Ligand-Ligand Interaction in $[Zn(1,10\text{-phenanthroline})_2(H_2O)_2](NO_3)_2$ and $[Zn(2,2'\text{-bipyridyl})_3](NO_3)_2$

Takeshi OHNO and Shunji KATO

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560

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The interaction between ligands in the excited state and in the ground state was examined by exploring the photophysical behaviors of ligands in the bis- and the tris-bidentate complexes. Although no exciton splitting was observed in the absorption spectra of $[Zn(bipy)_3](NO_3)_2$ and $[Zn(phen)_2(H_2O)_2](NO_3)_2$ at 77 K, the fluorescence yields of both complexes increased in comparison with those of the corresponding mono-bidentate complexes. It is probable that this change is caused by a delocalization of the excited singlet state, because a variation in Franck-Condon factors and a depolarization of the fluorescence accompanied it. In addition to the ligand-ligand interaction 1,10-phenanthroline and 2,2'-bipyridyl suffered from coordination effects. They have larger fluorescence yields and smaller phosphorescence yields than the free molecules. The decrease on the transition rate of the intersystem crossing is probably due to the changes in the energy levels of $^1(n\text{-}\pi^*)$ and $^3(n\text{-}\pi^*)$, caused by the metal-ligand bond using a "non-bonding" orbital in the free ligands.

The photochemistry of ligands in coordination compounds is affected not only by the metal-ligand bond, but also by ligand-ligand interaction. Some kinds of interaction between a ligand in its electronic excited state and ligand(s) in its ground state have been investigated in the case of β-diketonato complexes.[1] While a doubly- or a triply-degenerated state of the bis- or the tris-β-diketonato complexes was not split greatly by ligand-ligand interaction, three phenomena suggesting some weak interaction were observed: (i) an enhancement of spin-orbital interaction, (ii) a depolarization of the fluorescence, and (iii) a variation in the Franck-Condon factors of the radiative transition processes.

These interactions were examined in the cases of bis-1,10-phenanthroline* and tris-2,2'-bipyridyl** complexes of the zinc ion, which have more resolved spectra than the β-diketonato complexes of aluminium. These complexes were also examined with regard to the effects of the zinc-ligand bond on the excited states of the ligands. We will discuss the fact that ligands coordinating to Zn^{2+} have larger fluorescence yields than the free ligands, unlike the expectation based on the "heavy atom effect".[2]

Experimental

Materials. $[Zn(phen)_2(H_2O)_2](NO_3)_2$ and $[Zn(bipy)_3](NO_3)_2$ were prepared by heating a 50% ethanol solution of $Zn(NO_3)_2$ and the corresponding ligand. The prepared complexes were recrystallized from water two times. The free ligands, $1,10\text{-phenanthroline}\cdot 2H_2O$ and 2,2'-bipyridyl were recrystallized from ethanol. The water was distilled twice, while Wako G. R. methanol was used without further purification.

Procedure. All the materials were dissolved in a mixture of methanol and water (4 : 1 by volume). Solutions of the mono-bidentate complexes were prepared by the addition of $Zn(NO_3)_2$ (5×10^{-4} M) and free ligand (5×10^{-5} M) to the mixed solvent. The absence of the free ligand is practically supported by the large stability constants ($\log K=6.4$ for $[Zn(phen)]^{2+}$ [3]) and $\log K=5.4$ for $[Zn(bipy)]^{2+}$ [4]) in an aqueous solution) and the disappearance of the absorption spectrum due to the free bipy.

Measurements. The measurements of the absorption and emission spectra, the emission yields, the emission lifetimes and the emission polarizations at 77 K were carried out in the way reported in the previous paper.[1] The emission spectra were calibrated against the fluorescence spectra of phenol, benzene, naphthalene,[5] and β-naphthole.[6] The corrected spectra agreed with those obtained by Chen's method using rhodamin B.[7]

Results and Discussion

Effect of Coordination on the Excited States of Ligand Absorption and Emission Spectra: As Fig. 1 shows, at the temperature of boiling nitrogen, free bipy in a mixed solvent of metanol and water (4 : 1) has a broad absorption band in the near ultra violet region whereas the absorption band of bipy coordinating to Zn^{2+} was a well-resolved structure and is shifted to a lower frequency (0—0': 32400 cm^{-1}). Such a shifted spectrum has also been found by Schläfer in the case of the mono-bipy complexes of Zn^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Fe^{2+} in water at room temperature; Schläfer considered these changes to be caused by the Stark effect of central ions on the ligand.[8] This consideration has been proven by Hanazaki and Nagakura on the basis of their P-P-P SCF-CI calculation of π-π^* transitions.[9] However, the lack of any determination of the n-π^* level, a result of the strong π-π^* band, leaves the question open whether the lowest level in n–π^* or π-π^*.***

Moreover, the coordinating bipy emitted a well-resolved fluorescence (see Fig. 2), which took a good mirror image with the absorption spectrum. Consequently, the fine structure of the absorption may safely be attributed not to another electronic transition, but to the vibrational structure of a single electronic transition, because sub-bands of fluorescence other than 0'-0 band are usually assigned to the vibrational structure with no doubt. This is supported by the fact that the fluorescence has a high polarization value (0.40),

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* 1,10-phenanthroline will be abbreviated to "phen" heareafter.

** 2,2'-bipyridyl will be abbreated to "bipy" hereafter.

*** For pyridine, n-π is considerably lower (34769 cm^{-1}) than π-π^* (38350 cm^{-1}).[10]

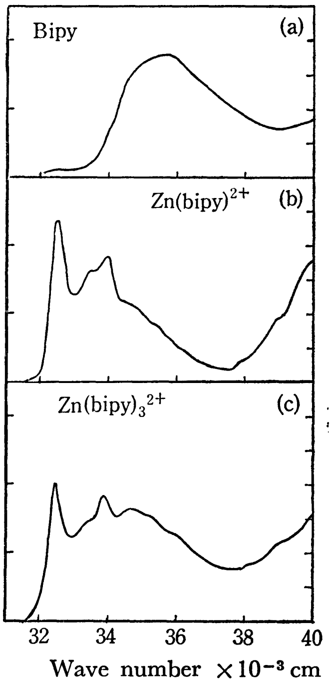

Fig. 1. Absorption spectra of bipy and its complexes of zinc ion in methanol and water (4 : 1 by volume) at 77 K.
(a) bipy: 4×10^{-5} M, (b) bipy: 4×10^{-5} M and $Zn(NO_3)_2$: 2×10^{-4} M, (c) $[Zn(bipy)_3](NO_3)_2$: 2×10^{-5} M and bipy: 4×10^{-5} M

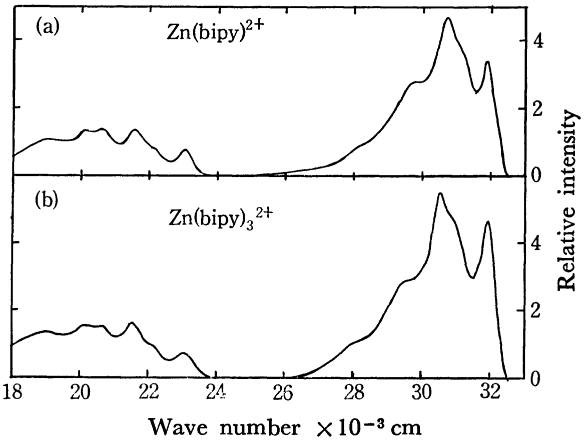

Fig. 2. Emission spectra of mono-bipy complex and $[Zn(bipy)_3](NO_3)_2$ in methanol and water (4 : 1 by volume) at 77 K.
(a) bipy: 5×10^{-5} M and $Zn(NO_3)_2$: 2×10^{-4} M
(b) $[Zn(bipy)_3](NO_3)_2$: 2.4×10^{-5} M

independent of the excitation ligand through 32~36 × 10^3 cm^{-1}. According to SCF-CI calculations of the free *cis*-bipy,[9,11] the transition moment to the first excited state of the B_1 symmetry is several tens of times as large as that to the second one of the A_1 symmetry lying 1×10^3 cm^{-1} above. Therefore, the assignments of the sub-bands are most probable.

It has been reported that the free form of phen has three kinds of transitions through 29~40 × 10^3 cm^{-1}. They have been assigned to ^1L_b, ^1L_a, and ^1B_a in the order of transition energy by measureing the fluorescence polarization with the excitation wavelength at 77 K[12] and by P-P-P SCF-CI calculations.[13] The coordination of phen to Zn^{2+} brought no essential change in the absorption spectrum, as Fig. 3 shows. However, one can recognize the following three changes; (i) the shoulders of the free form at 30000 and 31560 cm^{-1} disappear, (ii) the 0-0′ bands of the three transitions become more distinct (^1L_b: 29300, ^1L_a; 34200, and ^1B_a: 36900 cm^{-1}), and (iii) they shift to lower frequency by 250~600 cm^{-1} than those of the free form.

The fluorescence of the coordinating phen due to the transition from ^1L_b to the ground state has a structure similar to that of the free form (see Fig. 4). As for the fluorescence polarization, while the free phen has a constant polarization (0.19) on excitation with 29~36 × 10^3 cm^{-1}, the coordinating form has a different value (0.15) when observed on excitation to ^1L_b from that (0.11) when observed on excitation to ^1L_a.

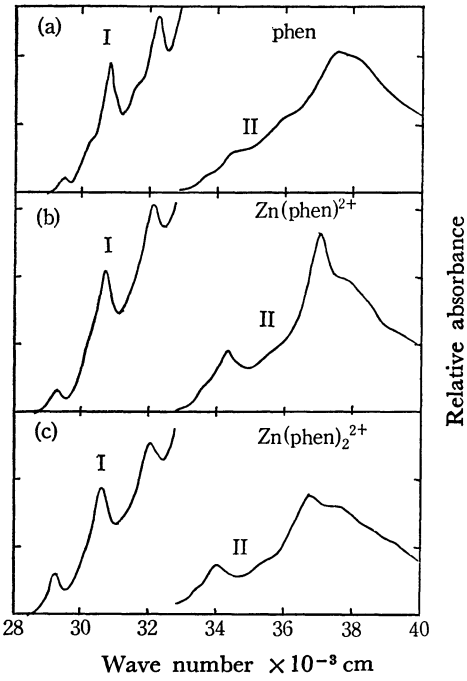

Fig. 3. Absorption spectra of phen and its complexes of zinc ion in methanol and water (4 : 1 by volume) at 77 K.
(a) I…phen: 8×10^{-4} M, II…phen: 2×10^{-5} M
(b) I…phen: 8×10^{-4} M, and $Zn(NO_3)_2$: 5×10^{-3} M, II…phen: 2×10^{-5} M and $Zn(NO_3)_2$: 1×10^{-3} M
(c) I…$[Zn(phen)_2(H_2O)_2](NO_3)_2$: 4×10^{-4} M, II…$[Zn(phen)_2(H_2O)_2](NO_3)_2$: 1×10^{-5} M

TABLE 1. QUANTUM YIELDS OF EMISSIONS IN METHANOL AND WATER (4 : 1) AT THE TEMPERATURE OF BOILING NITROGEN

	F	P	F/P	τ_p s
$[Zn(bipy)]^{2+}$	0.30	0.015	20	1.75
$[Zn(bipy)_3]^{2+}$	0.39	0.019	20	1.75
phen	0.014	0.07	0.2	1.49
H^+ phen	0.03	0.04	1.75	—
$[Zn(phen)]^{2+}$	0.050	0.040	1.25	2.81
$[Zn(phen)_2(H_2O)_2]^{2+}$	0.070	0.040	1.75	2.59
H_2^{2+} phen	—	—	2	—

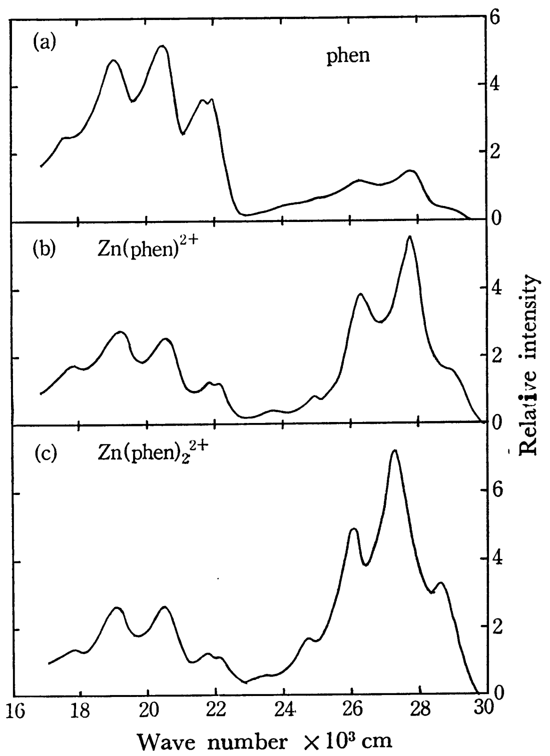

Fig. 4. Emission spectra of phen and its complexes of zinc ion in methanol and water (4 : 1 by volume) at 77 K.
(a) phen: 5×10^{-4} M, (b) phen: 5×10^{5} M and $Zn(NO_3)_2$: 2×10^{-4} M, (c) $[Zn(phen)_2(H_2O)_2](NO_3)_2$: 2×10^{-5} M

Yields of Emissions: While the free bipy emits only a weak phosphorescence at 77 K, the coordinating form emits a very strong fluorescence not only at the low temperature but also at room temperature. The yields of the fluorescence, listed up in Table 1, reach 0.30. The following considerations make it probable that such an appearance of the strong fluorescence originates from changing the lowest singlet excited state from the *n-π** state to the *π-π** state because of its coordination; (i) Coordination through nitrogen atoms of bipy to metal ions, not only Zn^{2+} but also Cd^{2+}, gives rise to a fall in the *π-π** level due to pyridyl-pyridyl interaction in the pseudo planar forms of *cis*-bipy and a rise of n-*π** level due to the coordination using "non-bonding" orbitals on nitrogen atoms. Therefore, the appearance of the strong fluorescence may be attributable to either a fall in the *π-π** level or a rise in the n-*π** level, or to both. (ii) Although no fluorescence was observed in 0.1 M HCl, in which mono-protonated bipy with the planar forms of *cis*-bipy is predominant, fluorescence was observed in an 80% sulfuric acid solution, in which bipy is changed into the di-protonated form of ***trans*** bipy. Therefore, a fall of *π-π** due to the pseudo planar forms of *cis*-bipy is not always needed for a strong fluorescence. (iii) It is generally believed that because n-*π** has a long radiative lifetime (10^{-7} s) because of a partly-allowed transition, other processes—intersystem crossing and internal conversion—take place much more easily, resulting in the absence of fluorescence. This is the case for pyridine. (iv) Because the coordination of bipy to metal ions raises the n-*π** states as hydrogen bonding and protonation do, the lowest singlet state of the coordinating bipy may be changed from n-*π** to *π-π**, of which, in the free form, the latter seems to be nearer to the former on account of pyridyl-pyridyl interation than in pyridine.

As for phen, the free form of which emits a fluorescence of a medium intensity in addition to a phosphorescence, its coordination to the zinc ion gave rise to an enhancement of the fluorescence and diminution of the phosphorescence (see Table 1). Because such a change in the emission yields was observed a little in 0.1 M HCl and moderately in a 90% sulfuric acid solution, as Table 1 shows, it is probable that a change in the energy level of n-*π** excited states with coordination or protonation results in the variation in the emission yields. However, since the weak lowest band may safely be regarded as a transition to the *π-π** state in all the forms and does not vary in intensity with coordination and protonation, the enhancement of the fluorescence is not caused by a change in the radiative transition rate, but by a change in the non-radiative transition rate. It has been reported that the yield of the phosphorescence of phen is the largest of the nine phenanthrolines.[14] Perkampus *et al.* assumed that the largest intersystem crossing rate was attributable to the small separation between ^1L_b and unknown higher triplet state(s). If the higher triplet state(s) is the n-*π** state, whose level is dependent on the positions of the nitrogen atoms in the free form, the coordination of phen will considerably raise ^{3}(n-*π**) as well as ^{1}(n-*π**) and make the rate of the ^{3}(*π-π**) formation ($^1L_b \rightarrow {}^3(n\text{-}\pi^*) \rightarrow {}^3(\pi\text{-}\pi^*)$ or $^1L_b \rightarrow {}^1(n\text{-}\pi^*) \rightarrow {}^3(n\text{-}\pi^*)$) slower. This change will give rise to a larger yield of fluorescence, which must be similar to those of other phenanthrolines (0.1~0.5 in a mixed solvent of ether and ethanol (1 : 1)) and phenanthrene (0.17 in EPA[15])). As Table 1 shows, this is indeed the case.

After all, the variation in the n-*π** levels with their coordination results in a large fluorescence yield in the cases of both bipy and phen. Moreover, the enhancement mechanism is different from that in the case of *β*-diketonates, in which the metal-ligand bond prevents their excited states from making a radiationless transition to the ground state.[1] It is worthwhile noticing that the fluorescence of ligands is enhanced by coordination to Zn^{2+}, contrary to the expectation deduced from the heavy-atom effect. In the case of porphyrin complexes, in fact, the enhancement of the phosphorescence yield with the complex formation has been accounted for in terms of the heavy-atom effect.[2]

Interaction between Ligands in the Excited State and in the Ground State. Absorption and Emission Spectra: Since the tris-bipy complex of Zn^{2+} has three large ligands with an allowed transition along their longer axes, it may be expected that an exciton interaction among the three ligands removes the three fold degeneracy of the excited state associated with the transition, resulting in some splitting between the states with E and A_2 symmetries as well as in the case of $[Fe(bipy)_3]^{2+}$. However, a comparison of the absorption spectra between the tris- and the mono-bipy complexes showed no difference not even at 77 K. As Fig. 1 shows, the tris-bipy complex has an absorption spectrum very similar to that of the mono-bipy complex. The broad band at the higher-frequency regions in the spectra for the tris-bipy complex is due to the free bipy, which is added to suppress the dissociation of the tris-bipy complex. Further, the band widths of the tris-bipy complex are seen to be the same as those of the mono-bipy complex for the sharpest 0-0′ band (its width: 460 cm^{-1}); therefore, the splitting of the vibronic bands should be very small if any. Such a weak interaction in $[Zn(bipy)_3]^{2+}$ has been suggested in view of the mirror-image relationship.[16] However, these results do not necessarily preclude any ligand-ligand interaction, because the change in the fluorescence yield and the fluorescence polarization may suggest a weak interligand interaction in addition to the circular dichroism of the tris-bipy complexes of Fe^{2+},[17] as will be discussed later.

For $[Zn(phen)_2(H_2O)_2](NO_3)_2$, which easily forms a tris-phen complex in the presence of excess phen, the coordinating nitrogen atoms of two phen are considered to locate at the apices of an octahedron and two H_2O at the vicinal apices. This is supported by the fact that two phen of some bis-phen complexes do not lie coplanar as a result of the repulsion between α-hydrogen atoms of two phen.[18] Therefore, the bis-phen complexes of zinc may also be expected to have such a ligand-ligand interaction, as was proposed in the tris-phen complex of Fe^{2+}.[17]

For the strongest band at 37,050 cm^{-1} (^1B_a in the free phen), which has been expected to have a large exciton interaction,[17] the absorption band of $[Zn(phen)_2(H_2O)_2]^{2+}$ has a similar structure, consisting of a strong peak (0-0′) and a shoulder (0-1′) on 700 cm^{-1} side higher than that of the mono-phen complex, as Fig. 3 shows. Since no splitting of the electronic transition is distinctly recognized, the exciton interaction can not be regarded as a "strong coupling" as defined by Simpson and Peterson.[19] And it is not possible to estimate the weak exciton interaction quantitatively on any vibronic coupling theory, because not all the electronic bands are distinctly resolved into sub-bands.

The difference in the relative intensities of the sub-bands, the Franck-Condon factors, are observed between the absorption spectra of $[Zn(phen)_2(H_2O)_2]^{2+}$ and the mono-phen complex (see Table 2). Generally speaking, the Franck-Condon factors of an intra-ligand transition may be expected to be varied by both the metal-ligand interaction and the ligand-ligand interaction, as are the energy and the total intensity of the transition. It is assumed that the ligand-ligand interaction, which gives rise to a delocalization of the excited state through two ligands and to a smaller distortion and displacement of the excited state, is reflected in the Franck-Condon factors of the lowest band of $[Zn(phen)_2(H_2O)_2]^{2+}$, which is larger than that of the mono-phen complex, and that the metal-ligand interaction is not so large as to change the Franck-Condon factors of the transition in the latter complex. Further, it is noticed that the Franck-Condon factors obtained by the analyses of the fluorescence spectra have a distribution similar to those obtained from the absorption spectra. These considerations show the existence of a weak interaction between a phen in the ground state and a phen in the excited state. On the other hand, it is assumed that, for the strong band (^1B in the free phen), the metal-ligand interaction has an effect on the relative intensities of the sub-bands, which are seen at 37,050 cm^{-1} (0-0′) and 37,800 cm^{-1} for the mono-phen complex, and at 36,800 cm^{-1} (0-0′) and 37,500 cm^{-1} for the bis-phen complex. This assumption is supported by the fact that the intensity of the 0-0′ band is stronger for the mono-phen complex than for the bis-phen complex, in which Zn^{2+} is shared by two phens. Though the variations in the Franck-Condon factors are not clear in the cases of the bipy complexes, a weak interaction between three bipys is probable.

TABLE 2. RELATIVE INTENSITIES OF VIBRONIC LINES NORMALIZED TO THE INTENSITY OF 0′-0

	Fluorescence		
	0′-0	0′-1	0′-2
$[Zn(bipy)]^{2+}$		1.00[a]	0.55
$[Zn(bipy)_3]^{2+}$		1.00[a]	0.52
phen	1.0	3.6	3.4
$[Zn(phen)]^{2+}$	1.0	3.51	2.51
$[Zn(phen)_2(H_2O)_2]^{2+}$	1.0	2.43	1.52

a) It is compared to the intensity of 0′-1 because 0′-0 is reduced by reabsorption.

Yields of Emission: As Table 1 shows, the fluorescence yields of the bis- and the tris-bidentate complexes were significantly greater than that of the corresponding mono-bidentate one; however, the absorption coefficient per ligand is not different. Therefore, it is likely that the fluorescence enhancement is due to a decrease in the rates of the non-radiative processes. Especially, the rate of internal conversion ($S_1 \rightarrow S_0$), which is affected by the Franck-Condon factors ($\langle 0' | v \rangle^2$) with very large v-values, according to Siebrand,[20] can be expected to be less than that of the mono-bidentate complex by taking account of the less distortion and displacement of the lowest excited state of $[Zn(phen)_2(H_2O)_2]^{2+}$. Therefore, it is reasonable to say that the fluorescence enhancement originates from the weak ligand-ligand interaction, as has been proposed in the preceding section.

Polarizations of Emission: Fluorescence in a rigid solvent depolarizes on the excitation of polarized light, when (a) an upper excited state with a moment in a different direction is directly excited, (b) an energy transfer takes place from an excited ligand to another ligand(s) in a complex ion, or (c) a new state with a transition moment along two or three axes is produced by interaction between ligands which individually have a transition moment along one axis. Therefore, the fluorescence polarization of the tris-bidentate complexes gives information about an energy transfer on excitation to the lowest excited state (S_1) or on the appearance of a new excited state. As Table 3 shows,

Table 3. Fluorescence polarization measured in methanol and water (4 : 1) at the temperature of boiling nitrogen on excitation to S_1

	P_F	P_P
$[Zn(bipy)]^{2+}$	0.40	
$[Zn(bipy)]_3^{2+}$	0.05	
phen	0.19, 0.19[a)]	−0.25, −0.25[a)]
$[Zn(phen)]^{2+}$	0.15, 0.11[a)]	−0.12, −0.18[a)]
$[Zn(phen)_2(H_2O)_2]^{2+}$	−0.014, 0.05[a)]	−0.038, −0.070[a)]

a) The value was observed on excitation to S_2 (^1L_a).

the fluorescence of the tris-bipy complex was considerably depolarized as compared with that of the mono-bidentate complex, on excitation to S_1. Therefore, it is certain that some interactions are operative between ligands in the excited state and the ground state. An energy transfer between ligands is unlikely, because neither excitation nor emission is localized in one ligand; both are delocalized through ligands, as was mentioned in the preceding sections. The next problem is in the estimation of the energy splitting between the two states of E and A_2 symmetry by means of the analysis of the fluorescence polarization. Although the states of E and A_2 symmetry participate in the absorption process because of the splitting between them, it depends on the energy splitting whether or not the upper state of A_2 symmetry participates in the fluorescence process. When the splitting is below 70 cm^{-1}, both E and A_2 are emissive at 77 K, while when it is over 100 cm^{-1}, only the state of E fluoresces practically. As Table 4 shows, the fluorescence polarization is determined by the direction of the transition moment of the emitting state(s). The observed value (0.05) for the tris-bipy complex is the nearest to the ideal value (0.09), which is calculated by assuming both states to be emissive.

The energy splitting (70 cm^{-1}) in $[Zn(bipy)_3]^{2+}$ is similar to that[17)] in $[Ni(bipy)_3]^{2+}$, which has been obtained by fitting the measured shape of the circular dichroism to the theoretical one based on the vibronic coupling theory of Perrin and Gouterman.[21)] Recently, Mason *et al.*[22)] reconstituted the observed intensity of circular dichroism by assuming the interaction to be 350 cm^{-1}, based on the vibronic coupling theory. However, since both the reconstituted spectra of circular dichroism were much more complex than the observed ones, the inter-ligand interaction of 350 cm^{-1} seems to be overestimated. Therefore, it is not improbable that the energy splitting in $[Zn(bipy)_3]^{2+}$ is smaller than 70 cm^{-1}.

Table 4. Ideal polarization of fluorescence on excitation to both states having E and A_2 symmetry

Emissive state	*P*
E	−0.174
A_2	0.222
E and A_2	0.090

The tris-phen complex is complicated, because the mono-phen complex had a considerable depolarization even, upon excitation to S_1 (^1L_b of the free phen).

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