Interactions between the Excited States of Ruthenium(II)−Diimine Complexes and Phenols in Aqueous Solution

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Interactions between the MLCT excited states of Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) or Ru(bpz)$_3^{2+}$ (bpz = 2,2′-bipyrazine) and phenol or monochlorophenols have been investigated in aqueous solution using steady-state and time-resolved spectrofluorimetry. The presence of phenol (PhOH), which does not quench *Ru(bpy)$_3^{2+}$ in mildly acidic solution, causes the emission to undergo a blue shift with increasing [PhOH]; the emission quantum yields and the excited-state lifetimes decrease with increasing [PhOH] at low temperatures (5−35 °C) but increase with increasing [PhOH] at higher temperatures (35−70 °C). This behavior is understood in terms of the variations in the rate constants of the temperature-independent radiative and nonradiative decays of *Ru(bpy)$_3^{2+}$ and the activation-controlled population of the metal-centered excited state as [PhOH] is changed. The presence of chlorophenols has no effect on the photophysics of *Ru(bpy)$_3^{2+}$; PhOH reductively quenches *Ru(bpz)$_3^{2+}$.

Introduction

The energetics and kinetics of the metal-to-ligand charge-transfer (MLCT) excited states of Ru(II)−diimine complexes in solution are sensitive to the microenvironment around the complex. For example, the emission lifetimes and intensities of many complexes are increased in the presence of DNA,[2−9] indicating the existence of electrostatic binding to the phosphate backbone and surface binding in the major and/or minor grooves; in some cases, intercalation occurs between the base pairs of the nucleic acid double strand. The photophysics of complexes is also dramatically altered in zeolites[10−20] and in micellar solutions.[21−27] The medium around the complex induces changes in the energy level of the dipolar MLCT state, resulting in variations in the rate constants for nonradiative return to the ground state (GS) and crossing to the metal-centered (MC) excited state. When the polarity of the microenvironment is decreased, the energies of the MLCT states increase, leading to a blue shift of the emission maxima and longer lifetimes of the excited states.[28] However, little is known about the interactions of the excited states with simple solutes that do not effect quenching.

In a recent communication[29] and a follow-up paper,[30] we reported on the ground-state interactions between Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) or Ru(bpz)$_3^{2+}$ (bpz = 2,2′-bypyrazine) and phenol (PhOH) or monochlorophenols (2-, 3-, and 4-ClPhOH) in aqueous (D$_2$O) solution. Specifically, we found that the presence of the phenols results in an upfield shift in the NMR spectra of the metal complexes; the results were interpreted in terms of an offset face-to-face orientation due to π-stacking interactions. The dependence of the shifts in the resonances on the concentration of the phenol led to estimates of the formation constants of 1:1 aggregates, which are on the order of 0.01 M^{-1} for Ru(bpy)$_3^{2+}$ and somewhat less for Ru(bpz)$_3^{2+}$.

Unlike PhOH, which does not quench *Ru(bpy)$_3^{2+}$ due to insufficient driving forces for energy or electron transfer, the phenolate ion (PhO$^-$) quenches it reductively, generating Ru(bpy)$_3^+$ and the phenoxyl radical (PhO$^\bullet$); the quenching rate constants (k_q) and cage escape yields of the redox products (η_{ce}) for quenching by PhO$^-$ and its derivatives were studied as a function of temperature and solution medium in alkaline aqueous solution by Miedlar and Das[31] and more recently by Thanasekaran et al.[32] *Ru(bpz)$_3^{2+}$ (bpz = 2,2′-bipyrazine), which is a much stronger excited-state oxidant than is *Ru(bpy)$_3^{2+}$ (1.68 and 0.93 V vs NHE, respectively),[33] is reductively quenched by PhOH; the products of the photoinduced electron transfer in the absence of air are hydroxyphenyl dimers.[34]

The observation that Ru(bpy)$_3^{2+}$ and Ru(bpz)$_3^{2+}$ interact with PhOH and ClPhOH in the ground state raises questions as to whether excited-state interactions are exhibited in the photophysics of these complexes and, if so, whether the excited-state quenching reactions show evidence of the interactions. To answer these questions, the photophysical properties of the excited states were examined at room temperature for mildly acidic aqueous solutions of Ru(bpy)$_3^{2+}$ or Ru(bpz)$_3^{2+}$ that contain PhOH or one of the monochlorophenols. Some preliminary information was recently presented.[29]

Experimental Section

Materials. Ru(bpy)$_3$Cl$_2$·6H$_2$O (GFS Chemicals) was recrystallized from water and dried over silica gel. PhOH and the monochlorophenols (Aldrich) were purified by sublimation. Aqueous solutions were prepared from doubly distilled water that had been passed through a Millipore purification train; D$_2$O (Aldrich) was used as received. Ru(bpz)$_3^{2+}$ as its PF$_6^-$ salt was prepared as described in the literature.[35] Buffer solutions (pH 5.5 and pH 12) were prepared by standard methods.[36]

Instrumentation. Emission spectra and quantum yield measurements were performed for 450 nm excitation with a Perkin-Elmer MPF2A fluorescence spectrometer or a SLM Instruments 48000 phase modulation spectrofluorimeter; in the latter case, corrections for phototube response and the spectral analyses were made with the programs supplied with the instrument. Pulsed-laser flash photolysis experiments for the

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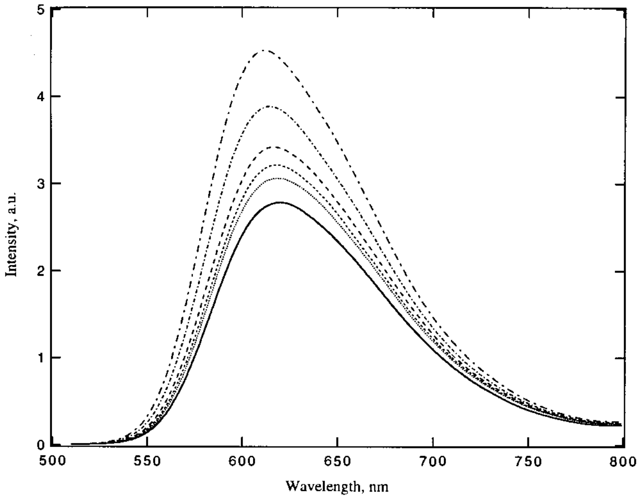


Figure 1. Corrected emission spectrum of $^*Ru(bpy)_3^{2+}$ in mildly acidic aqueous solution at 5 °C; $\lambda_{ex} = 450$ nm. [PhOH] = 0 (—), 0.1 (···), 0.2 (• • •), 0.3 (- - -), 0.5 (- • -), and 0.7 (— - —) M.

determination of τ_{obs} were conducted as a function of temperature on air-saturated or Ar-purged solutions with a Nd:YAG pulsed laser ($\lambda_{ex} = 532$ nm, 100 mJ/pulse);[37] temperature regulation was achieved to ±0.1 °C with the use of a Brinkmann model RM6 controller. The lifetime of $^*Ru(bpz)_3^{2+}$ as a function of [PhOH] (0.1−0.7 M) at ambient temperature was also made with the IBH single photon counting system 5000 at Istituto FRAE-CNR, Bologna, Italy. Absorption spectra were carried out with a HP 8452A diode array spectrophotometer.

Procedures. Values of the observed excited-state lifetimes (τ_{obs}) of the complexes (40 μM) were determined as a function of temperature and pH in the absence and presence of the phenols (0.05−0.7 M PhOH and 0.01−0.1 M ClPhOH) by measuring the decay of the excited-state emission at 605 nm. Fresh solutions were also used to measure the emission spectra of the complexes as a function of [PhOH] or [ClPhOH]. Except where noted, solutions were Ar-purged.

Results

Absorption and Emission Spectra. The presence of phenols did not result in any changes in the ground-state UV−visible absorption spectra of the complexes across the pH range at ambient temperature.

The emission spectrum of $^*Ru(bpy)_3^{2+}$ exhibited a distinct blue shift with increase in [PhOH] in mildly acidic Ar-purged aqueous solutions at 5 (Figure 1), 20, and 50 °C. At 5 and 20 °C, the emission intensity increased with increasing [PhOH]; at 50 °C, the intensity decreased with increasing [PhOH]. Values of the emission energy (E_{em}) were obtained from the corrected emission maximum (λ_{max}); values of the luminescent quantum yields (Φ_{em}) were obtained from the corrected integrated emission spectra relative to that of $Ru(bpy)_3^{2+}$ in the absence of PhOH[38] ($\Phi_{em} = 0.046$)[39] under identical absorbency conditions at 450 nm. The photophysical details (λ_{max}, E_{em}, Φ_{em}) in H_2O are given in Table 1; the corresponding data in D_2O are given in the Supporting Information. The values of Φ_{em} increase as [PhOH] is increased at 5° and 20 °C but decrease at 50 °C (Figure 2); a plot of E_{em} as a function [PhOH] is given in the Supporting Information. No effect on the emission spectrum of $Ru(bpy)_3^{2+}$ with increasing [PhOH] was seen in CH_3CN solutions.

Up to 0.1 M ClPhOH had no effect on the maximum or intensity of emission from $^*Ru(bpy)_3^{2+}$ in H_2O at pH 5.5. In alkaline solution, the emission from $^*Ru(bpy)_3^{2+}$ is quenched by the phenolate ions; no shift in the emission maximum was observed.

TABLE 1: Photophysical Parameters for the Decay of $^*Ru(bpy)_3^{2+}$ as a Function of [PhOH] and Temperature in H_2O

	[PhOH], M					
	0.00	0.10	0.20	0.30	0.50	0.70
k_1 (10^6 s^{-1})	1.36	1.28	1.22	1.12	0.870	0.620
k_2 (10^{14} s^{-1})	1.59	0.720	1.02	1.03	0.430	0.200
ΔE (cm^{-1})	4 174	3 959	4 022	3 996	3 739	3 517
			T = 5 °C			
λ_{max} (nm)	620	619	618	616	613	610
E_{em} (cm^{-1})	16129	16155	16181	16234	16313	16393
Φ_{em}	0.053	0.056	0.059	0.061	0.069	0.079
k_{rad} (10^4 s^{-1})	7.1	7.4	7.5	7.3	7.1	6.7
k_{nr} (10^6 s^{-1})	1.3	1.2	1.1	1.0	0.80	0.55
k' (10^6 s^{-1})	0.060	0.070	0.080	0.090	0.15	0.22
ϕ	0.044	0.053	0.063	0.075	0.15	0.26
			T = 20 °C			
λ_{max} (nm)	622	620	617	618	614	612
E_{em} (cm^{-1})	16077	16129	16207	16181	16287	16340
Φ_{em}	0.046	0.049	0.050	0.052	0.056	0.057
k_{rad} (10^4 s^{-1})	7.5	7.8	7.6	7.6	7.7	7.3
k_{nr} (10^6 s^{-1})	1.3	1.2	1.1	1.0	0.80	0.54
k' (10^6 s^{-1})	0.28	0.36	0.38	0.44	0.63	0.87
ϕ	0.17	0.23	0.25	0.30	0.46	0.67
			T = 50 °C			
λ_{max} (nm)	621	622	620	621	618	615
E_{em} (cm^{-1})	16103	16077	16129	16103	16181	16260
Φ_{em}	0.029	0.030	0.029	0.028	0.026	0.023
k_{rad} (10^4 s^{-1})	7.3	7.9	7.7	7.6	7.9	7.7
k_{nr} (10^6 s^{-1})	1.3	1.2	1.1	1.0	0.79	0.54
k' (10^6 s^{-1})	1.4	1.6	1.7	2.0	2.5	3.2
ϕ	0.53	0.61	0.65	0.71	0.83	0.95

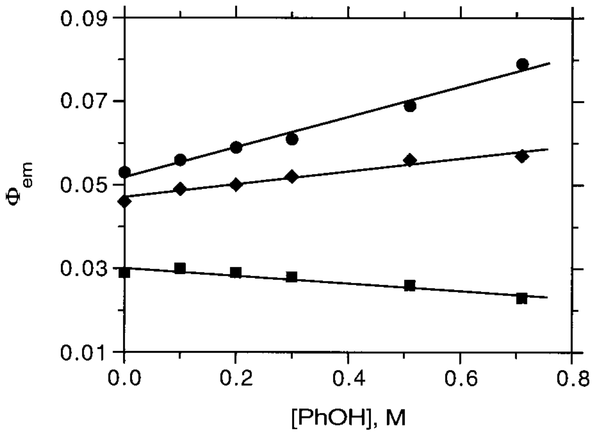


Figure 2. Luminescent quantum yields of $^*Ru(bpy)_3^{2+}$ as a function of [PhOH] and temperature in mildly acidic Ar-purged aqueous solution: 5 (●), 20 (◆), and 50 °C (■).

The emission spectrum of $^*Ru(bpz)_3^{2+}$ was quenched across the entire pH range in aqueous solution by PhOH and ClPhOH. No spectral shifts, corresponding to those seen for $^*Ru(bpy)_3^{2+}$, were observed. The Stern−Volmer plot of I_0/I (Supporting Information) in mildly acidic air-saturated solution shows no major deviations from linearity over a very large extent (≤99.6%) of quenching.

Emission Lifetimes. Figure 3 shows k_{obs} (=$1/\tau_{obs}$) vs [PhOH] for $^*Ru(bpy)_3^{2+}$ in mildly acidic, Ar-purged aqueous solutions at different temperatures; the corresponding plot in D_2O as well as the values of k_{obs} as a function of [PhOH] and temperature in H_2O and D_2O are given in the Supporting Information. In

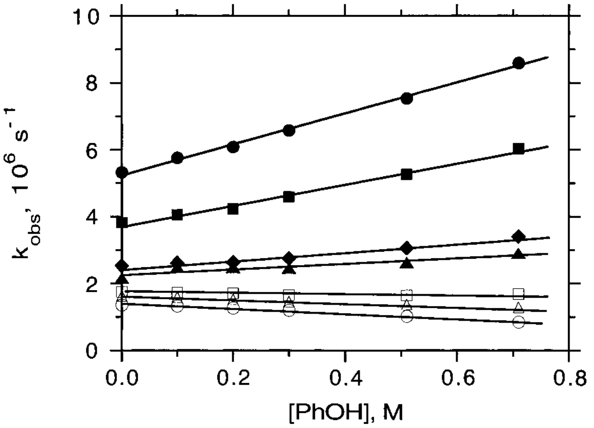


Figure 3. Observed decay rate constant for $^*Ru(bpy)_3^{2+}$ as a function of [PhOH] and temperature in mildly acidic Ar-purged aqueous solution: 5 (○), 20 (△), 30 (□), 40 (▲), 50 (◆), 60 (■), and 70 °C (●).

these solvents, k_{obs} decreases at low temperatures, but increases at high temperatures, as [PhOH] is increased.

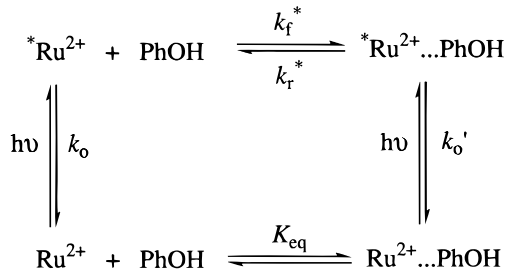
Quenching. A plot of τ_0/τ vs [PhOH] for $^*Ru(bpz)_3^{2+}$ in mildly acidic air-saturated solution overlays the I_0/I Stern−Volmer line (Supporting Information). Inasmuch as $\tau_0 = 0.84$ μs in air-saturated solution at ambient temperature, the slope of the line yields a value of $k_q = 4.2 \times 10^8$ M^{-1} s^{-1} for quenching by PhOH.

The emission lifetime of $^*Ru(bpy)_3^{2+}$ was determined as a function of $[O_2]$ in the presence and absence of PhOH; values of k_q for quenching by O_2 as a function of [PhOH] (0−0.5 M) at 20 and 50 °C averaged $(3.9 \pm 0.04) \times 10^9$ and $(7.0 \pm 0.3) \times 10^9$ M^{-1} s^{-1}, respectively, independent of [PhOH].[40]

Discussion

*Ru(bpy)$_3^{2+}$−PhOH Interaction. The significant changes in the emission spectrum and lifetime of $^*Ru(bpy)_3^{2+}$ that are observed upon the addition of PhOH indicate that a nonquenching interaction takes place, which may or may not be of the same origin as that observed for the ground-state species.[29,30] The Benesi−Hildebrand treatment[41] or alternative approaches[42] can be used to evaluate the equilibrium constant of a ground-state interaction from the determination of the quantum yield of fluorescence of the system as a function of the concentration of its constituents. These procedures carry the assumption that the spectrum and lifetime of the fluorescence from the complexed and uncomplexed excited states are the same; differences in Φ_{em}, which relate directly to the population of the excited states, reflect the concentrations of the ground-state species, their absorptivities, and the absorbed light intensities. However, in the case of the $^*Ru(bpy)_3^{2+}$−PhOH system, the variations in the emission spectra and the dependence of Φ_{em} on [PhOH] as a function of temperature indicate that these assumptions are not valid and that conventional approaches cannot be utilized.

SCHEME 1



Instead, the spectrofluorimetry data can be examined in terms of the dynamical mechanism in Scheme 1. Excitation of uncomplexed $Ru(bpy)_3^{2+}$ or the $Ru(bpy)_3^{2+}\cdots PhOH$ aggregate, which are in ground-state equilibrium with $K_{eq} \sim 0.01$ M^{-1} and have, apparently, the same absorption spectrum, creates the corresponding excited-state species. $^*Ru(bpy)_3^{2+}$ and $^*Ru(bpy)_3^{2+}\cdots PhOH$ engage in kinetically coupled transformations to the ground states (k_0 and k_0', respectively) and to each other; k_f^* and k_r^* represent the rate constants of the forward and reverse excited-state equilibrium reactions, respectively. If the rates of light absorption by $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}\cdots PhOH$ are I_a and I_a', respectively, and the rates of emission from $^*Ru(bpy)_3^{2+}$ and $^*Ru(bpy)_3^{2+}\cdots PhOH$ are R and R', respectively, the total integrated emission intensity ($R_{tot} = R + R'$) can be expressed in terms of the steady-state concentrations of the excited species (eq 1), where k_{rad} and k_{rad}' are the rate constants for radiative decay of $^*Ru(bpy)_3^{2+}$ and $^*Ru(bpy)_3^{2+}\cdots PhOH$, respectively.

$$R_{tot} = k_{rad}\left\{\frac{I_a + k_r^*[^*Ru(bpy)_3^{2+}\cdots PhOH]_{ss}}{k_0 + k_f^*[PhOH]}\right\} + k_{rad}'\left\{\frac{I_a' + k_f^*[^*Ru(bpy)_3^{2+}]_{ss}[PhOH]}{k_0' + k_r^*}\right\} \quad (1)$$

Dividing both sides of eq 1 by I_{tot} ($= I_a + I_a'$) yields the overall observed emission quantum yield (Φ_{em}). Unfortunately, the equation defies easy simplification; however, it can be seen that the unusual dependence of Φ_{em} on [PhOH] as a function of temperature results from the appearance of [PhOH] in the denominator and numerator of the first and second terms, respectively. Inasmuch as the various rate constants in the equation have their own temperature coefficients, the dependence of Φ_{em} on [PhOH] could shift smoothly from positive to negative as the temperature is raised, accounting, albeit qualitatively, for the results shown in Figure 3.

It is unfortunate that the results do not permit an evaluation of the excited-state equilibrium constant (K_{eq}^*). However, we showed for the ground-state equilibrium that increased electron-donating ability of the ligand results in a weaker π-stacking interaction and a correspondingly lower value of K_{eq};[30] the localization of the transferred electron on a unique ligand in the excited state $(Ru^{III}(bpy)_2(bpy^{\bullet-})^{2+})$[43] would not favor the equilibrium were it the locus of the interaction. On the other hand, $^*Ru(bpy)_3^{2+}$, unlike the ground state, possesses a large dipole moment;[44] the combined effect of π-stacking and dipole interactions could result in a value of K_{eq}^* that is higher than that of K_{eq}. Further, if the interaction were at the unreduced ligands, the value of K_{eq}^* would be expected to be similar to that of K_{eq}. Regardless, the fact that similarly high concentrations of PhOH are needed to effect both the ground- and excited-state interactions suggests that K_{eq}^* could be of the order of K_{eq} (0.001−0.1 M^{-1}). The failure to observe any effect with the monochlorophenols can be attributed to their lower solubilities and/or lower values of K_{eq}^* compared to the case of PhOH; both of these factors could keep any complexation from being observed.

The observation that the emission spectrum and photophysical parameters of $^*Ru(bpy)_3^{2+}$ are unaffected by the presence of PhOH in CH_3CN solutions is similar to that made for the ground state wherein the NMR spectrum is the same in the presence and absence of PhOH in neat CD_3CN;[30] it was argued that acetonitrile, which solvates both PhOH and $Ru(bpy)_3^{2+}$ more effectively than does water, results in a weaker π-stacking

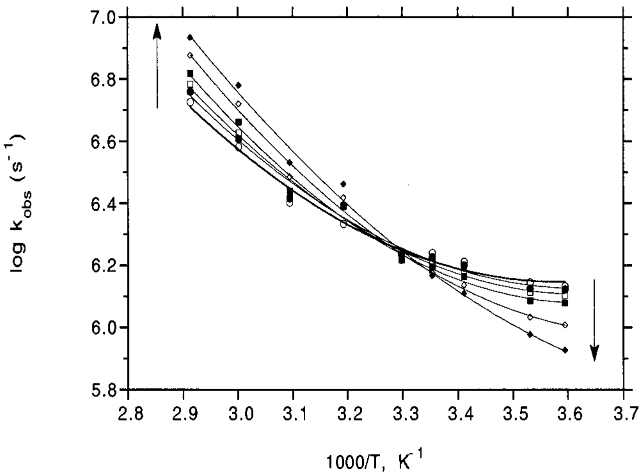


Figure 4. Plot of log k_{obs} vs $1/T$ as a function of [PhOH] (arrows in direction of increasing values: 0.00, 0.10, 0.20, 0.30, 0.50, 0.70 M) in H_2O.

interaction.[45] The same explanation can be applied to the excited-state behavior here.

Photophysics. The luminescent moiety in the presence and absence of PhOH is $^*Ru(bpy)_3^{2+}$. If the equilibrium between $^*Ru(bpy)_3^{2+}$ and $^*Ru(bpy)_3^{2+}\cdots PhOH$ were fast compared to their decays to the ground state, the variation in the photophysical parameters of energetics and dynamics with increasing [PhOH] would reflect the nature of the interaction of phenol with the excited state. The photophysical parameters serve as indicators of the microenvironment around the excited state. The increase in E_{em} with increasing [PhOH] at all temperatures indicates that the polarity of the microenvironment around the emitting species decreases as [PhOH] is increased; the different trend in Φ_{em} with increasing [PhOH] at high and low temperatures indicates that the rate constants for the competing decays of $^*Ru(bpy)_3^{2+}$ are altered in the presence of PhOH.

The temperature-dependent lifetimes of $^*Ru(bpy)_3^{2+}$ in the presence and absence of PhOH were fitted to eq 2,[46] where k_1 is a temperature-independent term and $k_2 \exp(-\Delta E/k_BT)$ is the overall rate constant (k') for the thermally activated population of the higher energy metal-centered d−d excited state that lies ΔE above the emitting state.

$$k_{obs} = k_1 + k_2 \exp(-\Delta E/k_BT) \qquad (2)$$

Plots of log k_{obs} vs $1/T$ as a function of [PhOH] show clearly the existence of isokinetic points at ~30 °C in H_2O (Figure 4) and at ~10 °C in D_2O (Supporting Information). These plots, which show the influence of a low mole fraction of a nonquenching solute in solution, are, remarkably, almost identical to those obtained earlier for Ru(II) complexes, including $Ru(bpy)_3^{2+}$, as a function of the composition of H_2O-CH_3CN solvent mixtures;[47] this effect was interpreted in terms of the variations of the values of k_1, k_2, and ΔE with changes in the polarity of the microenvironment surrounding the emitting state. Specifically, k_1 decreased, k_2 increased, and ΔE remained relatively unchanged (therefore, k' increased) as the mole fraction of CH_3CN was increased. It was concluded that it is the energy levels of the polar MLCT states that are sensitive to the polarity of the surroundings. The subtle differences in these parameters for complexes that possess different ligands cause the curves in the plots to intersect at different temperatures. It is for that reason the lifetime of $^*Ru(bpy)_3^{2+}$ is longer in CH_3CN than in water at room temperature, but the behavior of $^*Ru(bpz)_3^{2+}$ is exactly the opposite.

Temperature-independent values of k_1, k_2, and ΔE were obtained from the best computer fit of the plots of log k_{obs} vs $1/T$ as a function of [PhOH] in H_2O (Table 1) and D_2O (Supporting Information). The values of both k_1 and ΔE decrease significantly as [PhOH] is increased; the value of k_2, which has a much lower level of reliability due to the nature of the curve fitting,[47] generally decreases. Nevertheless, k' increases steadily at all temperatures as [PhOH] increases. The values of k_1, k_2, and ΔE are higher in H_2O than in D_2O. The efficiency of populating the MC state by thermal up-conversion from the MLCT state ($\phi = k'/k_{obs}$) is also given in the tables; ϕ increases significantly as [PhOH] is increased and is markedly greater in D_2O than in H_2O. These observations are consistent with a decrease in the MC−MLCT energy gap and a concomitant increase in the MLCT−ground state gap; a plot of ΔE vs E_{em} for the data in H_2O and D_2O at 5, 20, and 50 °C shows this linear relationship (Supporting Information).

Inasmuch as $k_1 = k_{rad} + k_{nr}$, where k_{rad} and k_{nr} are the rate constants for the radiative and nonradiative decay of the MLCT state, respectively, and $k_{rad} = \Phi_{em}/\tau_{obs}$,[48−51] it is possible to extract values of k_{rad} and k_{nr} (Table 1 and Supporting Information) as a function of temperature from the experimental data. As can be seen, k_{rad} is independent of [PhOH] and temperature within the uncertainty of the calculation; we saw previously that k_{rad} is insensitive to both solvent composition and temperature.[47] The nonradiative rate constant is usually examined on the basis of the energy gap law,[48−50] which predicts a linear dependence (negative slope) of the temperature-independent values of log k_{nr} on E_{em} if variations in the energy of reorganization of the solvent are not significant compared to variations in E_{em} as [PhOH] is changed; such a plot is given in the Supporting Information.

Whereas k_{obs} decreases with increasing [PhOH] at low temperatures but increases with increasing [PhOH] at high temperatures, the temperature-independent values of k_{nr} decrease with increasing [PhOH] in H_2O and D_2O at all temperatures (Supporting Information). As was pointed out by Meyer for hydroxylic solvents,[28] the high-frequency O−H (or O−D) stretching modes play an important role as energy acceptors in nonradiative decay, with k_{nr} increasing as the stretching frequency increases. This is the case here; the value of k_{nr} in the absence of PhOH is higher in H_2O (O−H stretch: 3200−3900 cm^{-1}) than in D_2O (O−D stretch: 2400−2900 cm^{-1}).[52] It is well established[53] that the O−H stretching frequency in H_2O is lowered by 300−400 cm^{-1} due to hydrogen bonding between PhOH and H_2O;[54] this may result in the decrease in k_{nr} with increasing [PhOH] in both solvents. This same explanation was used to account for the lowered radiationless decay rate in the $S_1 \rightarrow S_0$ transition of PhOH in H_2O compared to nonhydroxylic solvents.[55]

Finally, Barclay−Butler plots of log k_2 vs ΔE in H_2O and D_2O are linear (Supporting Information); a similar correlation was previously found for Ru(II) complexes.[56] It can be inferred from this relationship that an increase in the activation energy is accompanied by a greater density of vibrational levels at the point of barrier crossing, thus opening an increased number of reaction channels. The implication is that the low-frequency and collective dipole reorientation modes of the medium surrounding the complex are changed upon the addition of PhOH to H_2O and D_2O in a virtually identical manner.

Quenching. Despite the fact that $Ru(bpz)_3^{2+}$ exhibits ground-state complexation with PhOH,[30] there is no evidence for any excited-state interaction outside of reductive quenching. The diminished emission spectrum of $^*Ru(bpz)_3^{2+}$ with increasing

[PhOH] shows no spectral shifts; excellent linear Stern−Volmer behavior, with no evidence of curvature due to static quenching within a $^*Ru(bpz)_3^{2+}\cdots PhOH$ complex, is seen for up to 99.6% quenching. Although the equilibrium constant for the formation of a ground-state complex with $Ru(bpz)_3^{2+}$ is approximately a factor of 10 smaller than that of $Ru(bpy)_3^{2+}$,[30] it had been hoped that the sensitivity of the spectral and kinetic measurements would be sufficient to reveal an interaction of PhOH with $^*Ru(bpz)_3^{2+}$ superimposed upon electron-transfer quenching. Similarly, it had been hoped that energy-transfer quenching of $^*Ru(bpy)_3^{2+}$ by O_2 in the presence of PhOH would show a perturbation due to complexation. The failure to observe these effects is probably due to the magnitude of the excited-state complexation equilibrium constant, although it is intriguing, albeit premature, to speculate on how the act of quenching might destroy the π-interactions that are otherwise observed.

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Supporting Information Available: Table of photophysical parameters for the decay of $^*Ru(bpy)_3^{2+}$ as a function of [PhOH] and temperature in D_2O; k_{obs} for the decay of $^*Ru(bpy)_3^{2+}$ as a function of [PhOH] and temperature in H_2O and D_2O; plot of E_{em} for $^*Ru(bpy)_3^{2+}$ as a function of [PhOH] and temperature; Stern−Volmer plot of the quenching of $^*Ru(bpz)_3^{2+}$ by PhOH; plot of k_{obs} for $^*Ru(bpy)_3^{2+}$ as a function of [PhOH] and temperature in D_2O; plot of log k_{obs} vs $1/T$ as a function of [PhOH] in D_2O; plot of ΔE as a function of E_{em}; plot of log k_{nr} as a function of E_{em}; plot of k_{nr} as a function of [PhOH]; Barclay−Butler plot of log k_2 as a function of ΔE (11 pages). Ordering information is given on any current masthead page.

References and Notes

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