Circular Dichroism Spectra of Cobalt(III) Complexes of the Type, *trans*-[CoX_2(1,3-Diamine)$_2$]$^{n+}$ (X=Cl^-, CN^-, or NH_3)

Kazuo KASHIWABARA, Masaaki KOJIMA, and Junnosuke FUJITA*

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

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Four new complexes of the type, *trans*-[$Co(CN)_2$(1,3-diamine)$_2$]$^+$ were prepared, where 1,3-diamine is (*S,S*)-1,3-diphenyl-1,3-propanediamine, (*R,R*)-2,4-pentanediamine, (*S*)-1,3-butanediamine, or (*S*)-1-phenyl-1,3-propanediamine. Two diammine complexes of the same type with (*S*)-1,3-butanediamine and (*S*)-1-phenyl-1,3-propanediamine, and *trans*-[$Co(CN)_2$((*R,R*)-1,2-diphenyl-1,2-ethanediamine)$_2$]$^+$ were also newly prepared. The circular dichroism(CD) spectra of the new complexes measured in several solvents were compared with those of the corresponding dichloro and diammine complexes. The CD spectra of the dicyano complexes of (*S*)-1,3-butanediamine and (*S*)-1-phenyl-1,3-propanediamine showed remarkable solvent dependence, while those of the other complexes small or little dependence.

Bosnich and Harrowfield[1] found that the sign of circular dichroism(CD) under the $^1A_{2g}\leftarrow{}^1A_{1g}$ transition in the first absorption band of *trans*-[$CoCl_2$(*R*-pn)$_2$]$^+$ (*R*-pn=(*R*)-1,2-propanediamine) is negative in methanol, but positive in dimethyl sulfoxide(DMSO), and suggested that the effects of chiral distortions of the donor atoms and of chiral arrangements of the amino hydrogen atoms caused by solvation are important for such solvent dependence. Recently, Hawkins *et al.*[2] reported by both CD and PMR studies of the same complex and its related complexes in various solvents that the solvent dependence of the CD will be cussed by stereoselective solvation at the equatorial amino hydrogen atoms of the diamines, rendering the donor nitrogens chiral. This paper is concerned with the CD spectra of complexes of the type, *trans*-[CoX_2(1,3-diamine)$_2$]$^{n+}$ (X=Cl^-, CN^-, or NH_3) in several solvents, the abbreviations and the absolute configurations of the 1,3-diamines being shown in Fig. 1. The flexibility of six-membered chelate rings formed with the 1,3-diamines will affect the CD spectra of their complexes in a different way from that of the complexes of five-membered chelate rings. The *R*-pn and (*R,R*)-1,2-diphenyl-1,2-ethanediamine (*R,R*-dpen) complexes of the same type were also prepared to compare their CD spectra with those of the 1,3-diamine complexes.

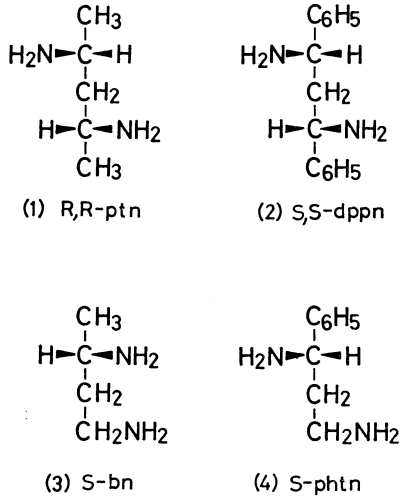

Fig. 1. Absolute configurations of the 1,3-diamines, (1) (*R,R*)-2,4-pentanediamine(*R,R*-ptn), (2) (*S,S*)-1,3-diphenyl-1,3-propanediamine(*S,S*-dppn), (3) (*S*)-1,3-butanediamine(*S*-bn), and (4) (*S*)-1-phenyl-1,3-propanediamine(*S*-phtn).

Experimental

Preparation of Ligands. Optically active diamines were prepared according to the references reported previously; *S,S*-dppn,[3] *R,R*-ptn,[4] *S*-phtn,[5] *S*-bn,[6] *R*-pn,[7] and *R,R*-dpen.[8]

Preparation of Complexes. *1)* The following complexes were prepared by the methods described previously; *trans*-[$CoCl_2$(*S,S*-dppn)$_2$]Cl·HCl·H_2O,[3] *trans*-[$CoCl_2$(*R,R*-ptn)$_2$]ClO_4,[9] *trans*-[$CoCl_2$(*S*-phtn)$_2$]Cl·H_2O,[5] *trans*-[$CoCl_2$(*R*-pn)$_2$]ClO_4,[1] *trans*-[$CoCl_2$(*R,R*-dpen)$_2$]ClO_4,[1] *trans*-[$Co(CN)_2$(*R*-pn)$_2$]Cl·1.5H_2O,[10] *trans*-[$Co(NH_3)_2$(*S,S*-dppn)$_2$]$(ClO_4)_3$·3H_2O,[11] and *trans*-[$Co(NH_3)_2$(*R,R*-ptn)$_2$]$(ClO_4)_3$·H_2O.[12]

2) trans-[*CoCl$_2$*(S-*bn*)$_2$]*ClO$_4$*: This complex was prepared by adding sodium perchlorate to an aqueous solution of the complex chloride.[13] Found: C, 23.88; H, 6.19; N, 13.56%. Calcd for [$CoCl_2(C_4H_{12}N_2)_2$]ClO_4: C, 23.69; H, 5.98; N, 13.82%.

3) trans-[*Co(CN)$_2$*(S,S-*dppn*)$_2$]*Cl·2H$_2$O*: To sodium cyanide (30 mg) in 12 cm^3 of DMSO was added *trans*-[$CoCl_2$-(*S,S*-dppn)$_2$]ClO_4 (140 mg) with stirring at 40 °C. The solution changed from green to orange instantly and was kept at 40 °C for 10 min. After cooling to room temperature, the solution was poured into a column (ϕ3×60 cm) of an SP-Sephadex C-25 ion exchanger and then the column was washed with water to remove DMSO. The adsorbed orange product was eluted with 0.1 mol/dm^3 sodium chloride in a mixture of methanol and water (1:4). The column showed only one orange yellow band. The eluate was concentrated under reduced pressure to give orange yellow crystals, which were recrystallized from a small amount of water. The yield was almost quantitative. Found: C, 60.36; H, 6.19; N, 13.15%. Calcd for [$Co(CN)_2(C_{15}H_{18}N_2)_2$]Cl·2$H_2O$: C, 60.51; H, 6.35; N, 13.23%.

4) trans-[*Co(CN)$_2$*(R,R-*ptn*)$_2$]*ClO$_4$·H$_2$O*: This complex was prepared from *trans*-[$CoCl_2$(*R,R*-ptn)$_2$]ClO_4 and sodium cyanide by the same method as that for *trans*-[$Co(CN)_2$-(*S,S*-dppn)$_2$]Cl·2H_2O except that the eluent was an aqueous solution of 0.05 mol/dm^3 sodium perchlorate. The yield was almost quantitative. Found: C, 33.62; H, 7.10; N, 19.65%. Calcd for [$Co(CN)_2(C_5H_{14}N_2)_2$]ClO_4·H_2O: C, 33.30; H, 6.94; 19.42%.

5) trans-[*Co(CN)$_2$*(S-*bn*)$_2$]ClO_4·H_2O: This complex was prepared from *trans*-[$CoCl_2$(*S*-bn)$_2$]ClO_4 and sodium cyanide according to the same method as described for the above *R,R*-ptn complex. Found: C, 29.94; H, 6.63; N, 20.80%.

Calcd for $[Co(CN)_2(C_4H_{12}N_2)_2]ClO_4 \cdot H_2O$: C, 29.67; H, 6.49; N, 20.76%.

6) trans-$[Co(CN)_2(S\text{-}phtn)_2]ClO_4 \cdot H_2O$: The procedure was the same as that for the *R,R*-ptn complex. However, two light yellow bands (probably the *cis*-Λ and *cis*-Λ isomers on the basis of the absorption spectra) followed after an orange band (*trans* isomer) by eluting with a 0.05 mol/dm^3 aqueous solution of sodium perchlorate. Yield: about 40%. Found: C, 45.65; H, 5.34; N, 15.69%. Calcd for $[Co(CN)_2(C_9H_{14}N_2)_2]ClO_4 \cdot H_2O$: C, 45.42; H, 5.72; N, 15.89%.

7) trans-$[Co(CN)_2(R,R\text{-}dpen)_2]ClO_4 \cdot 2H_2O$: To a DMSO solution (20 cm^3) of sodium cyanide (60 mg) was added *trans*-$[CoCl_2(R,R\text{-dpen})_2]ClO_4 \cdot H_2O$ (180 mg) at 50 °C with stirring. The solution changed from green to orange instantly and was kept at 50 °C for 10 min. After cooling to room temperature, the solution was poured into a column ($\phi 3 \times$ 90 cm) of an SP-Sephadex C-25 ion exchanger. DMSO in the column was washed out with water. The adsorbed orange product was eluted with an aqueous solution of 0.1 mol/dm^3 sodium acetate. An orange yellow band (the *trans* isomer) was eluted first and then two light yellow bands (the *cis* isomers) followed. The orange yellow eluate was mixed with a small amount of sodium perchlorate and concentrated under reduced pressure to give crystals. Yield: 50 mg. Found: C, 53.98; H, 5.39; N, 12.67%. Calcd for $[Co(CN)_2(C_{14}H_{16}N_2)_2]ClO_4 \cdot 2H_2O$: C, 53.70; H, 5.41; N, 12.52%.

8) trans-$[Co(NH_3)_2(S\text{-}bn)_2](ClO_4)_3$: When *trans*-$[CoCl_2(S\text{-bn})_2]ClO_4$ (100 mg) was dissolved in liquid ammonia (20 cm^3), the solution changed from green to orange instantly. After removal of liquid ammonia at room temperature, the residue was mixed with 2 mol/dm^3 hydrochloric acid (5 cm^3). The solution was diluted with water (500 cm^3) and passed through a column ($\phi 3 \times 120$ cm) of an SP-Sephadex C-25 ion exchanger. The adsorbed orange product was eluted with a 0.15 mol/dm^3 aqueous solution of sodium $(+)_D$-tartratoantimonate(III), yielding two orange yellow bands. The first eluting orange yellow band appeared to consist of one isomer because the CD patterns of all the fractions remained constant. On the other hand, the initial and final fractions of the second orange band gave different CD patterns, suggesting the presence of more than two isomers in this band. The fractions of the first orange yellow band were collected and concentrated to give crystals. Yield: 40 mg. Found: C, 16.94; H, 5.40; N, 14.67%. Calcd for $[Co(NH_3)_2(C_4H_{12}N_2)_2](ClO_4)_3$: C, 16.93; H, 5.33; N, 14.80%. The ^{1}H-NMR spectrum of the crystals in D_2O showed only one kind of methyl signal. Thus, we tentatively assigned this complex to the *trans* isomer. The chromatographic behavior that this isomer was eluted faster than did the other isomer(s) will support this assignment.[11,12]

9) trans-$[Co(NH_3)_2(S\text{-}phtn)_2](ClO_4)_3 \cdot 0.5H_2O$: This complex was prepared by the same method as that for the above *S*-bn complex. By eluting the product, the column gave five orange bands. The complex isolated from the first eluted orange band was tentatively assigned to the *trans* isomer, although no definite evidence for this structure was obtained from ^{1}H-NMR spectroscopy. Found: C, 30.82; H, 5.23; N, 11.67%. Calcd for $[Co(NH_3)_2(C_9H_{14}N_2)_2](ClO_4)_3 \cdot 0.5H_2O$: C, 30.84; H, 5.03; N, 11.99%.

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 and ^{1}H-NMR spectra with a JEOL PMX-60 spectrometer. All the solvents for optical measurements are of spectroscopic grade and used without further purification.

Results and Discussion

Figure 2 shows the absorption spectra of ptn and dppn complexes of the type, *trans*-$[CoX_2(diamine)_2]^+$ ($X = Cl^-$ or CN^-). Except the absorptions due to the phenyl group in the near ultraviolet region, the ptn and dppn complexes with the same X ligand show the same spectral pattern. The first absorption band ($^1T_{1g} \leftarrow {}^1A_{1g}$) in an octahedral field, CoN_6^{3+} splits into two components, $^1A_{2g} + {}^1E_g \leftarrow {}^1A_{1g}$ in a tetragonal field, *trans*-$CoX_2N_4^+$. According to Yamatera's theory,[14] the ^1E_g component should have lower energy than the $^1A_{2g}$ component when the axial ligand, X is lower than the ligating N atoms in the spectrochemical series, and inversely the ^1E_g component should be at higher energy for a complex in which the X ligand has a higher position than N in the series. All the complexes studied here obey this prediction as seen in Table 1. In the present paper, the CD spectra in this region are discussed . The CD spectra in the ultraviolet region are not described, because the spectra are complicated and no significant discussion can be made at present. The absorption and CD data of all the complexes are summarized in Table 1.

For the complexes of the present type with *R*-pn, *S*-bn, and *S*-phtn, there are two possible geometrical isomers, *cis* and *trans* with respect to the alignment of the substituents. The experiments gave neither the indication for the presence of these isomers nor the information for assigning such geometrical isomerism of the complexes obtained. The structure of *trans*-$[CoCl_2(R\text{-pn})_2]Cl \cdot HCl \cdot 2H_2O$ was determined by X-ray work to have a *trans*(CH_3, CH_3) configuration.[15] On the other hand, Boucher and Bosnich[16] reported that the *trans*-$[CoCl_2(R,S\text{-ptn})_2]^+$ complex prepared by oxidizing an aqueous solution containing cobalt(II) chloride and *R,S*-ptn with air consists mainly (>95%) of the *cis*(*R,R*) isomer (C_{2h}). The stable conformer of the *R,S*-ptn chelate ring is expected to be the *chair* form with the equatorially disposed methyl groups. In the crystals, *trans*-$[CoX_2(trimethylenediamine)_2]^+$ ($X = Cl^-$ [17] and NO_3^- [18]) also have the same skeletal structure as that of the *cis*(*R,R*) isomer. The *trans*-dichloro complexes of *S*-bn and *S*-phtn were prepared from cobalt(II) chloride and the diamines by air-oxidation. The stable conformations of these diamine chelate rings will be the *chair* form. (*vide post*) Therefore, these complexes may be assigned to the *cis*(CH_3,CH_3) and *cis*(phenyl, phenyl) isomers which correspond to the *cis*(*R,R*) isomer of the *R,S*-ptn complex. The corresponding dicyano and diammine complexes which were derived from the dichloro complexes may also have the same geometrical arrangement.

(1) Complexes of Five-membered Chelate Diamines. As Fig. 3 shows, the dichloro complex of *R*-pn in methanol gives a positive and a negative CD band in the ^1E_g and $^1A_{2g}$ transitions, respectively, while the *R,R*-dpen complex in the same solvent two positive CD bands in these transitions. Other dichloro complexes of *R*-1- or *R,R*-1,2-dialkyl-substituted 1,2-diamines

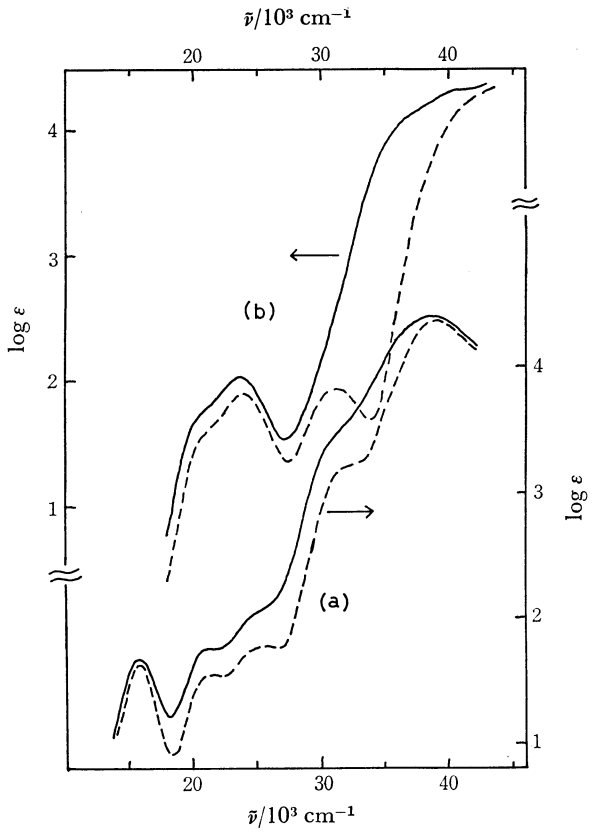

Fig. 2. Absorption spectra, (a) *trans*-$[CoCl_2(R,R\text{-ptn})_2]^+$ in methanol (— — —) and *trans*-$[CoCl_2(S,S\text{-dppn})_2]^+$ in methanol (——), (b) *trans*-$[Co(CN)_2(R,R\text{-ptn})_2]^+$ in water (— — —), and *trans*-$[Co(CN)_2(S,S\text{-dppn})_2]^+$ in methanol (——).

TABLE 1. ABSORPTION AND CD SPECTRAL DATA IN THE FIRST ABSORPTION BAND IN METHANOL

	Absorption $\tilde{\nu}/10^3$ cm^{-1} (ε)	CD $\tilde{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$)
trans-$[CoCl_2(R,R\text{-ptn})_2]$-$ClO_4$[9]	15.75 (43) 21.37 (37)	16.00 (+0.48) 20.92 (−0.58)
trans-$[CoCl_2(S,S\text{-dppn})_2]$-$Cl\cdot HCl\cdot H_2O$	15.70 (46) 21.16 (60)	15.57 (+0.70) 20.62 (−0.83)
trans-$[CoCl_2(S\text{-bn})_2]ClO_4$	15.70 (42) 21.10 (34)	15.87 (−0.04) 20.41 (−0.02)
trans-$[CoCl_2(S\text{-phtn})_2]Cl\cdot H_2O$	15.67 (47) 21.01 (46)	15.39 (−0.08) 20.62 (+0.30)
trans-$[Co(CN)_2(R,R\text{-ptn})_2]$-$ClO_4\cdot H_2O$[a]	21 (sh) 23.84 (82)	20.41 (−1.17) 24.10 (+2.44)
trans-$[Co(CN)_2(S,S\text{-dppn})_2]$-$Cl\cdot 2H_2O$	21 (sh) 23.53 (108)	20.10 (−1.69) 23.53 (+2.38)
trans-$[Co(CN)_2(S\text{-bn})_2]$-$ClO_4\cdot H_2O$[a]	21 (sh) 23.80 (78)	20.62 (+0.03) 24.10 (−0.11)
trans-$[Co(CN)_2(S\text{-phtn})_2]$-$ClO_4\cdot H_2O$	21 (sh) 23.58 (103)	20.83 (+0.14) 26.32 (−0.02)
trans-$[Co(CN)_2(R,R\text{-dpen})_2]$-$ClO_4\cdot 2H_2O$	21 (sh) 24.39 (120)	21.3 sh (+1.3) 24.00 (+1.95)

a) Solvent: water. sh: shoulder.

show the same CD patterns as that of the *R*-pn complex, and the CD pattern of the *R*-1-phenyl-1,2-ethanediamine(*R*-pen) complex is the same as that of the *R,R*-dpen complex.[19] The absolute configurations of *R,R*-dpen[20] and *R*-pen[21] have been determined

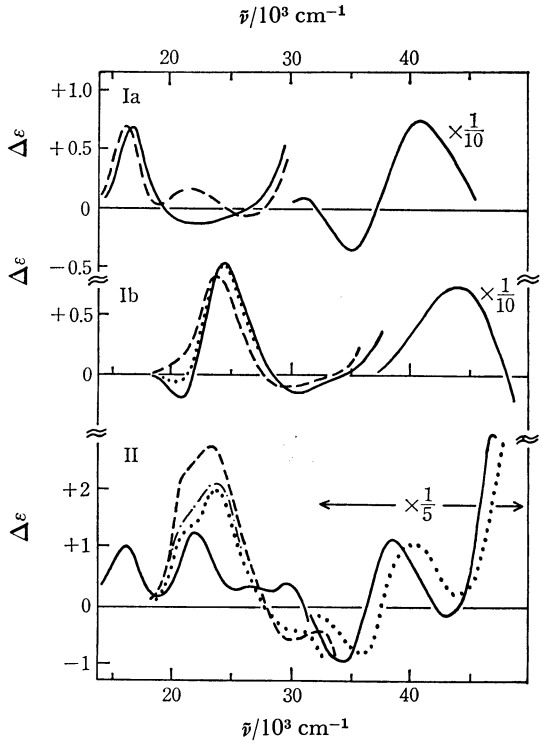

Fig. 3. CD spectra, (Ia) *trans*-$[CoCl_2(R\text{-pn})_2]^+$ in methanol (——) and in DMSO (— — —), (Ib) *trans*-$[Co(CN)_2(R\text{-pn})_2]^+$ in methanol (——), in DMF (·····), and in DMSO (— — —), (II) *trans*-$[CoCl_2(R,R\text{-dpen})_2]^+$ in methanol (——) and *trans*-$[Co(CN)_2(R,R\text{-dpen})_2]^+$ in methanol (·····), in DMF (—·—·—), and in DMSO (— — —).

by the X-ray and chemical methods, respectively, and these diamines will form chelate rings with the same λ-gauche conformation as that of *R*-pn upon coordination. Nevertheless, the *R,R*-dpen and *R*-pen complexes give the positive CD sign in the $^1A_{2g}$ band opposite to that of the *R*-pn complex. The corresponding dicyano complex of *R*-pn in methanol also exhibits a negative and a positive CD band in the $^1A_{2g}$ and ^1E_g transitions, respectively, and that of *R,R*-dpen two positive CD bands. Bosnich and Harrowfield,[1] however, found that in DMSO, the CD sign of the $^1A_{2g}$ band in *trans*-$[CoCl_2(R\text{-pn})_2]^+$ changes to positive, and the corresponding CD band of the dichloro *R,R*-dpen complex increases in the strength. The same phenomena are observed for the dicyano complexes as seen in Fig. 3. The weak negative CD band at 20410 cm^{-1} of *trans*-$[Co(CN)_2(R\text{-pn})_2]^+$ in methanol decreases its strength in *N,N*-dimethylformamide (DMF), and changes to positive sign in DMSO. The *R,R*-dpen complex shows the same trend. This fact suggests that the variations in CD sign or pattern with changes in solvent will be little related to the axial ligands in the complexes. As suggested by Bosnich and Harrowfield,[1] such solvent effect on CD spectra of the *trans*-bis(diamine) complexes may be caused by solvation of solvent molecules in chiral arrangements to the complex ions. Recently, Hawkins *et al.*[2] claimed that the solvation occurs stereoselectively at the equatorial amino hydrogens, rendering the donor nitrogens chiral. The new

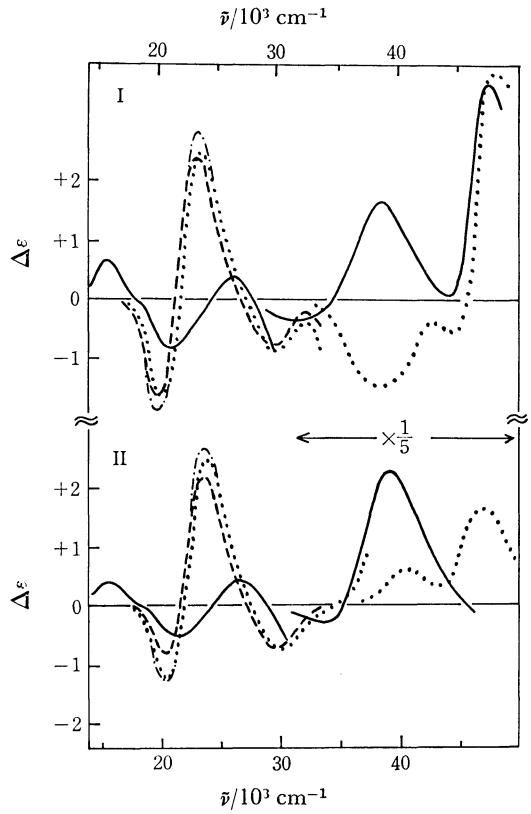

Fig. 4. CD spectra, (I) *trans*-$[CoCl_2(S,S\text{-dppn})_2]^+$ in methanol (——), and *trans*-$[Co(CN)_2(S,S\text{-dppn})_2]^+$ in methanol (·····), in DMF (—·—·—), and in DMSO (— — —). (II) *trans*-$[CoCl_2(R,R\text{-ptn})_2]^+$ in methanol (——), and *trans*-$[Co(CN)_2(R,R\text{-ptn})_2]^+$ in methanol (·····), in DMF (—·—·—), and in DMSO (— — —).

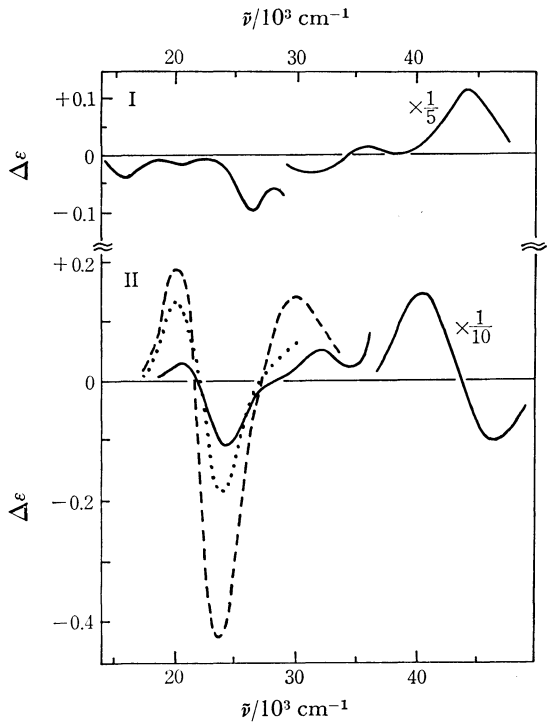

Fig. 5. CD spectra, (I) *trans*-$[CoCl_2(S\text{-bn})_2]^+$ in methanol (——), (II) *trans*-$[Co(CN)_2(S\text{-bn})_2]^+$ in water (——), in DMF (·····), and in DMSO (----).

chiral nitrogen atoms will affect the CD spectra of the diamine complexes. The dicyano complexes are probably the same case, since the variations in their CD spectra with changes in solvent quite resemble those in the CD spectra of the dichloro complexes.

(2) Dichloro and Dicyano Complexes of Six-membered Chelate Diamines. A 1,3-diamine chelate ring is known to take either the *chair* or the *skew* (δ or λ) conformation. When the chelate ring has substituent(s) attached to the skeletal carbon atom(s) of the ring, the conformation with the equatorially oriented substituent(s) will be more stable than the other. Thus the *R,R*-ptn and *S,S*-dppn chelate rings will be the most stable in the λ-*skew* conformation. The designation (*R* or *S*) of dppn which forms a chelate ring with the same conformational chirality as that of the ptn chelate ring is opposite to that of ptn according to the sequence rule.[22] The λ-*skew* form of the *R,R*-ptn chelate ring has been confirmed by X-ray crystallographic studies on $(-)_{546}$- and $(+)_{546}$-$[Co(R,R\text{-ptn})_3]^{3+}$.[23] On the other hand, the *S*-bn and *S*-phtn chelate rings can take the equatorially disposed substituent both in the *chair* and *skew* conformations. The δ-*skew* of the former diamine and the λ-*skew* of the latter diamine have the equatorial substituent on the basis of the sequence rule. Since a diamine chelate ring in the *chair* form is achiral in the skeleton, its vicinal effect should be much weaker than that of a diamine ring in the *skew* form.

Figure 4 shows the CD spectra of the dichloro and dicyano complexes of *R,R*-ptn and *S,S*-dppn. The dichloro complexes of all the 1,3-diamines studied here are stable in methanol, but unstable in DMF and DMSO to change the CD spectra during the measurement. The CD patterns of the dichloro complexes of *R,R*-ptn and *S,S*-dppn are very similar to each other and also to that of the *R*-pn complex, indicating the λ-chirality of the chelate rings, although the negative CD bands ($\approx$21000 cm^{-1}) assignable to the $^1A_{2g}$ transition are much stronger than that of the *R*-pn complex. The positive CD bands ($\approx$16000 cm^{-1}) can be assigned to the ^1E_g transition. The sign of the $^1A_{2g}$ band of the *S,S*-dppn complex is opposite to that of the *R,R*-dpen complex which gives the $^1A_{2g}$ band with the same sign as that of the ^1E_g band. The dicyano complexes of *R,R*-ptn and *S,S*-dppn also give a similar CD pattern to each other in the region of the first absorption band. The spectra show little variations with changes in solvent. The negative ($\approx$20000 cm^{-1}) and positive ($\approx$24000 cm^{-1}) CD bands can be assigned to the $^1A_{2g}$ and ^1E_g transitions, respectively, and these signs coincide with those of the corresponding CD bands of the dichloro complexes.

On the other hand, the dichloro complexes of *S*-bn and *S*-phtn give quite different CD spectra from each other, and from those of the *R,R*-ptn and *S,S*-dppn complexes, as seen in Figs. 5 and 6. The CD intensities of these complexes are very weak. The weakness suggests that the predominant conformations of the *S*-bn and *S*-phtn chelate rings are in the *chair* form. The CD pattern of the *S*-bn complex, however, is nearly enantiomeric to that of the *R*-pn complex in

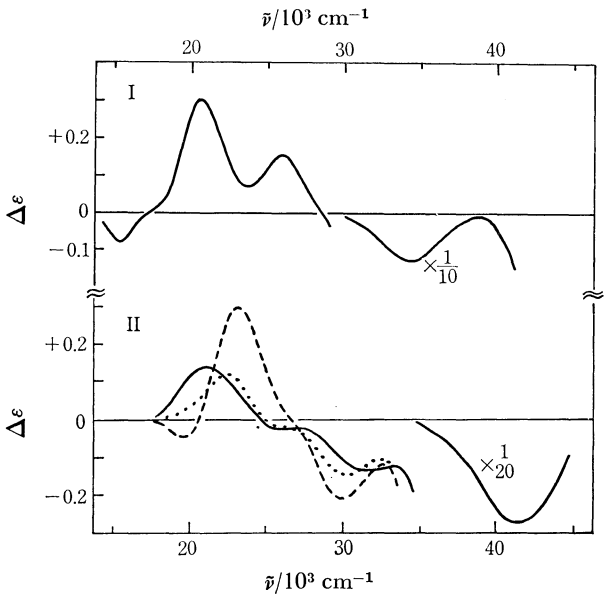

Fig. 6. CD spectra, (I) *trans*-$[CoCl_2(S\text{-phtn})_2]^+$ in methanol (——), (II) *trans*-$[Co(CN)_2(S\text{-phtn})_2]^+$ in water (——), in DMF (·····), and in DMSO (— — —).

DMSO. Hence the *S*-bn chelate ring will be in equilibrium between the *chair* and *δ-skew* forms in solution, the former being predominant. As stated previously, the *S*-bn chelate ring can have the equatorial methyl group in both the *δ-skew* and the *chair* conformations. The CD pattern of the *S*-phtn complex is nearly enantiomeric to that of the *S,S*-dppn complex, although the positive CD band at 20620 cm^{-1} ($^1A_{2g}$) is strong relative to the negative one at 15390 cm^{-1} (^1E_g). Such a pattern suggests the *δ-skew* conformation for the *S*-phtn chelate ring. This suggestion, however, is very unlikely, because the big phenyl group disposed axially interacts strongly with the apical ligand, Cl^-. The absolute configuration of *S*-phtn was confirmed by preparing an authentic sample from (*S*)-3-amino-3-phenyl propionic acid of known absolute configuration.[24] The reason for the anomalous CD of the *S*-phtn complex remains unknown. The vicinal effect of the asymmetric carbon atom, which has never been made clear but recognized to be weak, may appear on CD spectra explicitly to vary CD patterns of weak intensity.

The dicyano complexes of *S*-bn and *S*-phtn in water also show weak CD in the region of the first absorption band, indicating that the predominant conformations of these diamine chelate rings are the *chair* form. However, the CD patterns of the *S*-bn and the *R,R*-ptn complexes are nearly enantiomeric to each other, and it is concluded that the chelate rings will be in equilibrium between the *chair* and *δ-skew* conformations. The *S*-phtn complex gives again an anomalous pattern of only one CD band, although the positive sign of the band indicates the *λ-skew* conformation which is expected for the *S*-phtn chelate ring. The CD patterns of the *S*-bn complex in DMF and DMSO are the same as that in methanol, but the CD strengths increase to a large extent. Such variations in CD may be attributed to that the conformational equilibrium between the two forms, *chair* and *δ-skew* shifts toward the latter in these solvents. The *S*-phtn complex decreases the CD strength of smaller wave number side of the band in DMF, and exhibits a negative CD band in DMSO. The pattern in DMSO resembles that of the *S,S*-dppn complex, and suggests that the stability of the *λ-skew* conformer increases in such organic solvents.

The variations in CD for the dicyano complexes with changes in solvent seem to depend on the kind of diamines. In general, six-membered chelate rings formed with 1,3-diamines will be more flexible than five-membered ones with 1,2-diamines. Therefore, if the conformational change of a chelate ring is responsible for such variations in CD, the spectra of 1,3-diamine complexes should vary more remarkably than those of 1,2-diamine complexes. The dicyano complexes of *S*-bn and *S*-phtn will be this case. As stated previously, these chelate rings can have two stable conformations, the *chair* and the *skew* forms. The energy difference between these conformers has been calculated to be very small, the *chair* form being a little more stable than the other.[25] Hence, the relative stability of these conformers will be affected by many factors involving interactions with solvent molecules. The solvent dependence of the CD of the dicyano complexes of *S*-bn and *S*-phtn may be caused by such conformational changes of the chelate rings. In fact, the complexes of *R,R*-ptn and *S,S*-dppn which are expected to form less flexible six-membered chelate rings than those diamines show little solvent dependence in the CD spectra.

However, the solvent dependence of the *R,R*-ptn and *S,S*-dppn complexes seems to be even smaller than that of the complexes of 1,2-diamines, *R*-pn and *R,R*-dpen, although the chelate rings of the former 1,3-diamines may be more flexible than those of the latter 1,2-diamines. As suggested by Hawkins *et al.*,[2] if the variation in CD is caused by the stereoselective solvation of solvent molecules at the equatorial amino-hydrogens of diamines, the little solvent dependence of the *R,R*-ptn and *S,S*-dppn complexes indicates the followings; weak solvation, no stereoselective solvation, or weak contribution of new chiral nitrogen atoms introduced by stereoselective solvation to the CD. Details are not clear at present. However, molecular models indicate that in a *trans*-bis(1,3-diamine) complex, the distance between two equatorial amino-hydrogens in the *cis*-positions from each diamine chelate becomes much shorter than that in the corresponding 1,2-diamine complex. The crowded structure resulted from the shortening of distance between these hydrogen atoms may prevent them from strong interactions with solvent molecules. The little solvent dependence in the CD spectra of the *R,R*-ptn and *S,S*-dppn complexes may be interpreted by such a weak solvation effect.

(3) Diammine Complexes of Six-membered Chelate Diamines. Figures 7 and 8 show the CD spectra of diamine complexes of *R,R*-ptn and *S,S*-dppn, and *S*-bn and *S*-phtn, respectively. The *S,S*-dppn and *S*-phtn complexes were only stable in acidic solution, so that all

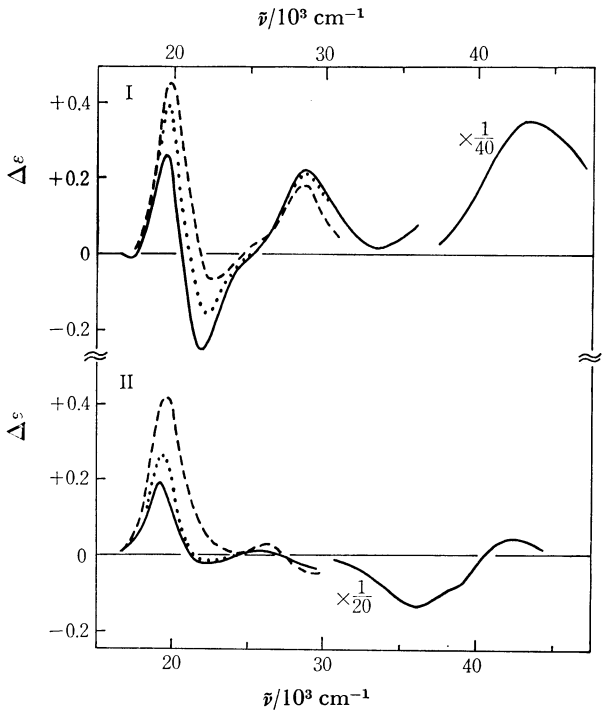

Fig. 7. CD spectra, (I) *trans*-[$Co(NH_3)_2$(*R*,*R*-ptn)$_2$]$^{3+}$ in water (——), in DMF (·····), and in DMSO (- - - -). (II) *trans*-[$Co(NH_3)_2$(*S*,*S*-dppn)$_2$]$^{3+}$ in methanol (——) in DMF (·····), and in DMSO (- - - -).

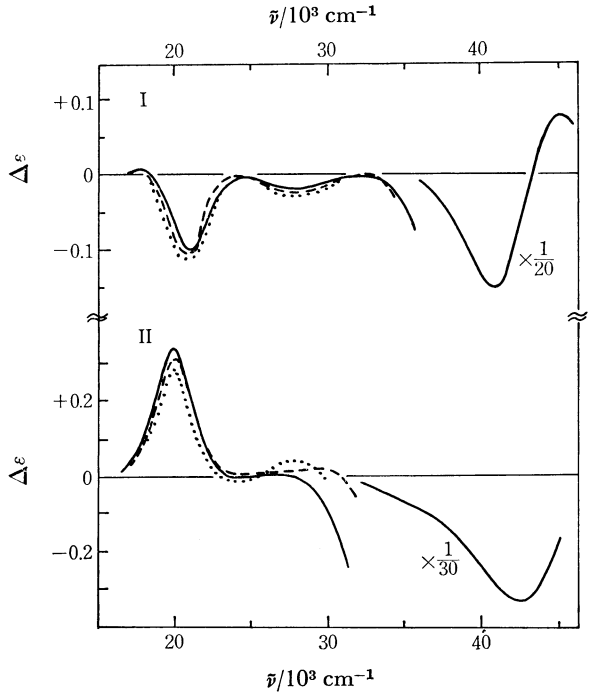

Fig. 8. CD spectra, (I) *trans*-[$Co(NH_3)_2$(*S*-bn)$_2$]$^{3+}$ in water (——), in DMF (·····), and in DMSO (- - - -). (II) *trans*-[$Co(NH_3)_2$(*S*-phtn)$_2$]$^{3+}$ in water (——), in DMF (·····), and in DMSO (- - - -).

the solutions were acidified with perchloric acid. The signs of the main CD bands or the patterns of CD spectra in the region of the first absorption band of these complexes suggest the *skew* conformation of the chirality expected from the equatorial preference of the substituent for the chelate rings, as stated previously. The CD strength of the *S*-bn complex is smaller than those of the other diamine complexes, indicating that the chelate rings are in equilibrium between the *chair* and the *δ-skew* conformations. In contrast to the cases of the *trans*-dicyano complexes, the CD spectra of the *S*-bn and *S*-phtn complexes show little solvent dependence, while those of the *R*,*R*-ptn and *S*,*S*-dppn complexes change the strength fairly remarkably with changes in solvent. Hawkins *et al.*[2] measured the CD spectra of *trans*-[$Co(NH_3)_2$(*R*-pn)$_2$]$^{3+}$ in various solvents and concluded that for such a tri-positive complex ion, ion-association with its counter anions is more important for the solvent dependence in CD rather than the stereoselective solvation as seen in the dichloro complexes. The *R*,*R*-ptn and *S*,*S*-dppn complexes increase the strengths of the positive CD components in DMF and DMSO compared with those in water or methanol. Since the vicinal effect due to a chiral chelate ring in the *λ*-conformation is known to exhibit positive CD in the region of the first absorption band, these rings may be more stabilized in the *λ-skew* form by ion-association in the former solvents.[13] The ion-association should be facilitated in organic solvents compared with that in water. However, the *S*-bn and *S*-phtn complexes show little solvent dependence, as seen in Fig. 8. Neither the ion-association nor the stereoselective solvation appears to operate in the CD spectra of these complexes. These systems should not be greatly different from those of *R*,*R*-ptn and *S*,*S*-dppn. The reason why these complexes show little solvent dependence is unknown at present.

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