Ground-State Interactions between Ruthenium(II)−Diimine Complexes and Phenol and Monochlorophenols in Aqueous Solution

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Ground-state interactions between $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) or $Ru(bpz)_3^{2+}$ (bpz = 2,2′-bipyrazine) and phenol (PhOH) or monochlorophenols (ClPhOH) have been investigated in aqueous (D_2O) solution by NMR. The upfield shifts of the resonances and the NOE difference spectra of the complexes in the presence of the phenols indicate the presence of offset face-to-face π-stacking interactions between the phenol and the aromatic ligands. Electron withdrawal from the phenol ring by the monochloro substituent and less effective solvation by aqueous (compared to acetonitrile) media favor the interaction. The formation constant for the 1:1 $Ru(bpy)_3^{2+}$−PhOH complex is estimated to be ~ 0.01 M^{-1}; K is smaller for $Ru(bpz)_3^{2+}$ than for $Ru(bpy)_3^{2+}$, and it increases for both complexes in the order PhOH < 4-ClPhOH < 3-ClPhOH < 2-ClPhOH.

Introduction

Inasmuch as the UV−visible absorption spectra of Ru(II)−diimine complexes, such as $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine), in solution are virtually independent of the solvent and the presence of other solutes, ground-state interactions cannot be easily observed by that technique. On the other hand, NMR spectroscopy enables interactions to be detected; metal−ligand interactions,[2−13] Ru(II)−EDTA ion-pairing in the presence of methylviologen (1,1′-dimethyl-4,4′-bipyridinium cation),[14] and oligonucleotide DNA binding[15−17] have been examined by that technique.

Little is known about the ground-state interactions of Ru(II) photosensitizers with small, neutral molecules; in contrast, the quenching of the excited states is very well documented.[18] In the case of phenol (PhOH), which does not quench $^*Ru(bpy)_3^{2+}$ due to insufficient driving forces for energy transfer or electron transfer, its presence ($\leq$0.7 M) results in a blue shift in the maximum of the emission spectrum of $^*Ru(bpy)_3^{2+}$; in addition, the observed excited-state lifetime is a function of both [PhOH] and temperature.[19] It was suggested that $^*Ru(bpy)_3^{2+}$ and PhOH engage in hydrophobic or π-stacking interactions, which affect the micropolarity of the medium around the complex and alter the photophysics of the luminescent MLCT state.

On the other hand, $^*Ru(bpz)_3^{2+}$ (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 in H_2O, respectively),[20] is reductively quenched by PhOH.[21] The question is whether both ground-state complexes exhibit interactions with phenol and its monochloro derivatives. If they do, it becomes important to see if excited-state interactions are manifest in the photophysics of the complexes, and if excited-state quenching reactions show evidence of these interactions; these latter concerns will be addressed in a future publication.[22]

In this paper, NMR techniques, which have been very well developed for organic and biological molecules,[23,24] are applied to the ground-state interactions of $Ru(bpy)_3^{2+}$ and $Ru(bpz)_3^{2+}$ with PhOH and the three monochlorophenols (2-, 3-, and 4-ClPhOH) in aqueous (D_2O) solution. Preliminary results on the $Ru(bpy)_3^{2+}$−PhOH ground-state system have recently been published.[19]

Experimental Section

Materials. $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (GFS Chemicals) was recrystallized from water and dried over silica gel. PhOH and the monochlorophenols (Aldrich) were purified by sublimation. Aqueous solutions were

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(1) (a) Boston University. (b) Université Blaise Pascal.
(2) Constable, E. C.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 34.
(3) Constable, E. C.; Lewis, J. *Inorg. Chim. Acta* **1983**, *70*, 251.
(4) Brevard, C.; Granger, P. *Inorg. Chem.* **1983**, *22*, 532.
(5) Cook, M. J.; Lewis, A. P.; McAuliffe, C. S. G. *Org. Magn. Reson.* **1984**, *22*, 388.
(6) Masuda, Y.; Yamatera, H. *J. Phys. Chem.* **1984**, *88*, 3425.
(7) Ohsawa, Y.; DeArmond, M. K.; Hanck, K. W.; Moreland, C. G. *J. Am. Chem. Soc.* **1985**, *107*, 5383.
(8) Crutchley, R. J.; Lever, A. B. P. *Inorg. Chem.* **1982**, *21*, 2276.
(9) Orellana, G.; Ibarra, C. A.; Santoro, J. *Inorg. Chem.* **1988**, *27*, 1025.
(10) Shirayil, S.; Thummel, R. P. *Inorg. Chem.* **1989**, *28*, 812.
(11) Hage, R.; Diemen, J. H.; Ehrlich, G.; Haasnoot, J. G.; Stufkens, D. J.; Snoeck, T. L.; Vos, J. G.; Reedijk, J. *Inorg. Chem.* **1990**, *29*, 988.
(12) Orellana, G.; DeMesmaeker, A. K.; Turro, N. J. *Inorg. Chem.* **1990**, *29*, 882.
(13) Von Zelewsky, A.; Gremaud, G. *Helv. Chim. Acta* **1988**, *71*, 1108.
(14) Kennelly, T.; Strekas, T. C.; Gafney, H. D. *J. Phys. Chem.* **1986**, *90*, 5338.
(15) Rehmann, J. P.; Barton, J. K. *Biochemistry* **1990**, *29*, 1701.
(16) DuPureur, C. M.; Barton, J. K. *J. Am. Chem. Soc.* **1994**, *116*, 10286.
(17) David, S. S.; Barton, J. K. *J. Am. Chem. Soc.* **1993**, *115*, 2984.
(18) Hoffman, M. Z.; Bolletta, F.; Moggi, L.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1989**, *18*, 219.
(19) Li, C.; Sun, H.; Hoffman, M. Z. *J. Photochem. Photobiol. A: Chem.* **1997**, *108*, 129.
(20) Sun, H.; Hoffman, M. Z.; Mulazzani, Q. G. *Res. Chem. Intermed.* **1994**, *20*, 735.
(21) Pizzocaro, C.; Bolte, M.; Sun, H.; Hoffman, M. Z. *New J. Chem.* **1994**, *18*, 737.
(22) Li, C.; Hoffman, M. Z.; Pizzocaro, C.; Mailhot, G.; Bolte, M. In preparation.
(23) Wuthrich, K. *NMR of Proteins and Nucleic Acids*; Wiley: New York, 1986.
(24) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: New York, 1989.

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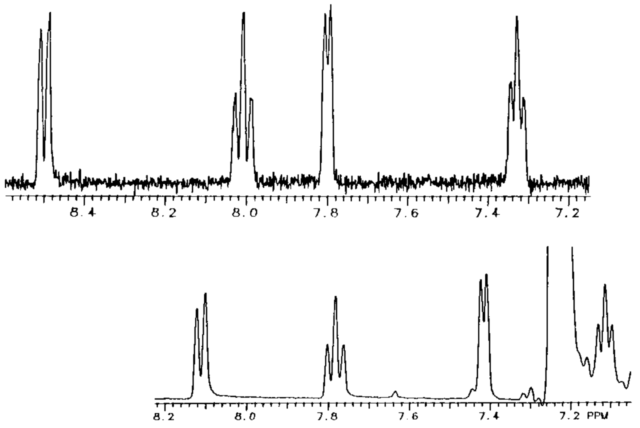

Figure 1. ^1H NMR (400 MHz) spectra of 5 mM $Ru(bpy)_3^{2+}$ (top) and 2 mM $Ru(bpy)_3^{2+}$ (bottom) in the presence of 0.5 M PhOH in D_2O at room temperature.

prepared from doubly distilled water that had been passed through a Millipore purification train; D_2O (Aldrich) was used as received. $Ru(bpz)_3^{2+}$, as its PF_6^- salt, was prepared as described in the literature.[25,26] Buffer solutions (pH 5.5 and 12) were prepared by standard methods.[27]

Instrumentation. NMR spectra were recorded on a Varian UNITYplus 400 MHz multichannel spectrometer at ambient temperature; the chemical shift of the solvent (D_2O) was used as the internal standard. The pH of the aqueous solutions was measured with a PHM82 pH meter (Radiometer America Inc.) with an accuracy of ±0.01 pH units, which was calibrated with standard buffers prior to use.

Procedures. The ^1H NMR spectra of $Ru(bpy)_3^{2+}$ and $Ru(bpz)_3^{2+}$ as a function of [ClPhOH] (0.01−0.1 M) and the ^1H NMR spectra of $Ru(bpz)_3^{2+}$ in the presence of PhOH (0.1−0.6 M) were recorded for air-equilibrated D_2O solutions at ambient temperature. The chemical shift of the solvent was used as an internal standard; for D_2O-CD_3CN mixtures, tetramethylsilane served as an external standard. The NOE difference spectra of the complexes (2 mM) in the presence of 0.1 M PhOH or ClPhOH were also recorded for D_2O solutions.

Results

The four aromatic resonances of the bpy ligand in $Ru(bpy)_3^{2+}$ have been unambiguously assigned in acetone−d_6;[2,3,9] the lowest field δ 8.83 ppm doublet, the δ 8.22 ppm triplet, the δ 8.07 ppm doublet, and the highest field δ 7.58 ppm triplet are due to the $H_{3,3'}$, $H_{4,4'}$, $H_{6,6'}$, and $H_{5,5'}$ protons, respectively; in D_2O, the resonances are 0.2−0.3 ppm upfield.[19] These resonances of $Ru(bpy)_3^{2+}$ shift dramatically and nonequivalently upfield in the presence of PhOH (Figure 1); for example, in the presence of 0.65 M PhOH, the $H_{3,3'}$ resonance shifts upfield by almost 0.62 ppm. The values of the resonances as functions of [PhOH] are given in the Supporting Information. Figure 2 summarizes the effect; the resonances of the $H_{5,5'}$ protons overlap those of PhOH and cannot be resolved.

The lower solubility of the chlorophenols in aqueous solution limits their highest concentration to 0.1 M. The data for the effect of 2-, 3-, and 4-ClPhOH on the resonances of $Ru(bpy)_3^{2+}$ are given in the Supporting Information; Table 1 gives the values of the resonances in the absence and presence of a 0.1 M concentration of each phenol for comparison. It is clear that, for the same concentration, the upfield shifts of the resonances are more significant for the chlorophenols than for PhOH.

It should be noted that the resonances of $Ru(bpy)_3^{2+}$ in the absence of PhOH are unchanged in the concentration range 2−50 mM, and that the resonances of PhOH shift upfield by only ~0.04 ppm for 0.01−0.65 M in the absence of $Ru(bpy)_3^{2+}$.

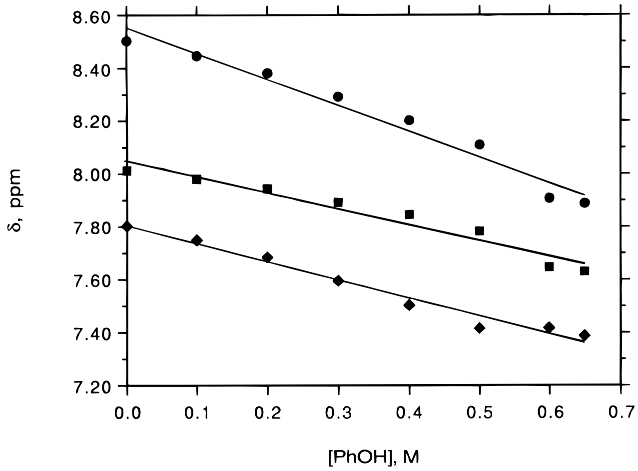

Figure 2. Resonances of $Ru(bpy)_3^{2+}$ (2 mM) as a function of [PhOH] in D_2O: $H_{3,3'}$ (●), $H_{4,4'}$ (■), $H_{6,6'}$ (◆).

Table 1. Chemical Shifts (ppm) of $Ru(bpy)_3^{2+}$ (2.0 mM) in the Absence and Presence of Phenols in D_2O at Ambient Temperature[a]

phenol (concn, M)	$H_{3,3'}$ (doublet)	$H_{4,4'}$ (triplet)	$H_{6,6'}$ (doublet)	$H_{5,5'}$ (triplet)
(0.0)	8.503 (8.4)	8.012 (8.0)	7.802 (5.6)	7.337 (6.0)
PhOH (0.1)	8.446 (8.0)	7.979 (8.0)	7.749 (5.2)	*b*
2-ClPhOH (0.1)	8.396 (8.4)	7.950 (8.0)	7.712 (6.0)	7.292 (6.4)
3-ClPhOH (0.1)	8.412 (8.4)	7.963 (7.6)	7.722 (5.6)	7.306 (6.4)
4-ClPhOH (0.1)	8.427 (8.4)	7.972 (8.0)	7.732 (6.0)	7.311 (6.8)

[a] Overlaps with resonances of PhOH and cannot be resolved. [b] The numbers in parentheses are the coupling constants.

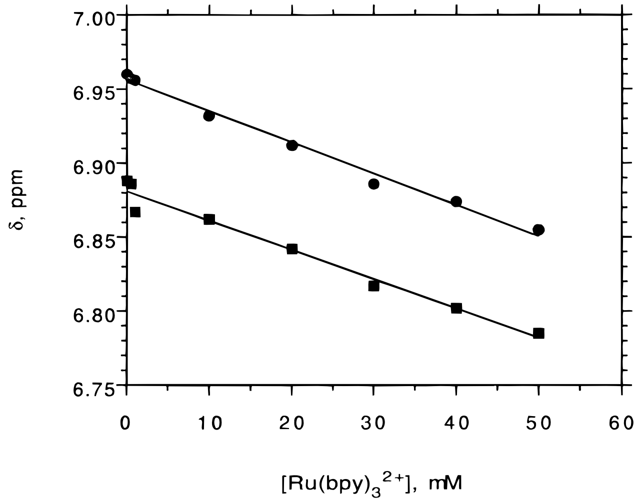

Figure 3. Resonances of PhOH (1 mM) as a function of $[Ru(bpy)_3^{2+}]$ in D_2O: H_4 (●), $H_{2,6}$ (■).

The NMR spectrum of PhOH in D_2O shows a triplet at δ 7.293 ppm, a triplet at δ 6.960 ppm, and a doublet at δ 6.888 ppm, corresponding to the $H_{3,5}$, H_4, and $H_{2,6}$ protons, respectively. In the presence of $Ru(bpy)_3^{2+}$, these resonances shift upfield; the data are given in the Supporting Information and are shown in Figure 3. The $H_{3,5}$ resonances overlap with those of $Ru(bpy)_3^{2+}$ and cannot be resolved.

The NMR spectrum of 2.0 mM $Ru(bpy)_3^{2+}$ in the presence of 0.5 M PhOH was determined in D_2O-CD_3CN mixtures; the data are given in the Supporting Information. The resonances shift downfield as the mole fraction of CD_3CN (χ_{AN}) is increased; the magnitude of the downfield shifts as a function

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(25) Lafferty, J. J.; Case, F. H. *J. Org. Chem.* **1967**, *32*, 1591.
(26) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613.
(27) Dean, J. A. *Lange's Handbook of Chemistry*, 14th ed.; McGraw-Hill: New York, 1992; pp 8.103−8.112.

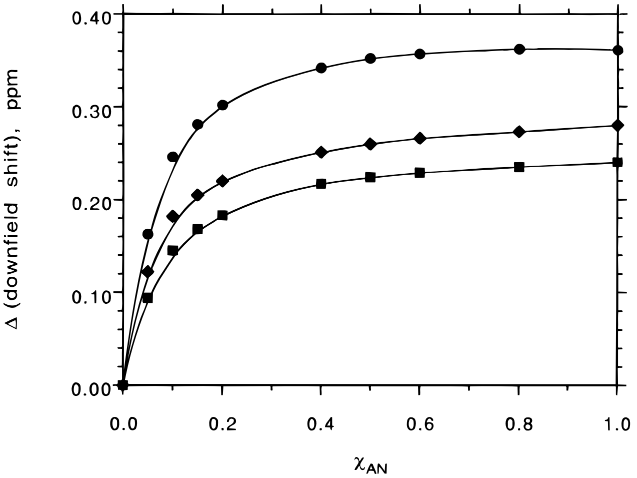

Figure 4. Magnitude of the downfield shifts in the resonances of Ru(bpy)$_3^{2+}$ as a function of the mole fraction of CD_3CN (χ_{AN}) in D_2O-CD_3CN mixtures at [PhOH] = 0.5 M: $H_{3,3'}$ (●), $H_{4,4'}$ (■), $H_{6,6'}$ (◆).

of χ_{AN} is shown in Figure 4. It should be noted that the spectrum of Ru(bpy)$_3^{2+}$ is the same in the presence and absence of PhOH in neat CD_3CN.

In the case of Ru(bpz)$_3^{2+}$, the lowest field δ 10.17 ppm singlet, the δ 8.76 ppm doublet, and the highest field δ 8.03 ppm doublet in DMSO-d_6 have been assigned to the $H_{3,3'}$, $H_{5,5'}$, and $H_{6,6'}$ protons, respectively.[8,9] The magnitude of the effect of the phenols on the resonances of Ru(bpz)$_3^{2+}$ is less than that observed for Ru(bpy)$_3^{2+}$; the data are given in the Supporting Information.

In order to assess the magnitude of any proton-spin coupling between the complexes and the phenols, NOE difference spectra were determined in the presence of each other. Proton coupling between Ru(bpy)$_3^{2+}$ and PhOH or 2-ClPhOH was observed; the resonances of the $H_{4,4'}$ and $H_{6,6'}$ protons of Ru(bpy)$_3^{2+}$ were enhanced when the $H_{3,5}$ resonance of PhOH was continuously irradiated at its central frequency (see Supporting Information). No NOE difference spectra could be detected for Ru(bpz)$_3^{2+}$ and the phenols.

No changes in the ground-state absorption spectra (200−800 nm) of the complexes in the presence of PhOH or the chlorophenols (up to the maximum concentrations used) were observed.

Discussion

Effect of Phenols on the NMR Spectra of the Complexes. The observed upfield shifts of the resonances of Ru(bpy)$_3^{2+}$ in the presence of PhOH could arise from a number of effects, which have been discussed in general terms:[28] (1) charge transfer from PhOH to Ru(bpy)$_3^{2+}$; (2) the effect of ring currents in PhOH on the Ru(bpy)$_3^{2+}$ protons; (3) electric field effects of PhOH on the Ru(bpy)$_3^{2+}$ protons; (4) modification of ring currents in Ru(bpy)$_3^{2+}$ through a binding interaction with PhOH; (5) alteration of the paramagnetic contribution to the Ru(bpy)$_3^{2+}$-proton shifts.

Effect 1 would result in a upfield shift in the Ru(bpy)$_3^{2+}$ resonances and a downfield shift in PhOH if the electron density in electron-deficient Ru(bpy)$_3^{2+}$ were to increase due to charge transfer from electron-rich PhOH; however, downfield shifts of the PhOH resonances were not observed. Effect 2 could result from the anisotropy generated by the π-systems of the aromatic rings;[29] the ring current from the circulating electrons of an aromatic ring can create a magnetic field that is opposed to the applied field at the center of the ring, but reinforcing of the applied field outside the ring. Inasmuch as both PhOH and the bpy ligands of the complex possess aromatic rings, the effect could arise through π-stacking. Effect 3 is anticipated to be very small due to the small dipole moment of PhOH. Effect 4 is unlikely to be important because binding could be only a very small perturbation on the complex. Effect 5 predicts a downfield shift of the resonances of Ru(bpy)$_3^{2+}$, which were not observed. The fact that there were no observed differences in the coupling constants of the Ru(bpy)$_3^{2+}$ resonances in the presence and absence of PhOH indicates that the rate of any proton exchange between the ligands and PhOH is very slow.[24]

The nonequivalent upfield shifts for the resonances of Ru(bpy)$_3^{2+}$ suggest that any π-stacking between the bpy aromatic rings and the PhOH ring may not overlap completely. The largest upfield shift is exhibited by the $H_{3,3'}$ protons, indicating that the anisotropic effect of PhOH on those protons is dominant.

Upfield shifts of the resonances of Ru(bpy)$_3^{2+}$ in the presence of 2-ClPhOH, 3-ClPhOH, and 4-ClPhOH follow the same trend as with PhOH: $\Delta(H_{3,3'}) > (H_{6,6'}) > (H_{4,4'})$. However, the magnitude of the upfield shifts are larger than were caused by PhOH, indicating stronger interactions with Ru(bpy)$_3^{2+}$ in the order Δ(2-ClPhOH) > (3-ClPhOH) > (4-ClPhOH) > (PhOH). It has been reported[30] that an electron-withdrawing group on the aromatic ring results in a stronger interaction due to the creation of a higher barrier of molecular rotation because of less favorable electrostatic interactions. It would be predicted that the π-stacking interaction should be stronger when the electron-withdrawing ability of the substituent is greater, i.e., the value of Δ would increase with an increasing value of the Hammett constant (σ(2-Cl) > σ(3-Cl) > σ(4-Cl)),[31] which is consistent with the observations here.

Upfield shifts of the resonances of Ru(bpz)$_3^{2+}$ in the presence of PhOH and the monochlorophenols were also observed; the magnitude of the effect is significantly less than that of Ru(bpy)$_3^{2+}$. It is well-known that the σ-donor strength of the bpz ligand is considerably less than that of bpy, giving rise to a greater effective nuclear charge on the metal center.[32,33] As a result, the lower electron density on bpy compared to bpz can result in a stronger interaction with PhOH as observed here. Alternatively, H-bonding between the noncoordinated nitrogen atoms in the bpz ring and the solvent or the phenols might be the origins of the effect.

Effect of Ru(bpy)$_3^{2+}$ on the NMR Spectrum of PhOH. As shown in Figure 3, the resonances of the H_4 and $H_{2,6}$ protons of PhOH shift upfield with increasing [Ru(bpy)$_3^{2+}$]; the upfield shifts of both components indicate the presence of the anisotropic effect. The data show that the values of the resonances of PhOH shift upfield by 0.1 ppm at [Ru(bpy)$_3^{2+}$]/[PhOH] = 50 while the resonances of Ru(bpy)$_3^{2+}$ shift upfield by only 0.03−0.06 ppm at [PhOH]/[Ru(bpy)$_3^{2+}$] = 50. Inasmuch as the bpy ligand has two aromatic rings, the effect of the ring current should be stronger for Ru(bpy)$_3^{2+}$ than for PhOH. As a result, the variation of [Ru(bpy)$_3^{2+}$] produces a more significant upfield shift in the resonances of PhOH.

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(28) Hanna, M. W.; Ashbaugh, A. L. *J. Phys. Chem.* **1964**, *68*, 811.

(29) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 4th ed.; McGraw-Hill: London, 1987; pp 69−76.

(30) Cozzi, F.; Ponzini, F.; Annuziata, R.; Cinquini, M.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1019.

(31) Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley: New York, 1979.

(32) Dutta, P.; Turbeville, W. *J. Phys. Chem.* **1992**, *96*, 9410.

(33) Bailey, S. L.; Ritchie, I. M.; Hewgill, F. R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 645.

Effect of Solvent on the NMR Spectrum of the $Ru(bpy)_3^{2+}$/PhOH System. As is seen in Figure 4, the magnitude of the downfield shift of the resonances of $Ru(bpy)_3^{2+}$ in the presence of 0.5 M PhOH is strikingly dependent on the composition of the D_2O−CD_3CN solvent mixture, indicating a dramatic change in the microenvironment around the interacting species. The solvent that effectively solvates the solute significantly reduces π-stacking interactions;[34,35] it is predicted that the π-interactions should be enhanced when the solubility of the solute is decreased. Inasmuch as the solubilities of both PhOH and $Ru(bpy)_3^{2+}$ are greater in CD_3CN than in D_2O, it can be concluded that CD_3CN solvates both PhOH and $Ru(bpy)_3^{2+}$ more effectively than does water, resulting in a weaker π-stacking interaction in CD_3CN-rich solution.

On the other hand, it has been suggested[36] that the especially high solvent reorganization energy in aqueous solution may be provided by the network of hydrogen bonds among the solvent molecules, with CH_3CN functioning as a structure breaker. This implies that the solvated solutes in water are in a highly organized structure, whereas they are in a very loose structure in CH_3CN. In the CD_3CN-rich systems, the interactions become weaker as χ_{AN} is increased; the highly organized structure provided by the hydrogen bonding among the water molecules and between H_2O and PhOH is largely broken. Therefore, the π-stacking interactions reduce significantly and ultimately disappear as χ_{AN} is increased.

Ground-State Equilibria between the Complexes and Phenols. The simple Benesi−Hildebrand expression[37] has been used extensively to evaluate the binding constant for the formation of 1:1 complexes from spectroscopic data. An analogous expression for use with changes in NMR resonances was derived by Hanna and Ashbaugh[28] and later modified by Foster and Fyfe.[38] With eq 1, the equilibrium formation constant (K) of a weak 1:1 complex (AD) can be determined by NMR measurements whereby a dilute component (A), which is maintained at a fixed total concentration ($[A]_0$), is titrated by the addition of a second component (D) with a total concentration of $[D]_0$.

$$K = \frac{[AD]}{[A][D]} = \frac{[AD]}{([A]_0 - [AD])([D]_0 - [AD])} \qquad (1)$$

The chemical shift of the protons of A, which are undergoing very rapid exchange between the associated and unassociated species ($\delta_{obs}{}^A$), is given by eq 2, where $\delta_0{}^A$ and $\delta_{AD}{}^A$ are the chemical shifts of the protons of A in the unassociated and associated forms, respectively.

$$\delta_{obs}{}^A = \frac{[A]}{[A]_0}\delta_0{}^A + \frac{[AD]}{[A]_0}\delta_{AD}{}^A \qquad (2)$$

The changes (Δ) before and after the addition of D can be expressed as $\Delta = \delta_{obs}{}^A - \delta_0{}^A$. When $[D]_0 \rightarrow \infty$, the limiting value of Δ_0 can be expressed as $\Delta_0 = \delta_{AD}{}^A - \delta_0{}^A$. Incorporation of these expressions into eq 2 followed by rearrangement and substitution into eq 1 yields eq 3, which can be further rearranged to eqs 4 (Hanna−Ashbaugh expression) and 5 (Foster−Fyfe expression).

$$\Delta = \frac{K[D]}{1 + K[D]}\Delta_0 \qquad (3)$$

$$\frac{1}{\Delta} = \frac{1}{K\Delta_0[D]} + \frac{1}{\Delta_0} \qquad (4)$$

$$\frac{\Delta}{[D]} = -K\Delta + K\Delta_0 \qquad (5)$$

It is to be noted that eqs 3−5 are valid only if $[D]_0 \gg [A]_0$ and the solutions are ideal, or if the ratio of the activity coefficients remains constant over the concentration range of the solutions studied. Both eqs 4 and 5 are linear expressions, which enable K and Δ_0 to be estimated from the slope and intercept of the appropriate plot. The value of $\delta_0{}^A$ is measured for a solution of A alone in order to give a reference point in the absence of any complex formation. A value of K can also be evaluated from a fitting of the data with eq 3.

A plot of $1/\Delta$ vs $1/[D]$ for $Ru(bpy)_3^{2+}$ and PhOH is shown in the Supporting Information; for all the other phenols, linear plots were also obtained. However, some of the intercepts of the plots are negative, resulting in negative (and meaningless) values of K and Δ_0. This problem could not be resolved even when other methods, with different equations, were used to estimate values of K: Bergeron and Channing's linear plot ($[PhOH]/\Delta$ vs $[PhOH] + [Ru(bpy)_3^{2+}]$) for inclusion complexes,[39] Wilcox and Cowart's curve fitting (Δ vs [PhOH]) for a receptor−substrate complex,[40] and the Horman−Dreux method for dimerization.[41] The problem encountered in this study has been seen by others,[28,34] who concluded that the values of K in their studies were close to 0; however, no satisfactory resolution was offered. It should be noted that if complexation were greater than 1:1, the plots of $1/\Delta$ vs $1/[D]$ would not be linear.[42]

The reasons for the appearance of undependable values of K and Δ_0 have been discussed by Deranleau[42,43] in terms of the low saturation fractions ($\alpha = [AD]/[A]_0$) when K is very small; it is important that measurements cover a large portion (>75%) of the saturation curve in order for the data extracted from plots such as Figure 5 to have meaning. No plateau in the plot of Δ vs [PhOH] is observed, doubtlessly due to the limitations in the solubility of the phenols in aqueous solution. However, the points can be fitted to eq 3 by assuming a value of K and minimizing the deviation in Δ_0. A good computer fit (see Supporting Information) and small deviations in Δ_0 were obtained for $K = 0.01\ M^{-1}$; a similar treatment of NMR data was used before.[37]

From the magnitude of the change (Δ) in the chemical shifts of the resonances as a function of [PhOH], the magnitudes of K, which indicate the strengths of the interactions between the Ru(II) complexes and the phenols, are in the following order for both $Ru(bpy)_3^{2+}$ and $Ru(bpz)_3^{2+}$: K(PhOH) < K(4-ClPhOH) < K(3-ClPhOH) < K(2-ClPhOH). In general, K is lower for $Ru(bpz)_3^{2+}$ than for $Ru(bpy)_3^{2+}$, which accounts for the absence of a detectable NOE difference spectrum in that case.

Structure of Ru(II)−Phenol Complexes. The nonequivalent upfield shifts of the NMR resonances of $Ru(bpy)_3^{2+}$ in the presence of PhOH indicate face-to-face (parallel) π-stacking

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(34) Shetty, A. S.; Zhang, J. S.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 1019.
(35) Sanders, G. M.; van Diji, M.; van Veldhuizen, A.; van der Plas, H. C.; Hofstra, U.; Schaafsma, T. J. *J. Org. Chem.* **1988**, *53*, 5272.
(36) Sun, H.; Hoffman, M. Z. *J. Phys. Chem.* **1993**, *97*, 11956.
(37) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
(38) Foster, R.; Fyfe, C. A. *Trans. Faraday Soc.* **1965**, 1626; *J. Chem. Soc., Chem. Commun.* **1966**, 642.
(39) Bergeron, R.; Channing, M. A. *Bioorg. Chem.* **1976**, *5*, 417.
(40) Wilcox, C. S.; Cowart, M. D. *Tetrahedron Lett.* **1986**, *27*, 5563.
(41) Horman, I.; Dreux, B. *Helv. Chim. Acta* **1984**, *67*, 754.
(42) Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4050.
(43) Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044.

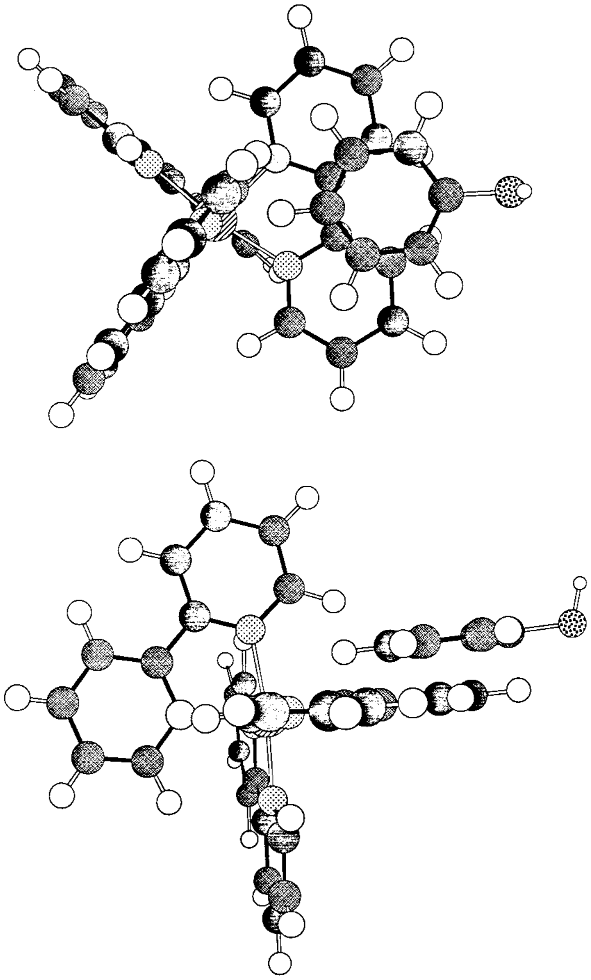

Figure 5. Top and side views of a computer-generated model of the interaction between $Ru(bpy)_3^{2+}$ and PhOH.

interaction rather than edge-to-edge (T-shape) orientation; in the latter case, the orientation would result in a very small upfield shift.[34] It has been pointed out[34] that aromatic−aromatic $\pi-\pi$ interactions are energetically favorable with driving forces of some tens of kJ/mol. CPK molecular models show that the phenol molecule can stack over the 2,2′-bridge of the bpy ligand by offset face-to-face orientation, with the para position oriented toward the metal center and the OH group pointing outward into the bulk solution where it can hydrogen-bond with the solvent. The NOE difference spectra support the assignment of a partial face-to-face π-stacking interaction; the $H_{3,5}$ protons of PhOH or 2-ClPhOH 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,[34] which can favorably contribute to the stability of the associating aromatic rings in a face-to-face geometry. Further to this point, a face-to-face orientation would be expected to minimize the steric effect when $Ru(bpy)_3^{2+}$ and PhOH stack; a face-to-edge geometry would encounter a large steric effect due to the restricted space of the interligand pockets. On the basis of the observations, a computer model of the orientation (Figure 5) was generated with the minimization of the energy of the individual molecules but not the aggregate. As a result, the figure is a cartoon that represents a possible orientation.

Conclusions

Face-to-face π-stacking interactions between Ru(II)−diimine complexes and phenols result in upfield shifts of the NMR resonances in the presence of each other due to the influence of the ring current from the neighboring molecule. The electronic character of the monochloro substituents on PhOH and the solvation of the solutes influence the interactions; the electron-withdrawing group and less effective solvation favor the π-stacking interaction. To the extent that π-stacking exists between the excited states of Ru−diimine complexes and molecules with aromatic moieties, such interactions may play an important role in mediating photoinduced electron transfer in these and similar systems.

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Supporting Information Available: Table of resonances of $Ru(bpy)_3^{2+}$ in the absence and presence of the phenols, table of resonances of PhOH in the absence and presence of $Ru(bpy)_3^{2+}$, table of resonances of $Ru(bpy)_3^{2+}$ as a function of the mole fraction of CD_3CN in D_2O-CD_3CN mixtures in the presence of PhOH, table of resonances of $Ru(bpz)_3^{2+}$ in the absence and presence of the phenols, NOE spectrum of $Ru(bpy)_3^{2+}$ in the presence of PhOH, Hanna−Ashbaugh plots for $Ru(bpy)_3^{2+}$, and a plot of a computer fit of the changes in the $Ru(bpy)_3^{2+}$ chemical shifts as a function of [PhOH] (10 pages). Ordering information is given on any current masthead page.

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