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Diastereomers and Circular Dichroism Spectra of the Tris(*trans*-1,2-cyclopentanediamine)cobalt(III) Complex

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The (*lel*$_3$), (*lel*$_2$*ob*), and (*lelob*$_2$) isomers of $[Co(rac\text{-}cptn)_3]^{3+}$ were obtained by the reaction of *trans*-$[CoCl_2(pyridine)_4]^+$ with *rac*-cptn, where cptn denotes *trans*-1,2-cyclopentanediamine. No indication for the formation of the (*ob*$_3$) isomer was found. The isomers were resolved into optical isomers by SP-Sephadex column chromatography. The circular dichroism spectra of these optical isomers were measured and the results compared with those of the related complexes. The anomalous circular dichroism pattern of the (*lel*$_3$) isomer in the region of the first absorption band was found to result from the contribution of the strong vicinal effect of the chiral cptn chelate ligand as compared with that of the configurational effect.

The tris(*rac*-*trans*-1,2-cyclopentanediamine)cobalt(III) ion, $[Co(rac\text{-}cptn)_3]^{3+}$ has four possible diastereomers, each of which exists in a pair of enantiomers (Δ and Λ). Since the ligand forms a gauche-type (δ and λ) chelate ring upon coordination, these diastereomers can be designated as *lel*$_3$($\Delta(\lambda\lambda\lambda)$ and $\Lambda(\delta\delta\delta)$), *lel*$_2$*ob* ($\Delta(\lambda\lambda\delta)$ and $\Lambda(\delta\delta\lambda)$), *lelob*$_2$($\Delta(\lambda\delta\delta)$ and $\Lambda(\delta\lambda\lambda)$), and *ob*$_3$($\Delta(\delta\delta\delta)$ and $\Lambda(\lambda\lambda\lambda)$).[1)]

Jaeger and Blumendal[2)] found in their studies on metal complexes with *rac*-cptn that $[M(rac\text{-}cptn)_3]^{3+}$ (M=Co(III), Rh(III)) exists in only one pair of enantiomers, $(+)_{589}$-$[M((-)\text{-}cptn)_3]^{3+}$ and $(-)_{589}$-$[M((+)\text{-}cptn)_3]^{3+}$. Ito *et al.*[3)] prepared $(-)_{589}$-$[Co((+)\text{-}cptn)_3]^{3+}$ and determined its absolute configuration by the X-ray method to be $\Lambda(\delta\delta\delta)$(*lel*$_3$)-$[Co(S,S\text{-}cptn)_3]^{3+}$. They found that this isomer shows a main circular dichroism (CD) band with the negative sign in the region of the first absorption band in contrast with Λ-$[Co(en)_3]^{3+}$ (en=ethylenediamine) and other Λ-tris(1,2-diamine)cobalt(III) complexes whose main CD bands are always positive in this region. Toftlund and Pedersen[4)] found that the reaction of *trans*-$[CoCl_2py_4]^+$ (py=pyridine) with (*R*,*R*)-cptn gives $\Delta(\lambda\lambda\lambda)$(*lel*$_3$)- and $\Lambda(\lambda\lambda\lambda)$(*ob*$_3$)-$[Co(R,R\text{-}cptn)_3]^{3+}$ in the formation ratio 10: 1. The Λ-*ob*$_3$ isomer, although it was not isolated as crystals but only separated as a fraction in the column chromatography, also showed an anomalous CD pattern in the region of the first absorption band, its main CD being negative.

In order to elucidate such anomalous CD spectra of $[Co(cptn)_3]^{3+}$, it is desirable to isolate all diastereomers of this complex. This paper deals with the preparation and resolution of diastereomers of $[Co(rac\text{-}cptn)_3]^{3+}$ and their CD spectra.

Experimental

Ligands. *Trans*-1,2-cyclopentanediamine (cptn) was prepared and resolved by the method of Toftlund and Pedersen.[4)] The (+)-cptn isomer has (*S*,*S*)-configuration, forming a δ-gauche chelate ring upon coordination.[3)]

$[Co(cptn)_3]^{3+}$. *a*): *Trans*-$[CoCl_2py_4]Cl\cdot 6H_2O$ was mixed with (−)-cptn in 2-methoxyethanol.[4)] The product was carefully chromatographed by use of a column of SP-Sephadex C-25 (ϕ 2.7×130 cm). By elution with 0.15 mol/dm^3 disodium hydrogenphosphate, 0.2 mol/dm^3 sodium sulfate, or 0.15 mol/dm^3 sodium $(+)_{589}$-tartratoantimonate (III), the column always gave only one band of the $\Delta(\lambda\lambda\lambda)$(*lel*$_3$) isomer. No indication for the presence of the $\Lambda(\lambda\lambda\lambda)$(*ob*$_3$) isomer was observed.

b): An *N*,*N*-dimethylformamide solution (50 cm^3) containing *trans*-$[CoCl_2(R,R\text{-}cptn)_2]ClO_4$[5)] (0.55 g, 1.3 mmol) and *R*,*R*-cptn (0.13 g, 1.3 mmol) was stirred at room temperature for a day. The resulting red solution was diluted with water to 1 dm^3, adjusted to pH 4 with hydrochloric acid, and poured on a column of SP-Sephadex C-25 (ϕ 2.7×130 cm). The adsorbed band was eluted by the same method as the above to give only one $\Delta(\lambda\lambda\lambda)$(*lel*$_3$) isomer, no $\Lambda(\lambda\lambda\lambda)$(*ob*$_3$) isomer being detected on the column.

c): To a 2-methoxyethanol solution (3 cm^3) of *rac*-cptn (3 g, 30 mmol) was added dropwise a 2-methoxyethanol solution (10 cm^3) of *trans*-$[CoCl_2py_4]Cl\cdot 6H_2O$ (5 g, 8.5 mmol). The red $[Co(cptn)_3]Cl_3$ complex was precipitated immediately and filtered at 0 °C after 1 h. It was washed three times with 3 cm^3 portion of ethanol and air dried. (yield: 85%). A small portion (*ca.* 0.2 g) of this crude complex was dissolved in water and the solution was poured on a column of SP-Sephadex C-25 (ϕ 2.7×130 cm). By elution with a 0.2 mol/dm^3 Na_2SO_4 solution, three red bands, T$_1$, T$_2$, and T$_3$ were obtained in succession. Each eluate was diluted with 10^{-2} mol/dm^3 HCl and poured again on a small column of SP-Sephadex C-25. The adsorbed band was eluted with 2 mol/dm^3 HCl after the column had been washed thoroughly with 10^{-2} mol/dm^3 HCl in order to remove Na^+ ions. The eluate was evaporated to dryness in a vacuum desiccator over NaOH and P_2O_5. The residue was washed with a small amount of ethanol and recrystallized from water to give red crystals. T$_1$, T$_2$, and T$_3$ formed in the ratio 10: 4: 1, are racemates of the *lel*$_3$, *lel*$_2$*ob*, and *lelob*$_2$ diastereomers, respectively.

The diastereomers were resolved by SP-Sephadex column chromatography.[6)] The T$_1$ isomer adsorbed on a column of SP-Sephadex C-25 (ϕ 2.7×130 cm) was eluted with a 0.3 mol/dm^3 sodium $(+)_{589}$-hydrogentartrate solution. Two bands were separately eluted. From the fast and the slowly eluted fractions, $(-)_{589}$-$\Lambda(\delta\delta\delta)$(*lel*$_3$)-$[Co(S,S\text{-}cptn)_3]Cl_3\cdot 4H_2O$ and $(+)_{589}$-$\Delta(\lambda\lambda\lambda)$(lel$_3$)-$[Co(R,R\text{-}cptn)_3]Cl_3\cdot 4H_2O$, respectively, were isolated by a method similar to that for the racemates described above. Elution with sodium $(+)_{589}$-tartratoantimonate (III) resulted in poor separation between the bands of the enantiomers.

The T$_2$ and T$_3$ isomers were resolved similarly with an eluent, a 0.15 mol/dm^3 sodium $(+)_{589}$-tartratoantimonate (III)

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Table 1. Analytical data of the cptn complexes

Complex	C/%		H/%		N/%	
	Found	Calcd	Found	Calcd	Found	Calcd
T_1: $(+)_{589}$-$[Co(cptn)_3]Cl_3\cdot 4H_2O$	33.44	33.49	8.15	8.26	15.46	15.63
T_2: $(+)_{589}$-$[Co(cptn)_3]Cl_3\cdot 5H_2O$	32.61	32.40	8.03	8.36	15.42	15.12
T_3: $(-)_{589}$-$[Co(cptn)_3]Cl_3\cdot 3H_2O$	34.32	34.65	8.04	8.16	15.90	16.17
$(+)_{589}$-Δ-$[Co(en)_2((-)\text{-cptn})]Cl_3\cdot H_2O$	26.78	26.77	7.69	7.51	21.00	20.82
$(+)_{589}$-Λ-$[Co(en)_2((-)\text{-cptn})]Cl_3\cdot 1.5H_2O$	26.57	26.19	7.26	7.59	20.02	20.37
$[Co(NH_3)_4((-)\text{-cptn})]Cl_3\cdot 1.5H_2O$	17.05	16.65	7.98	7.56	23.61	23.31

cptn = $C_5H_{12}N_2$.

solution, and the optical isomers were isolated by the same method as that for the T_1 isomer. The fast eluting enatiomers of T_2 and T_3 are $(-)_{589}$-$\Lambda(\delta\delta\lambda)$(*lel*$_2$*ob*)-[Co(*S*,*S*-cptn)$_2$(*R*,*R*-cptn)]$Cl_3\cdot 5H_2O$ and $(+)_{589}$-$\Lambda(\delta\lambda\lambda)$(*lelob*$_2$)-[Co(*S*,*S*-cptn)(*R*,*R*-cptn)$_2$]$Cl_3\cdot 3H_2O$, respectively. Their antipodes obtained from the slowly eluted bands are thus $(+)_{589}$-$\Delta(\lambda\lambda\delta)$(*lel*$_2$*ob*)-[Co(*R*,*R*-cptn)$_2$(*S*,*S*-cptn)]$Cl_3\cdot 5H_2O$ and $(-)_{589}$-$\Delta(\lambda\delta\delta)$(*lelob*$_2$)-[Co(*R*,*R*-cptn)(*S*,*S*-cptn)$_2$]$Cl_3\cdot 3H_2O$.

*[Co(en)$_2$(*R,R*-cptn)]$^{3+}$.* This complex was prepared from *trans*-$[CoCl_2(en)_2]Cl$ and (*R*,*R*)-cptn in dimethyl sulfoxide by a method similar to that reported.[7] The isomers were separated by an SP-Sephadex column chromatographic method. By elution with a 0.2 mol/dm^3 Na_2SO_4 solution, two orange bands of $\Delta(\lambda)$- and $\Lambda(\lambda)$-[Co(en)$_2$(*R*,*R*-cptn)]$^{3+}$ were eluted in succession. From the eluates, orange crystals of the complex chlorides were obtained by the same method as that for the tris(cptn) complex. Both isomers showed positive rotation at 589 nm.

*[Co(NH$_3$)$_4$(*R,R*-cptn)]$^{3+}$.* This complex was prepared from $[Co(NH_3)_5(H_2O)](ClO_4)_3$ and (*R*,*R*)-cptn by a method similar to that for the corresponding en complex.[8] Since an orange fraction obtained by chromatography with an eluent, 0.2 mol/dm^3 Na_2SO_4, was contaminated with the starting aqua complex, the fraction was rechromatographed with a 0.2 mol/dm^3 disodium tartrate solution. The complex chloride was isolated by the same method as that for the tris(cptn) complex and recrystallized from a mixture of water and methanol. Analytical data of all the complexes are given in Table 1.

Measurements. Absorption and CD spectra were recorded in aqueous solutions on a Hitachi 323 spectrophotometer, and a JASCO J-40 spectropolarimeter, respectively. Optical rotations were measured with a JASCO DIP-4 polarimeter. ^{13}C-NMR spectra were obtained with a Jeol JNM FX-60 spectrometer using TMS as an external reference in aqueous solutions by locking to D_2O. For the measurements, the tris (cptn) complex chlorides were converted into acetates with QAE-Sephadex A-25 anion exchanger in the acetate form in order to increase the solubility.

Results and Discussion

The Isomers of [Co(cptn)$_3$]$^{3+}$. Toftlund and Pedersen[4] obtained $\Delta(\lambda\lambda\lambda)$(*lel*$_3$)- and $\Lambda(\lambda\lambda\lambda)$(*ob*$_3$)-[Co(*R*,*R*-cptn)$_3$]$^{3+}$ in the ratio 10: 1 by the reaction of *trans*-$[CoCl_2py_4]Cl\cdot 6H_2O$ with *R*,*R*-cptn in 2-methoxyethanol. However, all attempts to prepare the (*ob*$_3$) isomer were unsuccessful (Experimental). On the other hand, three (T_1, T_2, and T_3) of the four possible diastereomers (*lel*$_3$, *lel*$_2$*ob*, *lelob*$_2$, and *ob*$_3$) were obtained in the ratio 10: 4: 1, by a method similar to that of Toftlund and Pedersen using *rac*-cptn instead of *R*,*R*-cptn. No indication for the presence of more than three isomers was observed in the column chromatography. The isomers were completely resolved by SP-Sephadex column chromatography.

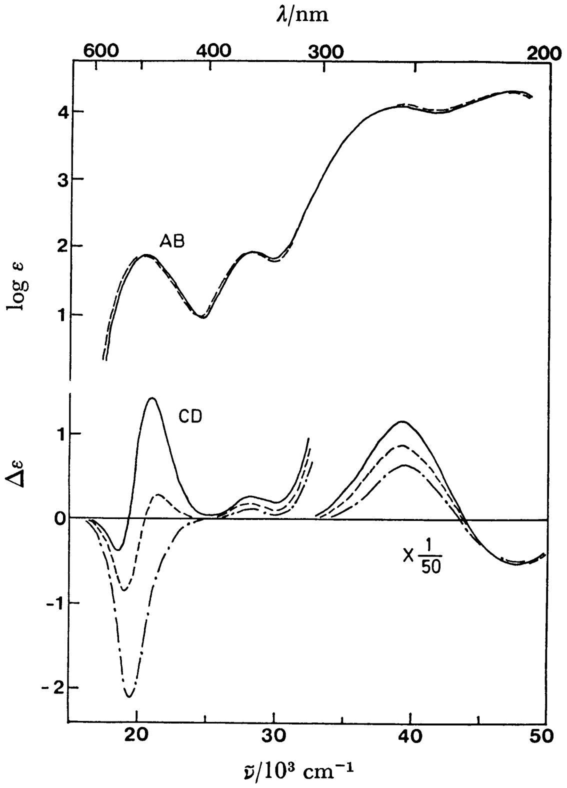

Fig. 1. Absorption and CD spectra of [Co(cptn)$_3$]$^{3+}$. ——: $(+)_{589}$-$\Delta(\lambda\lambda\lambda)$ (*lel*$_3$)-[Co(*R*,*R*-cptn)$_3$]$^{3+}$ (T_1), ------: $(+)_{589}$-$\Delta(\lambda\lambda\delta)$ (*lel*$_2$*ob*)-[Co(*R*,*R*-cptn)$_2$(*S*,*S*-cptn)]$^{3+}$ (T_2), -·-·-: $(-)_{589}$-Δ $(\lambda\delta\delta)$ (*lelob*$_2$)-[Co (*R*, *R*-cptn) (*S*, *S*-cptn)$_2$]$^{3+}$ (T_3).

The CD spectra of the enantiomers obtained from the more slowly eluted bands on the columns are given in Fig. 1 and the spectral data in Table 2. The CD spectrum of T_1 is the mirror image of that of $\Lambda(\delta\delta\delta)$(*lel*$_3$)-[Co(*S*,*S*-cptn)$_3$]$^{3+}$ whose absolute configuration has been determined by the X-ray method.[3] Thus T_1 is assigned to $\Delta(\lambda\lambda\lambda)$(*lel*$_3$)-[Co(*R*,*R*-cptn)$_3$]$^{3+}$. The other T_2 and T_3 isomers (Fig. 1) can be assigned to $\Delta(\lambda\lambda\delta)$(*lel*$_2$*ob*)-[Co(*R*,*R*-cptn)$_2$(*S*,*S*-cptn)]$^{3+}$ and $\Delta(\lambda\delta\delta)$(*lelob*$_2$)-[Co(*R*,*R*-cptn)(*S*,*S*-cptn)$_2$]$^{3+}$, respectively, for the following reasons: 1) The CD spectra in the region of the first absorption band change remarkably but regularly in the order T_1, T_2, and T_3, but those in the ultraviolet

Table 2. Absorption and CD spectral data

	Absorption $\tilde{\nu}/10^3$ cm^{-1} (log ε)	CD $\tilde{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$)
$(+)_{589}$-$\Delta(\lambda\lambda\lambda)$(*lel*$_3$)-[Co(*R*,*R*-cptn)$_3$]$^{3+}$(T$_1$)	20.3(1.88)	18.6(−0.39)
		21.0(+1.46)
	28.3(1.92)	28.3(+0.27)
	39.0(4.08)	39.2(+58.2)
	47.4(4.28)	47.6(−25.4)
$(+)_{589}$-$\Delta(\lambda\lambda\delta)$(*lel*$_2$*ob*)-[Co(*R*,*R*-cptn)$_2$(*S*,*S*-cptn)]$^{3+}$(T$_2$)	20.2(1.90)	19.0(−0.88)
		21.5(+0.29)
	28.3(1.93)	28.1(+0.19)
	39.1(4.08)	39.3(+43.7)
	46.7(4.28)	47.6(−25.1)
$(-)_{589}$-$\Delta(\lambda\delta\delta)$(*lelob*$_2$)-[Co(*R*,*R*-cptn)(*S*,*S*-cptn)$_2$]$^{3+}$(T$_3$)	20.1(1.88)	19.5(−2.13)
	28.3(1.93)	27.8(+0.10)
	39.1(4.08)	39.5(+30.2)
	47.2(4.28)	47.6(−25.2)
$(+)_{589}$-$\Delta(\lambda)$-[Co(en)$_2$(*R*,*R*-cptn)]$^{3+}$	21.1(1.93)	19.9(−1.41)
		22.4(+0.46)
	29.1(1.90)	28.4(−0.17)
	47.2(4.31)	44.5(+30.5)
$(+)_{589}$-$\Lambda(\lambda)$-[Co(en)$_2$(*R*,*R*-cptn)]$^{3+}$	21.1(1.93)	20.4(+1.95)
	29.1(1.90)	27.8(+0.08)
	47.6(4.33)	38.8(+3.68)
		45.9(−21.0)
[Co(NH$_3$)$_4$(*R*,*R*-cptn)]$^{3+}$	20.8(1.81)	21.1(+0.71)
	29.1(1.77)	28.2(−0.02)
	41.9(3.68)	41.7(+6.76)
	47.2(3.97)	

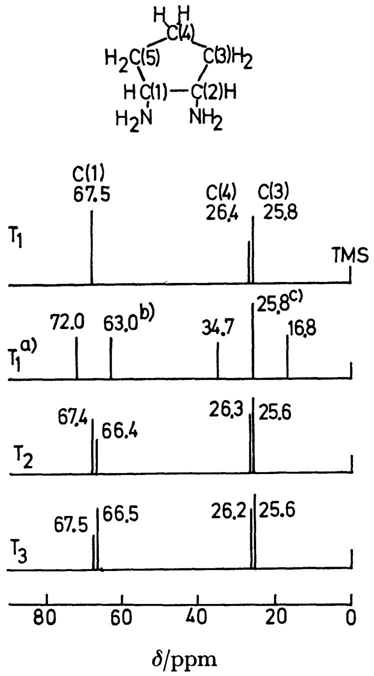

Fig. 2. ^{13}C-NMR spectra of the three isomers of [Co(cptn)$_3$] (CH$_3$COO)$_3$ in D$_2$O (15.04 MHz, The signals due to CH$_3$COO$^-$ are omitted).

a) The off-resonance spectrum, b) $J_{\text{C-H}}=135.5$ Hz. c) $J_{\text{C-H}}=134.3$ Hz.

region are very similar to one another, indicating the same absolute configuration.[9] 2) The reactions with optically active *R*,*R*-cptn give only one isomer of (*lel*$_3$), no (*ob*$_3$) isomer being obtained. 3) The yields of T$_1$, T$_2$, and T$_3$ decrease in this order. Since the stability of (*lel*$_{3-n}$*ob*$_n$) isomers of [Co(1,2-diamine)$_3$]$^{3+}$ decreases with an increase in the number of the *ob* ligands,[1,10] the order suggests the *lel*$_3$, *lel*$_2$*ob*, *lelob*$_2$ isomers for T$_1$, T$_2$, and T$_3$, respectively. The assignments are supported by ^{13}C-NMR spectroscopy (Fig. 2). The peak assignment can be made on the basis of the off-resonance and a comparison of relative intensities of the peaks. The T$_1$(*lel*$_3$) isomer which has D$_3$ symmetry[3] shows three kinds of carbons of the ligands. In the off-resonance spectrum, the lowest field peak at 67.52 ppm splits into two, while the two high field peaks at 26.37 and 25.80 ppm give a triplet due probably to accidental degeneracy of two triplets. The latter two peaks show a remarkable difference in intensity. Thus, the peaks at 67.52, 26.37, and 25.80 ppm can be assigned to the C(1), C(4), and C(3) atoms, respectively (Fig. 2). The T$_2$(*lel*$_2$*ob*) and T$_3$(*lelob*$_2$) isomers, both of which should have C$_2$ symmetry, each exhibits two C(1) peaks of different intensity. The T$_2$(*lel*$_2$*ob*) isomer shows a strong peak at a similar frequency value to that of the T$_1$(*lel*$_3$) isomer, and a weak peak in a little higher magnetic field. The T$_3$(*lelob*$_2$) isomer shows two similar peaks, but whose relative intensities are reversed (Fig. 2). Thus, the ^{13}C-NMR spectra strongly support the previous assignment that T$_1$, T$_2$, and T$_3$ are the *lel*$_3$, *lel*$_2$*ob*, and *lelob*$_2$ isomers, respectively.

The $\Lambda(\lambda\lambda\lambda)$(*ob*$_3$) isomer reported[4] seems to be the $\Delta(\lambda\lambda\delta)$(*lel*$_2$*ob*) isomer, the formation of which might have resulted from incomplete resolution of the ligand. The CD spectrum reported for this isomer is very similar to that of our $\Delta(\lambda\lambda\delta)$(*lel*$_2$*ob*) isomer. The reason for the *ob*$_3$ isomer not being formed under the experimental conditions given is not known. However, the formation ratio of T$_1$, T$_2$, and T$_3$ (10: 4: 1) suggests that the stability of isomer decreases a great deal with an increase in the number of the *ob* ligands. The analogous [Co(chxn)$_3$]$^{3+}$ (chxn=*trans*-1,2-cyclohexanediamine) complex gives the *lel*$_3$, *lel*$_2$*ob*, *lelob*$_2$, and *ob*$_3$ isomers in the formation ratio of *ca.* 14: 11: 4: 1 in equilibrium at 100 °C.[11] The differences among these values are small as compared with those of [Co(cptn)$_3$]$^{3+}$. The difference in the stability caused by replacing the *lel* ligand with the *ob* one in [Co(cptn)$_3$]$^{3+}$ would be much larger than that in [Co(chxn)$_3$]$^{3+}$. Attempts to equilibrate the isomers of [Co(cptn)$_3$]$^{3+}$ were unsuccessful because of the decomposition of the complex.

Absorption and CD Spectra. The three isomers of [Co(cptn)$_3$]$^{3+}$ give very similar absorption spectra, but the first absorption bands shift toward the smaller wavenumber side by *ca.* 100 cm^{-1} as the number of the *ob* ligands increases by one (Fig. 1 and Table 2). The magnitude of the shift is fairly large as compared with that of other tris(1,2-diamine) complexes. For [Co(chxn)$_3$]$^{3+}$ [11] and [Co(pn)$_3$]$^{3+}$ (pn=propylenediamine),[12] the differences in the absorption maxima between the *lel*$_3$ and *ob*$_3$ isomers are only 50 and 20 cm^{-1}, respectively. The large shift of the first absorption band due to replacement of the *lel* ligand with the *ob* one in $[Co(cptn)_3]^{3+}$ also suggests that the complex becomes unstable rapidly with an increase in the number of the *ob* ligands.

The red $[Co(cptn)_3]^{3+}$ complex gives all the absorption bands at wavenumbers smaller than those of the corresponding bands of the orange $[Co(chxn)_3]^{3+}$ [11] and $[Co(pn)_3]^{3+}$.[12] The red shift of the charge-transfer band, in particular, amounts to 5000—8000 cm^{-1}. Such red shifts might be brought about by a strained structure of the cptn chelate ring as pointed out by Ito *et al.*;[3] the N-N distance of 3.14 Å in a strain-free, free ligand decreases in length to 2.76 Å on forming a chelate ring, which give considerable strain in bond angles of the chelate ring. In cobalt(III) complexes with strain caused by various factors such as congestion due to bulky ligands or steric requirement, as in the case of cptn, the d-d absorption bands shift to the small wavenumber side.[13] The shift of the charge-transfer band might also be correlated with such a strained structure of the cptn chelate ring. No appreciable strain is observed for bond angles of the chelate rings in $[Co(chxn)_3]^{3+}$ [14] and $[Co(pn)_3]^{3+}$.[15]

The CD spectra of three isomers of the $[Co(cptn)_3]^{3+}$ complex are compared in Fig. 1. If we assume that all the isomers have the same Δ-configuration, the CD contributions due to the configurational and the vicinal effects can be estimated by the equations

$$\Delta\varepsilon(\Delta) = 1/2[\Delta\varepsilon(T_2: \Delta\lambda\lambda\delta) + \Delta\varepsilon(T_3: \Delta\lambda\delta\delta)]$$

$$\Delta\varepsilon(\lambda) = 1/2[\Delta\varepsilon(T_2: \Delta\lambda\lambda\delta) - \Delta\varepsilon(T_3: \Delta\lambda\delta\delta)]$$

where $\Delta\varepsilon(T_2: \Delta\lambda\lambda\delta)$ and $\Delta\varepsilon(T_3: \Delta\lambda\delta\delta)$ are the observed CD for $(+)_{589}$-T_2 and $(-)_{589}$-T_3 isomers, respectively, and $\Delta\varepsilon(\Delta)$ and $\Delta\varepsilon(\lambda)$ the CD of the Δ-configurational and the λ(*R,R*-cptn)-vicinal effects, respectively. The calculated CD curves of these two effects are shown in Figs. 3 and 4 in which CD curves of the related complexes are given for comparison. The CD curve calculated for $\Delta\varepsilon[\Delta(\lambda\lambda\lambda)]$ $(=\Delta\varepsilon(\Delta)+3\Delta\varepsilon(\lambda))$ agrees with the observed CD spectrum of $(+)_{589}$-$T_1\Delta(\lambda\lambda\lambda)$(*lel*$_3$)-$[Co(R,R\text{-cptn})_3]^{3+}$ over the whole region (Fig. 3). This indicates that the additivity[9,16] in CD between the configurational and the vicinal effects holds in the CD of $[Co(cptn)_3]^{3+}$. The $\Delta\varepsilon(\Delta)$ curve also resembles the Δ-configurational CD curve obtained similarly from the CD spectra of a diastereomeric pair, $\Delta(\lambda)$- and $\Lambda(\lambda)$-$[Co(en)_2(R,R\text{-cptn})]^{3+}$ $(1/2\{\Delta\varepsilon[\Delta(\lambda)]-\Delta\varepsilon[\Lambda(\lambda)]\})$. On the other hand, the λ(*R,R*-cptn)-vicinal CD curve, $\Delta\varepsilon(\lambda)$, is very similar in pattern and strength to the observed CD spectrum of $[Co(NH_3)_4(R,R\text{-cptn})]^{3+}$, and also to the vicinal CD curve obtained from $\Delta(\lambda)$- and $\Lambda(\lambda)$-$[Co(en)_2(R,R\text{-cptn})]^{3+}$ $(1/2\{\Delta\varepsilon[\Delta(\lambda)]+\Delta\varepsilon[\Lambda(\lambda)]\})$. All the results support the validity of the additivity. Hence the configurational and the vicinal CD of the $[Co(cptn)_3]^{3+}$ complex can be compared with those of other diamine complexes.

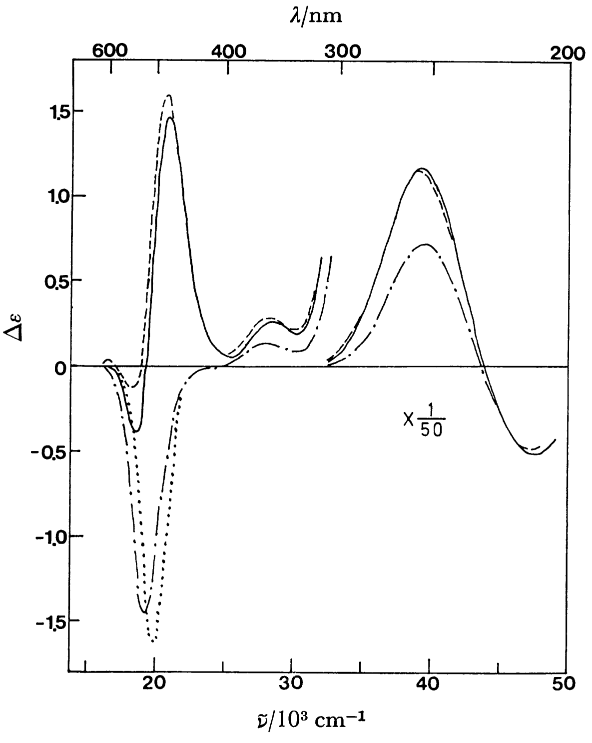

Fig. 3. Configurational effect CD $(\Delta\varepsilon(\Delta))$ of $[Co(cptn)_3]^{3+}$.
——: Observed CD of $\Delta(\lambda\lambda\lambda)$-$[Co(R,R\text{-cptn})_3]^{3+}$ (T_1), —·—·—: Calculated $\Delta\varepsilon(\Delta)=1/2[\Delta\varepsilon(T_2: \Delta\lambda\lambda\delta)+\Delta\varepsilon(T_3: \Delta\lambda\delta\delta)]$, ------: Calculated $\Delta\varepsilon[\Delta(\lambda\lambda\lambda)](=\Delta\varepsilon(\Delta)+3\Delta\varepsilon(\lambda))$, ······: Calculated $\Delta\varepsilon(\Delta)$ from $\Delta(\lambda)$- and $\Lambda(\lambda)$-$[Co(en)_2(R,R\text{-cptn})]^{3+}$ $(1/2\{\Delta\varepsilon[\Delta(\lambda)]-\Delta\varepsilon[\Lambda(\lambda)]\})$.

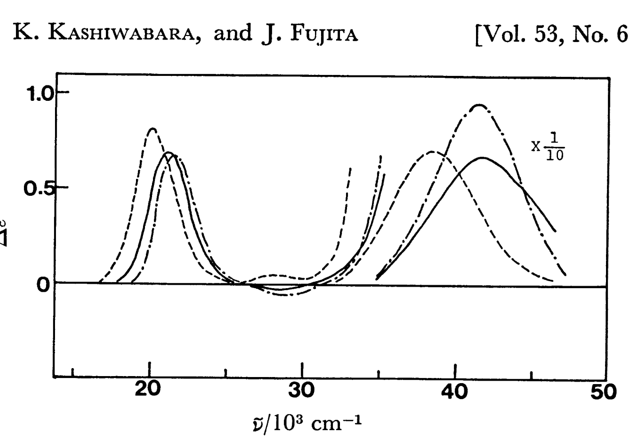

Fig. 4. Vicinal effect CD $(\Delta\varepsilon(\lambda))$ of the λ(*R,R*-cptn) ligand.
——: Observed CD of $[Co(NH_3)_4(R,R\text{-cptn})]^{3+}$, ------: Calculated $\Delta\varepsilon(\lambda)=1/2[\Delta\varepsilon(T_2: \Delta\lambda\lambda\delta)-\Delta\varepsilon(T_3: \Delta\lambda\delta\delta)]$, —·—·—: Calculated $\Delta\varepsilon(\lambda)$ from $\Delta(\lambda)$- and $\Lambda(\lambda)$-$[Co(en)_2(R,R\text{-cptn})]^{3+}$ $(1/2\{\Delta\varepsilon[\Delta(\lambda)]+\Delta\varepsilon[\Lambda(\lambda)]\})$.

The configurational $(\Delta\varepsilon(\Delta))$ and the vicinal $(3\Delta\varepsilon(\lambda))$ CD curves of $[Co(R,R\text{-cptn})_3]^{3+}$ in the region of the first absorption band are compared with those of $[Co(R,R\text{-chxn})_3]^{3+}$ [11,17] and $[Co(R\text{-pn})_3]^{3+}$ [9,17] (Fig. 5). The signs of the configurational and the vicinal CD of the *R,R*-cptn complex are the same as those of the corresponding CD of the other complexes. However, there is a big difference in the relative CD strength of these two effects. In the $[Co(R,R\text{-cptn})_3]^{3+}$ complex, the vicinal CD is much stronger than the configurational CD, the relation being reversed in the other complexes. However, if the CD strength is neglected, there is no anomaly in the CD of the *R,R*-cptn complex; the Δ-configurational and the λ-gauche vicinal effects give CD with negative and positive signs, respectively, in the region of the first absorption band, in line with the

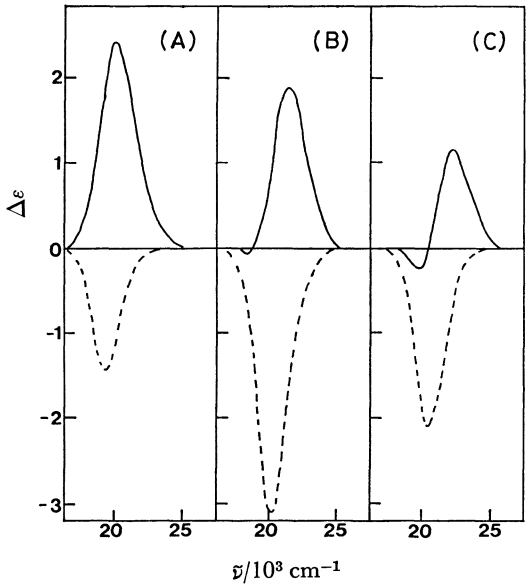

Fig. 5. Comparison of configurational ($\Delta\varepsilon(\Delta)$) (-----) and vicinal ($3\Delta\varepsilon(\lambda)$) (——) effect CD of the $\Delta(lel_3)$-$[\mathrm{Co(diamine)}_3]^{3+}$ complexes.
Diamine: (A) *R*,*R*-cptn, (B) *R*,*R*-chxn, (C) *R*-pn.

general rule concerning the CD sign in this region and the absolute configuration of a cobalt(III) complex. It is therefore concluded that the anomalous CD pattern, the positive sign of the main CD band of $\Delta(\lambda\lambda\lambda)$-$[\mathrm{Co}(R,R\text{-cptn})_3]^{3+}$ results from the contribution of the stronger positive vicinal effect than the negative configurational effect. The Δ-$[\mathrm{Co}(R,R\text{-chxn})_3]^{3+}$ and Δ-$[\mathrm{Co}(R\text{-pn})_3]^{3+}$ complexes which give the negative main CD band in line with the general rule have a strong negative configurational CD as compared with the positive vicinal CD.

The reason why the cptn complex shows such anomalous CD differing from those of the chxn and pn complexes is not clear. Ito *et al.*[3] suggested from a comparison of the data of X-ray crystal analyses on several tris(diamine) complexes that the important factor governing the rotatory strength of d-d transitions in metal complexes is the cumulative effect of various distortions of the ligand atoms. The cptn chelate ring involves strain. The bond angles, NC(1)C(5)(119°) and C(2)C(1)C(5)(110°) deviate from the normal tetrahedral angle.[3] The $[\mathrm{Co(tn)}_3]^{3+}$ complex (tn=trimethylenediamine) exhibiting an extremely weak CD in the region of the first absorption band[18] is also strained in the bond angle (CoNC=117.4°),[19] although the complex consists of six-membered chelate rings in the chair form. These strained complexes show CD spectra in the region of the first absorption band differing from those of other strain-free complexes. On the other hand, the vicinal effect CD of a 1,2-diamine chelate ligand depends on the chiral gauche conformation rather than on the asymmetric carbon atom.[20,21] The conformation of the chelate ring should be achiral, when it is in a *cis*, planar conformation. Thus the CD strength due to the vicinal effect of a chiral 1,2-diamine chelate ligand would depend on the dihedral angle of the N–C–C–N moiety of the puckered chelate ring. The strength of the vicinal CD increases in the order of the *R*-pn, *R*,*R*-chxn, and *R*,*R*-cptn complexes (Figs. 5 and 6). The order agrees with an increasing order of the observed dihedral angles of the chelate rings in (lel_3)-$[\mathrm{Co(diamine)}_3]^{3+}$; *R*-pn(51°),[15] *R*,*R*-chxn(59°),[14] and *R*,*R*-cptn(61.5°).[3] Thus, the anomalous CD pattern in the region of the first absorption band of $\Delta(\lambda\lambda\lambda)(lel_3)$-$[\mathrm{Co}(R,R\text{-cptn})_3]^{3+}$ is understandable in terms of the strong vicinal effect of the cptn chelate ligand.

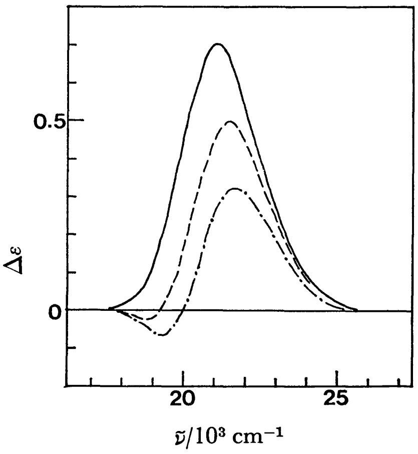

Fig. 6. CD spectra of the $[\mathrm{Co(NH_3)_4(diamine)}]^{3+}$ complexes.
Diamine: *R*,*R*-cpth (——), *R*,*R*-chxn (-----), *R*-pn (-·-·-).

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