J. Am. Chem. Soc. **1987**, *109*, 4895-4901

Unique Spectroscopic Properties of Mixed-Ligand Complexes with 2,2′-Dipyridylamine: A Dual Luminescence from a Ruthenium(II) Complex

Richard L. Blakley and M. Keith DeArmond*

Contribution from the Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204. *Received November 28, 1986*

Abstract: The 77 K absorption, emission, excitation, photoselection, and time-resolved emission spectra and emission lifetimes were obtained in aprotic and protic systems for the series of complexes $[Ru(bpy)_n(HDPA)_{3-n}]^{2+}$ (n = 0–3) and $[Ru(phen)_n(HDPA)_{3-n}]^{2+}$ (n = 0–3). The n = 2 species have d–π* MLCT emission characteristics indicative of the Ru–bpy and Ru–phen chromophores as do the n = 1 species in water, but in weak hydrogen-bonding solvents, as well as aprotic solvents, a second emission is observed producing a dual luminescence for the n = 1 species. This second emission is assigned to an n_{HDPA}–π_{bpy}^* (or n_{HDPA}–π_{phen}^*) interligand charge-transfer (ILCT) process. The absorption spectra for the deprotonated species $[Ru(bpy)_n(DPA^-)_{3-n}]^{(n-1)+}$ (n = 1, 2) were also obtained, and the absence of emission up to 800 nm for these complexes is discussed in terms of available emitting states and metal perturbations.

Two limiting cases are possible for the description of the emitting manifold of the MLCT luminescent orbital of $[Ru(bpy)_3]^{2+}$ and related ML_3^{n+} complexes: (1) a delocalized orbital in which the optical orbital extends over the electronic systems of all three bpy ligands and the metal or (2) a single chelate ring orbital in which the optical orbital involves a single bpy ring and the metal. The delocalized limit uses the D_3 symmetry of the ground-state molecule to describe the excited states so that a manifold of three spin–orbit states of A_2, E, and A_1 symmetry results.[1] In the single chelate ring localized orbital case, the molecule is considered a trimer containing three equivalent Ru–bpy chromophores; therefore, the excited state has an effective C_2 symmetry.[2-7]

One of the predictions of the localized orbital model is that $[Ru(bpy)_3]^{2+}$ has a multiple-state emission since each Ru–bpy chromophore of the trimer has an identical emitting state. Since emission from each of these states is identical, the emission cannot be time or energy resolved. But since isolated excited states exist for each ligand, mixed-ligand complexes may have a detectable dual emission. Indeed, a π–π* emission from *both* phen and bpy ligands is observed in $[Rh(phen)_{3-n}(bpy)_n]^{2+}$ (n = 1, 2).[8] A similar type of dual emission has also been observed for hetero bis-chelated Ir^{III} complexes where composite emission spectra of the parent homo bis chelates can be measured.[9,10] This type of multiple luminescence has been described as "spatially isolated" since the wave function of each emitting excited state is localized on a single chelate ring. In this case Kasha's rule[11] is not violated, since the dual emissions are best considered as arising from two nearly degenerate excited states in a "composite molecule".

A second type of multiple luminescence, "distinct orbital" type, occurs from states of distinct orbital origin, i.e., d–d* and d–π* or d–d* and π–π*. The first such multiple emission was reported for the $[Ir(phen)_2Cl_2]^+$ complex[12,13] and was corroborated by photoselection spectroscopy.[14] Other examples include the d–d* charge-transfer (CT) emissions from each of four tris sulfur chelates (two Rh^{III} and two Ir^{III})[15] CT and n–π* emissions for Re^{I} carbonyl complexes,[16,17] CT and π–π* emissions for Cu^{I} complexes with triphenylphosphine,[18,19] and d–d* and π–π* emissions from $[Rh(phen)_3]^{2+}$.[20]

Even though $[Ru(bpy)_3]^{2+}$ has been shown to have a single-ring MLCT emission, no bona fide dual emission has been reported for a Ru(II) complex to date.[21-23] Data obtained for $[Ru(phen)_{3-n}(bpy)_n]^{2+}$ (n = 1, 2) indicate no resolution of the two MLCT emission bands is possible since the energies, contours, and lifetimes are virtually identical.[24] (Recent results using time resolved photoselection have shown that the mixed bpy/phen complexes can be distinguished from the parent tris species and the data imply a dual emission does occur from these mixed complexes.[25]) In cases where the spectroscopic properties of the two ligands in the mixed-ligand complexes are sufficiently different to allow energy resolution of the two emissions, nonradiative relaxation frequently occurs from the higher energy chromophore to the lower energy chromophore consistent with Kasha's rule.

Since a dual emitting Ru(II) complex could have theoretical significance and also provide support for the localized excited-state model, a strategy was developed from the electrochemical[26] and spectroscopic[27] results of d^6 metal complexes with the ligand HDPA and its deprotonated form DPA^-. The complexes $[Ru(HDPA)_2(DPA^-)]^+$ and $[Ru(HDPA)(DPA^-)_2]^0$ give relatively strong emission at ~16 000 cm^{-1} (assigned LMCT) near the emission energy of the Ru–bpy chromophore (assigned MLCT),

---

[1] Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231.

[2] Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391.

[3] Carlin, C. M.; DeArmond, M. K. *Chem. Phys. Lett.* **1982**, *89*, 297.

[4] Carlin, C. M.; DeArmond, M. K. *Chem. Phys. Lett.* **1985**, *107*, 53.

[5] Milder, S. J.; Gold, J. S.; Kliger, D. S. *J. Phys. Chem.* **1986**, *90*, 548.

[6] Myrick, M. L.; Blakley, R. L.; DeArmond, M. K. *J. Am. Chem. Soc.* **1987**, *109*, 2841.

[7] DeArmond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325.

[8] Halper, W.; DeArmond, M. K. *J. Lumin.* **1972**, *5*, 225.

[9] Watts, R. J.; Brown, M. J.; Griffith, B. G.; Harrington, J. S. *J. Am. Chem. Soc.* **1975**, *97*, 6029.

[10] Watts, R. J.; Griffith, B. G.; Harrington, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 674.

[11] Kasha, M. *Discuss. Faraday Soc.* **1950**, *9*, 14.

[12] Watts, R. J.; White, T. P.; Griffith, B. G. *J. Am. Chem. Soc.* **1975**, *97*, 6914.

[13] Watts. R J.; Missimer, D. *J. Am. Chem. Soc.* **1978**, *100*, 5350.

[14] DeArmond, M. K.; Huang, W. L.; Carlin, C. M. *Inorg. Chem.* **1979**, *18*, 3388.

[15] Merrill, J. T.; DeArmond, M. K. *J. Am. Chem. Soc.* **1979**, *101*, 2045.

[16] Giordano, P. J.; Fredericks, S. M.; Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 2257.

[17] Fredricks, S. M.; Luang, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7415.

[18] Buckner, M. T.; Matthews, T. G.; Lytle, F. E.; McMillan, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 5846.

[19] Segers, D. P.; DeArmond, M. K.; Grutch, P. A.; Kutal, C. *Inorg. Chem.* **1984**, *23*, 2874.

[20] Indelli, M. T.; Carioli, A.; Scandola, F. *J. Phys. Chem.* **1984**, *88*, 2685.

[21] Belser, P.; von Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Chem. Phys. Lett.* **1984**, *104*, 100. This reference indicates in detail why the results of ref 22 and 23 cannot describe a bona fide dual emission for Ru(II) complexes.

[22] Cocks, A. T.; Wright, R.; Seddon, K. R. *Chem. Phys. lett.* **1982**, *85*, 369.

[23] Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A. *Israel J. Chem.* **1982**, *22*, 87.

[24] Crosby, G. A.; Elfring, W. H., Jr. *J. Am. Chem. Soc.* **1976**, *80*, 2206.

[25] Blakley, R. L.; DeArmond, M. K.; Myrick, M. L.; Arthur, Matt L. *J. Am. Chem. Soc.*, submitted for publication.

[26] Morris, D. E. Ohsawa, Y.; Segers, D. P.; DeArmond, M. K.; Hanck, K. W. *Inorg. Chem.* **1984**, *23*, 3010.

[27] Segers, D. P.; DeArmond, M. K. *J. Phys. Chem.* **1982**, *86*, 3768.

0002-7863/87/1509-4895$01.50/0

but the ligands HDPA and bpy in the complex have very different redox properties. Therefore, mixed-ligand complexes of bpy and HDPA were synthesized to determine if a dual emitting complex could be identified. The success of this approach led to a communication from this laboratory in which a dual emission from a Ru(II) system[28] was reported. This paper describes in more detail the properties of the dual emitting $[Ru(bpy)(HDPA)_2]^{2+}$ ($n = 1$) complex and in addition gives information on the $[Ru(bpy)_2(HDPA)]^{2+}$ ($n = 2$) species, the DPA^- complexes, and the phen analogues.

Experimental Section

A. Materials. Chemicals used in the preparation of the complexes were $RuCl_3 \cdot xH_2O$, 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and 2,2′-dipyridylamine (HDPA) from Fisher Scientific Co. HDPA was recrystallized from toluene, and bpy and phen were crystallized from MeOH prior to use.

The room temperature absorption spectra and the 77 K emission spectra were obtained in acetone (DMK), dimethyl sulfoxide (Me_2SO), CH_2Cl_2, $CHCl_3$, 2-propanol (2-PrOH), ethanol (EtOH), methanol (MeOH), H_2O, and EtOH/MeOH (4:1 by volume). EtOH/MeOH (4:1) was also used for the 77 K absorption and photoselection spectra. The 77 K absorption spectra were also obtained in 2-PrOH and EtOH, and the 77 K excitation spectrum was obtained in 2-PrOH. The solvent CH_3CN was used for the 77 K emission studies of the deprotonated species (vide infra).

Ethanol was purified by the method of Halper,[29] and water was purified by distillation. Acetonitrile (CH_3CN) was distilled three times from P_2O_5 and stored in a nitrogen atmosphere glovebox. Spectroanalyzed DMK, Me_2SO, CH_2Cl_2, $CHCl_3$, MeOH, and 2-PrOH were used as received from Fisher Scientific Co.

The complexes $[Ru(bpy)_n(HDPA)_{3-n}](ClO_4)_2$ ($n = 1, 2$) were available from previous work, and synthetic details are given elsewhere.[26] An alternative method for the synthesis of the $n = 1$ species involving $K[Ru(bpy)Cl_4]$ as an intermediate was also employed.[30] After purification of the intermediate on Sephadex LH-20 in MeOH, it was refluxed 4 h in EtOH with 20% excess HDPA. Precipitation by a metathesis reaction from an aqueous solution yielded the perchlorate salt of the tris-chelated mixed-ligand complex.

The series $[Ru(bpy)_n(DPA^-)_{3-n}](ClO_4)_{n-1}$ ($n = 1, 2$) were synthesized by using methods previously reported,[26] and the complexes $[Ru(phen)_n(HDPA)_{3-n}]^{2+}$ ($n = 1, 2$) were synthesized by using methods analogous to the bpy analogues.

Purity of the protonated complexes was assured by five successive recrystallizations from MeOH/2-PrOH mixtures and column chromatography using Sephadex LH-20 in MeOH and in EtOH, yielding only one band in each case. Excitation wavelength independent 77 K emission spectra in all solvents for $[Ru(bpy)_2(HDPA)]^{2+}$ and in H_2O for $[Ru(bpy)(HDPA)_2]^{2+}$ again indicate the purity of the complexes.

Elemental analysis was performed by Atlantic Microlab, Inc., Atlanta, GA. Anal. Calcd for $[Ru(bpy)(HDPA)_2](ClO_4)_2$: C 45.12; H, 3.28; N, 14.03. Found: C, 45.21; H, 3.31; N, 14.00.

B. Spectroscopic Measurements. Room- and low-temperature (77 K) absorption spectra were done with a Cary 2300 spectrometer using an Oxford Instruments Model DN1704 cryostat.

Low-temperature (77 K) emission and excitation spectra were obtained with an Aminco-Bowman spectrophotofluorometer. The excitation source was a Hanovia 200-W Hg-Xe lamp, and a Hammamatsu R955 photomultiplier tube (PMT) was used for detection. Spectra were not corrected for PMT or monochromator response, and the intensities of the time-resolved emission data, as well as the intensities of the excitation spectra, are not on the same scale.

Polarization spectra were measured with a high-resolution photoselection spectrometer.[31]

Emission decay curves and time resolved emission spectra were obtained by using a Princeton Applied Research (PAR) Model 162 boxcar averager with two Model 164 gated integrators. A Molectron DL-II tunable dye laser pumped by a Molectron model UV-12 pulsed $N_2(g)$ laser was employed as the excitation source. Detection of the emission was accomplished with a 3/4-m No. 1800 Czerny-Turner spectrometer (Spex Industries, Inc.) equipped with a Hamamatsu R955 PMT. Lifetimes were calculated by a published method.[32]

Table I. 77 K Absorption Bands in EtOH for Protonated Complexes

complex	λ,^{a} nm	$10^{-3}E$ cm^{-1}	$10^{-3}\epsilon$ M^{-1} cm^{-1}
$[Ru(HDPA)_3]^{2+}$	348 (s)^b	28.7	11.3
	383 (s)^b	26.1	10.3
	436 (sh)	22.9	3.23
$[Ru(bpy)_3]^{2+}$	320 (sh)	31.2	8.10
	344 (s)	29.1	4.39
	392 (sh)	25.5	3.08
	^{b}426 (s)	23.5	8.75
	^{b}455 (s)	22.0	12.4
$[Ru(bpy)(HDPA)_2]^{2+}$	356 (ba)^b	28.1	11.0
	433 (s)^c	23.1	4.19
	463 (s)^c	21.6	5.32
	506 (b)^d	19.8	3.12
$[Ru(bpy)_2(HDPA)]^{2+}$	350 (s)^b	28.6	9.70
	395 (s)	25.3	4.72
	425 (s)^c	23.5	6.08
	457 (sh)^c	21.9	6.84
	466 (s)^c	21.5	7.00
	512 (sh)^d	19.5	3.40

^{a} Abbreviations: s, sharp; sh, shoulder; ba, broad asymmetric; and b, broad. ^{b} Intense spin-allowed transitions involving HDPA. ^{c} Intense spin-allowed transitions involving bpy. ^{d} New transition only present in mixed-ligand species.

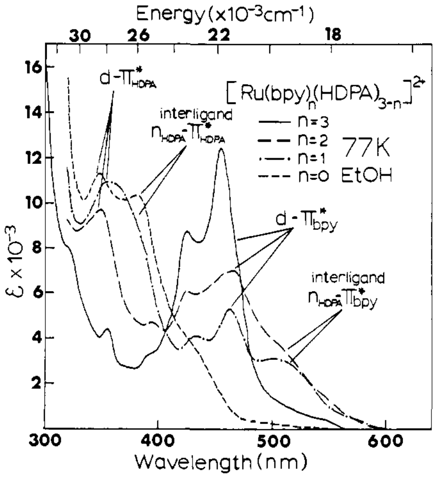

Figure 1. The 77 K absorption spectra in EtOH for the series $[Ru(bpy)_n(HDPA)_{3-n}]^{2+}$ (n = 0–3). Assignments for the absorption bands are made as shown (see text).

Results

Spectroscopy of Protonated Species. A. Absorption Spectra. The 30 000–24 000 cm^{-1} Region. The 77 K absorption transitions observed in the series $[Ru(bpy)_n(HDPA)_{3-n}]^{2+}$ (n = 0–3) in EtOH are given in Table I and Figure 1. Intense spin-allowed absorption bands characteristic of each of the two chromophores can be identified by comparison with the parent compounds. For example, the dominant transitions in $[Ru(HDPA)_3]^{2+}$ ($n = 0$) are at 28 700 and 26 100 cm^{-1}. The $[Ru(bpy)(HDPA)_2]^{2+}$ ($n = 1$) complex has a band at 28 100 cm^{-1} which is broad and asymmetric, indicating the presence of the 26 100 cm^{-1} transition with diminished intensity. A sharp absorption band at 28 600 cm^{-1} is observed in $[Ru(bpy)_2(HDPA)]^{2+}$ ($n = 2$) with no indication of the 26 100 cm^{-1} absorption. The displacement of the spectrum of $[Ru(HDPA)_3]^{2+}$ ($n = 0$) from the isosbestic point at 24 700 cm^{-1} seems to indicate that the 26 100 cm^{-1} band is due to chromophore interaction. Since this transition has its highest intensity in $[Ru(HDPA)_3]^{2+}$ ($n = 0$), is diminished in $[Ru(bpy)(HDPA)_2]^{2+}$ ($n = 1$), and does not occur in $[Ru(bpy)_2(HDPA)]^{2+}$ ($n = 2$) or $[Ru(bpy)_3]^{2+}$ ($n = 3$), it must be due to the interaction of two HDPA ligands. Interaction would be more likely to occur in the

---

[28] Blakley, R. L.; Myrick, M. L.; DeArmond, M. K. *J. Am. Chem. Soc.* **1986**, *108*, 7843.

[29] Halper, W. Ph.D. Thesis, North Carolina State University, Raleigh, NC, 1973, p 12.

[30] James, B. R.; McMillan, R. S. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 838.

[31] Carlin, C. M.; Hanck, K. W.; DeArmond, M. K. *Rev. Sci. Instrum.* **1981**, *52*, 137.

[32] Huang, W. L.; Segers, D. P.; DeArmond, M. K. *J. Phys. Chem.* **1981**, *85*, 2080.

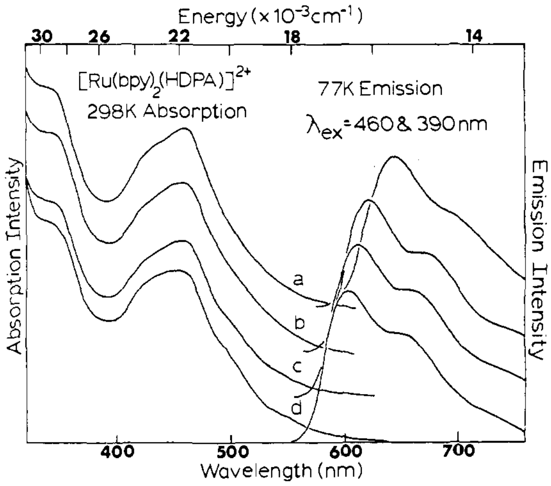

Figure 2. The room-temperature absorption and the 77 K emission spectra (using 460- and 390-nm excitations) for $[Ru(bpy)_2(HDPA)]^{2+}$ in the solvents (a) H_2O, (b) MeOH, (c) EtOH, and (d) 2-PrOH. The intensity scales are offset for clarity.

$n = 0$ than the $n = 1$ species and explains the differences in the observed transition intensities.

The 24000–21000 cm^{-1} Region. The $[Ru(bpy)_3]^{2+}$ ($n = 3$) complex has intense absorption peaks at 23 500 and 22 000 cm^{-1} assigned to metal to ligand charge-transfer absorption.[33] These absorption bands for $[Ru(bpy)(HDPA)_2]^{2+}$ ($n = 1$) occur slightly red shifted at 23 100 and 21 600 cm^{-1}. These sharp absorptions observed in the $n = 3$ and $n = 1$ complex indicate only one type of bpy chromophore. The red shift in band maxima could be attributed to ligand perturbations on the d_π ground-state orbital[34,35] (due to ligand π-back-bonding ability) and/or interaction of the HDPA and bpy chromophores. The $[Ru(bpy)_2(HDPA)]^{2+}$ ($n = 2$) absorption spectrum consists of a sharp band with its peak at 23 500 cm^{-1} and a broad asymmetric band which is a composite of a 21 900 and a 21 500 cm^{-1} band. This broad, two-component absorption could indicate the presence of more than one type of bpy chromophore, one like that in the $n = 3$ species and the other perturbed by an HDPA interaction as in the $n = 1$ complex resulting in a red shift in its absorption.

The 21000–16000 cm^{-1} Region. A new absorption band is present (~19 700 cm^{-1}) in both mixed-ligand complexes ($n = 1$, 2) that is not present in either of the parent complexes ($n = 0$, 3). This absorption is at 19 800 cm^{-1} in the $n = 1$ complex and while broad, has comparable intensity to the Ru–bpy absorption. For the $n = 2$ species the new absorption is at 19 500 cm^{-1} and has diminished intensity when compared to the $n = 1$ complex. The absence of an isosbestic point in the region of 20 800 cm^{-1} implies that this new absorption is due to chromophore interaction, and since it only occurs in the mixed-ligand species, the interaction must be between bpy and HDPA. The intensity change for this transition between the $n = 1$ and $n = 2$ complexes could be due to an increase in the number of HDPA ligands in the complex, which would increase the number of HDPA interactions with bpy.

B. Solvent Perturbation. A solvent perturbation absorption study was done at room temperature for the mixed-ligand complexes to better characterize the new absorption band unique to these species. In the aprotic solvents DMK, Me_2SO, CH_2Cl_2, and $CHCl_3$, no change was observed in the position of the ~19 800 cm^{-1} absorption band in either the $n = 1$ or the $n = 2$ complex. When the hydrogen-bonding ability of the solvent was increased in the protic solvent series 2-PrOH, EtOH, MeOH, and H_2O, a blue shift of this band was induced in both complexes (Figures 2 and 3). A blue shift in the absorption band accompanying an increase in solvent hydrogen-bonding ability has been observed for n-π^* transitions in many aromatic N-heterocyclics.[36]

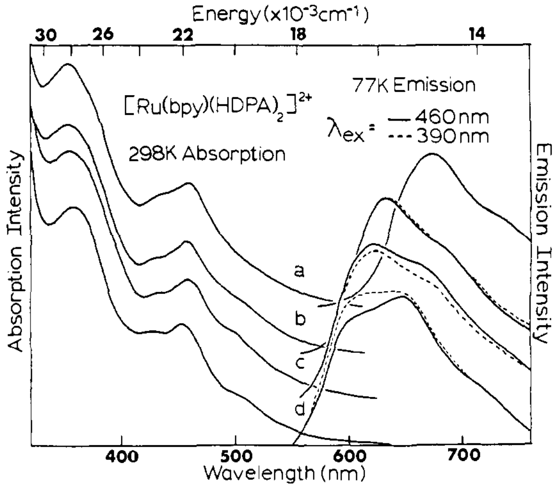

Figure 3. The room-temperature absorption and the 77 K emission spectra (using 460- and 390-nm excitations) for $[Ru(bpy)(HDPA)_2]^{2+}$ in the solvents (a) H_2O, (b) MeOH, (c) EtOH, and (d) 2-PrOH. The intensity scales are offset for clarity.

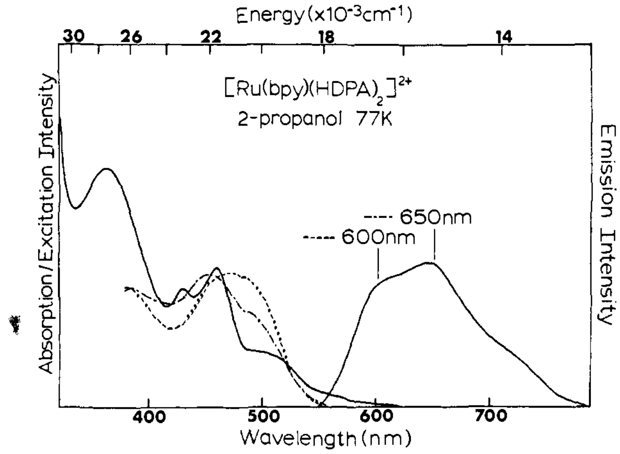

Figure 4. The 77 K absorption, excitation, and emission spectra in 2-PrOH for $[Ru(bpy)(HDPA)_2]^{2+}$. Excitation spectra are shown by using 600 (---) and 650 nm (– – –) emission monochromator settings.

C. **Emission/Excitation Data.** Emission spectra at 77 K were also obtained in the protic solvents (Figures 2 and 3). In each solvent tested the emission energy decreased as the number of HDPA ligands was increased in the complex, indicating d_π ground-state perturbations[34,35] and/or bpy–HDPA interactions are occurring. As the hydrogen-bonding ability of the solvents increased, the emission energy of the $n = 2$ species red-shifted, indicating differences in ground-state solvation,[37] but the emission remains excitation wavelength independent. The $n = 1$ species exhibited the same solvent dependence as the $n = 2$ complex; however, in the weaker hydrogen-bonding solvents EtOH and 2-PrOH, the $n = 1$ complex exhibits an additional emission band. The 77 K excitation spectra (Figure 4) of the $n = 1$ complex revealed that the new 16 800 cm^{-1} emission is associated with the new 19 800 cm^{-1} absorption band and is consistent with the occurrence of the new emission when the 19 800 cm^{-1} transition is present in the absorption spectrum.

The new low-energy absorption band was also present in the phen–HDPA complexes with analogous solvent dependence to the bpy complexes. Emission characteristics were also virtually identical with the bpy complexes, and maxima are listed in Table II.

D. Lifetimes. Lifetimes of the complexes were obtained at the emission maximum and at the shoulder (Table II). In all solvents, the emission lifetimes for the $n = 2$ complex were comparable to

---

(33) Lytle, F. E.; Hercules, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 253.
(34) Mabrouk, P. A.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 526.
(35) Rillema, D. P.; Allen, G.; Meyer, T. J. *Conrad, D.* **1983**, *22*, 1617.
(36) Kasha, M. Radiation Research, Supplement 2, **1960**, 264–269.
(37) Kosower, E. M. *An Introduction to Physical Organic Chemistry*; Wiley: New York, 1968; p 321.

Table II. 77 K Emission Energies and Liftimes in Protic Solvents

complex	solv	λ,[a] nm	$10^{-3}E$, cm^{-1}	ε,[a] μs
$[Ru(bpy)(HDPA)_2]^{2+}$	H_2O	674 (m)	14.8	254 ± 0.89
		736 (sh)	13.6	
	EtOH	610	16.4	13.3 ± 0.5
		621 (m)	16.1	
		670 (m)	14.9	5.04 ± 0.3
		734 (sh)	13.6	
	2-PrOH	600 (m)	16.7	14.4 ± 0.7
		640 (m)	15.6	2.69 ± 0.07
		716 (sh)	13.9	
$[Ru(bpy)_2(HDPA)]^{2+}$	H_2O	645 (m)	15.5	2.91 ± 0.08
		670	14.9	2.71 ± 0.08
		703 (sh)		
	EtOH	610 (m)	16.4	4.60 ± 0.11
		655 (sh)	15.3	4.26 ± 0.09
	2-PrOH	600 (m)	16.7	5.33 ± 0.08
		650 (sh)	15.4	5.14 ± 0.13
$[Ru(bpy)_3]^{2+}$	H_2O	590 (m)	16.9	3.67 ± 0.14
		640 (sh)	15.6	3.70 ± 0.14
	EtOH	578 (m)	17.3	6.01 ± 0.15
		328 (sh)	15.9	7.34 ± 0.26
	2-PrOH	575 (m)	17.4	6.24 ± 0.13
		625 (sh)	16.0	5.70 ± 0.16
$[Ru(phen)(HDPA)_2]^{2+}$	H_2O	630	15.9	3.74 ± 0.10
		659 (m)	15.2	4.02 ± 0.11
		730 (sh)	13.7	
	2-PrOH	590	16.9	10.5 ± 0.19
		598 (m)	16.7	
		636 (m)	15.7	11.4 ± 0.38
		670	14.9	7.89 ± 0.44
		706 (sh)	14.2	
$[Ru(phen)_2(HDPA)]^{2+}$	H_2O	636 (m)	15.7	
		648	15.4	4.38 ± 0.08
		690 (sh)	14.5	4.19 ± 0.07
	2-PrOH	590	16.9	10.0 ± 0.27
		597 (m)	16.8	
		630 (sh)	15.9	8.85 ± 0.19
$[Ru(phen)_3]^{2+}$	H_2O	590	16.9	2.32 ± 0.08
		598 (sh)	16.7	
		635	15.7	3.42 ± 0.07
		648 (m)	15.4	
	2-PrOH	575 (m)	17.4	5.75 ± 0.40
		620 (sh)	16.1	5.98 ± 0.33

[a] Abbreviations: sh, shoulder; m, maximum. [b] Errors are the 95% confidence limits.

those of the $n = 3$ complex, indicating d–π_{bpy}* charge-transfer (CT) character. For the $n = 1$ species, the emission in H_2O and the lower energy emission in EtOH and 2-PrOH is characteristic of the d–π_{bpy} CT emission, while the lifetime of the new higher energy emission was approximately 3–5 times longer depending upon the solvent. A longer lifetime could indicate less singlet state mixing and thus less metal character in the emission.

The lifetimes for the phen–HDPA complexes are not as easily understood as those of the bpy analogues. The lifetimes in water for the $n = 1$ and 2 species are much the same as in the $n = 3$ complex indicating d–π_{phen}* CT character, but in 2-PrOH the lifetimes of the $n = 2$ and 3 complexes are different and the two resolved lifetimes in the $n = 1$ species are not as different as in the bpy complexes (Table II).

E. Time-Resolved Emission. Time-resolved emission spectra were obtained for $[Ru(bpy)(HDPA)_2]^{2+}$ ($n = 1$) in 2-PrOH (Figure 5). At 3 μs after the laser pulse, the emission is dominated by the d–π_{bpy}* CT. The new longer lived emission is clearly present at 15 μs after the laser pulse. Analogous data was observed in EtOH. Time-resolved emission for $[Ru(bpy)_2(HDPA)]^{2+}$ ($n = 2$) was also obtained, but no second emission was resolved.

For the $[Ru(phen)(HDPA)_2]^{2+}$ complex time resolution of the emission was also possible (Figure 6). At 3 μs after the laser pulse the emission is dominated by the d–π_{phen}* CT, while a longer aperture delay range time, 24 μs, is needed to clearly observe the longer lived emission. As observed for the bpy analogue, no second emission could be time-resolved for the $n = 2$ species.

F. Photoselection Spectra. Excitation photoselection spectra obtained at 77 K in 4:1 EtOH/MeOH for the $n = 1$ and 2 species are shown in Figure 7. The $n = 2$ complex reached a maximum polarization of 0.28 at 21 300 cm^{-1}, which is a 180 cm^{-1} red shift from the maximum in the singlet state absorption. In the $n = 1$ species a polarization maximum of 0.075 occurs at 26 300 cm^{-1} confirming the presence of the absorption at ~26 100 cm^{-1}. Other values obtained for the $n = 1$ complex were 0.20 at 23 300 cm^{-1}, 0.055 at 22 100 cm^{-1}, –0.068 at 19 600 cm^{-1}, and –0.091 at 18 900 cm^{-1}. The peak at 22 100 cm^{-1} is ~500 cm^{-1} blue-shifted from the singlet state absorption maximum. Since the maximum of 0.23 in the photoselection spectrum of $[Ru(bpy)_3]^{2+}$ ($n = 3$) is red-shifted 1000 cm^{-1} from the singlet state absorption maximum,[3] it appears the bpy singlet states in the mixed-ligand complexes ($n = 1, 2$) differ in some detail from the $n = 3$ complex. The fact that the low-symmetry, $n = 1$ complex never attains the high value of >0.2 observed in other bpy complexes is curious but is perhaps due to the presence of overlapping bands in the absorption spectrum.

The emission photoselection spectra at 77 K in 4:1 EtOH/MeOH are shown in Figure 8. The nearly flat spectrum obtained for $[Ru(bpy)_2(HDPA)]^{2+}$ indicates that only one emission oscillator is present. The structured spectrum obtained for $[Ru(bpy)(HDPA)_2]^{2+}$ with 21 300 cm^{-1} excitation indicates more than one emission oscillator and confirms the presence of more than one emitting state.

Exactly analogous emission photoselection data were obtained for the mixed phen(HDPA) complexes at 77 K in EtOH.

Spectroscopy of the Deprotonated Complexes and Solution Equilibria. Absorption studies in H_2O and alcohol solvents for both the $n = 1$ and 2 complexes in the concentration range of 10^{-6} to 10^{-4} M follow the Beer–Lambert law, and acidification results in no spectral changes; therefore, only the fully protonated species

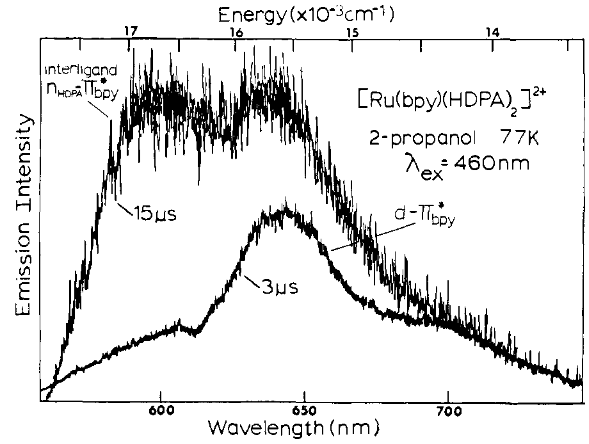

Figure 5. The time-resolved emission spectra obtained at 3 and 15 μs after the laser pulse for $[Ru(bpy)(HDPA)_2]^{2+}$ in 2-PrOH at 77 K. Assignments for the emissions are made as shown (see text).

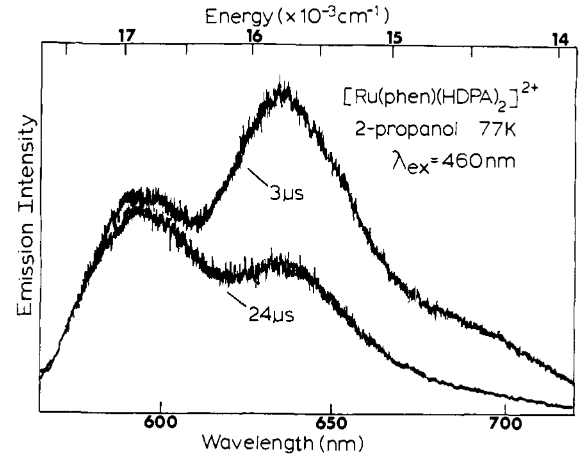

Figure 6. The time-resolved emission spectra obtained at 3 and 24 μs after the laser pulse for $[Ru(phen)(HDPA)_2]^{2+}$ in 2-PrOH at 77 K.

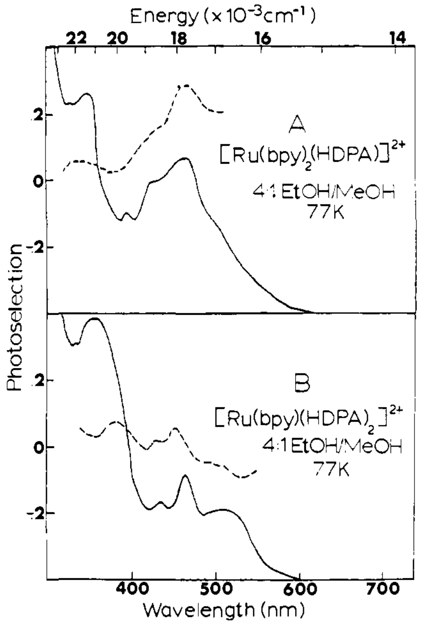

Figure 7. The 77 K excitation photoselection spectrum plotted across the 77 K absorption spectrum in 4:1 EtOH/MeOH for (A) $[Ru(bpy)_2(HDPA)]^{2+}$ (using a 603-nm emission monochromator setting) and (B) $[Ru(bpy)(HDPA)_2]^{2+}$ (using a 620-nm emission monochromator setting).

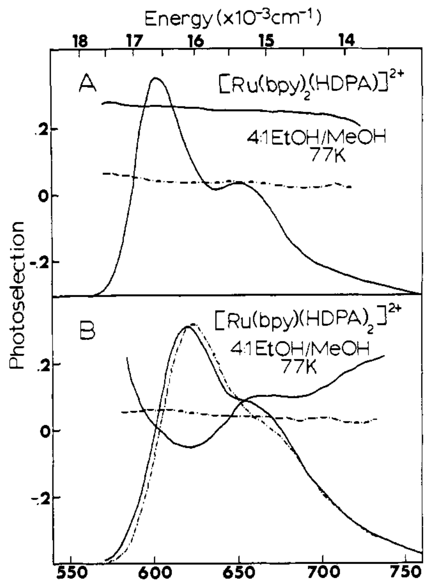

Figure 8. The 77 K emission photoselection (using 350- (-·-) and 460-nm (---) excitation) plotted across the 77 K emission spectrum in 4:1 EtOH/MeOH for (A) $[Ru(bpy)_2(HDPA)]^{2+}$ and (B) $[Ru(bpy)(HDPA)_2]^{2+}$.

exist in these solvents at these concentrations.

Reversible deprotonation of the $n = 1$ complex can be achieved in 4:1 EtOH/MeOH made basic with a sodium hydroxide pellet (Figure 9). This deprotonated complex can exist in two forms establishing equilibria similar to that previously reported for tris Ru(II)[27] and Co(III)[38] HDPA complexes:

$$[Ru(bpy)(HDPA)_2]^{2+} \leftrightarrow [Ru(bpy)(HDPA)(DPA^-)]^{1+} + H^+$$

$$[Ru(bpy)(HDPA)(DPA^-)]^{1+} \leftrightarrow [Ru(bpy)(DPA^-)_2]^0 + H^+$$

During deprotonation the color of the complex in solution changes from auburn, to brown, to jade green. The absorption of the deprotonated complex tails beyond 14 300 cm^{-1} (Table III).

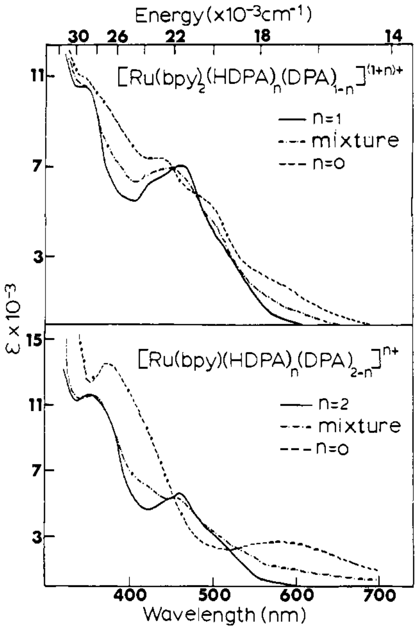

Figure 9. The room-temperature absorption spectra in 4:1 EtOH/MeOH made basic with a sodium hydroxide pellet for the series (A) $[Ru(bpy)_2(HDPA)_n(DPA^-)_{1-n}]^{(1+n)+}$, $n = 1$ (—), mixture of $n = 1, 2$ (-··-), and $n = 0$ (---), and (B) $[Ru(bpy)(HDPA)_n(DPA^-)_{2-n}]^{n+}$, $n = 2$ (—), mixture of $n = 2, 1, 0$ (-··-), and $n = 0$ (---).

Table III. Room-Temperature Absorption Bands for the Deprotonated Complexes in 4:1 EtOH/MeOH

complex	λ,[a] nm $10^{-3}E$	cm^{-1} $10^{-3}\epsilon$	M^{-1} cm^{-1}
$[Ru(bpy)(DPA^-)_2]^0$	374 (b)	26.7	13.5
	410 (sh)	24.4	10.8
	588 (b)	17.0	2.62
$[Ru(bpy)_2(DPA^-)]^{+1}$	340 (ba)	29.4	11.0
	366 (sh)	27.3	9.78
	434 (b)	23.0	7.33
	484 (b)	20.7	5.71
	580 (sh)	17.2	1.85

[a] Abbreviations: b, broad; sh, shoulder; ba, broad asymmetric.

Only one deprotonated form of the $n = 2$ complex can exist after the reversible deprotonation in basic 4:1 EtOH/MeOH:

$$[Ru(bpy)_2(HDPA)]^{2+} \leftrightarrow [Ru(bpy)_2(DPA^-)]^{1+} + H^+$$

In this case, deprotonation changes the color of the solution from auburn to brown. The energies for the singlet state absorption transitions for this species are listed in Table III, and the spectrum is shown in Figure 9.

Cooling the fully deprotonated complexes to 77 K in basic 4:1 EtOH/MeOH gives absorption spectra that are identical with the 77 K spectra of the fully protonated species; therefore, a shift in the K_a with temperature must be occurring.

To avoid the problems of equilibria associated with the deprotonated complexes in solution, the fully deprotonated solids were isolated (see synthesis). Room-temperature absorption spectra in dried CH_3CN were identical with the spectra obtained in the basic alcohol solutions. Attempts to glass the CH_3CN failed, and therefore, 77 K absorption data could not be obtained. However, cooling the CH_3CN solutions to 77 K produced no color change for either of the deprotonated complexes (reprotonation apparently not occurring in this aprotic solvent), so an attempt to obtain 77 K emission spectra was made, but no emission could be detected up to 800 nm for either of the deprotonated complexes.

Discussion

The difficulty in identifying a true dual emission for a Ru(II) complex has been previously discussed by Balzani and von Zelewsky.[21-24] Thus a substantial effort was made to ensure that the emission data reported here were not due to an impurity. Successive recrystallizations and column chromatographic methods

---

(38) Johnson, W. L., III; Geldard, T. F. *Inorg. Chem.* **1979**, *18*, 664.

cannot be expected to provide a satisfactory separation of $[Ru(bpy)_2(HDPA)]^{2+}$ ($n = 2$) and $[Ru(bpy)(HDPA)_2]^{2+}$ ($n = 1$) if the materials are mixed. So, the emission data might suggest that the $n = 2$ species is an impurity in the $n = 1$, especially since the emission energy of the former is isoenergetic with the higher energy emission of the latter. Only the different lifetimes of the emissions from the two complexes, 4.6 ($n = 2$) and 13 μs ($n = 1$) (in EtOH), and the disappearance of the 13-μs emission in H_2O, indicate that $[Ru(bpy)_2(HDPA)]^{2+}$ is not an impurity and that the dual emitting ($n = 1$) complex is pure. The synthesis of $[Ru(phen)(HDPA)_2]^{2+}$ complex and its dual emission behavior analogous to the bpy species again indicate the validity of the dual emission observed.

Insight into the origin of the higher energy luminescence observed in the $[Ru(bpy)(HDPA)_2]^{2+}$ ($n = 1$) and $[Ru(phen)(HDPA)_2]^{2+}$ ($n = 1$) complex is obtained from the 77 K absorption spectra in EtOH. Comparing the spectra for the $n = 0$–3 complexes (Figure 1), it is evident that spin-allowed transitions occur to states involving interligand interactions since the spectrum of $[Ru(HDPA)_3]^{2+}$ is displaced from the isosbestic point at 24 700 cm^{-1} and no isosbestic point exists in the region of 20 800 cm^{-1}. An interligand transition is also supported by the following. (1) Steric crowding due to the nonplanarity of the HDPA ligand which has been noted previously for tris complexes of Co(III).[38] (2) Examination of molecular models indicate that in one conformation the distance from the bridging nitrogen of HDPA to the bpy ring is 200 pm. (3) The 26 100 cm^{-1} absorption is only present in complexes with more than one HDPA ligand. (4) The 19 800 cm^{-1} absorption is only present in mixed-ligand complexes (an interligand transition between an HDPA and a bpy ligand). The blue shift in the 19 800 cm^{-1} absorption band upon increasing the hydrogen-bonding ability of the solvent, and its disappearance in water, is typical behavior of $n \rightarrow \pi^*$ transitions in hydroxylic solvents.[36] Therefore this transition is to an n_{HDPA}-π_{bpy}^* interligand charge-transfer (ILCT) excited state. Since from excitation spectra the higher energy, longer lived emission can be correlated with the lower energy 19 800 cm^{-1} absorption and since this emission disappears in water along with this absorption, this emission occurs from the n_{HDPA}–π_{bpy}^* interligand charge-transfer (ILCT) triplet state. The organic character of this state is supported by the small Stoke shift (3000 cm^{-1}) and the longer lifetime (13 μs) of the emission, both of which indicate less metal character than in the usual d–π_{bpy}^* emission.

Examination of the spectroscopic properties of $[Ru(bpy)(py)_4]^{2+}$ (in EtOH), where no bridging amine function is present, revealed no 19 800 cm^{-1} absorption, no asymmetry in the 28 700 cm^{-1} absorption, and no second emission.

The room-temperature resonance Raman (RR) spectra of $[Ru(bpy)(HDPA)_2]^{2+}$ complex in CH_3CN using 21 800 and 19 900 cm^{-1} excitation give characteristic bpy vibrations.[39,40] Excitation at these energies is into a d–π_{bpy}^* (MLCT) band. However, most of the absorption intensity at the 19 900 cm^{-1} exciting line is due to the electronic transition at 19 800 cm^{-1}. The proposed n–π^* (ILCT) assignment for this transition is also consistent with the observation of bpy vibrations in the RR spectrum at this excitation energy.[41]

Although a direct correlation with the electrochemistry for these complexes cannot be made since terms for electron exchange and repulsion[42] are not available, the HDPA complexes have oxidation waves that are indicative of amine functionalities.[26] This suggests that lone-pair orbitals of the bridging amine group of HDPA could be involved in optical transitions which is again consistent with our assignment.

The single emission observed in all solvents for $[Ru(bpy)_2(HDPA)]^{2+}$ ($n = 2$) and the low-energy emission observed in alcohol solvents, as well as the single emission observed in H_2O for $[Ru(bpy)(HDPA)_2]^{2+}$ ($n = 1$), by comparison to data for $[Ru(bpy)_3]^{2+}$, can be assigned as MLCT emission involving the bpy ligand.

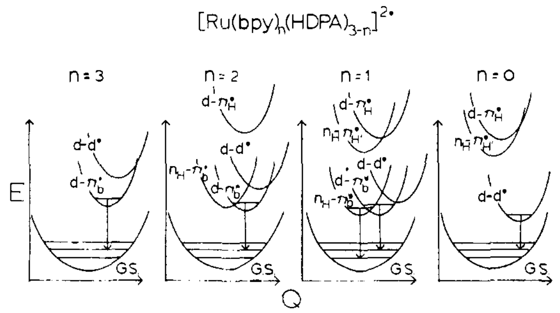

Figure 10. Potential energy diagrams of the ground and excited states for the complexes $[Ru(bpy)_n(HDPA)_{3-n}]^{2+}$ ($n = 0$–3). Energy is plotted vs. a vibrational mode Q, such as the totally symmetric Ru–N stretch. The orbital origin of the excited states are as indicated. No implication of relative force constants is intended (GS, ground state; H, HDPA; b, bpy).

While the emission band structure, energy, and lifetime for the $[Ru(phen)_n(HDPA)_{3-n}]^{2+}$ ($n = 1$ and 2) complexes in H_2O indicate an analogous emission assignment (MLCT, Ru–phen) as for the bpy complexes, the lifetime data in 2-PrOH indicates that even the $n = 2$ species has a longer lived emission than the $n = 3$ and shows a variation in lifetime across the emission band. The 2-PrOH and water data indicate that the $n = 2$ complex could have an n–π^* (ILCT) emission in weak H-bonding solvents and a d–π^* (MLCT) emission in H_2O. The inability to time-resolve two emission bands from this complex does not exclude the possibility of two isoenergetic emissions being present, although the photoselection data (in EtOH at 77 K) seem to indicate only one emitting oscillator is present (indicating only one emission).

To aid in the clarification of our assignments for these protonated complexes, potential energy drawings and orbital assignments for the excited states are given in Figure 10. The d–d* state is shown moving to lower energy as bpy ligands are replaced with HDPA ligands. This occurs since HDPA is similar to pyridine and therefore has a smaller crystal field effect than the bpy ligand. Also since HDPA forms six-membered chelate rings with the metal that are not well-conjugated, which increases the bond angle at the metal, resulting in σ bonds to the metal that are not as strong as in bpy. This destabilizes the d_σ orbitals, lowers the energy of the d_σ^* orbitals, and thus lowers the energy of the d–d* state. The $n = 2$ complex has a state of n–π^* orbital origin as indicated in the absorption spectrum, but the triplet state must be at higher energy than the emitting triplet of the d–π^* state resulting in only one emission for the complex. In the $n = 1$ complex the addition of the interligand state involving two HDPA ligands is shown. The energy levels in this complex are perturbed such that now the states involving the d–π_{bpy}^* and the n_{HDPA}–π_{bpy}^* orbitals are isoenergetic and a dual emission occurs from the complex. In the case of the tris HDPA complex, $n = 0$, all states involving bpy are absent and only emission from the previously assigned[27] d–d* state is observed.

The absence of the emission from the deprotonated forms of the mixed-ligand $bpy(DPA^-)$ complexes at first seems puzzling in view of the strong ~600 nm emission (assigned π–d*) reported for the series $[Ru(HDPA)_n(DPA^-)_{3-n}]^{(n-1)+}$ ($n = 0$–2.[27] But since a stable, nonemitting form of the fully deprotonated tris DPA^- complex ($n = 0$) was also reported at pH ≥11.9 and in equilibrated alcoholic solution with hydroxide ion concentrations beyond 3:1 NaOH/complex,[27] the absence of emission in the mixed $bpy(DPA^-)$ complexes may not be unique. Indeed, reassignment of the emission from the $[Ru(HDPA)_n(DPA^-)_{3-n}]^{(n-1)+}$ ($n = 1, 2$) complexes can provide a consistent rationale of the disappearance of the ILCT emission in these mixed-ligand $bpy(DPA^-)$ complexes. The data in this work and ref 27 indicate that the HDPA complexes are completely deprotonated only at high pH or with excess NaOH in alcohol; therefore, the absence of emission in [Ru-

---

(39) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441.

(40) Forster, M.; Hester, R. E. *Chem. Phys. Lett.* **1981**, *81*, 42.

(41) Blakley, R. L.; Tait, C. D.; Wertz, D. W.; DeArmond, M. K., unpublished results.

(42) Ohsawa, Y.; Hanck, K. W.; DeArmond, M. K. *J. Electroanal. Chem.* **1984**, *175*, 229.

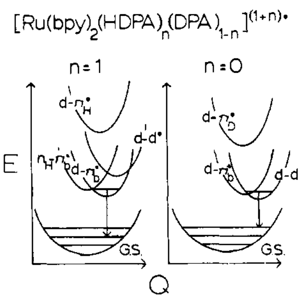

Figure 11. Potential energy diagrams of the ground and excited states for the complexes $[Ru(bpy)_2(HDPA)_n(DPA^-)_{1-n}]^{(1+n)+}$ (n = 1, 0). Energy is plotted vs. a vibrational mode Q, such as the totally symmetric Ru–N stretch. The orbital origin of the excited states are as indicated. No implication of the relative force constants is intended (GS, ground state; H, HDPA; D, DPA$^-$; b, bpy).

$(DPA^-)_3]^-$ would be due to the disappearance of the ILCT n_{HDPA}–$\pi_{DPA}{}^{-*}$ state since the lone-pair nitrogen electrons of the DPA$^-$ ligand are involved with "l-type"[43] conjugation and thus no low-energy n–π* state can exist.

However, turning off the n–π* ILCT emission in the mixed-ligand bpy(DPA$^-$) complexes still does not explain the disappearance of emission from the Ru-bpy chromophore. Deprotonation of the HDPA ligand, forming the more planar DPA$^-$ ligand that does not have complete conjugation (l-type instead of "true" π conjugation), would further destabilize the metal-to-ligand σ bonds and, as previously mentioned, lower the energy of the d–d* state (Figure 11). In addition geometric distortions have been suggested for the $[Ru(bpy)_n(DPA^-)_{3-n}]^{(n-1)+}$ (n = 1, 2) complexes[26] which again imply perturbations at the metal resulting in a lowering in energy of the d–d* states. This red-shifted, weak d–d* emission was not observed for any of these complexes.

Since the deprotonation of these complexes is totally reversible, photochemical deactivation pathways do not appear to be activated and are not likely the origin of the disappearance of the luminescence.

Conclusion

The identification of a dual emission for a Ru(II) complex as for all dual emissions has fundamental significance since the implication of the result is that independent deactivation pathways exist within the same molecule. Here the two types of emission, although "spatially isolated", are perhaps best categorized as "distinct orbital type" since the orbital origin of the two emitting excited states is different. The ILCT character of a the n_{HDPA}–π_{bpy}* emission is unique and does point up the donor (D)–acceptor (A) character of the optical process for this system. Mixed-ligand complexes as this may afford some practical photoredox possibilities since the optical properties of this system permit selective excitation of either the n_{HDPA}–π_{bpy}* chromophore or the d–π_{bpy}* chromophore. This ability to selectively excite one or the other emitting state is not a common feature among the dual emitting transition-metal complexes.

Acknowledgment. We are grateful to Mr. Michael Myrick for synthesizing the $[Ru(bpy)(py)_4]^{2+}$ complex and for obtaining the spectroscopic data for this complex. Gratitude is also extended to Dr. Yasuhiko Ohsawa for the original synthesis of the bpy/HDPA complexes and to Dr. David Morris and Dr. Donald Segers for earlier work on bpy/HDPA and related complexes. This work was supported by a grant the Army Research Office, Grant No. DAAL-03-86-K-0040.

---

[43] Kasha, M.; Rawls, H. R. *Photochem. Photobiol.* **1968**, *7*, 561.

Photochemistry of Multiply Bonded Dimolybdenum Phosphate Complexes in Acidic Solution: Photoinduced Two-Electron Oxidation of $Mo_2(HPO_4)_4{}^{4-}$ Ion

I-Jy Chang and Daniel G. Nocera*

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. *Received December 15, 1986*

Abstract: The multiply bonded dimolybdenum phosphate dimers $Mo_2(HPO_4)_4{}^{4-}$ and $Mo_2(HPO_4)_4{}^{3-}$ have been prepared and spectroscopically and electrochemically characterized. The electronic absorption spectrum of the quadruply bonded complex $Mo_2(HPO_4)_4{}^{4-}$ in H_3PO_4 is typical of many $M\overset{4}{-}M$ species with the $\delta^2 \rightarrow \delta\delta^*$ ($^1A_{2u} \leftarrow {}^1A_{1g}$) transition occurring at 516 nm. Cyclic voltammograms of phosphoric acid solutions of $Mo_2(HPO_4)_4{}^{4-}$ are characterized by two reversible waves at −0.67 and −0.25 V vs. SCE that we have attributed to the $Mo_2(HPO_4)_4{}^{3-/4-}$ and $Mo_2(HPO_4)_4{}^{2-/3-}$ couples, respectively. Oxidation of $Mo_2(HPO_4)_4{}^{4-}$ produces the mixed-valence dimer $Mo_2(HPO_4)_4{}^{3-}$, which exhibits an intense near-infrared absorption band that we have assigned to the $\delta \rightarrow \delta^*$ ($^2B_{1u} \leftarrow {}^2B_{2g}$) transition. Solid $K_3Mo_2(HPO_4)_4$ is paramagnetic and follows Curie law behavior (μ = 1.58 μ_B). The EPR spectrum of $K_3Mo_2(HPO_4)_4$ at 5 K shows an axial signal ($g_\perp$ = 1.894, $g_\parallel$ = 1.886). Whereas $Mo_2(HPO_4)_4{}^{4-}$ thermally reacts in 2 M H_3PO_4 to produce $Mo_2(HPO_4)_4{}^{3-}$ and hydrogen over a period of days, irradiation ($\lambda \geq 335$ nm) of phosphoric acid solutions of the dimer leads to the facile production of $Mo_2(HPO_4)_4{}^{2-}$ and hydrogen. The thermal reaction presumably results from the slow conversion of $Mo_2(HPO_4)_4{}^{4-}$ to yield hydrogen and $Mo_2(HPO_4)_4{}^{2-}$ which reacts in an ensuing comproportionation reaction with $Mo_2(HPO_4)_4{}^{4-}$ to produce $Mo_2(HPO_4)_4{}^{3-}$. In contrast, the photochemical reaction mechanism is consistent with sequential oxidation of the Mo_2 core [i.e., Mo_2(II,II) → Mo_2(II,III) → Mo_2(III,III)]. Electronic absorption spectra of the $Mo_2(HPO_4)_4{}^{n-}$ (n = 2–4) dimers in the ultraviolet spectral region, wavelength-dependent quantum yield measurements, and photochemical studies of Mo_2 phosphate dimers under N_2O atmospheres have led us to postulate a $\pi \rightarrow \pi^*$ ($^1A_{2u} \leftarrow {}^1A_{1g}$) parentage for the photoactive state of Mo_2 phosphato complexes. We propose that excitation of this transition leads to the direct production of hydrogen atoms which undergo subsequent reaction to produce hydrogen.

There has been a longstanding interest in the oxidation–reduction chemistry of transition-metal complexes in electronic excited states and in their application as catalysts for oxidation–reduction reactions. Although numerous studies have demonstrated the propensity of electronically excited metal complexes to exchange one electron,[1-3] many desirable redox reactions such

0002-7863/87/1509-4901$01.50/0