Ligand-Ligand Interaction in Tris(2,2′-bipyridyl) and Tris (1,10-phenanthroline) Complexes of Nickel(II)

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UV spectra of $[Ni(2,2'\text{-bipyridyl})_3]Cl_2$ and $[Ni(2,2'\text{-bipyridyl})(H_2O)_4]Cl_2$ in the mixed solvent of methanol and water (4: 1) were measured at 4.2 K. No difference between the spectra indicates a small splitting (<90 cm^{-1}) between the exciton states extending through the three 2,2′-bipyridyls. Since the UV spectrum of $[Ni(1,10\text{-phenanthroline})_3]Cl_2$ has a band with the progression as that of $[Ni(1,10\text{-phenanthroline})(H_2O)_4]SO_4$, a molecular exciton interaction between the three 1,10-phenanthrolines is not strong.

When some aromatic molecules coordinate to a metal ion through hetero atom(s) of the group(s) such as >–C<(O) >–O⁻, and >N, they suffer from such ligand-ligand interactions as a molecular exciton interaction and a Coulomb exchange interaction between the neighbouring ligands.[1-3] We have investigated the ligand-ligand interactions by comparing the excited states of the bis- or the tris-bidentate complexes with those of the corresponding mono-bidentate complexes in the cases of β-diketones, 2,2′-bipyridyl,* 1,10-phenanthroline,** and *N*-alkylsalicylideneimine[4] at 77 K, and have obtained some remarks as follows; (a) the higher intensity of 0–0′ band (absorption) and 0′–0 band (fluorescence) compared to those of the mono-bidentate complex suggests a delocalization of the excited singlet state through the two or three chelating ligands, (b) the increase in the yield of the triplet state formation is attributed to the overlap between the ligands nearly perpendicular with each other, (c) there was no distinct splitting of the absorption band, indicating a weak ligand-ligand interaction, (d) the depolarized fluorescence of $[Zn(bipy)_3]^{2+}$ at 77 K suggests that the energy splitting due to ligand-ligand interaction is so small (<70 cm^{-1}) that the upper state fluoresces as the lower does.

In contrast to the small splitting of the molecular exciton states, Mason *et al.* had concluded on the assumption of the strong coupling scheme that the molecular exciton splittings were nearly equal to differences (1200—2000 cm^{-1}) between the peaks of the positive and the negative bands of the circular dichroism observed at room temperature in the cases of trisacetylacetonato,[5] tris-phen[6] and tris-bipy[6] complexes. Recently, however, it was demonstrated[7] that either a medium or a weak coupling scheme was a suitable one, because the absorption and the circular dichroism spectra with a fine structure were observed in the case of $[Ni(bipy)_3]^{2+}$ below 0 °C: a small splitting value (<70 cm^{-1}) was inferred on the basis of the vibronic coupling theory proposed by Perrin and Gouterman.

In order to obtain the splitting in $[Ni(bipy)_3]^{2+}$, we tried to measure the well resolved absorption spectrum in a mixed solvent at 4.2 K, where the compound is free from a (crystal) exciton.

* 2,2′-Bipyridyl will be hereafter abbreviated to "bipy."

** 1,10-Phenanthroline will be hereafter abbreviated to "phen."

Experimental

Materials $[Ni(bipy)_3]Cl_2$, $[Ni(phen)_3]Cl_2$, and $[Ni(bipy)(H_2O)_4]SO_4$ were prepared from appropriate nickel (II) salts and the ligands and purified by recrystallization. G.R. methanol of Wako Chemical Co., and twice distilled water were used for the mixed solvent.

Procedure All the sample solutions except for $[Ni(phen)(H_2O)_4]^{2+}$ solution were prepared by dissolving a com plex in the mixed solvent of the methanol and the water (4:1 by volume). The sample solution of $[Ni(phen)(H_2O)_4]^{2+}$ is obtained by dissolving $NiSO_4 \cdot H_2O$ of $\sim 2 \times 10^{-4}$ M and the phenanthroline of 2×10^{-5} M in the solvent. It is assumed on the basis of the large formation constant ($\log K_1 = 8.60$[8]) that the free phen was reduced to 0.1% at most. The absorption spectra at 4.2 K were measured by using a thin cell (0.1×10 mm) plunged in the liq. He in a Dewar vessel, which was kindly offered by prof. N. Mataga. Although the sample solutions had a great number of fine cracks at 4.2 K, the cracks did not interfere with the measurement of the absorption spectrum owing to the following reasons. One is that the fine cracks running perpendicular to the window of the cell do not seriously scatter the light beam. The other is that a head-on-type photomultiplier with a wide aperture (A=12 cm^2) can catch the most of the scattered light. Though a polyvinylalcohol film (PVA) and a rod of polymethylmethacrylate (PMM) containing a complex, had no crack at 4.2 K, the doped complex has a broader spectrum, which is probably attributed to many kinds of doping cite in PVA or a thermal decomposition of the complex during the thermal polymerization.

Results

Absorption spectra of $[Ni(bipy)_3]^{2+}$ and $[Ni(bipy)(H_2O)_4]^{2+}$ in the region of the UV are shown in Figs. 1 and 2, respectively. The absorption bands at 4.2 K (solid line in Figs. 1 and 2) have well resolved structure which are almost common to the two ions. Figure 3 shows the absorption spectra of $[Ni(phen)_3]^{2+}$, $[Ni(phen)(H_2O)_4]^{2+}$ and the free phen in the region of the UV at 77 K. The three compounds have similar and weakly resolved spectra at 77 K.

Discussion

$[Ni(bipy)_3]Cl_2$. Since $[Ni(bipy)(H_2O)_4]^{2+}$ has a similar absorption spectrum to that of $[Zn(bipy)(H_2O)_4]^{2+}$ in the region of the UV, the well resolved spectrum is mainly attributed to the coordinating bipy with *cis*-conformation (not to d–d transition). The

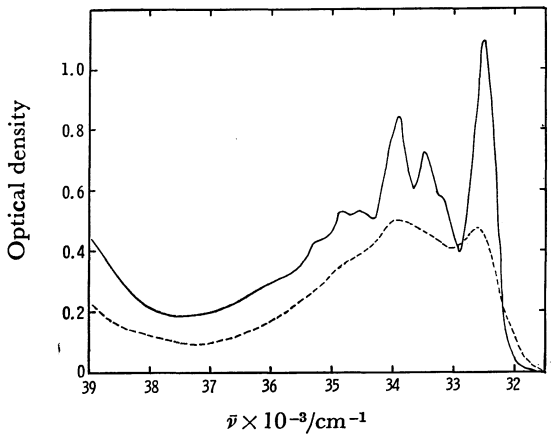

Fig. 1. Absorption spectra of 6×10^{-4} M solution of $[Ni(bipy)_3]^{2+}$
—— at 4.2 K, ----- at room temperature.

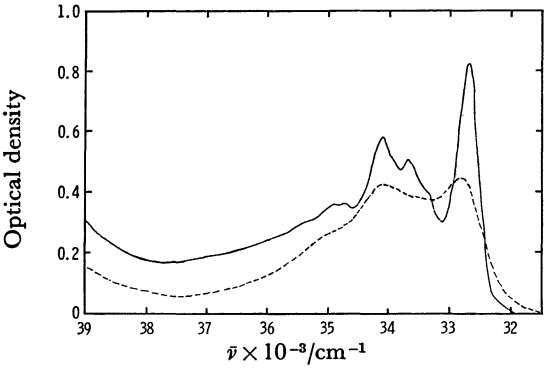

Fig. 2. Absorption spectra of $[Ni(bipy)(H_2O)_4]^{2+}$
—— [complex]: 1.28×10^{-3} M and at 4.2 K,
---- [complex]: 2.0×10^{-3} M and at room temperature.

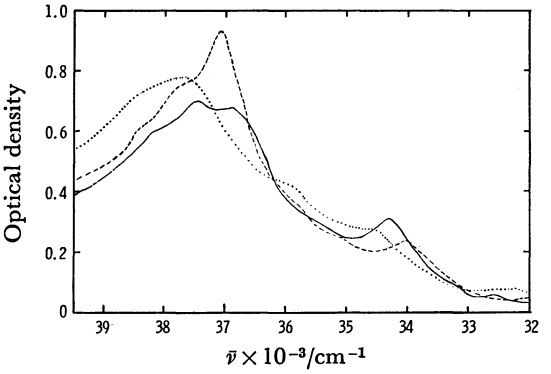

Fig. 3. Absorption spectra of phen and the phen complexes at 77 K
—— $[Ni(phen)_3]^{2+}$: 6.6×10^{-5} M,
---- $[Ni(phen)(H_2O)_4]^{2+}$ ($NiSO_4$: 2×10^{-4} M and phen: 2×10^{-5} M),
..... phen: 2×10^{-5} M.

coordinating bipy in the nickel complex is assumed to have practically one kind of transition ($A_1 \rightarrow B_1$) with the moment which is a several tens times as large as the other one ($A_1 \rightarrow A_1$),[9] as in the case of $[Zn(bipy)(H_2O)_4]^{2+}$ whose strong fluorescence at 77 K has a good mirror image relation to the absorption spectrum. Therefore, several sub-bands of $[Ni(bipy)(H_2O)_4]^{2+}$ are assigned to vibronic ones of the transition, $A_1 \rightarrow B_1$.

It is easily seen that the tris-bipy complex of nickel (II) keeps the vibronic band system of the mono-bipy complex and has neither new band nor splitting of the vibronic bands, which should be observed if there are any strong or intermediate coupling between the three ligands. The common width (460 cm^{-1}) of the 0–0′ bands to the two complexes, offers a contradictory proof to the inter-ligand interaction.

It is assumed that in the weak interaction scheme, a splitting of the vibronic band is produced by the interaction between the same vibronic states, the one of the splitted bands of the lower frequency is assigned to the transition to the E state and the other of the higher frequency to the A_2 state of $[Ni(bipy)_3]^{2+}$ with D_3 symmetry. And the spacing between the two 0–0′ bands may be equal to the splitting between the E and the A_2 states. When the splitting is much smaller than a spacing between the adjacent progression bands, the bands do not split but become broader. On assuming a Gaussian band shape and a moment ratio, 1 : 2, of $A_1 \rightarrow E$ to $A_1 \rightarrow A_2$, it is obtained that a greater bandwidth (473 cm^{-1}) than that (460 cm^{-1}) of the mono-bipy complex may be observed for $[Ni(bipy)_3]^{2+}$ when the splitting is 90 cm^{-1}. Therefore, the common band width (460 cm^{-1}) to the complexes implies a splitting less than 90 cm^{-1} between the two states. This possible largest value is supported by the fact that the splitting of $[Zn(bipy)_3]^{2+}$ is less than 70 cm^{-1}, which had been obtained by a measurement of the fluorescence polarization. Assuming that the total coupling energy is four times as great as the splitting of the 0–0′ band, of which the intensity is one-fourth of the total intensity, the possible maximum value of the coupling energy (360 cm^{-1}) is consistent with 210 cm^{-1} which Hawkins *et al.*[7] have obtained by the spectrum simulation of the circular dichroism on the basis of Perrin-Goutermans' vibronic coupling theory.

On the other hand, Mason has obtained a larger coupling energy (1050 cm^{-1}) by fitting the observed intensity of the circular dichroism with the calculated one on the Hückel M.O.[10] However, the reconstituted circular dichroism was so complex as to contain some extra shoulders (as Fig. 2 in the reference 10 shows). Because a surplus of shoulders or bands is originated from a larger coupling, the phantom shoulders of the reconstituted spectrum may be explained by an overestimation of the coupling energy.

$[Ni(phen)_3]^{2+}$. As in the case of the bipy complexes, all the absorption bands of the tris-phen and the mono-phen complexes in the region of $30—40 \times 10^3$

Table 1. The fine structure of the highest band

$[Ni(phen)(H_2O_4)]^{2+}$		$[Ni(phen)_3]^{2+}$	
ν cm^{-1}	$\Delta\nu$ cm^{-1}	ν cm^{-1}	$\Delta\nu$ cm^{-1}
37040		37760	
(37740)[a]	700	37450	690
(38460)	720	(38170)	720

a) Parenthesis shows shoulder.

cm^{-1} are assigned to the transition localized in the ligand(s). The mono-phen complex holds a weakly resolved structure for the transition of the largest wave number (^1B_a in the free phen). The structure may be caused by a metal effect, because the ^1B_a band of the free phen has no structure (but a great band width). Since the structure has a common spacing between the adjacent sub-bands (700 cm^{-1}) as Table 1 shows, the sub-bands are assigned to the vibronic bands. In the tris-phen complex, the less clear progression with the spacing of 700 cm^{-1} was observed and the feature of the band was similar to that of the free phen. It is probable that the less clear structure is caused by a sharing of the metal effect with the three ligands. A similar situation has been observed in the case of $[Zn(phen)_2(H_2O)_2]^{2+}$.[3]

Hawkins *et al.* has offered another explanation to the less stronger 0–0′ band of $[Ni(phen)_3]^{2+}$ than the 0–0′ band of $[Ni(phen)(H_2O)_4]^{2+}$; this explanation was that a molecular exciton interaction in $[Ni(phen)_3]^{2+}$ produced a broading of the 0–0′ band.[7] However, it must be noticed that $[Ni(phen)_3]^{2+}$ has a common spacing between the sub-bands as $[Ni(phen)(H_2O)_4]^{2+}$ has.

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