Quantum Efficiencies of Transition Metal Complexes. III. The Effect of Ligand Substituents on Radiative and Radiationless Processes[1]

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Abstract: Luminescence quantum yields and lifetimes of several complex ions of 4,4′-diphenyl-2,2′-bipyridine and 4,7-diphenyl-1,10-phenanthroline with ruthenium(II) and iridium(III) have been measured, and values of the radiative and radiationless decay constants have been calculated. From a comparison of these data with those from complexes of the parent 2,2′-bipyridine and 1,10-phenanthroline ligands, a quantitative assessment of the effects of ligand phenyl substituents on quantum yields, lifetimes, and decay constants has been made. A semiempirical spin–orbit coupling model provides an excellent interpretation of the changes in both the radiative and radiationless constants. Possible applications of ligand substituents for improving the efficiencies of luminescent materials are suggested.

The ligands 2,2′-bipyridine and 1,10-phenanthroline form complexes with a large number of the transition metals. A number of these complexes luminesce in the visible region, and several investigations have been devoted to the characterization and identification of the origins of the emitted light. In particular, the luminescence of the tris complexes of 2,2′-bipyridine and 1,10-phenanthroline with ruthenium(II) have been extensively studied.[2–9] The luminescence in each of these instances is now thought to arise primarily from a spin-forbidden charge-transfer $(d\pi^*) \rightarrow A_1$ transition. Recent studies have also revealed that the luminescence quantum yields of these complexes are high and that the radiative lifetimes at 77°K are on the order of 5–10 μsec.[9,10]

Although much less work has been done on the iridium(III) complexes of these ligands, the luminescence spectra of *cis*-dichlorobis(1,10-phenanthroline)-iridium(III) chloride[11] and *cis*-dichlorobis(2,2′-bipyridine)iridium(III) chloride[12,13] have been reported. The emission of the former ion has been assigned by Crosby and Carstens to a charge-transfer transition,[11] and we have made the same assignment in the case of the latter species.[12] Measurements of the quantum yield and lifetime of the luminescence of the phenanthroline complex at 77°K reveal that the emission occurs with high efficiency and that the radiative lifetime is 14 μsec.[10] Recently, DeArmond and Hillis[13] suggested that these emissions be labeled "delocalized molecular" due to large mixing of d and π orbitals, but our evidence does not support their contentions (*vide infra*).

In a previous publication we reported the effect of ligand substituents on the electronic spectra of several 2,2′-bipyridine and 1,10-phenanthroline complexes of ruthenium(II) and iridium(III).[12] Phenyl substitution on the 4,4′ positions of the 2,2′-bipyridine and 4,7 positions of the 1,10-phenanthroline ligands produced relatively small changes in the absorption and emission spectra of the complexes. In most instances, the phenyl substituents altered their optical properties without changing the fundamental nature of the observed transitions.

In the present work we report the effect of ligand phenyl substituents on the luminescence quantum yields, lifetimes, and low-temperature absorption spectra of some of these ruthenium(II) and iridium(III) complexes. Such data greatly expand our previous knowledge of the "fine tuning" capabilities of ligand substituents and establish additional guidelines for designing luminescent molecules. The data enable us to make quantitative estimates of both the radiative and radiationless lifetimes of the luminescing states and thereby provide a detailed analysis of the effect of substituents on the decay of the lowest electronic excited levels of these d^6 complexes.

Experimental Section

The synthetic methods and purification procedures for the complexes investigated here have been reported previously.[12] Absolute ethanol (U.S. Industrial Chemical Co., USP-NF) and absolute methanol (Baker Analyzed) were used without further purification. All spectroscopic measurements were performed at liquid nitrogen temperature on samples dissolved in a glass that consisted of four parts ethanol to one part methanol by volume.

Low-temperature absorption spectra were measured in clear-unfractured glasses in 1.76-cm cylindrical Pyrex cells. The baseline of the Cary Model 14 spectrophotometer was adjusted to zero from 350–600 nm with a blank ethanol–methanol glass submersed in liquid nitrogen in a Martin optical Pyrex dewar in the sample compartment and a 2-cm quartz cell containing ethanol–methanol at room temperature in the reference chamber. Care was taken to position the cylindrical sample cell such that the light from the source passed directly through the center of the cell. Once the

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[1] Research supported by AFOSR(NC)-OAR, USAF Grant No. 68-1342.

[2] J. P. Paris and W. W. Brandt, *J. Amer. Chem. Soc.*, 81, 5001 (1959).

[3] J. P. Paris, Ph.D. Dissertation, Purdue University, Lafayette, Ind., 1960.

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[6] D. M. Klassen and G. A. Crosby, *J. Chem. Phys.*, 48, 1853 (1968).

[7] J. N. Demas and G. A. Crosby, *J. Mol. Spectrosc.*, 26, 72 (1968).

[8] D. M. Klassen, Ph.D. Dissertation, University of New Mexico, Albuquerque, N. M., 1966.

[9] F. E. Lytle and D. M. Hercules, *J. Amer. Chem. Soc.*, 91, 253 (1969).

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

[11] 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 that in this partial study *cis*-dichlorobis(1,10-phenanthroline) ion was incorrectly identified as the tris species.

[12] R. J. Watts and G. A. Crosby, *J. Amer. Chem. Soc.*, 93, 3184 (1971).

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

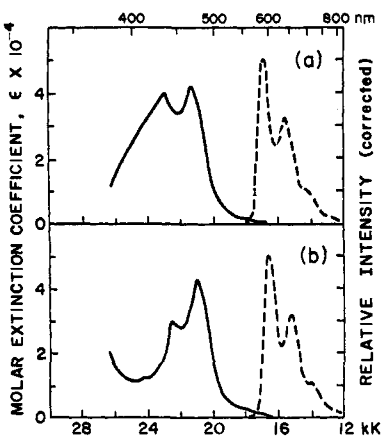

Figure 1. Absorption (——) and luminescence (- - -) spectra of phenyl-substituted ruthenium(II) complexes in ethanol–methanol glass (4:1, v/v) at 77°K: (a) [Ru(diphenylphen)$_3$]Cl$_2$; (b) [Ru(diphenylbipy)$_3$]Cl$_2$.

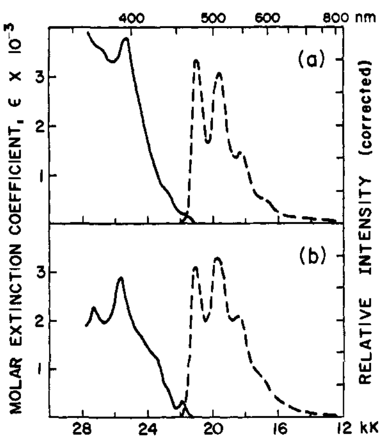

Figure 2. Absorption (——) and luminescence (- - -) spectra of unsubstituted iridium(III) complexes in ethanol–methanol glass (4:1, v/v) at 77°K: (a) [IrCl$_2$(phen)$_2$]Cl; (b) [IrCl$_2$(bipy)$_2$]Cl.

base line was adjusted, the blank was removed and the glass containing the sample was clamped into position. Sample concentrations were adjusted to yield solutions with optical densities less than 1.0 from 350 to 600 nm in order to minimize errors due to sample luminescence. Dry nitrogen gas was passed into the top portion of the optical dewar throughout both the baseline adjustment and the measurements to minimize the formation of ice crystals. Owing to the scattering of light from the round surfaces, no attempt was made to measure absorption spectra at wavelengths shorter than 350 nm by this technique. To calculate extinction coefficients from the low-temperature absorption spectra, a volume contraction of 20% between room temperature and 77°K was assumed.[14] Extinction coefficients reproducible with ±20% were obtained.

The flash lamp and firing circuit used for lifetime measurements have been described elsewhere.[7] Light from the EG&G FX-12 xenon flash lamp was passed through a filter system consisting of 2 cm of copper(II) sulfate solution (200 g/l.), a Corning 4-71 glass filter, and a Balzers 437-nm narrow-bandpass filter. For the iridium complexes, the emitted light was passed through 2 cm of nickel(II) sulfate solution (250 g/l.) and a Balzers 522 narrow-bandpass filter; for the ruthenium complexes the emission was directed through 2 cm of tris(2,2′-bipyridine)iron(II) chloride solution (0.6 g/l.) and a Corning 2-59 filter. Luminescence decays were monitored with an EMI 9558QC photomultiplier whose signal was displayed on a Tektronix 535A oscilloscope and photographed. Time marks from a Tektronix 184 time-mark generator were also superimposed upon each decay curve. The decay times and standard deviations were determined by a linear least-squares fit of ln *I vs. t*.

Quantum yields were measured by a modified Parker–Rees technique,[15,16] previously described in detail by Demas and Crosby.[14] Eastman White Label fluorescein was purified by the method of Orndorff and Hemmer.[17] A freshly prepared solution of this fluorescein in 0.1 *N* sodium hydroxide (less than 6×10^{-7} *M*) at 25° was assumed to have a quantum yield of 0.90, the value adopted in this laboratory.[14] A refractive index value of 1.41 was assumed for the ethanol–methanol glass at 77°K.[14] The sample and reference cells used for the quantum yield measurements were unblackened cylindrical Pyrex tubes, identical with those used for the low-temperature absorption spectra. Sample solutions were prepared and cooled to 77°K immediately prior to quantum yield determinations. No evidence of dissociation or photodecomposition of the complexes was noted. For excitation of both the complexes 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 set at a 5.5-nm bandpass. In addition to the monochromator, a Corning 3-73 glass filter and an Optics Technology 450-nm blue-edge filter were employed to improve the spectral purity. The absorbance values required for the quantum yield measurements were obtained by the same methods used for measuring the low-temperature absorption spectra. The absorbance was kept below 0.05/cm for the samples and 0.005/cm for the standard for the quantum yield measurements.

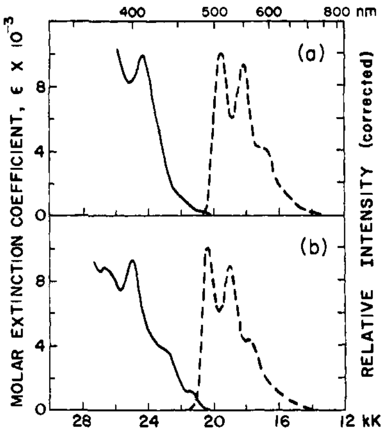

Figure 3. Absorption (——) and luminescence (- - -) spectra of phenyl-substituted iridium(III) complexes in ethanol–methanol glass (4:1, v/v) at 77°K: (a) [IrCl$_2$(diphenylphen)$_2$]Cl; (b) [IrCl$_2$(diphenylbipy)$_2$]Cl.

Results

The low-temperature absorption spectra of the iridium(III) complexes containing both the substituted and unsubstituted ligands and of the ruthenium(II) complexes containing substituted ligands are presented in Figures 1–3. For convenience, their luminescence spectra are also reproduced. The low-temperature absorption and emission spectra of [Ru(bipy)$_3$]Cl$_2$[18] and [Ru(phen)$_3$]I$_2$ have been presented elsewhere.[6]

In addition to the intense absorption bands between 400 and 500 nm, which are also evident in the room-temperature spectra,[12] the low-temperature absorption spectra of [Ru(diphenylbipy)$_3$]Cl$_2$ and [Ru(diphenylphen)$_3$]Cl$_2$ display slight shoulders at about 17.8 kK. These shoulders overlap the luminescence spectra in both instances.

Prominent bands, which were found in the room-temperature absorption spectra of the iridium(III)

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

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

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

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

(18) For identification of abbreviations, see footnote *a* in Table I.

Table I. Radiative Lifetimes of Iridium Complexes Calculated from Integrated Absorption Intensities

Complex[a]	$\bar{\nu}_a$, kK	$\bar{\nu}_e$, kK	f	τ_0 (calcd),[b] μsec
$[IrCl_2(bipy)_2]Cl$	21.8	19.2	0.000850	2.40
$[IrCl_2(diphenylbipy)_2]Cl$	21.1	18.9	0.00298	0.794
$[IrCl_2(phen)_2]Cl$	21.7	19.3	0.000517	4.39
$[IrCl_2(diphenylphen)_2]Cl$	20.7	18.2	0.000327	6.94

[a] Abbreviations of ligands: bipy = 2,2′-bipyridine, diphenylbipy = 4,4′-diphenyl-2,2′-bipyridine, phen = 1,10-phenanthroline, diphenylphen = 4, 7-diphenyl-1,10-phenanthroline. [b] Calculated from eq 1.

Table II. Quantum Yields, Lifetimes, and Rate Constants for Ruthenium and Iridium Complexes at 77°K[a]

Complex[b]	Quantum yield, Q	Measured lifetime, τ_m, μsec	Intrinsic lifetime,[c] τ_0, μsec	Radiative rate constant, k_r, μsec^{-1}	Quenching rate constant,[d] k_q, μsec^{-1}
$[Ru(bipy)_3]Cl_2$[e]	0.376 ± 0.036	5.21 ± 0.06	13.9	0.0719	0.1200
$[Ru(diphenylbipy)_3]Cl_2$	0.573 ± 0.032	4.68 ± 0.08	8.2	0.122	0.0913
$[Ru(phen)_3]I_2$[e]	0.584 ± 0.065	9.79 ± 0.12	16.8	0.0595	0.0426
$[Ru(diphenylphen)_3]Cl_2$	0.682 ± 0.029	9.58 ± 0.12	14.0	0.0714	0.0332
$[IrCl_2(bipy)_2]Cl$	0.516 ± 0.012	5.94 ± 0.05	11.5	0.0869	0.0815
$[IrCl_2(diphenylbipy)_2]Cl$	0.881 ± 0.022	5.03 ± 0.08	5.7	0.175	0.0237
$[IrCl_2(phen)_2]Cl$[e]	0.496 ± 0.017	6.92 ± 0.05	14.0	0.0714	0.0731
$[IrCl_2(diphenylphen)_2]Cl$	0.829 ± 0.054	14.95 ± 0.15	18.0	0.0556	0.0114

[a] Measured in ethanol–methanol (4:1, v/v). [b] For identification of abbreviations see Table I, footnote *a*. [c] Calculated from eq 2. [d] Calculated from eq 5. [e] Values from ref 10.

complexes between 24 and 26 kK,[11,12] are seen with somewhat higher resolution at low temperature. A number of additional well-resolved shoulders are also distinguishable. The low-temperature absorption spectra of all the iridium complexes display resolved peaks that overlap the emissions, whereas only $[IrCl_2(bipy)_2]Cl$ shows such a resolved peak in the low-energy tail of its room-temperature spectrum.[12] In the case of 2,2′-bipyridine complexes of iridium(III), 4,4′-phenyl substitution of the ligand brings about a red shift in the position of this overlapping peak from 21.8 kK for the parent molecule to 21.1 kK for the phenyl-substituted species. Its maximum extinction coefficient increases from about 400 l. mol^{-1} cm^{-1} for $[IrCl_2(bipy)_2]Cl$ to 1000 l. mol^{-1} cm^{-1} for $[IrCl_2(diphenylbipy)_2]Cl$. In the spectra of the 1,10-phenanthroline complexes, this low-energy band red shifts from 21.7 kK for $[IrCl_2(phen)_2]Cl$ to 20.7 kK for $[IrCl_2(diphenylphen)_2]Cl$, but its maximum extinction coefficient has roughly the same value of 200 l. mol^{-1} cm^{-1} for both molecules.

Oscillator strengths for these low-energy absorption bands of the iridium(III) complexes are listed in Table I. They are estimated to be accurate only within ±40% because of uncertainties in both the extinction coefficients and the band shapes. For the ruthenium complexes, no attempt was made to determine the oscillator strengths of these weak bands because of their poor resolution.

With the use of a modified version of the Strickler–Berg[19] formula given in eq 1, the radiative lifetimes of the iridium complexes reported in Table I were calculated. In eq 1, τ_0 represents the radiative lifetime

$$\tau_0^{-1} = 0.667n^2f(g_l/g_u)(\bar{\nu}_e^3/\bar{\nu}_a) \qquad (1)$$

of the excited state, n is the refractive index of the medium, f is the oscillator strength, g_l and g_u are the degeneracies of the ground and excited states, respectively, and $\bar{\nu}_e$ and $\bar{\nu}_a$ represent the average photon energies of the emission and absorption spectra, respectively. A value of 1.41 was used for n,[14] and the degeneracy factors were all assumed to be unity.

The measured quantum yields of the complexes are presented in Table II. In all instances phenyl substitution of the ligands produces a significant increase in the luminescence yield. Quantum efficiencies of the phenyl-substituted complexes are all in excess of 0.5, and those of $[IrCl_2(diphenylphen)_2]Cl$ and $[IrCl_2(diphenylbipy)_2]Cl$ are within experimental error of unity. Although estimated to be accurate only to ±30%, the precision in the quantum yield measurements, as indicated by the standard deviations, is considerably better than this. Therefore, the apparent trends are believed to be quite reliable.

Placing phenyl substituents on the ligands also slightly decreases the measured luminescence decay times of the emitting states (Table II). The lone exception is the 1,10-phenanthroline complex of iridium(III), where the lifetime shows a substantial increase from 6.92 μsec for the unsubstituted complex to 14.95 μsec for the phenyl-substituted one.

Radiative lifetimes (τ_0) for the emitting states reported in Table II were calculated from the equation

$$\tau_0 = \tau_m/Q_r \qquad (2)$$

where τ_m is the measured lifetime and Q_r is the quantum yield for the radiative decay of the emitting state. The latter was assumed to be equal to Q_m, the measured quantum yield for the overall luminescence from the complex. It is evident from these computed values that the same trends, shown by both the measured lifetimes and by the radiative lifetimes calculated by eq 1, are also shown by the radiative lifetimes determined from eq 2.

Discussion

Low-Temperature Absorption Spectra. Owing to the overlap of the low-temperature absorption and luminescence spectra, we feel that there can be little doubt that the long-wavelength absorption bands are due to direct transitions from the ground to the emitting states. Since the emission spectra of all the phenyl-substituted complexes, except one, have been assigned to charge-transfer $(d\pi^*) \rightarrow A_1$ transitions, we assign

(19) S. J. Strickler and R. Berg, *J. Chem. Phys.*, 37, 814 (1962).

the inverse long-wavelength absorption bands to charge-transfer transitions also. The single exception is [IrCl$_2$(diphenylphen)$_2$]Cl. Although the low-energy absorption band of this molecule also appears to be due to the inverse of the transition responsible for the luminescence, the orbital nature of the emissive state has not yet been assigned.

Further evidence that the transitions responsible for the low-energy absorption bands are the inverses of those responsible for the luminescence spectra is implicit in the band shifts occurring upon substitution. Phenyl substitution of the 2,2′-bipyridine in [IrCl$_2$(bipy)$_2$]Cl produces a red shift of 0.7 kK in the energy of the long-wavelength absorption band, whereas phenyl substitution of 1,10-phenanthroline in [IrCl$_2$(phen)$_2$]Cl causes a red shift of 1.0 kK. These figures are in reasonable agreement with the red shifts of 0.7 and 1.6 kK that have been previously observed for the luminescences of [IrCl$_2$(bipy)$_2$]Cl and [IrCl$_2$(phen)$_2$]Cl,[12] respectively, upon phenyl substitution of the ligands.

The data collected in Table II also provide further evidence in support of an intensity-borrowing model recently proposed to rationalize the values obtained experimentally for the radiative lives of luminescent complexes of this type.[10] The model invokes intensity borrowing through spin–orbit coupling by the emissive state from the first highly allowed charge-transfer state lying at higher energy. Significantly, for [IrCl$_2$(diphenylbipy)$_2$]Cl, the extinction coefficient of the low-energy absorption band is more than twice that for [IrCl$_2$(bipy)$_2$]Cl. This increase closely parallels the increase of a factor of 3 in the extinction coefficient of the charge-transfer band at 24–26 kK in line with expectations based on the model.

Owing to the lack of resolution of the absorption spectra in the low-energy region for the ruthenium(II) complexes, the extinction coefficients for transitions to these excited states are somewhat uncertain. In this general region, however, the intensities do increase roughly by a factor of 2 upon phenyl substitution of the ligands. These enhancements are again in good agreement with the factor of 2 increases in the extinction coefficients of the highly allowed charge-transfer bands at 20–22 kK. Thus the absorption spectra of the ruthenium complexes also lend support to the previously proposed intensity-borrowing model.

The only exception to this general behavior is found for the iridium(III) complexes of 1,10-phenanthroline. Although the intensity of the charge-transfer band at 24–26 kK increases by a factor of about 2.5 upon phenyl substitution of this ligand, the extinction coefficient of the low-energy band at 20–22 kK is not affected. This result suggests that the lowest excited state of [IrCl$_2$(diphenylphen)$_2$]Cl cannot be classified in the same way as it is for [IrCl$_2$(phen)$_2$]Cl or any of the other complexes we have discussed; rather, phenyl substitution of the ligands in this instance has brought about a major change in the nature of the lowest excited state instead of a simple modification of its features. The same conclusion was reached previously on the basis of the close proximity of a low-lying ligand-localized triplet state to the luminescing state of this complex.[12]

Quantum Yields. Before examining the means by which ligand substituents alter the luminescence quantum yields of these complexes, we consider the relationship between the experimentally measured quantum yield, Q_m, and the quantum yield for the radiative decay of the lowest excited level, Q_r. These two quantities are related by

$$Q_m = Q_r\phi_{isc}' \qquad (3)$$

where ϕ_{isc}' is the quantum yield for populating the emitting state from the state directly excited. The luminescence quantum yield may be altered by phenyl substituents through changes either in Q_r or ϕ_{isc}'.

It is apparent from eq 3 that in the limit of ϕ_{isc}' equal to unity, Q_r is equal to the measured quantum yield. This is a prerequisite for applying eq 2 to the determination of radiative lifetimes of the emitting states. The minimum possible value of ϕ_{isc}' is Q_m, in which case Q_r becomes unity. In this limit the radiative lifetime of the luminescing state is equal to the measured lifetime, and eq 2 is no longer applicable. Thus, the radiative lifetimes obtained by the use of eq 2 represent the maximum possible values of τ_0 consistent with the measured quantum yields for luminescence; the measured lifetimes represent the minimum possible values of τ_0.

Since the only luminescence observed from these complexes comes from the lowest excited level or set of levels, ϕ_{isc}' can be less than unity only if a direct radiationless transition from an upper excited level to the ground state occurs. Demas and Crosby[1c,14] have concluded that such transitions do not occur for several complexes of ruthenium(II), osmium(II), and rhodium(III) on the basis of the constancy of Q_m as the exciting wavelength is varied. Radiationless transitions from upper excited states to the ground state are also not expected to occur on the basis of the small Franck–Condon factors associated with the large energy gaps for such transitions.[20,21] Therefore, we proceed on the assumption that ϕ_{isc}' is unity and that phenyl substitution of the ligands alters the luminescence quantum yield only through changes in Q_r.

The quantum yield for the radiative decay of the luminescing state can be expressed by

$$Q_r = \tau_0^{-1}/(\tau_0^{-1} + k_q) \qquad (4)$$

where k_q is the rate constant for the radiationless decay of the level. An increase of the luminescence quantum yield may, therefore, be due to a decrease either in τ_0 or in k_q. The results from eq 2, as listed in Table II, indicate that a part of the increase in Q_m caused by phenyl substitution is due to a decrease in τ_0 in most cases. This conclusion is also supported by the trends in the radiative lifetimes obtained by the application of eq 1 (see Table I). The iridium(III) complex of 4,7-diphenyl-1,10-phenanthroline represents the only instance in which phenyl substitution of the ligand increases the luminescence quantum yield without causing an accompanying decrease in the radiative lifetime. Both the experimental measurement (Table II) and the calculated result (Table I) indicate that the radiative lifetime increases significantly.

The quenching rate constants, k_q, as determined from the relation

$$k_q = \tau_m^{-1} - \tau_0^{-1} \qquad (5)$$

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(20) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, 37, 1962 (1962).

(21) G. W. Robinson and R. P. Frosch, *ibid.*, 38, 1187 (1963).

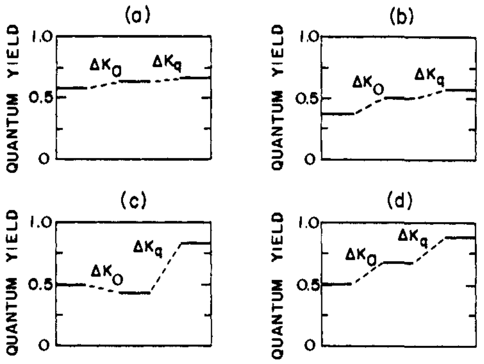

Figure 4. Resolution of substituent-induced quantum-yield changes into radiative and radiationless factors. The line on the left of each diagram represents the quantum yield of the parent complex. The line in the center represents the hypothetical quantum yield that the phenyl-substituted complex would have if only a change in the radiative rate constant (Δk_0) were caused by the ligand substituents. The line on the right represents the observed quantum yield of the phenyl-substituted complex due to the composite effect of Δk_0 and a change in the radiationless decay constant (Δk_q). (a) [Ru(phen)$_3$]I$_2$–[Ru(diphenylphen)$_3$]Cl$_2$; (b) [Ru(bipy)$_3$]Cl$_2$ –[Ru(diphenylbipy)$_3$]Cl$_2$; (c) [IrCl$_2$(phen)$_2$]Cl–[IrCl$_2$(diphenylphen)$_2$]·Cl; (d) [IrCl$_2$(bipy)$_2$]Cl–[IrCl$_2$(diphenylbipy)$_2$]Cl.

are listed in Table II. Phenyl substitution produces a decrease of k_q for all of the complexes. This decrease is responsible for at least part of the increase in the luminescence quantum yields, and, in the case of [IrCl$_2$(diphenylphen)$_2$]Cl, it is entirely responsible for it.

The means by which phenyl substituents affect the quantum yields of these complexes are illustrated in Figure 4. In most instances Q_m is larger for the phenyl-substituted complexes as a result of a decrease in both τ_0 and k_q. For [IrCl$_2$(diphenylphen)$_2$]Cl, however, the decrease of the quantum yield due to an increase in τ_0 relative to the value for [IrCl$_2$(phen)$_2$]Cl is more than compensated by the large decrease in k_q. The net effect is a substantial increase in Q_m.

Radiative Lifetimes. In order to interpret the effects of phenyl substitution on the radiative lifetimes of these complexes, we apply the model for intensity borrowing *via* spin–orbit coupling employed by Demas and Crosby.[1c] This model predicts that the magnitude of the spin–orbit coupling interaction between a triplet luminescing state and the singlet from which it borrows intensity is given by

$$K|M_{SO}|^2 = (1/\epsilon\tau_0)(E_S - E_T)^2(E_S/E_T^3) \qquad (6)$$

K is a proportionality constant that depends upon the geometry and the central metal ion of the complex, $|M_{SO}|^2$ is the magnitude of the spin–orbit coupling interaction, ϵ is the maximum molar extinction coefficient of the "lending" singlet state, τ_0 is the radiative lifetime of the emitting state, and E_S and E_T are the energies of the singlet and triplet states, respectively. In order to apply eq 6, we presume the emitting states of the complexes studied here to be triplets; we will return, however, to a consideration of the multiplicity later.

When applying eq 6, no attempt was made to evaluate K and $|M_{SO}|^2$ independently. Rather, the product of the two was computed as a single quantity proportional to the spin–orbit coupling interaction between the borrowing and lending states. The other quantities in eq 6 were determined by experimental measurements and used to calculate the value of $K|M_{SO}|^2$. The energy of the lending singlet was taken as the energy of the vibrational peak having the maximum extinction coefficient in the envelope of the intense charge-transfer band lying closest to the luminescing state. For each iridium(III) complex, the energy of the triplet was assumed to be the energy of the maximum extinction coefficient of the lowest lying absorption band. For the ruthenium(II) complexes, where no low-lying bands were resolved in absorption, the energies of the presumed 0–0 bands in the luminescence spectra were used for E_T.

The values that were found for $K|M_{SO}|^2$ by the application of eq 6 are listed in Table III. They reveal several interesting features about spin–orbit coupling in these molecules. It is immediately apparent that the magnitudes of $K|M_{SO}|^2$ are, in general, larger by a factor of about 3 for iridium(III) complexes than they are for analogous complexes of ruthenium(II). This trend is in qualitative agreement with the well-known increase of the atomic spin–orbit coupling constant with increasing atomic number. The values of $K|M_{SO}|^2$ for the iridium(III) complexes are also slightly larger than those that were reported previously for similar osmium(II) compounds.[10] These results are indeed gratifying and lend further support to the intensity-borrowing model, since they are in qualitative agreement with current knowledge of the dependence of spin–orbit coupling on the nuclear charge. Had this trend in $K|M_{SO}|^2$ not been observed, one would question the entire model concept.

Table III. Spin–Orbit Coupling in Ru(II) and Ir(III) Complexes

Complex	$K|M_{SO}|^2 \times 10^{7\,a}$
[Ru(bipy)$_3$]Cl$_2$	3.78[b]
[Ru(diphenylbipy)$_3$]Cl$_2$	2.62
[Ru(phen)$_3$]I$_2$	2.43[b]
[Ru(diphenylphen)$_3$]Cl$_2$	1.58
[IrCl$_2$(bipy)$_2$]Cl	10.9
[IrCl$_2$(diphenylbipy)$_2$]Cl	7.67
[IrCl$_2$(phen)$_2$]Cl	6.17
[IrCl$_2$(diphenylphen)$_2$]Cl	2.20

[a] Calculated from eq 6. [b] Reference 10.

The difficulties of making quantitative comparisons between the values of $K|M_{SO}|^2$ for complexes with different central metal ions and different geometries have been discussed previously.[10] In spite of such difficulties, the model provides a successful qualitative interpretation of the effect on radiative lifetimes caused by changing the central metal ion in several ruthenium(II) and osmium(II) complexes. One of the major triumphs of the model is, in fact, an interpretation of the slight lengthening of the radiative lifetimes of several osmium(II) complexes contrasted with those of similar complexes of ruthenium(II). Simple considerations of spin–orbit coupling suggest that the heavier osmium(II) should induce a larger mixing of singlets and triplets and produce shorter radiative lifetimes for complexes of osmium than for those of ruthenium. This is in contrast to the experimental results; factors other than spin–orbit coupling must be taken into account. The intensity-borrowing model indicates that $K|M_{SO}|^2$, *i.e.*, spin–orbit coupling, is indeed larger for osmium(II) than it is for ruthenium(II) complexes, but that the increase is compensated by a larger energy gap between the emitting triplet and the singlet from which it borrows intensity in osmium(II) complexes than in the ruthenium(II) species. The large energy gap negates the effect of an intrinsic increase in $K|M_{SO}|^2$ for osmium(II) relative to ruthenium(II) and produces a slight net increase in the radiative lifetimes of the former species.

The present data reveal that the radiative lifetimes of the iridium(III) complexes are only slightly shorter than those of the ruthenium(II) compounds, another anomalous result, insofar as one would expect much shorter lifetimes for iridium(III) compounds on the basis of an assumed larger spin–orbit coupling constant for the heavier metal. Application of the intensity-borrowing model, however, produces values of $K|M_{SO}|^2$ that are substantially larger for iridium complexes than for ruthenium species, as expected. The occurrence of only a slight shortening of the radiative lifetimes of the iridium(III) complexes cannot, however, be attributed to a larger energy gap between the singlet and triplet states in iridium than in ruthenium species; in fact, the gap is smaller. In this instance we find the key to the observed behavior in the magnitudes of the extinction coefficients of the singlet charge-transfer bands from which the triplets are assumed to borrow intensity. For the iridium(III) complexes the extinction coefficients are smaller than for the ruthenium(II) compounds by a factor of 5–10. This large decrease leads to a corresponding decrease in the radiative coupling of the excited and ground states. Thus, when comparing radiative lifetimes of iridium(III) complexes with those of ruthenium(II), we find that decreases in the energy gaps and increases in $K|M_{SO}|^2$ have effects that are opposed by decreases in the extinction coefficients of the lending charge-transfer states. The net effect of these compensating factors is to produce the small observed decreases in the radiative lifetimes when the central metal ion is changed from ruthenium(II) to iridium(III).

Although the comparison of values of $K|M_{SO}|^2$ for complexes with different central metal ions and geometries is fraught with inherent difficulties, a comparison of values for complexes that differ only by ligand substituents should be highly reliable. Table III shows that for all the compounds studied, phenyl substitution of the ligands leads to values of $K|M_{SO}|^2$ that are $\sim 30\%$ smaller than those found for the complexes of the unsubstituted ligands. These results point to a greater delocalization of the electron density over the organic moieties in the excited charge-transfer states of the phenyl-substituted complexes than in the unsubstituted compounds. Intuitively one expects such an increase in delocalization to lead to a smaller spin–orbit coupling within the molecules, because the latter is dominated by the heavy central-metal ion. We shall show in the following section that this observed decrease in the $K|M_{SO}|^2$ values for the complexes of the phenyl-substituted ligands also plays a key role in the interpretation of the trends observed in the radiationless decay rates of the luminescing states. For the present we conclude that the shortening of the radiative lifetimes brought about by phenyl substitution of the ligands is due to large increases in the extinction coefficients of the lending states. This factor overcomes the relatively small decrease in spin–orbit coupling matrix elements caused by phenyl substitution to produce a net decrease of the radiative lifetimes.

In the case of [IrCl$_2$(diphenylphen)$_2$]Cl we find a value of $K|M_{SO}|^2$ that, like its radiative lifetime, is completely out of line with what we would expect for a complex with a charge-transfer luminescence. We see that in this instance the value of $K|M_{SO}|^2$ is more typical of a ruthenium(II) than it is of an iridium(III) species. This small value of $K|M_{SO}|^2$ and the large value of the radiative lifetime provide further evidence that the luminescence of [IrCl$_2$(diphenylphen)$_2$]Cl cannot be assigned to a simple charge-transfer transition.

Radiationless Transitions. The substantial decrease in the quenching rate constants that accompanies phenyl substitution of the ligands in these compounds is, at first sight, a rather mysterious result. Changes in the rates of radiationless transitions for a series of similar compounds have, in the past, often been correlated with changes in the Franck–Condon factors responsible for the transitions.[22,23] The Franck–Condon factors, in turn, are found to be dependent upon such parameters as the energy gap between the initial and final states, the number of molecular vibrations, and the frequencies of the normal modes.[24] The primary effect of phenyl substitution of these complexes is to lower the energy gap between the emitting state and the ground state. This alteration should, however, increase the magnitude of the Franck–Condon factors, which would increase the radiationless decay constants.[20,21] A somewhat smaller increase in the Franck–Condon factors might be expected on the basis of an increase in the number of molecular vibrations in the phenyl-substituted complexes, although no significant changes in the magnitudes of vibrational frequencies are expected. The important point here is that there is no obvious way to explain the observed trends in the radiationless decay constants on the basis of alterations in the Franck–Condon factors brought about by the phenyl substituents. This leads us to the conclusion that the procedure of assuming a constant electronic matrix element for the radiationless coupling of two states in a series of similar compounds and of correlating changes in the radiationless decay rates with changes in the Franck–Condon factors[22,23] is not valid here.

Once one forsakes the idea that the electronic matrix elements responsible for the radiationless transitions are constant, a reasonable explanation for a decrease in the radiationless decay rates upon phenyl substitution of the ligands emerges. For a spin-forbidden radiationless process, the rate of decay depends upon matrix elements of both a spin–orbit and a vibronic perturbation. Lin[25] has presented a general treatment of this problem within the framework of perturbation theory. Bixon and Jortner[26] have provided a somewhat more detailed formalism for spin-forbidden radiationless transitions than that of Lin, but they arrive at matrix elements consistent with those of Lin. For our purposes the simpler formalism of Lin suffices.

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(22) W. Siebrand, *J. Chem. Phys.*, **47**, 2411 (1967).
(23) W. Siebrand, *ibid.*, **46**, 440 (1967).
(24) R. J. Watts and S. J. Strickler, *ibid.*, **44**, 2423 (1966).
(25) S. H. Lin, *ibid.*, **44**, 3759 (1966).
(26) M. Bixon and J. Jortner, *ibid.*, **48**, 715 (1968).

In Lin's treatment, the radiationless process is viewed as a result of breakdown of the Born–Oppenheimer approximation, and attention is therefore focused on the nuclear kinetic energy operator. Vibronic coupling of the Herzberg–Teller type is included in the basis functions used to describe the radiationless transition. For spin-forbidden processes, spin–orbit coupling is also included in the description of the initial and final states. Lin's theory therefore formally takes the point of view that a radiationless transition is a result of initial and final[27] states, corrected for spin–orbit and Herzberg–Teller coupling, being mixed by terms left out in the Born–Oppenheimer approximation.

Modified approaches to spin-forbidden radiationless processes have been presented by Henry and Siebrand[28] and by Burland and Robinson.[29] The former treatment places equal emphasis on spin–orbit coupling, Herzberg–Teller terms, and breakdown of the Born–Oppenheimer approximation as the source of the radiationless process. The latter treatment, which was applied specifically to the intersystem crossing process in benzene, places equal emphasis on spin–orbit and Herzberg–Teller coupling, but breakdown of the Born–Oppenheimer approximation is considered to be negligible. These treatments therefore formally view the radiationless transition as a mixing of initial and final[30] basis functions which are uncorrected for spin–orbit and Herzberg–Teller coupling and also breakdown of the Born–Oppenheimer approximation.

It is presently unclear to what extent these treatments differ for computational purposes. It is, however, quite clear that there are significant differences in the physical description of spin-forbidden radiationless transitions provided by these theories. These differences are centered around the description of the initial and final states for the radiationless process. In Lin's treatment, the basis functions used in the description of the radiationless transition are spin–orbit coupled, whereas those used in the Henry–Siebrand and Burland–Robinson approaches are pure spin functions. As point out by Henry and Siebrand,[28] there is a certain arbitrariness in the choice of basis functions for the calculation of the radiationless rate constant. However, the identification of the initial state as a spectroscopic state, which is actually produced in an experiment, removes this arbitrariness and necessitates the inclusion of certain terms in the Hamiltonian used to provide a description of this state.

The general problem of describing photon absorption as excitation to a particular nonstationary initial state followed by a radiationless transition to a final state has been discussed by Rhodes, Henry, and Kasha.[31] These authors point out that when the bandwidth of the exciting light is much less than the broadening due to interaction of the initial states chosen for the problem with the final states, it is meaningless to consider photon absorption as a real transition to this initial state followed by a radiationless transition. Although these authors discussed the problems in terms of Born–Oppenheimer states, a similar argument may be made for any choice of initial and final states. Whenever terms left out of the Hamiltonian used to derive the initial and final states are of such a magnitude as to broaden the initial state beyond the bandwidth of the exciting light, a time-dependent description of the radiationless transition from one of these initial states to a final state is inappropriate. Such an initial state is not a correct description of the real, spectroscopic state produced in the experiment. Rather, it is necessary to include all terms that are larger than the bandwidth of the excitation source in the description of the initial and final states.

In complexes of ruthenium and iridium, it is doubtful that all spin–orbit coupling terms are small enough to neglect in the initial–final state problem. It is quite possible, however, that certain of the spin–orbit coupling terms are small enough to neglect initially but to include in the description of the radiationless transition. The appropriate procedure would be to include all terms larger than the excitation bandwidth in the description of the initial and final states and to express the radiationless transition rate as a perturbation on these states by smaller terms. These smaller terms would presumably include both spin–orbit and vibronic contributions. Although Lin's formalism includes all spin–orbit coupling terms in the basis used for the expression of the radiationless transition rate, we prefer to use this formalism to emphasize that some spin–orbit coupling terms must be included in the basis set for the problem. Our choice of Lin's formalism is dictated by the fact that it provides what we feel to be the most realistic physical picture of a spin-forbidden process in a transition metal complex presently available.

Within the framework of Lin's treatment of a spin-forbidden radiationless transition, there are three basic types of coupling mechanisms that arise from the use of a zero-order basis consisting of pure-spin Born–Oppenheimer states. These are: (1) a direct spin-vibronic coupling of the triplet state with the ground state; (2) a vibronic coupling of the triplet state with a higher excited state of the same multiplicity, which is in turn spin–orbit coupled with the ground state; (3) a spin–orbit interaction of the triplet state with a higher singlet state that is vibronically coupled with the ground state. Of these three coupling mechanisms, the third is the most closely analogous to our previous description of the radiative properties of the emitting states in these complexes. Just as the radiative properties of the emissive charge-transfer state were described by assuming this state to be spin–orbit coupled with a higher energy singlet charge-transfer state, which could couple radiatively with the ground state, mechanism 3 would include the same spin–orbit coupling term but would replace the radiative term with a vibronic coupling term for the radiationless coupling of the singlet charge-transfer state with the ground state. There are,

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[27] The terms "initial" and "final" states as used in this discussion refer to the set of functions used as a basis for the expression of the radiationless decay rate. We differentiate our usage of these terms from our use of the term "zero-order" states, which refers to the original basis set in which the problem is cast. In the case of the Lin theory, the "zero-order" states are pure-spin Born–Oppenheimer states, while the "initial" and "final" states are spin-orbit-coupled Born–Oppenheimer states.

[28] B. R. Henry and W. Siebrand, *J. Chem. Phys.*, **54**, 1072 (1971).

[29] D. M. Burland and G. W. Robinson, *ibid.*, **51**, 4548 (1969).

[30] Although we maintain our previous usage of the terms "initial" and "final" states, these are identical to the "zero-order" states in the case of the Henry–Siebrand theory. In their treatment all spin–orbit coupling terms are included in the expression for the radiationless rate constant.

[31] W. Rhodes, B. R. Henry, and M. Kasha, *Proc. Nat. Acad. Sci. U. S.*, **63**, 31 (1969); W. Rhodes, *J. Chem. Phys.*, **50**, 2885 (1969).

of course, a large number of other coupling terms that could be considered in mechanism 3, as well as in the other two types of mechanisms described by Lin's formalism. For the present, however, we will explore the consequences of including only the single spin–orbit coupling term that is analogous to the term used in the intensity-borrowing model.

A comparison of the trends in the $K|M_{SO}|^2$ values listed in Table III with the trends in the quenching rate constants in Table II reveals that phenyl substitution of the ligands results in parallel decreases in both the spin–orbit coupling and quenching rate constants in all the cases studied. The ratios of the quenching rate constants for the ruthenium(II) complexes of the unsubstituted and substituted ligands are, in fact, nearly in quantitative agreement with ratios of the $K|M_{SO}|^2$ values. For the iridium(III) complexes, the ratios of the quenching rate constants for complexes of the unsubstituted and substituted ligands are somewhat larger than the ratios of the $K|M_{SO}|^2$ values, but a qualitative agreement in the trends shown by k_q and $K|M_{SO}|^2$ still exists. If only the single spin–orbit coupling term identical with that measured by $K|M_{SO}|^2$ is considered and if vibronic coupling terms and Franck–Condon factors are assumed to be only slightly affected relative to $K|M_{SO}|^2$ values by phenyl substitution of the ligands, then just such parallel trends in k_q and $K|M_{SO}|^2$ are expected. Although we cannot rule out the possibility that other spin–orbit and vibronic coupling mechanisms also contribute to k_q, the agreement found between the changes in k_q values upon phenyl substitution and those predicted on the assumption of this single coupling mechanism is highly suggestive that the same spin–orbit coupling term that is invoked in our description of radiative transitions also plays a dominant role in radiationless transitions. We thus conclude that the intensity-borrowing model is relevant not only to radiative but also to radiationless processes in these molecules.

Multiplicity of the Emitting Levels. In our applications of the model for intensity borrowing *via* spin–orbit coupling to these complexes, we have assumed the emitting level to be a triplet. Actually, in complexes with a central metal as heavy as iridium, spin–orbit coupling could be extremely large, and the classification of energy levels by their spin multiplicities could be a very crude approximation. The word "triplet" as it is used here is, therefore, simply meant to imply that there are three levels that are spin–orbit coupled with a lending state. Owing to the large spin–orbit interactions, which are expected to occur in the complexes, these excited levels may undergo a significant zero-field splitting. Recent studies of the temperature dependences of the lifetimes of several of these complexes[32] reveal that these zero-field splittings are indeed large (~10–50 cm^{-1}) and that a fourth level, possibly of a singlet origin, also contributes to the emission of the complexes at 77°K.

The important point is that the spectroscopic parameters reported here are based on measurements on a Boltzmann distribution of several excited levels at 77°K. Quantities such as the quantum yields, radiative lifetimes, and radiationless decay rates reported in this paper are not characteristic of distinct electronic states; rather, they must be interpreted as average quantities obtained from the weighted contribution of several electronic states. Thus, they are temperature dependent.

The occurrence of emission from several levels at 77°K will also have an important effect upon radiative lifetimes calculated from integrated absorption intensities by eq 1. Although absorption from the ground state to each of the emitting levels may occur in accordance with the appropriate extinction coefficient at any temperature, the Boltzmann equilibrium does not afford each of the excited levels an equivalent opportunity to undergo a corresponding emission process; rather, emission from the lowest excited levels is favored. For example, one may find a situation in which practically all of the oscillator strength is carried by the highest of a set of two closely spaced (~50 cm^{-1}) levels, whereas very little oscillator strength is contributed by the lowest member. A determination of the radiative lifetime for such a set of levels by quantum yield and lifetime measurements at low temperature ($kT \sim 50$ cm^{-1}) would yield an average value. This would approach the value of τ_0 for the lower level as the temperature was further decreased. Application of eq 1, however, would yield a value of the radiative lifetime closely approximating the value of τ_0 for the higher level, if a value of g_l/g_u of unity were assumed. In order to apply eq 1 correctly, it would be necessary to use a Boltzmann-averaged value of g_l/g_u appropriate to the temperature at which the radiative lifetimes of the set of levels was desired.[33] This would require a detailed knowledge of the splitting of the levels and their individual radiative lifetimes that is not currently available. The fact that the radiative lifetimes calculated by eq 1 are somewhat shorter than those obtained from quantum yield and lifetime measurements points to the necessity for such a procedure. Work is currently underway in this laboratory to determine the required zero-field splittings and lifetimes, and a detailed study of the use of these parameters to calculate g_l/g_u ratios is in progress.

Summary and Conclusion

Because of the success of the model of intensity borrowing *via* spin–orbit coupling for interpreting the effects of phenyl substituents on the optical properties of these complexes, we believe that it may be used with considerable confidence to predict the luminescence efficiencies of other complexes. Predictions are possible simply on the basis of measurements of the absorption spectrum and the luminescence decay time. From the absorption measurement, one can obtain the extinction coefficient and energy necessary to apply eq 6. A value of $K|M_{SO}|^2$ can be transferred from a similar complex to provide the final parameter necessary for a calculation of the radiative lifetime. Insertion of the measured luminescence lifetime into eq 4 yields the quantum efficiency. This procedure should prove somewhat more successful for the prediction of quantum yields than the use of integrated absorption intensities, owing to the difficulties discussed above.

Owing to the parallel trends found in $K|M_{SO}|^2$ and k_q values in this study, we feel that there is good reason to believe that the same spin–orbit coupling mechanism

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(32) R. J. Watts, R. W. Harrigan, and G. A. Crosby, *Chem. Phys. Lett.*, 8, 49 (1971).

(33) T. Azumi, C. M. O'Donnell, and S. P. McGlynn, *J. Chem. Phys.*, **45**, 2735 (1966).

that controls the radiative lifetimes of these complexes also plays a dominant role in determining the quenching rate constants. This mechanism corresponds to an indirect coupling of the luminescing and ground states through a higher energy charge-transfer state.

Our previous suggestion that a large $(d\pi^*) \rightarrow (\pi\pi^*)$ configuration interaction occurs in $[IrCl_2(\text{diphenylphen})_2]Cl$[12] is further supported by the results of the present study. The long radiative lifetime and small value of $K|M_{SO}|^2$ obtained for this complex indicate that its luminescence, in contrast to the others (see Figure 4), does not originate from a simple charge-transfer transition. The lowest excited state of this complex appears to be classified best as a level localized primarily on the ligands that is highly perturbed by the close proximity of a charge-transfer excited state.

For all but one of the iridium species studied here our observations indicate that a "delocalized molecular" description of the emitting states, as suggested by DeArmond and Hillis,[13] is not necessary. Our data show that, aside from $[IrCl_2(\text{diphenylphen})_2]Cl$, the $K|M_{SO}|^2$ values are large, indicating a strong admixture of singlet character in the emitting triplet level, a characteristic that we associate with a charge-transfer level. Although ligand-localized triplet states are certainly closer to the emitting levels in iridium complexes than they are in ruthenium ones,[13] the classification of an excited state as "delocalized molecular" should be necessary only when the energy gap between the zero-order $d\pi^*$ and $\pi\pi^*$ triplet states is comparable to the interaction matrix element. Only for $[IrCl_2(\text{diphenyl})_2]Cl$ do we infer that this condition obtains. Studies of several other iridium(III) molecules indicate that the matrix element mixing charge-transfer and ligand-localized triplet states is only on the order of several hundred wavenumbers.[34] Since the energy gaps between the unperturbed ligand triplets and the emitting levels are several times larger than this value for the unsubstituted iridium(III) species, we conclude that small $(d\pi^*) \rightarrow (\pi\pi^*)$ interactions occur and that the appellation "charge transfer" is an adequate description of the emitting levels.

The most striking effect of phenyl substitution of these nitrogen-coordinated ligands is the large increase produced in the luminescence yields of the respective chelates. Thus phenyl substitution can be used to "fine tune" the optical properties of a complex, in this instance, to improve the efficiency of the luminescence, without, in most cases, changing the fundamental nature of the transition responsible for it.[12] High efficiency is of paramount importance in the design of quantum converters and laser materials.

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Polymer Production in the γ Radiolysis of Methane, Ethane, and Ethylene Solutions in Liquid Argon

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Abstract: Further studies of the products of radiolysis of solutions of methane, ethane, and ethylene in liquid argon have been made. Our earlier work left the question of mechanism somewhat unanswered. The additional data seem to show that the most probable mechanism is ionization of the solutes with lowest ionization potential (IP) by electron transfer to the argon ions initially produced by the γ rays and subsequent ion molecule reactions and neutralization to form the heavy hydrocarbons. The limit on molecular weight is suggested to be an energetic one in which further growth of the polymer ion is energetically forbidden. Charge-transfer recharges the polymer when it is neutralized and this is thought to happen several times.

The reactions of hydrocarbons under the influence of ionizing radiation have been studied extensively for many years. One of the most interesting products found from methane, ethane, and ethylene under various conditions is an oily material referred to as a polymer as a matter of convenience. This polymer has been observed from gas discharge reactions,[1] methane photolysis,[2] and the radiolysis of methane under various conditions.[1c,3,4]

γ-Radiolysis of solid methane at 77°K produces a polymer with an average molecular formula $C_{20}H_{20}$.[4d-f] The yield is proportional to dose (constant G value) and the molecular weight is independent of dose as well. It was proposed that the reaction occurred *via* a chain

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