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Luminescence Tuning of 2,2′-Bipyridine and 1,10-Phenanthroline Complexes of Iridium(III) in Fluid Solution

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Luminescence quantum yields, lifetimes, and spectra of a series of *cis*-dichlorobis(2,2′-bipyridine) and -(1,10-phenanthroline) complexes of Ir(III) in water, methanol, acetonitrile, and dimethylformamide at 295 K are reported. Two emission bands originating from states of dd* and $d\pi^*$ or mixed $d\pi^*$–$\pi\pi^*$ parentage are observed when 2,2′-bipyridine, 1,10-phenanthroline, or 5,6-dimethyl-10-phenanthroline are the coordinated bidentate ligands. A single $d\pi^*$ or mixed $d\pi^*$–$\pi\pi^*$ emission is observed when 4,7-diphenyl-1,10-phenanthroline or 4,4′-diphenyl-2,2′-bipyridine occupies coordination sites. In all cases, the emitting states are found to be in thermal equilibrium in the fluid solvents at 295 K. The ratio of dd* to $d\pi^*$ or mixed $d\pi^*$–$\pi\pi^*$ emission intensity is solvent dependent; the dd* emission is generally favored by water whereas the $d\pi^*$ or mixed $d\pi^*$–$\pi\pi^*$ band is favored by the nonaqueous solvents. Lifetimes (τ) and overall quantum yields (Q) are strongly solvent dependent in all cases, displaying a range of values that differ by more than 2 orders of magnitude between water and acetonitrile in some instances. However, the τ/Q ratios are quite insensitive to solvent. The change of orbital parentage of the lowest excited state from dd* ($IrCl_2(bpy)_2^+$ or $IrCl_2(phen)_2^+$) to $d\pi^*$ or mixed $d\pi^*$–$\pi\pi^*$ ($IrCl_2(4,4'\text{-}Phbpy)_2^+$) indicate that these complexes would be useful to further studies of photochemical tuning.

Introduction

The initial studies[1-4] of photochemical "tuning" in complexes of the type $Ru(NH_3)_5(py\text{-}X)^{2+}$ (X = substituted pyridine or related aromatic heterocycle) by Ford and co-workers have stimulated widespread interest in this topic in the area of inorganic photochemistry. Subsequent studies have shown that complexes of the type $W(CO)_5(py\text{-}X)$,[5] $(\eta^5\text{-}C_5H_5)Re(CO)_2(py\text{-}X)$,[6] $(\eta^5\text{-}C_5H_5)Mn(CO)_2(py\text{-}X)$,[6] $Fe(CN)_5(py\text{-}X)^{3-}$,[7] and *cis*-$W(CO)_4(py\text{-}X)_2$[8] and several macrocyclic carbonyliron(III) complexes[9] display tuning effects similar to those observed in the $Ru(NH_3)_5(py\text{-}X)^{2+}$ complexes. Several basic features have been common to all of these studies. These include the following: (1) tuning has been effected by substituents of the pyridine ligand except in the case of the iron(III) macrocycles, (2) ligand substitution photoreactivity has been attributed to the presence of low-lying ligand field (dd*) excited states; and (3) tuning to the nonreactive situation has been due to a substituent-induced bathochromic shift of the charge-transfer ($d\pi^*$) levels to an energy below that of the reactive dd* levels.

Previous studies[10-14] of the photophysical properties of complexes of the type $IrCl_2(B)(B')^+$ (where B, B′ = 1,10-phenanthroline, 2,2′-bipyridine, or a substituted derivative) in low-temperature (77 K) glasses indicate that they are highly emissive from states whose orbital parentage is strongly dependent upon the nature of substituents attached to the bidentate ligands. Cases where the low-temperature luminescence arises from levels of distinct $d\pi^*$, distinct $\pi\pi^*$, or strongly mixed $d\pi^*$ and $\pi\pi^*$ parentage are known. Furthermore, the degree of mixing can be altered by taking advantage of the effects of the solvent environment on the energy gap between $d\pi^*$ and $\pi\pi^*$ levels.[15]

Studies of several of these complexes indicate that they undergo photoaquation[16-19] in ambient-temperature solutions due to the presence of low-lying dd* levels.[20] While emission from these levels is not evident in low-temperature glasses, evidence for dd* luminescence has been found[21-23] in ambient-temperature dimethylformamide solutions. Hence, both the photochemistry and fluid solution photoluminescence of these complexes indicate the presence of dd* levels near or below the energy of the $d\pi^*$ and $\pi\pi^*$ levels.

In spite of the complications introduced by the presence of low-lying dd* levels, these Ir(III) complexes have characteristics that may make them more amenable to quantitative studies of photochemical tuning than the two-level systems.[1-9] Generally, the two-level systems have been found to be weakly emissive or nonemissive at low temperatures, and no evidence for emission under photochemical conditions (fluid solutions, ambient temperatures) has been reported. In contrast, the Ir(III) complexes are generally emissive under photochemical conditions, sometimes from more than one state.[23] This provides a direct means of determining energy gaps between the lowest levels and their relative population, quantities which could only be estimated from indirect absorption measurements in previous tuning studies. More importantly, the measurement of luminescence lifetimes in conjunction with luminescence and photochemical quantum yields provides a straightforward means of determining photochemical reaction rate constants for product formation. This technique has been successfully applied to the determination of photosubstitution rate constants for d^6 complexes of Ru(II),[24] Rh(III),[25,26]

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Table I. Luminescence Lifetimes and Total Luminescence Yields of $IrCl(B)(B')^+$ Complex Ions in Several Solvents at 295 K

complex ion	water			methanol			acetonitrile			dimethylformamide		
	Q	τ, ns	τ/Q, μs	Q	τ, ns	τ/Q, μs	Q	τ, ns	τ/Q, μs	Q	τ, ns	τ/Q, μs
$IrCl_2(phen)_2^+$	4.1×10^{-5}	2^a	60	6.4×10^{-4}	31	48	2.7×10^{-3}	360	130	4.3×10^{-3}	320	73
$IrCl_2(bpy)_2^+$	3.0×10^{-5}	1^a	40	9.2×10^{-4}	36	38	6.6×10^{-3}	340	52	9.8×10^{-3}	330	33
$IrCl_2(bpy\text{-}d_8)_2^+$	4.1×10^{-5}	2^a	40	1.1×10^{-3}	44	40	1.3×10^{-2}	890	69	1.7×10^{-2}	710	42
$IrCl_2(5,6\text{-Mephen})_2^+$	5.6×10^{-4}	30	53	1.4×10^{-3}	64	46	8.9×10^{-3}	890	100	1.3×10^{-2}	840	65
$IrCl_2(bpy)(5,6\text{-Mephen})^+$	3.0×10^{-4}	29	97	5.2×10^{-4}	50	96	6.1×10^{-3}	610	99	1.1×10^{-2}	660	60
$IrCl_2(4,7\text{-Phphen})_2^+$	*b*	*b*	*b*	1.1×10^{-2}	268	24	1.8×10^{-1}	4700	26	1.7×10^{-1}	3580	21
$IrCl_2(4,4'\text{-Phbpy})_2^+$	*b*	*b*	*b*	7.5×10^{-3}	39	5	1.2×10^{-1}	570	4.8	2.1×10^{-1}	650	3.0

[a] Estimated from measurement of Q and average τ/Q values measured in methanol, acetonitrile, and dimethylformamide. [b] Complexes insufficiently soluble in water to measure τ or Q.

Table II. Emission Band Maxima of $IrCl_2(B)(B')^+$ Complex Ions in Several Solvents at 295 K

complex ion	E_{max}, μm^{-1} (orbital parentage)			
	water	methanol	acetonitrile	dimethylformamide
$IrCl_2(phen)_2^+$	2.05 ($d\pi^*$)	2.01 ($d\pi^*$)	2.02 ($d\pi^*$)	2.01 ($d\pi^*$)
	1.36 (dd^*)	1.34 (dd^*)	1.35 (dd^*)	1.35 (dd^*)
$IrCl_2(bpy)_2^+$ and $IrCl_2(bpy\text{-}d_8)_2^+$	1.90 ($d\pi^*$)	1.97 ($d\pi^*$)	1.97 ($d\pi^*$)	1.96 ($d\pi^*$)
	1.40 (dd^*)	1.40 (dd^*)	1.40 (dd^*)	1.35 (dd^*)
$IrCl_2(bpy)(5,6\text{-Mephen})_2^+$	1.98 ($d\pi^*$–$\pi\pi^*$)	2.00 ($d\pi^*$–$\pi\pi^*$)	2.02 ($d\pi^*$–$\pi\pi^*$)	2.02 ($d\pi^*$–$\pi\pi^*$)
	1.30 (dd^*)	1.30 (dd^*)	1.30 (dd^*)	1.30 (dd^*)
$IrCl_2(5,6\text{-Mephen})_2^+$	2.02 ($d\pi^*$–$\pi\pi^*$)	1.92 ($d\pi^*$–$\pi\pi^*$)	2.03 ($d\pi^*$–$\pi\pi^*$)	2.03 ($d\pi^*$–$\pi\pi^*$)
	1.30 (dd^*)	1.30 (dd^*)	1.30 (dd^*)	1.30 (dd^*)
$IrCl_2(4,7\text{-Phphen})_2^+$		1.80 ($d\pi^*$–$\pi\pi^*$)	1.88 ($d\pi^*$–$\pi\pi^*$)	1.87 ($d\pi^*$–$\pi\pi^*$)
$IrCl_2(4,4'\text{-Phbpy})_2^+$		1.88 ($d\pi^*$)	1.93 ($d\pi^*$)	1.93 ($d\pi^*$)

Re(I),[27] and Ir(III)[28] as well as for d^3 complexes of Cr^{3+} [29] but has not been applicable previously to those complexes that have been subjected to tuning studies. Hence, providing that substituents that bring about bathochromic shifts of the $d\pi^*$ and/or $\pi\pi^*$ levels to an energy substantially ($>kT$) below that of the dd^* levels can be found, the series of complexes of the type $IrCl_2(B)(B')^+$ should provide new, quantitative information pertinent to characterization of photochemical tuning.

Experimental Section

A. Preparation of Complexes. $IrCl_2(bpy)(5,6\text{-Mephen})^+$ was prepared for this study from iridium trichloride (Matthey-Bishop) and the appropriate ligands (G. F. Smith) with use of published techniques.[12,21,30,31] Good agreement between theoretical and observed elemental analyses for C, H, and N was obtained in all instances. Preparations of the other complexes studied here have been described previously.[21,23] Complexes were purified prior to use by repeated recrystallizations from alcoholic solvents or by column chromatography on CM-Sephadex cation-exchange resin. The purity of each sample used in the study was established by demonstration that additional recrystallization and column chromatography caused no change in the emission spectrum in fluid dimethylformamide.

B. Preparation of Solvents and Solutions. Water was purified by deionization followed by distillation with an all-glass Corning still. Dimethylformamide (Mallinckrodt, AR) was purified by double vacuum distillation and was stored over Linde Type 4A molecular sieves. Acetonitrile and methanol (Mallinckrodt, SpectrAR) were used without further purification.

Solutions were prepared immediately prior to use by bubbling with nitrogen until the emission intensity became constant (10–15 min). Fluorescein (Eastman) was purified by the method of Orndorff and Hemmer[32] and was dissolved in 0.1 M NaOH for use as a standard. Standard solutions were used within 4 h after their preparation.

C. Apparatus and Techniques. Quantum yields were determined by a modified Parker-Rees technique,[33,34] which has been described in detail.[35] A quantum yield of 0.90 was used for the standard fluorescein for excitation at 436 nm. Samples were also irradiated with the 436-nm line from a 1000-W Hg–Xe arc lamp, which was isolated with a Bausch and Lomb 0.25-m grating monochromator with slits to give a 5-nm band-pass. Additional copper sulfate solution and Corning CS 5-58 glass filters were used to improve spectral purity, and excitation was modulated with a PAR Model 191 chopper. Emission spectra were determined with a Perkin-Elmer Model 98 prism monochromator equipped with a dense flint prism and a dry-ice-cooled RCA 7102 photomultiplier. The signal from the photomultiplier was amplified with a PAR Model 124 lock-in amplifier and recorded with a Soltec Model 161-AA recorder. Emission spectra recorded with this apparatus were intensity corrected with calibration factors generated from an NBS standard quartz–iodine lamp by using a Hewlett-Packard Model V desk calculator.

Absorption measurements were performed with a Cary Model 15 spectrophotometer. The optical density of fluorescein solutions was adjusted to less than 0.005/cm, and the sample optical densities were adjusted to less than 0.05/cm.

Quantum yields were determined by application of the formula

$$Q_x = Q_r\left(\frac{A_r}{A_x}\right)\left(\frac{n_x^2}{n_r^2}\right)\left(\frac{D_x}{D_r}\right) \qquad (1)$$

where r and x refer to the reference standard (fluorescein) and the sample of the complex, A is the absorbance, n is the refractive index of the medium, and D is the area under the corrected emission spectrum.

Luminescence lifetimes were determined with excitation by the 337-nm pulse of an Avco C-950 nitrogen laser. Emitted light was passed through either a Balzers 497- or 547-nm interference filter to isolate the green $d\pi^*$ or $\pi\pi^*$ portion of the emission. When observed, the red dd^* emissions were isolated with a Balzers 704-nm interference filter.

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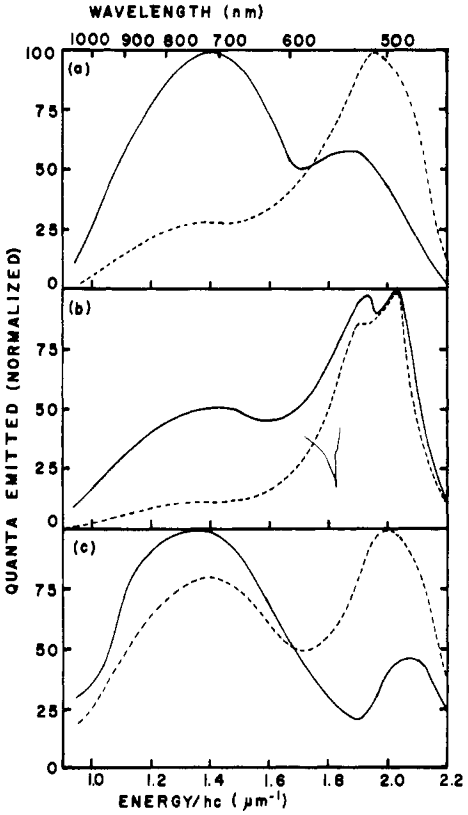

Figure 1. Emission spectra in water (—) and dimethylformamide (- - -) at 295 K: (a) $IrCl_2(bpy)_2^+$; (b) $IrCl_2(5,6\text{-Mephen})_2^+$; (c) $IrCl_2(phen)_2^+$.

Results

Luminescence lifetimes and yields are compiled in Table I, and the energies of emission-band maxima are listed in Table II. The series of complexes may be conveniently divided into two groups: (1) those complexes for which only a single emission is observed and (2) those complexes for which two emissions are evident in the various solvents. In general, the complexes that display a single emission are found to exhibit small shifts in emission maxima in the three nonaqueous solvents, but no major changes in the shapes of their emission spectra are observed; these complexes were insufficiently soluble in pure water to obtain reliable emission spectra. In contrast, those complexes that display two emissions are found to have luminescence spectra whose shapes are quite sensitive to the solvent environment. This is illustrated by the luminescence spectra shown in Figure 1. These spectra indicate that while the positions of the two band maxima are insensitive to the solvent environment, the ratio of the two emission intensities is strongly solvent dependent.

Luminescence quantum yields were generally found to be lower in the hydroxylic solvents than in the two nonhydroxylic solvents; in most instances the difference is nearly 2 orders of magnitude. In all four solvent systems quantum yields of the complexes for which a single emission is observed were found to be about 1 order of magnitude larger than those for the complexes with two emissions. The total quantum yields for these latter complexes can be decomposed into contributions from each of the two sets of levels by integration of the area under the emission spectrum of each component; results of this procedure are listed in Table III as the fraction of the total emission quantum yield contributed by the emission band in the red region.

All luminescence decay curves were found to be exponential, and equivalent lifetimes were obtained in both of the wavelength ranges monitored where two emissions were observed. This indicates that the two levels responsible for emission are in thermal equilibrium. Although both the luminescence lifetimes (τ) and quantum yields (Q) are very sensitive to the solvent medium, the ratio τ/Q, which represents the radiative lifetime of the emitting levels, is only weakly solvent dependent. This holds true even for those complexes for which two emissions are observed, where τ/Q represents the Boltzmann average of two radiative lifetimes. Although the luminescence lifetimes of $IrCl_2(phen)_2^+$ and $IrCl_2(bpy)_2^+$ could not be measured in aqueous solutions due to their shortness, they can be estimated from the measured luminescence quantum yields and values of τ/Q taken from other solvents. The values of τ/Q used for these estimates were 60 and 40 μs, respectively. The weak solvent dependence of τ/Q evident in Table I suggests that the estimated values of 2 and 1 ns are probably within a factor of about 2 of the true values.

Table III. Fractional Luminescence Quantum Yields for Red Component of Emission of $IrCl_2(B)(B')^+$ Complex Ions in Several Solvents at 295 K

	Q_R/Q_T[a]			
complex	water	methanol	acetonitrile	dimethylformamide
$IrCl_2(phen)_2^+$	0.77	0.27	0.33	0.27
$IrCl_2(bpy)_2^+$	0.81	0.54	0.68	0.60
$IrCl_2(bpy\text{-}d_8)_2^+$	0.67	0.30	0.31	0.32
$IrCl_2(5,6\text{-Mephen})_2^+$	0.36	0.17	0.18	0.13
$IrCl_2(bpy)(5,6\text{-Mephen})^+$	0.16	0.19	0.22	0.18

[a] Ratio of the quantum yield for the red portion of the emission spectrum (Q_R) to the total emission yield (Q_T).

Table IV. Values of $g_u k_{ur}/g_l k_{lr}$ and ΔE in Dimethylformamide from eq 2

complex ion	$g_u k_{ur}/g_l k_{lr}$	E, μm⁻¹	upper level	lower level
$IrCl_2(phen)_2^+$	7	0.050[a]	dπ*	dd*
$IrCl_2(bpy)_2^+$	9	0.037[b]	dπ*	dd*
$IrCl_2(5,6\text{-Mephen})_2^+$	$^1/_3$	0.010[a]	dd*	dπ*–ππ*

[a] Reference 23. [b] Reference 36.

Due to the establishment of thermal equilibrium among the two sets of emitting levels, it is possible to extract radiative lifetimes for each of the two levels in those complexes with two emissions. By forming the ratio Q_u/Q_l, which may be derived experimentally from the area under the corrected emission spectrum for each component, we obtain

$$Q_u/Q_l = (g_u k_{ur}/g_l k_{lr})e^{-\Delta E/kT} \tag{2}$$

In this equation l and u refer to the lower and upper levels, r represents the radiative process, g represents the degeneracy factor, and ΔE represents the energy gap between the emitting levels. ΔE can be obtained from the slope of a plot of ln (Q_u/Q_l) vs. $1/T$ and $g_u k_{ur}/g_l k_{lr}$ can be obtained from the intercept. Values of $g_u k_{ur}/g_l k_{lr}$ obtained by this procedure along with previously determined[23,36] ΔE values are listed in Table IV.

Discussion

Assignment of the Emitting States. 1. Model. The results for these complexes are consistent with the following model: (i) Two distinct types of low-energy excited states may be responsible for emission. These are classified as metal-localized (dd*) and delocalized-molecular[10] (dπ, ππ*, or mixed dπ*–ππ*) states. (ii) In all of the room-temperature solvent–complex systems studied, these two types of excited states attain thermal equilibrium with each other prior to emission. (iii) In several of the complexes ($IrCl_2(phen)_2^+$, for example) the equilibrium population of both types of excited states and

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the radiative decay rates are adequate to observe two distinct emissions at room temperature. (iv) In the complexes of the ligands with electron-withdrawing substituents (4,4′-Phbpy and 4,7-Phphen) only delocalized-molecular emission is observed because this level has been lowered sufficiently below the energy of the metal-localized level to prevent thermal back-population of the latter.

2. Energetics. The detailed energetics of the low-energy excited states taken from emission data are qualitatively in good agreement with this model if the large Stokes shifts of the metal-localized states are taken into account. Thus, although the emission of the metal-centered state is at 1.30–1.40 μm^{-1}, the 0–0 energy for this highly distorted excited state is estimated to lie at about 2.03 μm^{-1}.[23,36] This value is relatively insensitive to substituents on the bpy or phen ring systems since the immediate coordination sphere of the metal center is not altered. The low-temperature emission-band maxima of the delocalized-molecular emissions provide a relatively accurate estimate of the 0–0 energies of these states due to the small excited-state distortions. Comparison of these values[14] with the value of 2.03 μm^{-1} estimated for the metal-localized states indicates that the energy gap between the lowest excited states is generally in the range 0.00–0.20 μm^{-1}. Due to the small value of kT (0.02 μm^{-1}) it is quite reasonable that either thermal back-population of the upper of two levels could occur to give two emissions (energy gap <0.02 μm^{-1}) or that the lower level could lie sufficiently below the upper to prevent back-population and yield a single emission (energy gap >0.02 μm^{-1}). Unfortunately, quantitative correlation between 0–0 energies and the model would require an accuracy of about 0.01 μm^{-1}, which cannot be achieved in estimates of 0–0 energies from emission data due to uncertainties in Stokes shifts.

3. Decay Kinetics and Quantum Yield: Comparison with Previous Low-Temperature Results. Comparison of the lifetimes and quantum yields of the series of complexes reveals two immediate features that correlate with the model used in assigning the excited states: (i) the two complexes that display only one emission have somewhat higher quantum yields than those with two emissions and (ii) the two complexes with a single emission have smaller τ/Q values than those with two emissions. In correlating this information with the model, we apply the following generalization: the emission quantum yields of metal-localized states are reduced relative to delocalized-molecular states as a result of longer radiative lifetimes and larger quenching constants.

Since metal-localized emission is observed only for those complexes with two emissions, feature i follows immediately. Stated otherwise, this implies that population of the metal–localized excited state opens efficient radiationless decay channels available to the delocalized-molecular state. Since τ/Q is representative of the radiative lifetime of the delocalized-molecular state in those complexes with one emission while it represents a Boltzmann average of the radiative lifetimes of delocalized-molecular and metal-localized states in those complexes with two emissions, feature ii also follows from the model.

Further verification of the model can be obtained by a comparison of τ/Q values for these complexes in glasses at 77 K with the present room-temperature values. In making this comparison, one must be careful to recognize a point of contrast between the two sets of data. Whereas thermal equilibration between the excited states is attained in room-temperature fluid solutions, the excited states are unequilibrated at 77 K, and the dominant emission originates in the delocalized-molecular state regardless of whether it is the higher or lower energy state.[23] Hence, measurements at 77 K reflect properties of the delocalized-molecular states whereas room-temperature measurements of these quantitities reflect Boltzmann-averaged properties of both types of states.

The low-temperature radiative lifetimes for $IrCl_2(4,7\text{-}Phphen)_2^+$ and $IrCl_2(4,4'\text{-}Phbpy)_2^+$ (18.0 and 5.7 μs, respectively) are in good agreement with the room-temperature τ/Q values (see Table I). This indicates that the same set of delocalized-molecular levels that dominate the low-temperature emission are also responsible for the room-temperature emission. On the other hand, large changes between the τ/Q values at 77 K and room temperature are the rule for complexes such as $IrCl_2(bpy)_2^+$ and $IrCl_2(phen)_2^+$, which display two emissions. For example, the radiative lifetime of $IrCl_2(bpy)_2^+$ at 77 K is 11.5 μs whereas the room-temperature τ/Q value is about 40 μs. The room-temperature τ/Q value is attributed to contributions from both delocalized-molecular and metal-localized states. Hence, in the example of $IrCl_2(bpy)_2^+$ cited above, the τ/Q value measured at room-temperature represents a Boltzmann average of the 11.5-μs radiative lifetime of the delocalized-molecular state and a longer radiative lifetime of the metal-localized state. On the assumption that the two states have equivalent degeneracy factors, the radiative lifetime of the metal-localized state can be estimated from the k_{ur}/k_{ln} values in Table IV. This lifetime is estimated to be 104 μs for $IrCl_2(phen)_2^+$.

4. Solvent Effects. Tables I and III and Figure 1 serve to illustrate the large effect that the solvent medium has upon lifetimes, quantum yields, and emission spectra of these complexes. At room temperature, solvent effects are best viewed as the result of a combination of (i) modification of the radiative decay properties of the delocalized-molecular state analogous to the effect observed at low temperature,[14,15] (ii) modification of the relative Boltzmann populations of the delocalized-molecular states by alterations of the energy gap between them, and (iii) modification of the quenching of the excited state.

The solvent effects on the lifetimes and emission appear to stem primarily from modification iii since only a single emission is observed in all four solvents and the radiative lifetime is relatively insensitive to the solvent. From the substantial reduction of the lifetimes and quantum yields in methanol relative to acetonitrile and dimethylformamide, it is evident that the solvent O–H vibrational modes provide an efficient route for the quenching process.

The lifetimes and emission yields of the complexes that display two emissions follow a similar pattern, and enhanced quenching of the delocalized-molecular and metal-localized states by coupling to solvent O–H vibrations in methanol and water is again evident. That factors other than modification iii are also operating is evident from Table III and Figure 1, which indicate that the relative contribution of the metal-localized state is enhanced significantly in water relative to the other solvents. This may be interpreted by consideration of the effects of factors i and ii on the intensity ratio expressed by eq 2. Factor i will tend to decrease the radiative-decay rate in water in a manner analogous to that reported in previous low-temperature studies;[14] i.e., the $\pi\pi^*$ component of the delocalized-molecular state is enhanced in water by upward movement of the $d\pi^*$ components. This will affect the $g_u k_{ur}/g_l k_{lr}$ ratio in a manner that will enhance the metal-localized emission. Factor ii will also cause some enhancement of the metal-localized emission via upward movement of the delocalized-molecular state in water, resulting in alterations of the ΔE factor in eq 1.

It is interesting to note that both of these effects stem from an increase in the energy of the $d\pi^*$ configuration in the polar water solvent system. In the approach taken here, mixing of $d\pi^*$ and $\pi\pi^*$ configurations is considered to be an important factor, which alters the radiative lifetime of the delocalized-molecular state. On the other hand, mixing of $d\pi^*$ and dd^*

configurations is neglected, and the radiative lifetime of the metal-localized state is treated as a constant. The effects of movement of the $d\pi^*$ configuration relative to the dd* configuration are incorporated in the ΔE factor in eq 2. Justification of the approach lies in the fact that two distinct $d\pi^*$ and $\pi\pi^*$ emissions are not simulataneously observed, indicating that as these configurations approach one another, they interact strongly to yield delocalized-molecular states, which are sufficiently split to prevent thermal back-population of the upper level. On the other hand, the observation of simultaneous thermally equilibrated delocalized-molecular and metal-localized emissions indicates that these states can approach each other closely without being split by mixing of the $d\pi^*$ and/or $\pi\pi^*$ configurations with the dd* configuration.

This contrast in the degree of mixing of $d\pi^*$ and $\pi\pi^*$ configurations as opposed to $d\pi^*$ with dd* configurations probably stems from geometric considerations. Promotion of an electron from either a nonbonding d orbital or ligand π orbital to a ligand π^* orbital appears to lead to only a small excited-state distortion as evidenced by the highly structured low-temperature emissions observed in these complexes. Promotion from a nonbonding d orbital to an antibonding d orbital leads to a large geometric distortion as evidenced by the broad red-shifted metal-localized emission. The mixing of $d\pi^*$ and $\pi\pi^*$ configurations with similar geometries should be substantially larger than that of $d\pi^*$ and dd* configurations with very different geometries.

Summary and Conclusions. Luminescence Tuning and Its Applications

The present study provides evidence that inversion of metal-localized and delocalized-molecular states does occur when electron-withdrawing phenyl substituents are placed on the bpy or phen ligands in complexes of the type IrCl$_2$(B)(B′)$^+$. This evidence is found in the values of lifetimes, emission yields, and τ/Q as well as in shapes of emission spectra in room-temperature fluid solutions.

The photophysical data resulting from this study have several significant implications with regard to the photochemistry of these complexes. Since inversion of delocalized-molecular and metal-centered states has been shown to occur, a significant change in photochemical properties (photochemical tuning) is anticipated. For example, the photochemical properties of IrCl$_2$(4,7-Phphen)$_2$, which has a lowest energy delocalized-molecular state, may be quite different than those of IrCl$_2$(phen)$_2^+$, which has a low-energy metal-centered state. Furthermore, the availability of room-temperature lifetime data may render determination of photochemical rate constants feasible. This type of quantitative rate constant data has not been readily measurable in previous studies of photochemical tuning due to the absence of measurable room-temperature emissions.

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Registry No. IrCl$_2$(phen)$_2^+$, 17992-95-9; IrCl$_2$(bpy)$_2^+$, 47514-19-2; IrCl$_2$(bpy-d_8)$_2^+$, 75110-37-1; IrCl$_2$(5,6-Mephen)$_2^+$, 53822-52-9; IrCl$_2$(bpy)(5,6-Mephen)$^+$, 77320-95-7; IrCl$_2$(4,7-Phphen)$_2^+$, 77320-96-8; IrCl$_2$(4,4′-Phbpy)$_2^+$, 77320-97-9.

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Photochemistry of Copper(II) Complexes with Macrocyclic Amine Ligands

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The photochemical properties of Cu(*dl*-Me$_6$[14]aneN$_4$)$^{2+}$ and Cu(*rac*-Me$_6$[14]aneN$_4$)$^{2+}$ in the presence and absence of axially coordinated ligands have been investigated by continuous and flash irradiations. Flash photolysis of the complexes in deaerated aqueous solutions revealed the presence of copper–ligand radical complexes with closed- and open-cycle ligands. Flash photolysis of methanolic solutions of the complexes, in the presence of halides and pseudohalides, shows Cu(III) macrocyclic intermediates. The experimental observations can be explained in terms of two primary photoprocesses with origins in distinctive charge transfer to metal states. These states have been assigned as amino to copper(II) charge-transfer state and acido to copper(II) charge-transfer state.

Introduction

The photochemical properties of amino complexes of copper(II) have not been investigated in detail.[1] A report on the photochemistry of Cu(en)$_2^{2+}$ shows that ultraviolet irradiations induce the redox decomposition of the complex with formation of CO$_2$ and NH$_3$.[2] However, the irradiation and/or thermal decomposition of other species in solution complicate the interpretation of the results.[1,2] Some of the difficulties, introduced by the lability of Cu(en)$_2^{2+}$, can be resolved by using complexes of macrocyclic tetraamines, e.g., *dl*-Me$_6$[14]aneN$_4$ (I) and *rac*-Me$_6$[14]aneN$_4$ (II).[3] Moreover, these complexes, namely, Cu(en)$_2^{2+}$ and Cu(macrocycle)$^{2+}$, can be regarded as structuraly related species. Such a relationship makes it possible to extend the spectral assignments of the copper(II) ethylenediamines to the charge-transfer spectra of the macrocyclic amino complexes.[4,5]

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(3) Ligand abbreviations: *dl*-Me$_6$[14]aneN$_4$, *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; *rac*-Me$_6$[14]aneN$_4$, *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; Me$_6$-[14]dieneN$_4$, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetra-4,11-diene.

(4) Yokoi, H.; Isobe, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2187.

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