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A Study of the Electronic States of Iridium(III) Complexes Containing 1,10-Phenanthroline Ligands. The Contribution of a dd Excited State to the Lowest Triplet State

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To investigate the solvent dependence of the dd contribution to the lowest excited state of *cis*-$[IrCl_2L_2]Cl$ (L=1,10-phenanthroline (phen) and 5,6-dimethyl-1,10-phenanthroline (5,6-Mephen)), the triplet-triplet absorption spectra (15000—25000 cm^{-1}) were measured in *N,N*-dimethylformamide (DMF)–water mixed solvents. From a smaller solvent-dependence of the absorption intensity for $[IrCl_2(5,6\text{-Mephen})_2]Cl$ than for $[IrCl_2(phen)_2]Cl$, the lowest triplet state of the former is considered to have a $\pi\pi^*$ character in 95% v/v DMF–water and 45% v/v DMF–water. However, in pure water a considerable decrease in the triplet-triplet absorbance was observed. Because the molar extinction coefficient of the triplet-triplet absorption of the dd-dd type is 10^{-2} times smaller than that of the $\pi\pi^*$-$\pi\pi^*$ type, the observed decrease in the absorbance is elucidated by the increase in the contribution of the dd state to the lowest triplet state. Using ethanol–methanol (4 : 1, v/v) as a solvent, it was confirmed that the triplet-triplet absorption spectrum shows no change when the solutions are degassed and the temperature is lowered (77 K).

Recently, several studies have been reported on the electronic character of the emitting state of *cis*-$[IrCl_2(phen)_2]Cl$, which is sensitive to the solvents, the temperature, and the methyl substitution of a ligand molecule.[1–5] This characteristic has been interpreted in terms of a change in the character of the lowest triplet state. In this complex, the lowest triplet state of the $d\pi^*$ (metal-to-ligand charge transfer) character and the lowest triplet state of the $\pi\pi^*$ (locally excitation of a ligand) character lie very close to each other. From the studies of the solvent effects on the energies and the lifetimes of the emission in alcoholic solvents at 77 K, Crosby *et al.* concluded that the emittive state is a state of a mixed character of $d\pi^*$ and $\pi\pi^*$, and that the contribution to the lowest triplet state of the two characters is affected by the environment.[1–3] On the other hand, Ballardini *et al.* studied the quantum yield of the photosubstitution reaction of a chloride ion for $[IrCl_2(phen)_2]Cl$ and $[IrCl_2(5,6\text{-Mephen})_2]Cl$ by using mixed solvents of DMF and water at room temperature.[6] They reported that the photochemical quantum yields depend on the solvents and the temperature in a very similar way for both complexes. Generally, the ligand substitution takes place through a dd excited state. Therefore, the observed change in the quantum yield reveals the close-lying dd excited state near the lowest triplet state. Recently, Watts *et al.* measured the weak emission of $[IrCl_2(phen)_2]Cl$ and $[IrCl_2(5,6\text{-Mephen})_2]Cl$ at room temperature and reported the emission from a dd excited state, besides the emission from the $d\pi^*$-$\pi\pi^*$ mixed state previously reported.[5]

We previously measured the triplet-triplet absorption spectra of $[IrCl_2(phen)_2]Cl$ and the related complexes in DMF–water mixed solvents.[7] For these complexes, the relevant solvent effect on the triplet-triplet absorption spectrum was observed, and the changes were interpreted in terms of the decrease in the $d\pi^*$ component in the lowest triplet state with the increase in the solvent polarity. The excited-state absorption spectrum sharply reflects the character of the lowest excited state. Therefore, in the present work we investigated the dd contribution to the lowest triplet state of $[IrCl_2(phen)_2]Cl$ and $[IrCl_2(5,6\text{-Mephen})_2]Cl$ using excited-state spectroscopy.

Experimental

Materials. *cis*-Dichlorobis(1,10-phenanthroline)iridium(III) chloride trihydrate, $[IrCl_2(phen)_2]Cl\cdot 3H_2O$, and *cis*-dichlorobis(5,6-dimethyl-1,10-phenanthroline)iridium(III) chloride trihydrate, $[IrCl_2(5,6\text{-Mephen})_2]Cl\cdot 3H_2O$, were prepared by following the procedure of Broomhead and Grumley.[8] After the yellow band has been eluted with 0.1 M HCl[†] from a cellulose cation-exchange column, the emission spectra of the eluted fractions were measured in ethanol–methanol (4 : 1, v/v) at 77 K. The fraction is considered to be pure when the emission decay is exponential and when the lifetimes monitored at 480 nm and 500 nm have the same value, because the by-product has its strong emission at a longer wavelength than that of pure $[IrCl_2(phen)_2]Cl$. Moreover, the emission in 95% v/v DMF–water was measured at 77 K and at room temperature and confirmed to give the same spectrum as a sample B, reported by Ballardini *et al.*[9] The *N,N*-dimethylformamide was of a spectroscopic grade, while the water was distilled four times.

Apparatus. The triplet-triplet absorption spectra were measured at room temperature and at 77 K using a nitrogen laser (Molectron UV24) as an exciting-light source and a pulsed xenon flash as a monitoring-light source.

Results and Discussion

Environmental Effect on the Triplet-Triplet Absorption Spectra. Figures 1 and 2 show the triplet-triplet absorption spectra of $[IrCl_2(phen)_2]Cl$ and $[IrCl_2(5,6\text{-Mephen})_2]Cl$ at room temperature in the solvents of 95% v/v DMF–water (**1**), 45% v/v DMF–water (**2**), and water (**3**). The concentrations of the six complex solutions were adjusted to take the same optical density for the ground-state absorption at the wavelength of the exciting-light source (337 nm). The concentrations of the complex solutions used are $\approx 10^{-3}$ M. Since

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[†] $1M = 1\ mol\ dm^{-3}$.

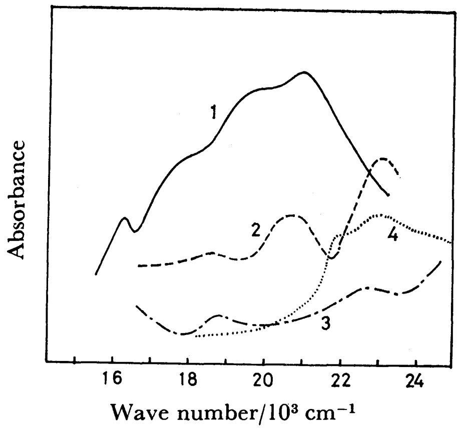

Fig. 1. Triplet-triplet absorption spectra at room temperature of [$IrCl_2(phen)_2$]Cl in 95% v/v DMF–water (curve 1), in 45% v/v DMF–water (curve 2), in water (curve 3), and of phenathroline molecule in ethanol–methanol (4 : 1, v/v) (curve 4).

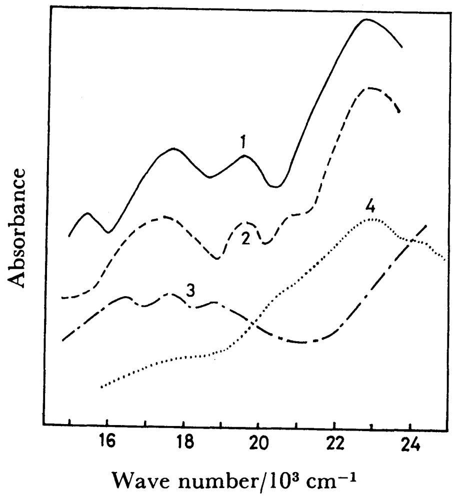

Fig. 2. Triplet-triplet absorption spectra at room temperature of [$IrCl_2$(5,6-Mephen$)_2$]Cl in 95% v/v DMF–water (curve 1), in 45% v/v DMF–water (curve 2), in water (curve 3), and of 5,6-dimethyl-1,10-phenanthroline molecule in ethanol–methanol(4 : 1, v/v) (curve4).

the two complexes show no fluorescence and contain a heavy atom (Ir^{3+}), the quantum yields of the intersystem crossing may safely be assumed to be very close to unity. Therefore, the concentrations of the singlet excited molecules populated by the laser radiation are assumed to be equal to that of the lowest triplet state. The absorbances of the six spectra (Curves 1—3 in Figs. 1 and 2) were measured under the same laser condition, so the changes in the absorbances correspond to the changes in the molar extinction coefficient of the triplet state. The absorbances of the free ligands in ethanol–methanol (4 : 1, v/v) are also shown in Figs. 1 and 2. The integrated absorbance of 5,6-Mephen is obtained to be larger by 1.5 times than that of phen.

At room temperature, the decay of the triplet-triplet absorption both of [$IrCl_2(phen)_2$]Cl and [$IrCl_2$(5,6-Mephen$)_2$]Cl is exponential in 95% v/v DMF–water and in ethanol–methanol (4 : 1, v/v). In 45% v/v DMF–water, it deviates slightly from exponential behavior, but no time-dependence of the triplet-triplet absorption spectrum was observed. In water, the decay is very rapid (τ=25 ns for the non-degassed solutions of both complexes), so that the deviation from the exponential decay is not clear. Since the dearation is not carried out for the DMF–water mixed solvents, the observed lifetimes at room temperature are shorter by 0.6—0.7 times than those of the degassed solutions obtained from the emission measurements.[6] The lifetime of a degassed ethanol–methanol (4 : 1, v/v) of [$IrCl_2(phen)_2$]Cl is determined from the absorption decay to be 59 ns. After a long radiation of 337 nm light, a dark violet material was produced, even at 77 K, in all the solvents examined. However, the emission and the triplet-triplet absorption spectra of the photoproducts were not found.

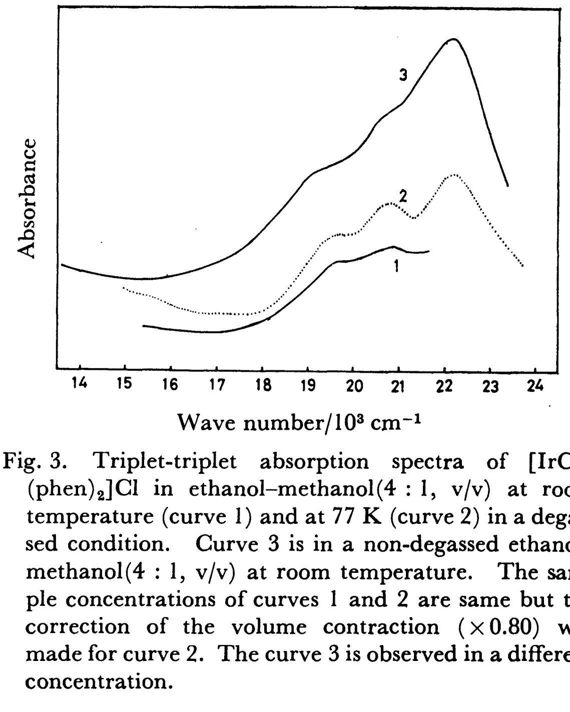

Fig. 3. Triplet-triplet absorption spectra of [$IrCl_2$-(phen$)_2$]Cl in ethanol–methanol(4 : 1, v/v) at room temperature (curve 1) and at 77 K (curve 2) in a degassed condition. Curve 3 is in a non-degassed ethanol–methanol(4 : 1, v/v) at room temperature. The sample concentrations of curves 1 and 2 are same but the correction of the volume contraction (×0.80) was made for curve 2. The curve 3 is observed in a different concentration.

In order to examine the temperature effect on the triplet-triplet absorption spectrum, the measurements were carried out by using a degassed ethanol–methanol (4 : 1, v/v) solution of [$IrCl_2(phen)_2$]Cl at 77 K and at room temperature (Fig. 3). The change in the absorption intensity and the spectrum is concluded to be insignificant between 77 K and room temperature after the correction for the volume contraction of the solvent. Over the range of 19500—21500 cm^{-1}, the emission is strong at 77 K, so that the correction was made for the emission contamination; the emission intensity is 1/4 of the decrease in the monitoring light by the absorption at the emission peak. From the comparison of the spectra of the non-degassed solution with that of the degassed solution (Fig. 3), no effect of the dearation on the spectra is observed at room temperature, but the triplet lifetime becomes longer upon dearation: 59 ns and 35 ns for the degassed and the non-degassed solutions respectively. Therefore, the absorption spectra observed without dearation at room temperature can be assigned to the triplet-triplet transitions.

The Character of the Lowest Triplet State. With respect to $[IrCl_2(phen)_2]Cl$ and $[IrCl_2(5,6\text{-Mephen})_2]Cl$, recently two models were proposed for the electronic structure of the low-lying states. Model A assumes the close-lying dd state and the dπ^* (or $\pi\pi^*$) state to be thermally equilibrated at room temperature, while at a low temperature a barrier is assumed to exist between the two potential minima by virtue of a rigid matrix perturbation; the dd state lies 500 cm^{-1} below the lowest dπ^* state for $[IrCl_2(phen)_2]Cl$ and 100 cm^{-1} above the lowest $\pi\pi^*$ state for $[IrCl_2(5,6\text{-Mephen})_2]Cl$ in DMF.$^{5)}$ The dd contribution to the emission is also determined by the use of the excitation and emission polarization spectra.$^{10)}$ On the other hand, Model B gives a common interpretation for both $[IrCl_2(phen)_2]Cl$ and $[IrCl_2(5,6\text{-MePhen})_2]Cl$. It is proposed that a dd state lies close above the emitting state and that the energy separation between the two states decreases with the increase in the solvent polarity.$^{6,9)}$

In order to discuss the relation between the above two models and the present environmental effects of the triplet-triplet absorption spectra shown in Figs. 1—3, knowledge of the values of the molar-extinction coefficients of the triplet-triplet transitions (ε_{T-T}) is necessary. With respect to the $\pi\pi^*$-$\pi\pi^*$ transitions in the region of our experiments, the values of ε_{T-T} are evaluated to be in the order of 10^5 l/(mol cm) from the oscillator strengths calculated for free-lignad molecules: 0.2 for 1,10-phenanthroline and 0.4 for 2,2′-bipyridine.$^{7)}$ The observed ε_{T-T} values for the ligands have not been reported, but the values for molecules with similar electronic structures have been reported:$^{11)}$ for phenanthrene, $\varepsilon_{T-T}=21000$ l/(mol cm) at 20730 cm^{-1} and 41500 l/(mol cm) at 20410 cm^{-1}, and for biphenyl, $\varepsilon_{T-T}=35400$ l/(mol cm) at 27700 cm^{-1}. From these values, ε_{T-T} of the $\pi\pi^*$-$\pi\pi^*$ transitions are estimated to be of the order of 10^4—10^5 l/(mol cm), assuming the perturbation by the complex formation to be not very large. On the other hand, because the dd-dd transitions are generally weak due to a symmetry-forbidden property, ε_{T-T} is estimated to be of the order of 10—10^2 l/(mol cm), like the ε_G of the ground-to-dd transition, which is 10^2 l/(mol cm) for $[RhCl_2(phen)_2]Cl^{12)}$ and 50 l/(mol cm) for $[IrCl_2(en)_2]Cl$ (en=ethylenediamine).$^{12)}$ The intensity for the dπ^*-dπ^* transitions becomes large only when the d orbital for the initial and the final states is common. Since the dπ^*-dπ^* transition energy can be estimated roughly from the difference in the π^* orbital energies (e_j; j=8—14), the transition energies and the oscillator strengths shown in Table 1 are obtained from the SCF calculation of a free 1,10-phenanthroline. The dπ^* transition from a d orbital to the antibonding π^* orbital j is described as (d-j). The lowest dπ^* state, (d-8), degenerates almost to the (d-9) state. Therefore, we assigned the lowest dπ^* state to $1/\sqrt{2}\{(d\text{-}8)+(d\text{-}9)\}$. Then, the oscillator strengths of the dπ^*-dπ^* transitions are calculated by means of the following equations:

$$f_j = 1.085 \times 10^{11}\,\sigma_j\,Q_j^{\,2} \quad (\sigma_j \text{ in cm}^{-1} \text{ and } Q_j \text{ in cm})$$

$$Q_j = \int 1/\sqrt{2}\,\{(d\text{-}8)+(d\text{-}9)\}\; r(d\text{-}j)\;dv$$

$$\sigma_j = e_j - 1/2(e_8 + e_9).$$

From the calculated results, the transitions to be observed in the present measurement are the transitions to (d-11) or (d-12). Therefore, their oscillator strengths are of the same order as those of the $\pi\pi^*$-$\pi\pi^*$ transitions. Judging from the above-mentioned estimation, the ε_{T-T} of the dd-dd transition seems to be smaller by 10^2—10^4 than those of the dπ^*-dπ^* and the $\pi\pi^*$-$\pi\pi^*$ transitions, so that the increase in the dd component in the lowest tripiet state causes a distinct intensity decrease in the triplet-triplet absorbances.

TABLE 1. TRANSITION ENERGY AND OSCILLATOR STRENGTH OF THE dπ^*-dπ^* TRANSITION OF $[IrCl_2(phen)_2]Cl$

Excited state	Transition energy σ_j/cm^{-1}	Oscillator strength
(d-8)	0	
(d-9)	81	
(d-10)	10500	0.05
(d-11)	13600	0.1
(d-12)	20200	0.1
(d-13)	30200	0.02
(d-14)	40300	0.007

By the use of Model A, for $[IrCl_2(phen)_2]Cl$ the population ratio of dπ^* to dd states is estimated as 1/9 at 300 K, based on the reported dd-dπ^* separation (500 cm^{-1}). However, at 77 K a selective internal conversion is assumed to occur to the lowest dπ^* state after the excitation to the higher $\pi\pi^*$ state, so that a large increase in the population ratio results.$^{5)}$ According to this scheme, the triplet-triplet absorbance should show a distinct increase with the temperature decrease. However, as may be seen in Fig. 3, the triplet-triplet absorption spectra at 77 K and at room temperature show no significant change in either the intensity or the peak position in ethanol–methanol (4 : 1, v/v). As far as the triplet-triplet absorption is concerned, the effect of the dd population was not observed at room temperature in this solvent, so that the lowest triplet state can be assigned to a dπ^* state, as was previously assigned.$^{2)}$ Since the **1** solvent has a dielectric constant (39) similar to that (26) of the above solvent, and since we observed that the absorption spectra and intensities of the triplet-triplet transitions of the two solvents resembles each other, it is reasonable to make the same assignment for the complex in the **1** solvent.

Mechanism of Solvent Effect for $[IrCl_2(5,6\text{-Mephen})_2]Cl$. In a previous work, the present author suggested that the $\pi\pi^*$ character in the lowest triplet state increases considerably in water for $[IrCl_2(phen)_2]Cl$.$^{7)}$ As may be seen in Fig. 1, this assignment is confirmed by the resemblance of the triplet-triplet absorption spectra of the complex in water and those of a free 1,10-phenanthroline.

The 5,6-dimethyl substitution of a 1,10-phenanthroline lowers the energy of the lowest $\pi\pi^*$ transition by 1500 cm^{-1} in ethanol–methanol (4 : 1, v/v) at 77 K.

Moreover, the emission energy does not show a solvent dependence, so that the lowest triplet state of [IrCl$_2$(5,6-Mephen)$_2$]Cl was assigned to a ππ* state in alcoholic solvents at 77 K, independent of the solvent polarity.[2] Figure 2 shows that the intensity change of the triplet-triplet transition is small with respect to the spectra for **1** and **2** solvents, in contrast to the spectra of [IrCl$_2$(phen)$_2$]Cl. Consistent with the expectation from the assignment, the spectra for the two solvents resemble that of a free ligand (Fig. 2). The small intensity difference between the two solvents may be attributed to the change in the dπ* component in the lowest triplet state. For this complex also, it has been reported that the lifetime changes from 66.3 μs to 236.1 μs at 77 K, but the emission energy does not change with the increase in the solvent dielectric constant (25—61).[2] Since the extent of the change in the lifetimes is comparable with that of [IrCl$_2$(phen)$_2$]Cl (6.95—20.1 μs under the same conditions), the contribution of the dπ* state to the emitting state can not be overlooked. Therefore, it is proposed that the lowest triplet state can be assigned to a ππ* state with a small dπ* component.

Considering the solvent dependence of the triplet-triplet absorption spectra,[7] the ground-state absorption spectra,[6] and the low-temperature emission energies[2] of [IrCl$_2$(phen)$_2$]Cl and [IrCl$_2$(5,6-Mephen)$_2$]Cl, the energy of the dπ* transition is confirmed to shift to the higher energy side with the increase in the solvent polarity. Therefore, the character of the lowest triplet state should be mainly of the ππ* character in water, so far as the contribution of the dπ* and ππ* states is concerned. However, as may be seen in Fig. 2, the absorbance in water shows a considerable decrease. This contradiction can be interpreted by means of Model B, which assumes the dd state to lie close above the emitting state and the energy separation to change with the solvent polarity. In the **1** and **2** solvents, the dd-ππ* energy separation is large, but in water it becomes so small that the thermal distribution to the dd state causes a decrease in the triplet-triplet absorbance. With respect to [IrCl$_2$(phen)$_2$]Cl, it may be considered that the intensity decrease in water is attributed partially to the increase in the dd component in the lowest triplet state, besides to the increase in the ππ* component. Since the emission energy of [IrCl$_2$(5,6-Mephen)$_2$]Cl is almost independent of the solvent polarity,[2] it may be suggested that the solvent shift of the dd state plays an important role and may be almost comparable to the small energy separation. This conclusion is reasonable because the dd transitions are generally sensitive to the environment, and the energy separation is suggested to be smaller for [IrCl$_2$(5,6-Mephen)$_2$]Cl than for [IrCl$_2$(phen)$_2$]Cl, judging from the work on photosubstitution.[6] For [IrCl$_2$(5,6-Mephen)$_2$]Cl, Model A does not involve a knowledge of the solvent dependence of the dd-ππ* energy separation, so the relation to the observed solvent dependence can not be discussed. From the above-mentioned discussion, it may be concluded that, in the polar solvents, the contribution of the dd state to the lowest triplet state can not be disregarded. The relevant evidence showing that the dd state is the lowest at room temperature for [IrCl$_2$(phen)$_2$]Cl was not obtained using the technique of the triplet-triplet absorption measurements. However, the fact that the emissions in several solvents deviate from the exponential behavior shows some complicated interaction with the environment.

The formation of a photoproduct is inevitable in the photophysical experiment of the metal complexes. When the lowest excited state is of the dπ* or ππ* character in the complex molecule and of the dd character in the photoproduct, the triplet-triplet absorption measurement is a very adequate method to study the excited states of the complex, for it is not disturbed by the photoproduct.

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