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**Excited States of Transition Metal Complexes. A Spectroscopic Measurement of  $d\pi^*-\pi\pi^*$  Interactions in Iridium(III) Complexes<sup>1</sup>**BY R. J. WATTS, G. A. CROSBY,\* AND J. L. SANSREGRET<sup>2</sup>

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The effect of solvent medium on the measured lifetimes of the emitting states of several iridium(III) complexes is interpreted in terms of a model invoking  $d\pi^*-\pi\pi^*$  configuration interaction. The model yields an interaction parameter,  $\beta$ , whose magnitude is  $280\text{ cm}^{-1}$  as determined from measured energies and decay times of the *cis*-dichlorobis(5,6-dimethyl-1,10-phenanthroline)iridium(III) ion. A quantitative scheme for classifying the emitting states of a number of iridium(III) complexes as "charge transfer" or "ligand localized" is developed in terms of the magnitude of  $\beta$ . Preparations of several iridium(III) complexes of methyl-substituted phenanthroline and bipyridine are reported. Absorption and emission spectra, lifetimes, and photoluminescence quantum yields of the complexes at 77°K are given.

**Introduction**

Profound changes of the optical properties of several ruthenium(II) and iridium(III) complexes with 2,2'-bipyridine and 1,10-phenanthroline are brought about by phenyl substitution of these ligands.<sup>3</sup> In general 4,4'-phenyl substitution of 2,2'-bipyridine and 4,7-phenyl substitution of 1,10-phenanthroline produce significant enhancements of the luminescence quantum yields of the substituted complexes over those of the parent species. The enhancements are due to a decrease in both the radiative lifetime and quenching rate constant of the luminescing state in most cases and generally occur without major alterations in the energies and orbital natures of the emitting levels. Both the unsubstituted and phenyl-substituted complexes usually display luminescence spectra and lifetimes which are characteristic of charge-transfer ( $d\pi^*-A_1$ ) transitions.<sup>4</sup>

In most instances it has been possible to correlate the decrease in the radiative lifetime with an increase in the extinction coefficient of a highly allowed charge-transfer state from which the emitting state presumably borrows intensity. The decrease in the quenching rate constant is thought to arise primarily from a decrease in spin-orbit coupling occurring upon substitution. Both of these conclusions stem from the application of a model for intensity borrowing *via* spin-orbit coupling in complexes with charge-transfer luminescences initially proposed by Crosby, *et al.*, for radiative processes<sup>5</sup> and later extended to radiationless ones.<sup>3</sup>

One outstanding exception to the aforementioned behavior has been noted in the case of *cis*-dichlorobis(4,7-diphenyl-1,10-phenanthroline)iridium(III) chloride. Although the quantum yield of this complex is greatly enhanced upon phenyl substitution of the ligands, the radiative lifetime of the complex is longer than that of the parent ion. The lengthening occurs in spite of a large increase in the extinction coefficient of the charge-transfer state that generally lends intensity to the borrowing luminescing state, and it appears that the intensity-borrowing model is not applicable in this instance. Phenyl substitution of the ligand in this complex shifts the emitting state to a somewhat

lower energy than expected on the basis of observed shifts of similar complexes, and also the free ligand phosphorescing state lies exceptionally close in energy to the luminescing state of the complex.<sup>4</sup> This information has led us to the conclusion that a large  $d\pi^*-\pi\pi^*$  configuration interaction occurs in *cis*-dichlorobis(4,7-diphenyl-1,10-phenanthroline)iridium(III) chloride.

When a ligand substituent brings the locally excited ligand triplet state in proximity to the charge-transfer state of the unsubstituted parent complex, a large  $d\pi^*-\pi\pi^*$  configuration interaction may be expected to occur. Although such a configuration interaction may produce relatively small effects on the absorption and emission spectra, large changes in the radiative and nonradiative decay rates of the emitting state are anticipated. DeArmond and Hillis have suggested that  $d$  and  $\pi^*$  orbitals may be strongly mixed when the relevant energy gaps become small and have proposed the term "delocalized molecular" to describe the state arising from a promotion to such a strongly mixed orbital.<sup>6</sup>

In order to investigate further the occurrence of configuration interactions between charge-transfer ( $d\pi^*$ ) and locally excited ligand triplet ( $\pi\pi^*$ ) states, we have prepared several methyl-substituted complexes of 2,2'-bipyridine and 1,10-phenanthroline with iridium(III). In this paper we report the results of a study of several optical properties of these compounds and relate the results to the occurrence of  $d\pi^*-\pi\pi^*$  configuration interactions. We further suggest several means by which this configuration interaction may be modulated and report the successful use of solvent perturbations to achieve such alterations.

**Experimental Section**

**Preparation and Purification of Complexes.** *cis*-Dichlorobis(5,6-dimethyl-1,10-phenanthroline)iridium(III) Chloride Trihydrate,  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$ .—5,6-Dimethyl-1,10-phenanthroline (0.490 g, G. Frederick Smith Chemical Co.) and 0.326 g of  $\text{Na}_2\text{IrCl}_6$  were ground together with mortar and pestle, sealed in a Pyrex tube under vacuum, and heated for 4 hr at 220°. The tube was allowed to cool, broken open, and boiled in 100 ml of water. The resulting dark green solution was filtered while hot and the yellow filtrate saved. Sodium chloride (10 g) in 50 ml of water was added to the filtrate to precipitate the desired yellow complex. This yellow precipitate was then washed with 50 ml of benzene and air-dried. The product was purified on a gel filtration column of Sephadex LH-20 (21 × 950 mm) using ethanol for

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(3) R. J. Watts and G. A. Crosby, *J. Amer. Chem. Soc.*, **94**, 2606 (1972).

(4) R. J. Watts and G. A. Crosby, *ibid.*, **93**, 3184 (1971).

(5) J. N. Demas and G. A. Crosby, *ibid.*, **93**, 2841 (1971).

(6) M. K. DeArmond and J. E. Hillis, *J. Chem. Phys.*, **54**, 2247 (1971).

elution. The yield of pure product was 90 mg. *Anal.* Calcd for  $[\text{IrCl}_2(\text{C}_{14}\text{H}_{12}\text{N}_2)_2]\text{Cl}\cdot 3\text{H}_2\text{O}$ : C, 43.72; H, 3.93; Cl, 13.83; N, 7.29. Found: C, 43.84; H, 4.40; Cl, 15.13; N, 7.36.

*cis*-Dichlorobis(4,7-dimethyl-1,10-phenanthroline)iridium(III) Chloride Pentahydrate,  $[\text{IrCl}_2(4,7\text{-Mephen})_2]\text{Cl}\cdot 5\text{H}_2\text{O}$ .—4,7-Dimethyl-1,10-phenanthroline (1.302 g, G. Frederick Smith Chemical Co.) and 0.998 g of  $\text{K}_3\text{IrCl}_6$  were ground together with mortar and pestle, sealed in a Pyrex tube under vacuum, and heated at 220° for 3.5 hr. The tube was allowed to cool, broken open, and boiled in 100 ml of water. This solution was filtered while hot, and 10 g of sodium chloride in 50 ml of water was added to the filtrate to precipitate the desired product. This was washed with ethyl ether and air-dried. The residue, olive drab in color, was washed very sparingly with ethanol to remove impurities. The desired product, yellow in color, was air-dried and purified on a gel filtration column of Sephadex LH-20 (9 × 400 mm) using methanol for elution. The total yield of pure product was 50 mg, which was then dried in a vacuum desiccator for 24 hr at room temperature. *Anal.* Calcd for  $[\text{IrCl}_2(\text{C}_{14}\text{H}_{12}\text{N}_2)_2]\text{Cl}\cdot 5\text{H}_2\text{O}$ : C, 41.77; H, 4.26; Cl, 13.21; N, 6.96. Found: C, 41.70; H, 4.54; Cl, 13.40; N, 7.30.

*cis*-Dichlorobis(4,4'-dimethyl-2,2'-bipyridine)iridium(III) Chloride Trihydrate,  $[\text{IrCl}_2(4,4'\text{-Mebipy})_2]\text{Cl}\cdot 3\text{H}_2\text{O}$ .— $\text{K}_3\text{IrCl}_6$  (0.470 g) and 0.515 g of 4,4'-dimethyl-2,2'-bipyridine (G. Frederick Smith Chemical Co.) were ground together with mortar and pestle, sealed in a Pyrex tube under vacuum, and heated for 4 hr at 220°. The tube was allowed to cool, broken open, and boiled in 200 ml of water. The solution was filtered while hot, and 10 g of sodium chloride in 50 ml of water was added to the filtrate, causing precipitation of a bright yellow solid. This solid was vacuum-dried overnight and dissolved in 10 ml of methanol. Insoluble material was discarded. The dissolved product was purified on a Sephadex LH-20 column (9 mm × 400 mm) using methanol for elution. Two bands separated, one green under uv excitation at ~360 nm and the other yellow. The green band came off first and was discarded. The yellow band contained the desired complex. The yield of pure product was 91 mg, which was vacuum-dried for 24 hr at room temperature. *Anal.* Calcd for  $[\text{IrCl}_2(\text{C}_{12}\text{H}_{12}\text{N}_2)_2]\text{Cl}\cdot 3\text{H}_2\text{O}$ : C, 39.97; H, 4.19; Cl, 14.75; N, 7.77. Found: C, 39.97; H, 4.02; Cl, 13.78; N, 7.72.

**Spectroscopic Measurements.**—Absolute ethanol (U. S. Industrial Chemical Co., USP-NF), absolute methanol (Baker Analyzed), and glycerol (Matheson Coleman and Bell, spectro-quality reagent) were used as spectroscopic solvents for absorption, emission, and quantum-yield measurements without further purification.

Low-temperature absorption spectra and absorbances for quantum-yield determinations were measured in clear glasses (77°K) in 1.76-cm cylindrical Pyrex cells with a Cary Model 14 spectrophotometer. Samples were kept at a distance of at least 15 cm from the detector to minimize errors due to sample luminescence. The techniques used for these measurements were reported previously.<sup>3</sup> For lifetime measurements, light from an EG&G FX-12 xenon flash lamp was passed through a filter system, which consisted of 2 cm of copper(II) sulfate solution (200 g/l.) and a Corning 7-60 glass filter. This filter system isolated a broad band of excitation light centered around 360 nm. Emitted light from the sample was passed through a Balzers 510-nm narrow band pass filter and a Corning 3-72 glass filter. Luminescence decays were monitored with an EMI 9558QC photomultiplier and displayed on a Tektronix 535A oscilloscope. The oscilloscope trace was photographed, and lifetimes were determined by a linear least-squares fit of  $\ln$  intensity *vs.* time.

Details of the modified Parker-Rees technique<sup>7,8</sup> used for measuring quantum yields have been published in a previous paper.<sup>5</sup> Our technique employs a freshly prepared solution of Eastman White Label fluorescein (purified by the method of Orndorff and Hemmer<sup>9</sup>) in 0.1 *N* sodium hydroxide (less than  $6 \times 10^{-7}$  *M*) as a standard. A value of 0.90 has been adopted in this laboratory for its quantum yield. For excitation of both the samples and the standard, the 436-nm region of a 1000-W Hanovia 977B-1 Hg-Xe lamp was isolated with an Aminco 4-8400 f/4 grating monochromator. The band pass of the monochromator was set at 5.5 nm, and a Corning 3-73 glass filter and an Optics

Technology 450-nm blue-edge filter were added to improve spectral purity. Emission spectra were analyzed with a red-sensitive apparatus constructed in the laboratory.<sup>10,11</sup> This apparatus uses a Perkin-Elmer Model 98 monochromator equipped with a Pyrex prism for analysis of the emitted light. The monochromator slits were set at 0.2 mm, which gave a band pass of ~100  $\text{cm}^{-1}$  over the range 400–1000 nm. No distortion of the emission spectra occurred under these conditions. An RCA-7102 photomultiplier cooled to Dry Ice temperature was used to monitor the emission. The exciting light was chopped with a Brower 312C chopper powered by a Brower 322 control. The output of the photomultiplier was amplified by a PAR lock-in amplifier. The emission apparatus was corrected for the wavelength dependence of the sensitivity with an NBS quartz-iodine lamp.

The sample cells used for emission were identical with those used for absorption measurements. Sample solutions were prepared immediately prior to use and cooled to 77°K. No dissociation or photodecomposition was detected. The absorbances of the samples were adjusted to less than 0.05/cm and that of the standard was adjusted to less than 0.005/cm to eliminate errors due to reabsorption of emitted light. The ethanol-methanol glass used in the measurements showed no detectable emission under the conditions employed. A value of 1.41 was adopted for the refractive index of the glass at 77°K.<sup>5</sup>

Phosphorescence spectra of the methyl-substituted ligands were recorded on a Hitachi Perkin-Elmer Model MPF-2A spectrophotometer with a phosphoscope attachment. All phosphorescence spectra were corrected for the wavelength dependence of the instrumental response.

## Results

In Figure 1 the absorption and emission spectra of

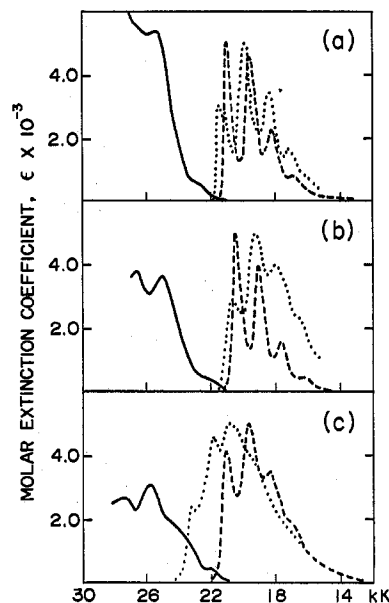


Figure 1.—Absorption (—) and luminescence (---) spectra of methyl-substituted iridium(III) complexes and phosphorescence (.....) of the ligands. All spectra were measured in ethanol-methanol glass (4:1, v/v) at 77°K: (a)  $[\text{IrCl}_2(4,7\text{-Mephen})_2]\text{Cl}$ ; (b)  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$ ; (c)  $[\text{IrCl}_2(4,4'\text{-Mebipy})_2]\text{Cl}$ .

the methyl-substituted phenanthroline and bipyridine complexes of iridium(III) are displayed. Phosphorescence spectra of the solvated ligands are included to aid comparisons.

All three of the complexes show a well-resolved absorption band in the 25–26-kK region having an extinction coefficient on the order of 3000–5000  $\text{l. mol}^{-1} \text{cm}^{-1}$ .

(7) C. A. Parker and W. T. Rees, *Analyst (London)*, **85**, 587 (1960).

(8) C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968.

(9) W. R. Orndorff and A. J. Hemmer, *J. Amer. Chem. Soc.*, **49**, 1272 (1927).

(10) J. N. Demas, Ph.D. Dissertation, University of New Mexico, Albuquerque, N. M., 1970.

(11) D. H. W. Carstens and G. A. Crosby, *J. Mol. Spectrosc.*, **34**, 113 (1970).

Similar bands are found in the absorption spectra of the parent  $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$  and  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  complexes. Methyl substitution of these ligands therefore appears to have only very slight effects on these bands, in contrast to the relatively large changes in their energies and extinction coefficients caused by phenyl substitution.<sup>3,4</sup>

Of the three complexes studied, only the  $[\text{IrCl}_2(4,4'\text{-Mebipy})_2]\text{Cl}$  complex displays a well-resolved absorption, which overlaps the emission spectrum. The absorption maximum in this region occurs at 22.0 kK with an extinction coefficient of about  $400 \text{ l. mol}^{-1} \text{ cm}^{-1}$ . This is again quite similar to the spectrum of the parent  $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$  complex. On the other hand, the methyl-substituted phenanthroline complexes show only weak ( $\epsilon \sim 50$ ) unresolved absorptions in this region, in contrast to the parent  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  complex, which shows a poorly resolved absorption at 21.7 kK with an extinction coefficient of about  $200 \text{ l. mol}^{-1} \text{ cm}^{-1}$ .

The emissions of these complex ions all occur in the blue-green region of the spectrum. The highest energy band of  $[\text{IrCl}_2(4,4'\text{-Mebipy})_2]\text{Cl}$  and  $[\text{IrCl}_2(4,7\text{-Mephen})_2]\text{Cl}$  occurs at 21.1 kK in the ethanol-methanol glass, whereas it is found at 20.5 kK for  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$ . The lowest triplet state of the 4,4'-Mebipy ligand lies at 23.3 kK, 2.2 kK higher in energy than the luminescing state of the iridium(III) complex of this ligand. In contrast the lowest triplet states of the solvated methyl-substituted phenanthroline ligands lie much closer to the luminescing states of their respective iridium(III) complexes. In the case of 4,7-Mephen, the triplet state emits at 21.6 kK, only 0.5 kK higher in energy than the emissive state of the corresponding iridium(III) complex. The energy difference between the lowest triplet of the parent ligand and its bis complex is even smaller for 5,6-Mephen, whose phosphorescing triplet state lies at 20.7 kK, just 0.2 kK above the luminescing state of  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$ . Methyl substitution of 1,10-phenanthroline is therefore seen to lower the energy of the ligand triplet state to a value that is very close to the energy of the iridium(III) complex emission.

A tabulation of the absorption and emission data for these complexes and the relevant ligands is presented in Table I. For purposes of comparison, previously reported data for the parent and phenyl-substituted complexes are included.

The overall photoluminescence quantum yields of these complexes under excitation at 436 nm in ethanol-methanol glasses are tabulated in Table II. The observed lifetimes of the luminescing states are also included. If it is assumed that the total luminescence quantum yields are equal to the quantum yields for radiative decay of the emitting states,<sup>3,5</sup> then the radiative lifetimes of the emitting states,  $\tau_0$ , are given by the ratio of the observed lifetimes to the observed yields. Values of  $\tau_0$  calculated by this procedure are also included in Table II. Although we have not measured the wavelength dependences of the quantum yields for these complexes, previous investigations on similar complexes revealed no changes.<sup>5</sup> The values of the quantum yield (0.534) and lifetime (5.91  $\mu\text{sec}$ ) of  $[\text{IrCl}_2(4,4'\text{-Mebipy})_2]\text{Cl}$  are nearly the same as those for the parent  $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$  complex, 0.516 and

TABLE I  
ABSORPTION AND EMISSION DATA FOR 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE COMPLEXES OF Iridium(III) AND THE SOLVATED LIGANDS IN 4:1 (v/v) ETHANOL-METHANOL GLASSES AT 77°K

Compound <sup>a</sup>	Emission, $\nu_e$ , <sup>b</sup> kK	Absorption	
		$\nu_{\text{max}}$ , kK	$\epsilon_{\text{max}} \times 10^{-3}$ , l. mol <sup>-1</sup> cm <sup>-1</sup>
$[\text{IrCl}_2(\text{bipy})_2]\text{Cl}^c$	21.1	25.6	2.8
	23.5 <sup>d</sup>	21.8	0.36
$[\text{IrCl}_2(4,4'\text{-Mebipy})_2]\text{Cl}$	21.1	26.0	3.1
	23.3	22.0	0.41
$[\text{IrCl}_2(4,4'\text{-phenylbipy})_2]\text{Cl}^e$	20.4	25.0	9.3
	23.2	21.1	0.90
$[\text{IrCl}_2(\text{phen})_2]\text{Cl}^{e,f}$	21.1	52.3	3.8
	22.2	21.7	0.20
$[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$	20.5	25.0	3.6
	20.7	21.0	0.05
$[\text{IrCl}_2(4,7\text{-Mephen})_2]\text{Cl}$	21.1	25.3	5.4
	21.6	21.2	0.05
$[\text{IrCl}_2(4,7\text{-phenylphen})_2]\text{Cl}^g$	19.5	24.3	9.3
	21.0	20.7	0.23

<sup>a</sup> Cis isomers. <sup>b</sup>  $\nu_e$  represents the energy of the highest energy member of the vibrational progression in the emission spectrum. <sup>c</sup> See ref 4. <sup>d</sup> See D. H. W. Carstens and G. A. Crosby, *J. Mol. Spectrosc.*, **34**, 113 (1970). <sup>e</sup> See ref 17. <sup>f</sup>  $\nu_e$  values for the solvated ligands are taken from phosphorescence spectra. Fluorescence data are not included.

TABLE II  
QUANTUM YIELDS, LIFETIMES, AND RATE CONSTANTS OF Iridium(III) COMPLEXES AT 77°K<sup>a</sup>

Complex <sup>b</sup>	Quantum yield, $\phi$	Measured lifetime, $\tau_m$ , $\mu\text{sec}$	Quenching rate constant, $k_q$ , $\mu\text{sec}^{-1}$	
			Intrinsic lifetime, $\tau_0$ , $\mu\text{sec}$	Quantum yield, $\phi_0$
$[\text{IrCl}_2(4,4'\text{-Mebipy})_2]\text{Cl}$	0.534 $\pm$ 0.021	5.91 $\pm$ 0.02	11.07	0.0789
$[\text{IrCl}_2(4,7\text{-Mephen})_2]\text{Cl}$	0.617 $\pm$ 0.024	21.7 $\pm$ 0.2	35.17	0.0176
$[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$	0.770 $\pm$ 0.015	66.3 $\pm$ 0.3	86.10	0.0034

<sup>a</sup> Measured in ethanol-methanol (4:1, v/v). <sup>b</sup> Cis isomers; see Experimental Section for proper chemical names and formulas.

5.94  $\mu\text{sec}$ , respectively. For  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ , however, substantial changes in the lifetime (6.92  $\mu\text{sec}$ ) and quantum yield (0.496) occur upon methyl substitution of the ligand in either the 4,7 or 5,6 positions.<sup>5</sup> A similar result was reported previously for 4,7-phenyl substitution of the ligand in this complex.<sup>3</sup>

The energies and lifetimes of the emissions from a series of substituted phenanthroline-iridium(III) complexes in eight different solvent systems are shown in Table III. The table has been arranged in such a way as to emphasize a correlation between the energy of the emitting state of the parent  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  complex and the observed lifetimes for the substituted species. In each case a change in the solvent system, which raises the energy of the charge-transfer emitting state of  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ , also causes a lengthening of the luminescence lifetime of the substituted complexes. No exceptions to this behavior were observed. In some instances the energy of the emitting state of the substituted complex is also raised, though in many cases no such change is observed. In all of the substituted complexes the lifetimes in several of the solvent systems exceed the radiative lifetimes reported in Table II for

TABLE III  
LIFETIMES AND ENERGIES OF LUMINESCING STATES OF IRIIDIUM(III)-PHENANTHROLINE  
COMPLEXES<sup>a</sup> IN VARIOUS SOLVENTS AT 77°K

Solvent	[IrCl <sub>2</sub> (phen) <sub>2</sub> ]Cl		[IrCl <sub>2</sub> (5,6-Mephen) <sub>2</sub> ]Cl		[IrCl <sub>2</sub> (4,7-Mephen) <sub>2</sub> ]Cl		[IrCl <sub>2</sub> (4,7-phenylphen) <sub>2</sub> ]Cl	
	ν <sub>e</sub> , <sup>b</sup> kK	τ, μsec	ν <sub>e</sub> , kK	τ, μsec	ν <sub>e</sub> , kK	τ, μsec	ν <sub>e</sub> , kK	τ, μsec
Ethanol	21.1	8.47	20.5	75.0	21.1	22.9	19.5	18.6
4:1 ethanol-methanol	21.1 <sup>c</sup>	6.95 <sup>d</sup>	20.5	66.3	21.1	21.8	19.6 <sup>e</sup>	15.0 <sup>e</sup>
1:1 glycerol-ethanol	21.2	11.0	20.5	116.5	21.1	29.7	19.7	23.7
2:1 glycerol-ethanol	21.3	11.3	20.5	128.8	21.1	35.0	19.7	25.2
Glycerol	21.4	12.8	20.5	158.3	21.2	41.3	19.9	27.8
4:1 glycerol-water	21.5	16.4	20.5	207.6	21.2	51.4	19.8	32.5
4:1 methanol-water	21.5	11.4	20.5	192.0	21.3	54.1	19.9	33.8
1:1 glycerol-water	21.6	20.1	20.5	236.1	21.3	72.2	19.9	35.0
9:10 MgCl <sub>2</sub> -H <sub>2</sub> O <sup>f</sup>	21.7	16.6	20.5	448.2	21.4	207.7	...	...

<sup>a</sup> Cis isomers. <sup>b</sup> ν<sub>e</sub> represents the energy of the highest energy member of the vibrational progression in the emission spectrum. <sup>c</sup> See ref 17. <sup>d</sup> See ref 5. <sup>e</sup> See ref 3. <sup>f</sup> Wt/wt; other ratios v/v.

samples in 4:1 (v/v) ethanol-methanol glasses. The largest increase in lifetime is observed for [IrCl<sub>2</sub>(5,6-Mephen)<sub>2</sub>]Cl where a change in solvent from 4:1 ethanol-methanol to 9:10 (wt/wt) MgCl<sub>2</sub>-H<sub>2</sub>O is accompanied by a sevenfold increase in the observed lifetime. In this instance the longest observed value of 448.2 μsec exceeds the radiative lifetime of 86.1 μsec for the complex in 4:1 ethanol-methanol by a factor of 5. This complex is also the only one of those studied whose emission energy is independent of the solvent system in which it is measured.

#### Interpretation of Solvent Effects

Although slight changes in the lifetime of an excited state are not uncommon when the solvent system is altered, large variations are rare. For the substituted phenanthroline complexes of iridium(III) investigated here, the strong solvent dependence of the observed luminescence lifetimes cannot be explained through changes in radiationless rates. Because the observed lifetimes of the complexes in several solvents exceed the radiative lifetimes determined in ethanol-methanol glasses by large factors, there is little doubt that the present results must be attributed, at least in part, to a change in the radiative lifetimes of the emitting states. Although small changes in the radiative lifetime may result from a refractive index effect, the large alterations observed in these systems are far beyond the range of such effects. We believe that the changes in the radiative lifetimes of these complexes must be attributed to alterations in the wave functions of the emitting states, which are brought about by solvent interactions.

We suggested previously that a large dπ\*-ππ\* configuration interaction is expected in [IrCl<sub>2</sub>(4,7-phenylphen)<sub>2</sub>]Cl because of the proximity of the anticipated low-lying charge-transfer and ligand-localized states of the complex.<sup>4</sup> This conjecture was further substantiated by the fact that the radiative lifetime for the luminescence of this complex far exceeded what would be expected for a charge-transfer state on the basis of an intensity-borrowing model.<sup>3</sup> These conditions, which we believe to be symptomatic of large interactions, are also found to be present in [IrCl<sub>2</sub>(4,7-Mephen)<sub>2</sub>]Cl and [IrCl<sub>2</sub>(5,6-Mephen)<sub>2</sub>]Cl. A large dπ\*-ππ\* configuration interaction is therefore expected to occur for these latter complexes. We believe that the alterations of the wave functions of the emitting states of these complexes may be interpreted in terms of changes in dπ\*-ππ\* interactions brought about by solvents.

This brings us to the question of how a change in the solvent system can alter the interaction of the lowest excited charge-transfer and ligand-localized states and therefore affect the wave functions and radiative lifetimes of the luminescing states. The answer lies in the fact that the energies of charge-transfer states are found to be solvent dependent, whereas those of ligand-localized states are virtually independent of the medium. As a result, a change in solvent may alter the energy gap between zero-order charge-transfer and ligand-localized states and, hence, change the wave functions of the luminescing states. Lim, *et al.*,<sup>12,13</sup> have suggested that, in a similar manner, a change in the energy gap between the <sup>3</sup>ππ\* and <sup>3</sup>nπ\* states of carbonyl compounds caused by switching from an alcoholic glass to a hydrocarbon glass may be responsible for a decrease in the quantum yields and lifetimes of the phosphorescences. In contrast to our belief that both the radiative and radiationless decay rates are sensitive to the energy gap in iridium(III) complexes, their evidence suggests that it is primarily the radiationless decay rate that is sensitive to the energy gap in carbonyl compounds. Gallivan and Brinen<sup>14</sup> have also studied the effects of solvent polarity on the lowest triplet state of several carbonyl compounds and have reported a reordering of <sup>3</sup>ππ\* and <sup>3</sup>nπ\* levels by solvent effects. They suggest, however, that it is primarily the radiative decay rate that is affected by alterations of the <sup>3</sup>ππ\*-<sup>3</sup>nπ\* interaction.

#### A Model for Modulation of dπ\*-ππ\* Configuration Interactions by Solvent Effects

**The Zero-Order Problem.**—To provide a quantitative interpretation of the effect of solvent medium upon the luminescence lifetimes of complexes having proximate low-lying charge-transfer and ligand-localized states, our approach is to incorporate the maximum amount of experimental information in the model. This empirical approach sidesteps the difficult problem of finding explicit wave functions and energies for these complex systems.

In the previous section it was proposed that solvent effects on the lifetimes of these complexes be attributed to changes in the wave functions brought about by alterations of the energy gaps between interacting charge-transfer and ligand-localized states. Our choice of zero-order wave functions will therefore be made in such a way as to emphasize this interaction term as well

- (12) E. C. Lim, Y. H. Li, and R. Li, *J. Chem. Phys.*, **53**, 2443 (1970).  
 (13) Y. H. Li and E. C. Lim, *Chem. Phys. Lett.*, **7**, 15 (1970).  
 (14) J. B. Gallivan and J. S. Brinen, *ibid.*, **10**, 455 (1971).

as to provide a starting point for which a solution is available. We assume a set of zero-order wave functions correct up to the postulated  $d\pi^*-\pi\pi^*$  configuration interaction between the two lowest excited states. Although interactions of the lowest excited pure spin states with higher energy pure spin states through spin-orbit coupling are known to be important, since they are the terms responsible for intensity borrowing, it is assumed that all of these other interactions are accounted for in the assumed zero-order wave functions. It is further assumed that all solvent interaction terms are diagonal in this basis set. The zero-order charge-transfer state,  $\phi_{CT}^0$ , is therefore defined as the hypothetical luminescing state of the complex in a given solvent that would exist if the ligand-localized state,  $\phi_{LL}^0$ , were moved far up in energy, but all the other states remained fixed. Conversely,  $\phi_{LL}^0$  is defined as the luminescing state that would exist in a given solvent if  $\phi_{CT}^0$  were moved far up in energy, but all other states remained fixed.

It is apparent that this definition of zero-order states would be unrealistic for a computational approach to this problem, since it presumes a basis set, which may not be adequately represented by single configuration wave functions. For an empirical treatment of the interaction, however, this definition of zero-order states proves to be quite convenient. Since these zero-order states are defined with reference to a specific solvent system,  $E_{CT}^0$ , the energy of  $\phi_{CT}^0$ , will depend upon the solvent. However,  $E_{LL}^0$ , the energy of  $\phi_{LL}^0$ , is assumed to be independent of the solvent as suggested in the previous section.

**The Interaction Terms.**—In our model,  $\phi_{CT}^0$  and  $\phi_{LL}^0$  are presumed to be coupled by a term in the Hamiltonian,  $H'$ , which is unimportant when the matrix element coupling these states,  $\beta$ , is much smaller than the energy gap between them. The interaction of these states leads to stationary states. The lower one,  $\Psi_e$ , will be the only emitting state of the complex if  $\beta$  is of sufficient magnitude to cause a splitting much greater than  $kT$ .<sup>15</sup> If  $\beta$  is very small, the splitting of the stationary states may be small enough to allow a significant population of both levels, and emission from the Boltzmann distribution of the states would then be anticipated. For the present we proceed on the assumption that  $\beta$  is of sufficient magnitude to cause the stationary states to be split by an energy gap that prohibits significant Boltzmann population of the upper state under normal experimental conditions ( $\leq 77^\circ\text{K}$ ). Classification of these stationary states as charge-transfer or ligand-localized states is not possible when the energy gap between the zero-order states becomes comparable to  $\beta$ . Although we do not propose a specific form for  $H'$ , it probably consists primarily of electron repulsion terms. Mixing of the zero-order states by vibronic coupling terms could also be of some importance. Finally,  $H'$  may also contain some terms due to spin-orbit coupling, but the importance of these terms cannot be assessed owing to our lack of knowledge of the appropriate spin and orbital classifications of the low-lying charge-transfer states of iridium(III) complexes. There is little doubt that the ligand-localized state can be classified with some accuracy as a triplet,

but the relative importance of spin-orbit interactions and of the electron repulsion terms within the  $d\pi^*$  configuration is unknown. The "state" we refer to as  $\phi_{CT}^0$  therefore probably consists of a group of spin-orbit-coupled electronic levels whose spin and orbital parentages are presently obscure. In our treatment of the interaction between  $\phi_{CT}^0$  and  $\phi_{LL}^0$ , we neglect any multiplicity considerations and treat  $H'$  as if it were responsible for coupling only two states. Because of our previous definition of the zero-order states,  $\phi_{CT}^0$  and  $\phi_{LL}^0$ , it is implicit that diagonal terms of  $H'$  are included in  $E_{CT}^0$  and  $E_{LL}^0$ . Although these terms do not affect the form of the zero-order wave functions directly, they do make a contribution to the energy of the zero-order states, which is independent of the energy gap between them.

The Hamiltonian matrix, including  $H'$ , for the two zero-order states may be written as

$$\mathcal{H} = \begin{pmatrix} E_{CT}^0 & \beta \\ \beta & E_{LL}^0 \end{pmatrix} \quad (1)$$

The solution of this problem by first-order perturbation theory for the case  $E_{LL}^0 < E_{CT}^0$  yields the corrected form for the emitting excited state given by

$$\Psi_e' = \phi_{LL}^0 - \frac{\beta}{\Gamma} \phi_{CT}^0 \quad (2)$$

where  $\Gamma = E_{CT}^0 - E_{LL}^0$ .

The simple Hamiltonian matrix given by eq 1 may also be diagonalized exactly to yield the stationary emitting state

$$\Psi_e = \left( \frac{\epsilon - \Gamma}{2\epsilon} \right)^{1/2} \phi_{CT}^0 - \left( \frac{\epsilon + \Gamma}{2\epsilon} \right)^{1/2} \phi_{LL}^0 \quad (3)$$

where  $\epsilon$  is given by  $(4\beta^2 + \Gamma^2)^{1/2}$ . The correct energy of this state is given by

$$E_e = \frac{1}{2}(E_{CT}^0 + E_{LL}^0 - \epsilon) \quad (4)$$

**The Effect of the Interaction on the Radiative Lifetime of the Luminescing State.**—The radiative lifetime of the emitting state,  $\tau_0$ , is given by

$$\frac{1}{\tau_0} = KE_e^3 |\langle \Psi_G | M | \Psi_e \rangle|^2 \quad (5)$$

where  $\Psi_G$  is the wave function for the ground state,  $M$  is the transition moment operator, and, although  $K$  does change slightly with solvent, it is treated as a constant.

The substitution of the corrected wave function given by eq 2 into this formula yields

$$\frac{1}{\tau_0} = KE_e^3 |\langle \Psi_G | M | \phi_{LL}^0 \rangle - \frac{\beta}{\Gamma} \langle \Psi_G | M | \phi_{CT}^0 \rangle|^2 \quad (6)$$

At this point we make the approximation that the matrix element of  $M$  between  $\Psi_G$  and  $\phi_{LL}^0$  is negligible. This is justified by the fact that ligand-localized states of complexes are generally found to have very long radiative lifetimes relative to those of charge-transfer states. This approximation leads to the expression

$$\frac{1}{\tau_0} = KE_e^3 \frac{\beta^2}{\Gamma^2} |\langle \Psi_G | M | \phi_{CT}^0 \rangle|^2 \quad (7)$$

(15) J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, **92**, 7262 (1970).

We now express the radiative lifetime of  $\phi_{CT}^0$ ,  $\tau_{0(CT)}$ , by

$$\frac{1}{\tau_{0(CT)}} = K(E_{CT}^0)^3 |\langle \Psi_G | M | \phi_{CT}^0 \rangle|^2 \quad (8)$$

and substitute this result in eq 7 to yield

$$\frac{1}{\tau_0} = \frac{1}{\Gamma^2 \tau_{0(CT)}} \left( \frac{E_e}{E_{CT}^0} \right)^3 \beta^2 \quad (9)$$

When an analogous procedure is followed using the stationary state given by eq 3, the following result is obtained.

$$\frac{1}{\tau_0} = \frac{1}{\tau_{0(CT)}} \left[ \frac{E_e}{E_{CT}^0} \right]^3 \left( \frac{\epsilon - \Gamma}{2\epsilon} \right) \quad (10)$$

As expected, the general result given by eq 10 reduces to eq 9 in the limit where first-order perturbation theory is applicable, *i.e.*, when  $\beta \ll \Gamma$ . Both eq 9 and 10 reveal that  $\tau_0$  is proportional to the square of the mixing coefficient of  $\phi_{CT}^0$  in  $\Psi_e$ . It is this mixing coefficient, along with  $\tau_{0(CT)}$ , that is primarily responsible for determining the lifetime of the emitting state.

#### Application of the Model to Experimental Results

**[IrCl<sub>2</sub>(5,6-Mephen)<sub>2</sub>]Cl.**—Although eq 10 represents a result, which should be applicable for all values of  $\Gamma$ , it is cumbersome to use to estimate  $\beta$ . Equation 9, though more approximate in nature, predicts a linear dependence of  $1/\tau_0$  on  $\beta^2$  and is convenient to use for a rough estimate of  $\beta$ . We choose, therefore, to begin our treatment by applying eq 9 to a case where we believe first-order perturbation theory to be applicable. Table III indicates that in all of the solvents studied the luminescing state of [IrCl<sub>2</sub>(5,6-Mephen)<sub>2</sub>]Cl is at 20.5 kK although the lifetime is quite solvent dependent. This behavior is expected for a complex in which  $\phi_{LL}^0$  lies significantly below  $\phi_{CT}^0$ , *i.e.*, when  $\beta \ll \Gamma$ . The other complexes listed in Table III have emitting states whose energies are solvent dependent, though less so than the emitting charge-transfer state of [IrCl<sub>2</sub>(phen)<sub>2</sub>]Cl. This behavior probably indicates a large interaction between  $\phi_{CT}^0$  and  $\phi_{LL}^0$  in these molecules due to a small energy gap between the zero-order states. Therefore, eq 9 will be applied only to [IrCl<sub>2</sub>(5,6-Mephen)<sub>2</sub>]Cl.

The pivotal element in our treatment lies in the method of extracting the quantities in eq 9 from the experimental results. The interaction element,  $\beta$ , is treated as an undetermined parameter. In order to determine  $E_{CT}^0$  and  $\tau_{0(CT)}$ , we turn to our measurements on the parent molecule, [IrCl<sub>2</sub>(phen)<sub>2</sub>]Cl. This complex represents a situation in which  $\phi_{CT}^0$  is thought to lie far below  $\phi_{LL}^0$ , since the phosphorescing ligand triplet state of 1,10-phenanthroline lies at 22.2 kK, a value well above the 21.1 kK observed for the luminescence of this complex in an ethanol-methanol glass. Although the lifetime for this complex lengthens slightly as the energy of its luminescing state moves up, we assume that the energy gap between  $\phi_{CT}^0$  and  $\phi_{LL}^0$  is always large enough such that  $E_{CT}^0$  is identical with the energy of the observed luminescence. We further assume that the position of the zero-order charge-transfer state of [IrCl<sub>2</sub>(5,6-Mephen)<sub>2</sub>]Cl is identical with the energy of the CT state of the parent complex observed in each solvent. This assumption is sub-

stantiated by the observation that the energy of the charge-transfer luminescing state of [Ru(phen)<sub>2</sub>]Cl<sub>2</sub> is not affected by the introduction of methyl substituents in the 5,6 position of the ligands.<sup>16</sup> For our value of  $\tau_{0(CT)}$  for [IrCl<sub>2</sub>(5,6-Mephen)<sub>2</sub>]Cl, we choose the value of 13.95  $\mu$ sec determined for an ethanol-methanol solution of the parent complex. This choice of  $\tau_{0(CT)}$  is a reasonable one, because Table I reveals that the extinction coefficients of the allowed charge-transfer bands at about 25 kK are identical for the two complexes within the accuracy of the measurements. Furthermore, the energy gap between this highly allowed charge-transfer state and the low-lying charge-transfer state is about the same in both cases, and we feel that the matrix element coupling these two states in each molecule should be nearly identical also. This situation leads us to predict identical radiative lifetimes of the charge-transfer state for [IrCl<sub>2</sub>(phen)<sub>2</sub>]Cl and [IrCl<sub>2</sub>(5,6-Mephen)<sub>2</sub>]Cl on the basis of the intensity-borrowing model.<sup>5</sup> These assumptions concerning  $\tau_{0(CT)}$  are further supported by the fact that the radiative lifetime for [IrCl<sub>2</sub>(4,4'-Mebipy)<sub>2</sub>]Cl (11.07  $\mu$ sec) is identical within experimental error with that of [IrCl<sub>2</sub>(bipy)<sub>2</sub>]Cl (11.5  $\mu$ sec).<sup>3</sup> The latter two complexes represent a case in which methyl substitution of the ligand does not introduce a low-lying ligand-localized state and provides telling evidence that  $\tau_{0(CT)}$  is not changed by methyl substitution of the ligand, provided the extinction coefficient of the lending state is unaltered in the process.

We next consider the choice of a value of  $E_{LL}^0$  for [IrCl<sub>2</sub>(5,6-Mephen)<sub>2</sub>]Cl. The energy of the phosphorescent triplet state of the 5,6-Mephen ligand is found to be identical in ethanol and in ethanol-methanol glasses. Table III shows that the luminescing state of this complex is also independent of the solvent medium, a behavior characteristic of a ligand-localized state whose energy is not perturbed by any close-lying charge-transfer states. Furthermore, the lowest value of  $E_{CT}^0$  for this complex is seen to be 21.1 kK as compared to 20.5 kK for the emitting state. It therefore seems reasonable to choose the value of 20.5 kK for  $E_{LL}^0$ . This choice implies that the energy of the low-lying ligand-localized state is not affected by the charge-transfer state although its lifetime is quite sensitive to the presence of the latter state. Such a situation is consistent with the application of first-order perturbation theory to the problem.

The final parameters necessary for the application of eq 9 are values of  $\tau_0$  for each of the solvent systems. The quantum yield of [IrCl<sub>2</sub>(5,6-Mephen)<sub>2</sub>]Cl has been measured only in the ethanol-methanol glass where the value of 0.77 leads to a  $\tau_0$  of 86.1  $\mu$ sec. Quantum-yield measurements in the other glasses employed in this study were not feasible owing to the severe fracturing which occurred at 77°K. We decided to assume that the quantum yield in all of the glasses studied was identical with the value found in the ethanol-methanol glass. We thus presume that any alteration in the wave function for the luminescing state that changes the radiative lifetime brings about an equivalent change in the lifetime for the radiationless decay process. The validity of this assumption is difficult to assess, and it must be considered crude at best. It is com-

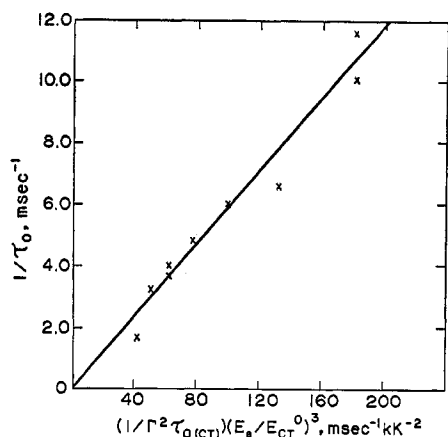


Figure 2.—Determination of  $\beta$  for  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$  by first-order perturbation theory (eq 9 in text). Experimental points are represented by  $\times$ 's. The square root of the slope yields  $\beta$ .

forting to notice, however, that the quantum yield of  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$  (0.77), which displays the closest approximation to a ligand-localized luminescence, is not too different from that of  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  (0.50), which is the closest approximation to a charge-transfer emitter. This relatively small change in the quantum yield between the two complexes is accompanied by large changes in both the radiative lifetime (86.10 to 13.95  $\mu\text{sec}$ ) and the radiationless lifetime (294.1 to 13.72  $\mu\text{sec}$ ). Although different molecules are being compared here, these data suggest that variation in the radiative and radiationless constants show parallel trends when a single complex is subjected to changes in solvent media.

We are now prepared to apply eq 9 to a calculation of  $\beta$  for  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$ . A complete list of the experimental parameters used in this determination is presented in Table IV. The most convenient method

TABLE IV  
PARAMETERS FOR THE DETERMINATION OF  $\beta$  FOR  
 $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$  BY  
FIRST-ORDER PERTURBATION THEORY<sup>a</sup>

Solvent	$E_{CT}^0$ , kK	$\Gamma$ , kK	$\tau_0$ , $\mu\text{sec}$
Ethanol	21.1	0.6	97.4
4:1 ethanol-methanol	21.1	0.6	86.1
1:1 glycerol-ethanol	21.2	0.7	151.3
2:1 glycerol-ethanol	21.3	0.8	167.3
Glycerol	21.4	0.9	205.6
4:1 glycerol-water	21.5	1.0	269.6
4:1 methanol-water	21.5	1.0	249.4
1:1 glycerol-water	21.6	1.1	306.6
9:10 $\text{MgCl}_2$ -water <sup>b</sup>	21.7	1.2	582.1

<sup>a</sup> See eq 9. <sup>b</sup> Wt/wt; other ratios, v/v.

of extracting  $\beta$  from the data is by plotting  $1/\tau_0$  vs.  $(1/\Gamma^2 \tau_0(CT))(E_e/E_{CT}^0)^3$ . Such a plot, displayed in Figure 2, should, according to eq 9, yield a straight line with a slope of  $\beta^2$ . In view of the numerous approximations and uncertainties encountered in our treatment, the plot is surprisingly linear, yielding a value for  $\beta$  of about  $250 \text{ cm}^{-1}$ . In this instance we deduce that first-order perturbation theory is a reasonable approximation, since the smallest energy gap encountered is  $600 \text{ cm}^{-1}$ . Some improvement is to be expected, however, by applying the more general result of eq 10.

When applying eq 10 to this complex, we used the

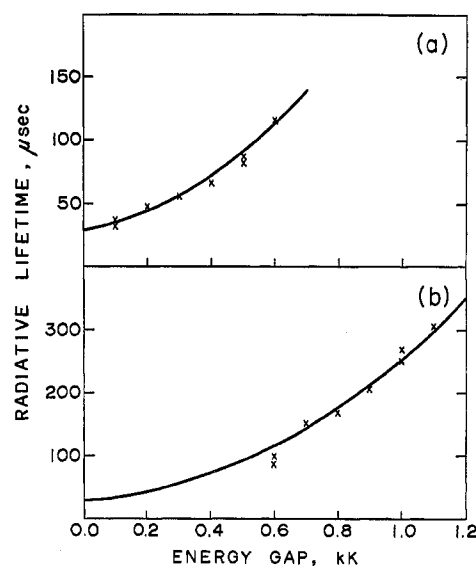


Figure 3.—Comparison of calculated and measured radiative lifetimes for (a)  $[\text{IrCl}_2(4,7\text{-Mephen})_2]\text{Cl}$  and (b)  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$ :  $\times$ 's, experimental radiative lifetimes; —, values calculated from eq 10 using  $\beta = 280 \text{ cm}^{-1}$ .

same zero-order parameters as used above. Values of  $\epsilon$  were first calculated from the initial guess of  $250 \text{ cm}^{-1}$ , and a final value of  $280 \text{ cm}^{-1}$  was found by varying  $\beta$  until a best fit to the experimental data was obtained. The final plot of  $\tau_0$  vs.  $\Gamma$  is shown in Figure 3 to illustrate the generally good agreement obtained between the experimental and calculated radiative lifetimes. The only experimental value that is in serious disagreement with the calculated lifetime is that observed for the  $\text{MgCl}_2\text{-H}_2\text{O}$  solvent system. This value was not used in the determination of  $\beta$  and is omitted in Figure 3. The disagreement was also encountered in the first-order perturbation treatment but was deemphasized by the reciprocal lifetime plot used in Figure 2.

**$[\text{IrCl}_2(4,7\text{-Mephen})_2]\text{Cl}$ .**—The phosphorescing triplet state of 4,7-dimethyl-1,10-phenanthroline is found to lie 0.9 kK above that of 5,6-dimethyl-1,10-phenanthroline suggesting that the ligand-localized state of the title complex should lie somewhat above that of  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$ . The charge-transfer state of this complex, however, is expected to lie very close to that of the parent  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  complex as was the case for  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$ . This set of circumstances is expected to lead to a much smaller energy gap between  $\phi_{CT}^0$  and  $\phi_{LL}^0$  than was previously encountered and to necessitate the use of eq 10 to interpret the solvent dependence of the lifetimes. Even the relative ordering of the zero-order states must be questioned here, since it is possible that the charge-transfer state could lie below the ligand-localized state in one or more of the solvent systems.

We begin our treatment of this complex with a discussion of the relative ordering of the zero-order states, considering first the possibility that a degeneracy of the zero-order states occurs. In this instance, eq 10 predicts that the radiative lifetime should be just twice  $\tau_0(CT)$ , aside from a small correction for  $(E_e/E_{CT}^0)^3$ . This prediction is independent of the value of  $\beta$ . If  $\phi_{CT}^0$  lies below  $\phi_{LL}^0$ , the predicted lifetime will be less than  $2\tau_0(CT)$ . As in the previous case, the  $\tau_0(CT)$  value is taken to be 13.95  $\mu\text{sec}$  from the parent complex,

and the experimental radiative lifetimes are calculated on the assumption of a solvent-independent quantum yield of 0.6 (measured in EtOH-MeOH). The smallest experimental value of  $\tau_0$  found in this way is about 35  $\mu\text{sec}$ , which is longer than  $2\tau_{0(\text{CT})}$  by a sufficient amount to suggest that  $\phi_{\text{LL}}^0$  lies below  $\phi_{\text{CT}}^0$  in all instances.

From Table III it is seen that the highest energy of the emitting state for this complex is 21.4 kK; this should provide a rough estimate of  $E_{\text{LL}}^0$ . That this value is a reasonable estimate is borne out by the fact that 21.4 kK is 0.2 kK below the energy of the observed triplet state of the ligand, as was the case in the choice of 20.5 kK for the  $E_{\text{LL}}^0$  value of  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$ . This choice of  $E_{\text{LL}}^0$  and the conclusion that  $E_{\text{LL}}^0 < E_{\text{CT}}^0$  in all instances forces us to use  $E_{\text{CT}}^0$  values that are somewhat higher than those observed for the parent complex. In order to obtain  $E_{\text{CT}}^0$  values, we choose to assume that  $\beta$  has the same value of  $280\text{ cm}^{-1}$  as found in the previous case and that  $E_{\text{CT}}^0$  is displaced from the values obtained for the parent complex by a constant amount. This reduces the number of variable parameters necessary for the application of eq 10 to just one, the constant energy difference between  $E_{\text{CT}}^0$  and the energy of the emitting state of the parent complex. A choice of 0.4 kK for this energy difference gives us good agreement between the experimental and calculated radiative lifetimes. With the exception of the experimental value of the  $\text{MgCl}_2\text{-H}_2\text{O}$  solvent (deleted in the figure), it is again evident from the plot shown in Figure 3 that the experimental and calculated values are in reasonable agreement. This treatment suggests that the zero-order states approach within  $\sim 100\text{ cm}^{-1}$  of each other in EtOH-MeOH. First-order perturbation theory is not applicable, and the luminescence of this complex cannot be classified either as charge transfer or as ligand localized.

**$[\text{IrCl}_2(4,7\text{-phenylphen})_2]\text{Cl}$ .**—A number of difficulties arise when attempts are made to apply eq 10 to the solvent dependence of the lifetime of this complex. It was previously concluded that the large increase in the extinction coefficient of the allowed charge-transfer band at 24–25 kK over that of the parent complex should lead to a shorter radiative lifetime for the low-lying charge-transfer state. It is therefore not possible to transfer  $\tau_{0(\text{CT})}$  directly from  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  to this complex. The best one can do is to calculate  $\tau_{0(\text{CT})}$  from the intensity-borrowing model by the relation<sup>5</sup>

$$\tau_{0(\text{CT})} = \frac{1}{K|M_{\text{SO}}|^2\epsilon} (E_{\text{S}} - E_{\text{T}})^2 \frac{E_{\text{S}}}{E_{\text{T}}^3} \quad (11)$$

The value of the energy (24.3 kK) of the lending state,  $E_{\text{S}}$ , and its extinction coefficient,  $\epsilon$ , are taken directly from Table I. The energy of the low-lying charge-transfer state,  $E_{\text{T}}$ , is estimated from the energy of the luminescing state, which is seen to be 20.7 kK from Table I. This leaves only the estimation of  $K|M_{\text{SO}}|^2$ , a quantity proportional to the spin-orbit-coupling matrix element for the interaction of the lending and borrowing charge-transfer states. As a first approximation, one might take the  $K|M_{\text{SO}}|^2$  value of  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  and transfer it to this complex. Although this would provide a rough estimate, previous studies have shown that phenyl substituents actually cause a decrease in  $K|M_{\text{SO}}|^2$ .<sup>3</sup> It is therefore assumed that phenyl substituents decrease the  $K|M_{\text{SO}}|^2$  value of

$[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  by 0.725, an amount equal to the decrease observed for  $[\text{Ru}(\text{phen})_3]\text{I}_2$  when phenyl substituents are introduced on the ligands. The  $K|M_{\text{SO}}|^2$  value of  $6.17 \times 10^{-7}$  for  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  is therefore assumed to be reduced to  $4.48 \times 10^{-7}$  for  $[\text{IrCl}_2(4,7\text{-phenylphen})_2]\text{Cl}$ . Substitution of these factors into eq 11 produces a  $\tau_{0(\text{CT})}$  value of 8.4  $\mu\text{sec}$ .

To obtain values of the zero-order energies,  $E_{\text{LL}}^0$  and  $E_{\text{CT}}^0$ , we begin, as before, with a consideration of the relative ordering of the zero-order states. In this instance  $2\tau_0 = 16.8\text{ }\mu\text{sec}$ , a value nearly equal to the  $\tau_0$  (18.0  $\mu\text{sec}$ ) observed for the complex in 4:1 ethanol-methanol solution. This suggests that the zero-order states are degenerate in this solvent. According to eq 4 the luminescing state lies below the degenerate zero-order states by  $\beta$ . Assuming that  $\beta$  is  $280\text{ cm}^{-1}$  for this complex, as was done for the previous two, we estimate  $E_{\text{CT}}^0$  and  $E_{\text{LL}}^0$  to be 19.8 kK in this solvent. This fixes the value of  $E_{\text{LL}}^0$  but still leaves  $E_{\text{CT}}^0$  to be determined for the remaining solvents.

There is unfortunately little that can be done to provide reliable estimates of  $E_{\text{CT}}^0$ . It is tempting to assume that there is a constant difference between the  $E_{\text{CT}}^0$  value of this complex and that of  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  as was done for  $[\text{IrCl}_2(4,7\text{-Mephen})_2]\text{Cl}$ . Since  $E_{\text{CT}}^0$  in 4:1 ethanol-methanol has been located at 19.8 kK, this would suggest the constant energy difference to be 1.3 kK. When such a procedure is followed, the calculated  $\tau_0$  values are found to lengthen through the range of solvents employed far more than the observed  $\tau_0$  values. One difficulty appears to be that the energy of the charge-transfer state of the phenyl-substituted complex probably does not move as far in these solvents as does that of the parent complex. For example, it is found that the energy of the charge-transfer state of  $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$  is moved by 0.7 kK upon changing from 4:1 ethanol-methanol to 4:1 methanol-water, whereas that of the phenyl-substituted analog is moved by only half of this amount. This suggests that the assumption of a constant energy difference between  $E_{\text{CT}}^0$  for the phenyl-substituted and parent complexes is invalid. A smaller movement of  $E_{\text{CT}}^0$  in the solvent systems employed would lead to less variation in the calculated  $\tau_0$  values and would therefore lead to better agreement with the experimental data. A second alternative would be to employ a larger value of  $\beta$  for this complex. The larger interaction of  $\phi_{\text{CT}}^0$  and  $\phi_{\text{LL}}^0$  would also cause a smaller variation in the calculated  $\tau_0$  values and would bring the calculation into better agreement with the experimental results.

Because of the uncertainties in estimating approximate values of  $E_{\text{CT}}^0$  and  $\beta$ , no further attempts to calculate the solvent dependence of the lifetimes of this complex have been made. In spite of our inability to determine the necessary parameters to apply eq 10 with any certainty in this instance, the trends in the lifetime leave little doubt that modulations of dπ\*-ππ\* interactions are also responsible for the observed solvent dependences.

### Summary and Conclusions

We have presented a study of the luminescence lifetimes of three complexes containing substituted phenanthroline ligands in eight different solvent systems. Of the 24 lifetimes, which were measured, there is no exception to the rule that an increase in the observed



lifetime produced by a change in solvent may be correlated with an increase in the energy of the luminescing state of the parent  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  molecule in the same solvent. This excellent correlation provides telling evidence that it is the alteration of the energy gap between the lowest lying charge-transfer and ligand-localized states that is responsible for the solvent effects on the luminescence lifetimes.

Our model for the interpretation of the solvent dependence of the radiative lifetimes of these complexes includes the assumption that the luminescence quantum yield is constant in all solvents. This is equivalent to assuming that both the radiationless and radiative decay rates change by an equivalent amount. While our results indicate that both the radiationless and radiative decay rates must change, we have no *a priori* evidence that they should change equally. Until the appropriate quantum yields can be determined, the validity of this approximation will remain unknown. The good agreement between the  $\tau_0$  values obtained under this assumption and those calculated by our model suggests that variations in the quantum yields with solvent must be small.

Our model for the interpretation of the solvent dependence of lifetimes is designed to utilize a maximum amount of experimental information; this is its great strength, since it permits the estimation of hypothetical parameters from measurable quantities and thus allows one to avoid the problems of calculating wave functions and energies. We also avoid the difficult problem of devising a mechanism to interpret the solvent shifts in the energy of charge-transfer states and, instead, simply take the energy of the charge-transfer state from a measurement in the appropriate solvent. The model thus glosses over many of the details, which might be considered in a calculation, by letting a molecule that is closely related to the one of interest solve the problem.

The general failure of the model to provide an interpretation of the lifetimes that were determined for the  $\text{MgCl}_2\text{-H}_2\text{O}$  solvent system is not too surprising. The solvent-solute interactions in this type of system are undoubtedly very large, and considerable ion pairing may result from the high  $\text{Cl}^-$  concentration. For these conditions our treatment is apparently inapplicable. We feel that the lack of agreement between the calculated and measured lifetimes in this case is symptomatic of the peculiarity of this unusual solvent and not of any great shortcomings of the model.

The most important single achievement of this model is that it provides a measure of the  $d\pi^*-\pi\pi^*$  configuration interaction between low-lying charge-transfer and ligand-localized states. The value of  $280\text{ cm}^{-1}$  obtained for  $\beta$  provides a quantitative estimate of this interaction and enables one to deduce when it is possible to classify emitting states by a  $d\pi^*$  or  $\pi\pi^*$  label. This value of  $\beta$  indicates that when zero-order ligand-localized and charge-transfer states lie within  $\sim 0.3\text{ kK}$  of each other, it is not valid to classify the resulting stationary states either as charge transfer or ligand localized. As the energy gap between the zero-order states becomes progressively larger than  $0.3\text{ kK}$ , however, it becomes more and more meaningful to label the states in that way. For example, our previous assignment of the emission of  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$  in 4:1 methanol-water as arising from a ligand-localized state

is quite justifiable, because the energy gap between the zero-order states is estimated to be  $1.0\text{ kK}$ . Even though this is a case where the energy of the ligand-localized state is unaffected by the presence of the higher lying charge-transfer state, it is interesting to note that the luminescence lifetime appears to be due entirely to the small charge-transfer contribution to the stationary state. It may quite possibly be true that the luminescence lifetimes of all complexes whose emitting states are ligand localized are really controlled by mixing with charge-transfer states. We feel, however, that the classification of such states as ligand localized is still meaningful whenever the contribution of the charge-transfer state to the stationary state wave function is small (less than 10%), so that the energy of the stationary state is nearly identical with that of the ligand-localized parent.

The prerequisites necessary to classify the luminescences of  $[\text{IrCl}_2(4,7\text{-Mephen})_2]\text{Cl}$  and  $[\text{IrCl}_2(4,7\text{-phenylphen})_2]\text{Cl}$  by the model, which neglects interactions between  $d\pi^*$  and  $\pi\pi^*$  configuration, are not present. The zero-order charge-transfer and ligand-localized states of these complexes are generally split by an energy gap, which is less than, or of the same order as,  $\beta$ , and the energies of the stationary states are substantially different from those of the zero-order states. The emitting states of these two complexes in the 4:1 ethanol-methanol glasses in which they are normally studied are best considered as nearly equal mixtures of charge-transfer and ligand-localized parentage.

Our estimation of  $\beta$  is entirely consistent with the assignment of the emitting states of  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  and  $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$  as charge transfer.<sup>4,17</sup> The energy gap between the solvated ligand triplet state and the emitting state is  $1.1\text{ kK}$  for the former complex and  $2.4\text{ kK}$  for the latter. If one assumes that these ligand-localized triplets are red shifted by  $0.2\text{ kK}$  in the complexes, then the energy gaps are estimated to be  $0.9\text{ kK}$  in  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  and  $2.2\text{ kK}$  in  $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$ . For  $\beta$  equal to  $0.280\text{ kK}$ , we calculate the contribution of the ligand-localized triplet,  $\beta^2/\Gamma^2$ , to the emitting state to be 10% in the former case and only 2% in the latter. Since a contribution of 10% by the ligand-localized triplet to the emitting state has practically no effect on its radiative properties and energy, we feel that the classification of the emitting states of these two complexes as charge transfer is quantitatively justified. These conclusions differ from those reached by DeArmond and Hillis<sup>6</sup> for the same molecules.

Prior to this study, one might have suspected that an enormous change in the lifetime of a complex could be caused by putting it in a medium that would invert the normal ordering of its charge-transfer and ligand-localized states. Our study reveals, however, that the lifetime is a rather insensitive function of the relative energies in the immediate area of a crossing of the zero-order states, because these states interact with one another when all the terms in the Hamiltonian are included. This leads to a stationary luminescing state that is nearly an equal admixture of the charge-transfer and ligand-localized contributions in the region where

(17) G. A. Crosby and D. H. W. Carstens in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 309. Note: In this partial study the *cis*-dichlorobis(1,10-phenanthroline)iridium(III) ion was incorrectly identified as the tris species.

the energy gap between these states is less than or comparable to  $\beta$ . This study shows that the largest solvent effects on the lifetimes are actually found for  $[\text{IrCl}_2(5,6\text{-Mephen})_2]\text{Cl}$  where the energy of the charge-transfer state is substantially above that of the ligand-localized state.

In conclusion, we wish to point out that this is, to the best of our knowledge, the first quantitative estimate of the validity of the widely used model to label states as charge transfer or ligand localized in these kinds of complexes. At present we have no way of deducing whether our determination of  $\beta$  for the species studied here will provide a rough estimate of such interactions

for other complexes. If  $\beta$  is determined primarily by electron repulsion terms rather than spin-orbit-coupling terms, as we have suggested, it is probably reasonable to assume that similar values of  $\beta$  will apply to complexes of similar ligands with different metals. The values of  $\beta$  might be quite sensitive, however, to large alterations of the ligands. Our study provides no means of estimating the magnitude of the interactions of crystal field (d-d) with either ligand-localized or charge-transfer states. If, in the future, the magnitude of such interactions can be deduced, a complete analysis of the range of validity of pure configuration labeling will be possible.

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## Pseudooctahedral Cobalt(III), Nickel(II), and Cadmium(II) Complexes of Linear, Sexadentate, Fluorinated Schiff Base Ligands

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New pseudooctahedral complexes,  $\text{Ni}(\text{BTAT})$ ,  $\text{Ni}(\text{BHAT})$ ,  $\text{Cd}(\text{BTAT})$ ,  $\text{Co}(\text{BTAT})\text{X}$ , and  $[\text{Co}(\text{BTAT})]_2\text{CoY}_4$  where  $\text{X}^- = \text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ , and  $\text{ClO}_4^-$  and  $\text{Y}^- = \text{Cl}^-$  and  $\text{SCN}^-$ , have been prepared from the linear Schiff base ligands bis(trifluoroacetylacetonate)triethylenetetramine, abbreviated  $\text{H}_2\text{BTAT}$ , and bis(hexafluoroacetylacetonate)triethylenetetramine, abbreviated  $\text{H}_2\text{BHAT}$ . Characterization of the complexes by elemental analyses, molecular weight, magnetic susceptibility, and conductivity measurements and by nmr, infrared, visible, and mass spectral data has shown that the reactions proceed stereospecifically with formation of only the *s-cis* isomer.

### Introduction

Studies on volatile metal chelates containing  $\beta$ -diketonate ligands have shown that maximum volatility results when the ligands are highly fluorinated and simultaneously satisfy the charge and coordination number of the metal ion.<sup>1-3</sup> We have used these criteria as guidelines in the synthesis of some potentially volatile transition metal complexes containing divalent metal ions and fluorinated Schiff base ligands.

The usual octahedral geometry of the dipositive transition metals dictates that if inner complexes are to result, the Schiff base ligands should be sexadentates and capable of coordinating to the metal as dinegative ions. While numerous metal complexes containing sexadentate Schiff base ligands have been prepared by Lions, *et al.*,<sup>4</sup> most of these were prepared from linear tetradentate ligands containing terminal  $\text{NH}_2$  groups with two bridging sulfur atoms in the backbone and various aldehydes or, in a few cases, acetylacetonate. For purposes of this study, ligands derived solely from linear tetramines and fluorinated  $\beta$ -diketonates were

used. Specifically, the sexadentate ligand obtained by condensation of 2 equiv of trifluoroacetylacetonate with 1 equiv of triethylenetetramine (trien), abbreviated  $\text{H}_2\text{BTAT}$ , and that obtained from 2 equiv of hexafluoroacetylacetonate and 1 equiv of trien, abbreviated  $\text{H}_2\text{BHAT}$ , have been prepared and used to synthesize complexes abbreviated  $\text{Ni}(\text{BTAT})$ ,  $\text{Ni}(\text{BHAT})$ ,  $\text{Cd}(\text{BTAT})$ ,  $[\text{Co}(\text{BTAT})]\text{X}$ , and  $[\text{Co}(\text{BTAT})]_2\text{CoY}_4$ , where  $\text{X}^- = \text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ , and  $\text{ClO}_4^-$  and  $\text{Y}^- = \text{Cl}^-$  and  $\text{SCN}^-$ .<sup>5</sup>

While none of the neutral complexes possess the desired high volatility,  $\text{Ni}(\text{BHAT})$  provides a new example of a Schiff base compound obtained by condensation of a carbonyl oxygen atom adjacent to a presumably deactivating  $\text{CF}_3$  group.<sup>6,7</sup> To date only one other metal complex of this type is known. It is the macrocyclic  $\text{Ni}(\text{II})$  complex  $\text{Ni}(\text{TAT})\text{X}$ , where TAT is the uninegative, fluorinated tetramine ligand 11-methyl-13-(trifluoromethyl)-1,4,7,10-tetraazacyclotrideca-10,12-diene, which can be prepared in several ways including rearrangement of the  $\text{Ni}(\text{BTAT})$  complex characterized in this paper.<sup>8</sup> Although four geometrical isomers are possible for the sexadentate complexes, studies suggest that the syntheses are stereospecific.

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