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Splitting of the 2nd d-d Band of *trans*-[$CoCl_2N_4$]X-Type Complexes Observed in the Solid State at 113 K

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The electronic spectra of *trans*-[$CoCl_2(NH_3)_4$]Cl and its analogues measured in the solid state at 113 K show four ligand field bands assignable to the Ia($^1E_g{}^a \leftarrow {}^1A_{1g}$), Ib($^1A_{2g} \leftarrow {}^1A_{1g}$), IIa($^1B_{2g} \leftarrow {}^1A_{1g}$), and IIb($^1E_g{}^b \leftarrow {}^1A_{1g}$) transitions in D_{4h} approximation. The ligand field parameters obtained from the observed data are; e_σ(N)=7400—8000 cm^{-1}, e_σ(Cl)=4500—5400 cm^{-1}, e_π(Cl)=300—830 cm^{-1}, and the Racah's parameter C estimated with the assumption of $C=4B$ is ca. 2000 cm^{-1}. A nearly linear relationship is obtained between the e_σ(Cl) and e_π(Cl) values; the stronger the coordination of Cl^- to Co(III), the stronger the π interaction of Cl^- with Co(III).

The splitting of the first d-d band ($^1T_{1g} \leftarrow {}^1A_{1g}(O_h)$) of octahedral Co(III) (d^6) complexes has often been observed in the spectra of solutions when the symmetry of the complexes becomes lower. However, no clear splitting has been reported on the second d-d band ($^1T_{2g} \leftarrow {}^1A_{1g}(O_h)$) except for *trans*-[$Co(CO_3$ or $C_2O_4)_2(pyridine)_2$]$^-$ in aqueous solutions.[1] In the previous paper,[2] we found a new band around 26000 cm^{-1} in the spectra of *trans*-[$CoCl_2(N_48)$]X (X=ClO_4^-, BF_4^-; N_48=1,4,7,10-tetraazacyclopentadecane) in the solid state at 113 K, which was not observed in the spectra both in the solid state and in solution at room temperature. The band is supposed to be a split component of the second d-d band as judged from the position and intensity. To examine whether other *trans*-[$CoCl_2N_4$]$^+$-type complexes show such a band, we have measured a number of complexes of this type in the solid state at 303 and 113 K and in methanol solutions at 293 and 193 K. Amine ligands used in this study are NH_3, ethylenediamine(en), trimethylenediamine(tn), 3,6-diazaoctane-1,8-diamine(trien), 1,4,8,11-tetraazacyclotetradecane(cyclam), 1,4,7,10-tetraazacyclotridecane(N_46), -tetradecane(N_47), and -hexadecane(N_49).

Experimental

Measurements. Electronic spectra were recorded on a HITACHI U-3400 spectrophotometer. Spectra of solid samples were measured by a Nujol mull method described previously,[2] and those of methanol solutions were done with a quartz cell (1 cm). Measurements at low temperatures were carried out with a stream of cold nitrogen, and the temperature was monitored by a Cu-constantan thermocouple. The volume of methanol solutions at 193 K was corrected by a factor of 0.893.[3] Gaussian curve fitting analyses of absorption spectra were performed with the modified LGNS program.[4]

Materials. *trans*-[$CoCl_2(en)_2$]BF_4, *trans*-[$CoCl_2(tn)_2$]ClO_4, and *trans*-[$CoCl_2(N_46)$]BF_4 were prepared by the addtion of $LiBF_4$ or $LiClO_4$ to methanol solutions of the corresponding chloride salts.[5-7] Other complexes were prepared as reported previously.[4,8-10]

Results and Discussion

Figure 1 compares the spectra of *trans*-[$CoCl_2(NH_3)_4$]Cl, *trans*-[$CoCl_2(en)_2$]BF_4, and *trans*-[$CoCl_2(tn)_2$]ClO_4 measured in the solid state at 113 and 303 K. Table 1 lists the data. Most of the other complexes show four bands in the d-d transition region at 113 K, while the bands in the region of 20000

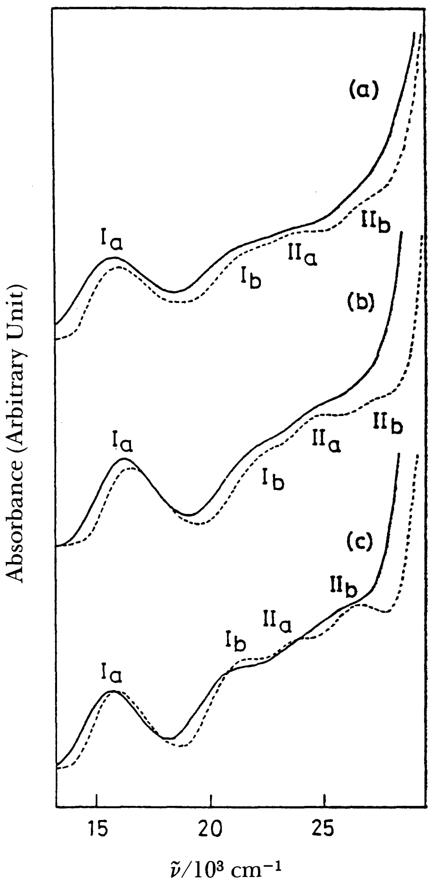

Fig. 1. Electronic spectra in the solid state at 303 K (——) and 113 K (----): (a) *trans*-[$CoCl_2(NH_3)_4$]Cl; (b) *trans*-[$CoCl_2(en)_2$]BF_4; (c) *trans*-[$CoCl_2(tn)_2$]ClO_4.

Table 1. Spectral Data of *trans*-[CoCl$_2$(L)]X in the Solid State

Complex	T	$\tilde{\nu}/10^3$ cm^{-1}			
	K	Ia	Ib	IIa	IIb
1. *trans*-[CoCl$_2$(NH$_3$)$_4$]Cl	303	15.8	ca. 21.0	—	—
	113	16.0	21.3	24.2	26.7
2. *trans*-[CoCl$_2$(en)$_2$]BF$_4$	303	16.2	ca. 21.8	ca. 24.4	—
	113	16.5	ca. 22.1	24.9	27.2
3. *trans*-[CoCl$_2$(tn)$_2$]ClO$_4$	303	15.7	ca. 21.0	—	—
	113	15.9	21.6	23.9	26.8
4. *trans*-[CoCl$_2$(trien)]ClO$_4$	303	16.1	ca. 22.8[c)]		—
	113	16.2	ca. 22.1	23.0	27.1
5. *trans*-[CoCl$_2$(cyclam)]Cl	303	15.9	ca. 23.5[c)]		—
	113	16.2	ca. 23.8[c)]		ca. 27.0
6. *trnas*-[CoCl$_2$(N$_4$6)]BF$_4$	303	16.3	23.5[c)]		—
	113	16.5	23.5[c)]		—
7. *trans*-[CoCl$_2$(N$_4$7)]ClO$_4$ (C$_2$)[a)]	303	15.6	ca. 22.1[c)]		ca. 26.1
	113	15.8	ca. 21.4	22.6	26.7
8. *trans*-[CoCl$_2$(N$_4$7)]ClO$_4$ (C$_1$)[a)]	303	15.8	ca. 21.0	22.6	—
	113	16.0	ca. 21.5	23.1	26.9
9. *trans*-[CoCl$_2$(N$_4$8)]BF$_4$ (C$_2$, green)[a,b)]	303	15.7	ca. 21.0	ca. 22.5	—
	113	15.9	21.2	22.7	26.2
10. *trans*-[CoCl$_2$(N$_4$8)]ClO$_4$ (C$_2$, brown)[a,b)]	303	15.4	ca. 20.5	ca. 22.0	—
	113	15.5	20.5	22.0	25.8
11. *trans*-[CoCl$_2$(N$_4$9)]ClO$_4$	303	15.7	20.2	22.4	—
	113	15.7	20.5	22.5	25.8

a) C$_1$ and C$_2$ represent the symmetry of geometrical isomers.[4] b) The complex crystallizes in different colors of green and brown.[2] c) Two bands are overlapped.

to 28000 cm^{-1} are less resolved at 303 K. At 113 K all the bands show a small blue-shift. In the spectra of chloride salts of these complexes, the highest energy band in this region is often hidden by an adjacent strong band which arises probably from association between the complex and chloride ions in crystals.[11] The four observed bands can be assigned as the two sets of split components, Ia, Ib and IIa, IIb resulting from the splitting of the 1st ($^1T_{1g}\leftarrow{}^1A_{1g}(O_h)$) and the 2nd ($^1T_{2g}\leftarrow{}^1A_{1g}(O_h)$) d-d bands, respectively in tetragonal symmetry of the complexes. When the symmetry of the complexes is approximated to D$_{4h}$, the bands in Fig. 1 can be assigned to the Ia($^1E_g{}^a\leftarrow{}^1A_{1g}$), Ib($^1A_{2g}\leftarrow{}^1A_{1g}$), IIa($^1B_{2g}\leftarrow{}^1A_{1g}$), and IIb($^1E_g{}^b\leftarrow{}^1A_{1g}$) transitions, and their energies represented by the angular overlap model (AOM) formulation[12] are

$$\nu_{\mathrm{Ia}} = 3/2e_\sigma(\mathrm{N}) + 3/2e_\sigma(\mathrm{Cl}) - 2e_\pi(\mathrm{Cl}) - C, \tag{1}$$

$$\nu_{\mathrm{Ib}} = 3e_\sigma(\mathrm{N}) - C, \tag{2}$$

$$\nu_{\mathrm{IIa}} = e_\sigma(\mathrm{N}) + 2e_\sigma(\mathrm{Cl}) + 16B - C, \tag{3}$$

$$\nu_{\mathrm{IIb}} = 5/2e_\sigma(\mathrm{N}) + 1/2e_\sigma(\mathrm{Cl}) - 2e_\pi(\mathrm{Cl}) + 16B - C, \tag{4}$$

where B and C represent the Racah's parameters. The e_π(N) parameter was assumed to be zero. With the assumption of $C=4B$, the values of parameters were obtained from the data as given in Table 2. The values of 7400—8000 cm^{-1} for e_σ(N), 4500—5400 cm^{-1} for e_σ(Cl), 300—830 cm^{-1} for e_π(Cl) , and ca. 2000 cm^{-1}

Table 2. Ligand Field Parameters of *trans*-[CoCl$_2$(L)]X Calculated from the Data in Table 1

Complex	e_σ(N)/cm^{-1}	e_σ(Cl)/cm^{-1}	e_π(Cl)/cm^{-1}	C/cm^{-1}
1. *trans*-[CoCl$_2$(NH$_3$)$_4$]Cl	7800	5200	700	2000
2. *trans*-[CoCl$_2$(en)$_2$)]BF$_4$	8000	5400	830	2000
3. *trans*-[CoCl$_2$(tn)$_2$)]ClO$_4$	7900	5000	700	2000
4. *trans*-[CoCl$_2$(trien)]ClO$_4$	8000	4700	450	1900
7. *trans*-[CoCl$_2$(N$_4$7)]ClO$_4$ (C$_2$)	7800	4500	380	1900
8. *trans*-[CoCl$_2$(N$_4$7)]ClO$_4$ (C$_1$)	7800	4700	430	2000
9. *trans*-[CoCl$_2$(N$_4$8)]BF$_4$ (C$_2$, green)	7700	4700	450	1800
10. *trans*-[CoCl$_2$(N$_4$8)]ClO$_4$ (C$_2$, brown)	7400	4500	300	1800
11. *trans*-[CoCl$_2$(N$_4$9)]BF$_4$	7500	4800	380	1900

for $C(=4B)$ seem to be appropriate. When the IIa and IIb bands are assigned as the ${}^1E_g{}^b \leftarrow {}^1A_{1g}$ and the ${}^1B_{2g} \leftarrow {}^1A_{1g}$ transitions, respectively, the e_σ(Cl) and e_π(Cl) values become exceptionally large. For example, the values for *trans*-$[CoCl_2(NH_3)_4]Cl$ are $e_\sigma(N)=7700\ cm^{-1}$, $e_\sigma(Cl)=6800\ cm^{-1}$, $e_\pi(Cl)=2000\ cm^{-1}$, and $C=1800\ cm^{-1}$. There seems to be no correlation between the e_σ(N) and the e_σ(Cl) values, while a nearly linear relationship is seen between the e_σ(Cl) and the e_π(Cl) values as shown in Fig. 2. The result indicates that the stronger the coordination of Cl^- to Co(III), the stronger the repulsive π interaction of Cl^- with Co(III).

The spectra of a series of *trans*-$[CoCl_2(N_4x)](BF_4$ or $ClO_4)$ (x=6—9) are shown in Fig. 3. In the spectra of the N_46 and N_47 complexes both at 113 and 303 K, only two and three bands are detected, respectively. From a comparison of the four spectra with one another, however, it can be concluded that the Ib and IIa bands of the N_46 and N_47 complexes overlap each other, and the IIb band of the former complex is hidden by a charge-transfer band. In this series of complexes, with a decrease in the size of chelate rings the e_σ(N) value increases, while the e_σ(Cl) one does not change or decreases (Table 2). Since the energy of the Ib band depends only on the e_σ(N) (Eq. 2), and that of the IIa band on both the e_σ(N) and e_σ(Cl) (Eq. 3), the increase in energy of the Ib band occurred with the decrease in size of chelate rings should be much larger than that of the IIa band. Consequently, the energy difference between the Ib and IIa bands becomes small with the decreasing size of chelate rings, and they overlap in the N_46 and N_47 complexes, although the latter complex shows a small shoulder due to the Ib band in the spectrum at 103 K.

The spectra of the en, tn, cyclam, and N_47 complexes in methanol solutions were measured to compare with those in the solid state. Except for the N_47 complex, all the complexes show no clear IIb band both at 193 and 293 K. The N_47 complex exhibits the

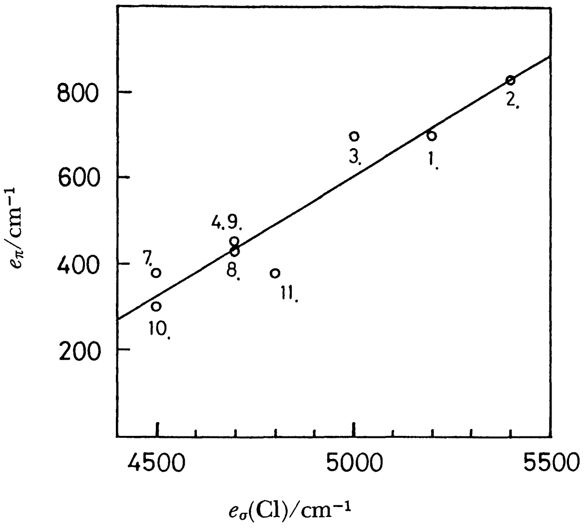

Fig. 2. Plots of e_π (Cl) vs. e_σ (Cl). The least-squares line is e_π (Cl)=0.56 e_σ (Cl) −2200, correlation coefficient: 0.95.

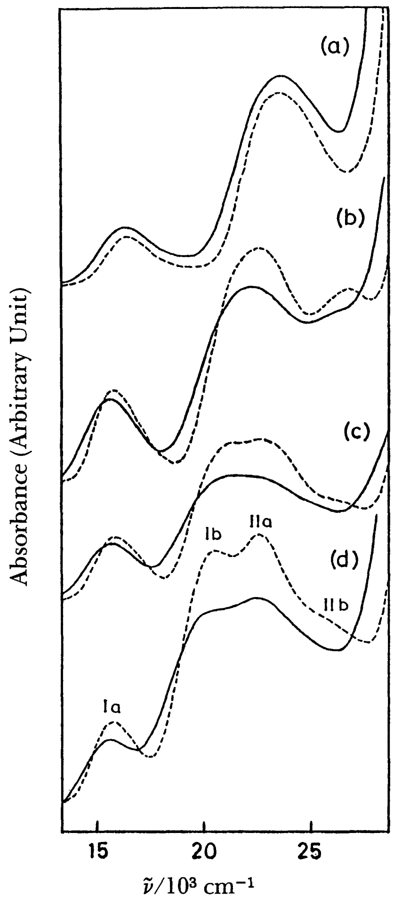

Fig. 3. Electronic spectra in the solid state at 303 K (——) and 113 K (----): (a) *trans*-$[CoCl_2(N_46)]BF_4$; (b) *trans*-$[CoCl_2(N_47)]ClO_4$ (C_2); *trans*-$[CoCl_2(N_48)]BF_4$ (C_2, green); (d) *trans*-$[CoCl_2(N_49)]BF_4$.

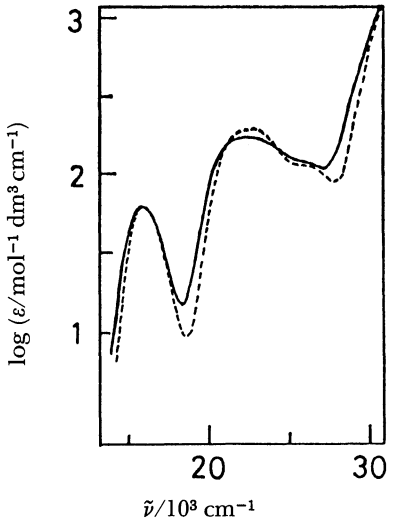

Fig. 4. Electronic spectra of *trans*-$[CoCl_2(N_47)]Cl$ (C_2) at 293 K (——) and 193 K (----) in methanol.

Table 3. Ligand Field Bands of *trans*-[$CoCl_2(N_47)$]Cl (C_2) in Methanol Solution Obtained by Gaussian Curve Fitting Analysis ($\tilde{\nu}/10^3$ cm^{-1})

T	Ia		Ib		IIa		IIb	
K	$\tilde{\nu}_{max}$(log ε)	Half width	$\tilde{\nu}_{max}$(log ε)	Half width	$\tilde{\nu}_{max}$(log ε)	Half width	$\tilde{\nu}_{max}$(log ε)	Half width
293	15.9(1.80)	2.51	21.2(2.10)	3.05	23.5(2.08)	3.67	26.8(1.94)	4.46
193	16.0(1.81)	2.35	21.5(2.18)	2.77	23.6(2.16)	3.12	26.8(1.99)	3.05

IIb band around 27000 cm^{-1}. The broad band around 22000 cm^{-1} will be a overlapping one of the Ib and IIa components (Fig. 4). In the previous paper,[4] we assigned this broad band as the Ib band, and the IIb band as the unsplitting II band. The positions of the Ia, Ib, IIa, and IIb bands of *trans*-[$CoCl_2(N_47)$]Cl in methanol solution were obtained by the Gaussian curve fitting analysis (Table 3). At 193 K, the band positions remain almost unchanged, but the band widths are reduced fairly largely.

References

1) Y. Ida, S. Fujinami, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **50**, 2665 (1977).

2) M. Tsuchimoto, H. Takazawa, M. Kita, M. Nonoyama, S. Ohba, Y. Saito, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 785 (1990).

3) "Landolt-Börnstein Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," Springer-Verlag, (1971), 6 Aufl., II Band, 1 Teil, S. 662.

4) M. Tsuchimoto, M. Kita, M. Nonoyama, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 227 (1990).

5) *Inorg. Synth.*, Vol. II, p. 222.

6) Y. Kojima, *Bull. Chem. Soc. Jpn.*, **48**, 2033 (1975).

7) Y. Hung, L. Y. Martin, S. C. Jackels, A. M. Tait, and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 4029 (1977).

8) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).

9) A. M. Seargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).

10) S. M. Jörgensen, *Z. Anorg. Chem.*, **14**, 415 (1897).

11) Y. Kondo, *Bull. Chem. Soc. Jpn.*, **28**, 497 (1955).

12) C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.*, **9**, 401 (1965).