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Circular Dichroism Spectra of Cobalt(III)-Ammine Complexes Containing Optically Active 1,3-Diphenyl-1,3-propanediamine or 1,2-Diphenyl-1,2-ethanediamine*

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A series of optically active cobalt(III) ammine complexes containing (*S,S*)-1,3-diphenyl-1,3-propanediamine (dppn) or (*S,S*)-1,2-diphenyl-1,2-ethanediamine (stien) were prepared. The sign of circular dichroism (CD) of $[Co(NH_3)_4(S,S\text{-dppn})]Br_3$ depends on solvents in the first absorption band region. The CD magnitude of *trans*-$[Co(NH_3)_2(S,S\text{-dppn})_2]^{3+}$ varies significantly with solvent variations in the same energy region. The CD curve of the vicinal effect of (*S,S*)-dppn derived from the two diastereomers of *cis*-$[Co(NH_3)_2(S,S\text{-dppn})_2]^{3+}$ is different from the CD spectra of both $[Co(NH_3)_4(S,S\text{-dppn})]^{3+}$ and *trans*-$[Co(NH_3)_2(S,S\text{-dppn})_2]^{3+}$. The CD spectra of the (*S,S*)-stien complexes are insensitive to solvent variations and the vicinal contributions of the (*S,S*)-stien calculated from a variety of the (*S,S*)-stien complexes are similar to one another.

It has been suggested that circular dichroism (CD) of metal complexes are sensitive to environment around a metal ion, *i.e.* conformational change of ligands, the deviation of ligating atoms from the octahedral positions, and interactions between solute and solvent. Recently, cobalt(III) complexes containing six-membered chelate rings have been investigated to show remarkable variations in CD spectra with change in solvent.[1-3] These variations have been primarily ascribed to the flexibility of six-membered chelate rings.

Such a conformational flexibility will differ depending on the kind of substituent on six-membered chelate rings. In a previous paper,[4] we have reported that the CD sign of $[Co(NH_3)_4(S,S\text{-dppn})]Br_3$ in water is opposite to that of $[Co(NH_3)_4(R,R\text{-ptn})](ClO_4)_3$ (*R,R*-ptn=(*R,R*)-2,4-pentanediamine) in water in the first absorption band region, although both the diamine ligands are expected to have the same λ-skew conformation. In order to investigate further detailed features of the dppn chelate ligand, we have prepared a series of complexes of the type $[Co(NH_3)_{2n}(S,S\text{-dppn})_{3-n}]^{3+}$ (n=0, 1, 2). This paper will report the preparation and the CD spectra of these complexes together with those of the corresponding (*S,S*)-1,2-diphenyl-1,2-ethanediamine (stien) complexes.

Experimental

Preparation of Ligands. The optically active diamines used were prepared by the methods previously reported; (*S,S*)-dppn[4] and (*S,S*)-stien.[5]

Preparation of the Complexes. *(1)* $[Co(NH_3)_4(S,S\text{-dppn})]Br_3 \cdot H_2O$: Method 1). Sodium hydroxide (2 g) in water (5 cm^3) was added dropwise to a suspension of $(-)_D$-dppn-di-*O*-benzoyltartrate (0.6 g) in cold water (5 cm^3). The released dppn was extracted with chloroform (20 cm^3). After removal of the chloroform under reduced pressure, the oily residue was dissolved in 5 cm^3 of dimethyl sulfoxide (DMSO). The solution was mixed with a DMSO solution (10 cm^3) of $[Co(NH_3)_5(H_2O)](ClO_4)_3$ (0.46 g) and allowed to stand at room temperature for 10 h with stirring. The resultant solution was passed through a column ($\phi 3\times 20$ cm) of an SP-Sephadex ion exchanger. After washing with water, the adsorbed band was eluted with a 0.5 M aqueous solution of potassium bromide. The first eluted orange yellow band was $[Co(NH_3)_6]^{3+}$. The second orange yellow eluate was concentrated to give orange crystals, which were recrystallized from warm water (50 °C) acidified with a few drops of 60% hydrobromic acid. Yield; 0.1 g. Found: C; 29.67, H; 5.36, N, 13.78%. Calcd for $[Co(NH_3)_4(S,S\text{-dppn})]Br_3 \cdot H_2O$ ($C_{15}H_{32}N_6OBr_3Co$): C; 29.48, H; 5.28, N; 13.76%.

Method 2). A DMSO solution (30 cm^3) of racemic dppn (1.4 g) was added to a DMSO solution (50 cm^3) of $[Co(NH_3)_5(H_2O)](ClO_4)_3$ (2.3 g). The solution was allowed to stand at 50 °C for 4 h with stirring, diluted to 1 dm^3 with water and acidified with concd hydrochloric acid. A red precipitate of by-products was filtered off and the orange filtrate was passed through a column ($\phi 5\times 30$ cm) of an SP-Sephadex C-25 ion exchanger. After washing with water, the adsorbed band was eluted with a 0.3 M aqueous solution of potassium bromide. The orange yellow eluate was concentrated to give orange crystals, which were recrystallized from water (25 cm^3) by adding ethanol (25 cm^3) and by cooling the solution in a refrigerator. Yield: 0.9 g. Found: C; 28.98, H; 5.36, N; 13.63%. Calcd for $[Co(NH_3)_4(dppn)]Br_3 \cdot 1.5H_2O$ ($C_{15}H_{33}N_6O_{1.5}Br_3Co$): C; 29.05, H; 5.36, N; 13.55%.

An aqueous solution of the orange yellow crystals was passed through a column ($\phi 4\times 60$ cm) of an SP-Sephadex C-25 ion exchanger. After washing with water, the adsorbed band was eluted with a 0.36 M aqueous solution of sodium $(+)_D$-tartratoantimonate(III). When the adsorbed band was separated into two bands, the eluent was changed to a 0.3 M aqueous solution of potassium bromide. The first eluted orange yellow band was concentrated to give orange crystals, which were the same compound as that prepared by method 1) on the basis of the elemental analysis and the CD spectra. Found: C; 29.24, H; 5.31, N; 13.90%.

The second orange yellow eluate was concentrated to give crystals, the CD spectrum of which is mirror image of that of the first eluted complex. Found: C; 29.47, H; 5.29, N; 14.00%. Calcd for $[Co(NH_3)_4(dppn)]Br_3 \cdot H_2O$ ($C_{15}H_{32}N_6OBr_3Co$): C; 29.48, H; 5.28, N: 13.76%.

(2) $[Co(NH_3)_4(R,S\text{-dppn})]Br_3$: A DMSO solution (5 cm^3) of (*R,S*)-dppn prepared from (*R,S*)-dppn·2HCl (1.6 g) was mixed with a DMSO solution (20 cm^3) of $[Co(NH_3)_5(H_2O)](ClO_4)_3$ (2.3 g). The resultant solution was warmed at 70 °C for 10 min with stirring, diluted with water (100 cm^3) and acidified with concd hydrochloric acid. A red orange precipitate of by-products was filtered off and the orange filtrate was

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passed through a column ($\phi 5\times 30$ cm) of an SP-Sephadex C-25 ion exchanger. After washing with water, the adsorbed band was eluted with a 0.3 M aqueous solution of potassium bromide. The first eluted orange band was $[Co(NH_3)_6]^{3+}$. The second orange eluate was concentrated to give orange crystals, which were recrystallized from hot water (200 cm^3) acidified with a few drops of 47% hydrobromic acid. Yield; 0.7 g. Found: C; 29.98, H; 5.38, N; 13.39%. Calcd for $[Co(NH_3)_4(R,S\text{-dppn})]Br_3\cdot H_2O$ ($C_{15}H_{32}N_6OBr_3Co$): C; 29.48, H; 5.28, N; 13.76%.

(3) $[Co(NH_3)_4(S,S\text{-}stien)](ClO_4)_3\cdot 4H_2O$: (*S*,*S*)-Stien (1.0 g) was added to a DMSO solution (50 cm^3) of $[Co(NH_3)_5(H_2O)](ClO_4)_3$ (2.24 g). The resultant solution was allowed to stand at room temperature for 20 h, and passed through a column ($\phi 5\times 30$ cm) of an SP-Sephadex C-25 ion exchanger. After washing with water, the adsorbed band was eluted with a 0.5 M aqueous solution of sodium perchlorate. The first eluted red band was $[Co(NH_3)_5(H_2O)]^{3+}$. The second yellow orange eluate was concentrated to give orange crystals, which were recrystallized from ethanol. Yield; 0.4 g. Found: C; 23.99, H; 5.00, N; 11.39%. Calcd for $[Co(NH_3)_4(S,S\text{-stien})](ClO_4)_3\cdot 4H_2O$($C_{14}H_{36}N_6O_{16}Cl_3Co$): C; 23.69, H; 5.11, N; 11.84%.

(4) trans- *and* cis-$[Co(NH_3)_2(S,S\text{-}dppn)_2]^{3+}$: When *trans*-$[CoCl_2(S,S\text{-dppn})_2]Cl\cdot HCl\cdot H_2O$[4] (600 mg) was dissolved in liquid ammonia, the color of solution changed from green to orange instantly. After removal of liquid ammonia at room temperature, the residue was mixed with 2 M hydrochloric acid (10 cm^3) and then dissolved in DMSO. The resultant solution was passed through a column ($\phi 4\times 45$ cm) of an SP-Sephadex C-25 ion exchanger. After washing with a mixture of water and DMSO (4 : 1), the adsorbed band was eluted with a 0.15 M solution of sodium (+)$_D$-tartratoantimonate(III) in a mixture of DMSO and water (1 : 4). When the adsorbed orange band was separated into two bands (I and II in the order of elution), the eluent was changed to a 0.7 M solution of sodium perchlorate in a mixture of water and methanol (2 : 1). The slowly eluted band, II, was further separated into two bands (IIa and IIb). The eluate of I was concentrated to give crystals, which were recrystallized from a mixture of acetone and ethanol (1 : 5), filtered off, and washed with ethanol and diethyl ether. Yield; 0.2 g. Found: C; 40.33, H; 5.39, N; 9.41%. Calcd for $[Co(NH_3)_2(S,S\text{-dppn})_2](ClO_4)_3\cdot 3H_2O$($C_{30}H_{48}N_6O_{15}Cl_3Co$): C; 40.09, H; 5.39, N; 9.36%. This complex was assigned to the *trans* isomer on the basis of the PMR and CD spectra.

The eluate IIa was diluted about ten times with water and passed through a column ($\phi 2\times 20$ cm) of an SP-Sephadex C-25 ion exchanger. The adsorbed band was eluted with 1 M hydrochloric acid. Orange crystals (20 mg) were obtained by concentrating the eluate. Found: C; 53.77, H; 6.52, N; 12.47%. Calcd for $[Co(NH_3)_2(S,S\text{-dppn})_2]Cl_3\cdot H_2O$ ($C_{30}H_{44}N_6OCl_3Co$): C; 53.78, H; 6.62, N; 12.54%. This complex was assigned to the *cis-Λ* isomer on the basis of the CD spectrum.

The precipitate formed by concentrating the eluate IIb was filtered off and dissolved in a mixture of water and methanol (2 : 1). The solution was passed through a column ($\phi 2\times 20$ cm) of an SP-Sephadex C-25 ion exchanger. The adsorbed band was eluted with 1 M hydrochloric acid. The orange eluate was evaporated to almost dryness and the residue was again dissolved in methanol. The solution was filtered and the filtrate was concentrated to give orange crystals, which were recrystallized from a mixture of methanol and water. Yield; 0.2 g. Found: C; 51.97, H; 6.49, N; 12.26%. Calcd for $[Co(NH_3)_2(S,S\text{-dppn})_2]Cl_3\cdot 2H_2O$($C_{30}H_{46}N_6O_2Cl_3Co$): C; 52.37, H; 6.74, N; 12.21%. This complex was assigned to the *cis-Δ* isomer on the basis of the PMR and CD spectra.

(5) trans- *and* cis-$[Co(NH_3)_2(S,S\text{-}stien)_2]^{3+}$: To liquid ammonia (50 cm^3) was added *trans*-$[CoCl_2(S,S\text{-stien})_2]ClO_4\cdot H_2O$[1] (0.57 g). The color of the solution changed from green to orange instantly. After removal of liquid ammonia at room temperature, the residue was mixed with 2 M hydrochloric acid (10 cm^3) and then dissolved in DMSO. The resultant solution was passed through a column ($\phi 4\times 45$ cm) of an SP-Sephadex C-25 ion exchanger. After washing with a mixture of DMSO and water (1 : 4), the adsorbed band was eluted with a 0.15 M solution of sodium (+)$_D$-tartratoantimonate(III) in a mixture of DMSO and water (1 : 4). When the orange band was separated into two bands, the eluent was changed to a 0.7 M solution of sodium perchlorate in a mixture of water and methanol (2 : 1). The first eluted orange band was concentrated to give crystals, which were recrystallized from methanol. Yield; 0.3 g. Found: C; 40.40, H; 5.13, N; 9.82%. Calcd for $[Co(NH_3)_2(S,S\text{-stien})_2](ClO_4)_3$($C_{28}H_{38}N_6O_{13}Cl_3Co$): C; 40.33, H; 4.83, N; 10.08%. This complex was assigned to the *trans* isomer on the basis of the CD spectrum.

The second orange eluate was concentrated to give orange precipitate. The product was dissolved in a mixture of water and DMSO (4 : 1) and rechromatographed with a column ($\phi 4\times 45$ cm) of an SP-Sephadex C-25 ion exchanger. The adsorbed band was eluted with a 0.15 M solution of sodium (+)$_D$-tartratoantimonate(III) in a mixture of DMSO and water (1 : 4). When the orange band was separated into two bands, the eluent was changed to a 0.5 M aqueous solution of sodium chloride. The first eluted band was concentrated to give orange precipitate. Recrystallization from a mixture of water and methanol (1 : 4) gave orange crystals, which were filtered off and washed with ethanol. Yield; 20 mg. Found: C; 49.42, H; 6.45, N; 12.35%. Calcd for $[Co(NH_3)_2(S,S\text{-stien})_2]Cl_3\cdot 3H_2O$($C_{28}H_{44}N_6O_3Cl_3Co$): C; 49.60, H; 6.54, N; 12.40%. This complex was assigned to the *cis-Λ* isomer on the basis of the CD spectrum.

The second eluted band was concentrated to give orange precipitate, which was recrystallized from water. Yield; 0.1 g. Found: C; 49.74, H; 6.78, N; 12.75%. Calcd for $[Co(NH_3)_2(S,S\text{-stien})_2]Cl_3\cdot 3H_2O$($C_{28}H_{44}N_6O_3Cl_3Co$): C; 49.60, H; 6.54, N; 12.40%. This complex was assigned to the *cis-Δ* isomer on the basis of the CD spectrum.

Measurements. Visible and ultraviolet absorption spectra were recorded on a Hitachi 323 spectrophotometer. CD spectra were obtained with JASCO J-20 and J-40 spectropolarimeters. PMR spectra were recorded on Varian A-60 and HA-100 spectrometers in deuterated solvents using tetramethylsilane (TMS) as the internal standard. All the solvents for optical measurements are of spectroscopic grade and used without further purification.

Results and Discussion

Conformation of the Chelate Rings and Geometrical Isomers of the Complexes. The PMR spectral data for the methylene and methine resonances of the (*R*,*S*)- and (*S*,*S*)-dppn complexes are summarized in Table 1 together with those of the (*R*,*S*)- and (±)-ptn platinum(II) and platinum(IV) complexes. Appleton and Hall[6] suggested that the chair conformation is preferred in the (*R*,*S*)-ptn platinum complexes and the skew conformation in the (±)-ptn platinum(IV) complex on the basis of the coupling constant $J_{\text{Pt-N-C-H}}$. The coupling constants, J_{AX} and J_{AB} of the (*R*,*S*)-dppn

Table 1. The methylene proton (H_A, H_B) resonances and the coupling constants with the methine proton (H_X) of the dppn and ptn complexes (δ/ppm)

	H_A	H_B	J_{AX}
$[Co(NH_3)_4(R,S\text{-dppn})](ClO_4)_3$	3.01	2.17	11
$[Pt(NH_3)_2(R,S\text{-ptn})]Cl_2$ 6)	2.03	3.08	11.0
$[Pt(H_2O)_2(R,S\text{-ptn})_2](ClO_4)_4$ 6)	2.68	3.75	11.0
$[Co(NH_3)_4((\pm)\text{-dppn})](ClO_4)_3$	2.62		8
trans-$[Co(NH_3)_2(S,S\text{-dppn})_2](ClO_4)_3$	2.70		8
cis-Δ-$[Co(NH_3)_2(S,S\text{-dppn})_2](ClO_4)_3$	2.53,	2.78	8
$[Pt((\pm)\text{-ptn})(NH_3)_2]Cl_2$ 6)	2.87		5.5
$[Pt((\pm)\text{-ptn})(NH_3)_2(H_2O)_2](ClO_4)_4$ 6)	3.42		7.5

Solvent: $(CD_3)_2CO$ for dppn complexes and D_2O for ptn complexes. Internal references: TMS for dppn complexes and DSS for ptn complexes.

cobalt(III) complexes are similar to those of the (R,S)-ptn platinum complexes. The constants, J_{AX} of the (($\pm$) or S,S)-dppn cobalt(III) complexes are also similar to that of $[Pt((\pm)\text{-ptn})(NH_3)_2(H_2O)_2](ClO_4)_4$ as seen in Table 1. It is, therefore, concluded that the (R,S)-dppn and the (R,R or S,S)-dppn chelate rings take chair and skew conformations, respectively. In a previous paper,4) it was clarified from the CD spectrum of *trans*-$[CoCl_2(S,S\text{-dppn})_2]^+$ that the (S,S)-dppn takes a λ-skew conformation upon coordination.

The assignment of the geometrical isomers of $[Co(NH_3)_2(S,S\text{-dppn})_2]^{3+}$ was made on the basis of the PMR spectral patterns (Table 1). This assignment will be supported by the elution order of the isomers of $[Co(NH_3)_2(S,S\text{-dppn})_2]^{3+}$ in SP-Sephadex column chromatography; *trans*>*cis*-Λ>*cis*-Δ. This order is the same as that for the corresponding isomers of the (R,R)-ptn complexes.3)

Circular Dichroism Spectra. The CD data of the (S,S)-dppn and (S,S)-stien complexes in the first absorption band region are summarized in Table 2 together with the absorption data.

(1) $[Co(NH_3)_4L]^{3+}$ *(L=(S,S)-dppn and (S,S)-stien)*: The CD spectra of the complexes, $[Co(NH_3)_4L]^{3+}$ in water are shown in Fig. 1. Both the complexes give only a negative CD band in the first absorption band region. The (S,S)-stien is known to take a δ-gauche conformation, the two phenyl groups on the asymmetric carbons adopting equatorial orientation.7,8) A single negative CD sign of the (S,S)-dppn complex predicts that the chelate ring also takes a δ-skew conformation. However, this conformation is unlikely for the (S,S)-dppn because the two phenyl groups on the asymmetric carbons become axial orientation. The (S,S)-dppn chelate is expected to be stable in the λ-skew conformation with two equatorial phenyl groups. The designation of the absolute configuration for both the diamines is opposite to each other for the same conformation on the basis of the sequence rule.9) The CD pattern of $[Co(NH_3)_4(S,S\text{-dppn})]^{3+}$ in water is also different from either CD curve of the vicinal contribu-

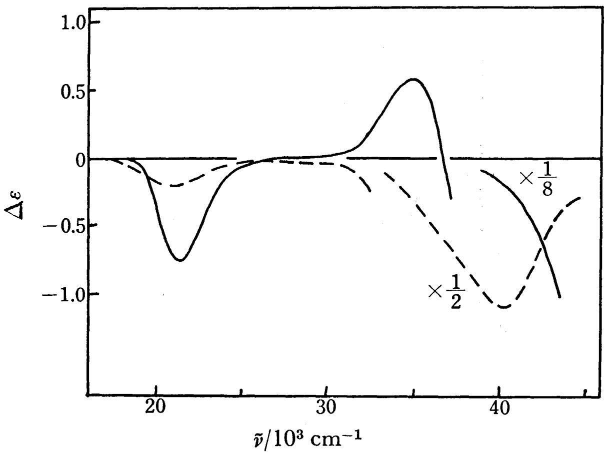

Fig. 1. CD spectra of $[Co(NH_3)_4(S,S\text{-dppn})]Br_3$ (----) and $[Co(NH_3)_4(S,S\text{-stien})](ClO_4)_3$ (——) in water.

Table 2. Absorption (AB) and CD spectral data of the (S,S)-dppn and the (S,S)-stien complexes in the first absorption band region

	L=(S,S)-dppn		L=(S,S)-stien	
	AB $\tilde{\nu}/10^3\ cm^{-1}$ (ε)	CD $\tilde{\nu}/10^3\ cm^{-1}$ ($\Delta\varepsilon$)	AB $\tilde{\nu}/10^3\ cm^{-1}$ (ε)	CD $\tilde{\nu}/10^3\ cm^{-1}$ ($\Delta\varepsilon$)
$[Co(NH_3)_4L]^{3+}$	20.88(79.0)*1)	20.83(−0.17)*1)	21.28(83.3)*1)	21.37(−0.75)*1)
	20.83(85.4)*3)	19.34(−0.10)*3)	21.19(91.1)*3)	21.14(−1.49)*3)
		22.94(−0.02)*3)		
		17.24(−0.01)*4)	21.19(91.1)*2)	21.46(−1.02)*2)
		20.62(+0.21)*4)		
		25.32(−0.01)*4)		
$[Co(NH_3)_2L_2]^{3+}$, *cis*-Λ	20.45(106.5)*2)	18.18(−0.03)*2)	21.32(100)*1)	19.49(+0.31)*1)
		20.41(+0.62)*2)		21.88(−0.54)*1)
cis-Δ	20.53(87.7)*2)	19.34(−0.31)*2)	21.32(87)*1)	21.23(−1.69)*1)
trans	20.66(121.9)*2)	19.23(+0.21)*2)	21.46(118)*2)	18.52(+0.04)*2)
		21.83(−0.01)*2)		
	20.75(109.9)*3)	19.57(+0.48)*3)	21.51(119)*3)	19.32(+0.32)*3)
				21.85(−2.03)*3)
		19.76(+0.75)*4)		21.44(−3.17)*4)

* Solvent: 1) water, 2) methanol, 3) DMSO, and 4) KBr matrix.

tion of (*S*,*S*)-dppn calculated from the two diastereomers, Δ- and Λ-$[Co(S,S\text{-dppn})_3]^{3+}$ or from Δ- and Λ-$[Co(en)_2(S,S\text{-dppn})]^{3+}$.[4,10] One explanation for the CD spectrum of $[Co(NH_3)_4(S,S\text{-dppn})]^{3+}$ can be based on the flexibility of the (*S*,*S*)-dppn ligand in connection with the observation that the cobalt(III) complexes containing 2,4-pentanediamine are susceptible to solvent effect.[3]

The solvent effect on the CD spectra of both the (*S*,*S*)-dppn and the (*S*,*S*)-stien complexes is shown in Figs. 2 and 3, respectively. The former complex shows a marked solvent effect in the first absorption band region. The CD pattern in KBr matrix resembles that of the vicinal contribution of (*S*,*S*)-dppn derived from the Δ- and Λ-$[Co(S,S\text{-dppn})_3]^{3+}$ complexes in DMSO. On the other hand, $[Co(NH_3)_4(S,S\text{-stien})](ClO_4)_3$ shows little variations. The pattern is the same as that of the vicinal contribution of (*S*,*S*)-stien derived from the two diastereomers of Δ- and Λ-$[Co(S,S\text{-stien})_3]^{3+}$.[1] Several explanations have been proposed for the solvent effect; 1) the conformational change of the diamine chelate ring, 2) asymmetric deviation of the coordinated nitrogen atoms from the octahedral positions, 3) asymmetric interaction of the solvent molecule with the solute. These factors are not independent of one another. The fact that the CD spectrum of $[Co(NH_3)_4(S,S\text{-dppn})]^{3+}$ is much more susceptible to solvent ef-

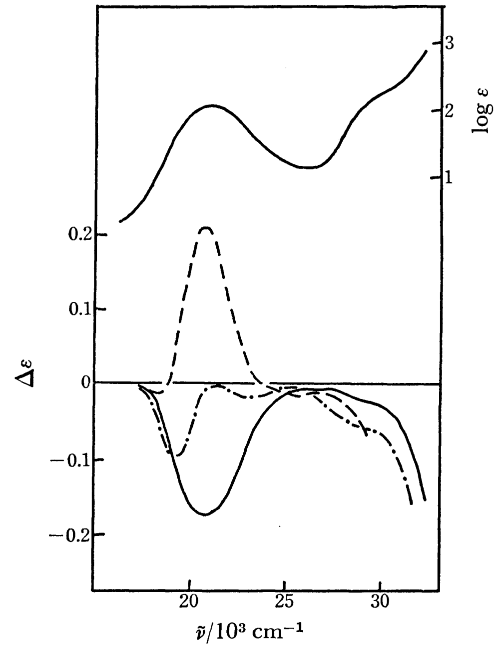

Fig. 2. Absorption and CD spectra of $[Co(NH_3)_4(S,S\text{-dppn})]Br_3$ in water (——), in DMSO (—·—), and KBr matrix (----).

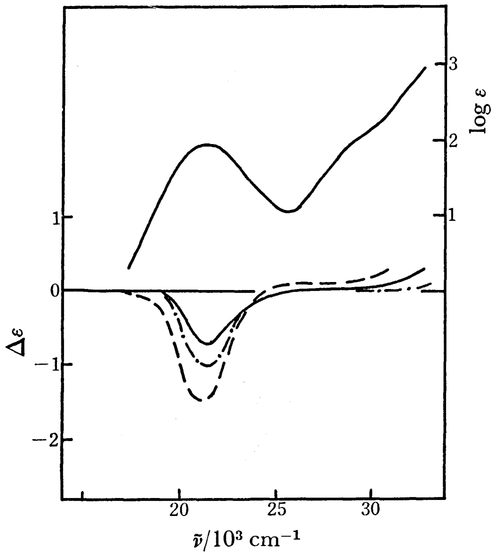

Fig. 3. Absorption and CD spectra of $[Co(NH_3)_4(S,S\text{-stien})](ClO_4)_3$ in water (——), in DMSO (—·—), and KBr matrix (----).

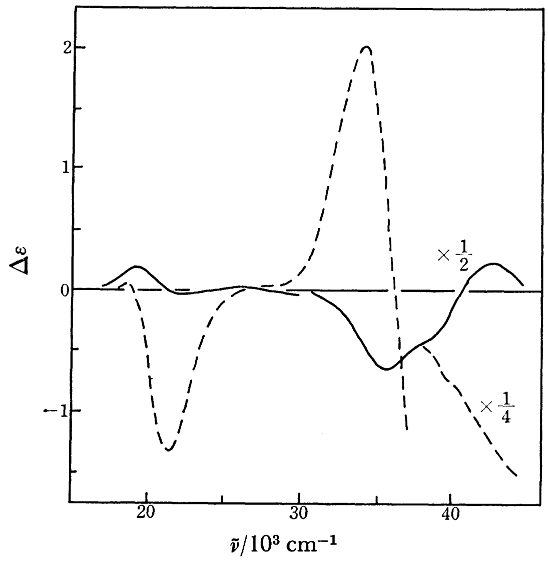

Fig. 4. CD spectra of *trans*-$[Co(NH_3)_2(S,S\text{-dppn})_2](ClO_4)_3$ (——) and *trans*-$[Co(NH_3)_2(S,S\text{-stien})_2](ClO_4)_3$ (----) in methanol.

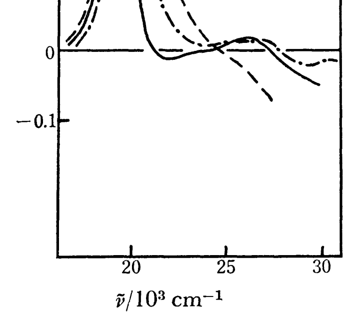

Fig. 5. CD spectra of *trans*-$[Co(NH_3)_2(S,S\text{-dppn})_2](ClO_4)_3$ in methanol (——), in DMSO (—·—), and KBr matirx (----).

fect than that of the corresponding stien complex indicates that the variations may be associated with the flexibility of the six-membered chelate ring. However, the main factor for the solvent variations is not clear at present.

(2) trans-$[Co(NH_3)_2L_2]^{3+}$ *(L=(S,S)-dppn and (S,S)-stien)*: The CD spectra of the complexes, *trans*-$[Co(NH_3)_2L_2]^{3+}$ in methanol are shown in Fig. 4. Both the complexes give two CD peaks in the first absorption band region and the sign of the main component is positive for the former and negative for the latter. These patterns coincide with the anticipation that the (*S*,*S*)-dppn takes a λ-skew conformation and the (*S*,*S*)-stien a δ-gauche form. The CD strength of the (*S*,*S*)-dppn complex in the second absorption band region is very weak, in contrast to that of the corresponding (*R*,*R*)-ptn complex.[11]

The solvent effect on both the (*S*,*S*)-dppn and the (*S*,*S*)-stien complexes is shown in Figs. 5 and 6, respectively. The CD strength of the (*S*,*S*)-dppn complex varies significantly with the solvent variations in the first absorption band region. On the other hand, the CD spectrum of the (*S*,*S*)-stien complex is rather insensitive to the solvent variations. The CD pattern of *trans*-$[Co(NH_3)_2(S,S\text{-dppn})_2]^{3+}$ is entirely different from that of $[Co(NH_3)_4(S,S\text{-dppn})]^{3+}$ in water, while the (*S*,*S*)-stien complex gives the same pattern as that of $[Co(NH_3)_4(S,S\text{-stien})]^{3+}$. The difference in the CD behavior between the (*S*,*S*)-dppn and the (*S*,*S*)-stien complexes may be related with the difference in the conformational behavior of the chelate rings.

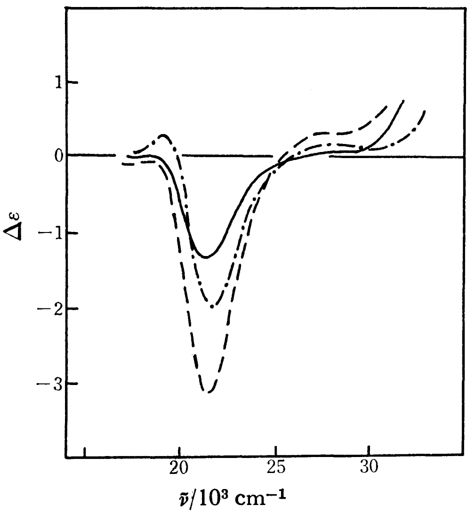

Fig. 6. CD spectra of *trans*-$[Co(NH_3)_2(S,S\text{-stien})_2](ClO_4)_3$ in methanol (——), in DMSO (—·—) and KBr matrix (----).

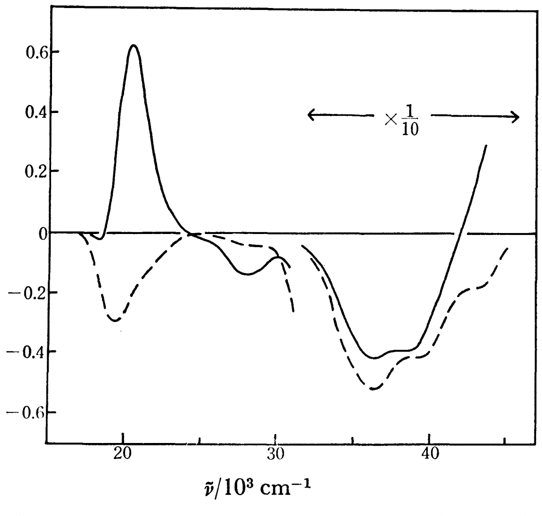

Fig. 7. CD spectra of *cis* 1 (——) and *cis* 2 (----) of $[Co(NH_3)_2(S,S\text{-dppn})_2]Cl_3$ in methanol. The solution of *cis* 2 was acidified with hydrochloric acid.

(3) cis-$[Co(NH_3)_2L_2]^{3+}$*(L=(S,S)-dppn and (S,S)-stien)*: Figures 7—10 show the CD spectra of the isomers of *cis*-$[Co(NH_3)_2L_2]^{3+}$ and the calculated configurational and vicinal (per mole of the ligands) contributions to the CD spectra. The *cis* 1 in Figs. 7 and 9

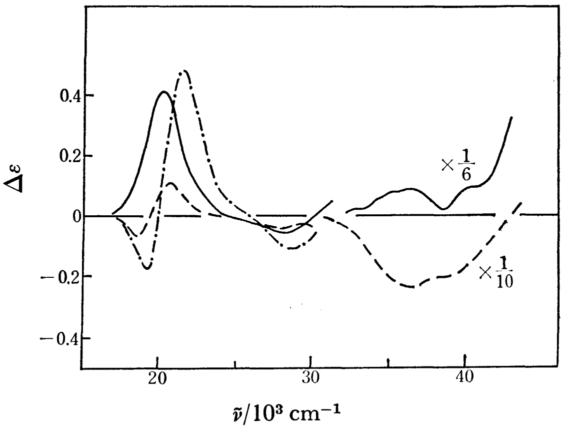

Fig. 8. The configuration (Λ) (——) and the vicinal (----) contribution in the CD calculated from the spectra of the two diastereomers of *cis*-$[Co(NH_3)_2(S,S\text{-dppn})_2]Cl_3$ in methanol, and the vicinal (—·—) contribution from Δ- and Λ-$[Co(S,S\text{-dppn})_3]^{3+}$.

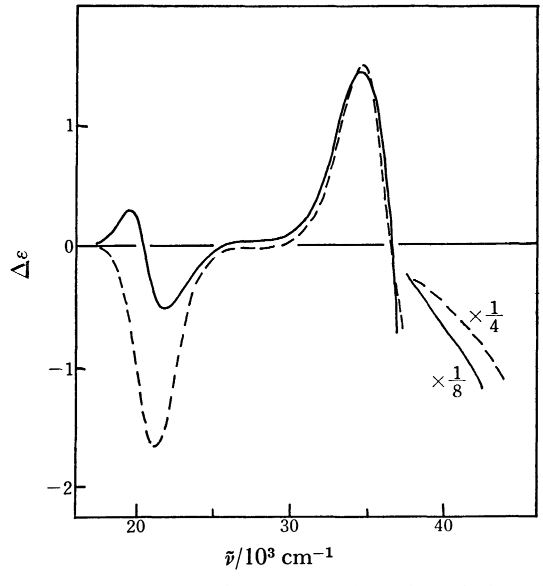

Fig. 9. CD spectra of *cis* 1 (——) and *cis* 2 (----) of $[Co(NH_3)_2(S,S\text{-stien})_2]Cl_3$ in 0.02 M aqueous hydrochloric acid.

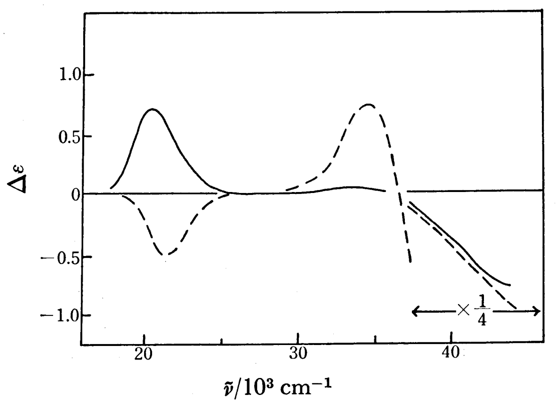

Fig. 10. The configurational (Λ) (——) and the vicinal (----) contribution in the CD calculated from the spectra of the two diastereomers of *cis*-$[Co(NH_3)_2$(*S*,*S*-stien)$_2]Cl_3$ in methanol.

were obtained from the first orange eluate and the *cis* 2 from the second orange yellow eluate. The absolute configuration of each isomer can be assigned on the basis of the empirical rule.[12)] The calculated configurational contribution of the CD spectra shown in Fig. 8 also supports the assignment: *cis* 1 to Λ and *cis* 2 to Δ.

Boucher and Bosnich[11)] reported that the calculated vicinal contribution of (*R*,*R*)-ptn derived from the two diastereomers of *cis*-$[Co(NH_3)_2$(*R*,*R*-ptn)$_2]^{3+}$ is entirely different from the CD spectrum of *trans*-$[Co(NH_3)_2$(*R*,*R*-ptn)$_2]^{3+}$. Mizukami *et al.*[13)] also claimed that the vicinal contribution of (*R*,*R*)-ptn derived from [Co(*R*,*R*-ptn)$_3]^{3+}$ differs from the CD spectrum of $[Co(NH_3)_4$(*R*,*R*-ptn)$]^{3+}$. The calculated vicinal contribution of (*S*,*S*)-dppn derived from the two diastereomers of *cis*-$[Co(NH_3)_2$(*S*,*S*-dppn)$_2]^{3+}$ also differs from the CD spectra of both *trans*-$[Co(NH_3)_2$(*S*,*S*-dppn)$_2]^{3+}$ and $[Co(NH_3)_4$(*S*,*S*-dppn)$]^{3+}$. The spectral pattern of the calculated vicinal contribution, however, is similar to that obtained from the CD spectra of Δ- and Λ-[Co(*S*,*S*-dppn)$_3]^{3+}$ in Fig. 8, although the CD strength of the former is weak compared with that of the latter.

The vicinal contribution of the (*S*,*S*)-stien chelate ring in Fig. 10 is almost the same as the CD spectra of both $[Co(NH_3)_4$(*S*,*S*-stien)$]^{3+}$ and *trans*-$[Co(NH_3)_2$(*S*,*S*-stien)$_2]^{3+}$. This is common to five-membered chelate ring systems such as 1,2-propylenediamine cobalt(III) complexes.[14)]

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