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Ground- and excited-state interactions between the tris(2,2′-bipyridine)ruthenium(2+) ion and phenol in aqueous solution

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Abstract

Although phenol (PhOH) does not quench $^*\mathrm{Ru(bpy)}_3^{2+}$ due to unfavorable energetics, its presence in aqueous solution results in a blue shift in the emission spectrum and a change in the observed lifetime (τ_{obs}). The effect of temperature (5–70 °C) and [PhOH] (0.1–0.7 M) on τ_{obs} is complex; at low T, where nonradiative decay is the dominant process, τ_{obs} increases with increasing [PhOH]; at high T the opposite effect is seen, reflecting the dominance of the thermal population of the d–d* excited state. The NMR spectra of both $\mathrm{Ru(bpy)}_3^{2+}$ and PhOH are altered in the presence of each other, indicating the existence of ground-state interactions that are, undoubtedly, hydrophobic or π-stacking in nature. The NOE difference spectra show that the $H_{3,5}$ protons of PhOH couple with the $H_{4,4'}$ and $H_{6,6'}$ protons of $\mathrm{Ru(bpy)}_3^{2+}$, indicating the existence of an offset face-to-face orientation. © 1997 Elsevier Science S.A.

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The photophysics of $\mathrm{Ru(bpy)}_3^{2+}$ (bpy = 2,2′-bipyridine) in solution, specifically the emission spectrum and lifetime of the luminescent MLCT excited state, is very well known [1]; that complex serves as the paradigm for transition-metal photosensitizers. The photophysical properties are sensitive to the immediate environment around the excited cation; for example, the emission maximum and decay rate constant are a function of the solvent composition in H_2O, CH_3CN, and their mixtures [2]. The subtle variations in these parameters have been used as markers for the interaction between Ru(II)-diimine cations and large microheterogeneous structures: DNA [3], micelles [4], starburst dendrimers [5], polyelectrolytes [6], bacteriorhodopsin [7], zeolites [8], layered compounds [9], and semiconducting oxides [10]. These electrostatic and intercalation interactions arise from the large negative charges and/or the many hydrophobic and hydrophilic regions on and within those structures. Much less is known about the interaction of $\mathrm{Ru(bpy)}_3^{2+}$ and simpler solutes; ion-pairing between simple electrolytes and $\mathrm{Ru(bpy)}_3^{2+}$ occurs in the ground and excited states [11], but observations of the interactions of the complex with simple organic solutes, especially in aqueous solution, are hampered due to limited solubility and efficient excited-state quenching. In this note, we report on the interaction of ground- and excited-state $\mathrm{Ru(bpy)}_3^{2+}$ with a small, neutral, nonquenching organic molecule at modest concentrations in aqueous solution.

Phenol (PhOH; pK_a 9.98) does not quench $^*\mathrm{Ru(bpy)}_3^{2+}$ by energy or electron transfer; the energetics of those reactions are unfavorable. Nevertheless, the presence of PhOH in mildly acidic (pH ~ 5), unbuffered aqueous solutions at $T \leq 35$ °C results in a blue shift of the luminescence spectrum (Fig. 1), and an increase in the observed lifetime (τ_{obs}) and the emission quantum yield (Φ_{em}) of $^*\mathrm{Ru(bpy)}_3^{2+}$ as [PhOH] is increased. At higher temperatures (40–70 °C), an increase in [PhOH] causes a decrease in τ_{obs} and Φ_{em} while the blue-shifted spectra are still seen. Fig. 2 shows the dependence of k_{obs} on [PhOH] as a function of temperature.

The temperature-dependence of k_{obs} can be treated by the simple model [12] in which the radiative and nonradiative decays from the MLCT excited state compete with the thermally activated population of the lowest-lying metal-centered d–d* excited state. Thus, $k_{obs} = k_1 + k'$, where $k_1 = k_{rad} + k_{nr}$, $k' = k_2 \exp(-\Delta E/kT)$, and ΔE is the energy gap between the MLCT and the d–d* excited states. Values of k_1, k_2, and ΔE were obtained from the best computer fits of the dependence of k_{obs} on T. The calculations show k_{rad} and k_{nr} to be temperature-independent, and k_{rad} to be insensitive to the presence of PhOH. However, as [PhOH] is increased, the energy of the emitting state (E_{em}) increases, resulting in an increase in the value of k' and a decrease in the values of k_{nr}

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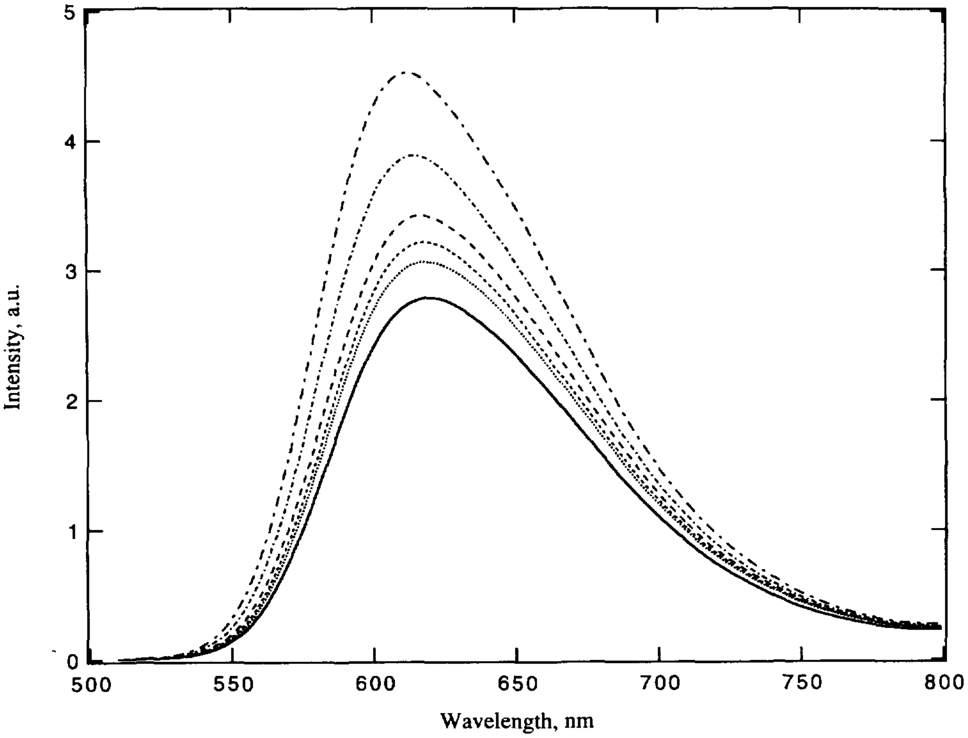

Fig. 1. Corrected emission spectrum of *Ru(bpy)$_3^{2+}$ in aqueous solution at 5°C; λ_{ex}=450 nm. [PhOH] = 0 (———), 0.1 (· · ·), 0.2 (· · ·), 0.3 (– – –), 0.5 (– · –), and 0.7 (— — —) M.

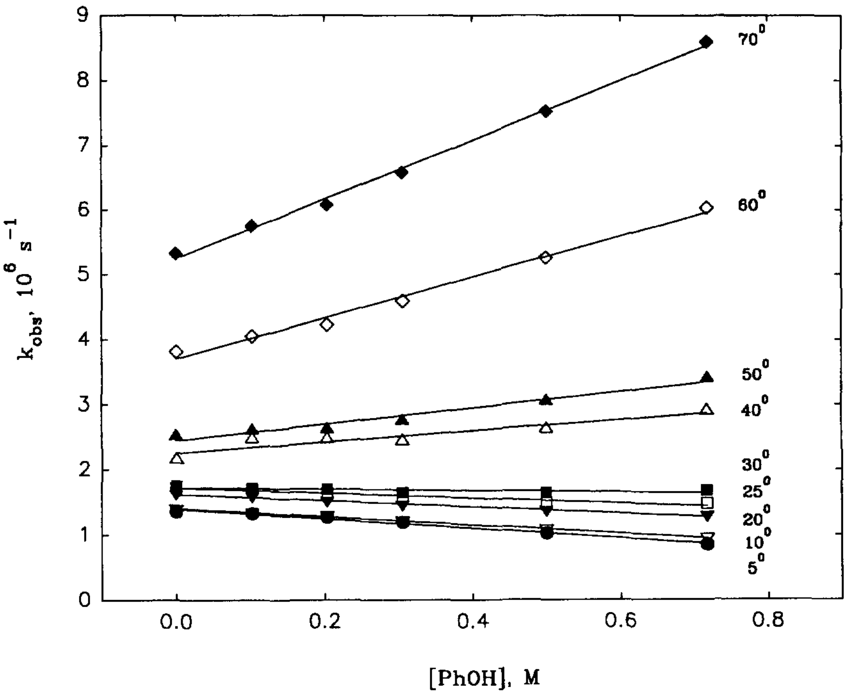

Fig. 2. Dependence of k_{obs} for the decay of *Ru(bpy)$_3^{2+}$ on [PhOH] as a function of temperature in Ar-purged aqueous solution.

and ΔE. These effects are fully in accord with the energy gap law [13]. The dependence of log k_{obs} on $1/T$ as a function of [PhOH] strikingly resembles the same plot as a function of solution composition in H_2O/CH_3CN mixtures [2].

It has been pointed out [14] that E_{em} for *Ru(bpy)$_3^{2+}$ is higher in nonpolar than in polar solvents. The observations reported here suggest that the polarity of the medium immediately surrounding the excited state decreases in the presence

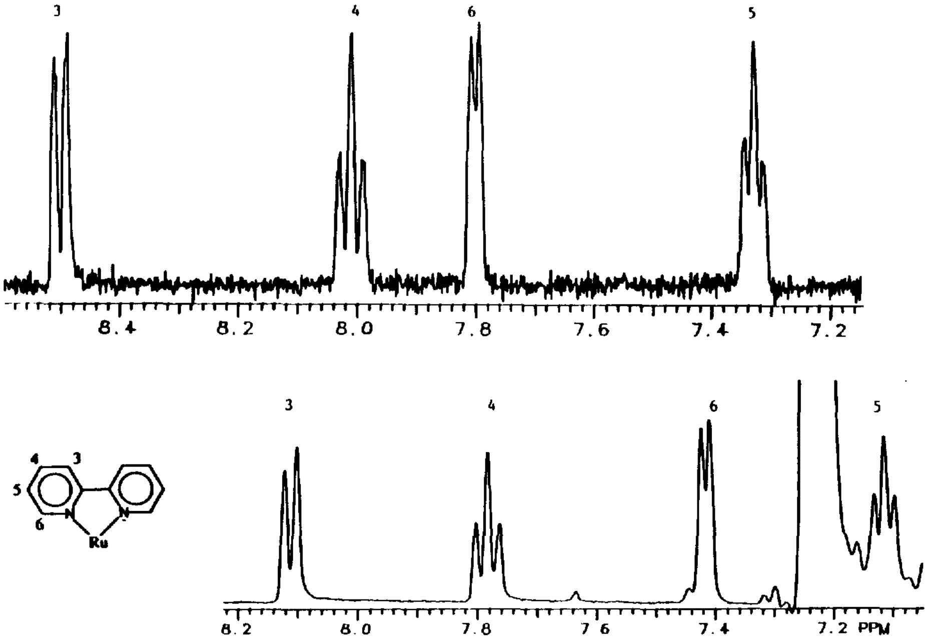

Fig. 3. ^{1}H NMR (400 MHz) spectra of 5 mM Ru(bpy)$_3^{2+}$ (top) and 2 mM Ru(bpy)$_3^{2+}$ with 0.5 M PhOH (bottom) in D_2O at room temperature.

of fairly modest mole fractions of PhOH; one can visualize the formation of π-stacked complexes between *Ru(bpy)$_3^{2+}$ and the aromatic solute.

In order to investigate interactions of the ground state of the complex, which cannot be discerned due to the lack of any change in its optical absorption spectrum as a function of [PhOH], the 400-MHz ^{1}H NMR spectra of Ru(bpy)$_3^{2+}$ in the presence and absence of PhOH in D_2O at ambient temperature were examined. The four aromatic protons of the bpy ligand in the complex have been unambiguously assigned [15]; their resonances shift dramatically and nonequivalently upfield in the presence of PhOH (Fig. 3). The upfield shifts of the individual proton resonances are proportional to [PhOH]; in the presence of 0.6 M PhOH, the $H_{3,3'}$ resonance shifts upfield by almost 0.6 ppm. The binding constant was evaluated to be of the order of < 0.1 M^{-1} on the basis of the Benesi–Hildebrand treatment [16]; the exact value of K_{eq} could not be obtained due to the small saturation fraction of PhOH [17]. It is to be noted that the resonances are unchanged for [Ru(bpy)$_3^{2+}$] = 2 μM–50 mM in the absence of PhOH, and that the resonances of PhOH shift upfield by only ~0.04 ppm for [PhOH] = 0.01–0.6 M in the absence of Ru(bpy)$_3^{2+}$.

Nonequivalent shifts in the resonances, seen also in the intercalation of Ru(II) and Rh(III) complexes with DNA [18], are indicative of a direct interaction between Ru(bpy)$_3^{2+}$ and PhOH. However, the observations suggest that the interaction is not charge-separation, which would result in upfield shifts for the electron-deficient complex and downfield shifts for electron-rich PhOH; rather, the shifts arise from the anisotropic effect produced by the π-system of the aromatic ring [19]. This conjecture is supported by the observation of a uniform upfield shift of the aromatic protons of PhOH as [Ru(bpy)$_3^{2+}$] is increased due to the influence of the ring current from the neighboring Ru(bpy)$_3^{2+}$; the magnitude of the shift is 0.1 ppm in the presence of 50 mM Ru(bpy)$_3^{2+}$. The fact that there is no change in the coupling constant of the Ru(bpy)$_3^{2+}$ resonances in the absence and presence of PhOH indicates that the rate of any proton exchange between the complex and PhOH is very slow [20]. The nonequivalent shifts in the Ru(bpy)$_3^{2+}$ resonances also indicate face-to-face (parallel) stacking rather than an edge-to-face (perpendicular) orientation. CPK molecular models show that the PhOH molecule can stack nicely over the 2,2′-bridge by offset face-to-face orientation [21], with the *para* position toward the metal center and the –OH group pointed outward into the bulk solution. Another piece of evidence suggesting a partial face-to-face π-stacking interaction is shown by the NOE difference spectra, which show that the $H_{3,5}$ protons of PhOH couple with the $H_{4,4'}$ and $H_{6,6'}$ protons of Ru(bpy)$_3^{2+}$; they may also couple with the $H_{5,5'}$ protons of the complex, although these chemical shifts are too close to each other to resolve the interaction by NOE. A simple explanation for the face-to-face orientation is based on the dipole–dipole and dipole–quadrupole interaction terms for unsymmetrical molecules [22]. Fig. 4 shows a computer-generated model of the orientation.

The proposed model is consistent with the interactions of PhOH with both the ground and excited states. Phenol, with its hydrophobic and hydrophilic regions can be visualized as engaging in both π-stacking with the complex and H-bonding with water, forming a pseudo-micellar structure. The change in the H-bonding of the solvation shell around the complex due to the presence of PhOH may also cause a lowering of the micropolarity. The importance of H_2O in the observed phenomena is supported by the observation of a lack of any ground- or excited-state effects when CH_3CN is the solvent. The interactions reported here could be very important in the

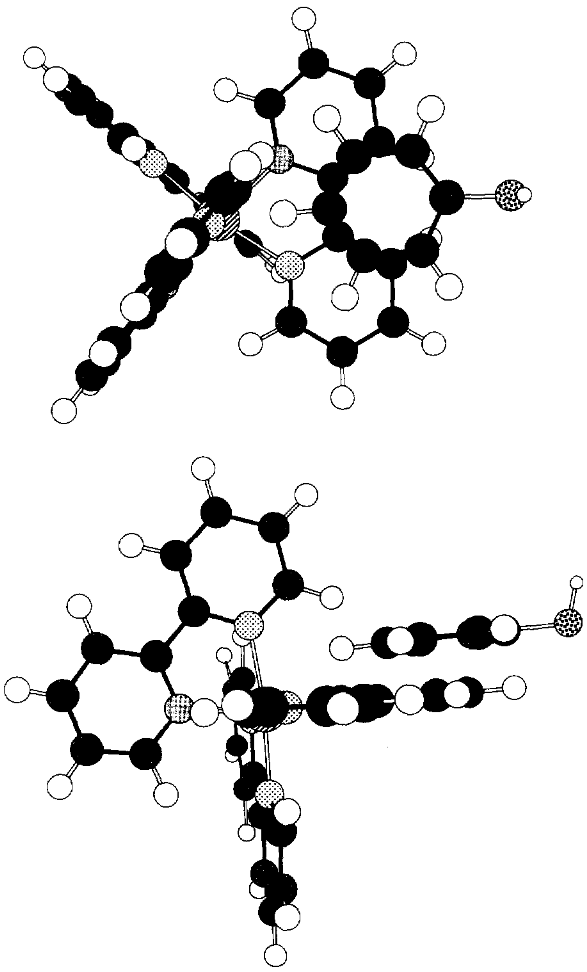

Fig. 4. Side and top views of a computer-generated model of the interaction between Ru(bpy)$_3^{2+}$ and PhOH.

mediating of photoinduced electron-transfer between Ru(II)-photosensitizers and solutes that possess aromatic moieties.

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