terligand interactions, we find evidence for the binding of cytidine(cytosine), although the formation constants are very small, Table VI.

As a general conclusion, then, we have selected a system which differentiates in its binding to the four common nucleosides, clearly favoring the binding to adenosine with the exclusion of binding to guanosine or uridine and with only a very minor contribution by cytidine. The stability constant data were obtained in Me_2SO and the proton at N(3) in uridine is less readily displaced in this solvent than in water. However, our preparative studies, which *were* carried out in water, clearly show the same selectivity by $Na[Co(acac)_2(NO_2)_2]$.

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Supplementary Material Available: Listings of structure factors and final fractional atomic parameters (29 pages). Ordering information is given on any current masthead page.

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A Stable Monodentate 2,2′-Bipyridine Complex of Iridium(III): a Model for Reactive Intermediates in Ligand Displacement Reactions of Tris-2,2′-bipyridine Metal Complexes

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Abstract: A complex containing monodentate 2,2′-bipyridine bound to Ir(III) has been prepared and isolated. The complex, which contains two bidentate bpy's, one water, and one monodentate bpy can be converted to the hydroxo form and isolated by treatment with base. The pK_a for the conversion is 3.0 ± 0.1. Spectroscopic data indicate strong hydrogen bonding between coordinated water and monodentate bpy in the aquo form of the complex. The $[Ir(bpy)_2Cl(H_2O)]^{2+}$ and $[Ir(bpy)_2(H_2O)_2]^{3+}$ complex ions have been prepared and isolated by photolysis of $[Ir(bpy)_2Cl_2]^+$. These complexes have been converted to $[Ir(bpy)_2Cl(OH)]^+$ and $[Ir(bpy)_2(OH)_2]^+$ by treatment with base, and the pK_a's for the conversions have been determined. Comparison of the effects of protonation of these complexes on their visible absorption and emission spectra with protonation of the monodentate bpy complex illustrates the contrasting effects of protonation of π-donating and π-accepting ligands on charge-transfer-to-ligand (CTTL) transitions. The luminescence lifetimes of the monodentate bpy complexes are long in fluid solution ($\sim$10 μs) and their luminescence quantum yields are high ($\sim$0.3). These properties indicate that they may be useful as high-energy sensitizers and in flash-lamp-pumped dye lasers. The structures of these complexes provide a model for the structures of reactive intermediates formed in the photolysis of tris-2,2′-bipyridine metal complexes such as $[Ru(bpy)_3]^{2+}$.

I. Introduction

The ligand 2,2′-bipyridine (bpy) has been used extensively by inorganic chemists due to the ease with which it chelates most transition metal ions. Although similar ligands such as ethylenediamine (en) form well-characterized complexes in which en may act as either a monodentate[1-4] or a bidentate ligand, the extra rigidity present in bpy apparently leads to a high preference for the bidentate binding mode. However, recent x-ray crystallographic studies of the binding of the still-more-rigid 1,10-phenanthroline (phen) ligand to Pt(II) indicate that (phen) acts as a monodentate ligand in $[PtCl(PEt_3)_2(phen)]BF_4$.[5] Furthermore, studies of the photolysis of $Ru(bpy)_3^{2+}$ in DMF indicate that an intermediate monodentate bpy species is formed in solution prior to formation of the final product, $[Ru(bpy)_2(NCS)_2]$.[6] Attempts to isolate this species as a crystalline solid have not been successful.[7] We have also found evidence for formation of a species containing monodentate bpy in the photolysis of $Ru(bpy)_3^{2+}$ in aqueous solution, but have likewise been unable to isolate the material.[8]

Most of the d^6 ions of the group 8 transition metals are known to easily form tris complexes with bidentate-bound bpy. Thus, $Fe(bpy)_3^{2+}$, $Co(bpy)_3^{3+}$, $Ru(bpy)_3^{2+}$, $Rh(bpy)_3^{3+}$, and $Os(bpy)_3^{2+}$ are all well-known species. However, $IrCl_2(bpy)_2^+$ is the principal product of the reaction of $IrCl_3$ with bpy,[9-12] and $Ir(bpy)_3^{3+}$ has only recently been prepared by reaction of iridium sulfates with bpy in a halide-free medium.[13] It is apparently considerably more difficult to bind three bpy's to Ir(III) than it is to the other metal ions mentioned above.

In this paper we report the preparation and characterization of the bis-2,2′-bipyridineaquo-2,2′-bipyridineiridium(III) ion, a stable Ir(III) species containing monodentate bpy. We have also characterized the chloroaquobis-2,2′-bipyridineiridium(III), $\{[Ir(bpy)_2(H_2O)Cl]^{2+}\}$ and the diaquobis-2,2′-bipyridineiridium(III), $\{[Ir(bpy)_2(H_2O)_2]^{3+}\}$, complex ions. The acid–base properties of these complexes are compared with those of the monodentate bpy species to illustrate the contrasting effects of protonations of π-donating and π-accepting ligands on charge-transfer states in Ir(III).

II. Experimental Section

A. Synthesis of Complexes. Bis-2,2′-bipyridineaquo-2,2′-bipyridineiridium(III) Chloride, $[Ir(bpy)_2(H_2O)(bpy)]Cl_3\cdot 3H_2O$. Iridium trichloride (Mathey Bishop, 1 g) and 2,2′-bipyridine (G. F. Smith, 2 g) were mixed in 10 mL of glycerol. The mixture was heated at 180 °C for 2 h to give a clear orange-red solution. After cooling, 20 mL of water was added to the mixture, and excess 2,2′-bipyridine was removed by three extractions with diethyl ether. The solution containing the product was cooled overnight at 5 °C, and the golden yellow crystals which precipitated were collected, dried, and recrystallized from methanol to yield 0.53 g of *cis*-dichlorobis-2,2′-bipyridineiridium(III) chloride. The supernatant was passed through a 25 × 200 mm column of carboxymethylcellulose cation exchange resin (Macherey-Nagel MN 2100CM) in the Na^+ form buffered to pH 6. The column was washed with 250 mL of water to remove glycerol, and the product was eluted with 0.1 M HCl. The solution of product was flash evaporated to near dryness and dissolved in a minimum volume (15 mL) of hot methanol. Upon cooling, an additional 0.25 g of $[IrCl_2(bpy)_2]Cl$ was collected by filtration of the solution. Sodium methoxide was added to the methanol solution of the product to make it 0.01 M in methoxide. This solution was passed onto a 25 × 500 mm column of Sephadex LH-20 which was prepared with 0.01 M sodium methoxide in methanol. The position of the product during elution with the sodium methoxide-methanol solvent could be easily followed by its blue-green emission under excitation with a black light. The main product was the first fraction to be eluted. This was followed by several unidentified fractions. The methanol solution of the product was evaporated to dryness and dissolved in a minimum volume of boiling 0.01 M sodium methoxide in 1-propanol. The hot orange solution of the product was acidified with a few drops of concentrated HCl, and the solution changed to a light yellow color. Light yellow crystals of the product formed on cooling. These were collected on a filter and washed with ice-cold propanol to yield 0.26 g of the product. This was further purified by additional recrystallizations from acidic 1-propanol. The chloride salt was converted to the less-soluble perchlorate salt by recrystallization in 0.1 M perchloric acid.

Anal. Calcd for $[Ir(H_2O)(C_{10}H_8N_2)_3]Cl_3\cdot 3H_2O$: C, 42.94; H, 3.84; Cl, 12.67; N, 10.01. Found: C, 42.44; H, 3.76; Cl, 13.23; N, 9.77.

Bis-2,2′-bipyridineaquo-2,2′-bipyridineiridium(III) Bromide, $[Ir(bpy)_2(H_2O)(bpy)]Br_3\cdot 3H_2O$. The bromide salt was prepared from iridium tribromide (Englhard, 1 g) and 2,2′-bipyridine (G. F. Smith, 2 g) by a procedure analogous to the one described above. A reduced yield of 0.13 g of the product was obtained in addition to several other components which have not been identified.

Anal. Calcd for $[Ir(H_2O)(C_{10}H_8N_2)_3]Br_3\cdot 3H_2O$: C, 37.05; H, 3.32; Br, 24.65; N, 8.64. Found: C, 36.92; H, 3.16; Br, 24.23; N, 8.60. Ionic bromide was determined by passing an aqueous solution of the complex through a 1 × 10 cm column of Biorad AG-50W × 8 cation exchange resin in the Na^+ form. The aqueous solution of sodium bromide from the column was collected and bromide was determined by potentiometric titration with silver nitrate using a silver electrode. The value of 24.12% obtained indicates that the complex ion contained no coordinated halide.

Chloroaquobis-2,2′-bipyridineiridium(III) Perchlorate, $[Ir(bpy)_2Cl(H_2O)][ClO_4]_2\cdot XH_2O$. *cis*-Dichlorobis-2,2′-bipyridineiridium(III) chloride (0.2 g) was dissolved in 0.01 M nitric acid (100 ml). The solution was placed in a Pyrex flask and photolyzed with the Pyrex filtered output of a General Electric AH-4 100-W Hg lamp for 4 h under a continuous nitrogen purge. Ionic chloride was precipitated immediately after photolysis by addition of silver nitrate to the solution. The silver chloride was removed by centrifugation, and the clear yellow supernatant was flash evaporated to dryness. The product was dissolved in methanol (10 mL) and placed on a 25 × 500 mm column of Sephadex LH-20 in methanol. Elution with methanol gave three fractions. The first of these contained mainly the diaquo species, $[Ir(bpy)_2(H_2O)_2]^{3+}$, which was formed in only small quantities. No distinct separation between this fraction and the second fraction could be obtained. Rather, both fractions constituted a long band which was light yellow at the front and darker yellow at the tail. The second fraction, which was the darker-yellow tail portion of the first band, contained the desired product. The third fraction, which was a separate band well-removed from the first, contained unreacted $[Ir(bpy)_2Cl_2]^+$. The second fraction was evaporated to dryness at room temperature and dissolved in a minimum of hot water. The solution was allowed to cool, and several drops of concentrated perchloric acid were added. Yellow crystals of the product formed when the solution was allowed to cool overnight at 5 °C. These were collected on a filter and washed with cold 1-propanol and a few drops of cold water to yield 0.12 g of the product. The hydroxo form of the complex, $[Ir(bpy)_2Cl(OH)]ClO_4$, was isolated by recrystallization of the aquo complex from 0.1 M NaOH–1.0 M $NaClO_4$.

Anal. Calcd for $[IrCl(H_2O)(C_{10}H_8N_2)_2][(ClO_4)_2]\cdot H_2O$: C, 31.00; H, 2.60; N, 7.23; Cl, 13.72. Found: C, 30.86; H, 2.58; N, 7.44; Cl, 13.81.

Diaquobis-2,2′-bipyridineiridium(III) Nitrate $[Ir(bpy)_2(H_2O)_2](NO_3)_3$. *cis*-Dichlorobis-2,2′-bipyridineiridium(III) chloride (0.2 g) was dissolved in 0.01 M sodium hydroxide (100 mL). The solution was placed in a quartz tube and continuously purged with nitrogen during 24 h of photolysis in a Ultra-Violet Products Model PCQXI photochemical reactor equipped with low pressure Hg lamps. Concentrated nitric acid (1 mL) was added and chloride ion was precipitated by addition of silver nitrate. After removal of silver chloride by centrifugation, the solution was flash evaporated to dryness and washed with three 10-mL portions of hot methanol. The resulting yellow solid was dissolved in 20 mL of hot 50% 1-propanol-0.1 M nitric acid and crystallized by slow evaporation of the solvent. The resulting light yellow crystals were collected on a filter and washed with cold methanol to yield 0.10 g of the product. The nitrate salt could be converted to the perchlorate salt by recrystallization from 1.0 M $HClO_4$ and to the dihydroxo complex by recrystallization from 0.1 M NaOH–1 M $NaClO_4$.

Anal. Calcd for $[Ir(H_2O)_2(C_{10}H_8N_2)_2](NO_3)_3$: C, 33.06; H, 2.77; N, 13.49. Found: C, 33.16; H, 2.76; N, 13.60.

B. Experimental Measurements. Infrared absorption spectra were determined with either a Perkin-Elmer 225 or a Perkin-Elmer 283 spectrometer. Visible-UV absorption spectra were determined with a Cary Model 15 spectrophotometer. Corrected emission spectra from 400 to 700 nm were obtained with a Perkin-Elmer Hitachi Model MPF-3 spectrophotofluorimeter. Corrected emission spectra from 450 to 1000 nm were obtained by excitation of samples at 365 nm through a 250-mm Bausch and Lomb grating monochromator blazed at 300 nm with a 1000-W Hanovia 977B-1 Hg-Xe lamp. A 7-cm $CuSO_4$ (150 g/L) solution filter and a Corning 7-60 glass filter were placed in the exciting beam to further improve the spectral purity of the exciting light, which was then passed through a PAR Model 191 chopper modulated at 318 Hz. Emission at right angles to the excitation was passed through a Perkin-Elmer Model 98 monochromator

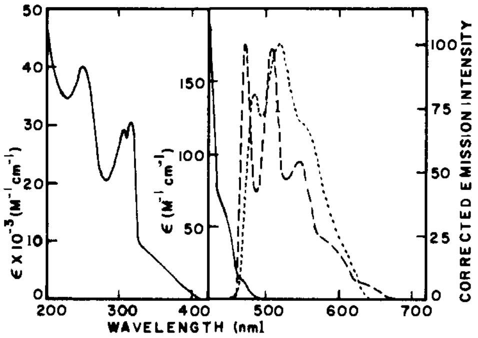


Figure 1. Visible-ultraviolet absorption and emission spectra of $[Ir(bpy)_2(H_2O)(bpy)]Cl_3$: —, absorption in 0.1 M HCl at 295 K; - -, emission in 0.01 M HCl ethanol-methanol glass at 77 K; - - -, emission in deoxygenated 0.1 M HCl at 295 K.

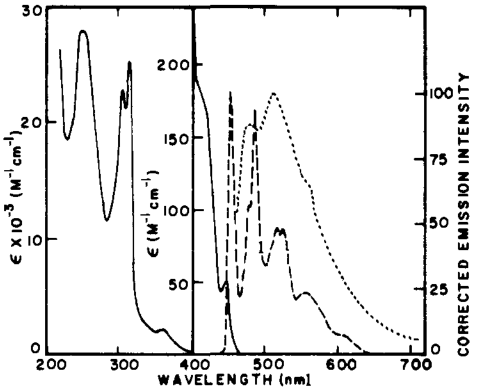


Figure 2. Visible-ultraviolet absorption and emission spectra of $[Ir(bpy)_2Cl(H_2O)][ClO_4]_2$: —, absorption in 0.1 M $HClO_4$ at 295 K; - -, emission in 0.01 M HCl ethanol-methanol glass at 77 K; - - -, emission in deoxygenated 0.1 M $HClO_4$ at 295 K.

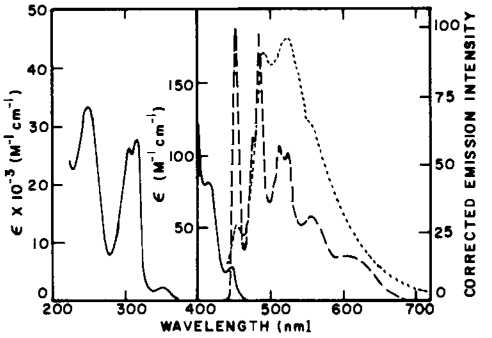


Figure 3. Visible-ultraviolet absorption and emission spectra of $[Ir(bpy)_2(H_2O)_2][NO_3]_3$: —, absorption in 0.1 M HNO_3 at 295 K; - -, emission in 0.01 M HCl ethanol-methanol glass at 77 K; - - -, emission in deoxygenated 0.1 M HNO_3 at 295 K.

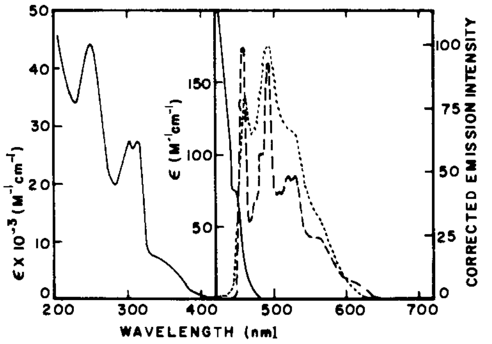


Figure 4. Visible-ultraviolet absorption and emission spectra of $[Ir(bpy)_2(OH)(bpy)]Cl_2$: —, absorption in 0.1 M NaOH at 295 K; - -, emission in 0.01 M $NaOCH_3$ ethanol-methanol glass at 77 K; - - -, emission in deoxygenated 0.1 M NaOH at 295 K.

equipped with a dense flint prism and detected with a dry-ice-cooled RCA 7102 photomultiplier whose output was amplified by a PAR Model 124 lock-in amplifier with a Model 184 preamplifier. Emission spectra were recorded with a RDK Model B161 strip-chart recorder, and corrected for the wavelength sensitivity of the instrument by calibration against an NBS standard tungsten-iodine lamp. Luminescence quantum yields were also measured on this apparatus by a modified Parker-Rees method using a 5-nm excitation bandwidth centered at 365 nm. A 7-cm $CuSO_4$ (150 g/L) solution filter, two Corning 9-58, and one 7-60 glass filter were used to assure the spectral purity of the exciting light. Quinine sulfate in 1.0 N sulfuric acid at 25 °C was used as a standard with a yield of 0.546.[14,15]

Luminescence lifetimes were determined by excitation at 337 nm with an Avco C-950 pulsed nitrogen laser. For lifetimes at 77 K, emitted light was passed through a Fastie-Ebert 0.8 m grating monochromator with 1-nm resolution set at the wavelength of maximum emission intensity. Emitted light was detected with an EMI 9558 QA photomulitplier whose output was applied to the 50-ohms input of a PAR Model 162 boxcar averager with a Model 164 gated integrator. The 50-ns aperture of the boxcar averager was scanned from 0 to 20 μs or 0 to 50 μs with a 100-s scan time using a 60 pps repetition rate on the laser. For determination of lifetimes at 295 K, solutions of the samples were deoxygenated by bubbling with N_2 for 15-30 min. In order to avoid photolysis of the samples in fluid solution emitted light following laser excitation was passed through a Balzers 493-nm interference filter and two Corning 3-52 glass filters. The emission was detected with the EMI 9558QA photomultiplier and applied to the input of a Tektronix type 1A1 plug-in unit in a Tektronix 549 oscilloscope. Decay curves were photographed with a Tektronix C-12 camera. Using this technique, lifetimes could be determined on the basis of one to ten laser pulses.

Potentiometric acid-base titrations were performed with a glass electrode and a Sargent-Welch Model NX pH meter. The NaOH solution used for the acid-base titrations was prepared from carbonate-free saturated NaOH and freshly double-distilled water, and standardized by titration with potassium hydrogen phthalate. Ionic chloride was also determined by potentiometric titration with a silver electrode and a calomel reference electrode. The silver nitrate solution was standardized by titration of NaCl.

III. Results

A. Visible-UV Absorption Spectra. The absorption spectra of the three aquated Ir(III) complexes in both 0.1 M acid and 0.1 M base are presented in Figures 1-6. In acid solution, all three complexes show intense bands at 250, 305, and 315 nm which are characteristic of 2,2′-bipyridine when it is complexed to a metal center. In addition to these bands, each complex shows three features in the longer-wavelength UV-visible region. These features are clearest in the $[Ir(bpy)_2(H_2O)_2]^{3+}$ complex ion which has well-defined peaks at 350, 418, and 448 nm. Peaks are also evident at 360 and 448 nm in $[Ir(bpy)_2Cl(H_2O)]^{2+}$, and a shoulder appears at 418 nm. No well-defined peaks are observed in this region for $[Ir(bpy)_2(H_2O)(bpy)]^{3+}$, although shoulders are found at 360, 448, and 470 nm.

The absorption spectra of the $[Ir(bpy)_2Cl(H_2O)]^{2+}$ and $[Ir(bpy)_2(H_2O)_2]^{3+}$ complex ions (Figures 2 and 3) are grossly altered by conversion of the coordinated water to coordinated hydroxide (Figures 5 and 6) while the hydroxo species containing monodentate bpy (Figure 4) shows the features at 250, 305, and 315 nm which appear in all three aquo species. The $[Ir(bpy)_2(OH)(bpy)]^{2+}$ species also has shoulders at 360 and 448 nm as seen in $[Ir(bpy)_2(H_2O)(bpy)]^{3+}$, but the shoulder at 470 nm is absent in the hydroxo species. The visible absorption spectrum of $[Ir(bpy)_2(OH)_2]^+$ is dominated by an intense peak at 400 nm and a shoulder at 430 nm. A similar peak appears in $[Ir(bpy)_2Cl(OH)]^+$ at 386 nm although no additional shoulder is observed.

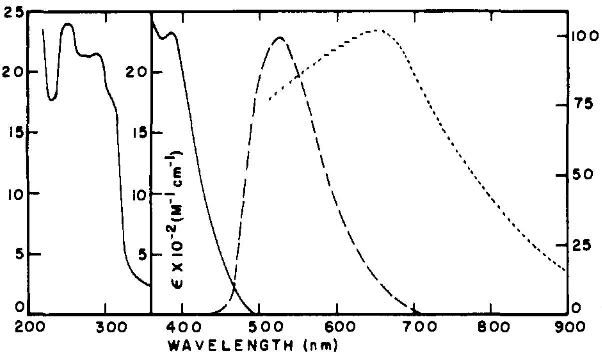


Figure 5. Visible-ultraviolet absorption and emission spectra of $[Ir(bpy)_2Cl(OH)][ClO_4]$: —, absorption in 0.1 M NaOH at 295 K; - -, emission in 0.01 M $NaOCH_3$ ethanol-methanol glass at 77 K; - - -, emission in deoxygenated 0.1 M NaOH at 295 K.

B. Luminescence Spectra. The emission spectra of the three aquated complexes are shown in Figures 1-6 in both acidic and basic ethanol-methanol glasses at 77 K and in acidic and basic water at 295 K. The emission spectra of the aquated species in acidic ethanol-methanol at 77 K are all highly structured. The structure is broadened but remains apparent in acidic water at 295 K. The emission of $[Ir(bpy)_2Cl(H_2O)]^{2+}$ is very weak in acidic water at 295 K, and we were unable to detect the emission at wavelengths less than 460 nm. The similarity in the shape of the emission spectrum of $[Ir(bpy)_2Cl(H_2O)]^{2+}$ and that of $[Ir(bpy)_2(H_2O)_2]^{3+}$ at wavelengths longer than 460 nm suggests that a weak emission peak also occurs at about 455 nm in the 295 K spectrum of $[Ir(bpy)_2Cl(H_2O)]^{2+}$. The emission of the complex containing monodentate bpy shows a blue shift when it is converted from the aquo to the hydroxo form in contrast to the large red shifts observed in the emission of $[Ir(bpy)_2Cl(H_2O)]^{2+}$ and $[Ir(bpy)_2(H_2O)_2]^{3+}$ when they are converted to $[Ir(bpy)_2Cl(OH)]^{+}$ and $[Ir(bpy)_2(OH)_2]^{+}$. Like the aquo complexes, the emission of $[Ir(bpy)_2(OH)(bpy)]^{2+}$ is highly structured in ethanol-methanol glass at 77 K, and is slightly broadened but still structured in basic water at 295 K. In contrast, the emissions of $[Ir(bpy)_2Cl(OH)]^{+}$ and $[Ir(bpy)_2(OH)_2]^{+}$ are unstructured at 77 K and show large red shifts with substantial broadening in basic water at 295 K.

C. Luminescence Lifetimes and Quantum Yields. The luminescence lifetimes of the acid and base forms of all three complexes in ethanol-methanol glass at 77 K are listed in Table I. Although the decay curves of all three complexes were exponential in acidic glasses, the $[Ir(bpy)_2Cl(OH)]^{+}$ and $[Ir(bpy)_2(OH)_2]^{+}$ complexes showed substantial departure from exponential behavior in alcoholic glasses containing sodium methoxide. The same result was obtained when the lifetimes were measured in methanol-water glasses containing sodium hydroxide. The result was obtained for base concentrations as high as 1 M, indicating that the nonexponential decays are not due to the presence of the protonated aquo species in equilibrium with the hydroxo complexes. The decay curve of the complex containing monodentate bpy was found to be exponential in the methoxide-containing alcohol glass at 77 K.

We have also tabulated the lifetimes of those complexes with measurable decay curves in acidic or basic water and heavy water at 295 K in Table I. The complexes containing monodentate bpy were found to have lifetimes which were dependent on the concentration of the complex in 0.1 M HCl or 0.1 M NaOH at complex concentrations from 10^{-3} to 10^{-5} M. Luminescence lifetimes were found to be relatively independent of concentration between 10^{-5} and 10^{-7} M. In contrast, the luminescence lifetime of $[Ir(bpy)_2(H_2O)_2]^{3+}$ in 0.1 M acid was found to be independent of the complex ion concentration over the measurable concentration range (10^{-3} to 10^{-6} M). We were unable to measure the luminescence lifetimes of $[Ir(bpy)_2Cl(H_2O)]^{2+}$, $[Ir(bpy)_2Cl(OH)]^{+}$, or $[Ir(bpy)_2(OH)_2]^{+}$ in aqueous room temperature solutions due to their weak emissions and short lifetimes.

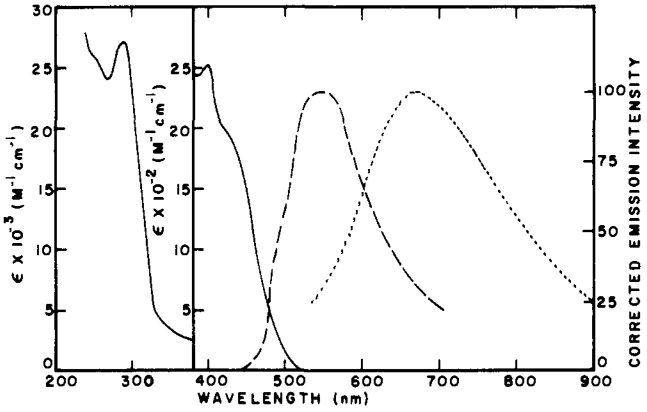


Figure 6. Visible-ultraviolet absorption and emission spectra of $[Ir(bpy)_2(OH)_2][NO_3]$: —, absorption in 0.1 M NaOH at 295 K; - -, emission in 0.01 M $NaOCH_3$ ethanol-methanol glass at 77 K; - - -, emission in deoxygenated 0.1 M NaOH at 295 K.

Table I. Luminescence Lifetimes and Quantum Yields of Aquated 2,2′-Bipyridine Complexes of Ir(III)

	Lifetime, μs (quantum yield)		
Complex ion	77 K (EtOH/MeOH)	295 K (H_2O)	295 K (D_2O)
$[Ir(bpy)_2(H_2O)(bpy)]^{3+}$	15.6 ± 0.3	12.2^{a} ± 0.2 (0.30 ± 0.01)	14.7^{a} ± 0.2 (0.35 ± 0.01)
$[Ir(bpy)_2(OH)(bpy)]^{2+}$	19.5 ± 0.3	10.0^{a} ± 0.2 (0.35 ± 0.01)	11.6^{a} ± 0.3 (0.40 ± 0.02)
$[Ir(bpy)_2Cl(H_2O)]^{2+}$	7.2 ± 0.2	<0.1[b]	<0.1[b]
$[Ir(bpy)_2Cl(OH)]^{+}$	~6[c]	<0.1[b]	<0.1[b]
$[Ir(bpy)_2(H_2O)_2]^{3+}$	11.4 ± 0.4	10.1 ± 0.2	10.7 ± 0.4
$[Ir(bpy)_2(OH)_2]^{+}$	~4[c]	<0.1[b]	<0.1[b]

[a] Lifetime dependent on complex concentrations; tabulated value measured at 10^{-5} M in 0.1 M H^+ (aquo complexes) or 0.1 M OH^- (hydroxo complexes). [b] Emission too weak and short for accurate lifetime determinations. [c] Nonexponential emission, lifetime taken from long-time tail of decay curve.

D. Infrared Spectra.[16] Infrared absorption bands which are pertinent to the characterization of the complexes prepared for this study are tabulated in Table II. The band at 2650 cm^{-1} in $[Ir(bpy)_2(H_2O)(bpy)]Cl_3$ is characteristic of an N-H immonium stretch.[16] The band is absent in the hydroxo form of this complex as well as in $[Ir(bpy)_2Cl(H_2O)][ClO_4]_2$, $[Ir(bpy)_2Cl(OH)][ClO_4]$, $[Ir(bpy)_2(OH)_2][ClO_4]$, and $[Ir(bpy)_2Cl_2]Cl$. However, it does appear in both the nitrate and perchlorate salts of $[Ir(bpy)_2(H_2O)_2]^{3+}$. The band at 1600-1610 cm^{-1} is characteristic of a skeletal stretch of the heterocyclic bpy rings. This band appears at 1573 cm^{-1} in uncomplexed bpy and 1600 cm^{-1} in protonated bpy when it is not bound to a metal. Hence, we believe that 1600-1610-cm^{-1} absorption is symptomatic of coordinated bpy. The bands in the 1230-1320-cm^{-1} region have not been rigorously assigned, but are generally associated with C-C stretching frequencies.[16] There are two such bands in $[Ir(bpy)_2(OH)(bpy)][ClO_4]_2$, $[Ir(bpy)_2Cl(H_2O)][ClO_4]_2$, $[Ir(bpy)_2Cl(OH)]ClO_4$, $[Ir(bpy)_2(OH)_2]ClO_4$, and [Ir-

Table II. Selected Bands in the Infrared Absorption Spectra of Aquo- and Hydroxo-2,2′-bipyridine Complexes of Iridium(III)

Complex	Freq (cm^{-1}), intens							
$[Ir(bpy)_2(H_2O)(bpy)]Cl_3$	2650 s	1600 vs	1310 s	1292 s	1274 m	1243 s	—	—
$[Ir(bpy)_2(OH)(bpy)][ClO_4]_2$	—	1605 vs	1310 s	—	—	1242 s	—	—
$[Ir(bpy)_2Cl(H_2O)][ClO_4]_2$	—	1610 vs	1318 s	—	—	1250 m	335 w	—
$[Ir(bpy)_2(H_2O)_2][ClO_4]_3$	2680 vs	1610 vs	1320 s	—	1280 w	1250 s	—	—
$[Ir(bpy)_2Cl_2]Cl$	—	1602 vs	1310 s	—	—	1240 s	327 s	307 w
$[Ir(bpy)_2Cl(OH)][ClO_4]$	—	1605 vs	1315 s	—	—	1248 m	329 m	—
$[Ir(bpy)_2(OH)_2][ClO_4]$	—	1602 s	1318 s	—	—	1245 s	—	—

Table III. pK_a Values of Iridium(III) Aquo-2,2′-bipyridine Complexes

Complex	pK_1	pK_2
$[Ir(bpy)_2(H_2O)_2]^{3+}$	3.9 ± 0.1	5.9 ± 0.1
$[Ir(bpy)_2Cl(H_2O)]^{2+}$	5.1 ± 0.1	—
$[Ir(bpy)_2H_2O(bpy)]^{3+}$	—	3.0 ± 0.1

$(bpy)_2Cl_2]Cl$, but four bands in $[Ir(bpy)_2(H_2O)(bpy)]Cl_3$ and three in $[Ir(bpy)_2(H_2O)_2][ClO_4]_3$. By comparison, uncoordinated bpy shows only one band at 1245 cm^{-1} and protonated bpy has two bands at 1235 and 1275 cm^{-1}. The Ir-Cl stretching frequencies[16] of $[Ir(bpy)_2Cl_2]Cl$ appear at 327 and 307 cm^{-1}. One band also appears in $[Ir(bpy)_2Cl(H_2O)][ClO_4]_2$ (335 cm^{-1}), and in $[Ir(bpy)_2Cl(OH)][ClO_4]$ (329 cm^{-1}). The two monodentate bpy complexes show no infrared absorption bands in the 300-400-cm^{-1} region, nor do the $[Ir(bpy)_2(H_2O)_2][ClO_4]_3$ and $[Ir(bpy)_2(OH)_2][ClO_4]$ complexes.

E. pK_a Values of Complexes. The pK_a values for the complexes prepared for this study are listed in Table III. As expected, the $[Ir(bpy)_2(H_2O)_2]^{3+}$ complex has two acidic protons and the $[Ir(bpy)_2Cl(H_2O)]^{2+}$ has one acidic proton. The open-ended bpy complex has only one labile proton corresponding to conversion of $[Ir(bpy)_2(H_2O)(bpy)]^{3+}$ to $[Ir(bpy)_2(OH)(bpy)]^{2+}$. We found no evidence for formation of the diprotonated $[Ir(bpy)_2(H_2O)(Hbpy)]^{4+}$ complex at pH as low as 0.

IV. Discussion

A. Characterization of $[Ir(bpy)_2(H_2O)(bpy)]^{3+}$; Evidence for a Monodentate 2,2′-Bipyridine. In spite of evidence that an intermediate monodentate bpy complex is formed in the photolysis of $[Ru(bpy)_3]^{2+}$,[6,8] we know of no evidence which indicates that such a complex has been isolated. Elemental analysis of the complex we have isolated indicates that it contains 3 mol of bpy, 3 mol of Cl, and 4 mol of H_2O per mole of Ir. This would suggest tris-2,2′-bipyridineiridium(III) trichloride tetrahydrate as the most likely formulation. This complex has been prepared as the perchlorate salt (trihydrate) and characterized by absorption, emission, and ^{13}C NMR spectroscopy.[13] The emissions of both acid and base forms of the present complex are at lower energy than those reported for the tris complex. Furthermore, the visible absorption bands of the acid (470 nm shoulder, $\epsilon \sim 10$ M^{-1} cm^{-1}) and base (448 nm broad shoulder, $\epsilon \sim 75$ M^{-1} cm^{-1}), forms of our complex do not match those of the tris complex (448 nm peak, ϵ 12 M^{-1} cm^{-1}). Finally, the luminescence lifetime of our complex is somewhat shorter in acidic and basic glasses at 77 K than the ~80 μs luminescence lifetime reported for the tris complex at 77 K. Thus, we conclude that our complex cannot contain three bidentate bpy's bound to a six-coordinate Ir(III).

The most likely alternatives to a tris complex are: (1) a six-coordinate Ir(III) bound to two bidentate bpy's, one monodentate bpy, and one water, $[Ir(bpy)_2(H_2O)(bpy)]Cl_3 \cdot 3H_2O$; (2) a six-coordinate Ir(III) bound to two bidentate bpy's and one "covalently hydrated"[17,18] bpy, $[Ir(bpy)_2(HbpyOH)]Cl_3 \cdot 3H_2O$; (3) a six-coordinate Ir(III) bound to two bidentate bpy's, one monodentate bpy, and one chloride, $[Ir(bpy)_2Cl(bpy)]Cl_2 \cdot 4H_2O$; (4) a seven-coordinate Ir(III) bound to three bidentate bpy's and one water, $[Ir(bpy)_3H_2O]Cl_3 \cdot 3H_2O$. A seven-coordinate Ir(III) bound to three bpy's and one chloride is excluded from consideration due to the absence of acidic protons in this structure.

Several compelling facts indicate that (3) is not an adequate formulation of the structure of our complex. Our ionic halide analysis by titration with $AgNO_3$ gives us the same result as the total halide analysis. The emission spectrum of the solution of the complex after the titration followed by reacidification was found to be identical with that prior to the titration, ruling out the possibility of removal of coordinated chloride by the ion exchange column. We also find no evidence of an Ir-Cl stretch in the infrared spectrum of the complex. Finally, the absorption, emission, and infrared spectra of the complex prepared from iridium tribromide are identical with those of the complex prepared from iridium trichloride. Since a change in all of these spectra would be expected to accompany a change from a structure containing coordinated chloride to one containing coordinated bromide, we conclude that halide is absent in the coordination sphere.

This leaves us with (1), (2), and (4), which are far more difficult to distinguish. We feel that the most compelling pieces of evidence to rule out a seven-coordinate Ir(III) are in the pH dependence of the visible absorption and luminescence of the complex and in the infrared absorption. As indicated by the absorption and emission of $[Ir(bpy)_2(H_2O)_2]^{3+}$ and $[Ir(bpy)_2Cl(H_2O)]^{2+}$ in acidic and basic solutions, conversion of coordinated water to coordinated hydroxide leads to large red-shifts in both the visible absorption and emission spectra. This effect may be related to the influence of σ- and π-donating ligands on transitions which are formally classified as charge-transfer from Ir(III) to bpy (vide infra). The blue-shift of the emission spectrum of our complex in base and the disappearance of the longest wavelength (470 nm) absorption band cannot be reconciled with a simple conversion of coordinated water to hydroxo, as would be required by (4) above. Furthermore, the appearance of an immonium N-H stretch in the infrared spectrum of the acidic form of our complex and the disappearance of this band in the basic form are not consistent with all three bpys chelated to Ir(III). Hence, we eliminate (4) as an acceptable structure.

This leaves us with our formulation of the complex as either the monodentate bpy structure or the complex containing "covalently hydrated"[17,18] bpy. According to previous formulations by Gillard,[18] these two species are related by an intramolecular shift of hydroxyl within the covalent hydrate as shown by (7b) and (7e) in Figure 7. In this formulation the tris complex **7a**, the covalent hydrate **7b**, and the monodentate bpy complex **7e** are all believed to be in equilibrium in aqueous solutions. In addition the covalent hydrate may be either protonated to form **7c** or deprotonated to form **7d**. Both **7c** and **7d** can form monodentate bpy complexes by either a hydroxyl shift, **7g**, or a water shift, **7f**.

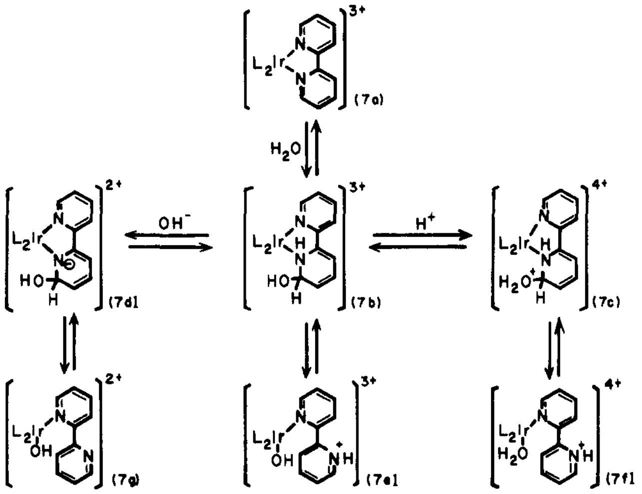


Figure 7. Hypothetical effects of pH and covalent hydration on aqueous solutions of $[Ir(bpy)_3]^{3+}$.[18]

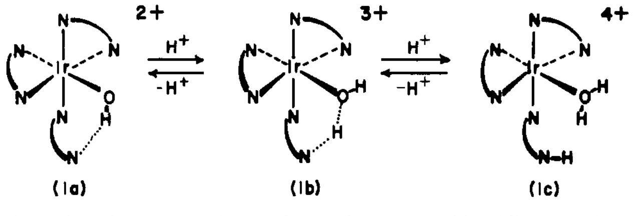


Figure 8. Acid-base equilibria of monodentate 2,2′-bipyridine complexes of Ir(III).

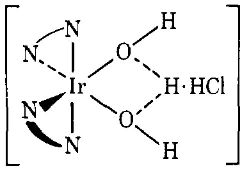
Although numerous examples of kinetic, NMR, and UV-visible spectroscopic results have been cited[18] to support the covalent hydrate formulation, there is very strong evidence that the equilibria indicated in Figure 7 are not an accurate representation of the present results. As shown in Figures 1 and 4, the emission and absorption of the complex we have prepared are different in acid and base solutions. We have examined the emission at intermediate pH values, and have found that the emission spectrum is always identical to the ones in Figures 1 and 4, or a combination of the two (simultaneous contributions from both species are evident at pH 3-4). Comparison of these emission spectra with that of $[Ir(bpy)_3]^{3+}$ indicates that neither species is the tris(bidentate) bound complex. The emission spectrum of $[Ir(bpy)_3]^{3+}$ has its highest energy peak at a shorter wavelength than that of either of the two species we have prepared, so any contribution of $[Ir(bpy)_3]^{3+}$ would be immediately evident. Furthermore, we have prepared the $[Ir(bpy)_3]^{3+}$ complex ion according to the procedure described by Flynn and Demas.[13] The material we have isolated has an emission spectrum identical with that reported by these authors, and the *emission spectrum in 0.1 M base is identical with that in 0.1 M acid.* As a result we conclude there is no evidence to support a facile equilibrium between the tris complex of Ir(III) and a covalent hydrate.

We therefore formulate the complex as $[Ir(bpy)_2(H_2O)(bpy)]Cl_3{\cdot}3H_2O$, which may have as many as two sites for protonation. The various pH dependent forms anticipated for this complex are indicated in Figure 8. Thus, we correlate our measurements of the complex in 0.1 M acid with structure **Ib** and our measurements in 0.1 M base with structure **Ia**. Structure **Ic** might theoretically exist at high acid concentrations. The value of pK_2 for bpy has been reported to be −0.2,[19] which probably places an upper limit on pK_2 for interconversion of **Ib** and **Ic**. Several considerations suggest this conclusion. Firstly, **Ib** is undoubtedly stabilized by hydrogen bonding between coordinated water and monodentate bpy, as indicated by the appearance of the N-H immonium stretch in the infrared. Secondly, **Ic** is destabilized by steric hindrance to rotation of the monodentate bpy into the transoid configuration which is favored in diprotonated bpy.[19] This forces the two acidic protons in **Ic** into close proximity. Thus, we conclude that $pK_2 < -0.2$, and **Ic** is not expected to be present in measurable concentration between pH 0 and 14.

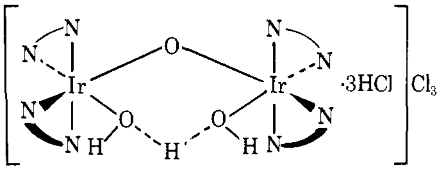
Interconversion of structures **Ib** and **Ia** on going from acid to basic solution correlates well with our results. Hydrogen bonding between coordinated water and monodentate bpy should be much stronger than that between coordinated hydroxo and monodentate bpy in agreement with the appearance of an N-H immonium stretch in the infrared spectrum of the complex recrystallized from 1 M acid, and the absence of this band in the complex recrystallized from 1 M base. The appearance of four bands in the infrared spectrum of the aquo complex between 1230 and 1320 cm^{-1} and only two bands in the hydroxo complex may indicate that the two pyridine rings of the monodentate bpy are skewed in the former complex and cisoid in the latter. Solvated protonated bpy, which is presumably cisoid, has two bands in this region (1235, 1275 cm^{-1}), as have most of the bidentate complexes of bpy studied (e.g., 1245, 1312 cm^{-1} for $[Ir(bpy)_2Cl_2]Cl{\cdot}3H_2O$), whereas unprotonated bpy, presumably transoid,[16] has one band (1245 cm^{-1}). The appearance of two additional bands suggests an intermediate geometry, presumably due to steric hindrance of the cisoid monodentate bpy configuration by coordinated water in the aquo complex and/or due to requirements for optimum hydrogen bonding in the complex. The small blue shift in the visible absorption and luminescence spectra of our complex in basic medium also correlates well with conversion of **Ib** to **Ia**. Deprotonation of **Ib** should not follow the pattern of red-shifting the Ir(III) to bpy charge-transfer bands illustrated by deprotonation of $[Ir(bpy)_2(H_2O)_2]^{3+}$ or $[Ir(bpy)_2ClH_2O]^{2+}$. Rather, deprotonation of **Ib** should give rise to combined effects due to partial deprotonation of both π-accepting (bpy) and π-donating (H_2O) ligands. The net effect is expected to be small as our results indicate it is. Finally, titration of **Ib** with base should give a single endpoint to form **Ia**. This should occur with a pK_a in the neighborhood of pK_1 for $[Ir(bpy)_2(H_2O)_2]^{3+}$ (3.9) due to the absence of negatively charged ligands in the coordination sphere of this complex and **Ib**. The pK_2 value of the monodentate bpy complex is somewhat lower (3.0) than that of $[Ir(bpy)_2(H_2O)_2]^{3+}$, and this is probably due to the presence of an additional π-accepting ligand in the coordination sphere of Ir(III) which draws additional electron density from the coordinated water. An additional contributing factor may be steric hindrance from the other ligands in the coordination sphere of Ir(III) which could facilitate the loss of a proton from **Ib**.

B. Infrared Absorption Spectra. Although the appearance of a band at 2650 cm^{-1} in the infrared spectrum of $[Ir(bpy)_2(H_2O)(bpy)]^{3+}$ is consistent with our formulation of the structure of this complex, the appearance of this band at 2680 cm^{-1} in $[Ir(bpy)_2(H_2O)_2]^{3+}$ is not consistent with a formulation of this complex as Ir(III) bound to two waters and two bidentate bpy's. This band is absent in $[Ir(bpy)_2(OH)_2]^{+}$ as it is in $[Ir(bpy)_2(OH)(bpy)]^{2+}$. We also find no evidence of it in $[Ir(bpy)_2Cl(H_2O)]^{2+}$ or in $[Ir(bpy)_2Cl(OH)]^{+}$. This would seem to suggest that $[Ir(bpy)_2(H_2O)_2]^{3+}$ may also contain monodentate bpy. Furthermore, the appearance of four bands in the 1230-1320-cm^{-1} range seems to correlate with a relative twisting of the two pyridine rings of bpy to a configuration between cisoid and transoid in $[Ir(bpy)_2(H_2O)(bpy)]^{3+}$, and the only other complex to display more than two bands in this region is $[Ir(bpy)_2(H_2O)_2]^{3+}$. However, one of the three bands displayed by this complex is very weak, making it difficult to draw any definite conclusions from this region of its infrared spectrum.

Our other studies of the diaquo complex, which were performed in either aqueous or alcoholic solutions, give no evidence for the presence of a monodentate bpy in the coordination sphere of Ir(III). This suggests several alternative interpretations of the 2680-cm^{-1} absorption band of the diaquo complex. It is possible that one or both bpy ligands open substantially to accommodate the crystal lattice preferred by the solid complex, but close to the bidentate structure in solution. Alternatively, the 2680-cm^{-1} band may arise from another source, the most likely being an interaction between two coordinated waters. For example, a structure such as **9a** below, which could be formed on crystallization, might have an O···H···O stretching frequency very similar to the O···H···N immonium stretch. A second source of this type of interaction could occur if the complex were formulated as a dimeric oxo-bridged species analogous to that formed by Ru(III)[20] as shown by **9b** below. Again, this type of structure could give rise to an O···H···O stretching frequency similar to the immonium stretch. At present we have no evidence which would strongly favor any of these alternatives.



9a



9b

C. Absorption Spectra of Aquated Iridium(III)–2,2′-Bipyridine Complexes. Photoaquation of $[Ir(bpy)_2Cl_2]^+$ to form $[Ir(bpy)_2Cl(H_2O)]^{2+}$ and $[Ir(bpy)_2(H_2O)_2]^{3+}$ leads to substantial changes in the visible absorption bands, as well as a sharpening of the features observed in the ultraviolet region. In assigning these spectra, three basic principles are applied. Firstly, the absorption spectrum of $[Ir(bpy)_2Cl_2]^+$ is dominated by Ir(III) to bpy charge-transfer bands (CTTL) in the visible and internal bpy bands (IL) in the ultraviolet. Secondly, substitution of H_2O for Cl^- in the coordination sphere of Ir(III) should lead to a small increase in the crystal field parameter, Δ_O, and should therefore raise the energy of any crystal field states. Finally, this substitution represents replacement of a good π-donating ligand with a negative charge (Cl^-) by a neutral weak π-donating ligand (H_2O). To the extent that electron donation to Ir(III) by π-donors contributes to the CTTL bands, this will raise the energy of CTTL bands.[21]

The visible absorption spectrum of $[Ir(bpy)_2Cl_2]^+$ consists of a weak band ($\epsilon \sim 300\ M^{-1}\ cm^{-1}$) at 450 nm and a stronger band ($\epsilon \sim 2500\ M^{-1}\ cm^{-1}$) at 380 nm. Both of these bands have been assigned as CTTL transitions.[22,23] The 448-nm absorption of $[Ir(bpy)_2Cl(H_2O)]^{2+}$ is much sharper than the 450-nm absorption of $[Ir(bpy)_2Cl_2]^+$ and has a much lower extinction coefficient ($\epsilon \sim 50\ M^{-1}\ cm^{-1}$). This band also appears in $[Ir(bpy)_2(H_2O)_2]^{3+}$ with a further reduced extinction coefficient ($\epsilon \sim 25\ M^{-1}\ cm^{-1}$). It is significant that this band also has been reported in the absorption of $[Ir(bpy)_3]^{3+}$ with an extinction coefficient of $\sim 10\ M^{-1}\ cm^{-1}$, where it has been assigned as a triplet IL transition.[13] We concur with that assignment, and attribute the variation in extinction coefficients to underlying contributions from the tail of the CTTL band which moves to shorter wavelength in the order $[Ir(bpy)_3]^{3+} < [Ir(bpy)_2(H_2O)_2]^{3+} < [Ir(bpy)_2Cl(H_2O)]^{2+} < [Ir(bpy)_2Cl_2]^+$. The shoulder at 416 nm ($\epsilon \sim 170\ M^{-1}\ cm^{-1}$) in $[Ir(bpy)_2Cl(H_2O)]^{2+}$ also appears in $[Ir(bpy)_2(H_2O)_2]^{3+}$ ($\epsilon \sim 80\ M^{-1}\ cm^{-1}$) and in $[Ir(bpy)_3]^{3+}$ ($\epsilon \sim 25\ M^{-1}\ cm^{-1}$). We concur with the assignment of this band as vibrational structure on the 448-nm IL band and again attribute the ϵ variation to an underlying CTTL band.

The CTTL band at 380 nm in $[Ir(bpy)_2Cl_2]^+$ moves to 360 nm in $[Ir(bpy)_2Cl(H_2O)]^{2+}$ ($\epsilon \sim 2500\ M^{-1}\ cm^{-1}$) and to 352 nm in $[Ir(bpy)_2(H_2O)_2]^{3+}$ ($\epsilon \sim 2500\ M^{-1}\ cm^{-1}$). We attribute these bands to a CTTL transition in the two aquated complexes, and we believe that their progressive movement to shorter wavelengths illustrates the influence of the π-donating Cl^- ligand on the energy of CTTL states.[21] The location of this state in $[Ir(bpy)_3]^{3+}$ has not been assigned, but on the basis of our results we assign the shoulder which has been reported at $\sim$340 nm ($\epsilon \sim 3000\ M^{-1}\ cm^{-1}$) as the corresponding CTTL band in this complex.

Our interpretation of the absorption spectra of the hydroxo complexes is based upon the same principles we apply to the aquo complexes with the following exception; the OH^- ligand is a better π-donor than Cl^-, and should therefore lower the energy of the CTTL bands.[21] This influence is apparent in the movement of the 380-nm CTTL absorption band of $[Ir(bpy)_2Cl_2]^+$ to 386 nm ($\epsilon \sim 2300\ M^{-1}\ cm^{-1}$) in $[Ir(bpy)_2Cl(OH)]^+$ and to 400 nm ($\epsilon \sim 2500\ M^{-1}\ cm^{-1}$) in $[Ir(bpy)_2(OH)_2]^+$. These bands are extremely broad and tail out beyond 500 nm. An additional CTTL band analogous to the 450-nm absorption of $[Ir(bpy)_2Cl_2]^+$ is presumably buried in these tails.

The absorption spectra of the aquo and hydroxo complexes containing monodentate bpy show significant differences in their visible bands from the complexes containing only bidentate bpy. The shoulder at 470 nm in $[Ir(bpy)_2(H_2O)(bpy)]^{3+}$ ($\epsilon \sim 10\ M^{-1}\ cm^{-1}$) lies at a longer wavelength than the 448-nm IL band of the complexes discussed above. However, due to its small extinction coefficient, this band is likely to be due to a $^3(\pi\pi^*)$ transition also. We therefore assign this band to an IL transition of the strongly hydrogen-bonded monodentate bpy ligand. Although no shoulder is present in the absorption of $[Ir(bpy)_2(OH)(bpy)]^{2+}$ at 470 nm, this complex also has an extinction coefficient of about 10 $M^{-1}\ cm^{-1}$ at 470 nm. The shoulder at 448 nm in this complex is slightly more intense ($\epsilon \sim 75\ M^{-1}\ cm^{-1}$) than the 440-nm shoulder of $[Ir(bpy)_2(H_2O)(bpy)]^{3+}$ ($\epsilon \sim 65\ M^{-1}\ cm^{-1}$). This suggests that both complexes have an IL transition of the bidentate bpy ligands at 440–448 nm. However, the IL transition of the monodentate bpy ligand is apparently shifted to shorter wavelengths in the hydroxo complex due to decreased hydrogen bonding. As a result, it is buried in the bidentate bpy absorption.

The shoulder at 360 nm in the absorption spectra of both of the monodentate bpy complexes ($\epsilon \sim 5000\ M^{-1}\ cm^{-1}$) is probably due to the CTTL transition which appears at 360 nm in $[Ir(bpy)_2Cl(H_2O)]^{2+}$ also. This shoulder is much more clearly defined in the $[Ir(bpy)_2OH(bpy)]^{2+}$ complex than it is in $[Ir(bpy)_2H_2O(bpy)]^{3+}$, suggesting that the CTTL band may be moved to slightly shorter wavelength in the latter complex where it is buried in the strong $\pi\pi^*$ absorption which peaks at 316 nm. Both complexes presumably have lower energy CTTL levels, analogous to the 450-nm absorption of $[Ir(bpy)_2Cl_2]^+$ which are buried in the tail of the strong 360-nm CTTL absorption, at shorter wavelengths than the 440–448-nm IL bands.

C. Luminescence Spectra and Lifetimes. (1) Emissions at 77 K. The luminescence spectra of $[Ir(bpy)_2Cl(H_2O)]^{2+}$ and $[Ir(bpy)_2(H_2O)_2]^{3+}$ are nearly identical in their structure and wavelength. Due to the sharpness of these spectra, the wavelength of the first vibrational band is extremely well defined and occurs at 453 nm in the chloroaquo complex in ethanol-methanol at 77 K and 452 nm in the diaquo complex. The 1-nm shift is reproducible. These emissions show small blue shifts to 452 nm for the chloroaquo complex in methanol-water at 77 K and 450 nm for the diaquo complex which are also reproducible. These emissions are very similar to the emission of $[Ir(bpy)_3]^{3+}$ in ethanol-methanol at 77 K, which has been assigned as an IL transition from a $^3\pi\pi^*$ state of bidentate bpy.[13] Due to this similarity and to the low-lying IL transitions found at 448 nm in the absorption spectra of these complexes, we believe both emissions have major contributions from IL states of bidentate bpy. However, the shortening of the luminescence lifetime from ~80 μs in $[Ir(bpy)_3]^{3+}$ to 11.4 μs in $[Ir(bpy)_2(H_2O)_2]^{3+}$ and 7.2 μs in $[Ir(bpy)_2Cl(H_2O)]^{2+}$ suggests a progressively increasing mixing of CTTL states with the IL states occurs as π-donating ligands are introduced into the coordination sphere of Ir(III). The emission of $[Ir(bpy)_2Cl_2]^+$ is substantially red-shifted from these emissions (473 nm in ethanol-methanol at 77 K) and has a somewhat shorter lifetime (5.9 μs). The emission of this complex is also much more sensitive to the solvent polarity than the emission of the chloroaquo and diaquo complexes. This emission has been assigned a CTTL, and illustrates that two π-donating Cl^- ligands lower the CTTL levels below the IL states.

This effect of π-donating ligands on the luminescence is further illustrated by the chlorohydroxo and dihydroxo complexes. The large red-shifts and broadening of the emissions of these complexes relative to the chloroaquo and diaquo complexes suggest that both emissions are due to CTTL states which are largely influenced by the strong π-donating effect of OH^- in the coordination sphere of Ir(III). The emission maximum of $[Ir(bpy)_2Cl(OH)]^+$ is shifted from 530 nm in ethanol-methanol at 77 K to 510 nm in methanol-water at 77 K. A large shift from 550 to 540 nm is also found in $[Ir(bpy)_2(OH)_2]^+$ as expected for CTTL emissions.

The absence of structure in these emissions is in stark contrast to the highly structured emission encountered in $[Ir(bpy)_2Cl_2]^+$. There are several factors which may contribute to this phenomenon. Firstly, the participation of the strongly π-donating hydroxo ligands in the CTTL transitions will probably lead to a large distortion of the iridium-oxygen bonds. In a sense, this is similar to the situation encountered in charge-transfer-to-metal (CTTM) states of complexes such as $[Rh(NH_3)_5I]^{2+}$ which are believed to undergo major metal-negative ligand bond distortions.[24] Such distortions would broaden the structure of the CTTL emission spectra. A second factor which could broaden these emissions would be strong hydrogen-bonding interactions between coordinated hydroxide and the alcoholic solvent. The nonexponential decays encountered in these complexes are likely due to these types of interactions also, and are probably best viewed as extreme examples of the red-edge effect.[25,26] These types of interactions would lead to a variety of sites in the glass which would cause broadening of the emission spectrum of the solvent-sensitive CTTL states. Finally, some broadening of the CTTL states may occur due to interactions with crystal field states in these complexes. Photoaquation of $[Ir(bpy)_2Cl_2]^+$ presumably occurs via population of crystal field states by analogy with $[Ir(phen)_2Cl_2]^+$.[27,28] Replacement of Cl^- by OH^- should lead to some increase in Δ_0 according to the traditional spectrochemical series. However, one must keep in mind that this series reflects the relative energy of Franck-Condon states formed by absorption, but may not be a correct measure of the relative energy of thermally relaxed crystal field states. As a result, it is possible that the thermally relaxed crystal field states of the chlorohydroxo and dihydroxo complexes may be very close in energy to the CTTL states. Mixing of these states with the CTTL states would lead to distortion of the metal-ligand bonds and would broaden the emission spectra.

As pointed out previously, conversion of $[Ir(bpy)_2(H_2O)(bpy)]^{3+}$ to $[Ir(bpy)_2(OH)(bpy)]^{2+}$ leads to a small blue shift in the emission rather than the large red shift encountered in the complexes containing only bidentate bpy. The structure of the emission of $[Ir(bpy)_2(OH)(bpy)]^{2+}$ is very much like that of $[Ir(bpy)_2(H_2O)_2]^{3+}$ and $[Ir(bpy)_2Cl(H_2O)]^{2+}$, but is at somewhat longer wavelength (460 nm). The emission of $[Ir(bpy)_2(H_2O)(bpy)]^{3+}$ is at 470 nm, and lacks much of the structure of the other three complexes. We believe that the emission of the aquo complex is from the same state which gives rise to the absorption band at 470 nm. Hence, it contains major contributions from an IL transition of the monodentate bpy. The 15.6-μs lifetime of this emission suggests that there is substantial mixing of CTTL configurations into the IL transition. Since partially protonated monodentate bpy should be a better electron acceptor than bidentate bpy, we believe that the lowest energy CTTL configurations arise from transfer of electron density from Ir(III) to monodentate bpy.

While the emission of $[Ir(bpy)_2(OH)(bpy)]^{2+}$ also has large contributions from an IL transition, it is difficult to deduce whether it is associated with bidentate or monodentate bpy. The vibrational structure would suggest bidentate bpy, but the emission wavelength is somewhat longer than anticipated for bidentate bpy. Our absorption data suggest that the IL transitions on monodentate and bidentate bpy are nearly degenerate in this complex. Due to this fact and to the likelihood of substantial steric crowding of monodentate and bidentate bpy, we believe that this emission is best viewed as a delocalized IL transition over all three bpy's. The 19.5-μs lifetime again suggests mixing of CTTL configurations in the IL state.

(2) Emissions at 295 K. The lifetimes of the monodentate bpy complexes in deoxygenated water (Table I) are the longest luminescence lifetimes we have encountered for any metal complex in aqueous solution. The quantum yields are also very high for these conditions, exceeding even the quantum yield of $[Ru(bpy)_3]^{2+}$ at 77 K. The lifetimes are very sensitive to oxygen, particularly that of the hydroxy complex whose lifetime is reduced to ~2.8 μs in air-saturated 0.1 M NaOH. The lifetime of the aquo complex is reduced to ~4.6 μs in air-saturated 0.1 M HCl. These are also the first complexes we have encountered which display self-quenching in fluid solution. The lifetime of the aquo complex is reduced to ~9 μs at 10^{-3} M complex in 0.1 M deoxygenated HCl, while that of the hydroxo complex is ~7 μs at 10^{-3} M complex in 0.1 M deoxygenated NaOH. In contrast, the $[Ir(bpy)_2(H_2O)_2]$ complex, which also has a long lifetime in fluid solution and is strongly quenched by oxygen, shows no sign of self-quenching over a concentration range of 10^{-3} to 10^{-6} M in 0.1 M HCl.

The very short lifetimes and red shifts of the emission spectra of $[Ir(bpy)_2Cl(OH)]^+$ and $[Ir(bpy)_2(OH)_2]^+$ in aqueous solutions are consistent with our contention that coordinated hydroxide hydrogen bonds strongly to hydroxylic solvents. They are also consistent with our viewpoint that the thermally relaxed crystal field states of these complexes may be close in energy to the CTTL states. The decrease in viscosity in going from a glass at 77 K to a fluid medium at 295 K may very well remove viscosity-dependent potential barriers presented by the solvent cage,[29] thus enabling the complex to relax to low-energy nuclear configurations of the crystal field states not accessible at the higher viscosity. This could lead to larger contributions from the crystal field states at lower viscosities, resulting in a red shift in the emission and shortening the lifetime.

Although the lifetime of $[Ir(bpy)_2Cl(H_2O)]^{2+}$ is very short in fluid solution, the emission is only slightly broadened. This excludes shortening of the lifetime of this complex by interactions with crystal field states which should red shift the emission. We believe that the short lifetime encountered here is due to thermal population of CTTL states at 295 K. The absence of low-lying crystal field states in this complex is also consistent with its relative photoinertness, since we found little $[Ir(bpy)_2(H_2O)_2]^{3+}$ in solutions of $[Ir(bpy)_2Cl(H_2O)]$ photolyzed in aqueous acid.

In view of their long lifetimes and high quantum yields in aqueous solutions, the monodentate bpy complexes are excellent candidates for high-energy sensitizers. Their sensitivity to oxygen and particularly to self-quenching suggests that they undergo facile intermolecular energy transfer. The $[Ir(bpy)_2(OH)(bpy)]^{2+}$ species in particular may be a useful sensitizer. Since it is a +2 ion it should transfer energy to neutral or negatively charged species readily. However, it also possesses an electron-rich site at the monodentate bpy as evidenced by its ready conversion to $[Ir(bpy)_2(H_2O)(bpy)]^{3+}$. Hence, it may be able to easily transfer energy to positively charged species also. A second possible application of these complexes could be in a flash lamp pumped dye laser. Their lifetimes are appropriate for pumping on the microsecond time scale, and their quantum yields are high. We are currently preparing analogous complexes from deuterated 2,2′-bipyridine in an attempt to further increase these quantum yields.

Although we have no evidence for stable monodentate bpy complexes of other transition metals, it is quite likely that such species are reactive intermediates in the photochemical and thermal reaction of tris(bipyridine)metal complexes. For example, we have evidence for the formation of a monodentate bpy complex as an intermediate in the photolysis of $[Ru(bpy)_3]^{2+}$ in acidic water solution.[8] By analogy with our present work this would be formulated as $[Ru(bpy)_2H_2O(bpy)]^{2+}$. Excitation of this species could lead to charge transfer to monodentate bpy, and, perhaps, reduction of coordinated water to a hydrogen atom and a coordinated hydroxide. This may provide a mechanism to account for the recent report of H_2 production by excitation of monolayer-bound $[Ru(bpy)_3]^{2+}$ in water.[30] This process would be cyclic due to concomitant formation of $[Ru(bpy)_2OH(bpy)]^{2+}$ when H atoms are formed. This species should be reduced back to $[Ru(bpy)_3]^{2+}$ by coordinated hydroxide with formation of OH·.[31] We are currently searching for further evidence of monodentate bpy in the photolysis of tris-2,2′-bipyridine metal complexes.

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