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Circular Dichroism Studies of a Series of (Ammine)[(*RR*)-2,4-pentanediamine]cobalt(III) Complexes

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The circular dichroism spectra of a series of complexes of the type $[Co(NH_3)_{2n}(RR\text{-ptn})_{3-n}]^{3+}$($n$=0, 1, 2), where the *RR*-ptn is (*RR*)-2,4-pentanediamine, were recorded in aqueous solutions with and without the addition of electrolytes such as chloride or sulfate, and in DMSO solutions. The circular dichroism spectra in the region of the first absorption band of Δ-$[Co(RR\text{-ptn})_3]^{3+}$ and *cis*-Δ-$[Co(NH_3)_2(RR\text{-ptn})_2]^{3+}$ were extremely sensitive to the environment of the complexes and showed a remarkable variation, while those of the corresponding diastereomers, Λ-$[Co(RR\text{-ptn})_3]^{3+}$ and *cis*-Λ-$[Co(NH_3)_2(RR\text{-ptn})_2]^{3+}$ were little affected by the given environment. The other complexes, *trans*-$[Co(NH_3)_2(RR\text{-ptn})_2]^{3+}$ and $[Co(NH_3)_4(RR\text{-ptn})]^{3+}$ exhibited small variations in the circular dichroism spectra. These variations seem to be accounted for by the conformational change of the flexible six-membered chelate ring brought about by ion-pair formation between the complex cations and anions.

In a previous paper,[1] we have reported that the solution CD spectra of $\Delta(lel_3)$-$[Co(RR\text{-ptn})_3]^{3+}$(*RR*-ptn=(*RR*)-2,4-pentanediamine) in the region of the first absorption band are seriously affected by its counter ions which comprise the complex salts; the chloride salt in water (2.7 mM) gives two CD bands, a strong negative and a weak positive band, while the perchlorate salt a single negative band in the same solvent. Such influences of counter ions have generally been reckoned to be negligibly small for the corresponding tris-chelated complexes formed with 1,2-diamines.

The *RR*-ptn chelate rings in the crystals of $\Delta(lel_3)$-[2] and $\Lambda(ob_3)$-$[Co(RR\text{-ptn})_3]Cl_3 \cdot nH_2O$[3] have been shown by X-ray analyses to have the λ-*skew*(*twist*) conformation with two equatorially orientated methyl groups. However, PMR studies suggest that the *RR*(or *SS*)-ptn chelate ring is conformationally labile in solution at room temperature; in planar complexes such as [Pt(*RR*-(or *SS*)-ptn)$_2$]$^{2+}$ [4,5] where no appreciable interaction is expected between the ligands, the chelate rings prefer to take the *chair* form with one axial methyl group rather than the *skew* form, while in octahedral complexes such as $[PtCl_2(NH_3)_2(RR(\text{or } SS)\text{-ptn})]^{2+}$ [5] and $[Ni(H_2O)_4(RR(\text{or } SS)\text{-ptn})]^{2+}$ [6] the stability of the *skew* form increases to reduce interactions between an apical ligand and the axial methyl group of the *RR*(or *SS*)-ptn in the *chair* form. Thus the stable conformation of *RR*(or *SS*)-ptn chelate ring in a complex seems to depend primarily on the magnitude of intramolecular interactions with other ligands. The conformation in solution may also be affected by various other factors such as the kind of solvent, the presence of excessive electrolyte, and temperature. That the CD spectrum of Δ-$[Co(RR\text{-ptn})_3]^{3+}$ in water is very sensitive to the kind of counter ion seems to be correlated with such a conformational behavior of the chiral six-membered *RR*-ptn chelate ring. In order to investigate this correlation, we have prepared a series of complexes of the type $[Co(NH_3)_{2n}(RR\text{-ptn})_{3-n}]^{3+}$ and measured their CD spectra in various matrices.

Very recently Boucher and Bosnich[7] reported the CD spectra of a number of complexes of the type, $[CoX_2(RR\text{-ptn})_2]^{n+}$, involving three isomers of the diammine complex, and found some unusual features in the CD spectra of the diammine complexes.

Experimental

Ligand. (*RR*)-2,4-pentanediamine was prepared by the method of Bosnich *et al.*,[8] and its hydrochloride (*RR*-ptn·2HCl) was used to prepare the complexes.

$(-)_{546}$-Δ-tris[(RR)-2,4-pentanediamine]cobalt(III) Complex. Mizukami *et al.*[9] prepared this complex from *trans*-$[CoCl_2(RR\text{-ptn})_2]ClO_4$ and *RR*-ptn. However, the following method gives pure Δ-isomer stereoselectively in a high yield.

RR-ptn·2HCl (2.7 g, 15.4 mmol) was dissolved in water (3 cm^3), and the pH of the solution was adjusted to 9 with NaOH. To this solution were added $[CoBr(NH_3)_5]Br_2$ (1.8 g, 4.6 mmol) and active charcoal (0.5 g). The mixture was stirred for 10 h at 50 °C, filtered off in hot to remove the charcoal, and the residue was washed with hot water. The resulting orange filtrate was then diluted with 1 dm^3 of water and poured on SP-Sephadex. The complex adsorbed on SP-Sephadex was found to be pure Δ-$[Co(RR\text{-ptn})_3]^{3+}$ by an SP-Sephadex column chromatography using a 0.2 M aqueous Na_2SO_4 solution as the eluent. The complex was isolated as various salts by the following methods.

$(-)_{546}$-Δ-$[Co(RR\text{-ptn})_3](ClO_4)_3 \cdot 3H_2O$. The complex adsorbed on SP-Sephadex was eluted with a 1.0 M $NaClO_4$ solution. The effluent was concentrated at 40 °C under reduced pressure to give orange needle crystals. They were filtered off, and recrystallized from water.

$(-)_{546}$-Δ-$[Co(RR\text{-ptn})_3]Cl_3 \cdot 2.5H_2O$. The complex was eluted similarly with 0.5 M HCl. Orange needle crystals were obtained by evaporating the effluent to almost dryness in a vacuum desiccator over NaOH and P_2O_5. They were recrystallized from a small amount of water by the addition of concd HCl.

$(-)_{546}$-Δ-$[Co(RR\text{-ptn})_3]Br_3 \cdot 2H_2O$. This complex was obtained by converting the perchlorate into bromide with the anion exchanger, Dowex 1×8, in the bromide form and recrystallized from water.

$(-)_{546}$-Δ-$[Co(RR\text{-ptn})_3]I_3$. This complex was obtained by adding a NaI solution to an aqueous solution of the perchlorate. Orange crystals were filtered off, washed with cold water and recrystallized from ethanol.

$(+)_{546}$-Λ-tris[(RR)-2,4-pentanediamine)]cobalt(III) Complex. The preparative method reported by Mizukami *et al.*[9] was modified as follows. A suspension of *RR*-ptn·2HCl (0.256 g, 1.46 mmol) and sodium methoxide (0.158 g, 2.92 mmol) in methanol (5 cm^3) was added to a solution of *trans*-$[CoCl_2(RR\text{-ptn})_2]Cl$[9] (0.54 g, 1.46 mmol) in DMSO (20 cm^3). The reaction took place immediately to give a brown solution.

It was then diluted with about 1 dm^3 of water and passed through an SP-Sephadex column (ϕ 2.7×5 cm). A small portion of the Sephadex saturated with the product was poured on the top of an SP-Sephadex column (ϕ 2.7×120 cm), and the adsorbed complexes were eluted with a 0.2 M aqueous solution of Na_2SO_4. Two separate bands were obtained. The first and the second were Δ- and Λ-$[Co(RR\text{-}ptn)_3]^{3+}$, respectively. The formation ratio of the former to the latter was 10: 1. The effluent containing the Λ-isomer was poured again on an SP-Sephadex column (ϕ 1.5×3 cm) after dilution with water and the adsorbed complex was eluted by the following method.

(+)$_{546}$*-Λ-[Co(RR-ptn)*$_3$*](ClO*$_4$*)*$_3$*.* This complex was obtained from the SP-Sephadex adsorbed the Λ-isomer in a similar way to that for Δ-$[Co(RR\text{-}ptn)_3](ClO_4)_3\cdot 3H_2O$.

(+)$_{546}$*-Λ-[Co(RR-ptn)*$_3$*]Cl*$_3$*·3H*$_2$*O.* An aqueous solution of the complex perchlorate was passed through a column containing the anion exchanger, Dowex 1×8, in the chloride form to convert into the chloride. Needle crystals were obtained by evaporating the effluent to almost dryness in a vacuum desiccator over P_2O_5.

trans, (+)$_{470}$*-cis-Δ-, and (−)*$_{470}$*-cis-Λ-diamminebis[(RR)-2,4-pentanediamine]cobalt(III) Complexes.* To a solution cf sodium methoxide (0.227 g, 4.2 mmol) in methanol (3 cm^3) was added *RR*-ptn·2HCl (0.45 g, 2.6 mmol) with stirring, and the mixture was filtered to remove NaCl. The filtrate was added to a solution of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ (1 g, 2.2 mmol) in DMSO (20 cm^3). The solution was stirred for 25 min at 85 °C, diluted with 1 dm^3 of water and acidified (pH≈3) with HCl. This was poured on SP-Sephadex, and the adsorbed complexes were chromatographed by a method similar to that for $[Co(RR\text{-}ptn)_3]^{3+}$ with a 0.2 M aqueous Na_2SO_4 solution. The column gave three separate bands, I, II, and III in the order of elution, which were $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_4(RR\text{-}ptn)]^{3+}$, and a mixture of three isomers of $[Co(NH_3)_2(RR\text{-}ptn)_2]^{3+}$, respectively. The effluent of the band III was reloaded on an SP-Sephadex column after dilution with water, and the adsorbed band was eluted with a 0.18 M sodium $(+)_{589}$-tartratoantimonate(III) solution. Two separate bands, III_A and III_B were eluted in this order. The band III_B was $(+)_{470}$-*cis*-Δ-$[Co(NH_3)_2(RR\text{-}ptn)_2]^{3+}$, but the band III_A was still a mixture of *trans*- and $(-)_{470}$-*cis*-Λ-$[Co(NH_3)_2(RR\text{-}ptn)_2]^{3+}$. However, these two isomers were successfully separated by a repeated SP-Sephadex column chromatography using a 0.2 M Na_2SO_4 solution as the eluent. The *trans*-isomer(III_A-1) moved faster than did the $(-)_{470}$-*cis*-Λ-isomer(III_A-2). The formation ratio, *trans*: *cis*-Λ: *cis*-Δ was about 1: 1: 20.

trans-[Co(NH$_3$*)*$_2$*(RR-ptn)*$_2$*](ClO*$_4$*)*$_3$*·H*$_2$*O, (+)*$_{470}$*-cis-Δ- and (−)*$_{470}$*-cis-Λ-[Co(NH*$_3$*)*$_2$*(RR-ptn)*$_2$*](ClO*$_4$*)*$_3$*.* These complexes were obtained from each separated eluate described above by a method similar to that for Δ-$[Co(RR\text{-}ptn)_3](ClO_4)_3\cdot 3H_2O$ using 1.0 M $HClO_4$ as the eluent. The effluent was concentrated to a small volume with a rotary evaporator under a reduced pressure. Orange crystals which formed were filtered off and washed with ethanol.

(+)$_{470}$*-cis-Δ-[Co(NH*$_3$*)*$_2$*(RR-ptn)*$_2$*]Cl*$_3$*·1.5H*$_2$*O.* This complex was obtained by a method similar to that for Δ-$[Co(RR\text{-}ptn)_3]Cl_3\cdot 2.5H_2O$.

[Co(NH$_3$*)*$_4$*(RR-ptn)]Cl*$_3$ *and [Co(NH*$_3$*)*$_4$*(RR-ptn)](ClO*$_4$*)*$_3$*·H*$_2$*O.* These complexes were isolated from the reaction product of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ and *RR*-ptn in DMSO described before and crystallized by methods similar to those for the chloride and the perchlorate salts of Λ-$[Co(RR\text{-}ptn)_3]^{3+}$.

(−)$_{589}$*-Λ-Tris(trimethylenediamine)cobalt(III) Perchlorate* The racemic complex was prepared by the method of Bailar and Works[10] and resolved by the method of Fujita *et al.*[11] The Λ-isomer was isolated as the perchlorate salt by a method similar to that for Δ-$[Co(RR\text{-}ptn)_3]$ $(ClO_4)_3\cdot 3H_2O$.

Table 1 shows the results of chemical analyses of all the complexes obtained.

Measurements. Absorption spectra were obtained on a Hitachi 323 and a Carl Zeiss PMQ-II spectrophotometer, and CD spectra on a JASCO model J-20 spectropolarimeter. CD spectra in Nujol mulls were measured by a method simliar to that used for IR measurement with two quartz plates. PMR spectra were recorded in D_2O at 60 MHz on a JEOL PMX-60 spectrometer taking HOD signal as the internal reference. FT ^{13}C NMR spectra were obtained in D_2O at 15.04 MHz on a JEOL FX-60 spectrometer using dioxane as the internal reference, the chemical shift of which is at 67.69 ppm downfield from TMS sealed in an external capillary.

Results and Discussion

Preparation and Characterization of the Complexes. Mizukami *et al.*[9] prepared first a pair of diastereomers, $(+)_{546}$- and $(-)_{546}$-$[Co(RR\text{-}ptn)_3]^{3+}$ by the reactions of *trans*-$[CoCl_2(RR\text{-}ptn)_2]^+$ with *RR*-ptn in 50% aqueous methanol in the absence of active charcoal, and in water in the presence of active charcoal, respectively. In the

Table 1. Analytical data of the complexes

Complex	H/%		C/%		N/%	
	Found	Calcd	Found	Calcd	Found	Calcd
Δ-$[Co(RR\text{-}ptn)_3]Cl_3\cdot 2.5H_2O$	9.38	9.16	35.10	34.86	16.27	16.26
Δ-$[Co(RR\text{-}ptn)_3]Br_3\cdot 2H_2O$	7.45	7.23	27.97	28.10	13.14	13.11
Δ-$[Co(RR\text{-}ptn)_3]I_3$	6.00	5.67	24.63	24.15	10.62	11.26
Δ-$[Co(RR\text{-}ptn)_3](ClO_4)_3\cdot 3H_2O$	6.28	6.74	25.13	25.10	11.73	11.71
Λ-$[Co(RR\text{-}ptn)_3](ClO_4)_3$	6.37	6.38	27.23	27.14	12.65	12.66
Λ-$[Co(RR\text{-}ptn)_3]Cl_3\cdot 3H_2O$	8.74	9.20	34.11	34.26	16.10	15.98
$[Co(NH_3)_4(RR\text{-}ptn)]Cl_3$	7.76	7.81	17.77	17.90	24.74	25.04
$[Co(NH_3)_4(RR\text{-}ptn)](ClO_4)_3\cdot H_2O$	4.88	5.17	11.05	11.01	15.46	15.40
trans-$[Co(NH_3)_2(RR\text{-}ptn)_2]Cl_3\cdot 1.5H_2O$	8.71	8.66	27.79	27.89	19.82	19.51
trans-$[Co(NH_3)_2(RR\text{-}ptn)_2](ClO_4)_3\cdot H_2O$	5.55	5.91	19.77	19.57	13.59	13.69
cis-Δ-$[Co(NH_3)_2(RR\text{-}ptn)_2]Cl_3\cdot 1.5H_2O$	8.32	8.66	27.81	27.89	19.93	19.51
cis-Δ-$[Co(NH_3)_2(RR\text{-}ptn)_2](ClO_4)_3$	5.98	5.75	20.05	20.16	13.91	14.11
cis-Λ-$[Co(NH_3)_2(RR\text{-}ptn)_2](ClO_4)_3$	5.66	5.75	20.02	20.16	13.96	14.11

present study, these two isomers are formed by the same reaction in DMSO without the addition of active charcoal at room temperature, and separated by SP-Sephadex column-chromatography with a 0.2 M Na_2SO_4 solution as the eluent. On the other hand, the reaction of $[CoBr(NH_3)_5]Br_2$ with *RR*-ptn in water in the presence of active charcoal gives only the $(-)_{546}$-isomer. It is known that the $(+)_{546}$- and the $(-)_{546}$-isomers have $\Lambda(ob_3)$[3] and $\Delta(lel_3)$[2] configurations, respectively, all the *RR*-ptn chelate rings taking *λ-skew-(twist)* conformation. Niketic and Woldbye[12] showed by the conformational analysis that the $(+)_{546}$-$\Lambda(ob_3)$ isomer is about 18.8 kJ·mol^{-1} less stable than the $(-)_{546}$-$\Delta(lel_3)$ isomer. This value implies that the complexes formed under an equilibrium condition are almost all (>99.9%) the $\Delta(lel_3)$ isomer. The fact that only the $\Delta(lel_3)$ isomer is formed stereoselectively in the presence of active charcoal agrees well with this implication. The formation of the $(+)_{546}$-$\Lambda(ob_3)$ isomer in the absence of active charcoal may be related with a kinetic route to form $[Co(RR\text{-ptn})_3]^{3+}$ in the reaction between *trans*-$[CoCl_2(RR\text{-ptn})_2]^+$ and *RR*-ptn.

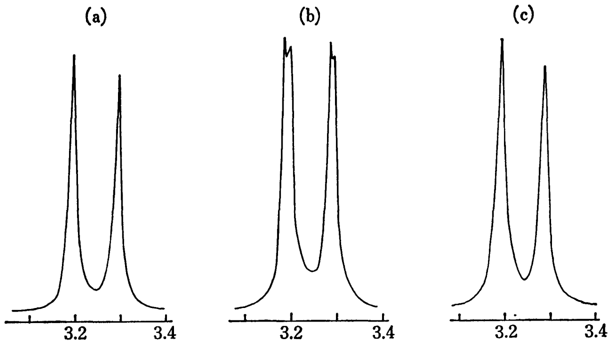

Fig. 1. PMR spectra of methyl signals of the isomers (a) III_A-1(*trans*), (b) III_A-2(*cis*)-Λ, and (c) III_B(*cis*-Δ) in D_2O.
Chemical shifts in ppm from HOD signal.

The complex, $[Co(NH_3)_2(RR\text{-ptn})_2]^{3+}$ exists in three isomers, *trans*, *cis*-Δ, and *cis*-Λ configurations, all of which have been obtained. Figure 1 shows the PMR spectra of these three isomers in D_2O at 60 MHz. The *trans*(D_2 symmetry) and the *cis*(C_2 symmetry) isomers are expected to show one and two kinds of doublet signal due to the methyl protons, respectively. The III_A-2 isomer exhibits two kinds of doublet in the methyl signal region and is assigned safely to the *cis* configuration. However, each isomer of the other two(III_A-1 and III_B) gives only one doublet methyl signal. To distinguish them ^{13}C-NMR spectroscopy has been utilized. As Fig. 2 shows, the III_A-1 isomer gives only one kind of signal for each resonance of the methyl, the methylene, and the methine carbons, while the III_B isomer two, one, and two signals for the corresponding carbons, respectively. The III_A-2 isomer exhibits the same spectral pattern as that of the isomer III_B. Thus, all of the NMR data lead to the conclusion that the III_A-1, the III_A-2, and the III_B isomers are *trans*, *cis*, and *cis* configurations, respectively. For the two *cis* III_A-2 and III_B isomers, the $\Lambda(ob_2)$ and $\Delta(lel_2)$ configurations are assigned, respectively on the basis of their CD patterns in the region of the first absorption band, as shown in Figs. 3 and 4. These assignments will be supported by the fact that the formation ratio of the $\Lambda(ob_2)$ to the $\Delta(lel_2)$ isomer is 1 : 20 as described in the Experimental part, since the yield of one diastereomer

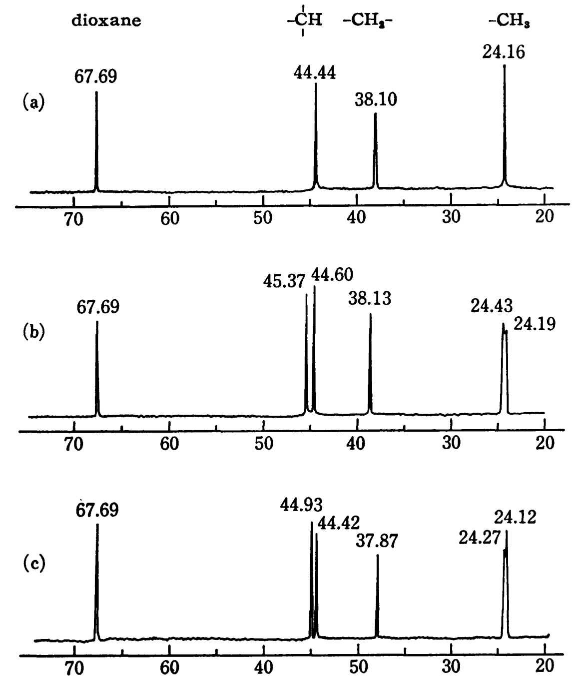

Fig. 2. Proton-decoupled 15.04 MHz ^{13}C-NMR spectra of the isomers (a)III_A-1(*trans*), (b)III_A-2(*cis*-Λ), and (c)III_B(*cis*-Δ) in D_2O.
Tantaive assignments for the signals are also given.

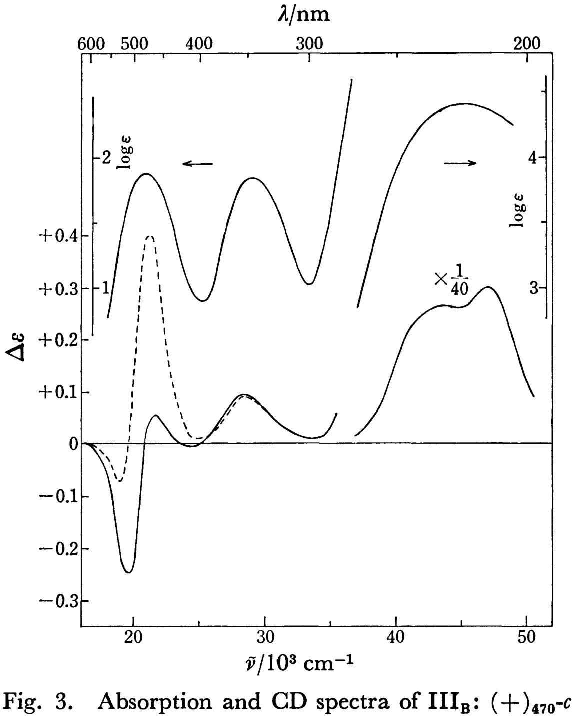

Fig. 3. Absorption and CD spectra of III_B: $(+)_{470}$-*cis*-Δ-$[Co(NH_3)_2(RR\text{-ptn})_2](ClO_4)_3$($3.31\times10^{-3}$ M in visible region and 1.32×10^{-4} M in UV region) in water(——) and in 0.2 M Na_2SO_4(----).

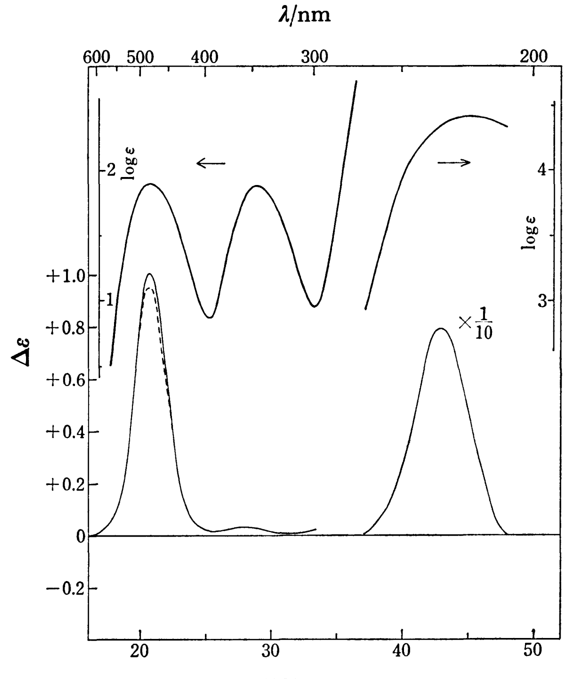

Fig. 4. Absorption and CD spectra of III$_A$-2: (—)$_{470}$-*cis*-Λ-[Co(NH$_3$)$_2$(*RR*-ptn)$_2$](ClO$_4$)$_3$(3.30×10^{-3} M in visible region and 1.32×10^{-4} M in UV region) in water(——) and in 0.2 M Na$_2$SO$_4$ (----).

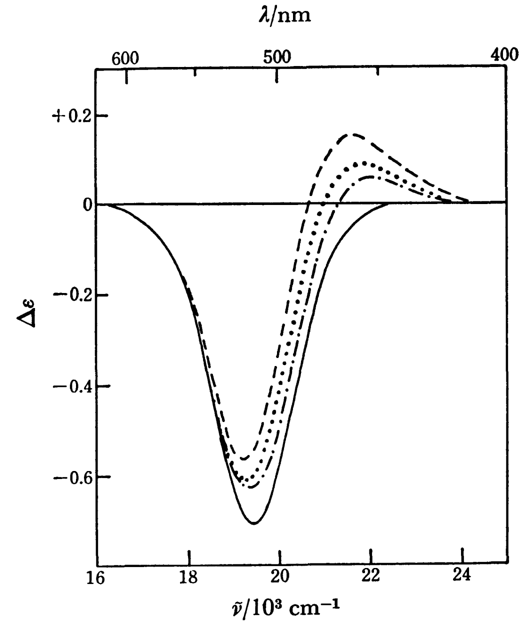

Fig. 5. CD spectra of Δ-[Co(*RR*-ptn)$_3$](ClO$_4$)$_3$·3H$_2$O (——, 3.45×10^{-3} M), Δ-[Co(*RR*-ptn)$_3$]I$_3$(-·-·-, 3.51×10^{-3} M), Δ-[Co(*RR*-ptn)$_3$]Br$_3$·2H$_2$O(······, 1.75×10^{-3} M), and Δ-[Co(*RR*-ptn)$_3$]Cl$_3$·2.5H$_2$O(----, 3.90×10^{-3} M) in water.

involving more steric interactions is expected to be lower than that of the other.[13] Molecular models indicate that the $\Lambda(ob_2)$ structure involves such interactions to a greater extent than the $\Delta(lel_2)$ structure. The assignments for these three isomers of the diammine complex agree with those made by Boucher and Bosnich.[7]

The *cis*-$\Lambda(ob_2)$ isomer gives the first absorption band at a longer wavelength (482 nm) than does the *cis*-$\Delta(lel_2)$ isomer (480 nm). These results agree with the observations reported by Mizukami *et al.*[9] that in a pair of diastereomers, the d-d absorption bands of the one involving more steric interactions lie at a longer wavelength than those of the other. For [Co(*RR*-ptn)$_3$]$^{3+}$, the first absorption band of the $\Lambda(ob_3)$ isomer is at a longer wavelength side by 6 nm than that of the $\Delta(lel_3)$ isomer, as shown in Table 2.

Circular Dichroism Spectra. As stated previously, the solution CD spectra of Δ-[Co(*RR*-ptn)$_3$]$^{3+}$ in the region of the first absorption band are seriously affected by its counter ion. Figure 5 and Table 2 show the CD data of various salts of this complex ion in water. The positive CD component at a shorter wavelength side of the first absorption band, which has been assigned to the $^1A_2\leftarrow{}^1A_1$ transition (D$_3$ symmetry) based on the analysis of the solid state CD spectrum of the chloride,[14] increases the magnitude in the order of perchlorate< iodide<bromide<chloride. The absorption spectra are all nearly identical with one another in this region. Since all the anions have uni-negative charge and the sizes of ions decrease in this order, such CD changes are suggested to be correlated with ion-pair formation between the complex cation and anions. Figure 6 shows dependence of the CD spectra of Δ-[Co(*RR*-

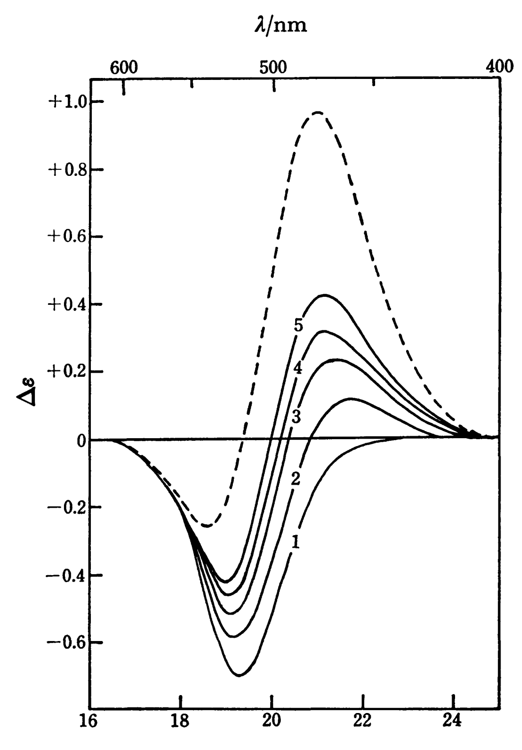

Fig. 6. Dependence of CD of Δ-[Co(*RR*-ptn)$_3$](ClO$_4$)$_3$·3H$_2$O(2.80×10^{-3} M) on the concentration of chloride ion at 25 °C and I=0.091(NaClO$_4$).
1. [Cl$^-$]=0, 2. [Cl$^-$]=1.66×10^{-2} M, 3. [Cl$^-$]=3.33×10^{-2} M, 4. [Cl$^-$]=4.99×10^{-2} M, and 5. [Cl$^-$]=7.49×10^{-2} M.
Calculated CD curve of the ion-paired species, Δ-[Co(*RR*-ptn)$_3$]$^{3+}$·Cl$^-$(----).

TABLE 2. ABSORPTION AND CD SPECTRAL DATA

Complex	Absorption $\log\varepsilon$ ($\tilde{\nu}_{\max}$/cm^{-1})	CD $\Delta\varepsilon$ $\tilde{\nu}$/cm^{-1}	Concentration C/M
Δ-$[\mathrm{Co}(RR\text{-ptn})_3](\mathrm{ClO_4})_3\cdot 3\mathrm{H_2O}$	1.90 (20750)	−0.704 (19340)	3.45×10^{-3}
	1.89 (28800)	+0.058 (28600)	
	4.49 (43500)	+18 (42200)	3.81×10^{-4}
Δ-$[\mathrm{Co}(RR\text{-ptn})_3]\mathrm{Cl_3}\cdot 2.5\mathrm{H_2O}$	1.90 (20750)	−0.565 (19190)	3.90×10^{-3}
		+0.154 (21550)	
	1.88 (28800)	+0.051 (28600)	
	4.47 (43500)	+18 (42200)	4.20×10^{-4}
Δ-$[\mathrm{Co}(RR\text{-ptn})_3]\mathrm{Br_3}\cdot 2\mathrm{H_2O}$	1.88 (20750)	−0.613 (19310)	1.75×10^{-3}
		+0.086 (21790)	
	1.84 (28800)	+0.061 (28300)	
	4.46 (43500)	+18 (42200)	4.01×10^{-4}
Δ-$[\mathrm{Co}(RR\text{-ptn})_3]\mathrm{I_3}$	1.88 (20750)	−0.628 (19460)	3.51×10^{-3}
		+0.059 (21980)	
		+0.047 (28200)	
Λ-$[\mathrm{Co}(RR\text{-ptn})_3](\mathrm{ClO_4})_3$	1.98 (20500)	+3.22 (20750)	2.88×10^{-3}
	1.95 (28600)	−0.31 (28400)	
	4.46 (43100)	+5.9 (42000)	1.15×10^{-4}
		−4.1 (48800)	
Λ-$[\mathrm{Co}(RR\text{-ptn})_3]\mathrm{Cl_3}\cdot 3\mathrm{H_2O}$	1.98 (20500)	+3.18 (20790)	3.03×10^{-3}
	1.96 (28600)	−0.33 (28600)	
	4.52 (43100)	+6.5 (42000)	1.21×10^{-4}
		−4.5 (48800)	
$[\mathrm{Co}(\mathrm{NH_3})_4(RR\text{-ptn})](\mathrm{ClO_4})_3\cdot \mathrm{H_2O}$	1.85 (20920)	+0.104 (20410)	7.77×10^{-3}
		−0.012 (23370)	
	1.79 (29200)	+0.075 (28700)	
	4.38 (48300)	+5.8 (46500)	7.06×10^{-4}
$[\mathrm{Co}(\mathrm{NH_3})_4(RR\text{-ptn})]\mathrm{Cl_3}$	1.82 (20920)	+0.103 (20410)	6.91×10^{-3}
		−0.011 (23470)	
	1.78 (29200)	+0.070 (28700)	6.28×10^{-4}
	4.34 (48300)	+5.5 (46500)	
trans-$[\mathrm{Co}(\mathrm{NH_3})_2(RR\text{-ptn})_2](\mathrm{ClO_4})_3\cdot \mathrm{H_2O}$	1.92 (20920)	+0.271 (19530)	3.12×10^{-3}
		−0.266 (21980)	
	1.92 (28900)	+0.234 (28800)	
	4.39 (43700)	+14 (43100)	1.25×10^{-4}
cis-Δ-$[\mathrm{Co}(\mathrm{NH_3})_2(RR\text{-ptn})_2](\mathrm{ClO_4})_3$	1.88 (20830)	−0.245 (19380)	3.31×10^{-3}
		+0.055 (21550)	
	1.85 (28900)	+0.098 (28500)	
	4.41 (45000)	+10sh (43500)	1.32×10^{-4}
		+12 (47400)	
cis-Δ-$[\mathrm{Co}(\mathrm{NH_3})_2(RR\text{-ptn})_2]\mathrm{Cl_3}\cdot 1.5\mathrm{H_2O}$	1.89 (20830)	−0.220 (19340)	3.78×10^{-3}
		+0.088 (21510)	
	1.86 (28900)	+0.093 (28400)	
	4.41 (45000)	+6.9sh (42600)	1.51×10^{-4}
		+11 (47400)	
cis-Λ-$[\mathrm{Co}(\mathrm{NH_3})_2(RR\text{-ptn})_2](\mathrm{ClO_4})_3$	1.90 (20750)	+1.01 (20750)	3.30×10^{-3}
	1.87 (28900)	+0.031 (27600)	
	4.42 (45000)	+7.9 (43100)	1.32×10^{-4}
Λ-$[\mathrm{Co}(\mathrm{tn})_3](\mathrm{ClO_4})_3$	1.88 (20450)	+0.081 (18800)	5.68×10^{-3}
		−0.117 (21050)	
	1.88 (28500)	−0.018 (28400)	
	4.37 (43300)	−13 (40000)	2.27×10^{-4}
		+12 (45300)	
		−9.1 (50500)	

ptn)$_3$]$^{3+}$ on the concentration of chloride ion. The measurements were carried out at 25 °C, and at the ionic strength of 0.091 adjusted with NaClO$_4$, and using a 2.8 mM aqueous solution of the complex perchlorate. The CD spectrum of this perchlorate was little affected by the addition of NaClO$_4$ up to its 0.5 M concentration. From the change of CD strengths at 475 nm, association constant, K=13.8 was obtained by the method of Tanaka *et al.*[15] for the following equilibrium; Δ-$[\mathrm{Co}(RR\text{-ptn})_3]^{3+}+\mathrm{Cl}^- \rightleftharpoons \Delta\text{-}[\mathrm{Co}(RR\text{-ptn})_3]^{3+}\cdot\mathrm{Cl}^-$. On the other hand, the constant K determined from the absorbancies[15] at 290 nm was 12.6 for the same equilibrium system. That the two K values obtained by both the CD and the UV methods are nearly the same strongly suggests that the CD variation of Δ-[Co(*RR*-ptn)$_3$]$^{3+}$ in the region of the first absorption band is brought about by ion-pair formation between the complex ion and counter ions. A further evidence to support this suggestion is that the CD spectra of the complex chloride in aqueous solutions depend clearly on its concentration as shown in Fig. 7. Figure 6 includes the calculated CD curve of the ion-paired species, Δ-[Co(*RR*-ptn)$_3$]$^{3+}\cdot$Cl$^-$ (K=13.8). The A$_2$ component is considerably enhanced and the sign of the so-called main CD band is reversed.

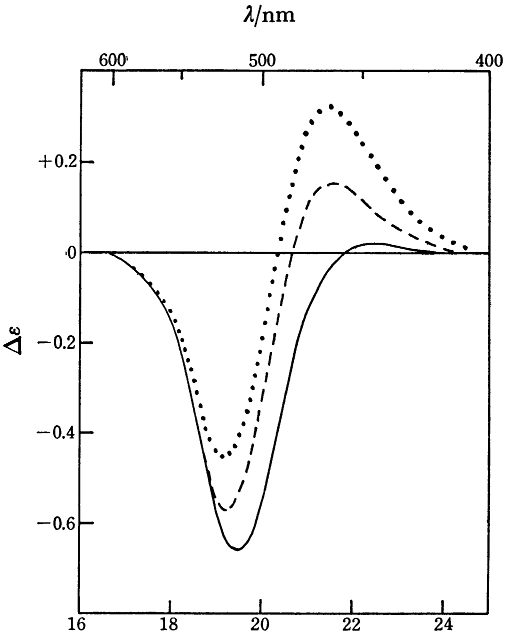

Fig. 7. Dependence of CD of Δ-[Co(*RR*-ptn)$_3$]Cl$_3\cdot$2.5 H$_2$O on its concentration in water; 1.76×10^{-4}M (——), 3.90×10^{-3} M(----), and 1.71×10^{-2} (······).

The effect of sulfate ion on the CD spectrum of Δ-[Co(*RR*-ptn)$_3$]$^{3+}$ is very similar to that of chloride ion and the CD curve of the ion-paired species, Δ-[Co(*RR*-ptn)$_3$]$^{3+}\cdot$SO$_4{}^{2-}$ closely resembles that of the Δ-[Co(*RR*-ptn)$_3$]$^{3+}\cdot$Cl$^-$ (Fig. 8). The association constant K of the complex ion with a sulfate ion was determined to be 61.7 by the CD method under the same condition as that measured for chloride ion. This value and 13.8 (or 12.6) in the case of chloride ion may be reasonable for the constants of ion-pair formation in the systems of ions of a tripositive-dinegative and a tripositive-uninegative, respectively.[15,16] Thus, the CD pattern of Δ-[Co(*RR*-ptn)$_3$]$^{3+}$ in the region of the first absorption band seems to be affected in a similar manner by ion-pair formation with counter anions irrespective of their kinds.

The ion-pair formation should be facilitated in an organic solvent to a greater extent than in an aqueous solution. Figure 9 shows the CD spectra of Δ-[Co(*RR*-ptn)$_3$]Br$_3\cdot$2H$_2$O in DMSO at various concentrations. The spectra give strong A$_2$ components without the addition of excessive bromide ion and depend clearly

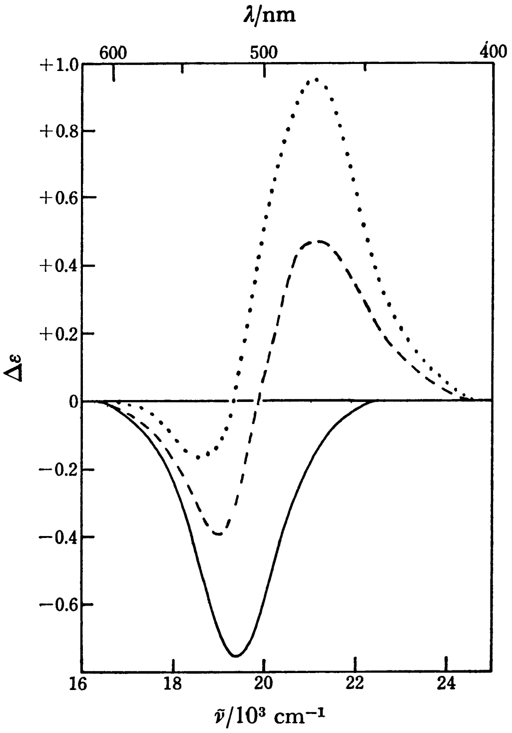

Fig. 8. CD spectra of Δ-[Co(*RR*-ptn)$_3$](ClO$_4$)$_3\cdot$3H$_2$O(3.45×10^{-3} M) in water(——) and in 0.1 M Na$_2$SO$_4$(----). Calculated CD curve of the ion-paired species, Δ-[Co(*RR*-ptn)$_3$]$^{3+}\cdot$SO$_4{}^{2-}$(······).

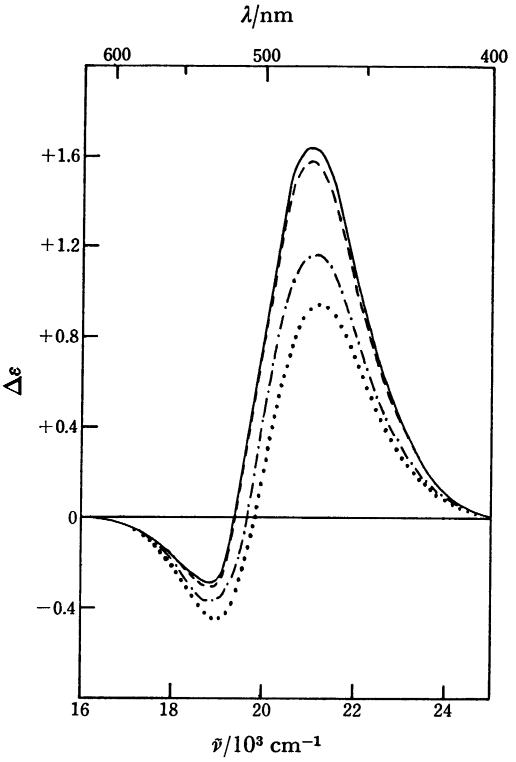

Fig. 9. CD spectra of Δ-[Co(*RR*-ptn)$_3$]Br$_3\cdot$2H$_2$O in DMSO; 4.52×10^{-5} M (······), 2.09×10^{-4} M(-·-·-), 1.93×10^{-3} M(----), and 9.33×10^{-3} M(——).

on the concentration of the complex. The complex chloride in DMSO gives a CD pattern very similar to that of the ion-paired species shown in Fig. 6 even at a very dilute solution (6.13×10^{-5} M). With increase in the concentration of the complex chloride, both CD components, the A_2 and the E, increase their strengths. Since the association constant between the complex cation and a chloride ion is expected to be larger than that between the complex ion and a bromide ion, this might be attributed to the formation of higher ion-paired species, 1 : 2 or 1 : 3 than 1 : 1. The complex perchlorate in DMSO exhibits a marked A_2 component which is never observed in an aqueous solution, but shows no dependence on the concentration of the complex in the range between 9.75×10^{-3} and 7.05×10^{-5} M. The reason for this is not clear at present, but it is clear that a perchlorate ion is weak in ability to form an ion-pair with the complex ion in DMSO.

In marked contrast to the large variety of solution CD spectra of $\Delta(\mathit{lel}_3)$-$[\mathrm{Co}(RR\text{-ptn})_3]^{3+}$, the CD spectra of $\Lambda(\mathit{ob}_3)$-$[\mathrm{Co}(RR\text{-ptn})_3]^{3+}$ show little solvent dependence in the region of the first absorption band. As Fig. 10 shows, the CD patterns of the latter isomer are nearly the same in water, 0.2 M Na_2SO_4, and DMSO solutions, although the spectrum in the last solution gives a small negative CD band at a longer wavelength side.

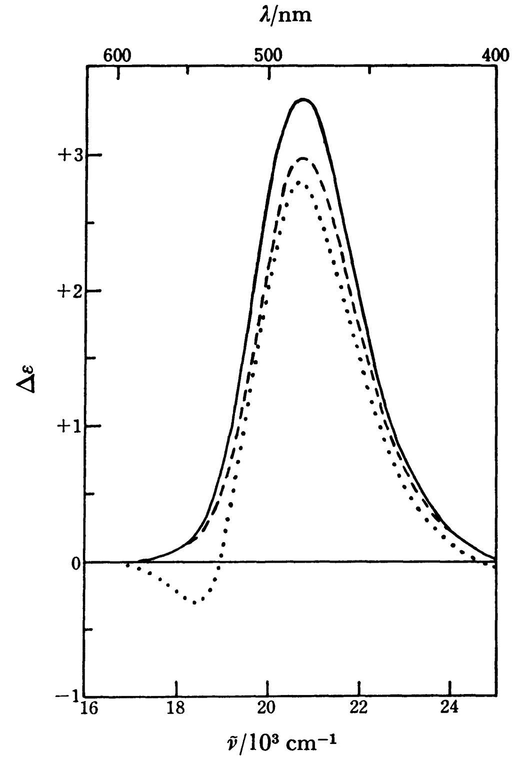

Fig. 10. CD spectra of Λ-$[\mathrm{Co}(RR\text{-ptn})_3](\mathrm{ClO}_4)_3$; 2.88×10^{-3} M in water (——), 2.88×10^{-3} M in 0.2 M Na_2SO_4 (----), and 1.81×10^{-3} M in DMSO(······).

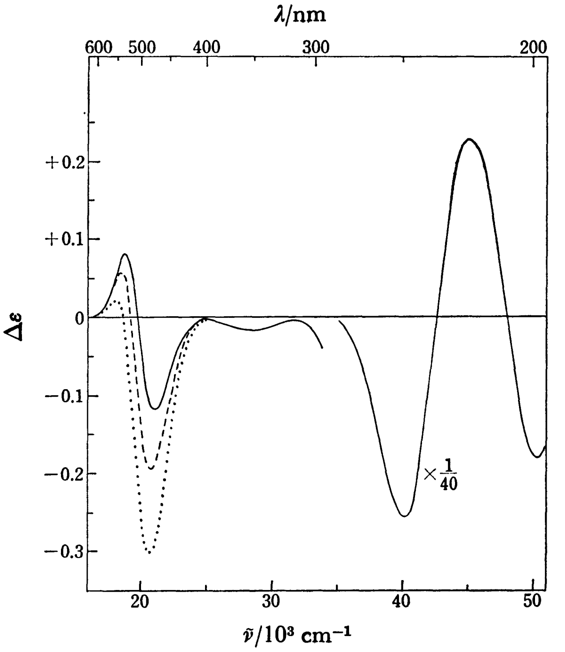

Fig. 11. CD spectra of Λ-$[\mathrm{Co}(\mathrm{tn})_3](\mathrm{ClO}_4)_3$($5.68\times10^{-3}$ M in visible region and 2.27×10^{-4} M in UV region) in water(——), in 1 M NaCl(----), and in 0.2 M Na_2SO_4 (······).

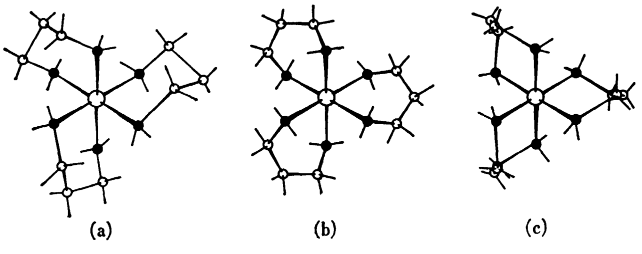

Fig. 12. Schematic structures of tris(trimethylenediamine)cobalt(III) complexes; (a) $\Lambda(\mathit{chair}_3)$, (b) $\Lambda(\mathit{ob}_3, \lambda\lambda\lambda)$, and (c) $\Lambda(\mathit{lel}_3,\delta\delta\delta)$.

It is known that the polarizable oxoanions such as phosphate and selenite have a marked effect on the CD spectra of some tris(diamine)cobalt(III) complexes. The CD spectrum of Δ(or Λ)-$[\mathrm{Co}(\mathrm{tn})_3]^{3+}$(tn: trimethylenediamine) is particularly sensitive to the excessive presence of these oxoanions.[17,18] Figure 11 shows that a chloride ion affects also the CD of Λ-$[\mathrm{Co}(\mathrm{tn})_3]^{3+}$ in a similar way, giving rise to the increase in the major negative CD band(A_2) at the expense of the minor positive CD band(E). Beddoe and Mason[17,19] found that the CD spectra of Δ-$[\mathrm{Co}(\mathrm{tn})_3]^{3+}$ in the presence of phosphate or selenite resemble that of the solid Δ-$[\mathrm{Co}(\mathrm{tn})_3]\mathrm{Br}_3\cdot\mathrm{H}_2\mathrm{O}$ in a KBr disk. Since all the tn chelates in the crystals adopt the chair conformation,[20] they suggested that on the addition of oxoanions, $[\mathrm{Co}(\mathrm{tn})_3]^{3+}$ in an aqueous solution is stabilized to have the tris-*chair* conformation by ion-pair formation (Fig. 12). However, CD spectra in KBr disks should be viewed with some caution for such conformationally labile complexes as $[\mathrm{Co}(\mathrm{tn})_3]^{3+}$, because these spectra depend often on the condition such as pressure and its duration time employed for the preparation of KBr disk. In fact, Λ-$[\mathrm{Co}(\mathrm{tn})_3]\mathrm{Br}_3\cdot\mathrm{H}_2\mathrm{O}$ in Nujol mull exhibits no detectable CD in the region of the first absorption band, indicating that the tris-*chair* form has substantially very small CD. Furthermore, molecular models indicate that either the tris-*chair* or the ob_3 conformation ($\Delta(\delta\delta\delta)$ and $\Lambda(\lambda\lambda\lambda)$) of $[\mathrm{Co}(\mathrm{tn})_3]^{3+}$ has no set of N–H bonds parallel to the C_3 axis of the complex ion to form an ion-pair most effectively with the oxoanion through hydrogen bonding, while that only the *lel*$_3$ conformation ($\Delta(\lambda\lambda\lambda)$ and $\Lambda(\delta\delta\delta)$) has a set of three N–H bonds suitable for forming such hydrogen bonds with the oxoanion.[21] This suggests that the conformer stabilized by ion-pair formation is not the tris-*chair* proposed by Beddoe *et al.*,[19] but the *lel*$_3$ conformation. Then, the increase in the magnitude of the negative CD band of Λ-[Co(tn)$_3$]$^{3+}$ in the presence of excessive anions can be attributed to the contribution of the vicinal effect of the δ-*skew* chelate rings in the *lel*$_3$-$\Lambda(\delta\delta\delta)$ conformer stabilized by ion-pair formation (Fig. 11). It is known that the vicinal effect due to a chiral chelate ring in δ form gives negative CD in the region of the first absorption band and that the vicinal and the configurational effect contribute additively to the CD in this region.[22] The addition of other anions such as a chloride ion than the oxoanions may result in a similar stabilization of the *lel*$_3$ form, since the effect of chloride ion on the CD spectrum of [Co(tn)$_3$]$^{3+}$ quite resembles that of sulfate ion. Thus the CD variation of [Co(tn)$_3$]$^{3+}$ on the addition of anions can resonably be explained by the stabilization of the *lel*$_3$ conformer due to ion-pair formation and by the contribution of the vicinal effect due to the chiral, skew tn chelate rings in this conformer. The interconversion between the tris-*chair* and the *lel*$_3$ conformation seems to occur easily in solution, since the energy difference between them has been calculated to be very small.[23] The *ob*$_3$ conformation has been shown to have a substantially higher energy.[23]

A similar discussion can be made on the CD variation of [Co(*RR*-ptn)$_3$]$^{3+}$ in solution. As stated previously, the *RR*-ptn chelate ring has been shown to prefer to take the *chair* conformation with one axial methyl group rather than the *skew* conformation in solution, although those in the crystals of Δ(*lel*$_3$)-[2] and Λ(*ob*$_3$)-[Co(*RR*-ptn)$_3$]Cl$_3\cdot n$H$_2$O[3] are all in the λ-*skew* conformation with two equatorial methyl groups. As molecular models (Fig. 12) show, Δ(*lel*$_3$)[Co(*RR*-ptn)$_3$]$^{3+}$ has much less crowded structure than Λ(*ob*$_3$)[Co(*RR*-ptn)$_3$]$^{3+}$ and the chelate rings in the former seem to be able to convert their conformations without difficulty into others, the *chair* or some intermediate conformations between the λ-*skew* and the *chair*. On the other hand, the more crowded Λ(*ob*$_3$)-isomer seems to have too rigid a structure to change the conformation.

If it is assumed that the conformations of Δ-[Co(*RR*-ptn)$_3$]$^{3+}$ in an aqueous solution are in an equilibrium among the tris-*skew* and some others involving the *chair* conformation, the CD variation on the addition of anions can be explained by the same ion-pair effect as that described for [Co(tn)$_3$]$^{3+}$; on the addition of anions the Δ(*lel*$_3$, $\lambda\lambda\lambda$) conformer is stabilized by ion-pair formation and the positive CD component in the region of the first absorption band is strengthened by the contribution of the vicinal effect due to the increasing amount of the λ-*skew* chelate ring (Figs. 6 and 8). This explanation will be supported by the fact that the CD spectrum of Δ(*lel*$_3$, $\lambda\lambda\lambda$)-[Co(*RR*-ptn)$_3$]Cl$_3\cdot$2.5H$_2$O in Nujol mull shows a pattern very similar to that of the ion-paired species.

The small CD variation of Λ(*ob*$_3$)-[Co(*RR*-ptn)$_3$]$^{3+}$ on the addition of anions may be due to the conformational rigidity resulted from the crowded and strained structure. Although this isomer will be thermodynamically much unstable than the Δ(*lel*$_3$)-isomer[12] as stated previously, the Λ(*ob*$_3$)-isomer seems to be stable from the viewpoint of conformational lability.

The same difference in the CD variation on the addition of anions is seen between *cis*-Δ(*lel*$_2$)- and *cis*-Λ(*ob*$_2$)-[Co(NH$_3$)$_2$(*RR*-ptn)$_2$]$^{3+}$. As Figs. 3 and 4 show, the positive CD band of the *cis*-Δ(*lel*$_2$) isomer in the region of the first absorption band gives rise to a pronounced increase in the presence of sulfate ion, while the CD change of the *cis*-Λ(*ob*$_2$) isomer is negligible under the same condition. The CD spectrum of the chloride of *cis*-Δ(*lel*$_2$) isomer in the region of the first absorption band also differs from that of the perchlorate in an aqueous solution, as shown in Table 2. The structures of *cis*-Δ(*lel*$_2$)- and Λ(*ob*$_2$)-[Co(NH$_3$)$_2$(*RR*-ptn)$_2$]$^{3+}$ may be compared to those of Δ(*lel*$_3$)- and Λ(*ob*$_3$)-[Co(*RR*-ptn)$_3$]$^{3+}$, respectively, and the *RR*-ptn chelate rings in the *cis*-Δ(*lel*$_2$) isomer are expected to be more conformationally flexible than those in the more crowded *cis*-Λ(*ob*$_2$) isomer. Thus, on the addition of sulfate ion the Δ(*lel*$_2$) isomer is stabilized by forming an ion-pair in a mechanism similar to that described for Δ(*lel*$_3$)-[Co(*RR*-ptn)$_3$]$^{3+}$. A set of three N–H bonds suitable for hydrogen bonding may be provided by two *RR*-ptn and one ammonia ligands in the complex. The Λ(*ob*$_2$) isomer which is insensitive to the ion-pair effect seems to have a rigid structure similar to that of Λ(*ob*$_3$)-[Co(*RR*-ptn)$_3$]$^{3+}$, although the crowded structure of Λ(*ob*$_2$) isomer might be reduced to some extent by coordinating two ammonia molecules in place of a bulky bidentate *RR*-ptn.

The CD spectra of *trans*-[Co(NH$_3$)$_2$(*RR*-ptn)$_2$]$^{3+}$ in water, 0.2 M Na$_2$SO$_4$, and DMSO solutions show small variations in the region of the first absorption band, giving rise to an increase and a decrease in the magnitudes of the positive and the negative CD bands, respectively in the latter two solutions (Fig. 13). The [Co(NH$_3$)$_4$(*RR*-ptn)]$^{3+}$ ion exhibits similar small variations, as shown in Fig. 14. Thus, the observed CD variations are rather small, although the tendency to increase the magnitude of the positive CD band in 0.2 M Na$_2$SO$_4$ and DMSO solutions is consistent with that observed for Δ-[Co(*RR*-ptn)$_3$]$^{3+}$ and *cis*-Δ-[Co(NH$_3$)$_2$(*RR*-ptn)$_2$]$^{3+}$. The *RR*-ptn chelate rings in *trans*-[Co(NH$_3$)$_2$(*RR*-ptn)$_2$]$^{3+}$ and [Co(NH$_3$)$_4$(*RR*-ptn)]$^{3+}$ seem to be more flexible than those in the more crowded *tris*- and *cis*-bis(*RR*-ptn) complexes. Furthermore, the ability to form ion-pairs between the present series of complexes, [Co(NH$_3$)$_{2n}$(*RR*-ptn)$_{3-n}$]$^{3+}$ and sulfate ions will not differ greatly from one another.[15] However, molecular models seem to indicate that *trans*-[Co(NH$_3$)$_2$(*RR*-ptn)$_2$]$^{3+}$ can not provide a set of three N–H bonds to form effective hydrogen bonds with a sulfate ion without distorting the λ-*skew* conformation of the *RR*-ptn chelate ring. On the other hand, [Co(NH$_3$)$_4$(*RR*-ptn)]$^{3+}$ can have such a set of N–H bonds provided by two ammonia molecules and one *RR*-ptn chelate in the λ-*skew* conformation, but similar two sets of three N–H bonds can also be formed by the three ammonia ligands in the facial positions without the participation of the *RR*-ptn. An ion-pair may also be formed by hydrogen

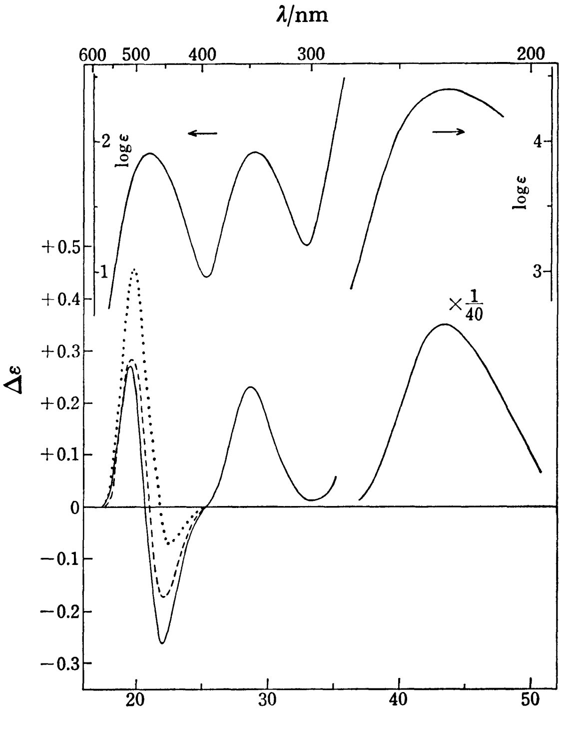

Fig. 13. Absorption and CD spectra of *trans*-[Co(NH$_3$)$_2$(*RR*-ptn)$_2$](ClO$_4$)$_3$·H$_2$O; 3.12×10^{-3}M in visible region and 1.25×10^{-4} M in UV region in water (——), 3.12×10^{-3} M in 0.2 M Na$_2$SO$_4$(----), and 2.59×10^{-3} M in DMSO(······).

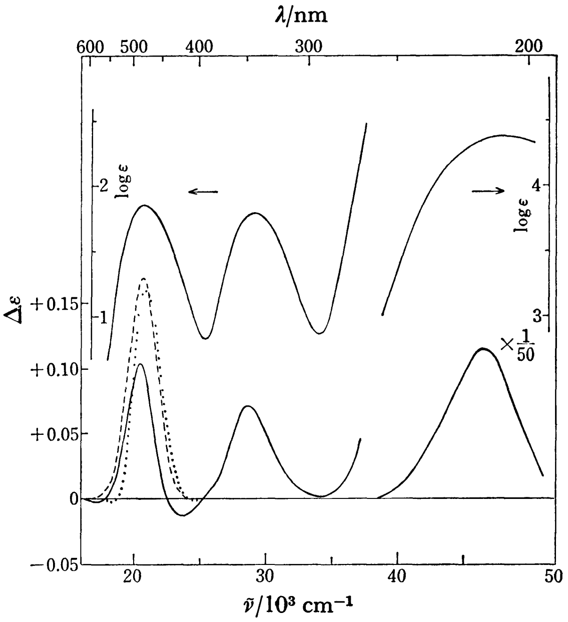

Fig. 14. Absorption and CD spectra of [Co(NH$_3$)$_4$(*RR*-ptn)](ClO$_4$)$_3$·H$_2$O; 7.77×10^{-3} M in 0.1 M in visible region and 7.06×10^{-4} M in UV region in water(——), 7.77×10^{-3} M in 0.1 M Na$_2$SO$_4$(----), and 4.59×10^{-3} M in DMSO(······).

bonding between such N–H bonds provided by three ammonia ligands and a sulfate ion. In this case, the λ-*skew* conformation of the *RR*-ptn chelate ring will not be stabilized by the ion-pair formation.

Other proposals[24,25] have been put forth in an attempt to rationalize the effect of electrolyte on the CD spectra in the region of the first absorption band of tris(diamine)-cobalt(III) complexes. However, so far as complexes containing puckerd six-membered chelate rings are concerned, a conformational change of the chelate ring seems to play the most important role in determining a pattern of CD bands in the region of the first absorption band. Such a conformational change may also account for the lack of the additivity of the vicinal (conformational) and the configurational contributions to the CD of these six-membered chelate complexes.[7,9]

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