2$Cl$_2$.[14] In fact, the first absorption in pH ≈1 solutions is very close, in position, appearance, and intensity, to that for [Ru(phen)$_3$]$^{2+}$ and [Ru(bpy)$_3$]$^{2+}$.

What is remarkable is the substantial red shift of the first maximum in going from acidic to basic solution. The assignment of the first absorption in the basic solution is still Ru(II) → ligand CT, but owing to the deprotonation of 4,7-dihydroxy-1,10-phenanthroline, the three ligands are no longer nearly equivalent. Deprotonation of the complex results in a situation where resonance structure (b) in eq 1 apparently contributes significantly. ^{1}H NMR studies show that in going from acidic to basic media the complexes do undergo a large change in electronic structure: in the protonated form the aromatic protons give a complex signal in the range τ 1.2–3.0 and upon deprotonation two doublets appear (integration 1:1) significantly upfield, in the range τ 3.2–3.9. These two doublets are attributable to the protons in the 2,3 and 8,9 positions of the deprotonated 4,7-dihydroxy-1,10-phenanthroline in resonance structure (b). Given that (b) is a significant contributor to the ground-state structure, we conclude that the deprotonated 4,7-dihydroxy-1,10-phenanthroline can function as a π donor. Note that in (b) the electron density on the N atoms is in an orbital of π symmetry for strong interaction with the dπ orbitals on Ru. We assign the lowest energy spectral bands to Ru(dπ)^6 → Lπ^*CT (L = 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, 1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline). The deprotonated 4,7-dihydroxy-1,10-phenanthroline can clearly participate in the CT to some extent, but the key role of this ligand is as a π donor such that the resulting CT state is stabilized by π donation to the hole on Ru from deprotonated 4,7-dihydroxy-1,10-phenanthroline. The decrease in electron density in the π-donor ligand accounts

Table II. Excited State Properties of $[L_2Ru(4,7\text{-dihydroxy-1,10-phenanthroline})]^{2+}$ Complexes and Their Conjugate Bases

L	$pK_a \pm 0.1$ [a]	$pK_a^* \pm 0.1$ [b]	emission max, $cm^{-1} \times 10^{-3}$ (lifetime, ns) [c]		
			protonated	deprotonated	pK_a^* (calcd) [d]
bpy	10.1	5.1	15.34 (350)	13.70 (33)	6.7
4,4′-Me_2bpy	10.0	5.4	15.20 (280)	13.55 (42)	6.5
phen	10.0	4.7	15.75 (650)	13.91 (150)	6.1
3,4,7,8-Me_4phen	9.8	5.6	15.90 (600)	13.95 (400)	6.1

[a] Observed pK_a from spectrophotometric titration curves; pK_a is twice the pH at the inflection point in the curve. [b] Observed pK_a^* from luminescence titration curves and emission lifetimes. $pK_a^* = 2pH + \log [(\tau \text{ protonated})/(\tau \text{ deprotonated})]$ where the pH is taken at the inflection point in the luminescence titration curve and the lifetimes are those given for the protonated and deprotonated forms under the conditions of the titration. [c] Corrected emission maxima; luminescence lifetimes are for air-saturated solutions, i.e., they are measured under the same conditions as for the luminescence titrations. [d] Calculated from the relationship given in ref 1 and 13 using the emission maxima and the value of pK_a.

Table III. Excited State Properties for $[L_2Ru(4,7\text{-dihydroxy-1,10-phenanthroline})]^{2+}$ Complexes

L	T, K	solvent	emission max, $cm^{-1} \times 10^{-3}$ (lifetime, ns) [a]		luminescence quantum yield ± 25% [b]	
			protonated	deprotonated	protonated	deprotonated
2,2′-bipyridine	298	H_2O	15.34 (455)	13.70 (38)	0.01	0.001
2,2′-bipyridine	298	D_2O	15.34 (800)	13.70 (76)	0.02	0.002
2,2′-bipyridine	77	EtOH	16.75	15.25	0.27	0.02
			15.50 (3900)	(1200)		
			13.90	13.80		
1,10-phenanthroline	298	H_2O	15.75 (1250)	13.91 (175)	0.04	0.003
1,10-phenanthroline	298	D_2O	15.75 (2100)	13.91 (310	0.07	0.006
1,10-phenanthroline	77	EtOH	16.95	15.40	0.38	0.01
			15.90 (3000)	(1000)		
			14.20	14.20		
4,4′-dimethyl-2,2′-bipyridine	298	H_2O	15.20 (340)	13.55 (49)	0.01	0.001
4,4′-dimethyl-2,2′-bipyridine	298	D_2O	15.20 (610)	13.55 (93)	0.02	0.002
4,4′-dimethyl-2,2′-bipyridine	77	EtOH	16.80	15.30	0.15	0.01
			15.45 (10 500)	(2000)		
			14.00	13.80		
tetramethyl-1,10-phenanthroline	298	H_2O	15.90 (1250	13.95 (650)	0.03	0.003
tetramethyl-1,10-phenanthroline	298	D_2O	15.90 (2250	13.95 (1100	0.05	0.005
tetramethyl-1,10-phenanthroline	77	EtOH	16.95	15.35	0.39	0.002
			15.60 (11 000)	(3500)		
			14.10	13.80		

[a] Corrected emission maxima; luminescence lifetimes are for rigorously degassed solutions. [b] Luminescence quantum yields are measured relative to rhodamine B in EtOH, and corrected for refractive index of solvent.

for the increase in acidity upon excitation of the complexes. Species like *cis*-$Cl_2Ru(bpy)_2$ have lowest Ru → bpy CT bands significantly to the red of $[Ru(bpy)_2]^{2+}$;[15] the Cl^- ligands are bona fide π-donor ligands and produce the effect we find for deprotonated 4,7-dihydroxy-1,10-phenanthroline. That remote proton transfer can have a large effect on the position of a MLCT state is demonstrated by the absorption spectral changes accompanying the protonation of the coordinated CN^- ligands in *cis*-$(CN)_2RuL_2$ complexes,[16,17] *Thus, the increased acidity in the complexes is a consequence of Ru(II) → ligand CT principally to ligands not involved in the proton transfer; there is a net drain of electron density from the deprotonated 4,7-dihydroxyphenanthroline in the excited state via electron donation to the hole of π symmetry on the Ru.*

Some additional features of the optical spectra are noteworthy; consider the 298 and 77 K spectra of the complexes in Figure 5. The features of the protonated complexes in the low-energy region are quite similar to those for $[Ru(bpy)_3]^{2+}$ itself. Further, the emission properties in solution at 298 and at 77 K are similar for the protonated species and $[Ru(bpy)_3]^{2+}$ (Table III and Figures 1, 3, and 6). In comparing the emission properties note the emission quantum yields and the degree of structure at 77 K. All of these spectral features support the conclusion that the protonated form of the $[L_2Ru(4,7\text{-dihydroxy-1,10-phenanthroline})]^{2+}$ complexes behaves like a slightly perturbed $[RuL_3]^{2+}$ species. However, for the deprotonated form, the absorption and emission spectral properties are qualitatively different: the emission yields are much lower and the low-temperature spectrum is less structured; the absorption spectra of the deprotonated species clearly show a substantive perturbation of the $[RuL_3]^{2+}$ behavior. Some aspects of the absorption spectra of the deprotonated species are quite similar to those for *cis*-$Cl_2Ru(bpy)_2$, but the changes upon cooling from 298 to 77 K are quite different (Figure 5). At this point, we do not have a detailed understanding of the spectral changes accompanying the change in temperature, but the fact remains that the lowest excited state (from the emission position) is much lower in energy than for the protonated species (Table III and Figure 6).

Since the low-temperature optical spectra are sharper than those at room temperature, there exists a better prospect for assigning the 0–0 band positions. Unfortunately, though, there is a long tail on the 77 K absorptions which precludes an accurate location of the 0–0 band in these cases. Calculation of pK_a^* values using the highest energy emission maxima at 77 K and the value of pK_a gives a value of pK_a^* which is more in error than the calculation using the 298 K emission maxima. In the absence of emission, pK_a^* values have been calculated from pK_a and the absorption maxima of the protonated and deprotonated forms;[18] such values are likely to be inaccurate, owing to the noncoincidence of the 0–0 band and the absorption

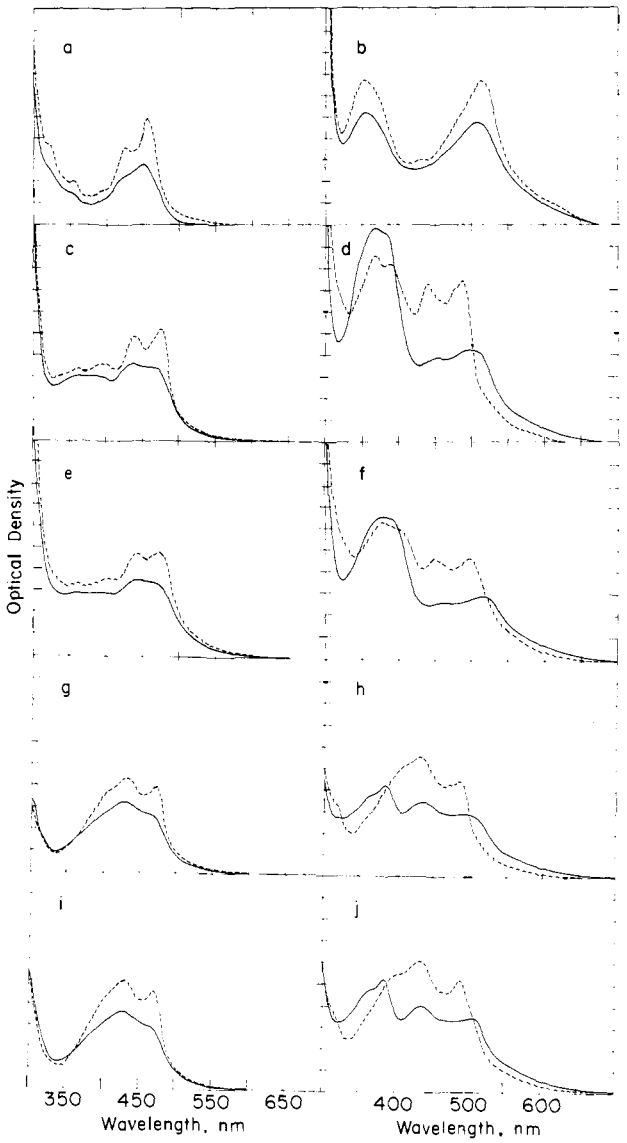


Figure 5. Absorption spectra at 298 (—) and 77 K (- - - -) in C_2H_5OH solution for (a) $[Ru(bpy)_3]^{2+}$; (b) *cis*-$Cl_2Ru(bpy)_2$; (c) [(4,7-dihydroxy-1,10-phenanthroline)$Ru(bpy)_2]^{2+}$ and its deprotonated form, (d); (e) [4,7-dihydroxy-1,10-phenanthroline)Ru(4,4′-dimethyl-2,2′-bipyridine)$_2]^{2+}$ and its deprotonated form, (f); (g) [(4,7-dihydroxy-1,10-phenanthroline)Ru(1,10-phenanthroline)$_2]^{2+}$ and its deprotonated form, (h); and (i) [(4,7-dihydroxy-1,10-phenanthroline)Ru(3,4,7,8-tetramethyl-1,10-phenanthroline)$_2]^{2+}$ and its deprotonated form (j). Spectra are not corrected for solvent contraction upon cooling from 298 to 77 K; band positions and absorptivities are given in Table I.

maximum. But also, the absorptions in Ru(II) complexes are to excited states which have considerable singlet character, whereas the lowest excited states have considerable triplet character. For the emissive pairs the measurement of pK_a^* is a *direct* measure of the equilibrium in the lowest (emissive) excited state.

The comparison of 298 K emission properties in D_2O and H_2O of the complexes reveals that both the emission quantum yield and lifetime are approximately a factor of 2 greater in D_2O compared to H_2O. Interestingly, nearly the same effect is found for $[Ru(bpy)_3]^{2+}$;[19] such data were taken to reflect a significant component of intermolecular coupling of the excited state to solvent vibrational modes. The effect we find for the 4,7-dihydroxy-1,10-phenanthroline complexes suggests that there is no special role for the –OH substituent in the phenanthroline ring in nonradiative decay, despite the fact that the O–H stretch is the highest energy vibrational mode in the complex.

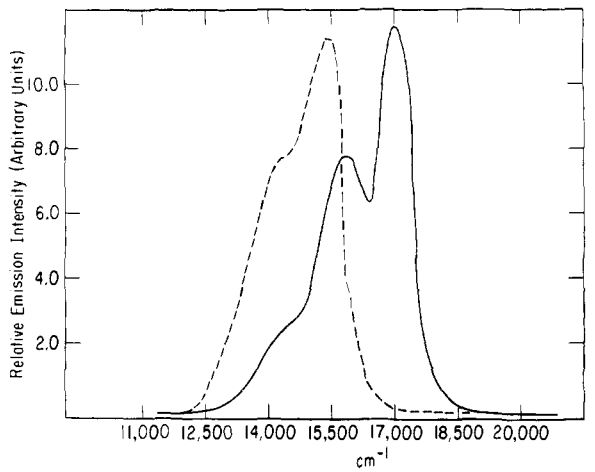


Figure 6. Emission of protonated (highest energy) and deprotonated [(4,7-dihydroxy-1,10-phenanthroline)Ru(3,4,7,8-tetramethyl-1,10-phenanthroline)$_2]^{2+}$ in EtOH solution at 77 K. Spectra are corrected for variation in detector sensitivity with wavelength but are not plotted on the same sensitivity; cf. Table III for quantum yield and emission maxima.

Experimental Section

Solvents. Acetonitrile, ethanol, and methanol used for spectroscopic studies were commercially available in spectroscopic grade. All other solvents were used as commercially available either as reagent or analytical grade; distilled water was used for all studies in aqueous solvent.

Ligands. 2,2′-Bipyridine, 1,10-phenanthroline, and related ligands were commercially available from either Aldrich or G. F. Smith Chemical Co. and were used as provided, or, if necessary, filtered before use to remove insoluble impurities.

Preparation and Purification of Starting Materials. Synthesis of *cis*-Cl_2RuL_2 Compounds. The synthesis of *cis*-Cl_2RuL_2 compounds where L = 2,2′-bipyridine, 1,10-phenanthroline, 4,4′-dimethyl-2,2′-bipyridine, or 3,4,7,8-tetramethyl-1,10-phenanthroline all follow the same procedure described for the synthesis of $Ru(bpy)_2Cl_2 \cdot 2H_2O$.

Commercial ruthenium trichloride (Alfa-Ventron) (1.56 g, 5.97 mmol) and 2,2′-bipyridine (Aldrich) (1.87 g, 12.0 mmol) were refluxed together in dimethylformamide (~60 mL) for 3 h. The solvent was then reduced and the sample was cooled in an ice bath for several hours. The resulting solid was collected by filtration and washed several times with cold water. Final purification was achieved by recrystallization from an aqueous solution treated with 30 g of LiCl. The product precipitate was collected by suction filtration, washed well with several portions of cold water, and dried under vacuum. The dark, nearly black, microcrystalline product, $Ru(bpy)_2Cl_2 \cdot 2H_2O$, is formed in 68% yield (2.11 g). Product purity was determined by comparison of its electronic spectrum with published reports.[15]

Synthesis of L_2Ru(4,7-dihydroxy-1,10-phenanthroline)$(PF_6)_2$ Compounds. The synthesis of [L_2Ru(4,7-dihydroxy-1,10-phenanthroline)]$^{2+}$ compounds where L = 2,2′-bipyridine, 1,10-phenanthroline, 4,4′-dimethyl-2,2′-bipyridine, or 3,4,7,8-tetramethyl-1,10-phenanthroline follows the procedure described for $Ru(bpy)_2$(4,7-dihydroxy-1,10-phenanthroline)$(PF_6)_2$.

$Ru(bpy)_2Cl_2 \cdot 2H_2O$ and 4,7-dihydroxy-1,10-phenanthroline (G. F. Smith) previously dissolved in 1 M NaOH aqueous solution and filtered to remove solid impurities were refluxed together in EtOH/1.0 M NaOH aqueous solution, 50/50 by volume. The dark red solution was then neutralized to pH 6 and excess ligand filtered off. The product was then isolated by precipitation from a pH 2 aqueous solution by addition of concentrated aqueous NH_4PF_6. The complex was further purified by precipitation from an acetone solution by addition of concentrated aqueous NH_4PF_6. The complex was further purified by precipitation from an acetone solution by addition of an acidic (pH 2) aqueous solution of dilute NH_4PF_6. Final purification was achieved by chromatographing on Sephadex LH-20 (Pharmacia Fine Chemicals) eluting with acetone. The elemental analysis (Alfred Bernhardt, West Germany) is satisfactory. Anal. Calcd: C, 41.96; N, 9.18; H, 2.62. Found: C, 42.20; N, 9.30; H, 2.78.

Techniques. Spectra. All electronic spectra were recorded using a Cary 17, and low-temperature spectra were obtained using an all-

quartz liquid N_2 Dewar equipped with optical quality flats for windows.

All luminescence spectra were recorded using an Aminco-Bowman spectrophotofluorometer set for emission measurements in the 300–900-nm range and equipped with a grating blazed at 750 nm. The detectors used were either a Hamamatsu R136 PMT operated at 780 V and 25 °C or an RCA 7102 PMT operated at 1400 V and cooled with a dry ice/2-propanol bath. Both the emission and excitation monochromators were calibrated using a low-pressure Hg lamp. The relative sensitivity of the entire detection system (and for both PMT detectors) has been calibrated in the 300–600-nm range using the rhodamine B quantum counter[20] and over the entire 300–900-nm range by a standard lamp obtained from and calibrated by E,G, & G, Inc., Salem, Mass. The standard lamp is a 200-W tungsten halogen lamp operated at 6.5 A having serial no. B115A and calibrated from NBS standards QM 197, QM 198, and QM 199. The relative intensity of the excitation source (150-W xenon lamp) as a function of wavelength was determined by monitoring the front surface emission at 630 nm of an ethanol solution of rhodamine B.[20]

Luminescent Lifetimes. Luminescent lifetimes, τ, were measured using a TRW Model 75A decay time fluorometer equipped with a Xenon Corp. nanopulser excitation source. The Hamamatsu R446 UR PMT detector was powered by a Kepco Model 2500 ABC regulated high-voltage supply. Output from the PMT following the excitation pulse was monitored by a Tektronix 453 oscilloscope and recorded with a Polaroid camera. Lifetimes shorter than ~200 ns were determined by comparing the luminescence intensity in rigorously degassed, air-saturated, and oxygen-saturated solutions. A quenching constant of 3×10^9 M s^{-1} for O_2 quenching was assumed and the O_2 concentration was determined by quenching a complex whose lifetime could be measured directly in the same solvent system.[6] For the pK_a* determinations only the ratio of lifetimes is needed; the absolute lifetime by this technique are ±20%. Luminescent lifetimes which can be measured directly show excellent agreement with values obtained via the quenching method. Plots of log (emission intensity) vs. time are linear and the value of τ is taken as the time required for the luminescent intensity to decay in $1/e$ of its original value. All luminescent lifetimes are the average of at least three measurements.

^{1}H NMR Spectra. All ^{1}H NMR spectra were recorded using either the Perkin-Elmer R20B or R22 at 60 or 90 MHz, respectively. Samples were prepared in Me_2SO-d_6 (Merck Sharp and Dohme) and deprotonated using LiOD. NMR tubes were Willmad grade 256 or better.

Measurement of pH. The pH values of the aqueous solutions were measured with a Corning Model 7 pH meter equipped with a Fisher microprobe combination electrode. Calibration of the apparatus was achieved using pH buffers at pH 4.0, 7.0, and 10.0. The instrument was checked several times during the course of an experiment. Equivalence titrations were determined for several of the $[L_2Ru(4,7\text{-dihydroxy-}1,10\text{-phenanthroline})]^{2+}$ complexes, and in all cases the equilibrium was shown to be a two-proton process. For a typical equivalence titration, ~100 mg of the metal complex was dissolved in a 10% MeOH–90% H_2O solution and titrated with 0.01 M NaOH which had been standardized immediately prior to use.

Evaluation of Ground and Excited State Acid Dissociation Constants. For all compounds the ground-state and excited-state pK_as were determined in the same manner; a typical experiment is described. $[(bpy)_2Ru(4,7\text{-dihydroxy-}1,10\text{-phenanthroline})]^{2+}$ (~5 mg) is dissolved in a minimum amount of MeOH and then diluted to ~100 mL with distilled H_2O and filtered to remove any undissolved solid, and the volume adjusted with H_2O to make the optical density of the Ru → LCT absorption ~0.8 ODU. Emission intensity was measured exciting at one of the isosbestic points. The pH was monitored continuously and varied by adding small amounts of concentrated aqueous HCl or NaOH. At a set pH reading, a 3-mL aliquot is removed from the solution and both its electronic absorption and emission spectra are recorded. Isosbestic points in the electronic spectra, when they occur, are maintained throughout the experiment. Stability of the Aminco is confirmed by using a standard solution and determining its emission intensity several times during the experiment.

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