Photochemical and Photophysical Behavior of Dichloro Complexes of Iridium(III) Containing Phenanthroline Ligands[1]

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Abstract: Photochemical (continuous and flash photolysis) and photophysical (luminescence intensity and lifetime) measurements have been made on $Ir(phen)_2Cl_2^+$ and $Ir(Me_2phen)_2Cl_2^+$ in aqueous solution. The predominant photochemical step is Cl^- release with wavelength (254–404 nm) and pH (2–11) independent quantum yields ($\phi_{Cl^-} = 0.05$ for $Ir(phen)_2Cl_2^+$ and 0.09 for $Ir(Me_2phen)_2Cl_2^+$). Increasing temperature causes an increase in ϕ_{Cl^-} which is also decreased upon addition of dmf (up to 95% v/v). Flash photolysis produces a transient species that does not appear to be a precursor of the aquation process but rather arises from excitation in the deep ultraviolet. The emission intensity, which is very weak in water, is strongly increased in dmf solutions. The emission lifetime also increases with increasing [dmf]. In all media, the intensity and lifetime of the emission decreases with increasing temperature. Quenching experiments demonstrate that at least part of the photoaquation reaction originates from an excited state different from that responsible for emission. Temperature and medium dependence show that the reactive state is higher in energy than the emitting state and that the reactive state can be populated from the emitting state through thermal activation. The evidence indicates that the reactive state is the lowest triplet dd state in both complexes. Because these complexes are relatively inert photochemically and exhibit very intense and relatively long-lived emission in dmf, they can be conveniently used as sensitizers in energy transfer reactions.

In the last decade, a large number of studies have been performed on the photochemical[3,4] and photophysical[4,5] behavior of transition metal coordination complexes. However, the photochemistry and luminescence investigations have proceeded almost independently in the past. The unfortunate result of this situation is that the complexes whose photochemistry is reasonably well known have not yet been studied from a photophysical point of view, and *vice versa.*[6] Moreover, most photochemistry studies have been carried out in fluid solution and near ambient temperature (~300°K), while luminescence experiments have generally been performed in rigid media at liquid nitrogen temperature (77°K).

Parallel photochemical and photophysical investigations on the same systems and under the same experimental conditions may make significant contribution toward a complete understanding of the factors which determine the photochemical and photophysical behavior. Mixed ligand complexes of Ir(III) such as $Ir(AA)_2X_2^+$ and $Ir(AA)X_4^-$ (where AA is 1,10-phenanthroline or α,α'-dipyridyl or their derivatives, and X is a halide ion) seem to be particularly suitable for such studies. Their photophysical properties in rigid glasses at 77°K have been investigated by Crosby and coworkers[11-16] who discovered several interesting features such as the possibility of "tuning" the luminescence of these compounds by appropriate changes of ligands or ligand substituents. Relevant studies on these complexes have also been carried out by DeArmond, *et al.*[17,18] It is known[19] that some of these complexes are luminescent even at room temperature in fluid solution, *i.e.*, under the usual experimental conditions of the photochemical studies. Moreover, qualitative experiments have shown that $Ir(phen)_2Cl_2^+$,[20,21] $Ir(phen)_2Br_2^+$,[20,21] $Ir(phen)Cl_4^-$,[20,22] and $Ir(phen)Br_4^-$ [22] are photosensitive toward release of X^-. While this work was in progress, relative quantum yield values for Cl^- aquation of $Ir(phen)_2Cl_2^+$ at 254 and 350 nm were reported by Muir and Huang.[23] We thought it important to carry out a detailed investigation on the photochemical and photophysical behavior of these systems under the same experimental conditions. In this paper, we wish to report the results of continuous and flash photolysis and luminescence studies on $Ir(phen)_2Cl_2^+$ and $Ir(5,6\text{-dimethylphen})_2Cl_2^+$ in fluid solution and consider the relationships between their photochemical and photophysical behavior.

Experimental Section

Materials. *cis*-Dichlorobis(1,10-phenanthroline)iridium(III) nitrate trihydrate, $[Ir(phen)_2Cl_2]NO_3 \cdot 3H_2O$, was obtained by adding KNO_3 to a saturated solution of $[Ir(phen)_2Cl_2]Cl$. The chloride salt was prepared following the procedure indicated by Broomhead and Grumley.[22] *Anal.*[24] Calcd for $C_{24}H_{22}N_4Cl_3O_3Ir$: C, 40.37; H, 3.10; N, 7.85; Cl, 14.9; Ir, 27.04. Found: C, 40.35; H, 3.14; N, 8.00; Cl, 15.10; Ir, 27.05. *cis*-Dichlorobis(5,6-dimethyl-1,10-phenanthroline)iridium(III) nitrate trihydrate, $[Ir(Me_2phen)_2Cl_2]NO_3 \cdot 3H_2O$, was prepared following the same procedure indicated for the previous complex.[22] *Anal.*[24] Calcd for $C_{28}H_{30}N_4Cl_3O_3Ir$: C, 43.67; H, 3.93; N, 7.28; Cl, 13.81; Ir, 25.07. Found: C, 41.62; H, 4.24; N, 6.77; Cl, 13.46; Ir, 23.64. Spectrophotometric grade dimethylformamide (dmf) and 2-propanol were used. Trifluoromethylsulfonic acid (HTFMS) was distilled before use. Water was triply distilled, and all of the other chemicals used were of reagent grade.

Luminescence Measurements. The emission spectra were recorded on a Hitachi-Perkin-Elmer MPF-3 spectrofluorimeter. Emission lifetimes were measured with the equipment previously described.[25] For the luminescence intensity measurements, excitation was at 400 nm for both complexes. The emission intensity was monitored at 540 nm for $Ir(phen)_2Cl_2^+$ and at 530 nm for $Ir(Me_2phen)_2Cl_2^+$. For each complex, solutions having the same absorbance were used and the excitation and emission slits were kept constant. For the decay measurements, excitation was at 487 nm and the emission was monitored at 548 nm using cutoff and interference filters.

Continuous Photolysis. Radiations of 254, 313, 365, and 404 nm were produced as previously described.[26] The intensity of the incident light, measured by means of the ferrioxalate actinometer,[27] was of the order of 5×10^{-7} $Nh\nu$/min at each of the irradiation wavelengths used. The absorbance measurements and the recording of the spectra were performed with an Optica CF4 NI spectrophotometer. Differential titration of Cl^- was made by using a Knick KpH 34 pH meter as a potentiometer. A SP-Sephadex C25

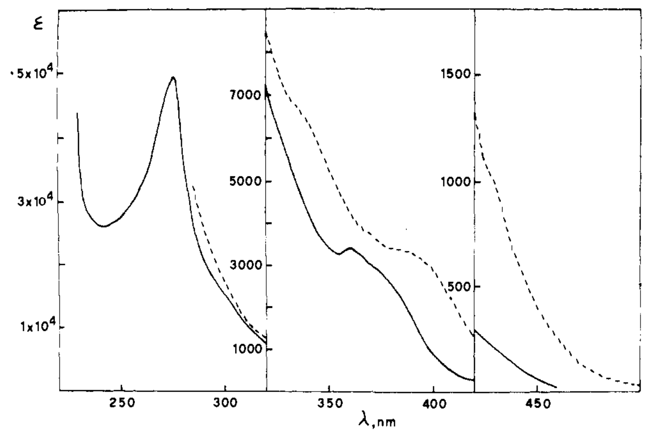


Figure 1. Absorption spectrum of Ir(phen)$_2$Cl$_2$$^+$ in water (—) and in 95% v/v dmf–water (- - -).

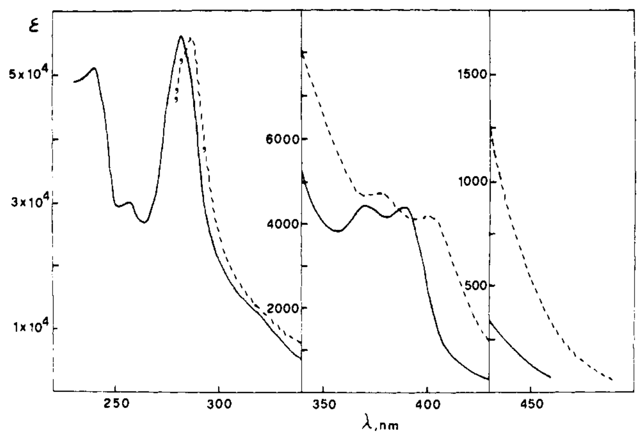


Figure 2. Absorption spectrum of Ir(Me$_2$phen)$_2$Cl$_2$$^+$ in water (—) and in 95% v/v dmf–water (- - -).

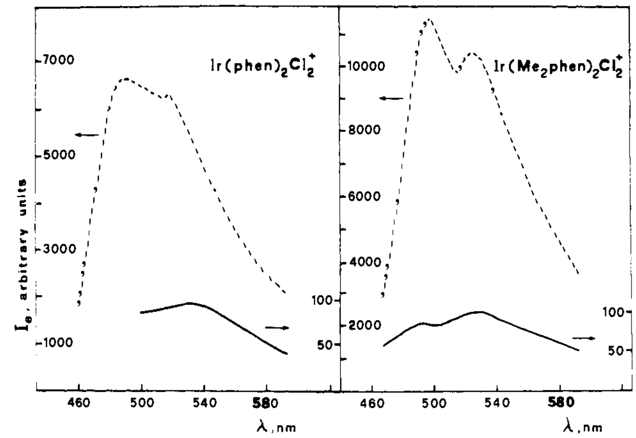


Figure 3. Emission spectra of Ir(phen)$_2$Cl$_2$$^+$ and Ir(Me$_2$phen)$_2$Cl$_2$$^+$ in water (—) and 95% v/v dmf–water (- - -). The absolute intensities are much higher for Ir(Me$_2$phen)$_2$Cl$_2$$^+$ than for Ir(phen)$_2$Cl$_2$$^+$ under the same experimental conditions.

resin was used for ion-exchange chromatography. The general procedure for the photochemical experiments was as follows. A weighed amount of the complex to be irradiated was dissolved in the selected medium under red light. The concentration of the complex was 1×10^{-3} *M* for Ir(phen)$_2$Cl$_2$$^+$ and 5×10^{-4} *M* for Ir(Me$_2$phen)$_2$Cl$_2$$^+$. Phosphate and borate buffers were used for the experiments at pH 7 and 10. The reaction cell (optical path 4 cm, capacity 12 ml) was filled with the solution and placed in the thermostated cell holder of the irradiation equipment. Under these conditions, the incident light was completely absorbed at each of the irradiation wavelengths. A sample of the same solution was maintained in the dark at the same temperature in order to provide a control for thermal reactions and a reference for spectrophotometric and potentiometric measurements. When necessary, deoxygenation or oxygen saturation of the solutions was obtained by bubbling a stream of purified nitrogen or oxygen for 45 min. Unless otherwise indicated, solutions were air-equilibrated. After suitable irradiation periods, the light beam was interrupted and the irradiated solution was analyzed either spectrophotometrically or potentiometrically. The quantum yields for Cl$^-$ release, ϕ_{Cl^-}, were obtained from potentiometric titration. In some cases, ϕ_{Cl^-} was evaluated from the spectral changes that occur on irradiation. Such changes had previously been calibrated by the potentiometric titrations. In all cases where ϕ_{Cl^-} was determined, the irradiation period was chosen so that <10% decomposition occurred. Upper limits for the amount of phen or Me$_2$phen released were obtained by spectrophotometric determination after addition of Fe^{2+}. Chromatographic analyses were performed on completely (>98%) photolyzed solutions.

Flash Photolysis. Solutions containing 1×10^{-5} *M* Ir(phen)$_2$Cl$_2$$^+$ and Ir(Me$_2$phen)$_2$Cl$_2$$^+$ (as the nitrate salts) were prepared from triply distilled water. The pH of the solutions was adjusted using HClO$_4$, HTFMS, NaOH, or KOH and 1×10^{-4} *M* phosphate was used as a buffer in the pH range 4–9. Solutions were purged with N$_2$ for 45 min before use and were introduced into the flash photolysis optical cell under a positive pressure of N$_2$. For some runs, the solutions were saturated with O$_2$.

The flash photolysis apparatus and the procedures followed have already been described in detail.[28] The photolysis cell was 22 cm in length and was unjacketed except when Pyrex sleeves were used to restrict the photolysis flash to λ >300 nm. Because of the photosensitivity of the complexes, exposure of the solution to the 150-W xenon analyzing lamp was minimized by the use of an electric shutter which was opened for short periods of time (a few seconds) during the experiment. In addition, cutoff filters (380 or 300 nm) were always in place in front of the analyzing lamp to remove the light of wavelengths shorter than that being monitored by the monochromator-photomultiplier detector. Because of the strong uv absorption by the complexes themselves, it was not possible to monitor λ <300 nm. The weak transient absorption observed necessitated the use of the photolysis flash at its highest intensity. Spectra were recorded 30 μsec after the initiation of the flash.

Results

Thermal Behavior. In agreement with previous results[20,22] Ir(phen)$_2$Cl$_2$$^+$ was found to be thermally inert. Neither spectral variations nor Cl$^-$ or phen release could be observed for basic or acidic aqueous solutions and solutions containing 1.2 *M* 2-propanol or dmf kept in the dark for several weeks. Solutions in 45% v/v dmf–water and pure dmf were also stable for weeks.

Ir(Me$_2$phen)$_2$Cl$_2$$^+$ proved to be as inert as the previous complex under all the experimental conditions used.

Absorption and Emission Measurements. The electronic absorption spectra of the two complexes in water and 95% v/v dmf–water are shown in Figures 1 and 2. In agreement with a previous report,[29] the spectra of Ir(phen)$_2$Cl$_2$$^+$ in aqueous solution shows maxima at 360 (ϵ 3.3×10^3 M^{-1} cm^{-1}) and 276 nm (4.9×10^4) and shoulders at about 430 and 300 nm. The spectrum of Ir(Me$_2$phen)$_2$Cl$_2$$^+$, which had previously been reported in rigid solution at 77°K,[16] shows maxima at 240 (5.2×10^4), 257 (3.0×10^4), 282 (5.6×10^4), 370 (4.4×10^3), and 390 nm (4.4×10^3) in water solution. Both spectra were unchanged upon changing pH from 2 to 11. The presence of 1.2 *M* dmf or 2-propanol caused a general increase in absorption (~10%) above 300 nm, without changing the shape of the spectra. In 95% v/v dmf–water a general red shift of the absorption spectra was observed (Figures 1 and 2).

The emission spectra in aqueous solution showed a maximum at ~530 nm for Ir(phen)$_2$Cl$_2$$^+$ and two maxima at ~495 and ~530 nm for Ir(Me$_2$phen)$_2$Cl$_2$$^+$ (Figure 3). For Ir(phen)$_2$Cl$_2$$^+$ the emission intensity in aqueous solution was too low to allow the recording of the emission spectrum below 500 nm. Deaeration or the changing of pH did not affect the emission intensity and band position. The emission

Table I. Quantum Yields of Cl^- Release and Relative Emission Intensities for $Ir(phen)_2Cl_2^+$, at 22°

Experimental conditions	Quantum yields[a] 254 nm	313 nm	365 nm	404 nm	Relative emission intensity[b]
HCl, 1×10^{-2} *M*			0.050[c]		100
HCl, 1×10^{-2} *M*; 0.5 *M* Cl^-			0.050[c]		
HCl, 1×10^{-2} *M*; 1.2 *M* dmf		0.029[c]			
HCl, 1×10^{-2} *M*; 1.2 *M* 2-propanol		0.030[c]			
pH 7			0.055		100
pH 7; 1 *M* Cl^-			0.050[c]		
pH 10	0.050	0.050	0.050	0.050	100
NaOH, 1×10^{-3} *M*			0.050		100
NaOH, 1×10^{-3} *M*; deoxygenated			0.050		100
NaOH, 1×10^{-3} *M*; oxygenated			0.050		100
NaOH, 1×10^{-3} *M*; 0.04 *M* dmf		0.050[c]			
NaOH, 1×10^{-3} *M*; 1.2 *M* dmf	0.031[c]	0.033[c]		0.032[c]	130[d]
NaOH, 1×10^{-3} *M*; 45% v/v dmf			0.007	0.009	380[d]
NaOH, 1×10^{-3} *M*; 45% v/v dmf; 1 *M* Cl^-			0.007[c]		
NaOH, 1×10^{-3} *M*; 95% v/v dmf				~0.001	6700[d]
NaOH, 1×10^{-3} *M*; 1.2 *M* 2-propanol	0.039[c]	0.038[c]		0.038[c]	110[d]

[a] Precision, ±15%; unless otherwise noted, the quantum yields were obtained by Cl^- titration. [b] Precision, ±10%. [c] From spectral measurements. [d] Natural pH.

Table II. Quantum Yields of Cl^- Release and Relative Emission Intensities for $Ir(Me_2phen)_2Cl_2^+$, at 22°

Experimental conditions	Quantum yields[a] 254 nm	313 nm	365 nm	404 nm	Relative emission intensity[b]
HCl, 1×10^{-2} *M*				0.090[c]	100
pH 7		0.10	0.090	0.090	100
pH 10	0.090			0.090	
pH 10; 0.5 *M* Cl^-				0.090[c]	
NaOH, 1×10^{-3} *M*				0.090	100
NaOH, 1×10^{-3} *M*; 45% v/v dmf			0.020	0.020	1100[d]
NaOH, 1×10^{-3} *M*; 95% v/v dmf				~0.002	6600[d]

[a] Precision, ±15%; unless otherwise noted, the quantum yields were obtained by Cl^- titration. [b] Precision, ±10%. [c] From spectral measurements. [d] Natural pH.

Table III. Temperature Dependence for the Cl^- Release and Emission of $Ir(phen)_2Cl_2^+$ and $Ir(Me_2phen)_2Cl_2^+$

		Complex and medium[a]					
		$Ir(phen)_2Cl_2^+$			$Ir(Me_2phen)_2Cl_2^+$		
	T, °C	H_2O	dmf 45% v/v	dmf 95% v/v	H_2O	dmf 45% v/v	dmf 95% v/v
Quantum yields[b]	8	0.025	0.006		0.070	0.012	
	22	0.050	0.009	~0.001	0.090	0.020	~0.002
	45	0.065	0.014		0.16	0.025	
	65	0.095	0.018		0.21	0.050	0.014
	E_{app}[c]	4	4		4	5	
Relative emission intensities[d]	8	130	610	7000	160	1700	11500
	22	100	380	6700	100	1100	10500
	45	71	190	6400	53	590	9600
	65	49	110	6100	32	370	8900
	E_{app}[c]	−4	−5	−0.5	−5	−5	−1
Emission lifetimes (nsec)[e]	22		60	270		90	360
	45			200		50	290
	65			130			240
	E_{app}[c]			−2		~−5	−2

[a] For the quantum yield measurements, 1×10^{-3} *M* NaOH was present in the solution. [b] Excitation at 404 nm; precision ±15%. [c] Apparent activation energy in kcal $mole^{-1}$; precision, ±1 kcal $mole^{-1}$. [d] Precision, ±10%. The absolute intensities are much higher for $Ir(Me_2phen)_2Cl_2^+$ than for $Ir(phen)_2Cl_2^+$ under the same experimental conditions. [e] Precision, ±10%.

intensity was greater in 1.2 *M* dmf or 2-propanol than in water under identical conditions (Tables I and II). As the dmf concentration was increased above 1.2 *M*, an additional maximum was observed at shorter wavelengths (~490 nm) for $Ir(phen)_2Cl_2^+$, and the 495 nm maximum of $Ir(Me_2phen)_2Cl_2^+$ increased in intensity more than the 530-nm band (Figure 3). Increasing temperature decreased the emission intensity, as is shown in Table III where the apparent activation energies are also reported.

In 45% v/v dmf-water, the emission intensity of both complexes was noticeably quenched by oxygen. The results are shown in Table IV, where the quenching results obtained using some Cr(III) complexes are also reported.

With our equipment, luminescence lifetimes for aqueous solutions could not be measured because of the low emission intensity of the two complexes and also because excitation was only possible at 487 nm, where the absorption of aqueous solutions is very low. The luminescence lifetimes in 95% v/v and 45% v/v dmf-water solutions at various temperatures are given in Table III.

Continuous Photolysis. In aqueous solution the general pattern of the two complexes at all the wavelengths examined was the same. The irradiation caused (i) the release of Cl^- ions, (ii) changes in the absorption spectra, and (iii) a decrease in pH when the initial pH was higher than 7. For short irradiation periods (less than 10% of reactant decom-

Table IV. Quenching of the Emission Intensity and Quantum Yield of Cl^- Release in 45% v/v dmf–Water[a]

Experimental conditions	$Ir(phen)_2Cl_2^+$ I^0/I	$Ir(phen)_2Cl_2^+$ $\phi^0_{Cl^-}/\phi_{Cl^-}$	$Ir(Me_2phen)_2Cl_2^+$ I^0/I	$Ir(Me_2phen)_2Cl_2^+$ $\phi^0_{Cl^-}/\phi_{Cl^-}$
oxygen saturated; 22°[b]	1.40 ± 0.05	1.05 ± 0.10	1.50 ± 0.10	1.0 ± 0.1
oxygen saturated; 65°[b]	1.25 ± 0.05	1.25 ± 0.10	1.15 ± 0.05	1.20 ± 0.10
$Cr(CN)_6^{3-}$, 1×10^{-2} *M*; 22°[c]	1.20 ± 0.05	1.00 ± 0.05		
$Cr(ox)_3^{3-}$, 2×10^{-3} *M*; 22°[c]			1.6 ± 0.1	1.3 ± 0.1

[a] Error limits reported are deviations from the mean. [b] Relative to nitrogen saturated solutions at the same temperature. [c] Relative to a l saturated solutions at the same temperature.

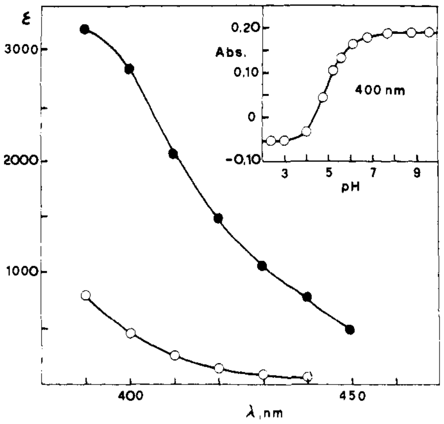


Figure 4. Absorption spectrum of the primary photoproduct from the continuous irradiation of $Ir(phen)_2Cl_2^+$ at pH 2 (○) and 11 (●). Insert shows the variation of the absorption spectrum with pH.

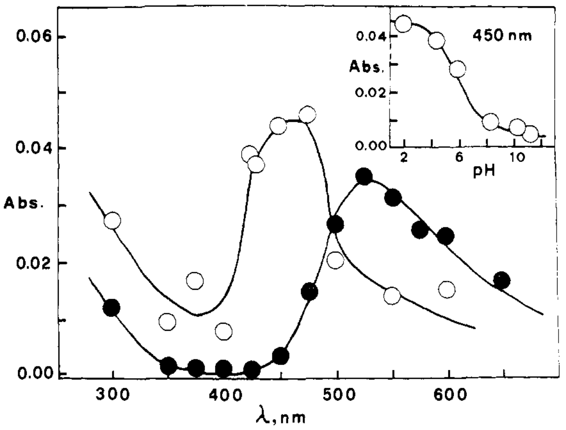


Figure 5. Absorption spectrum of the transient generated in the flash photolysis of $Ir(phen)_2Cl_2^+$ at pH 2 (○) and pH 11 (●). Insert shows the variation of absorbance with pH. Absorbances measured relative to the final absorbance of the solution after the flash.

posed) the Cl^- release and the spectral variations were linear functions of the absorbed light intensity. No postirradiation process was observed. The spectral changes were different in acidic and basic solutions. However, acidic and basic solutions irradiated for the same lengths of time showed the same spectrum, within the experimental error, when brought to the same (basic or acidic) pH after the irradiation.

Quantum yields for Cl^- release are given in Tables I–III under different experimental conditions of irradiation wavelength, pH, presence of added solutes, solvent composition, and temperature. Deaeration, oxygen saturation, presence of up to 1 *M* Cl^-, and presence of 4×10^{-2} *M* dmf did not affect ϕ_{Cl^-} in aqueous solutions (Tables I and II). However, the quantum yield decreased in solutions containing 1.2 *M* dmf or 2-propanol. A strong decrease of ϕ_{Cl^-} was observed with further increasing dmf concentration. Increasing temperature caused an increase in ϕ_{Cl^-} (Table III). In 45% v/v dmf-water, ϕ_{Cl^-} was not appreciably quenched by oxygen at 22°, but it was quenched at 65° (Table IV).

From the spectra of the irradiated aqueous solutions and the knowledge of the extent of Cl^- release, the spectrum of the primary photoproduct could be synthesized in a narrow spectral range. Figure 4 shows the spectra of acidic and basic solutions and the variation of the absorbance as a function of pH for the product from $Ir(phen)_2Cl_2^+$; pK_a values of 5.0 and 5.4 for the primary photoproducts from $Ir(phen)_2Cl_2^+$ and $Ir(Me_2phen)_2Cl_2^+$ were obtained.

For long irradiation periods in aqueous solution the rate of Cl^- release and the spectral variations were no longer a linear function of the absorbed light intensity. After very long irradiation periods (up to several days) at all wavelengths, the spectra of the solutions did not exhibit any further change. A kinetic analysis of the spectral changes[30] showed that this stage was reached through two consecutive photochemical reactions. Here, potentiometric titration showed that two Cl^- ions had been released for each complex molecule contained in the irradiated solutions, whereas no detectable free phen or Me_2phen was present ($<5 \times 10^{-5}$ *M*). The presence of 1.2 *M* dmf or 2-propanol did not affect the stoichiometry of Cl^- release. The same final spectrum was obtained by adding dmf (up to 1.2 *M*) to a completely photolyzed basic aqueous solution of $Ir(phen)_2Cl_2^+$ as from the complete photolysis of a 1.2 *M* dmf basic solution of the complex. The same pattern was followed for 2-propanol. Chromatographic analyses carried out (after acidification) on completely photolyzed $Ir(phen)_2Cl_2^+$ basic solutions showed that the same cationic complex was the sole final product regardless of the presence of 1.2 *M* dmf or 2-propanol in the irradiated solutions.

Flash Photolysis. The flash photolysis of aqueous solutions of $Ir(phen)_2Cl_2^+$ and $Ir(Me_2phen)_2Cl_2^+$ results in almost identical transient absorptions (λ 300–600 nm) and absorbing final products (λ 300–600 nm). Inasmuch as the substrates themselves absorb strongly so that the solution absorbance changes when the complexes are photolyzed by the flash, it is not possible to determine the absorption spectra of transient or product until the interrelationship of these species with the substrate is established. For reasons that will be discussed later, we have chosen to present the transient absorption spectra relative to the final absorbance of the solution after the flash.

In Figure 5 the spectrum of the transient intermediate from the flash photolysis of $Ir(phen)_2Cl_2^+$ is shown. The spectrum is dependent upon pH and the figure insert shows that the transient undergoes acid–base equilibrium with an apparent pK_a value of ~6. The $Ir(Me_2phen)_2Cl_2^+$ complex gave a virtually identical transient absorption and pH dependence.

Because of the low absorbance of the transients even under optimum conditions, it was difficult to evaluate the kinetics of their decays to the final solution absorbance. For example, it was not possible to apply a half-life test to the decays to establish the order of the reaction inasmuch as a decrease in flash intensity, and thus diminished absorbance, rendered the results even less precise. Graphical and computer fit of the decay data to the usual first- and second-

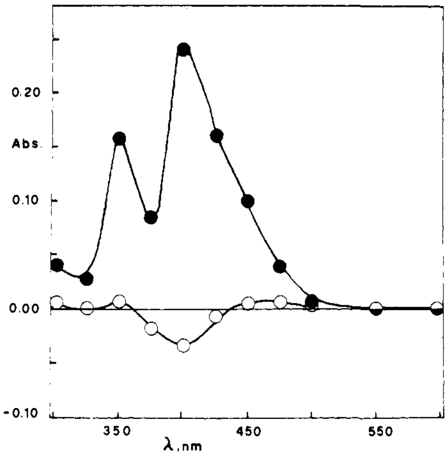


Figure 6. Absorption spectrum of $Ir(phen)_2Cl_2^+$ solution after the flash relative to the initial absorbance of the solution at pH 2 (○) and pH 11 (●).

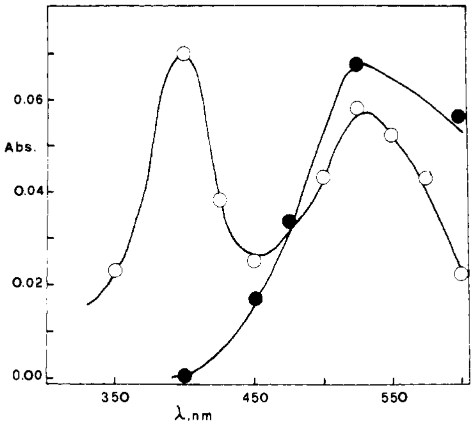


Figure 7. Transient absorption spectrum from the flash photolysis of $Ir(phen)_2Cl_2^+$ containing 1.0 *M* 2-propanol at pH 2 (○) and pH 11 (●). Absorbance measured relative to the final absorbance of the solution after the flash.

order equations indicated that second-order kinetics were most applicable. Decay kinetics in acidic solution were monitored at 475 nm and at 525 nm in basic solution. Because the values of ϵ are not known for the transients, (slope) × (cell path length) = k/ϵ are reported. For $Ir(phen)_2Cl_2^+$, k/ϵ at 475 nm at pH 2.0-3.4 is 4.1 (±0.8) × 10^5.[31] At 525 nm at pH 9.0-11.0, k/ϵ = 1.5 (±0.3) × 10^6. The relative absorbances of the 475- and 525-nm bands in acidic and basic solution, respectively, should reflect their relative ϵ values assuming that the intensity of absorbed radiation and the quantum yield of transient formation are pH independent. Making these assumptions and recognizing that the 475-nm band is approximately 40% more intense than the 525-nm band, the conclusion is reached that $k_{525} = \sim 2.5 k_{475}$ or that the basic form of the intermediate decays ~2.5 times more rapidly than does the acidic form. The decay kinetics of the transients from $Ir(Me_2phen)_2Cl_2^+$ followed a similar pattern with k/ϵ = 3.9 (±0.8) × 10^5 at pH 2 monitored at 475 nm and 1.2 (±0.3) × 10^6 at pH 11 monitored at 525 nm.

The final absorbance of the solution after the flash was evaluated relative to the initial absorbance of the solution. Figure 6 shows the results for the $Ir(phen)_2Cl_2^+$ complex in acidic and basic solution. Except for minor variations in the intensity of the absorbances, the behavior of both complexes was identical. From the variation of the final absorption (relative to the initial absorption) with pH, an apparent pK_a value of 6 (±1) was obtained.

The effect of saturating the solutions with O_2 was to cause the transient to be virtually quenched at both pH 2 and 11. The presence of dmf in the solution of $Ir(phen)_2Cl_2^+$ at pH 2 (0.01-1.0 *M* dmf) and pH 11 (1.0 *M* dmf) also quenched the transient. The addition of 0.1 *M* KCl to $Ir(phen)_2Cl_2^+$ at pH 11 had no effect on the amount of transient or final product formed nor on their absorption spectra or decay kinetics.

The presence of 2-propanol (0.1-1.0 *M*) in the solution had the effect of producing new transient spectra in acidic and basic solution, and they are shown in Figure 7 for $Ir(phen)_2Cl_2^+$. The same results were obtained for $Ir(Me_2phen)_2Cl_2^+$.

Restricting the photolyzing light to λ >300 nm caused the transient to be undetectable with only a slight (up to 30%) decrease in the yield of the final product consistent with the reduction of the intensity of absorbed radiation.

Discussion

The continuous photolysis of aqueous solutions of both complexes leads exclusively to loss of Cl^- with wavelength independent quantum yields. The kinetics and stoichiometry of the observed photolysis indicate that two consecutive photoreactions take place for our complexes (AA stands for phen or Me_2phen).

$$\mathrm{Ir(AA)_2Cl_2^+} \xrightarrow[\mathrm{H_2O}]{h\nu} \mathrm{Ir(AA)_2(OH_2)Cl^{2+}} + \mathrm{Cl^-} \quad (1)$$

$$\mathrm{Ir(AA)_2(OH_2)Cl^{2+}} \xrightarrow[\mathrm{H_2O}]{h\nu} \mathrm{Ir(AA)_2(OH_2)_2^{3+}} + \mathrm{Cl^-} \quad (2)$$

The quantum yield data (Tables I-IV) were obtained for short irradiation periods and therefore they refer to reaction 1. The quantum yield values reported by Muir and Huang[23] for $Ir(phen)_2Cl_2^+$ in water (0.02-0.036 at 350 nm and 0.014 at 254 nm) are substantially lower than our values. The disagreement could be due to the indirect method used by those authors to evaluate the absolute quantum yields.

The spectra displayed in Figure 4 can be identified with the acidic and basic forms of the chloroaquo product. From the observed spectral changes, the pK_a of reaction 3 is deduced to be 5.0 for $Ir(phen)_2(OH_2)Cl^{2+}$ and 5.4 for $Ir(Me_2phen)_2(OH_2)Cl^{2+}$. These p$K_a$ values for coordinated H_2O are in the range shown for other aquo complexes of the same ionic charge.[32]

$$\mathrm{Ir(AA)_2(OH_2)Cl^{2+}} \rightleftarrows \mathrm{Ir(AA)_2(OH)Cl^+} + \mathrm{H^+} \quad (3)$$

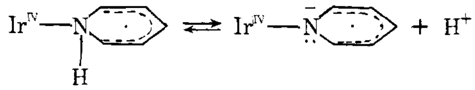
In the flash photolysis experiments, the final change of the solution absorbance (Figure 6) can be reasonably accounted for by assuming that the chloroaquo complex is the only permanent product (reaction 1). Moreover, the pH dependence of these spectral variations for both complexes correspond to apparent pK_a values of ~6, in agreement with those obtained from the continuous photolysis experiments. Thus, at the start the conclusion is made that the transient intermediate does not contribute to the formation of final product nor to a substantial depletion of the substrate and actually constitutes a minor component in the photolysis scheme. This conclusion is based on the spectral correlation discussed above and on the following facts: (1) the transient is produced only from high energy (<300 nm) radiation while the loss of Cl^- is independent of wavelength; (2) the transient is quenched by O_2 and 4 × 10^{-2} *M* dmf while ϕ_{Cl^-} is unaffected under these conditions; (3) although 1.2 *M* dmf quenches the transient and 1.2 *M* 2-propanol apparently reacts with it, the diaquo complex is the sole final product of the continuous photolysis experiments regardless of the presence of these solutes. Thus, we conclude that the chloroaquo product exists in solution independent of the formation and decay of the intermediate. We further assume that the chloroaquo product is generated in a period short compared to the flash photolysis time resolution (~30 μsec).

It is for these reasons that the transient absorption spectra shown in Figures 5 and 7 are displayed relative to the final absorbance of the solution after the flash which reflects the presence of chloroaquo product and the unphotolyzed substrate. From the knowledge of the absorbance differences between product and substrate, we can conclude that the conversion according to reaction 1 in the flash is of the order of $2.5 \times 10^{-6}\ M$.

Nature of the Transient. The transient intermediate arises from the absorption of radiation of $\lambda < 300$ nm and very likely, because of the independence of product yield on wavelength in the continuous irradiation, from $\lambda < 254$ nm. Furthermore, the transient does not appear to be the precursor, or related in any way, to the chloroaquo product. It is the near-quantitative correlation between the spectrum of the final product from the flash and chloroaquo product from the continuous illumination that supports the conclusion that the loss of substrate is coupled with the formation of the chloroaquo complex and that the transient comprises a low-quantum yield component of the total photochemical process, perhaps no more than 10% of the aquation step. Thus, assuming that the quantum yield of aquation is the same under continuous and flash intensities (ϕ = 0.05–0.09), the quantum yield of transient formation would be <0.01. The concentration of transient species formed in the flash would be $\leq 2.5 \times 10^{-7}\ M$ which corresponds to $\epsilon \geq 5 \times 10^3\ M^{-1}\ \mathrm{cm}^{-1}$ for its absorption bands.

We suggest that the transient arises from excitation of metal-to-ligand charge-transfer states in the ultraviolet. The transient can then be viewed formally as a (phen)$^-$ ligand radical anion coordinated to an Ir(IV) center: $[\mathrm{Cl_2(phen)Ir^{IV}(phen)^-}]^+$. The electron adduct to *o*-phenanthroline, (phen)$^-$, generated free in solution by pulse radiolysis[33] does not show absorption bands at $\lambda > 300$ nm and coordination of (phen)$^-$ would not be expected to cause extensive shifts in its absorption maxima. In fact, radicals show virtually the same spectra whether coordinated or free in solution.[34] However, $\mathrm{IrCl_6}^{2-}$ shows an intense absorption band, probably of charge-transfer origin, in the visible[35] so that the transient absorption could be derived from its Ir(IV) nature.

The pH dependence of the transient spectrum indicates that the Ir$^{\mathrm{IV}}$(phen)$^-$ intermediate is involved in an acid-base equilibrium. Inasmuch as an aromatic radical anion with the charge localized on the ring is very basic and susceptible to rapid protonation on the ring by the solvent,[36] we suggest that the site of protonation of the coordinated radical is the nitrogen atom with pK_a ~ 6.



A similar suggestion was made by Endicott[37] in the metal-to-ligand charge-transfer photochemistry of $\mathrm{Ru(NH_3)_5py^{2+}}$ and $\mathrm{Ru(bipy)_3}^{2+}$, systems which are electronically very similar to the Ir(III) complexes discussed here. It is not surprising that the protonation–deprotonation of the ligand results in a spectral shift; there are many examples of this effect in the spectra of Co(III) complexes containing deprotonatable ligands.[38]

The estimated values of ϵ for the transient absorption bands in the visible lead to values of $k > 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ for the bimolecular decay of the intermediate. Such values are compatible with the proposed free radical nature of that species. The larger estimated rate constant for the bimolecular decay of the intermediate at pH 11 is consistent with the +1 charge on the complex in basic solution and the +2 charge in acidic solution due to the proposed protonation of the ligand. The factor of 2.5 in the values of the rate constants estimated above is also consistent with the Debye relationship for the diffusion-controlled interaction of the charged species.[39] Of course, the mode of this bimolecular reaction, whether *via* combination or disproportionation, is not known. It must be pointed out, however, that the second-order decay observed under flash illumination may not be operative under continuous irradiation where the steady-state concentration of the intermediate, generated in a very low quantum yield process, is very small. If the intrinsic lifetime of the Ir$^{\mathrm{IV}}$(phen)$^-$ species toward ligand-to-metal intramolecular electron transfer is on the order of milliseconds, then no final product derived from the intermediate would be detected in the continuous photolysis.

The quenching of the transient absorption by O_2, 2-propanol, and dmf can be attributed to the rapid scavenging of the coordinated radical by these species. The exact mode of reaction is not known but it is important to note that continuous photolysis in the presence of these scavengers did not produce any observed spectra that could be attributed to final products other than the diaquo product. The transient spectrum we detected in the presence of 2-propanol has many characteristics similar to those of the original intermediate which suggests that 2-propanol interacts with the ligand radical in such a way as to maintain the Ir(IV) nature of the intermediate. The decay of the transient from 2-propanol scavenging was not monitored.

The Role of the Excited States in the Photochemical and Photophysical Behavior. The absorption and emission spectra of the $\mathrm{Ir(AA)_2Cl_2}^+$ type complexes have been discussed by Crosby, *et al.*,[11-16,40] and by DeArmond.[17,18] In principle,[3,11] the excited states of these complexes may be classified according to orbital as well as spin labels. From the orbital point of view, in these complexes there are three different categories of excited states: (i) metal centered (dd) excited states in which an electron is promoted from an essentially nonbonding d orbital to a higher energy (σ^* antibonding) d orbital; (ii) metal-to-ligand charge transfer (dπ^*) excited states, in which an electron is promoted from an essentially nonbonding d orbital of the metal to an antibonding π^* orbital associated with the aromatic ligands; (iii) ligand centered ($\pi\pi^*$) excited states, in which an electron in a bonding orbital derived from the ligand π system is promoted to an antibonding π^* orbital also essentially localized on the aromatic ligands. As far the spin labels are concerned, since the Ir(III) complexes have singlet ground state, singlet and triplet excited states are (in principle) expected for each of the three categories of orbitally different excited states.

Using the above classification, the absorption (Figure 1) and emission (Figure 3) spectra of $\mathrm{Ir(phen)_2Cl_2}^+$ were assigned by Crosby, *et al.*,[11-13] as follows. The very high intensity bands in the uv region, which are very similar to those displayed by the free aromatic ligand, are due to spin-allowed π–π^* transitions. Those high intensity absorption bands present in the uv and visible regions which are not present in the spectrum of free aromatic ligand are due to spin allowed d–π^* transitions. The absorption tail in the 450-nm region, where a poorly resolved band at 21.7 kK (~460 nm) can be observed at 77°K,[16] is assigned to a d–π^* singlet-triplet transition.[13-16] No d-d bands can be observed in the absorption spectrum because they are expected to appear in the same spectral region as the more intense CT bands (see also below). The emission band of $\mathrm{Ir(phen)_2Cl_2}^+$ is well structured and shows its high energy peak at 21.1 kK in 4:1 v/v ethanol–methanol glasses at 77°K.[11,13,16] Since this emission band overlaps significantly with the absorption tail and is 1.1 kK red shifted with respect to the π-π^* phosphorescence of the free ligand, it has been attributed to a dπ^* triplet state.[11,13,16]

The absorption spectrum of $Ir(Me_2phen)_2Cl_2^+$ (Figure 2) is similar to that of the parent complex. According to Crosby, *et al.*,[13,16] a significant difference between the two absorption spectra at 77°K in ethanol-methanol glasses is given by the fact that the poorly resolved absorption band at about 21.7 kK with $\epsilon \sim 200\ M^{-1}\ cm^{-1}$, which can be seen in the spectrum of the parent complex, is not present in the spectrum of $Ir(Me_2phen)_2Cl_2^+$, which in that region only exhibits a weak unresolved absorption ($\epsilon \sim 50$). This difference, however, is not apparent in the room temperature spectra (Figures 1 and 2). The emission spectrum of $Ir(Me_2phen)_2Cl_2^+$ (Figure 3) is well structured at 77°K and shows its high energy peak at 20.5 kK, that is, only 0.2 kK red-shifted with respect to the emission of the free aromatic ligand under the same conditions.[11,16] These facts, as well as others which will be discussed below, led Crosby to assign the emission of $Ir(Me_2phen)_2Cl_2^+$ to a ligand localized $\pi\pi^*$ triplet state.[11,15,16]

Crosby[11-16,40] and DeArmond[17,18] have also emphasized that the orbital and spin classifications may lose much of their value owing to configuration interaction and spin-orbital coupling. According to DeArmond and Hillis,[17a] the red shift of the $Ir(phen)_2Cl_2^+$ emission with respect to that of the free ligand is too small to assign the emission of the complex to a dπ^* excited state. They affirm that a significant mixing of metal d orbitals and π or π^* ligand orbitals of appropriate symmetry must occur, so that the d-π^* "charge transfer" and the π-π^* "ligand localized" labels for the electronic transitions should be replaced by a more general (dπ)-(dπ)* "delocalized molecular" label. The importance of the dπ^*-$\pi\pi^*$ configuration interaction has also been discussed by Crosby, *et al.*[13,15,16] They have found that the relation between the dπ^* and $\pi\pi^*$ excited states of these complexes is similar to that occurring for the nπ^* and $\pi\pi^*$ excited states of aromatic carbonyl compounds.[15] The energy of the dπ^* states of the complexes decreases with decreasing polarity of the solvent, whereas the energy of the $\pi\pi^*$ states is substantially unaffected by changing solvent. It follows that the extent of dπ^*-$\pi\pi^*$ configuration interaction can be modulated by solvent perturbation.[15,16] Using various solvent mixtures at 77°K, they found that the energy of the emitting state of $Ir(Me_2phen)_2Cl_2^+$ (20.5 kK) was independent of the solvent nature, whereas the energy of the emitting state of $Ir(phen)_2Cl_2^+$ changed from 21.1 kK in 4:1 ethanol-methanol to 21.6 kK in 1:1 glycerol-water.[15,16] These results led Crosby to suggest that the dπ^* and $\pi\pi^*$ orbital labels are substantially meaningful for the emitting states of $Ir(phen)_2Cl_2^+$ and $Ir(Me_2phen)_2Cl_2^+$, although a contribution of at least 10% by the $\pi\pi^*$ triplet to the emitting dπ^* triplet of $Ir(phen)_2Cl_2^+$ must be present. For other complexes, such as the 4,7-diphenyl substituted complex, the configuration interaction is so large that the dπ^* or $\pi\pi^*$ labels for the emitting state are completely meaningless.[13,15]

As far as the singlet and triplet spin labels are concerned, they can reasonably be used for the $\pi\pi^*$ states because these states are not much perturbed by the metal atom, but they lose part of their meaning for the dd excited states because of the strong spin-orbit coupling caused by the heavy metal atom on the d electrons. For the dπ^* excited states, singlet and triplet labels have always been used up until now,[11-19] but a very recent paper by Crosby, *et al.*,[40] claims that any spin label is apparently not justified either experimentally or theoretically for these types of excited states.

It is also very important to evaluate the energy position of the lowest dd triplet state which in these complexes is not seen either in absorption or in emission.[11,13] Using the rule of the average environment and the known spectra of $IrCl_6^{3-}$[41] and $Ir(phen)Cl_4^-$,[42] a value of about 22 kK for the absorption maximum of the lowest dd triplet state of $Ir(phen)_2Cl_2^+$ is obtained. A comparison between the triplet dd emission of some Rh(III) and Ir(III) complexes together with the knowledge of the triplet dd emission of $Rh(phen)_2Cl_2^+$[17a] gives a value of about 14 kK for the emission maximum of the triplet dd state of $Ir(phen)_2Cl_2^+$. While being admittedly rough, these estimates indicate that the zero-energy level of the lowest triplet dd state of $Ir(phen)_2Cl_2^+$ should not be much higher than 20 kK, *i.e.*, in the same energy range of the dπ^* emitting state.

The results from the quenching experiments (Table IV) show that, at room temperature, Cl^- release is not appreciably quenched under conditions in which the luminescence emission is quenched. *This demonstrates that most, if not all, of the Cl^- release must take place from an excited state different from that responsible for the luminescence emission.* On the other hand, the general pattern of our results (particularly, the increase of ϕ_{Cl^-} and the decrease of I_e and τ_e passing from dmf to water) strongly suggests that there is a competition between emission and photoreaction. In other words, emission and photoreaction appear to originate from different but "communicating" excited states. Thus, the following problems arise: (1) what are the orbital and spin labels of the reacting state; (2) what is the relative energy position of the emitting and reacting state; (3) which of these two states is first populated following the deactivation of the excited states originally obtained with light absorption; (4) what channels allow the communication between the emitting and reacting state; (5) what is the role played by temperature and solvent composition?

As far as the first point is concerned, there is no doubt that the reacting state must be a dd triplet. This statement is based on the following reasons: (i) the $\pi\pi^*$ and dπ^* excited states are not expected to cause the release of Cl^- from the complex because the π-π^* transitions should not affect the Ir-Cl bonds and the d-π^* transitions are expected to reinforce the Ir-Cl bonds by increasing the positive charge on the metal; (ii) our quenching results directly show that the dπ^* emitting state of $Ir(phen)_2Cl_2^+$ and the $\pi\pi^*$ emitting state of $Ir(Me_2phen)_2Cl_2^+$ are not directly responsible for most of the observed Cl^- release; (iii) the dd excited states are known[3,4] to cause halide ion release in a number of transition metal complexes; (iv) the dd singlet excited states are expected to lie at higher energies than that needed (404 nm, ~25 kK) to obtain photoreaction; (v) the lowest dd triplet state is expected to lie in the same energy range as the emitting state of the two complexes, *i.e.*, <404 nm.

In order to discuss the second problem, *i.e.*, the relative energy position of the reacting and emitting states, we must consider the change in ϕ_{Cl^-}, I_e, and τ_e with temperature and solvent composition. Since the lifetime and intensity of the emission exhibit apparent *negative* activation energies (Table III), there must be some important deactivation process, which is thermally controlled, involving the emitting state. The results also show that the decrease in τ_e and I_e with increasing temperature is accompanied by an increase in ϕ_{Cl^-}. This suggests that the thermally controlled deactivation path of the emitting state leads to the population of the reactive dd triplet.[43] Thus, for both complexes the emitting state must lie at lower energy than the reacting dd triplet. This conclusion is in agreement with the general rule that emission can only originate from the lowest excited state of a complex,[44] and particularly with the previously reported assignments of dπ^* triplet[11,13,16] or "molecular delocalized" triplet[17] for the lowest (emitting) state of $Ir(phen)_2Cl_2^+$, and of $\pi\pi^*$ triplet[11,15,16] for the lowest (emitting) state of Ir(Me$_2$phen)$_2$Cl$_2^+$.

As far as problems 3 and 4 are concerned, the following points are relevant: (a) ϕ_{Cl^-} is independent of excitation wavelength (Tables I and II), requiring a nearly unitary efficiency of conversion from the high energy excited states to the one directly populated by the lowest energy radiation (404 nm); (b) evidence for a near unitary population of the emitting level following optical pumping of any upper excited state has been reported by Demas and Crosby[12] for Ir(phen)$_2$Cl$_2^+$ and several Ru(II) and Os(II) complexes in rigid alcoholic glass at 77°K, where the photochemical reaction probably does not occur; (c) as discussed above, the reactive state is higher in energy than the emitting state; (d) in these complexes there is a noticeable density of states which are strongly mixed by configuration interaction and spin-orbit coupling, so that there is no reason to believe that the state responsible for the reaction is by-passed in the cascade from the high-energy states populated upon light absorption; (e) the reaction is less quenched than the emission (Table IV), which means that the emitting state cannot be a precursor of the reactive state in the cascade from the higher energy states; (f) as we have seen above, there is a thermally activated path from the emitting to the reactive state.

The simplest energy level diagram for Ir(phen)$_2$Cl$_2^+$ which fits these points is shown in Figure 8. Since ϕ_{Cl^-} is very small, k_r is much smaller than (k_c + k_d). Moreover, assuming that Demas and Crosby's finding[12] of a near unitary population of the emitting level (see above) still holds at room temperature, k_c should be much larger than k_d.

On the basis of the scheme of Figure 8 we will discuss some specific aspects of our results, with particular regard to problem 5 mentioned above, *i.e.,* to the role played by temperature and solvent composition. A steady state treatment gives the following equations for the emission lifetime, τ_e, the emission intensity, I_e, and the quantum yield of the photoreaction, ϕ_{Cl^-}

$$\tau_e = \frac{K_R}{K_R K_E - k_c k_c'} = \frac{K_R}{A + Bk_c'} \tag{4}$$

$$I_e = \alpha \phi_e = \alpha \frac{k_e k_c'}{K_R K_E - k_c k_c'} = \alpha \frac{C}{A + Bk_c'} \tag{5}$$

$$\phi_{Cl^-} = \frac{k_r K_E}{K_R K_E - k_c k_c'} = \frac{D + k_r k_c'}{A + Bk_c'} \tag{6}$$

where

$$K_R = k_r + k_c + k_d$$

$$K_E = k_e' + k_c' + k_d'$$

$$A = K_R(k_e' + k_d')$$

$$B = k_d + k_r$$

$$C = k_e' k_c$$

$$D = k_r(k_e' + k_d')$$

and α is a constant related to the experimental conditions under which the emission intensity was measured.[45] According to these equations, if k_c' is the only step that can exhibit a substantial activation energy (eq 7), and if in the temperature range explored

$$k_c' = k_c'^0 e^{-\Delta E/RT} \tag{7}$$

Bk_c' is not negligible with respect to A in eq 1 and 2, the lifetime and intensity emission are expected to show the same apparent *negative* activation energy. This is in reasonable agreement with what we have found from our experiments (Table III). Moreover, since $D \ll A$ and k_d should not be larger than k_r (remember that k_c should be the most important deactivation step for the reacting state), the temperature dependence of k_c' may affect the numerator of eq 6 more than the denominator so that increasing temperature may cause an increase in ϕ_{Cl^-}, as we have found experimentally (Table III). It should also be noted that if k_r also has an activation energy, it would contribute to cause an apparent *positive* activation energy for ϕ_{Cl^-} without affecting the apparent negative activation energies of I_e and τ_e since k_r is much smaller than (k_c + k_d). Moreover, when k_c' is an important deactivation path for the emitting state, both prompt and delayed reaction should take place from the triplet dd state, so that a partial quenching of the photoreaction by the emission quenchers can be expected, especially at high temperature. This is again in agreement with the experimental results (Table IV).

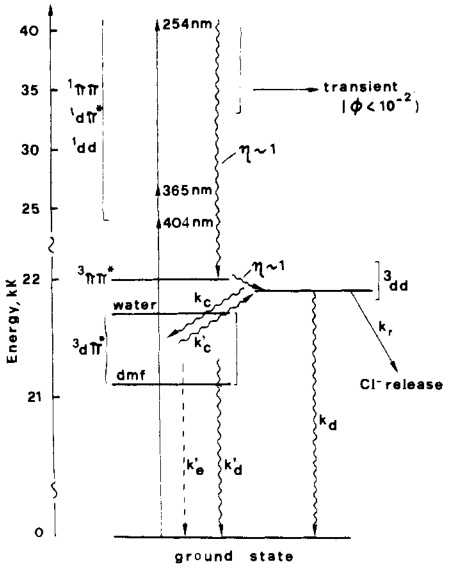


Figure 8. Schematic energy level diagram for Ir(phen)$_2$Cl$_2^+$. For sake of simplicity, the excited states are labeled according to the nomenclature proposed in ref 11 (for discussion, see text). The exact energy positions of the "singlet" excited states are not specified since they do not affect our discussion. The exact energy position of ^{3}dd is not known and the square bracket indicates approximately the energy range where this state should lie (see text). The full-line arrows show the irradiation wavelengths used in the continuous photolysis experiments.

The results show that increasing dmf concentration has the same qualitative effect as decreasing temperature. Although one cannot rule out that other factors may contribute to explain this effect, the observed behavior can be simply reconciled by Crosby's finding that the energy of the emitting state of Ir(phen)$_2$Cl$_2^+$ decreases with decreasing polarity of the solvent.[15,16] This will cause an increase in the energy separation between the emitting and reacting states (Figure 8), and an increase in ΔE of eq 7, with the same consequences that result from a decrease in temperature. In 95% v/v dmf-water, ΔE may be so high, and thus k_c' so small, that the term A may be more important than Bk_c' in eq 4 and 5. This would explain the very small value of the apparent negative activation energy of τ_e and I_e in this medium.

For Ir(Me$_2$phen)$_2$Cl$_2^+$, the energy of the emitting state, which is $\pi\pi^*$ in the Crosby nomenclature, is not affected by the nature of the solvent for a series of mixed solvents at 77°K.[15,16] Therefore, the energy gap between the emitting state and the reacting triplet dd state (the energy of which is also solvent independent) should not change in going from water to dmf, and the photochemical and photophysical behavior should be solvent independent. From the experimental point of view, however, Ir(Me$_2$phen)$_2$Cl$_2^+$ behaves in practically the same manner as Ir(phen)$_2$Cl$_2^+$; *i.e.,* it exhibits a strong solvent-dependent behavior. The most plausible explanation appears to be as follows. Crosby has shown that although the energy of the $\pi\pi^*$ state is not solvent dependent, its lifetime is profoundly affected by the solvent nature.[16] This is attributed to the change in the degree of configuration interaction between the $\pi\pi^*$ state and the $d\pi^*$ state which lies just above the former one and whose energy is solvent dependent. In other words, the lifetime of the $\pi\pi^*$ state is really controlled by mixing with the $d\pi^*$ state, even though the $\pi\pi^*$ energy is unaffected.[16] Similarly, it may be that the communication between the emitting $\pi\pi^*$ state and the reacting dd state might be strongly affected by the energy position of the $d\pi^*$ state which changes in going from dmf to water. It is apparent that the use of the more general nomenclature proposed by DeArmond[17,18] would facilitate the explanation of the similar behavior of the two complexes. In any case, the very similar photochemical and photophysical behavior of $\mathrm{Ir(phen)_2Cl_2^+}$ and $\mathrm{Ir(Me_2phen)_2Cl_2^+}$ in fluid solutions should be taken into consideration in any further discussion of the labeling of the excited states of these complexes.

Conclusion

The results displayed in this paper show that both the photochemical and the photophysical behavior of certain transition metal complexes can be "tuned" at room temperature by a change of the solvent. This may help in the design of systems having desired photochemical and photophysical properties, as Crosby has emphasized since 1970.[11] A particularly appealing goal is that of obtaining new inorganic sensitizers which can complement the widely used $\mathrm{Ru(dipy)_3^{2+}}$ complex.[46] Both $\mathrm{Ir(phen)_2Cl_2^+}$ and $\mathrm{Ir(Me_2phen)_2Cl_2^+}$ are not suitable sensitizers in water because of their relatively high photosensitivity, weak emission intensity, and short emission lifetime. In dmf solution, and presumably also in other solvents having low dielectric constants, these complexes are relatively inert photochemically and exhibit a very intense and relatively long-lived emission, so that they can be conveniently used as energy donors.

Finally, these results, as well as preliminary observations[42] carried out on $\mathrm{Ir(phen)Cl_4^-}$ which only undergoes $\mathrm{Cl^-}$ release in continuous photolysis experiments, show that, contrary to a common belief, the photochemical behavior is not always dictated by the nature of the lowest lying excited state. For $\mathrm{Ir(phen)Cl_4^-}$, $\mathrm{Ir(phen)_2Cl_2^+}$, and $\mathrm{Ir(Me_2phen)_2Cl_2^+}$, the lowest lying excited state is dd, $d\pi^*$, and $\pi\pi^*$, respectively,[11] but all three complexes give the same type of photoreaction ($\mathrm{Cl^-}$ release) with very similar quantum yields.

References and Notes

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