A Study on Electronic Excited States of Iridium(III) Complexes Containing Bipyridine and Phenanthroline Ligands. Solvent Effect on Triplet-Triplet Absorption Spectra

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In order to study the solvent effect on the lowest excited state of *cis*-$[IrCl_2L_2]Cl$ (L=2,2′-bipyridine, 1,10-phenanthroline, and 4,7-dimethyl-1,10-phenanthroline), the triplet-triplet absorption spectra (15000 cm^{-1}—27000 cm^{-1}) were measured by the use of *N*,*N*-dimethylformamide–water mixed solvents. For the triplet-triplet spectra of the three iridium complexes, remarkable spectral changes were observed with the change of the solvent polarity. An SCF calculation of the triplet-triplet transitions was carried out for free bipyridine and free phenanthroline. By comparing the calculated results and the observed spectra, the solvent effect can be interpreted in terms of a model invoking $d\pi^*$-$\pi\pi^*$ interaction, as proposed by Crosby. The lowest triplet state of $[IrCl_2(phen)_2]Cl$ is predominantly a $d\pi^*$ state in 95% v/v DMF–water, but in water, by the reversal of the state ordering, the lowest state becomes a $\pi\pi^*$ state. Furthermore, a quite similar solvent effect which was observed on the lowest triplet state of $[IrCl_2(bpy)_2]Cl$ is discussed; this state is not expected to have a $d\pi^*$-$\pi\pi^*$ interaction.

It has been pointed out that, in contrast to the ruthenium(II) complexes,[1–4] the character of the lowest excited state of *cis*-$[IrCl_2(phen)_2]Cl$ (phen: phenanthroline) is very sensitive to the solvent. The emission spectra and lifetimes at 77 K show a distinct solvent effect as the solvent polarity changes. This effect has been interpreted in terms of a change in the character of the lowest excited state.[1–3] Since the lowest $d\pi^*$ state (metal-to-ligand charge transfer excited state) and the lowest $\pi\pi^*$ state (locally excited state of a ligand) lie very close to each other, the solvent polarity affects their energy separation, which changes the electronic character of the lowest excited state. Recently, the contribution of the lowest d-d (locally excited state of a metal) level to the lowest excited state was also shown to be important by photochemical measurements[4] and the temperature dependence of the emission spectra.[5]

Since the excited-state absorption spectrum is assumed to change sharply, as the character of the lowest excited state changes, we measured the triplet-triplet absorption spectra of three *cis*-biscoordinated complexes($[IrCl_2(phen)_2]Cl$, $[IrCl_2(4,7\text{-}Mephen)_2]Cl$, and $[IrCl_2(bpy)_2]Cl$) (bpy: bipyridine) and one triscoordinated complex ($[Ir(bpy)_3](NO_3)_3$) at room temperature, by using the mixed solvents of *N*,*N*-dimethylformamide (DMF) and water. Large solvent effects on the triplet-triplet absorption spectra were observed for the three biscoordinated complexes, but almost no solvent effect was seen for the triscoordinated complex. Using these results, we discuss the electronic structure of these biscoordinated complexes.

Experimental

Materials. *cis*-Dichlorobis(1,10-phenanthroline)iridium(III) chloride trihydrate, $[IrCl_2(phen)_2]Cl\cdot 3H_2O$, was prepared by following the procedure of Broomhead and Grumly.[6] *cis*-Dichlorobis(4,7-dimethyl-1,10-phenanthroline)iridium(III) chloride pentahydrate, $[IrCl_2(4,7\text{-}Mephen)_2]Cl\cdot 5H_2O$, wa prepared by the same procedure. *cis*-Dichlorobis(2,2′-bipyridine)iridium(III) chloride dihydrate, $[IrCl_2(bpy)_2]Cl\cdot 2H_2O$, was synthetized by the method of Watts and Crosby.[7] Tris(bipyridine)iridium(III) nitrate, $[Ir(bpy)_3](NO_3)_3$, was prepared by the method of Flynn and Demas.[8] The purity of the complexes was checked by measuring the phosphorescence spectra, decay times, and the excitation spectra. Dimethylformamide was of spectrophotometric grade and water was distilled four times.

Apparatus. The triplet-triplet absorption spectra were obtained at room temperature using a nitrogen laser as an exciting light source and a pulsed xenon flash as a monitoring light source.[9] In order to discuss the relative absorbance of the triplet-triplet spectrum, we made a correction for the concentration of the excited molecules. Since in iridium(III) complexes no fluorescence was observed and the phosphorescence quantum yield does not depend on the exciting wavelength, we can assume that the quantum yield of triplet formation is very close to unity. Then, the absorbance at 337 nm of the ground-state absorption of each sample is proportional to the concentration of the excited triplet molecules. The ethanol–methanol solution (4: 1, v/v) of $[IrCl_2(phen)_2]Cl$ was used as a standard sample. The absorbance of the standard solution was measured in the same laser conditions as that for each sample solution. With the use of the relative concentration of the excited molecules estimated by the 337 nm absorbance, we obtained the corrected triplet-triplet absorption spectra corresponding to the same concentration of the excited molecules.

Results and Discussion

Figure 1 shows the triplet-triplet absorption spectra of $[IrCl_2(bpy)_2]Cl$ in water, 45% v/v DMF–water and 95% v/v DMF–water, and the triplet-triplet spectrum of $[Ir(bpy)_3](NO_3)_3$ in ethanol–methanol (4: 1, v/v). In our present experiment, the measurements were carried out at concentrations of $\approx 10^{-3}$ mol dm^{-3}. An absorbance of less than 0.01 could not be measured.

In the case of $[IrCl_2(bpy)_2]Cl$, the absorbance in the spectral region below 21000 cm^{-1} decreases and the absorbance above 23000 cm^{-1} increases, as the solvent becomes more polar. However, for $[Ir(bpy)_3](NO_3)_3$, no solvent effect on the absorption spectra was observed for water, 95% v/v DMF–water, and ethanol–methanol (4: 1, v/v). Figures 2 and 3 show the triplet-triplet

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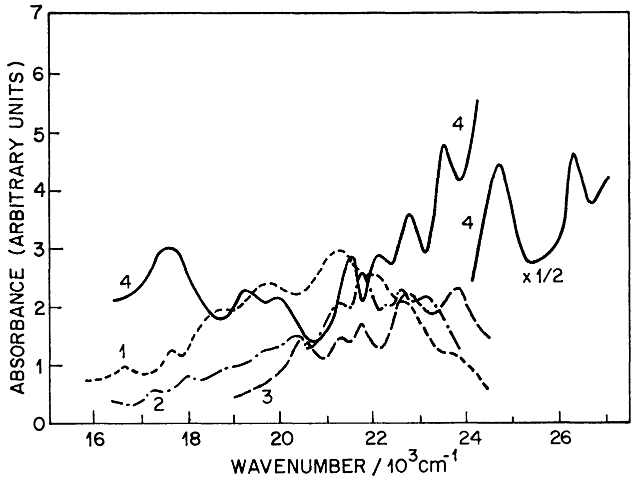

Fig. 1. Triplet-triplet absorption spectrum of [IrCl$_2$(bpy$_2$)]Cl in 95% v/v DMF–water(curve 1), in 45% v/v DMF–water(curve 2) and in water(curve 3). The triplet-triplet spectrum of [Ir(bpy)$_3$](NO$_3$)$_3$ in ethanol–methanol(4: 1, v/v)(curve 4).

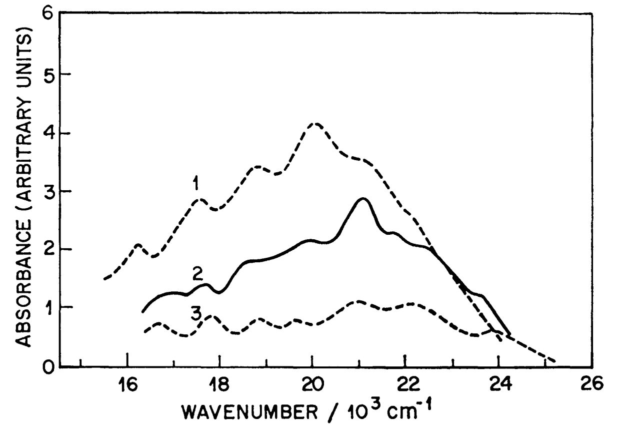

Fig. 2. Triplet-triplet absorption spectrum of [IrCl$_2$(phen)$_2$]Cl in 95% v/v DMF–water(curve 1), in 45% v/v DMF–water(curve 2) and water(curve 3).

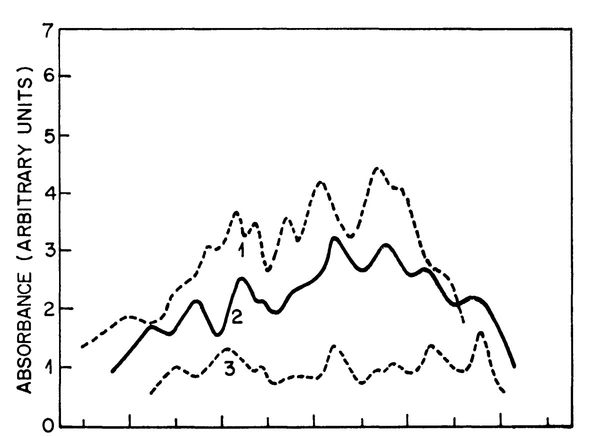

Fig. 3. Triplet-triplet absorption spectrum of [IrCl$_2$(4,7-Mephen)$_2$]Cl in 95% v/v DMF–water(curve 1), in 45% v/v DMF–water(curve 2) and water(curve 3).

absorption spectra of [IrCl$_2$(phen)$_2$]Cl and [IrCl$_2$(4,7-Mephen)$_2$]Cl in DMF–water mixed solvents. In both complexes, the absorbance decreases remarkably as the solvent polarity increases. Furthermore, the same shift of the spectra was observed as for the bis(bipyridine) complex.

Assignment of Excited States. The absorption spectrum of [Ir(bpy)$_3$](NO$_3$)$_3$ has no low-energy ^{1}dπ^* band and resembles that of free bipyridine molecules.[8] Since the singlet-triplet energy separation of a $\pi\pi^*$ state is generally much larger than that of a dπ^* state, the emitting level of the tris(bipyridine) complex(E_0= 22350 cm^{-1}) was assigned to a $^3\pi\pi^*$ state. The phosphorescence lifetime we observed is 49 μs at 77 K in degassed methanol. This value is ten times as long as the typical lifetimes of dπ^* phosphorescence.[10]

From the absorption spectrum measurements,[1] the lowest singlet state of [IrCl$_2$(bpy)$_2$]Cl at 21900 cm^{-1} and [IrCl$_2$(phen)$_2$]Cl at 21700 cm^{-1} was assigned to a ^{1}dπ^* state. The singlet-triplet energy separation is generally small for a dπ^* state, hence the ^{3}dπ^* level lies just below the ^{1}dπ^* level. On the other hand, both of the free ligands also have a $^3\pi\pi^*$ emission in this region: E_0=23500 cm^{-1} for free bipyridine and 22200 cm^{-1} for free phenanthroline, at 77 K in ethanol–methanol (4: 1, v/v). Thus, the energy separation between the lowest ^{3}dπ^* state and the lowest $^3\pi\pi^*$ state is expected to be small. The stabilization energy by solvent polarization is different depending upon the types of the electronic structures, that is, the ground state, dπ^* states, and $\pi\pi^*$ states. These differences of polarization energy are assumed to be of the same order as the energy separation between the lowest ^{3}dπ^* and $^3\pi\pi^*$ states. Therefore, the character of the observed lowest triplet state of biscoordinated complexes is sensitive to the environment, as is seen from Figs. 1 and 2. The emitting state of [IrCl$_2$(bpy)$_2$]Cl is 21400 cm^{-1} and that of [IrCl$_2$(phen)$_2$]Cl is 21000 cm^{-1}, in ethanol–methanol (4: 1, v/v). Since the $^3\pi\pi^*$ energy of free bipyridine is 1300 cm^{-1} higher than that of free phenanthroline, the interaction in [IrCl$_2$(bpy)$_2$]Cl between ^{3}dπ^* and $^3\pi\pi^*$ states is thought to be small, in contrast to the case of [IrCl$_2$(phen)$_2$]Cl.[2] However, the lowest $^3\pi\pi^*$ state of [Ir(bpy)$_3$](NO$_3$)$_3$ appears at 22350 cm^{-1}, 1200 cm^{-1} lower than that of free bipyridine. The red shift of the $\pi\pi^*$ peak upon complex formation is thus large for a bipyridine complex but very small for a phenanthroline complex. Therefore, the energy separation between the lowest $^3\pi\pi^*$ and ^{3}dπ^* of [IrCl$_2$(bpy)$_2$]Cl is very similar to that of [IrCl$_2$(phen)$_2$]Cl.

For the bis(phenanthroline) complex, the emission lifetime at room temperature decreases from 270 ns[4] to 13 ns(our data), when the solvent is changed from 95% v/v DMF–water to water. This rapid decrease of the lifetime is also observed for bis(bipyridine) complex. From this similarity we can conclude that the character of the lowest triplet state of [IrCl$_2$(bpy)$_2$]Cl is analogous to [IrCl$_2$(phen)$_2$]Cl.

Recently, from the large temperature dependence of the emission spectra in glycerol, the lowest triplet state of [IrCl$_2$(phen)$_2$]Cl and [IrCl$_2$(5,6-Mephen)$_2$]Cl was assigned to an excited state localized on the metal(dd).[5]

However, in ethanol–methanol (4: 1, v/v), we observed no shift between the emission spectra at 77 K and 300 K for $[IrCl_2(phen)_2]Cl$. Furthermore, in water and 95% v/v DMF–water, the emission of $[IrCl_2(phen)_2]Cl$ and $[IrCl_2(5,6\text{-Mephen})_2]Cl$ at room temperature also does not show any shift from the low-temperature emission.[4] Therefore, in the solvents used in our experiments, the contribution of a dd level to the lowest triplet state can be neglected.

Solvent Effect of Triplet-Triplet Absorption Spectra. For the three biscoordinated complexes, the ground-state absorption peaks show a blue shift of 400—1000 cm^{-1}, when the solvent is changed from 95% v/v DMF–water to water. The observed stabilization of the singlet energy levels in polar solvents were almost equal for the same type of transition. On the other hand, the observed strong triplet-triplet transitions are primarily assigned to the transitions between electronic states of the same type($d\pi^*$-$d\pi^*$ or $\pi\pi^*$-$\pi\pi^*$). For the triplet-triplet transition the solvent effect on both states is almost counterbalanced. Therefore, the observed solvent effects on the triplet-triplet absorption spectra shown in Figs. 1, 2, and 3 can not be explained only by the above-mentioned solvent shifts of the energy levels.

The lowest triplet state in a tris(bipyridine) complex is $^3\pi\pi^*$; hence the observed triplet-triplet absorption spectrum is assigned to a $\pi\pi^*$-$\pi\pi^*$ transition. In a bis(bipyridine) complex, since the $^3d\pi^*$-$^3\pi\pi^*$ energy separation is of the same order as the solvent shift of the energy levels, a reversal of the states can occur by changing the solvent polarity. If the lowest triplet state(T_1) is denoted as $T_1 = A_{CT}\Psi(d\pi^*) + A_{LE}\Psi(\pi\pi^*)$, where A_{CT} and A_{LE} are coefficients of the wave function, the observed triplet-triplet absorption spectrum changes from T_1-higher $d\pi^*$ transitions to T_1-higher $\pi\pi^*$ transitions, as the coefficient A_{LE} increases.

We carried out an SCF-CI calculation on the triplet-triplet transitions for free bipyridine and free phenanthroline molecules. Figure 4 shows the calculated transition energies. The observed triplet-triplet absorption spectrum of free phenanthroline and the $^3\pi\pi^*$-$^3\pi\pi^*$ absorption spectrum of $[Ir(bpy)_3](NO_3)_3$ in ethanol–methanol (4: 1, v/v) are shown in Fig. 4. SCF-CI calculations generally gives an over-estimate of the transition energy, so the observed spectrum of tris(bipyridine) complex can be assigned to one strong and three weak $^3\pi\pi^*$-$^3\pi\pi^*$ transitions, and the observed one of free phenanthroline to several weak $^3\pi\pi^*$-$^3\pi\pi^*$ transitions. With respect to the $^3d\pi^*$-$^3d\pi^*$ transitions, the energies can be estimated from the differences in orbital energies. Using the orbital energies of our calculation, for a bipyridine complex, two bands at 16200 cm^{-1} and 29500 cm^{-1} are expected; for a phenanthroline complex, two bands at 20200 cm^{-1} and 30200 cm^{-1} are expected. Thus from our SCF-CI calculations, we conclude that the triplet-triplet transitions both to the higher $^3d\pi^*$ states and to higher $^3\pi\pi^*$ states from the lowest triplet state are expected in the wave number range of our experiment.

It was pointed out that in the bis(bipyridine) complex the lowest $^3\pi\pi^*$ state lies a little higher than the lowest $^3d\pi^*$ state in ethanol–methanol (4: 1, v/v).[1] 95% DMF–water has a similar polarity to that of ethanol–methanol, so spectrum 1 in Fig. 1 is assigned to $^3d\pi^*$-$^3d\pi^*$ transition. On the other hand, spectrum 3 in Fig. 1 shows the vibrational structure, which resembles closely that of a tris(bipyridine) complex. Therefore, in water the $\pi\pi^*$ component of the lowest triplet state is predominant. The spectrum in 45% v/v DMF–water is interpreted as a superposition of almost equal contributions from the T_1-$^3\pi\pi^*$ and T_1-$^3d\pi^*$ transitions.

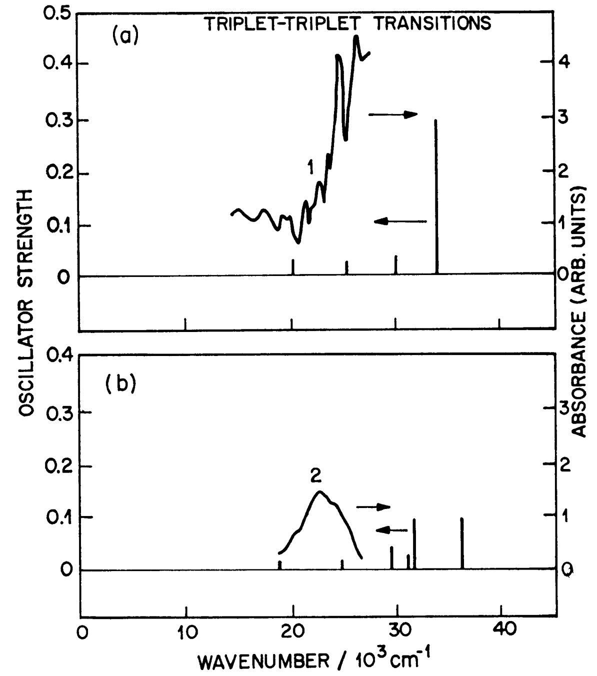

Fig. 4. Calculated triplet-triplet transition energies and their oscillator strength. (a) Free bipyridine, (b) free phenanthroline. Curves are the observed triplet-triplet absorption spectra of $[Ir(bpy)_3](NO_3)_3$ in 95% v/v DMF–water (curve 1) and free phenanthroline in ethanol–methanol(4: 1, v/v)(curve 2).

In the bis(phenanthroline) complex, the most distinct characteristics of the solvent effect on the triplet-triplet absorption spectrum is the large change in the absorption intensity. In 95% v/v DMF–water, the lowest triplet state is assigned to mainly $^3d\pi^*$, as in the bis(bipyridine) complex.[1] As the solvent becomes polar, the absorption intensity decreases rapidly and the peak maxima shift to slightly higher energy. This intensity decrease can be interpreted as a change in the character of T_1. In a bipyridine complex, the solvent affects only the absorption frequency, so the observed T_1-$^3\pi\pi^*$ transitions and T_1-$^3d\pi^*$ transitions have almost equal intensity. However, as is shown in Fig. 4, $^3\pi\pi^*$-$^3\pi\pi^*$ transitions of phenanthroline are weaker than the strong band of bipyridine. Therefore, an increase in the $\pi\pi^*$ component of T_1 results in a decrease of the intensity of the triplet-triplet absorption. Spectrum 3 in Fig. 2 can be assigned mainly to $^3\pi\pi^*$-$^3\pi\pi^*$ transitions. An analogous solvent effect was observed for bis(4,7-dimethyl-1,10-phenanthroline) complex (Fig. 3).

In conclusion, the excited states of the iridium(III) complexes with such ligands as bipyridine, phenanthroline, and their derivatives are very sensitive to the environment. Changing the mixing ratio of DMF and water can cause changes in the character of the lowest triplet state as well as a reversal in the order of the state. Such solvent effects may become an important factor in the reactivity of these complexes in various solvents.

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