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(35) The shortest metal–metal bond known to date is the Cr–Cr quadruple bond in Cr$_2$(2,6-dimethoxyphenyl)$_4$ (1.847 Å)[36a] and in Cr$_2$(o-C$_6$H$_4$O)$_4{}^{4-}$ (1.83 Å).[36b] All other known metal–metal bond lengths are greater than 1.96 Å.[14,17] The shortest Mo–Mo quadruple bond known has a length of 2.067 Å.[36] Typical values for Cr–Cr and Mo–Mo triple bonds are around 2.28[37] and 2.20 Å.[14] The bridged Cr–Cr bond in Cr$_2$(CH$_2$SiMe$_3$)$_4$(PMe$_3$)$_2$ has a length of 2.10 Å.[38]

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Luminescence Quenching of the Bis(2,2′-bipyridine)aquo-2,2′-bipyridineiridium(III) Ion and Its Conjugate Base

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Abstract: Quenching of Ir(bpy)$_2$(H$_2$O)(bpy)$^{3+}$ and Ir(bpy)$_2$(OH)(bpy)$^{2+}$ by a variety of charged metal complexes and neutral biacetyl has been studied. Stern–Volmer and quenching constants have been determined and diffusional rate constants for each donor–acceptor combination have been estimated. Quenching efficiencies are comparable to those of Ru(bpy)$_3{}^{2+}$ with similar quenchers. Quenching is believed to occur by both energy-transfer and electron-transfer mechanisms. The reduction potential of the luminescent state of Ir(bpy)$_2$(OH)(bpy)$^{2+}$ is estimated to be +1.84 V.

Introduction

Since the initial studies of the use of the tris(bipyridyl)ruthenium(II) ion [Ru(bpy)$_3{}^{2+}$] as a sensitizer,[1] there has been an enormous growth of interest in the use of this and other transition-metal ions to initiate photoinduced energy- and/or electron-transfer processes. Three broad areas of bimolecular photoinduced processes which have come under study are (1) quenching by oxidation electron transfer;[2-10] (2) quenching by reductive electron transfer;[11-16] (3) quenching by energy transfer.[17-23] A fourth photoinduced bimolecular process which has been reported for transition-metal complexes, though not widely studied, is excited-state proton transfer (4).[24,25]

$$^*D^{n+} + A^{m+} \rightarrow D^{(n+1)+} + A^{(m-1)+} \qquad (1)$$

$$^*D^{n+} + A^{m+} \rightarrow D^{(n-1)+} + A^{(m+1)+} \qquad (2)$$

$$^*D^{n+} + A^{m+} \rightarrow D^{n+} + {}^*A^{m+} \qquad (3)$$

$$^*D^{n+} + HX^{+} \rightleftarrows {}^*HD^{(n+1)+} + X \qquad (4)$$

The versatility of transition-metal complexes is illustrated by the fact that a single donor, such as Ru(bpy)$_3{}^{2+}$, may undergo all of the first three processes with appropriate selection of acceptors.

In a previous study[26] we reported the isolation of a stable complex of Ir(III) which contains bpy bound as a monodentate ligand, and noted that its photophysical properties (luminescence quantum yield, lifetime, emission energy) indicated that it might be useful as a high-energy sensitizer. Since then the complex [Ir(bpy)$_2$H$_2$O(bpy)]$^{3+}$ has been found to sensitize the norbornadiene to quadricyclene isomerization with high efficiency (~70% at 366 nm).[27] The conjugate base of this complex, [Ir(bpy)$_2$OH(bpy)]$^{2+}$, has photophysical properties similar to those of the acid, and also should be useful as a high-energy sensitizer. We report here the results of a study of the quenching of the emissions of the acid and base forms of this complex by a variety of acceptor species.

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Experimental Section

A. Materials. Bis(2,2′-bipyridine)aquo-2,2′-bipyridineiridium(III) perchlorate was synthesized and purified initially according to previously published procedures.[26] After successive recrystallization from water the purity was checked by exciting a nitrogen-purged aqueous acid solution of the complex at 340, 400, and 420 nm and monitoring the emission spectrum at each exciting wavelength. For pure samples, the ratio of the emission maxima at 482 and 517 nm remains constant at the different excitation wavelengths. Samples found to be impure by this technique could be purified by warming a solution of the complex in 0.1 M NaOH for several hours and then recrystallizing the complex as $[Ir(bpy)_2OH(bpy)](ClO_4)_2$ by adding $NaClO_4$. The most likely impurity appears to arise from substitution of chloride for the water ligand during the initial synthesis and purification procedures; this impurity is converted to the hydroxo complex by treatment with NaOH.

Potassium hexacyanochromate and tetrabutylammonium hexacyanochromate were prepared according to published techniques. Purity was checked by comparison of the UV-visible absorption spectrum and emission spectrum in dimethylformamide against published data.[28]

Ferric chloride hexahydrate, cobaltous chloride hexahydrate, silver nitrate, and nickel(II) nitrate hexahydrate were all analytical reagent grade from Mallinckrodt. Europium(III) nitrate hexahydrate, 99.9%, was obtained from Research Organic/Inorganic Chemical Corp. and sodium perchlorate was G. F. Smith reagent grade. Thallic acetate (Eastman Kodak) was recrystallized several times from glacial acetic acid. Biacetyl (Mallinckrodt) was redistilled and the middle fraction (bp 88 °C) was retained. Its purity was established by NMR spectroscopy and by comparison of UV-visible absorption and emission spectra with published data.[29,30]

B. Excited-State pK_a* Determination. Corrected emission spectra from 400 to 700 nm were obtained with a Perkin-Elmer Hitachi Model MPF-3 spectrophotofluorimeter. Measurements of pH were made with a Leeds and Northrop pH meter standardized with Mallinckrodt buffers.

The luminescence titration was performed with a 1 mM solution of the complex (aquo form) in 0.1 M sodium perchlorate . A 20-mL sample of this solution was placed in a stirred titration cell and nitrogen purged for 10 min. The pH of the solution was determined, and a 2-mL aliquot was transferred to a 1-cm quartz fluorescence cell. After several minutes of nitrogen purging the cell was capped and an emission spectrum of the aliquot was recorded using 350-nm excitation. The aliquot was then transferred back to the titration cell and the pH was lowered by addition of a small increment of perchloric acid. The procedure was repeated until incremental addition of perchloric acid led to no further spectral changes (pH 1.5). A second 20-mL sample was then added to a clean titration cell and the procedure was repeated using sodium hydroxide to raise the pH until no further spectral changes occurred (pH 4.5).

Emission spectra of the pure acid and base forms of the complex were determined at pH 1.3 and 5.25, respectively. Owing to a red shift in the emission of the acid form relative to the base form of the complex, only the base form contributes to the emission intensity at 460 nm in a mixture of the two. As a result, the total emission spectrum at any pH can be decomposed into the two component contributions by scaling the emission spectrum of the pure base form to the intensity observed at 460 nm in a mixture of the two forms. The contribution of the acid form to the total emission intensity can then be obtained from the difference between the total emission intensity and the portion due to the base form. The integrated emission intensity due to each form was obtained by tracing the total emission spectrum onto tracing paper, superimposing the appropriately scaled contribution from the base form, and cutting out the two pieces and weighing them.

C. Luminescence Quenching Measurements. A stock solution containing 1 mM of the perchlorate salt of the iridium complex was prepared and used for all quenching experiments. Stock solutions of the Fe^{3+}, Tl^{3+}, Co^{2+}, Ni^{2+}, and biacetyl were prepared in 1 M perchloric acid and in a pH 4.66 buffer of 0.2 M acetic acid and 0.16 M sodium acetate. The initial quencher concentration ranged between 0.5 and 400 mM, depending on the charge of the quenching species. A series of solutions of varying quencher concentration was prepared by successive dilution of these stock solutions with either 1 M perchloric acid or 0.2 M acetic acid and 0.16 M sodium acetate. Owing to the instability of the hexacyanochromate ion in acid solutions, stock solutions of potassium hexacyanochromate were prepared in and diluted with 0.05 M sodium bicarbonate (pH 8.6). Final sample solutions for quenching measurements were prepared by pipetting 5 mL of the donor stock solution into 10-mL volumetric flasks and adding 5 mL of the solution containing the desired concentration of quencher at the desired pH. Portions (2 mL) of the resulting solutions were transferred to 1-cm quartz cells and deoxygenated by nitrogen bubbling for 10–20 min. The nitrogen used for purging was passed through an oxygen scrubber (13.3 g of chromium trichloride per 100 mL of 1 M HCl over Zn/Hg amalgam) prior to bubbling through the sample solution. Europium(II) solutions for quenching studies were prepared by reducing solutions of known europium(III) nitrate concentration (0.5–100 mM) over Zn/Hg amalgam in a nitrogen atmosphere. These were combined with an equal volume of 1 mM iridium complex in 1 M nitric acid to give sample solutions ranging from 0.25 to 50 mM in Eu(II).

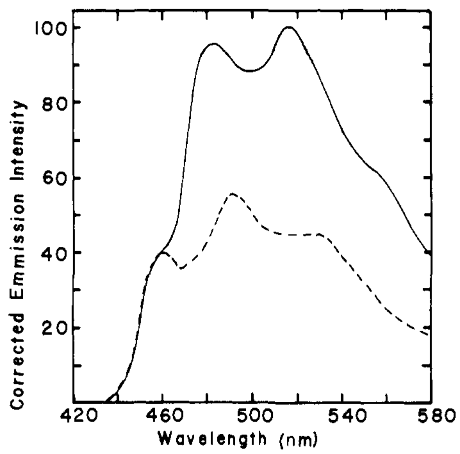


Figure 1. Sample luminescence spectrum used in luminescence titration of $Ir(bpy)_2(H_2O)(bpy)^{3+}$ at pH 3.2; —, total emission; - - - -, contribution of base form.

Intensity measurements were made with either the Perkin-Elmer Hitachi MPF-3 using 390-nm excitation or with a device employing phase-sensitive amplification which has been described in previous publications,[31] using 365-nm excitation. Emission intensities were monitored at 493 (base form) or 517 nm (acid form). For lifetime measurements samples were excited at 337 nm with an Avco C-950 pulsed nitrogen laser. Emitted light was passed through a 0.8-m Fastie-Ebert grating monochromator set at either 493 or 517 nm, and detected with an EMI 9558 QA photomultiplier. Decay curves were monitored with a Tektronix 549 oscilloscope and photographed prior to least-squares analysis with a 9829A Hewlett-Packard calculator. All absorption spectra were recorded with a Cary Model 15 spectrophotometer.

Results

A. Excited-State pK_a*. From the observed values of the emission band maxima in room temperature aqueous acid and aqueous base (517 and 492 nm, respectively) a Förster cycle calculation[32] yields a value of 4.94 for pK_a*.

A sample corrected luminescence spectrum (at pH 3.2) which was used in the determination of pK_a* via the luminescence titration technique is illustrated in Figure 1 along with the decomposition of the spectrum into intensity contributions from the acid and base forms. The ratio of the concentrations of the acid and base forms of the complex was obtained by dividing the observed ratio of integrated emission intensities by the ratio of the luminescence quantum yields (0.30/0.35).

Figure 2 shows a complete luminescence titration curve for the complex. This sharp-breaking luminescence titration curve is consistent with either of two interpretations:[33] (1) The excited-state acid–base equilibrium is established much more rapidly than the excited-state decay back to the ground state, and the curve is a measure of the excited-state acid–base properties. (2) The excited-state acid–base equilibration is

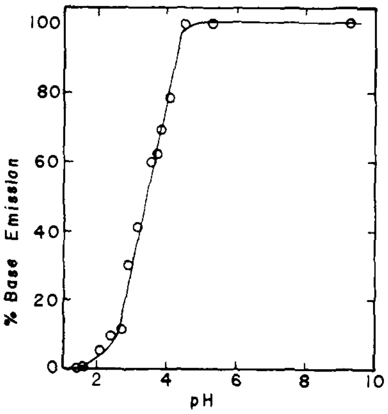


Figure 2. Luminescence titration of $Ir(bpy)_2(H_2O)(bpy)^{3+}$.

much slower than the deactivation of the excited states, and the titration curve reflects ground-state acid–base properties. Since comparable excited-state proton exchange and luminescence decay rates generally lead to a broadening of the titration curve, which is not observed here, the intermediate case is neglected. If case (1) above is applicable then the value of pK_a* can be extracted from the luminescence titration curve with the relationship[34]

$$pK_a^* = pH_i + \log\,[\tau(\text{acid})/\tau(\text{base})] \qquad (5)$$

where pH_i is the value of the pH at the inflection point of the titration curve and τ(acid) and τ(base) are the luminescence lifetimes of the acid and base forms (12.2 and 10.0 μs, respectively). This procedure yields a pK_a* value of 3.5 ± 0.1 compared to the previously reported[26] ground-state pK_a value of 3.0 ± 0.1. From this value of pK_a* and an assumed value of $k_1 \gtrsim 10\tau^{-1}$ ($\gtrsim 10^6\ s^{-1}$) for the deprotonation rate constant in order to establish acid–base equilibrium in the excited state prior to deactivation, the second-order rate constant for protonation, k_{-1}, would be estimated to be $\gtrsim 3.3 \times 10^9\ M^{-1}\ s^{-1}$. Since rate constants for protonation processes are typically diffusion controlled[33] ($k_{-1} \lesssim 10^{11}\ M^{-1}\ s^{-1}$), the value of k_{-1} estimated for applicability of case (1) is quite reasonable. If case (2) were to apply ($k_1 \lesssim 0.1\tau^{-1} \sim 10^4\ s^{-1}$) then $k_{-1} \lesssim 3.3 \times 10^7\ M^{-1}\ s^{-1}$, a value far too small for a typical protonation process. These estimates of k_{-1} rely upon the value of K_a*, and, if K_a* is much smaller than the luminescence titration indicates, the values of k_{-1} estimated for applicability of cases (1) and (2) above would be much larger. Hence, while our estimates are consistent with case (1), they by no means prove that excited-state acid–base equilibration occurs.

Further evidence for applicability of case (1) is found in the use of buffers in the luminescence titration. It is known that high concentrations of buffer species can bring about acid–base equilibration in excited states which are otherwise unequilibrated.[33] The use of buffer species with concentrations as high as 1 M has no measurable effect on the ratio of acid to base emission in the present system in the pH region around equivalence point. This strongly supports case (1) above, and indicates that the luminescence titration yields a value of the acid dissociation constant in the excited state.

B. Luminescence Quenching. Quenching data obtained by either lifetime measurements (τ method) or steady-state intensity measurements (I method) were fit to eq 6 to yield Stern–Volmer quenching constants, K_{sv}.

$$\left(\frac{I_0}{I}\right)_{cor} = \frac{\tau_0}{\tau} = 1 + K_{sv}[Q] \qquad (6)$$

In (6) I_0 and τ_0 represent the emission intensity and lifetime with no added quencher and I and τ represent the emission intensity in the presence of a concentration, Q, of added quencher. All measured intensity ratios were corrected for trivial absorption of exciting and emitting light by the quencher.[5] Bimolecular quenching constants k_q obtained from Stern–Volmer plots (Figure 3a,b) are listed in Table I along with K_{sv} values for the quenching species which were studied.

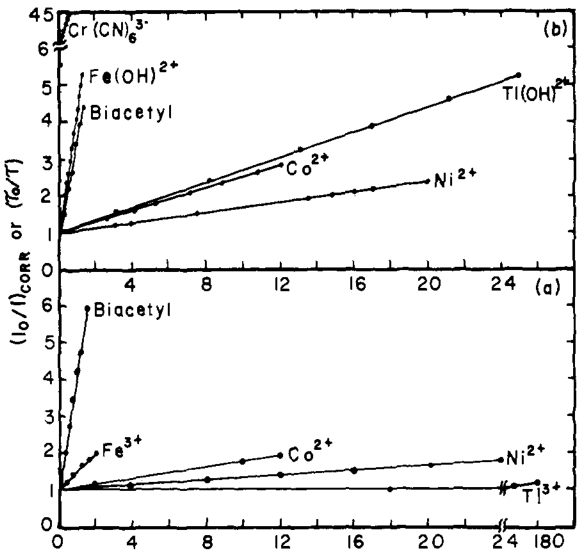


Figure 3. Stern–Volmer quenching plots: (a) quenching of the acid form, $Ir(bpy)_2(H_2O)(bpy)^{3+}$ in 0.5 M $HClO_4$; (b) quenching of the base form, $Ir(bpy)_2(OH)(bpy)^{2+}$ in pH 4.66 acetate buffer.

Bimolecular diffusion rate constants for donor–acceptor collisions, k_d, were estimated using standard formulas for spherical molecules with corrections for Coulombic potentials between charged species. A value of 0.916 nm, used as the hard-sphere diameter of the iridium(III) donor, was estimated from the known dimensions of pyridine[35] and an ionic radius of 0.07 nm for Ir(III). Estimates of the hard-sphere diameters of the quenching species were made from ionic radii and bond lengths available in the literature. Estimated values of k_d are indicated in Table I. From values of k_q and k_d it is possible to estimate the fraction of collisions which lead to bimolecular quenching, β, which is given by k_q/k_d (see Table I).

Owing to the necessity of having electrolytes other than the donor and quencher in solution in order to maintain the desired pH values for quenching measurements, the possibility of ionic strength effects on k_q was investigated. The Co^{2+} quencher was chosen for this study since it required the largest variation of concentrations to obtain k_q. Constant ionic strength of 0.5 was maintained by addition of a calculated amount of solid $NaClO_4$ to the donor solution prior to mixing with the Co^{2+} quencher solutions. The study indicates that k_q values are increased by ~20–30% with Co^{2+} at this ionic strength.

Possible quenching by counterions present in the donor–acceptor solutions was checked over the concentration range in which they were present. No quenching of the donor emission was found for acetate (0–0.2 M), bicarbonate (0–0.05 M), chloride (0–0.2 M), nitrate (0–1.0 M), perchlorate (0–0.5 M), or zinc(II) (0–0.5 M).

The possibility of ground-state donor–quencher pairing which would lead to a static quenching contribution to the Stern–Volmer analysis was checked by absorption spectroscopy of the donor–quencher solutions. In all cases, no new bands were found in the absorption spectra which were identical with the sum of the donor and quencher spectra. This was further checked by emission spectroscopy in the case of a donor–$Cr(CN)_6^{3-}$ solution in dimethylformamide due to the potential for ion pairing between the oppositely charged complex ions. The shape of the emission spectra of both species

Table I. Luminescence Quenching Results at ~23 °C

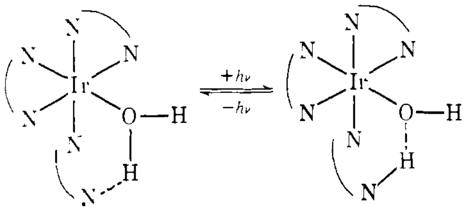
	$Ir(bpy)_2(H_2O)(bpy)^{3+}$ [a,b]					$Ir(bpy)_2(OH)(bpy)^{2+}$ [b,c]			
quencher	K_{sv}, M^{-1}	$k_q \times 10^{-7}$, M^{-1} s^{-1}	k_d, M^{-1} s^{-1}	$\beta = k_q/k_d$	quencher	K_{sv}, M^{-1}	$k_q \times 10^{-7}$, M^{-1} s^{-1}	k_d, M^{-1} s^{-1}	$\beta = k_q/k_d$
Fe^{3+}	450	3.7	0.69	5.4	$Fe(OH)^{2+}$	3100	31	55	0.56
Tl^{3+}	0.75	0.006	0.83	0.007	$Tl(OH)^{2+}$	160	1.6	61	0.026
Co^{2+}	74	0.61	11	0.057	Co^{2+}	150	1.5	56	0.027
Co^{2+} [d]	110	0.91	11	0.085	Co^{2+} [d]	190	1.9	56	0.033
Ni^{2+}	34	0.28	10	0.028	Ni^{2+}	42	0.42	56	0.008
Eu^{3+}	0	0	0.83	0	Eu^{3+}	0	0	12	0
biacetyl	3100	26	740	0.035	biacetyl	2800	28	740	0.038
Eu^{2+} [e]	~2400	~20	24	~1	$Cr(CN)_6^{3-}$ [f]	89 000	890	3800	0.23

[a] In 0.5 M perchloric acid except as noted. [b] Donor concentration 5.0×10^{-4} M. [c] In pH 4.66 buffer of 0.1 M acetic acid and 0.08 M sodium acetate except as noted. [d] At constant ionic strength of 0.5. [e] In 0.5 M nitric acid. [f] In 0.05 M sodium bicarbonate (pH 8.6).

was found to be unaltered by the presence of the other, and no new emission bands were found. The intensity of the $Cr(CN)_6^{3-}$ was clearly enhanced in dimethylformamide solutions containing the donor iridium complex, indicating sensitization of the emission. However, no quantitative Stern–Volmer analysis of the $Cr(CN)_6^{3-}$ emission was possible owing to a rapid photoreaction which took place in dimethylformamide. This photoreaction was found to occur in solutions of the donor iridium complex in dimethylformamide without added $Cr(CN)_6^{3-}$, but was not further characterized. No evidence of photodecomposition was found in studies with $Cr(CN)_6^{3-}$ or any of the other quenchers in aqueous solutions containing the donor, as indicated by donor emission intensities which were independent of irradiation time.

Discussion

A. Identity of Donor and Acceptor Species in Solution. The excited-state pK_a^* value of 3.5 indicates that the site of proton ionization is more basic than it is in the ground state. Since this is not consistent with proton ionization from the coordinated water, which should lose some electron density due to the contribution of charge-transfer to monodentate bpy in the luminescent state, we believe that the complex undergoes proton phototautomerization prior to ionization as indicated in (7).[36] This formulation is also consistent with a red shift of the luminescence of the aquo complex in fluid solutions compared to rigid glasses.[26] Owing to this phototautomerization, calculation of pK_a^* from room temperature emission maxima by the Förster cycle, which yields a value of 4.94, is inaccurate. However, the calculation does correctly predict the direction of the shift in pK_a^* compared with the ground-state pK_a value.



(7)

The establishment of pK_a^* for the donor complex permits identification of which of the two species is present in the excited state at a given pH. Thus, at pH less than about 1.5, the tautomeric form of the aquo complex (eq 7) is the dominant donor species, whereas at pH greater than about 4.5 the normal hydroxo form of the complex is the primary donor species in solution. Taking the 0–0 bands of the room temperature aqueous emission spectra of the base and tautomeric acid forms of the complex, the donor energies available in bimolecular energy transfer processes are estimated to be 259 and 246 kJ/mol, respectively.

By choosing 0.5 M perchloric acid and acetate buffer for the solvent media for quenching experiments, the identity of the donor species is assured to be either the tautomeric acid form or the base form of the iridium complex, respectively. Comparison of the donor efficiencies as measured by β (Table I) or the quenching rate constants, k_q (Table I), of the two forms is complicated by potential changes in the identity of the quencher in the two solvent media. For example, comparison of the absorption spectra of Co(II) and Ni(II) in perchloric acid and acetate buffer with published absorption spectra[37] of the aquated species confirms the identity of the quencher as the aquated complex in both solvent systems; however, Fe(III) clearly exists in different complexed forms in the two solvent media as evidenced by changes in its absorption spectrum. It is known that Fe(III) tends to hydrolyze and/or form polynuclear complexes in aqueous solutions. At pH less than 1 the predominant species is the hexaaquo complex, the quenching species in 0.5 M perchloric acid. In the acetate buffer, there are several possible Fe(III) species including the hydroxopentaaquoiron(III) complex, polynuclear complexes, and a basic iron acetate complex, $[Fe_3(CH_3COO)_6 \cdot 3H_2O]^+$. The third possibility can be eliminated owing to the severe conditions known to be necessary for its formation.[38] At the pH of the acetate buffer hydroxopentaaquoiron(III) is the primary species present at Fe(III) concentrations less than 2 mM.[39,40] Thus, the hydroxopentaquoiron(III) complex ion is believed to be the dominant quencher species in the Fe(III)-acetate buffer. Similar information suggests that Tl(III) exists as the aquo complex in 0.5 M perchloric acid as the hydroxopentaaquothalium(III) cation at the pH of the acetate buffer.[41]

B. Quenching Mechanisms. Excited states of Ru(II) complexes similar to the Ir(III) donor used here are known to undergo several quenching mechanisms over the range of acceptors employed in this study. These include (1) oxidative quenching;[2-10] (2) reductive quenching;[11-16] (3) energy-transfer quenching.[17-23] Recent electrochemical studies[42] of the hydroxo form of the iridium donor complex in acetonitrile by cyclic voltammetry indicate that a single irreversible ground-state oxidation wave comes at an anodic peak potential of +2.1 V (vs. SCE) whereas the first of a series of reversible reduction waves appears with a cathodic peak potential of −1.1 V (vs. SCE). From this information a reduction potential of about −0.76 V (vs. NHE) can be estimated for the hydroxo complex. Assuming a negligible entropy change between the ground and luminescent states, an excited-state potential of 2.68 V is available in the hydroxo complex (2.55 V in the aquo form). From this information, the reduction potential for the excited state (eq 8) can be estimated to be +1.84 V (vs. NHE).

$$*Ir(bpy)_2OH(bpy)^{2+} + e^- \rightarrow Ir(bpy)_2OH(bpy)^+ \qquad E_0 = +1.84\ V \qquad (8)$$

Although this estimate is rather crude owing to the transference of the ground-state reduction potential from acetonitrile to water and to the neglect of entropy changes, it is clear that the excited state of the iridium complex is a far better oxidizing agent than *Ru(bpy)$_3$$^{2+}$, for which a reduction potential of +0.84 V has been estimated.[14] A similar estimate based on cyclic voltammetry[42] and luminescence[43] results for Ir(bpy)$_3$$^{3+}$ suggest that the excited-state reduction potential of that species is +2.26 V, even higher than that of the iridium complex studied here.

Little can be deduced with regard to oxidative quenching owing to the large, irreversible ground-state oxidation potential obtained from cyclic voltammetry. However, it appears likely that the excited *Ru(bpy)$_3$$^{2+}$ is a far better reducing agent than the iridium complex. With regard to energy-transfer quenching, the donor energy of the iridium complex (259 kJ/mol, base form; 246 kJ/mol, acid form) considerably exceeds that of Ru(bpy)$_3$$^{2+}$ (205 kJ/mol)[44] and is slightly below that of Ir(bpy)$_3$$^{3+}$ (271 kJ/mol).[43]

The information above suggests that quenching mechanisms (2) and (3) are likely to be efficient in the iridium complex, but that (1) would only be expected for acceptors which are reasonably good oxidizing agents. Of the quenchers used in this study, only Eu^{3+}, Tl^{3+}, and Tl(OH)$^{2+}$ are known with some certainty to lack low energy states necessary for the energy-transfer mechanisms.[7] While this may also be the case for Eu^{2+}, little information is presently available concerning the low-energy states of this ion in an aqueous environment.[16] Thus, energy-transfer quenching may contribute to the k_q values observed for all of the acceptors studied, save the four above.

The only reasonably good oxidizing agent among the acceptors is Fe^{3+}. Comparison of the quenching efficiency of Fe^{3+} with β values of otther species capable of energy-transfer quenching indicates that the efficiency of Fe^{3+} is substantially higher than that of the other energy-transfer quenchers. Thus, it appears likely that the oxidative mechanism contributes to quenching by Fe^{3+}. This mechanism is presumed to be the only one possible for quenching by Tl^{3+}, Tl(OH)$^{2+}$, and Eu^{3+}. Very small k_q and β values were observed for the thallium species, whereas no Eu^{3+} quenching was found. These observations are in qualitative agreement with the relative reduction potentials of Tl^{3+} and Eu^{3+} (−0.37 and −0.43 V, respectively), which indicate that Tl^{3+} is a better oxidizing agent than Eu^{3+}. It is interesting to note that oxidative quenching of Ru(bpy)$_3$$^{2+}$ by Tl^{3+} is quite efficient (β = 0.59),[7] presumably owing to the favorable oxidation potential of *Ru(bpy)$_3$$^{2+}$ compared to that of *Ir(bpy)$_2$OH(bpy)$^{2+}$.

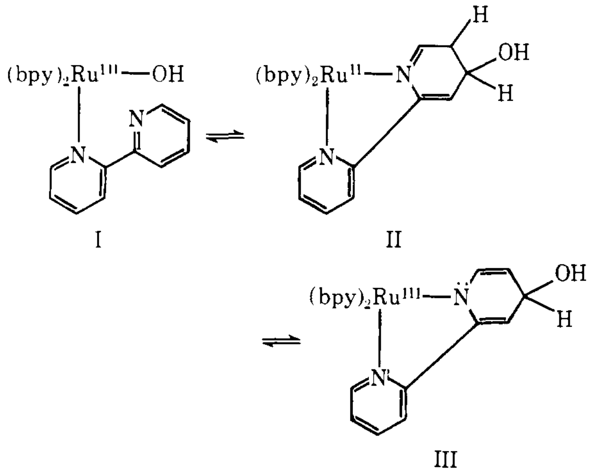
Of the quenchers studied here, only Eu^{2+} is expected to quench via reductive electron transfer, and quenching appears to proceed at a diffusion-controlled rate in this case. Thus, as anticipated on the basis of the highly favorable reduction potential of *Ir(bpy)$_2$OH(bpy)$^{2+}$, the iridium complex is quenched by Eu^{2+} with a somewhat higher efficiency than is Ru(bpy)$_3$$^{2+}$ (β = 0.12).[16] One cannot entirely rule out the possibility of some energy-transfer quenching by Eu^{2+} in any of the quenching studies where it has been employed. However, the high quenching efficiency of Eu^{2+} relative to species which are limited to energy-transfer quenching mechanisms leaves little doubt that reductive quenching is significant with Eu^{2+} The absence of any net photochemical changes due to irradiation of the Ir(bpy)$_2$H$_2$O(bpy)$^{3+}$–Eu^{2+} solutions indicates that the back electron transfer from Eu^{3+} to Ir(bpy)$_2$H$_2$O(bpy)$^{2+}$ efficiently regenerates the starting complex and Eu^{2+} analogously to the Ru(bpy)$_3$$^{2+}$–Eu^{2+} results.[16]

C. Comparisons of Quenching Efficiencies. Table I indicates that the quenching efficiency for the acid form of the complex is higher than that of the base form in several instances. However, this is based upon a crude calculation of k_d, which involves a correction for a 3+ ion in the case of the acid and a 2+ ion in the case of the base form of the complex. The unreasonably high value of β in the case of quenching of the acid form by Fe^{3+}, and the near equivalence of β for the acid and base forms for uncharged biacetyl, where no charge correction is applied, suggests that our calculation of k_d overestimates the charge effect for the acid form. For an ionic model, as assumed in the calculation, this can be attributed to screening of the 3+ charge of the metal by the first and second coordination spheres. Since the observed k_q value of 3.7×10^7 M^{-1} s^{-1} represents a lower limit for k_d, we can estimate the maximum effective charge on iron(III) which is consistent with this k_d value. We find that for an effective charge of 2.5+ the k_d value for iron(III) is equal to its minimum possible value. Values of β for the acid form of the complex which are estimated using an effective charge of 2.5+ in the calculation of diffusion constants are in all instances in good agreement with β values for the base form. Thus, it appears that no significant differences exist in the quenching efficiencies of the two forms. Hence, the base form is generally preferable for positively charged species and the acid form for negatively charged species to ensure maximum diffusion rates and k_q values.

It is interesting to compare quenching efficiencies for the base form of the iridium complex with those for Ru(bpy)$_3$$^{2+}$ since both are 2+ ions with nearly equal hard-sphere diameters, and the quenching of the latter by a wide variety of quenchers has been studied. For Co^{2+} and Ni^{2+} the iridium complex is quenched more efficiently than is the ruthenium complex;[21] for Cr(CN)$_6$$^{3-}$ the ruthenium complex is more efficient.[21] Comparison for Fe^{3+} and Tl^{3+} is complicated by the fact, noted above and in Table I, that these species probably exist as Fe(OH)$^{2+}$ and Tl(OH)$^{2+}$ in the acetate buffer used to maintain the base form whereas they have been studied in acid solutions with Ru(bpy)$_3$$^{2+}$.[7,10] Nonetheless, the enhanced efficiency of the ruthenium complex in these cases and the increased efficiency for the acid form of the iridium complex with Eu^{2+} appear to qualitatively correlate with potentials for oxidative and reductive electron transfer quenching mechanisms as noted above.

D. Considerations of Solar Energy Storage. Interest in solar energy storage via photocatalytic hydrogen and oxygen production from water is currently high, as is the interest in the use of metal complexes as catalytic agents for this purpose. General considerations relevant to this problem have been discussed,[45] and more detailed considerations of the requisite electron-transfer steps for Ru(bpy)$_3$$^{2+}$, including evidence for dioxygen production from hydroxide ion and Ru(bpy)$_3$$^{3+}$, have been presented.[46] Recent success in hydrogen generation by visible irradiation of a solution of Ru(bpy)$_3$$^{2+}$ containing triethanolamine, a rhodium–bipyridine complex, and a platinum catalyst has been reported,[47] although no report of the equally important oxygen-production cycle for this system has been published.

The thermodynamic requirements for photocatalytic cleavage of water are satisfied by Ru(bpy)$_3$$^{2+}$, whose excited-state oxidation potential is adequate to reduce water to diatomic hydrogen and hydroxide ion.[46] The Ru(bpy)$_3$$^{3+}$ so produced would be thermodynamically capable of oxidizing hydroxide ion to diatomic oxygen and water; indeed, the oxidative step has been shown to occur in a relatively narrow pH range around pH 9.[46] Although the mechanism for dioxygen production is not known with certainty, it is thought to involve a species in which hydroxide has been added to a bound bipyridine ring; the Ru(bpy)$_3$$^{3+}$ species is believed to chaperone hydroxyl through a reaction sequence to produce diatomic oxygen without hydroxyl radical production.[46] It is interesting to note that the intermediate ruthenium species, as depicted below (eq 9, structures II and III), is tautomerically analogous, via the Gillard[48,49] formulation of covalent hydration, to the



(9)

monodentate iridium species used in this study (eq 9, structure I). In this equation structure I is formed by hydroxide ion migration from the bound bpy ring to the metal center whereas II and III are the proposed intermediates in the hydroxide oxidation.[46]

The apparent similarity between these structures and that of the hydroxo form of the iridium complex studied here suggests that it too may have application to the water-cleavage problem. Our estimate of the reduction potential of $^*\mathrm{Ir(bpy)_2OH(bpy)^{2+}}$ suggests that this species is capable of oxidizing water to oxygen or even to hydrogen peroxide. The $\mathrm{Ir(bpy)_2OH(bpy)^{+}}$ so produced is capable of reducing protons to diatomic hydrogen according to the cyclic voltammetry results.[42] Hence, photochemical cleavage of water, according to (10–12), is thermodynamically feasible.

$$\mathrm{Ir(bpy)_2OH(bpy)^{2+}} \xrightarrow{h\nu} {}^*\mathrm{Ir(bpy)_2OH(bpy)^{2+}} \tag{10}$$

$$\begin{aligned}&{}^*\mathrm{Ir(bpy)_2OH(bpy)^{2+}} + \mathrm{H_2O}\\&\qquad \rightarrow \mathrm{Ir(bpy)_2OH(bpy)^{+}} + \tfrac{1}{2}\mathrm{H_2O_2} + \mathrm{H^+}\end{aligned} \tag{11}$$

$$\begin{aligned}&\mathrm{Ir(bpy)_2OH(bpy)^{+}} + \mathrm{H^+}\\&\qquad \rightarrow \mathrm{Ir(bpy)_2OH(bpy)^{2+}} + \tfrac{1}{2}\mathrm{H_2}\end{aligned} \tag{12}$$

While the mechanism by which one might accomplish the photochemical cleavage of water is obscure, the analogy between $\mathrm{Ru(bpy)_3}^{3+}$, which is known to oxidize $\mathrm{OH^-}$ to diatomic oxygen, and the *excited state* of $\mathrm{Ir(bpy)_2OH(bpy)^{2+}}$ is striking. As indicated in eq 9, the proposed intermediate in the oxidation of $\mathrm{OH^-}$ by $\mathrm{Ru(bpy)_3}^{3+}$ is tautomerically analogous to the structure of ground-state $\mathrm{Ir(bpy)_2OH(bpy)^{2+}}$. Furthermore, the excited hydroxo complex, like $\mathrm{Ru(bpy)_3}^{3+}$, is thermodynamically capable of the $\mathrm{OH^-}$ oxidation. Hence, a pathway for dioxygen production by irradiation of the iridium complex might be available. In view of the strong pH dependence for dioxygen production by $\mathrm{Ru(bpy)_3}^{3+}$, a similarly strong pH dependence is likely to occur should dioxygen production prove possible with the iridium complex.

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