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Ligand-Ligand Interaction in the β-Diketonato Complexes of Be^{2+}, Al^{3+}, and Zn^{2+}

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The fluorescence yield (Φ_F) and the phosphorescence yield (Φ_P) of acetylacetone, benzoylacetone, and dibenzoylmethane were enhanced by coordination of Zn^{2+}, Al^{3+}, and Be^{2+} in an increasing order. In the bis- and the tris-bidentate complexes, not only did the ratios of Φ_P to Φ_F increase, but also the lifetimes of the phosphorescences became a little longer than that of the corresponding mono-bidentate complex. This change originates from some kinds of interaction between the ligands in the excited and ground states. Such an inter-ligand interaction was supported by the measurement of the polarization. However, the interaction energy is smaller than the expected values in the analyses of the absorption spectra and the circular dichroism in the region of the ligand band. A difference in the absorption spectra between the mono- and the bis- or the tris-bidentate complexes was seen only in the Franck-Condon factors; this finding supports the extension of the excited state through the two or the three ligands due to the weak inter-ligand interaction.

It can be easily expected that an excited state of a ligand in a coordination compound has a different character from that of the free ligand because of the coordination bond and the other ligand(s) in close proximity. An enhancement of the ligand-triplet yield is caused by spin-orbit interaction due to a heavy metal ion,[1] and the excitation in the ligand is transferred to that in the metal ion,[2] with an excited state below that of the ligand. Further, the circular dichroism due to intra-ligand transition in some tris-bidentate complexes implies the presence of an inter-ligand effect through dipole-dipole interaction. However, effect of inter-ligand interaction on the excited state of ligand has been examined, through many types of inter-molecular interaction—redox reaction, dimer formation, luminescence quenching, and energy transfer—have been reported between molecules in the excited state and in the ground state. Because such a type of reaction has been known to depend on the extent of interaction between the molecules (see Table 1), one may ascertain the extent of the inter-ligand interaction by exploring the photochemistry of ligand. Consequently, each ligand in the bis- and tris-bidentate complexes suffers from ligand-ligand interaction and coordination effects; first, we examined the corresponding mono-bidentate complex, in which the coordination effect was revealed, and then the bis- and the tris-bidentate complexes were compared with it.

TABLE 1. PHENOMENA CAUSED BY INTERACTION BETWEEN MOLECULES IN THE EXCITED STATE AND THE GROUND STATE

Interaction	Phenomena
Strong	Excimer formation[3] Electron transfer[3]
Intermediate	Splitting of the vibronic band in the absorption spectrum[4]
Weak	Change of emission yield and lifetime[5] Energy transfer[6]

Three kinds of metal ions—beryllium(II), zinc(II), and aluminium(III)—were chosen as central metal ions, as they are practically inactive to electron-transfer reaction on photoexcitation and have no excited state below 45×10^3 cm^{-1}. Because these three metal ions arrange ligands in different conformations, the magnitudes and the characters of ligand-ligand interactions can be expected to be different. All the metal ions were easily chelated by various β-diketones, which showed strong luminescences at lower temperatures.[7] The acetylacetonato complexes emitted phosphorescence only, whereas the complexes of dibenzoylmethane and benzoylacetone emitted both fluorescence and phosphorescence. Therefore, some characteristics (yield, lifetime, and spectrum) of the emission in addition to the absorption spectrum were measured in order to ascertain the interaction between ligands in the excited state and the ground state.

Experimental

Materials. *Free Ligands*: The acetylacetone(AcAc), benzoylacetone(Ba), and dibenzoylmethane (Dbm) were purified in the following ways: vacuum distilation for AcAc, three recrystallizations from ethanol for Ba, and four recrystallizations from ethanol and benzene for Dbm.

Metal Complexes and Metal Salts: The metal complexes were prepared in the usual ways except of $Be(AcAc)_2$, which was obtained from Wako Pure Chemical Industries. The complexes of zinc prepared had the following molecular formula: $Zn(AcAc)_2(H_2O)$, $Zn(Ba)_2\cdot C_2H_5OH$, $Zn(Dbm)_2(H_2O)_2$. In aluminium and beryllium complexes, three β-diketones coordinate to Al^{3+}, and two, to Be^{2+}. The results of the elementary analyses agreed with the theoretical values within a deviation of 0.58% for carbon and that of 0.14% for hydrogen. The purifications of the metal salts, $BeSO_4$, $Zn(NO_3)_2$, $KAl(SO_4)_2\cdot 12H_2O$, and H_3BO_3, were carried out through two recrystallizations from aqueous solutions.

Solvents: The ethanol was refluxed with silver nitrate and over calcium oxide, and then distilled. The methanol was purified in a similar way without drying. The water was distilled two times. The ether and isopentane were dried over calcium chloride and distilled over metalic sodium.

Procedure. All the solutions were buffered by 0.2 M borate at pH=8.0. The bis-bidentate and tris-bidentate complexes were examined soon after preparation, because, in solution, 10% of the complex was dissociated in a day. The spectrum of the mono-bidentate complex was measured for the solution containing β-diketone (10^{-5} M), together with a large excess of a metal ion ($10^{-4}\sim10^{-3}$ M), in which only the mono-β-diketonato complex was expected to exist.

This was supported by the set of successive formation constants,[8] by the changes in both the absorption and emission spectra and in the lifetime in the presence of excess metal ions. We used a mixture of water and methanol (1 : 4 by volume) as the solvent.

Measurements. The absorption spectra were measured by means of a Shimadzu MPS-50L spectrophotometer. For the measurements at the temperature of boiling nitrogen (77.4 K), a quartz Dewar vessel (diameter : 55 mm) filled with liquid nitrogen was set very near to the wide aperture of the head-on type photomultiplier in order to diminish the error due to light scattering.

For the luminescence studies, all the complexes and ligands were studied at 77 K at a concentration of about 10^{-5} M. The emission spectra were obtained by using MPF-2A Hitachi fluorescence spectrophotometer with a band-width of 2~8 nm; it had been calibrated by the method of Lippert[9] against the fluorescence of β-naphthol. The emission yields were determined relative to an EPA solution of benzophenone with a band-width of 6 nm.[10]

To measure the polarization of the emission, a Polacoat film (105 UV), put between two quartz plates, or a Gram-Thomson prism was used as the polarizer, and a Toshiba polarizing filter, as the analyzer. The emission monochromator, which had different transmittance with polarized lights perpendicular to each other, was corrected by means of unpolarized light scattered from a frosted glass.

Results and Discussion

Semi-empirical calculations have shown that the absorption band of AcAc in the near ultraviolet region is attributable to the π-π^* transition[11] with a transition moment along the x-axis, as is shown in Fig. 1.

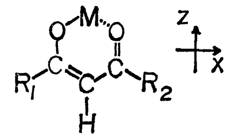

Fig 1. Structure of the ligand.
AcAc: $R_1=R_2=CH_3$
Ba: $R_1=CH_3$, $R_2=C_6H_5$
Dbm: $R_1=R_2=C_6H_5$

For Ba and Dbm, the intense band observed in a frequency region a little lower than AcAc can safely be assigned to the π-π^* transition. Although the n-π^* transitions are hidden by the strong π-π^* transition, one of n-π^* transitions may be shifted to a higher frequency because of the formation of an enol form†, this lifting one of the non-bonding orbitals. It is certain that, just as with the hydrogen bond, coordination to the metal ion makes a six-membered ring. However, because neither coordination nor protonation greatly changes the energy level of the other non-bonding orbital in the ring comformation, the non-bonding orbital may interact with the π-orbital of the neighboring ligand(s) in the complexes of aluminium, as will be discussed below.

Effect of Coordination on the Excited States of β-Diketones. *Absorption and Emission Spectra*: A broad absorption band was observed at room temperature in the near-ultraviolet region for all the β-diketones examined, independent of the presence or absence of

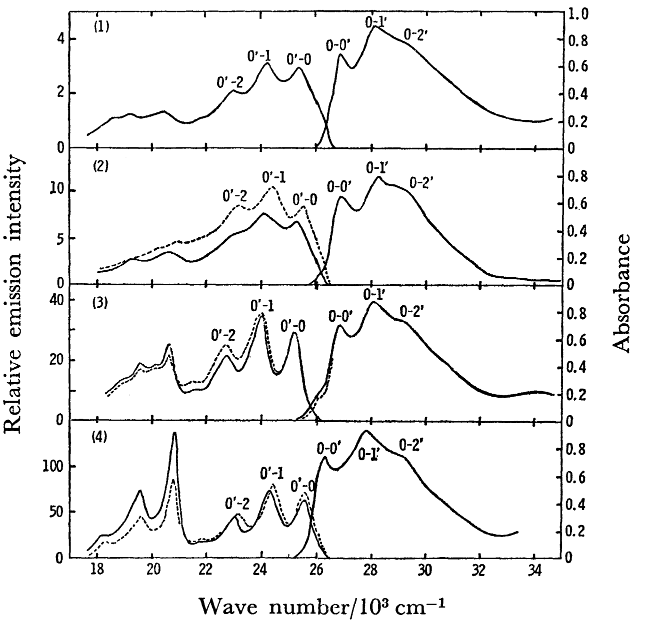

Fig 2. Absorption and emission spectra of dibenzoylmethane and the dibenzoylmethanato complexes at 77 K in methanol and water (4 : 1 by volume).
(1) Dbm, (2) solid line : $Zn(Dbm)_2$, broken line : $Zn(Dbm)^+$, (3) solid line : $Al(Dbm)_2^+$, broken line : $Al(Dbm)^{2+}$, (4) solid line : $Be(Dbm)_2$, broken line : $Be(Dbm)^+$

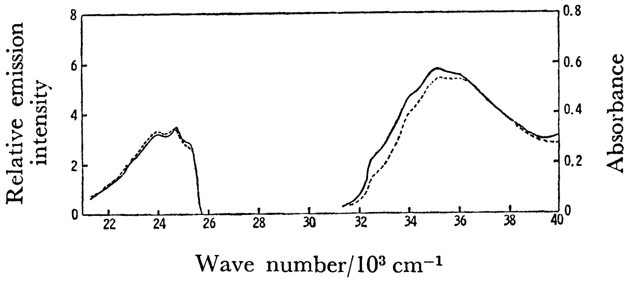

Fig. 3. Absorption and emission spectra of $Al(AcAc)_3$ (solid line) and $Al(AcAc)^{2+}$ (dashed line) at 77 K in methanol and water (4 : 1 by volume)

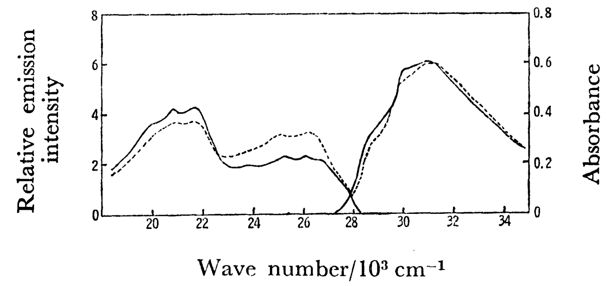

Fig. 4. Absorption and emission spectra of $Al(Ba)_3$ (solid line) and $Al(Ba)^{2+}$ (broken line) at 77 K in methanol and water (4 : 1 by volume).

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† Burdett and Rogers reported, on the basis of PMR analysis, that 80% of the free AcAc, 100% of the Ba and 100% of the Dbm exists as the enol form in $CHCl_3$ or CCl_4.[12]

TABLE 2. SPECTRAL DATA OF ABSORPTION, FLUORESCENCE AND PHOSPHORESCENCE IN METHANOL AND WATER AT 77 K

Compound	Abs. 10^3 cm^{-1}	Fluo. 10^3 cm^{-1}	Phos. 10^3 cm^{-1} 0″—0
AcAc	(33.7),[a] (35.0), 36.23	—	—
Be(AcAc)$^+$	(32.5), (33.1), 34.25	—	25.45
Be(AcAc)$_2$	(32.5), (33.1), 34.25	—	25.45
Al(AcAc)$^{2+}$	(32.6), (33.8), 35.22	—	25.40
Al(AcAc)$_3$	(32·6), (33.8), 35.22	—	25.40
Zn(AcAc)$_2$	(32.6), (33.9), 35.21	—	25.45
Ba	(28.7), (30.0), 31.25	—	—
Be(Ba)$^+$	(28.4), (29.9), 30.08	27.76, 26.04, 25.25	22.08
Be(Ba)$_2$	(28.4), (29.9), 30.08	27.47, 26.04, 24.88	22.08
Al(Ba)$^+$	(28.7), (30.0), 31.10	27.2 25.87, 24.75	21.98
Al(Ba)$_3$	(28.7), (30.0), 31.10	27.14, 25.77, 24.47	21.88
Zn(Ba)$^+$	(28.7), (30.1), 31.2	27.4 26.2 25.00	—
Zn(Ba)$_2$	(28.9), (30.0), 31.3	27.2 25.8 24.7	21.83
Dbm	26.81, 28.01, (28.9)	26.04, 24.88, 23.7	20.70
Be(Dbm)$^+$	26.25, 27.55, (28.7)	25.57, 24.30, 23.04	20.88
Be(Dbm)$_2$	26.11, 27.40, (28.7)	25.45, 24.15, 22.94	20.88
Al(Dbm)$^{2+}$	(25.8), 26.74, 28.09, 29.15	25.31, 24.10, 22.78	20.75
Al(Dbm)$_2^+$	(25.8), 26.74, 28.09, 29.15	25.31, 24.10, 22.78	20.79
Zn(Dbm)$^+$	26.74, 28.17, (29.2)	25.55, 24.39, 23.26	—
Zn(Dbm)$_2$	26.74, 28.09, (29.1)	25.32, 24.2, 22.94	20.79

a) Parenthesis shows shoulder.

metal ions. Each of the mono-bidentate complexes had a broad absorption band, not greatly different from the free β-diketone. At 77 K, the fine structure of the absorption spectra emerged as is shown in Fig. 2—4; one may easily recognize that the peaks and shoulders of the coordinating β-diketones shift to a lower frequency than those of the free β-diketones (see Table 2). However, an exception is found in the case of Al(Dbm)$^{2+}$, in which a new band is weakly observed on the lower-frequency side of the 0—0′ band.

Coordination enhanced the emission intensity of β-diketones in all cases at 77 K, as is shown in Fig. 2. The fluorescence spectra of these mono-coordinated complexes have a well-resolved structure at 77 K and are practically independent of the metal ions (Fig. 2). The numerical data on the peaks and shoulders are shown in Table 2. As Fig. 2 shows, there are mirror-image relations between the absorption and the fluorescence spectra. Therefore, all of the peaks and the shoulders of the absorption may be regarded as 0—0′ bands or vibronic bands. However, Al(Dbm)$^{2+}$ is an exception; it is different from the others in its absorption spectrum, though similar in its fluorescence spectrum.

On the basis of rough analyses of the fine structures of the spectra, symmetric vibrations coupled with the π-π^* transition are assigned to C–C stretching in the six-membered ring and to C–R (R : CH_3 or C_6H_5) stretching (1300 cm^{-1}) (except for the case of Be (AcAc)$^+$) on the basis of Nakamoto's assignment of Al(AcAc)$_3$.[13]

Yields and Polarizations of Emission: All the free β-diketones showed a weak emission with quantum yields below 0.008 at 77 K. Fluorescence was observed only for Dbm. However, the coordination increased the emission very much, as has been mentioned above, and the fluorescence was easily observed even in the case of Ba. In view of all the emission yields listed in Table 3, it is noticeable that the emission yield was enhanced with the coordination in the following order: Be>Al>Zn. The simultaneous enhancement of the fluorescence and phosphorescence yields indicates that the strong metal-ligand bond restricts the internal rotation of the ligand in the singlet excited state and prevents it from making a radiationless transition. In fact, the fluorescence yields increase in an order of that of the ionic radii of metal ions (Be^{2+}: 0.34, Al^{3+}: 0.57, Zn^{2+}: 0.69 Å). Further, this presump-

TABLE 3. EMISSION YIELDS OBSERVED AT 77 K IN METHANOL AND WATER (4 : 1)

Compound	Φ_F	Φ_P	Φ_P/Φ_F	τ_P, s
Be(AcAc)$^+$	—	0.028	—	0.098
Be(AcAc)$_2$	—	0.031	—	0.098
Al(AcAc)$_3$	—	0.006	—	—
Zn(AcAc)	—	0.012	—	—
Ba	0.0001	0.001	—	—
Be(Ba)$^+$	0.023	0.065	2.8	0.32
Be(Ba)$_2$	0.020	0.10	5.0	0.35
Al(Ba)$^{2+}$	0.030	0.019	0.63	0.39
Al(Ba)$_3$	0.023	0.025	1.1	0.48
Zn(Ba)$_2$	0.0004	0.0015	3.8	—
Dbm	0.008	0.0003	0.33	—
Be(Dbm)$^+$	0.15	0.077	0.52	0.29
Be(Dbm)$_2$	0.11	0.13	1.1	0.40
Al(Dbm)$^{2+}$	0.088	0.032	0.37	0.60
Zn(Dbm)$^+$	0.028	0.007	0.24	0.45
Zn(Dbm)$_2$	0.019	0.007	0.31	0.45

tion is supported by the fact that an intense fluorescence is observed at low temperatures for all the complexes which have no emission at room temperature.

It is important that beryllium complexes do not have the smallest ratio of the phosphorescence yields to the fluorescence yield, contrary to the expectation that the ratio in the lightest metal complex would be the smallest on account of having the smallest spin-orbit interaction. This abnormality will be discussed later.

The polarization of emission is defined by Eq. (1) when excited with polarized light:

$$P=\frac{I_{\parallel}-I_{\perp}}{I_{\parallel}+I_{\perp}} \tag{1}$$

where $I_{\parallel}$ and $I_{\perp}$ are the emission intensities with electric vectors parallel and perpendicular to that of the exciting light respectively. When the emission moment at an angle(θ) with the absorption one, P is written as Eq. (2), assuming the random orientation of a solute in the solution:

$$P=\frac{3\cos^2\theta-1}{\cos^2\theta+1} \tag{2}$$

Moreover, the polarization is calculated to be 1/2 when the transition moment of the emission is the same in direction as that of absorption ($\theta=0°$), and $-1/3$ when it is perpendicular ($\theta=90°$). The fluorescence polarizations obtained have a small deviation from the ideal value (1/2) and are independent of the excitation light throughout the near-ultraviolet region for all the samples except $Al(Dbm)^{2+}$, as Table 4 shows. Phosphorescence polarizations have negative or small positive values, depending on the metal ions, for all the series of β-diketones; they are also independent of excitation wavelength except for the dibenzoylmethanato complex of aluminium. The independence of P for the mono-β-diketonato complex suggests that the broad absorption band in the near-ultraviolet region consists of one kind of transition except for the case of dibenzoylmethanato complexes, one of which has a new and weak absorption band in the lower frequency region, as has been mentioned above. The negative and small positive values of the phosphorescences indicate that the lowest triplet state is a π-π^* state in all cases, just as McGlynn *et al.* reported.[14] The assignment of the phosphorescence is supported by both the semi-empirical calculation of acetylacetone[13] and the relatively longer lives of the phosphorescences. The shortest lifetime, 0.1 s, which was found for $Be(AcAc)^+$, was longer than any other reported life-times of the n-π^* triplet state.

TABLE 4. POLARIZATION OF EMISSION ON EXCITATION TO THE FIRST EXCITED STATE IN METHANOL AND WATER (4 : 1) AT 77 K

Compound	P_{Fluo}	P_{Phos}
$Be(AcAc)_2$		0.10
$Al(AcAc)_3$		−0.018
$Zn(AcAc)_2$		−0.097
$Be(Ba)^+$	0.35	
$Be(Ba)_2$	0.14	
$Al(Ba)^{2+}$	0.28	
$Al(Ba)_3$	0.03	
$Zn(Ba)_2$	0.35	0.17
$Be(Dbm)^+$	0.33, 0.36[a]	0.01, 0.14[a]
$Be(Dbm)_2$	0.30, 0.12[a]	−0.13, 0.07[a]
$Al(Dbm)^{2+}$	0.25, 0.13[a]	0.020
$Al(Dbm)_2{}^+$	0.15, 0.11[a]	
$Zn(Dbm)^+$	0.40	
$Zn(Dbm)_2$	0.40	

a) The values were obtained on the excitation of the 0—1′ or 0—2′ band; they were different from the value on the excitation of the 0—0′.

It is interesting that the shortest lifetimes of the AcAc and Dbm complexes were found not for the zinc complexes but for the beryllium complexes, contrary to the expectation based on the spin-orbit coupling through the metal-ligand bond. Because the shortest lifetimes were accompanied by extraordinary enhancements of the yields in all the beryllium complexes, it is probable that the intersystem crossing rates ($S_1 \rightarrow T_0$, $T_0 \rightarrow S_0$) increase with the strength of the metal-ligand bond.

After all, the metal-ligand bond in a complex brings about: (i) a small radiationless transition rate in the singlet excited state, resulting in increasing yields of emission, and (ii) a large intersystem crossing rate, resulting in a larger yield and the shortest lifetime of the phosphorescence.

Ligand-ligand Interactions in Bis- and Tris-bidentate Complexes. *Conformations of Ligands in Bis- and Tris-bidentate Complexes*: The conformations of the coordinating β-diketones are different depending on the metal ions. In beryllium complexes, the six-membered rings of two ligands hold planes which are vertical with each other, so that the Coulomb exchange interaction of π-π electrons (inter-ligand π-π) between two ligands

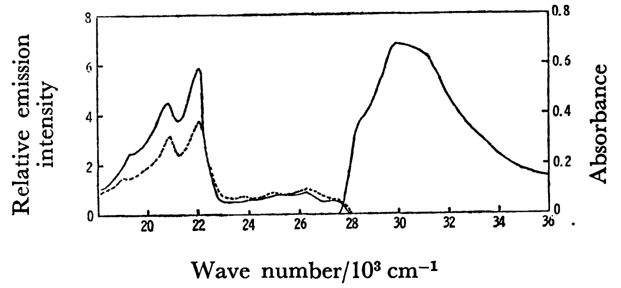

Fig. 5. Absorption and emission spectra of $Be(Ba)_2$ (solid line) and $Be(Ba)^+$ (broken line) at 77 K in methanol and water (4 : 1 by volume).

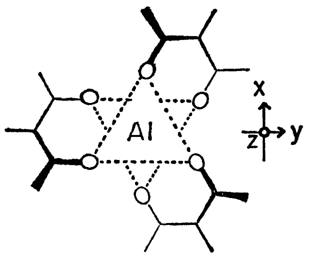

Fig. 6. Comformation of the tris-acetylacetonato complex of aluminium(III).

is impossible as the first approximation. However, weak interactions of two types cannot be ignored. One is the dipole-dipole interaction due to a weak component of the transition moment along the z-axis. The other is the interaction between non-bonding electrons localized on the oxygen atoms of one ligand and the π-electrons on the six-membered ring of the other ligand (inter-ligand n-π).

Aluminium complexes with the three same ligands have a conformation as in Fig. 6, belonging to the D_3 group. In these complexes, both Coulomb exchange interaction (inter-ligand π-π and n-π) and dipole-dipole interaction may be operative between the ligands. Especially, the circular dichroism of tris-(acetylacetonato)-silicon(IV) in the near-ultraviolet region has been understood on the basis of the dipole-dipole interaction,[15] which splitted the triply-degenerated state into two exciton-like state with A_2 and E symmetry with an allowed transition.

As for zinc complexes—$Zn(AcAc)_2 \cdot (H_2O)$[16] and $Zn(Ba)_2 \cdot C_2H_5OH$,[17] X-ray analysis has shown that two ligands of AcAc or Ba are approximately coplanar and that H_2O or C_2H_5OH is located at an apical position. It is probable that $Zn(Dbm)_2 \cdot (H_2O)_2$ has a similar structure, with two Dbm in the same plane and two H_2O at apical positions. Such a structure has also been reported in the case of Zn(8-hydroxyquinolinato)$_2$(H_2O)$_2$.[18] Two ligands in the same plane may interact with each other through both Coulomb-exchange (π-π and n-π) and dipole-dipole interactions; the latter produces a lower symmetric state with a forbidden transition and an antisymmetric higher one with an allowed transition.

Absorption Spectra and Emission Spectra: Each of the bis- and the tris-β-diketonato complexes has an absorption spectrum similar to that of the corresponding mono-β-diketonato complex, as is shown in Figs. 2—4. Although they are not finely resolved, some peaks and shoulders of the absorption spectra of the bis- and the tris-β-diketonato complexes can be assigned to a vibrational structure, just as those of the corresponding mono-β-diketonato complexes are (see Table 2). This assignment is supported by the fluorescence spectra in the case of the dibenzoylmethanato complexes (see Fig. 2). The fluorescence spectra of the bis-β-diketonato complexes, whose peaks and shoulders can be assigned to one kind of progression without ambiguity, have a good mirror image with the absorption spectra. After all, it is reasonable to say that there is not so strong an interaction between ligands in the bis- and tris-bidentate complexes as to produce a distinct new electronic transition.

This is contrary to the proposition which explains the absorption spectra and the circular dichroism of some tris-acetylacetonato complexes. Hanazaki *et al.*[11] have regarded the separation (1500 cm^{-1}) between the absorption maximum and the shoulder on the lower-frequency side observed at room temperature as the energy difference between the A_2 and E states for $Al(AcAc)_3$. For $Si(AcAc)_3^+$, 1500 cm^{-1} has been obtained in a similar way to that reported by Mason and Searle.[15] However, there remain some ambiguities in the assignments which are deduced without considering that the vibrational structure might appear as some sub-bands in the absorption spectra. Moreover, it must be recalled that the dipole-dipole interaction comes vibronically into play, according to Simpson,[19] when the vibrational interval (1300 cm^{-1}) is larger than the interaction energy (850 cm^{-1}=1/3× (the energy difference between E and A_2 states), which has been calculated by the method of P-P-P SCF-CI[11]). The splitting of the individual sub-band is calculated approximately to be one fourth of 2560 cm^{-1}, on the average, if the absorption spectrum is considered to consist of four sub-bands. Therefore, the absorption spectrum becomes more complex and broader, so that small splitting cannot be observe deasily. Moreover, if the dipole-dipole interaction in $Al(AcAc)_3$ is retained in the case of $Al(Dbm)_2^+$, which has a less broad absorption spectrum, a splitting of the individual sub-band should be observed.

In the case of α,α′-bipyridyl complexes of nickel(III) whose absorption spectra are well resolved into several sharp sub-bands, the splitting of the sharp individual sub-band may be expected to be visible since the total dipole-dipole interaction in [Ni(α,α′-bipyridyl)$_3$]$^{2+}$ has been calculated to be 2680 cm^{-1}.[20] However, Bray *et al.* observed no difference between the well-resolved spectra of the mono- and the tris-α,α′-bipyridyl complexes at 77 K.[21] After all, then it is not improbable that the dipole-dipole interaction in the tris-β-diketonato complexes is smaller than the calculated values in the cases of $Al(AcAc)_3$ and $Si(AcAc)_3^+$.

However, in the relative intensities of the sub-bands of the absorption spectra, a distinct difference is observed between the bis- or the tris-bidentate complexes and the mono-bidentate complexes (Figs. 3 and 4). The intensities of the 0—0′ and 0—1′ bands are higher, and those of the 0—2′ and 0—3′ bands are a little lower, for $Al(AcAc)_3$ and $Al(Ba)_3$ than for the respective monobidentate complexes. As for the fluorescence, the intensity ratios of the vibronic bands to the 0—0′ band for the bis- and the tris-bidentate complexes in

TABLE 5. RELATIVE INTENSITIES OF THE VIBRONIC BANDS OF EMISSION NORMALIZED TO THE INTENSITY OF THE 0′—0 OR 0″—0 BAND

Compound	Fluorescence		Phosphorescence	
	0′—1	0′—2	0″—1	0″—2
$Be(AcAc)^+$	—		1.10	0.90
$Be(AcAc)_2$	—		1.07	0.87
$Al(AcAc)^{2+}$	—		0.92	
$Al(AcAc)_3$	—		0.88	
$Be(Ba)^+$	—		0.65	
$Be(Ba)_2$	—		0.62	
$Al(Ba)^{2+}$	1.88	1.95	0.96	
$Al(Ba)_3$	1.87	1.92	0.95	
$Be(Dbm)^+$	1.56	0.84	0.42	
$Be(Dbm)_2$	1.55	0.77	0.41	
$Al(Dbm)^{2+}$	1.30	0.72	0.74	0.68
$Al(Dbm)_2^+$	1.19	0.66	0.69	0.64
$Zn(Dbm)^+$	1.20	0.77	0.48	
$Zn(Dbm)_2$	1.15	0.65	0.42	

any case, are lower than those for the mono-bidentate complexes as is shown in Table 5; for instance, the ratio of the 0′—1 is 1.30 for $\mathrm{Al(Dbm)}^{2+}$ while it is 1.19 for $\mathrm{Al(Dbm)_2}^{+}$. A similar situation is also seen in the phosphorescence. The intensity ratios of the vibronic bands are lower for the bis- and the tris-bidentate complexes than for the mono-bidentate complexes except in the case of $\mathrm{Al(Ba)_3}$.

These changes in the spectral pattern are reduced to the change in the Franck-Condon factors ($\langle 0|v'\rangle^2$, $\langle 0'|v\rangle^2$ and $\langle 0''|v\rangle^2$ where v and v' are zero or near to zero). The situation in which the Franck-Condon factors for the sub-bands of the bis- and the tris-bidentate complexes decrease compared to that of the mono-bidentate complexes may correspond to the reduction of the configurational deformation or displacement in the excited state with the bis- and the tris-bidentate complexes. Since a smaller deformation or displacement can be expected when a ligand-ligand interaction causes an extended excited state, the variation in the Franck-Condon factors can be understood in terms of ligand-ligand interaction. Further, it may be expected that the Franck-Condon factors of phosphorescence ($\langle 0''|v\rangle^2$, v: much higher) are smaller in the bis- and the tris-bidentate complexes. If this is the case, the phosphorescence may also be expected to have a larger yield and a longer lifetime, because smaller Franck-Condon factors with higher v-values reduce the rate of the radiationless transition for polyatomic molecules.[22)]

Yields and Polarizations of Emissions: The sharing of excitation and emission by two or three ligands results in a depolarization of the emission. When the excited state of the bis-bidentate complexes of beryllium is a doubly degenerate state of E symmetry, with a transition moment of two components, the fluorescence polarization is calculated to be 0.14 (see Table 6). The polarizations measured for $\mathrm{Be(Ba)_2}$ and $\mathrm{Be(Dbm)_2}$ were nearly 0.14 as Table 4 shows*. Though these results do not enable us to decide what kind of inter-ligand interaction is operative, they support the idea that an interaction exists between ligands in the excited state and in the ground state. As for the tris-β-diketonato complexes belonging to the D_3 group, it can easily be seen that the transition moments of the three ligands couple to give a transition (z-polarized) with the A_2 symmetry and a transition (x- and y-polarized) with the E symmetry. Since the splitting of the two states is too small to be observed in the spectra, it is plausible that both of the states fluoresce at 77 K. In that case, the fluorescence polarization can be calculated to be 0.09 on excitation to both states. In fact, the measured polarization (0.03) of $\mathrm{Al(Ba)_3}$ was near to the ideal value. Therefore, these results confirm the existence of the excited state extending through three ligands which has been proposed on the basis of the changes in the sub-band intensities.

TABLE 6. IDEAL VALUES OF THE FLUORESCENCES OF BIS AND TRIS-BIDENTATE COMPLEXES[a)]

Complex (symmetry group)	Absorption (moment)	Fluorescence (moment)	Polarization
Tris-bidentate (D_3)	$A_1 \to A_2$, E (x, y, z)	$A_2 \to A_1$ (z)	0.22
	$A_1 \to A_2$, E (x, y, z)	$E \to A_1$ (x, y)	−0.17
	$A_1 \to A_2$, E (x, y, z)	A_2, $E \to A_1$ (x, y, z)	0.09
Bis-bidentate (D_{2d})	$E \to E$ (x, y)	$E \to E$ (x, y)	0.14

a) The ideal values are calculated on the following conditions in the case of tris-β-diketonato complexes: (i) the ratio of the transition probability of $A_2 \leftrightarrow A_1$ to that of $E \leftrightarrow A_1$ is two, and (ii) the internal conversion rate between A_2 and E is very rapid.

No difference in fluorescence polarization between the mono- and bis-β-diketonato form was observed for zinc complexes. However, this does not imply that no delocalization of the excited state occurs through the two ligands of zinc complexes, because the two ligands have parallel transition moments.

As for the phosphorescence, the bis- and tris-β-diketonato complexes have longer lifetimes than the corresponding mono-β-diketonato complexes except for zinc complexes, as Table 3 shows. These changes may be caused by a decrease in the radiationless transition rate, because the rate is reduced with the decrease in Franck-Condon factors for higher v'-values which was expected from the change in the vibronic band intensities of the phosphorescences mentioned above.

There was a distinct change in the emission yields from the mono-β-diketonato complexes to the bis- and tris-β-diketonato ones (see Table 3). The fluorescence yields of the latter decreased, while the phosphorescence yields increased. The increase in the phosphorescence yields seems to arise from the same origin (a decrease in the radiationless transition rate of the triplet state) as the longer lifetime. However, because the increase in the yield was much larger than that in the lifetime, it may be assumed that it is mainly due to the increase in the intersystem crossing rate of the singlet-excited state and partially due to a decrease in the radiationless transition rate of the triplet state. This assumption is supported by the fact that the fluorescence yields decrease in the case of the bis- and tris-β-diketonato complexes. It is reasonable that the increase in the intersystem crossing rate is brought about by the spin-orbit coupling through the inter-ligand interaction as well as by inter-phenyl interaction in diphenylmethane and triphenylmethane.[5)]

References

1) P. Yuster and S. I. Weissman, *J. Chem. Phys.*, **17**, 1182 (1949).

2) M. A. El-Sayed and M. L. Bhaumik, *ibid.*, **39**, 2391 (1963), Y. Ohashi, K. Yoshihara, and S. Nagakura, *J. Mol.*

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* The polarization of $\mathrm{Be(Dbm)_2}$ was different between the 0′—0 excitation and the 0—1′ or 0—2′ excitation. It is probable that ligand-ligand interaction produces such a splitting as was observed in the case of $\mathrm{Al(Dbm)}^{2+}$ as has been described.

Spectrosc., **38**, 43 (1971).

3) B. Stevens, "Advance in Photochemistry," Vol. 8, John Wiley & Sons, New York (1971), p. 161.

4) L. O. Edwards and W. T. Simpson, *J. Chem. Phys.*, **53**, 4237 (1970); M. E. Long, Y. H. Li, and E. Lim, *Chem. Phys. Lett.*, **16**, 445 (1972).

5) F. H. Watson and M. A. El-Bayoumi, *J. Chem. Phys.*, **55**, 5464 (1971).

6) Th. Förster, *Discuss. Faraday Soc.*, **27**, 7 (1959).

7) R. S. Becker and J. B. Allison, *J. Phys. Chem.*, **67**, 2669 (1963).

8) R. M. Izatt, W. C. Fernelius, B. P. Blck, and C. G. Hass, Jr., *ibid.*, **59**, 170 (1955).

9) E. Lippert, W. Nagele, I. Seibold-Blankenstein, U. Straiger, and W. Voss, *Z. Anal. Chem.*, **170**, 1 (1960).

10) E. H. Gilmore, G. E. Gibson, and D. S. McClure, *J. Chem. Phys.*, **20**, 829 (1952).

11) I. Hanazaki, F. Hanazaki, and S. Nagakura, *ibid.*, **50**, 265 (1969).

12) J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, **86**, 2105 (1964).

13) K. Nakamoto, Y. Morimoto, and A. E. Martell, *ibid.*, **66**, 346 (1962).

14) S. P. McGlynn, T. Azumi and M. Kinoshita, "Molecular Spectroscopy of The Triplet State," Prentice-Hall, New Jersey (1966), p. 246.

15) E. Larsen, S. F. Mason, and G. H. Searle, *Acta Chem. Scand.*, **20**, 191 (1966).

16) E. L. Lippert and M. R. Truter, *J. Chem. Soc.*, **1960**, 4996.

17) R. L. Belford, N. D. Chasteen, M. A. Hitchman, P. K. Hon, C. E. Pflungan, and I. C. Paul, *Inorg. Chem.*, **8**, 1312 (1969).

18) G. J. Palenik, *Acta Crystallogr.*, **17**, 696 (1964).

19) W. T. Simpson and D. L. Peterson, *J. Chem. Phys.*, **26**, 588 (1957).

20) S. F. Mason, *J. Chem. Soc.*, *Ser. A*, **1969**, 1428.

21) R. G. Bray, J. Ferguson, and C. J. Hawkins, *Aust. J. Chem.*, **22**, 2091 (1969).

22) W. Siebrand, *J. Chem. Phys.*, **46**, 440 (1967).