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Luminescence Quenching of the Tris(2,2′-bipyrazine)ruthenium(II) Cation and Its Monoprotonated Complex

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The MLCT excited state of Ru(bipyrazine)$_3^{2+}$ is quenched by a series of organic amines and methoxybenzenes, in acetonitrile solution. Linear Stern–Volmer plots were obtained, and various rate parameters were extracted from the data. The excited state is also quenched in neutral aqueous solution by a range of metal ions and complexes. Rate constants for both oxidative and reductive quenching mechanisms were obtained. In general the rates are faster for this ion than for the corresponding Ru(bipyridine)$_3^{2+}$ excited state. Similar data were also obtained for the monoprotonated complex in 2 M sulfuric acid and the hexaprotonated species in concentrated sulfuric acid.

Introduction

The excited-state chemistry of Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) has been extensively investigated during the past decade.[1] Excited states may undergo various bimolecular processes, namely (1) energy transfer, (2) quenching by oxidative electron transfer, (3) quenching by reductive electron transfer, and (4) excited-state proton transfer. With appropriate choice of systems the Ru(bpy)$_3^{2+}$ cation may undergo processes 1–3.[1-3] These studies have been extended to the photochemical decomposition of water into hydrogen and oxygen by using Ru(bpy)$_3^{2+}$ as a sensitizer.[4]

Recently, we have shown that the analogous Ru(bpz)$_3^{2+}$ cation (bpz = 2,2′-bipyrazine)[5] is an excellent photocatalyst for methylviologen (MV^{2+}) reduction. Table I shows a comparison of the properties of the two complexes. The metal-to-ligand charge-transfer (MLCT) band of Ru(bpz)$_3^{2+}$ is slightly shifted to higher energy, and the lifetime of the emissive state is slightly longer than that of Ru(bpy)$_3^{2+}$ in water. A major difference between the two systems lies in their redox potentials, those of Ru(bpz)$_3^{2+}$ being shifted 0.5 V positive relative to those of Ru(bpy)$_3^{2+}$. Furthermore, the Ru(bpz)$_3^{2+}$ cation has six peripheral uncoordinated nitrogen atoms that can be protonated step by step in sulfuric acid.[6] We report here the systematic bimolecular quenching of Ru(bpz)$_3^{2+}$ and its monoprotonated complex by simple ions and organic compounds.

Experimental Section

Materials. [Co(NH$_3$)$_6$]Cl$_3$,[7] [Co(NH$_3$)$_5$Cl]Cl$_2$,[7] Ru(bpz)$_3$Cl$_2$,[5] [Ru(bpz)$_3$](PF$_6$)$_2$,[5] and Ru(bpy)$_3$Cl$_2$[8] were synthesized and purified as described previously. H$_2$SO$_4$, KCl, KBr, KI, AgNO$_3$, KNO$_3$, CoCl$_2$·6H$_2$O, Mn(NO$_3$)$_2$·6H$_2$O, FeSO$_4$·6H$_2$O, (NH$_4$)$_2$Fe(SO$_4$)$_2$, CuSO$_4$·5H$_2$O, FeNH$_4$(SO$_4$)$_2$·12H$_2$O, K$_4$[Fe(CN)$_6$], and K$_3$[Fe(CN)$_6$] were all analytical reagent grade. A loan of RuCl$_3$·3H$_2$O from the Johnson Matthey Co. is gratefully acknowledged. *N,N′*-Diphenyl-*p*-phenylenediamine was purchased from Fischer Scientific Co. and recrystallized from benzene. All other organic quenchers were purchased from Aldrich. Aniline, *N,N*-dimethylaniline, and *N,N*-dimethyl-*p*-toluidine were purified by vacuum distillation before use. Phenothiazine, diphenylamine, and triphenylamine were recrystallized from ethanol. A series of methoxybenzenes were used without further purification.

Water doubly distilled over KMnO$_4$ was used to make all solutions. Acetonitrile for quenching measurements was dried over P$_2$O$_5$ and distilled before use. Tetrabutylammonium perchlorate (Eastman) (TBAP) was recrystallized from ethanol and vacuum-dried.

Luminescence Quenching Measurements. Emission spectra were recorded with a Varian SF-330 spectrofluorimeter. The exciting wavelength was 423 nm, and the emission intensity was monitored at the wavelengths 595 nm (neutral complex), 717 nm (monoprotonated complex), and 620 nm (hexaprotonated complex). In neutral solution and in CH$_3$CN, the concentrations of Ru(bpz)$_3^{2+}$ and the quencher were about 10^{-5} and 10^{-2}–10^{-6} M, respectively. The ionic strength of solutions was adjusted to 0.1 M with TBAP in acetonitrile, 1 M with KCl in neutral aqueous solution, and 2 M with sulfuric acid in acidic aqueous solutions. KNO$_3$ (1 M) was used instead of 1 M KCl for the quenching experiment with the Ag$^+$ ion. For the experiments in CH$_3$CN, Ru(bpz)$_3$(PF$_6$)$_2$ was used because of its higher solubility.

In a typical experiment, the appropriate quenchers were added in microliter "spikes" to the Ru(bpz)$_3^{2+}$ solution in a quartz or Pyrex cuvette closed by a rubber serum cap. The solutions were bubble degassed with dry nitrogen for at least 15 min. The emission intensities were corrected for absorption of the incident light by the quenchers, from the equation[9]

$$\left(\frac{I_0}{I}\right)_{\text{corr}} = \left(\frac{I_0}{I}\right)_{\text{app}}\left[\frac{1-10^{-(A_D+A_Q)l}}{1-10^{-A_Dl}}\right]\frac{A_D}{A_D+A_Q}10^{-A_Q'l'}$$

where $(I_0/I)_{\text{app}}$ is the observed ratio of luminescence intensity in an unquenched solution to that in a quenched solution and $(I_0/I)_{\text{corr}}$ is the ratio corrected for the inner filter effect. A_D and A_Q are the absorbances at the exciting wavelength for Ru(bpz)$_3^{2+}$ and the quencher, respectively. A_Q' is the absorbance of the quencher at the emission wavelength, l is the excitation path length within the cell, and l' is the effective path length for reabsorption of the emitted radiation, estimated to be 0.5 cm. For each quencher, the luminescence intensity was measured with at least four different quencher concentrations. Several sets of quenching experiments were carried out, and quenching constants are averages obtained from the separate experiments.

Lifetime and lifetime quenching measurements were carried out with a York University constructed 0.5-MW pulsed nitrogen laser and a Princeton Applied Research (PAR) Model 162 boxcar averager with a Model 165 gated integrator. Absorption spectra were recorded on a Perkin-Elmer Hitachi Model 340 microprocessor spectrometer.

Formation of Ion-Pair Complexes. [Ru(bpz)$_3$]$_2$[Fe(CN)$_6$]·12H$_2$O. Concentrated solutions of Ru(bpz)$_3$Cl$_2$ and K$_4$Fe(CN)$_6$ were mixed together in an approximately 1:1 molar ratio, in water. A dark copper-colored crystalline precipitate formed immediately. The product was recrystallized from hot water, yielding black platelike crystals and a green filtrate. The infrared spectrum shows ν(CN) stretching vibrations at 2022 and 2031 cm^{-1}. Anal. C, H, N, Fe.

[Ru(bpz)$_3$]$_3$[Fe(CN)$_6$]$_2$·22H$_2$O was prepared as above, but with K$_3$Fe(CN)$_6$. An orange-brown precipitate was recrystallized to yield orange-brown flaky crystals. The infrared spectrum shows ν(CN) stretching vibrations at 2108 and 2113 cm^{-1}. Anal. C, H, N.

[Ru(bpz)$_3$]$_3$[Co(CN)$_6$]$_2$·22H$_2$O was prepared as above, but with K$_3$Co(CN)$_6$. An orange precipitate formed. The infrared spectrum shows a ν(CN) stretching vibration at 2114 cm^{-1}. Anal. C, H, N.

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(1) (a) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1. (b) Balzani, V.; Moggi, L.; Manfrin, M. F.; Boletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321. (c) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94. (d) Sutin, N. *J. Photochem.* **1979**, *10*, 19. (e) Kemp, T. J. *Prog. React. Kinet.* **1980**, *10*, 301. (f) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (g) Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834. (h) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83.

(2) Meyer, T. J. *Prog. Inorg. Chem.* **1982**, *30*, 389.

(3) (a) Energy-transfer: Scandola, F.; Balzani, V. *J. Chem. Educ.* **1983**, *60*, 814. (b) Electron-transfer: Sutin, N.; Creutz, C. *J. Chem. Educ.* **1983**, *60*, 809.

(4) (a) Kirch, M.; Lehn, J. M.; Sauvage, J. P. *Helv. Chim. Acta* **1979**, *62*, 1345. (b) Kalyanasundaram, K.; Kiwi, J.; Gratzel, M. *Helv. Chim. Acta* **1978**, *61*, 2720. (c) Kiwi, J.; Kalyanasundaram, K.; Gratzel, M. *Struct. Bonding (Berlin)* **1982**, *49*, 37. (d) Julliard, M.; Channoy, M. *Chem. Rev.* **1983**, *83*, 425.

(5) (a) Crutchley, R. J.; Lever, A. B. P. *J. Am. Chem. Soc.* **1980**, *102*, 7128. (b) Crutchley, R. J.; Lever, A. B. P. *Inorg. Chem.* **1982**, *21*, 2276. (c) Crutchley, R. J.; Lever, A. B. P.; Poggi, A. *Inorg. Chem.* **1983**, *22*, 2647. (d) Gonzales-Velasco, J.; Rubinstein, I.; Crutchley, R. J.; Lever, A. B. P.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 822.

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

(7) Brauer, G., Ed. "Handbook of Preparative Inorganic Chemistry", 2nd ed.; Academic Press: New York, **1965**; Vol. 2, p 1531.

(8) Burstall, F. H. *J. Chem. Soc.* **1936**, 173.

(9) Demas, J. N.; Adamson, A. W. *J. Am. Chem. Soc.* **1973**, *95*, 5159.

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Table I. Photophysical, Photochemical, and Electrochemical Data

	$Ru(bpy)_3^{2+}$	$Ru(bpz)_3^{2+}$	$Ru(bpz)_2(bpzH)^{3+}$	$Ru(bpzH_2)_3^{8+}$
absorption $\lambda_{max}(H_2O)$, nm	452	441 (443)^a	475	458
emission λ_{max}, nm	607	595 (591)^a	717	620
lifetime τ, ns	620 ($\phi = 0.042$)	920 (1 M KCl) 740 (CHCN)	50 (2 M H_2SO_4)	520 (conc H_2SO_4)
ϕ(photoanation) (CH_3CN/Cl^-)	0.01	0.37	...	...
mech of quenching in MV^{2+}/TEOA system	oxidative by MV^{2+}	reductive by TEOA	...	...
$E(RuL_3^{3+/2+})^b$	1.29	1.86 (1.95)^c	+2.27^d	
$E(RuL_3^{2+/+})^b$	−1.33	−0.80 (−0.71)^c	−0.28^d	
$E(RuL_3^{3+/2+*})^b$	−0.81	−0.26^d	+0.55^d	
$E(RuL_3^{2+*/+})^b$	+0.77	+1.45	+1.44^d	

^{a}In CH_3CN. ^{b}V vs. SCE in CH_3CN. ^{c}Data from ref 5d. ^{d}Calculated.

Table II. Quenching Rate Constants For $Ru(bpz)_3^{2+}$ in Acetonitrile (μ = 0.1 M, 22 °C)

quencher	$E[Q/Q^+]$, V vs. SCE[10-12]	k_q, $M^{-1}\,s^{-1}$	$RT \ln k_q$	
			calcd^a	obsd
1. *N*,*N*′-diphenyl-*p*-phenylenediamine	0.35	1.1×10^{10}	0.591	0.593
2. phenothiazine	0.53	7.9×10^9	0.591	0.586
3. *N*,*N*-dimethyl-*p*-toluidine	0.71	8.6×10^9	0.590	0.588
4. *N*,*N*-dimethylaniline	0.81	8.4×10^9	0.589	0.587
5. diphenylamine	0.83	5.6×10^9	0.589	0.577
6. aniline	0.98	5.2×10^9	0.585	0.575
7. triphenylamine	1.06	6.2×10^9	0.580	0.579
8. 1,2,4-trimethoxybenzene	1.12	2.9×10^9	0.574	0.560
9. 1,4-dimethoxybenzene	1.34	8.6×10^8	0.514	0.529
10. 1,2,3-trimethoxybenzene	1.42	6.5×10^7	0.478	0.462
11. 1.2-dimethoxybenzene	1.45	1.7×10^8	0.464	0.486
12. 1,3,5-trimethoxybenzene	1.49	2.7×10^7	0.444	0.440

^{a}See text for parameters fitted to eq 5.

Results and Discussion

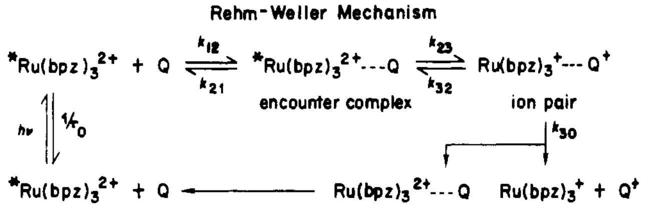
(i) Quenching in CH_3CN by Aromatic Amines and Methoxybenzenes. The emission intensities gave linear Stern–Volmer plots as a function of the quencher concentrations for all systems. The quenching rate constants, k_q, were calculated from eq 1, where

$$I_0/I = 1 + K_{SV}[Q] = 1 + \tau_0 k_q[Q] \qquad (1)$$

I_0 and I are the emission intensities of a solution of $Ru(bpz)_3^{2+}$ in the absence and presence of quencher, respectively. τ_0 is the lifetime of $Ru(bpz)_3^{2+}$ with no added quencher (Table I). The bimolecular quenching rate constants are shown in Table II.

Bimolecular quenching may take place by various mechanisms. However, where rate constants are greater than 10^7 M^{-1} s^{-1}, only energy- and electron-transfer processes need to be considered. Amines and methoxybenzenes do not have appropriate low-lying excited states so that energy-transfer quenching of $Ru(bpz)_3^{2+}$ in CH_3CN is energetically unfavorable. In this case, the k_q values increase with decreasing oxidation potential of the quenchers (Table II). Thus, the most probable quenching mechanism for reaction of the $Ru(bpz)_3^{2+}$ cation with amines and methoxybenzenes is reductive quenching.

Scheme I



The theory of electron-transfer quenching[13] is based on the relationship between the quenching rate constants and free energy change of outer-sphere electron transfer.[10-15] Only a brief summary will be presented here. The reaction scheme for electron-transfer quenching can be described by Scheme I, where k_{12} is the diffusion rate constant, k_{21} is the rate constant for dissociation of the precursor complex, k_{23} and k_{32} are rate constants for electron transfer between encounter complex and ion pair, and k_{30} is a combined rate constant for disappearance of the ion pair leading to net quenching.

The driving force for quenching may be written in terms of ΔG_{23}, where, in the case here of quenching by amines (Q), reductive quenching is involved:[10,12]

$$\Delta G_{23} = E_{1/2}[Q^+/Q] - E_{1/2}[Ru^{2+*}/Ru^+] + w_p - w_r \qquad (2)$$

w_p and w_r are the work terms required to bring the products (Ru^+, Q^+) and reactants (Ru^{2+}, Q) together at the separation distance in the encounter complex. Since the amines are uncharged, w_r may be neglected and w_p is small; we assume a value of 0.01 V.[12]

The free energy of activation for electron transfer, ΔG^*_{23}, may be related to this driving force by various different equations,[16] but they generally give very similar results. We use here (eq 3)

$$\Delta G^*_{23} = \Delta G_{23} + (\Delta G^*(0)/\ln 2) \times \ln\,[1 + [\exp(-\Delta G_{23})](\ln 2)/\Delta G^*(0)] \qquad (3)$$

the equation derived by Agmon and Levine,[17] where $\Delta G^*(0)$ is the free energy of activation for $\Delta G_{23} = 0$ and is the so-called "intrinsic barrier" or reorganization energy.

We are concerned here with whether our experimental data can be fitted to reasonable values of these various parameters, based upon previous experience in the bipyridine series. Values of $E_{1/2}[Q^+/Q]$ are available in the literature. A value for $E_{1/2}[Ru^{2+*}/Ru^+]$ can be estimated from the ground-state potential and the emission energy via

$$E_{1/2}[Ru^{2+*}/Ru^+] = E_{0,0} + E_{1/2}[Ru^{2+}/Ru^+]$$

and

$$E_{1/2}[Ru^{3+}/Ru^{2+*}] = E_{1/2}[Ru^{3+}/Ru^{2+}] - E_{0,0} \qquad (4)$$

This last equation has some uncertainty, depending upon whether all the spectroscopic energy in the excited state can be used as redox energy, and generally predicts a value that may be too low by up to 0.1 V.

The relationship between the observed quenching rate constants and the above-mentioned parameters may be written[13]

$$k_q = k_{12}/[1 + (k_{12}/(\Delta V)k_{30})(\exp(\Delta G^*_{23}/RT) + \exp(\Delta G_{23}/RT))] \qquad (5)$$

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(10) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219.

(11) Shioyama, H.; Masuhaya, H.; Mataga, N. *Chem. Phys. Lett.* **1982**, *88*, 161.

(12) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.

(13) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(14) Gandolfi, M. T.; Maestri, M.; Sandrini, D.; Balzani, V. *Inorg. Chem.* **1983**, *22*, 3435.

(15) Balzani, V.; Scandola, F.; Orlandi, G.; Sabbatini, N.; Indelli, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 3370.

(16) Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1979**, *101*, 6140.

(17) Agmon, N.; Levine, R. D. *Chem. Phys. Lett.* **1977**, *52*, 197.

Table III. Quenching Rate Constants for $Ru(bpz)_3^{2+}$ and Protonated Species

	$Ru(bpz)_3^{2+\,a}$			$Ru(bpz)_2(bpzH)^{3+\,b}$			$Ru(bpzH_2)_3^{8+\,c}$
quencher	$10^{-8}k_q$, M^{-1} s^{-1}	$10^{-8}k_d$,[d] M^{-1} s^{-1}	reaction[e]	$10^{-8}k_q$, M^{-1} s^{-1}	$10^{-8}k_d$,[d] M^{-1} s^{-1}	reaction[e]	$10^{-8}k_q$, M^{-1} s^{-1}
$Fe(H_2O)_6^{2+}$[f]	6	100	2	7	115	2	1.1
$Fe(H_2O)_6^{3+}$[g]	105	100	3	1	130	3	0.1
$Cu(H_2O)_4^{2+}$	5	100	3	5	115	1	0.3
I^-	70	40	2				
$Fe(CN)_6^{4-}$	100	6	2	53	5		
$Fe(CN)_6^{3-}$	56	12	3	410	10		
$Co(NH_3)_6^{3+}$	1.3	100	3				
$Co(NH_3)_5Cl^{2+}$	5.7	100	3				

[a] In aqueous solution, $\mu = 1.0$ M (KCl), 20 °C. [b] In 2 M sulfuric acid. [c] In concentrated sulfuric acid. [d] Calculated rate constants for diffusion-controlled quenching. The Debye–Hückel expressions are not good models at high ionic strength so values for 2 M sulfuric acid are only approximate. [e] Reaction responsible for quenching: energy transfer (1); reductive quenching (2); oxidative quenching (3). [f] Ferrous sulfate was used as a quencher. The use of ferrous ammonium sulfate with the unprotonated ruthenium species yielded a quenching rate constant of 20×10^{-8} M^{-1} s^{-1}. [g] Ferric ammonium sulfate was used as a quencher.

where $\Delta V = k_{12}/k_{21}$ is the encounter volume, $k_{12} = k_d$ (the diffusion rate constant), and k_q is the observed rate constant. In common with Balzani,[10] in a study of the quenching of $Cr(bpy)_3^{3+}$ and $Ru(bpy)_3^{2+}$ with aromatic amines, the values $k_d = 1 \times 10^{10}$ M^{-1} s^{-1} and $(\Delta V)k_{30} = 8 \times 10^{11}$ M^{-1} s^{-1} were assumed. Values of $E_{1/2}[Ru(bpz)_3^{2+*}/Ru(bpz)_3^{+}]$ and $\Delta G^*(0)$ (cf. eq 3) were then sought by obtaining a best fit between observed and calculated rate constants. There is some correlation in fit between these two variables, and it does not seem possible, by this method alone, to define each parameter independently. In the case of the $E_{1/2}[Ru(bpy)_3^{2+*}/Ru(bpy)_3^{+}]$ couple, the accepted value is some 0.08 V higher than predicted by eq 4.[12] We assume a similar situation with the bipyrazine complex and fix $E_{1/2}[Ru(bpz)_3^{2+*}/Ru(bpz)_3^{+}] = 1.45$ V. With this value an acceptable fit between observed and calculated k_q values (Figure 1) is seen, with $\Delta G^*(0) = 0.24$ eV (5.5 kcal/mol). This compares with ca. 4 kcal/mol for $Ru(bpy)_3^{2+}$.[12] The parameters correlate positively; if the electrode potential is slightly over-estimated, so will be the reorganization energy parameter. Note that permitting k_d and $(\Delta V)k_{30}$ to vary from the assumed values offered no improvement of fit; the values assumed seem acceptable.

Thus, the bipyrazine system behaves similarly to the bipyridine system but with a much larger value for the excited-state potential couple, as previously proposed.

Using the Marcus "cross-reaction" equation,[12,18,19] one may obtain the self-exchange rate of the ruthenium couple (k_{ii}) using the expression

$$RT \ln k_q'(0) = 0.5RT \ln (k_{ii}k_{jj}) + \text{(work terms)} \qquad (6)$$

where the work terms, to bring reactants together, are small and are neglected here and k_{jj} is the self-exchange rate of the quencher. The term $k_q'(0)$ is the quenching rate (corrected for diffusion) when the driving force is zero. This value can be derived from our data, as the rate when $\Delta G_{23} = 0$ (eq 5), i.e. when $E_{1/2}[Q^+/Q] = 1.45$ V. Thus (Table II), $RT \ln k_q'(0) = RT \ln k_q = 0.46$ (the correction for diffusion is negligible), and assuming with Meyer an average quencher self-exchange rate of 8.7×10^8 M^{-1} s^{-1} in this medium, eq 6 yields a self-exchange rate for the $Ru(bpz)_3^{2+}$ system of 4×10^6 M^{-1} s^{-1}. This is an approximate lower limit for this exchange rate. The upper limit could be derived on the basis that the true excited redox potential for the $Ru(bpz)_3^{2+*}/Ru(bpz)_3^{+}$ couple will not be less than 1.37 V. This yields, from the quenching data, a self-exchange rate constant of 4×10^7 M^{-1} s^{-1}. The corresponding value for the bipyridine–ruthenium system is ca. 4×10^8 M^{-1} s^{-1}.[12] Thus, the rate for the bipyrazine system appears to be slower, even allowing for possible experimental error.

(ii) Quenching in Neutral Aqueous Media by Metal Ions. Many metal cations, and several anions, will quench the luminescence of the $Ru(bpz)_3^{2+}$ ion, and a brief survey of these has been made, in both neutral and acidic media. In the latter case, the protonated ruthenium–bipyrazine system is involved and is discussed separately below. No quenching was observed with Cl^-, Br^-, $[Mn(H_2O)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$, or Ag^+ (this last ion in nitrate medium), under neutral or acidic conditions. However, $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Cu(H_2O)_4]^{2+}$, $[Fe(CN)_6]^{n-}$ (n = 3, 4), $[Co(NH_3)_6]^{3+}$, and $[Co(NH_3)_5Cl]^{2+}$ were effective quenchers in both neutral and acidic media. The $[Co(CN)_6]^{3-}$ ion was also an effective quencher, but the Stern–Volmer plots were nonlinear and further study was postponed. The other complexes yielded linear Stern–Volmer polts, and the rate constants obtained therefrom are shown in Table III. Table III also contains the hypothetical diffusion rates corrected for ionic strength (1 M KCl) from Debye–Huckel expressions in the literature.[20,21]

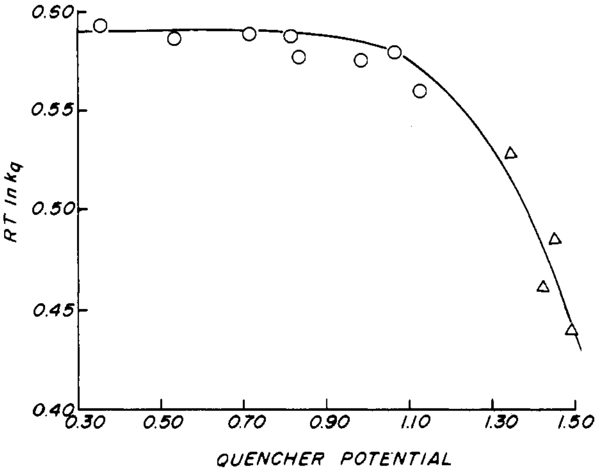

Figure 1. Plot of $RT \ln k_q$ vs. the quencher potential $E[Q^+/Q]$. The circles and triangles are experimental points, and the solid line is the theoretical line based upon eq 5, from the parameters presented in the text.

The lowest excited state of $Ru(bpz)_3^{2+}$ lies at 16 800 cm^{-1}, and for energy transfer there should be some overlap between the emission band of the donor (ruthenium) and the lower energy absorption band of the acceptor (quencher) excited state;[22] there are also some spin selection rules.[23] While energy transfer has been considered in the past, as a mechanism for the quenching of the excited state of the $Ru(bpy)_3^{2+}$ ion by quenchers of this type, it is not now considered likely in most cases.[24-29] Except

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(18) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

(19) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213 and references therein.

(20) (a) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265. (b) Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129. (c) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

(21) We assume here a value of r equal to the sum of the radii of the two reactants, $r_A + r_D$. The following values of radii have been used for calculation: $Ru(bpz)_3^{2+}$, 7.1 Å; Fe^{2+} and Fe^{3+}, 3.5 Å; Cu^{2+}, 3.8 Å; I^-, 2.16 Å; $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, 3.8 Å; $Co(NH_3)_6^{3+}$, 3.5 Å; $Co(NH_3)_5Cl^{2+}$, 4 Å. Equation 6:[20c] $k_0 = [8RT/3\eta][(b/r)/(e^{b/r} - 1)]$ where $b = Z_AZ_De^2/\epsilon kT4\pi\epsilon_0$. All constants are in SI units.

(22) Farmilo, A.; Wilkinson, F. *Chem. Phys. Lett.* **1975**, *34*, 575.

(23) Porter, G.; Wright, M. R. *Discuss. Faraday Soc.* **1959**, *27*, 18.

Chart I

reductive quenching

	$[Fe(CN)_6]^{4-}$ >	I^- >	$[Fe(H_2O)_6]^{2+}$
$10^{-8}k_q$, M^{-1} s^{-1}	100	70	6
driving force, V	1.33	1.14	0.92

oxidative quenching

	$Fe(H_2O)_6^{3+}$ >	$Fe(CN)_6^{3-}$ >	$Cu(H_2O)_4^{2+}$ >	$Co(NH_3)_5Cl^{2+}$ >	$Co(NH_3)_6^{3+}$
$10^{-8}k_q$, M^{-1} s^{-1}	105	56	5	5.7	1.3
driving force, V	0.79	0.38	0.54	0.34	0.12

Table IV. Thermodynamic Driving Forces (eV) for Reductive and Oxidative Quenching[a]

species	pH	oxidative quenching	reductive quenching
$Fe(H_2O)_6^{2+}$	7	−0.42	0.92
	−0.3	−1.23	0.91
$Fe(H_2O)_6^{3+}$	7	0.79	0.19
	−0.3	−0.02	0.18
$[Fe(CN)_6]^{4-}$	7	−0.48	1.33
	−0.3	−1.29	1.32
	−0.3	−0.86*	0.89*
$[Fe(CN)_6]^{3-}$	7	0.38	<0.19
	−0.3	−0.43	<0.18
	−0.3	0*	<−0.25*
$Cu(H_2O)_4^{2+}$	7	0.54	−0.11
	−0.3	−0.25	<−0.12
$[Co(NH_3)_6]^{3+}$	7	0.12	<−0.11
	−0.3	−0.69	<−0.12
$[Co(NH_3)_5Cl]^{2+}$[b]	7	0.34	<−0.11
	−0.3	−0.12	<−0.5
I^-	7	<−1.5	1.14
$Co(H_2O)_6^{2+}$	7	−0.26	−0.12
	−0.3	−1.07	−0.13
$Mn(H_2O)_6^{2+}$	7	−1.16	0.18
	−0.3	−1.97	0.17
Ag^I/NO_3^-	7	0.82	−0.29
	−0.3	0.01	−0.30

[a] The < sign means more negative than. An asterisk signifies corrected for Nernstian shift. M^{n+}/M^{n-1+} couples taken from: Huheey, J. E. "Inorganic Chemistry"; Harper and Row: New York, 1972; p 258. [b] From: Curtis, N. J.; Lawrance, G. A.; Sargeson, A. M. *Aust. J. Chem.* **1983**, *36*, 1327. Note that, with respect to neutral solution, the corresponding driving forces for quenching of the $Ru(bpy)_3^{2+}$ ion are approximately 0.5 V greater than for oxidative quenching and approximately 0.7 V smaller for reductive quenching.

in one or two cases, as noted below, it is probably not important in the bipyrazine system.

The driving force for reductive quenching is as shown in (2), while the corresponding equation for oxidative quenching is

$$\Delta G_{23} = -E_{1/2}[Q^+/Q] + E_{1/2}[Ru^{3+}/Ru^{2+*}] + w_p - w_r \qquad (7)$$

where a value of −0.26 V is calculated for $E_{1/2}[Ru(bpz)_3^{3+}/Ru(bpz)_3^{2+*}]$ on the basis of the ground-state potential and excited-state energy (Table I).

Table IV includes the driving forces for both oxidative and reductive quenching for the various quenchers at pH 7 (and also −0.3). They were calculated from the excited-state potentials shown in Table I and the standard quencher potentials, $E[Q^+/Q]$ and $E[Q/Q^-]$ (in the presence where relevant, such as for Cu(II), of chloride ion). In general, considering the pH 7 data, one of these processes dominates. With the most downhill process chosen as the most probable mechansim, the observed rate constants tend to increase with the driving force as shown in Chart I. An exact correlation should not be expected in view of the variation in the nature of the quenchers, especially the variation in charge.

Table V. Quenching Rate Constants for the $Ru(bpy)_3^{2+}$ Ion[a]

quencher	medium	k_q, M^{-1} s^{-1}	ref
$Fe(H_2O)_6^{3+}$	0.5 M H_2SO_4	2.7×10^9	24
	1.0 M KCl	4.8×10^9	tw
$Fe(H_2O)_6^{2+}$	1.0 M KCl	3.3×10^6	tw
$Cu(H_2O)_4^{2+}$	0.5 M H_2SO_4	6.2×10^7	25
	1.0 M KCl	8.3×10^8	tw
$Co(NH_3)_6^{3+}$	0.5 M H_2SO_4	1×10^7	28
$Co(NH_3)_5Cl^{2+}$	0.5 M H_2SO_4	9.3×10^8	28
$Fe(CN)_6^{4-}$	0.5 M NaCl	49×10^8	27

[a] Room temperature, uncorrected for diffusion. tw = this work.

The Co(II) ion has uphill driving forces for both reductive and oxidative quenching, thereby explaining its lack of reaction. Mn(II) has a small downhill driving force for reductive quenching, but it is evidently not enough, in view of the positive charge on the quencher, for any quenching to be observed. The absence of oxidative quenching by Ag(I) is, however, puzzling.

We conclude that the dominant quenching mechanism is as shown in Chart I although we recognize that this does not constitute a proof. However, comparing these data with those for the $Ru(bpy)_3^{2+}$ ion shows that the mechanisms proposed here are identical with those proposed or proven with the tris(bipyridine) ion, specifically for Fe(III),[24] Cu(II),[25] $[Fe(CN)_6]^{4-}$,[26,27] and $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5X]^{2+}$.[28,29]

It is difficult to compare these data (Table III) in depth because of the varying charges and types of quencher. However, note that the $[Fe(H_2O)_6]^{3+}$, I^-, and $[Fe(CN)_6]^{n-}$ (n = 3, 4) ions all quench at the diffusion rate. The last two are undoubtedly assisted by their negative charge while the first has a very substantial driving force for quenching. Other ions quench at a lower than diffusion rate generally because of lower driving forces and their positive charge; however, note that the $[Fe(H_2O)_6]^{2+}$ ion has an unexpectedly low k_q value in this context.

The data in Table III were obtained via intensity quenching. Two systems were also studied by lifetime quenching. The $[Fe(CN)_6]^{3-}$ ion yielded a lifetime quenching rate constant of 40 × 10^8 M^{-1} s^{-1}, essentially the same as that shown in Table III; thus, static quenching is not significant despite the interaction in concentrated solution (see below). On the other hand, the lifetime quenching rate constant for the $[Fe(CN)_6]^{4-}$ ion is a maximum of 2.4 × 10^9 M^{-1} s^{-1}, which may be indicative of some static quenching. However, there is a slow thermal chemical reaction between the $Ru(bpz)_3^{2+}$ and ferrocyanide ions in the presence of chloride ion; this undeniably complicates the issue and may also be responsible for the apparently much greater than diffusion rate quenching observed for this ion.

Comparison of these data with the quenching of $Ru(bpy)_3^{2+}$ is illuminating (Table V). In general, the $Ru(bpy)_3^{2+}$ quenching rates are at least 1 order of magnitude slower than those of the bipyrazine species, for both oxidative and reductive quenching processes. The only exception is for quenching with the $[Co(NH_3)_5Cl]^{2+}$ ion (oxidative). Since the bipyrazine species is a stronger oxidizing agent in the excited state than the bipyridine species, reductive quenching is expected to proceed more rapidly.

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(24) (a) Lin, C.-T.; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97. (b) Lin, C.-T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536.

(25) Hoselton, M. A.; Lin, C.-T.; Schwartz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 2383.

(26) Toma, H. E.; Creutz, C. *Inorg. Chem.* **1977**, *16*, 545.

(27) (a) Juris, A.; Manfrin, M. F.; Maestri, M.; Serpone, N. *Inorg. Chem.* **1978**, *17*, 2258. (b) Juris, A.; Gandolfi, M. T.; Manfrin, M. F.; Balzani, V. *J. Am. Chem. Soc.* **1976**, *98*, 1047.

(28) (a) Navon, G.; Sutin, N. *Inorg. Chem.* **1974**, 13, 2159. (b) Natarajan, P.; Endicott, J. F. *J. Am. Chem. Soc.* **1973**, *95*, 2470.

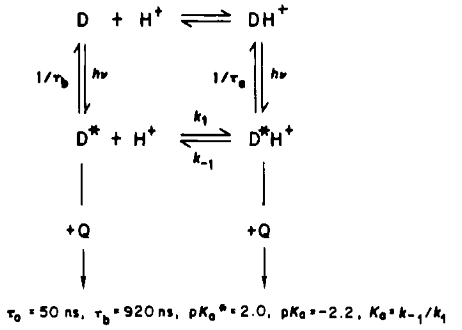
(29) Lehn, J.-M.; Sauvage, J.-P.; Ziessel, R. *Nouv. J. Chim.* **1979**, *3*, 423.

Certainly the rates for oxidation of the various amine species discussed in the previous section are significantly more rapid with $Ru(bpz)_3^{2+}$ than with $Ru(bpy)_3^{2+}$.[10,11]

The excited ruthenium tris(bipyridine) system is, however, a significantly better reducing agent than the bipyrazine analogue, and it is difficult to understand why oxidative quenching should generally be slower with this species.

(iii) Quenching in Acidic Aqueous Media by Metal Ions. In 2 M H_2SO_4 the most important excited-state species is $[Ru(bpz)_2(bpzH)]^{3+*}$. In concentrated sulfuric acid, the ground-state species is the hexaprotonated $Ru(bpzH_2)_3^{8+}$ (no doubt heavily ion paired)[6] but the predominant excited-state species is probably pentaprotonated. Both these excited species emit, so that it is possible to probe their electron-transfer photochemistry.

However, it is necessary to be sure that the protonation equilibrium is fully achieved prior to deactivation by the quencher. The situation (8) may prevail for the monoprotonated species.



(8)

Using the reported pK_a^* value and an assumed value of $k_{-1} > 10\tau_a^{-1}$ ($>2 \times 10^8$ s) for the deprotonation constant and following the discussion for $Ir(bpy)_2(bpyH)^{3+}$,[30] the second-order rate constant for protonation, k_1, would be estimated to be $>2 \times 10^{10}$ M^{-1} s^{-1}. On the other hand, if it were assumed that the deactivation were faster than the acid–base equilibrium, e.g. $k_{-1} < 0.1\tau_a^{-1}$, then $k_1 < 2 \times 10^8$ M^{-1} s^{-1}. Since rate constants for protonation processes are typically diffusion controlled (10^{10}–10^{11} M^{-1} s^{-1}),[31] the value estimated for this latter situation is far too slow. One may therefore conclude that the excited-state protonation equilibrium is established much faster than decay back to the ground state.

Although the excited-state species in 2 M H_2SO_4 is protonated, this is not the case for the ground-state species; it is therefore difficult to measure the ground-state redox potential of the monoprotonated species directly. It may be estimated via the Nernst equation:

$$E = E^\circ + 2.303(RT/nF)\text{pH} \tag{9}$$

Assuming pH −0.3 in 2 M H_2SO_4 and E° values reported in Table I for the unprotonated species, the data for the monoprotonated species, which are also shown in Table I, are derived from eq 9.

The monoprotonated species emits at 13 900 cm^{-1} (1.72 eV), and assuming this represents the (0, 0) transition, use of eq 4 provides estimates for the excited-state potentials also shown in Table I.

Thus, the monoprotonated species is seen to be a much weaker reducing agent than the unprotonated species, but a comparable oxidizing agent. It had been hoped that this species would have been a much stronger oxidizing agent in the excited state, because of the Nernstian shift in potentials due to the extra positive charge. That it is not so is due almost entirely to the significant shift to lower energy of the emission frequency.

The quenching rate constants from Stern–Volmer analysis are shown in Table III, and the calculated driving forces are shown in Table IV. To calculate the driving forces for the Cu(II), Fe(II), and Fe(III) aquo ions, which are not expected to be protonated in 2 M H_2SO_4, the same electrode potentials were used as for the neutral-species calculations. However, the hexacyano anions will be protonated in acidic media, and although some data are available in the literature[32] for the redox potentials of protonated hexacyanoiron species, we have simply assumed a Nernstian dependence to derive appropriate numbers. This is not expected to be far from the true situation.

Compared with the neutral species, oxidative quenching of the monoprotonated species should be much more difficult (slower), while driving forces for reductive quenching of both species are comparable. For the simple Fe(II) and Fe(III) and for the ferrocyanide ions this expectation is achieved. For Cu(II) we anticipate oxidative quenching and hence a marked reduction in rate. Such a reduction is observed, but it is small. The calculated driving force is now strongly uphill, yet considerable quenching is observed.

It is possible that there has been a switch to a dominant energy-transfer mechanism. The aquocopper(II) ion has a broad d–d adsorption centered near 12 500 cm^{-1},[33] relatively close to the emission of the protonated $[Ru(bpz)_2(bpzH)]^{3+}$ ion at 13 800 cm^{-1}. Overlap between donor and acceptor should be good, and thus an energy-transfer mechanism may be appropriate at least in acid solution.

The strong affinity for nitrogen ligands of the copper ion, and the higher basicity of the excited ruthenium–bipyrazine entity, may result in some binding of the Cu(II) to the excited-state species, facilitating quenching.

The ferricyanide ion is a much more effective quencher than anticipated. Oxidative quenching should be greatly inhibited, and there are no low-lying transitions[27a] to allow energy transfer. Formation of an iron(IV) species may be occurring (reductive quenching), but we know of no evidence for such a species in strong acidic media. Quenching by free cyanide ion would be much more effective than quenching by ferricyanide ion, and it is possible that, under the strongly acidic conditions, dissociation of cyanide ion may be fast enough to provide an alternate quenching mechanism.[32] Alternatively, in view of the high negative charge on the quencher and high positive charge on the excited ruthenium species, some kind of exciplex may be formed. Further study of these two last systems is in progress.

(iv) Quenching of Hexaprotonated $[Ru(bpzH_2)_3]^{8+}$ in Concentrated Sulfuric Acid. No electrochemical data exist for this species in concentrated sulfuric acid. However, the ground-state potentials will be more positive than those for the monoprotonated material. Moreover, the emission is at a higher energy (2.0 eV). Thus, the excited hexaprotonated species should be a stronger oxidizing agent than the excited monoprotonated species, and perhaps a comparable reducing agent.

It is difficult to adequately probe the photophysics of this species because concentrated sulfuric acid is such an unforgiving solvent. Most quenchers will be protonated by this medium, resulting in an increase in their redox potentials. Even simple metal aquo ions are likely to be modified. Thus, most quenchers will carry a positive charge and their approach to the excited hexaprotonated species is likely to be greatly inhibited by charge repulsion. Moreover, the solution is very viscous, reducing the diffusion rates. Thus, greatly reduced quenching rates are expected and are observed (Table III).

(v) Formation of Donor–Acceptor Ion Pairs. The possibility of complex formation between the positively charged $Ru(bpz)_3^{2+}$ ion and negative quenchers such as the hexacyano ions could not be neglected, especially as there is much evidence in the literature for similar types of species.[34,35] It is possible to isolate complexes of the type $[Ru(bpz)_3]_2Fe(CN)_6$ and $[Ru(bpz)_3]_3[M(CN)_6]_2$ (M = Fe(III), Co(III)), but this does not require that these ions interact significantly in dilute solution. Indeed, solutions of these

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(30) Bergeron, S. F.; Watts, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 3151.

(31) Bell, R. P. "The Proton in Chemistry"; Cornell University Press: Ithaca, New York, 1959.

(32) Sharpe, A. G. "The Chemistry of Cyano Complexes of the Transition Metals"; Academic Press: New York, **1976**.

(33) Lever, A. B. P. "Inorganic Electronic Spectroscopy", 2nd ed.; Elsevier: New York, 1984.

(34) Hennig, H.; Rehorek, A.; Rehorek, D.; Thomas, P. *Inorg. Chim. Acta* **1984**, *86*, 41.

(35) Curtis, J. C.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1562.

complexes show visible-region CT spectra typical of the ruthenium(II) component. In the solid state the complexes are intensely colored, have FTIR ν(CN) frequencies differing from the simple alkali-metal hexacyano anions, and presumably do involve some charge transfer under these conditions. A strong solution of the ferricyanide ion pair in aqueous solution shows a broad band centered about 15 150 (670) cm^{-1}. This is not present in either of the components and may be an intervalence transition.[33-35]

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Registry No. $Ru(bpz)_3^{2+}$, 75523-96-5; $Fe(H_2O)_6^{3+}$, 15377-81-8; $Fe(H_2O)_6^{2+}$, 15365-81-8; $Cu(H_2O)_4^{2+}$, 22174-11-4; $[Fe(CN)_6]^{4-}$, 13408-63-4; $[Fe(CN)_6]^{3-}$, 13408-62-3; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Co(NH_3)_5Cl]^{2+}$, 14970-14-0; $Co(H_2O)_6^{2+}$, 15276-47-8; $Mn(H_2O)_6^{2+}$, 15365-82-9; $Ru(bpz)_2(bpzH)^{3+}$, 95865-85-3; $Ru(bpzH_2)_3^{8+}$, 95865-86-4; Ag^I/NO_3^-, 7761-88-8; I^-, 20461-54-5; *N*,*N'*-diphenyl-*p*-phenylenediamine, 74-31-7; phenothiazine, 92-84-2; *N*,*N*-dimethyl-*p*-toluidine, 99-97-8; *N*,*N*-dimethylaniline, 121-69-7; diphenylamine, 122-39-4; aniline, 62-53-3; triphenylamine, 603-34-9; 1,2,4-trimethoxybenzene, 135-77-3; 1,4-dimethoxybenzene, 150-78-7; 1,2,3-trimethoxybenzene, 634-36-6; 1,2-dimethoxybenzene, 91-16-7; 1,3,5-trimethoxybenzene, 621-23-8.

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Protonation and Lewis Acid–Lewis Base Equilibria in (Bipyrazine)molybdenum and (Bipyrazine)tungsten Tetracarbonyls

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The title complexes react with boron trifluoride etherate to generate mono- and diadducts of BF_3. In H_2SO_4/ethanol solution one proton is coordinated. In each case reaction is assumed to occur at the peripheral uncoordinated nitrogen atoms of the bipyrazine unit. New metal-to-ligand charge-transfer bands are observed for these various species. Analysis of the spectra shows that $pK_a(1)$ for the first uncoordinated nitrogen atom is about −0.3 (Mo complex) and that extensive mixing of ground and excited states must be occurring to account for the oscillator strengths and band widths observed.

Introduction

Ground- and excited-state protonation equilibria involving the $Ru(bpz)_3^{2+}$ ion (bpz = bipyrazine) have recently been reported.[1] This species binds up to six protons in a stepwise fashion, providing an interesting series of electronic absorption and emission data. Of special interest was the variation in metal-to-ligand charge-transfer (MLCT) energy as a function of the degree and site of protonation. Stepwise protonation provides a useful mechanism for "tuning" excited-state redox potentials[2] and is of obvious interest in the design of photocatalytic redox reagents. Previous studies of protonation equilibria involving inorganic complexes have discussed protonation at the nitrogen atom of coordinated cyanide ion in species such as $M(CN)_4L$ and $M(CN)_2L_2$ (M = Fe, Ru; L = diimine),[3,4] considered the enhanced acidity of ruthenium(II) complexes of 4,7-dihydroxy-1,10-phenanthroline[5], and analyzed the pH dependence of ruthenium bipyridine[6] and bipyrimidine[7] species. As is evident, much of the work has been associated with ruthenium or its congeners. The binding of Lewis acids to cyanide complexes and its effect on their charge-transfer spectra has also been studied.[8] For these reasons we considered it useful to probe the protonation equilibria in a complex other than ruthenium having only one bipyrazine unit to provide a data set that might be capable of more detailed analysis and additional insights.

The species $M(CO)_4(bpz)$ (M = Mo, W)[9] are soluble in organic solvents and give rise to intense absorption in the visible region, attributed to metal-to-ligand charge-transfer (MLCT) M → bpz(π^*). Addition of mineral acid, or the Lewis acid BF_3 (etherate) causes changes in the visible absorption spectra that can be interpreted in terms of mono- and diacid equilibria. FTIR and NMR data are reported in support of the equilibria proposed.

Table I. Electronic Spectra of $M(CO)_4bpz$ in the Presence of $Et_2O{\cdot}BF_3$[a]

approx concn of $Et_2O{\cdot}BF_3$, mol L^{-1}	color	λ_{max}, nm					
		$Mo(CO)_4bpz$			$W(CO)_4bpz$		
		II	I/Ib	Ia	II	I/Ib	Ia
0	pink	368.5	520		371	533	
0.07	pink	369	523	sh	371	534	sh
0.13	mauve	370	527	618	371	539	616
0.17	blue	371	sh	625	371	sh	620
0.20	blue	371	494	640	sh	482	630
0.33	gray-blue	sh	490	653	...	480	640
7.9[b]	gray-blue				322	490	654

[a] Spectra recorded using approximately 10^{-4} M $M(CO)_4bpz$ in acetone. Solutions were deoxygenated with dry N_2 before addition of $Et_2O{\cdot}BF_3$. [b] Complex dissolved in pure $Et_2O{\cdot}BF_3$.

Experimental Section

The complexes $Mo(CO)_4(bpz)$ and $W(CO)_4(bpz)$ were prepared according to literature methods.[9] Acetone and 96% H_2SO_4 were BDH Analar grade. The acid was diluted with absolute ethanol. Boron trifluoride etherate was purified according to a literature method[10] and stored under nitrogen or dry air. Electronic spectra were recorded on a Perkin-Elmer Hitachi Model 340 microprocessor spectrophotometer. The cell holder was cooled to ca. 10 °C to minimize decomposition of the complexes. ^1H NMR spectra were recorded on a Varian EM360 60 MHz spectrometer at ambient temperature. Tetramethylsilane at 0.00 ppm or the residual protons of acetone-d_6 at 2.05 ppm were used as internal references. FTIR spectra were recorded on a Nicolet SX20 instrument (courtesy of Nicolet Co.) as acetone solutions in a sodium chloride cell. Computer simulations were obtained with a Commodore

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(1) Crutchley, R. J.; Kress, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1983**, *105*, 1170.
(2) Haga, M.-A.; Dodsworth, E. S.; Eryavec, G.; Seymour, P.; Lever, A. B. P. *Inorg. Chem.*, paper in this issue.
(3) Schilt, A. A. *J. Am. Chem. Soc.* **1963**, *85*, 904.
(4) Peterson, S. H.; Demas, J. N. *J. Am. Chem. Soc.* **1979**, *101*, 6571.
(5) Giordano, P. J.; Bock, C. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 6960.
(6) Giordano, P. J.; Bock, C. R.; Wrighton, M. S.; Interrante, L. V.; Williams, R. F. X. *J. Am. Chem. Soc.* **1977**, *99*, 3187.
(7) Hunziger, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370.
(8) Shriver, D. F.; Posner, J. *J. Am. Chem. Soc.* **1966**, *88*, 1672.
(9) Crutchley, R. J.; Lever, A. B. P. *Inorg. Chem.* **1982**, *21*, 2276.
(10) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals", 2nd ed.; Pergamon Press: Elmsford, NY, 1980.

0020-1669/85/1324-1906$01.50/0