

Preparation of Optically Active 1,3-Diphenyl-1,3-propanediamine (dppn) and the Circular Dichroism of *trans*-[CoCl₂-(*S,S*-dppn)₂]⁺ and [Co(*S,S*-dppn)₃]³⁺ *

Sumio ARAKAWA, Kazuo KASHIWABARA,** Junnosuke FUJITA,** and Kazuo SAITO

Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980

**Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

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1,3-Diphenyl-1,3-propanediamine (dppn) was prepared from 1,3-diphenyl-2-propen-1-one. The meso and racemic isomers were isolated. The racemate was resolved into enantiomers with (+)-*D*-di-*O*-benzoyltartrate. The absolute configuration of the free diamine was determined by comparing the circular dichroism (CD) spectrum of *trans*-[CoCl₂(*S,S*- or *R,R*-dppn)₂]⁺ with that of *trans*-[CoCl₂(*R,R*-2,4-pentanediamine)₂]⁺. The absolute configurations of *Δ*- and *Λ*-[Co(*S,S*-dppn)₃]³⁺ were also assigned on the basis of the CD spectra.

Recently, several groups have reported the stereochemistry and circular dichroism (CD) of cobalt(III) complexes containing 2,4-pentanediamine (ptn) which forms a six-membered chelate ring upon coordination.¹⁻⁴ Among possible conformations of coordinated ptn, the chair and skew forms are energetically preferred as indicated by conformational energy calculation.⁵ X-Ray crystallographic studies confirm the skew form of coordinated (*R,R*)-ptn in (−)₅₄₆[−] and (+)₅₄₆[−][Co(*R,R*-ptn)₃]³⁺ and the chair form of (*R,S*)-ptn in (+)₅₁₀[−][Co(ox)(*R,S*-ptn)₂]ClO₄·H₂O (ox=oxalate).⁷ The chair form of coordinated trimethylenediamine (tn) was found in (−)₅₈₉[−][Co(tn)₃]³⁺.⁸ These results indicate that chelated 1,3-diamines can take a variety of conformations in the solid state.

An equilibrium among these conformations of 1,3-diamines will be expected in solution. We have pointed out in a previous paper that the CD spectra of *Δ*-[Co(*R,R*-ptn)₃]³⁺ and *cis-Δ*-[Co(NH₃)₂(*R,R*-ptn)₂]³⁺ in the first absorption band region show a remarkable variation on the addition of electrolytes such as chloride and sulfate, and that the variation is accounted for the conformational change of the flexible (*R,R*)-ptn ligands.⁹ Such a conformational stability of coordinated 1,3-diamines will differ depending on the kind of substituent on the six-membered chelate ring. In order to investigate the effect of substituent on the conformation of a chelate ring, we have prepared optically active 1,3-diphenyl-1,3-propanediamine (dppn) which forms a six-membered chelate ring with two phenyl groups on the asymmetric carbons. This paper will report the preparation of dppn as well as the CD spectra of *trans*-[CoCl₂(*S,S*-dppn)₂]⁺ and *Δ*- and *Λ*-[Co(*S,S*-dppn)₃]³⁺.

Experimental

Preparation of Ligand. (1) *Racemic and meso-1,3-Diphenyl-1,3-propanediamine:* The dioxime of 1,3-diphenyl-1,3-propanediamine was prepared by modifying slightly the method of Auwers and Müller.¹⁰ An ethanol solution (95%, 1.2 dm³) of 1,3-diphenyl-2-propen-1-one (208 g) was mixed dropwise with hydroxylamine hydrochloride (183 g) in water (200 cm³), and then with potassium hydroxide (240 g) in water (200 cm³) at

50 °C. The solution was refluxed for 20 min, cooled in ice water, and filtered to remove potassium chloride. The ethanol was removed under reduced pressure in a rotary evaporator. Enough water was added to the concentrate to give white precipitate. After a day the precipitate was filtered off and dried at 70 °C and then over P₂O₅ *in vacuo*. Recrystallization from hot ethanol gave white needle-like crystals of the dioxime (160 g). Mp 207 °C (dec). Found: C; 71.12, H; 5.53, N; 11.02%. Calcd for the dioxime (C₁₅H₁₁N₂O₂): C; 70.87, H; 5.51, N; 11.02%. Recrystallization from hot benzene gave the hydroxyamino oxime. Mp 145 °C. Found: C; 70.77, H; 6.41, N; 11.27%. Calcd for the hydroxyamino oxime (C₁₅H₁₆N₂O₂): C; 70.31, H; 6.25, N; 10.94%. These compounds were identified by IR spectra.

The dioxime was reduced with metallic sodium in ethanol according to the method used for preparing 2,4-pentanediamine.^{11,12} The dioxime (80 g) was suspended in absolute ethanol (1.5 dm³) in a three necked round bottom flask (3 dm³) equipped with a large reflux condenser. Small pieces (5–8 cm³) of metallic sodium (300 g) were added in portions to the suspension, to which was added additional amount of absolute ethanol from time to time. The mixture was allowed to stand for 30 min. Aqueous ethanol was added carefully to hydrolyze excess of sodium in the mixture and then 1 dm³ of water was added. Ethanol was removed by evaporation. The aqueous solution was shaken with diethyl ether and ether layer was washed with water several times. Hydrogen chloride was bubbled into the ether solution to give white precipitate, which was filtered off and dried in air. Yield 70 g. Found: C; 56.78, H; 6.99, N; 8.83%. Calcd for 1,3-diphenyl-1,3-propanediamine dihydrochloride monohydrate (C₁₅H₂₂N₂OCl₂): C; 57.00, H; 6.70, N; 8.49%. This diamine is a mixture of meso(*R,S*) and racemic(*R,R* and *S,S*) isomers.

(2) *Separation of the meso- and dl-1,3-Diphenyl-1,3-propanediamine Dihydrochloride: Method 1).* The purified mixture of meso and racemic dihydrochloride (140 g) was suspended in boiling ethanol (400 cm³) containing concd hydrochloric acid (20 cm³). The suspension was stirred for 30 min and filtered in hot to remove a small amount of residue. White crystals were obtained on cooling the filtrate to room temperature. Both the products (residue and crystals) are the pure meso dihydrochloride. The PMR spectrum is shown in Fig. 1.

The filtrate was concentrated to 100 cm³ and cooled to room temperature. White crystals (28 g) of the racemic dihydrochloride, contaminated by a small amount of the meso isomer, were filtered off. They were dissolved again in boiling ethanol (400 cm³) and mixed with concd hydrochloric acid (10 cm³). The solution was concentrated to 100 cm³ to yield white crystals (9 g), which were filtered off. The pure racemic dihydrochloride (18 g) was obtained by evaporating the fil-

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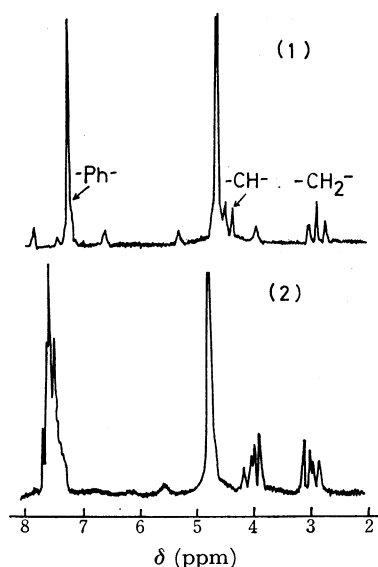


Fig. 1. PMR spectra of (1) *meso*-dppn·2HCl and (2) *dl*-dppn·2HCl in D₂O (60 MHz).

trate to almost dryness and by the addition of acetone. The PMR spectrum is shown in Fig. 1. The two isomers, *meso* and *racemic*, can be distinguished by the PMR spectra. Found for the *meso* isomer: C; 60.08, H; 6.99, N; 9.31%. Found for the *racemic* isomer: C; 59.58, H; 6.93, N; 9.22%. Calcd for 1,3-diphenyl-1,3-propanediamine dihydrochloride (C₁₅H₂₀N₂Cl₂): C; 60.21, H; 6.74, N; 9.36%.

Method 2. Sodium hydroxide (30 g) in water (50 cm³) was added dropwise to a mixture of *meso*- and *dl*-dppn dihydrochloride (8.3 g) in cold water (50 cm³). The released dppn, insoluble in water, was extracted with chloroform (100 cm³). After removal of chloroform under reduced pressure, the oily residue was dissolved in ethanol (100 cm³). To the ethanol solution was added dropwise (+)-*D*-tartaric acid (8.3 g) in water (100 cm³). White crystals were obtained on cooling the solution in a refrigerator overnight. The crystals are *meso*-dppn (+)-*D*-tartrate. No crystal was obtained from the concentrated filtrate. The oily residue is *dl*-dppn (+)-*D*-tartrate. These isomers were identified by comparison with those prepared by method 1.

(3) **Resolution of *dl*-1,3-Diphenyl-1,3-propanediamine:** Potassium hydroxide (20 g) in water (20 cm³) was added dropwise to a cold aqueous solution (50 cm³) of *dl*-dppn dihydrochloride (9.2 g). The released dppn was extracted with chloroform (100 cm³), which was evaporated off and the oily residue was dissolved in methanol (40 cm³). The methanol solution was mixed with a methanol solution (40 cm³) of (+)-*D*-di-*O*-benzoyltartaric acid (10.7 g), and then with diethyl ether. The solution was allowed to stand overnight at room temperature. The precipitated white crystals were filtered off and washed with a mixture of methanol and diethyl ether (1:1) and then with diethyl ether. Recrystallization from methanol by the addition of diethyl ether gave white crystals (7.8 g), [α]_D = -52.1° (c: 0.0048 g in 100 cm³ of a mixture of ethanol and water (1:1)). This rotation did not change with further recrystallization. The absolute configuration of dppn in the less soluble diastereomer was assigned to the (*S,S*) configuration as described later.

Preparation of the Complexes. (1) *trans*-[CoCl₂(*S,S*-dppn)₂]·Cl·HCl·H₂O: Sodium hydroxide (15 g) in water (20 cm³) was added dropwise to a suspension of (-)-*D*-dppn-di-*O*-benzoyltartrate (6 g) in cold water (50 cm³). The released dppn was extracted with chloroform (100 cm³). The chloroform was

removed under reduced pressure, and methanol (25 cm³) was added to the residue. The methanol solution was added dropwise with stirring to a mixture (60 cm³) of water and ethanol (2:1) containing Na₃[Co(NO₂)₆] (2 g). The total volume of the solution was adjusted to 200 cm³ with methanol. The solution was allowed to stand at 50 °C for 5 h. Hydrogen chloride was bubbled into the solution for 30 min until the color changed from orange to brown. The solution was kept in an evaporating dish at 50 °C with the addition of concd hydrochloric acid and methanol from time to time. The precipitated green solid was filtered off. Recrystallization from ethanol containing a small amount of concd hydrochloric acid gave green crystals (2 g). Found: C; 54.01, H; 5.68, N; 8.61%. Calcd for [CoCl₂(*S,S*-dppn)₂]Cl·HCl·H₂O (C₃₀H₃₉N₄OCl₄Co): C; 53.59, H; 5.85, N; 8.33%. The perchlorate was obtained by adding sodium perchlorate to a methanol solution of the chloride.

(2) *trans*-[CoCl₂(*R,S*-dppn)₂]Cl·H₂O: To an aqueous solution (35 cm³) of Na₃[Co(NO₂)₆] (2.7 g) was added dropwise (*R,S*)-dppn (3 g) in ethanol (20 cm³). Yellow brown precipitate formed immediately. The suspension was stirred at 50 °C for 5 h and the yellow brown precipitate was filtered off (5.6 g), which was dissolved in methanol (1 dm³). When hydrogen chloride was bubbled for 10 min, the color changed from yellow to violet. The violet solution was concentrated in an evaporating dish to yield green precipitate, which was filtered off and washed with 4 M hydrochloric acid, then cold ethanol and diethyl ether. Yield 4 g. Found: C; 56.19, H; 6.09, N; 8.75%. Calcd for [CoCl₂(*R,S*-dppn)₂]Cl·H₂O (C₃₀H₃₉N₄OCl₃Co): C; 56.66, H; 6.02, N; 8.81%.

(3) [Co(*S,S*-dppn)₃]Cl₃: A dimethyl sulfoxide (DMSO) solution (25 cm³) of dppn obtained from (-)-*D*-dppn-di-*O*-benzoyltartrate (2.4 g) was added dropwise to a DMSO solution (25 cm³) of *trans*-[CoCl₂(*S,S*-dppn)₂]Cl·HCl·H₂O (1.8 g). The solution was allowed to stand at 25 °C for 7 h and then passed through a column (5 × 30 cm) of SE-Cellulose. The adsorbed band was eluted with a mixture of ethanol and water (1:1). Orange yellow eluates were cooled in a refrigerator overnight to yield orange crystals (1.2 g), which were recrystallized from warm methanol (50 cm³, 60 °C). Found: C; 57.35, H; 6.73, N; 8.39%. Calcd for [Co(*S,S*-dppn)₃]Cl₃·5.5H₂O (C₄₅H₆₅N₆O_{5.5}Cl₃Co): C; 57.29, H; 6.94, N; 8.91%. This complex has the Δ configuration as described later.

The unremoved band on the column was eluted with 0.5 M sodium perchlorate in a mixture of ethanol and water (1:1). The orange eluates were concentrated to give red orange solid, which was dissolved in a mixture of water and methanol (4:1). The solution was passed through a column (2 × 20 cm) of an SP-Sephadex C-25 ion exchanger. After washing with water, the adsorbed band was eluted with 1 M hydrochloric acid. The orange eluates were concentrated under reduced pressure to give orange crystals, which were filtered off and dried *in vacuo*. Yield 20 mg. Found: C; 57.62, H; 6.80, N; 8.42%. Calcd for [Co(*S,S*-dppn)₃]Cl₃·5.5H₂O (C₄₅H₆₅N₆O_{5.5}Cl₃Co): C; 57.29, H; 6.94, N; 8.91%. This complex has the Δ configuration as described later.

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 sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the internal standard. All the solvents for optical measurements are of spectroscopic grade and used without further purification.

Results and Discussion

1,3-Diphenyl-1,3-propanediamine (dppn) is a six-membered chelate ligand, an analogue of 1,2-diphenyl-1,2-ethanediamine (stien) which forms a five-membered chelate ring. The skeleton is the same as that of 2,4-pentanediamine (ptn) in which the substituents on the asymmetric carbons are methyl groups. Therefore, there are two aspects for the cobalt(III) complexes of dppn: the first is the comparison with the ptn complexes and the second with the stien complexes.

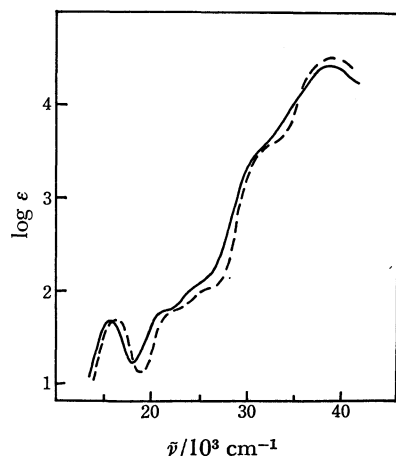


Fig. 2. Absorption spectra of $\text{trans}[\text{CoCl}_2\text{L}_2]^+$ in methanol, $\text{L}=(\text{S},\text{S})\text{-dppn}$ (—) and $(\text{S},\text{S})\text{-stien}$ (---).

TABLE 1. ABSORPTION DATA IN THE FIRST ABSORPTION BAND REGION

	$\bar{\nu}/10^3 \text{ cm}^{-1} (\epsilon)$
$\Delta\text{-}[\text{Co}(\text{S},\text{S}\text{-dppn})_3]\text{Cl}_3 \cdot 5.5\text{H}_2\text{O}$	19.76(115.5)* ²⁾
$\Delta\text{-}[\text{Co}(\text{S},\text{S}\text{-dppn})_3]\text{Cl}_3 \cdot 5.5\text{H}_2\text{O}$	20.28(84.2)* ²⁾
$\Delta\text{-}[\text{Co}(\text{R},\text{R}\text{-ptn})_3]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ ^{a)}	20.58(97.7)* ¹⁾
$\Delta\text{-}[\text{Co}(\text{R},\text{R}\text{-ptn})_3](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ ^{a)}	20.75(75.9)* ¹⁾
$\text{trans}[\text{CoCl}_2(\text{S},\text{S}\text{-dppn})_2]\text{Cl} \cdot \text{HCl} \cdot \text{H}_2\text{O}$	15.63(45.7)* ³⁾ 22(sh) ^{d)}
$\text{trans}[\text{CoCl}_2(\text{R},\text{S}\text{-dppn})_2]\text{Cl} \cdot \text{H}_2\text{O}$	15.63(49.5)* ³⁾ 22(sh)
$\text{trans}[\text{CoCl}_2(\text{R},\text{R}\text{-ptn})_2]\text{ClO}_4$ ^{a)}	15.75(42.7)* ⁴⁾ 21(sh)
$\text{trans}[\text{CoCl}_2(\text{R},\text{S}\text{-ptn})_2]\text{Cl}$ ^{a)}	15.75(39.0)* ⁴⁾ 21(sh)
$\text{trans}[\text{CoCl}_2(\text{S},\text{S}\text{-stien})_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ ^{b)}	16.50(50.1)* ³⁾ 23(sh)
$[\text{Co}(\text{NH}_3)_4(\text{S},\text{S}\text{-dppn})]\text{Br}_3 \cdot \text{H}_2\text{O}$ ^{c)}	20.83(85.4)* ²⁾
	20.88(79.0)* ¹⁾
$[\text{Co}(\text{NH}_3)_4(\text{R},\text{S}\text{-dppn})]\text{Br}_3 \cdot \text{H}_2\text{O}$ ^{c)}	20.79(88.6)* ¹⁾
$[\text{Co}(\text{NH}_3)_4(\text{R},\text{R}\text{-ptn})](\text{ClO}_4)_3$ ^{a)}	20.96(69.2)* ¹⁾
$[\text{Co}(\text{NH}_3)_4(\text{S},\text{S}\text{-stien})](\text{ClO}_4)_3 \cdot 4\text{H}_2\text{O}$ ^{c)}	21.19(91.1)* ²⁾
	21.28(83.3)* ¹⁾

*Solvent: 1) water, 2) DMSO, 3) methanol, 4) ethanol.

a) Ref. 1. b) Ref. 19. c) The preparation for these complexes will be reported elsewhere. d) sh=shoulder.

Absorption Spectra. In Fig. 2, the absorption spectra of $\text{trans}[\text{CoCl}_2(\text{S},\text{S}\text{-dppn})_2]^+$ and $\text{trans}[\text{CoCl}_2(\text{S},\text{S}\text{-stien})_2]^+$ are compared in methanol. The absorption data are summarized in Table 1. We should point out some features of six-membered chelate rings from these

data. (1) Red shift is observed for the complexes with six-membered chelate rings as compared with those containing five-membered chelate rings. This is commonly expected for complexes containing large chelate rings.¹³⁾ (2) The diastereomers, Δ - and Λ - $[\text{Co}(\text{S},\text{S}\text{-dppn})_3]^{3+}$ as well as Δ - and Λ - $[\text{Co}(\text{R},\text{R}\text{-ptn})_3]^{3+}$, give different absorption energies from each other in the first absorption band region. Such a difference is very small for the Δ - and Λ - $[\text{Co}((\text{R})\text{-propylenediamine})_3]^{3+}$ complexes.¹⁴⁾ (3) The absorption peaks of the $(\text{S},\text{S})\text{-dppn}$ complexes lie at lower energies than those of the corresponding $(\text{R},\text{R})\text{-ptn}$ complexes. Hence, the ligand field strength may be $(\text{R},\text{R})\text{-ptn} > (\text{S},\text{S})\text{-dppn}$.

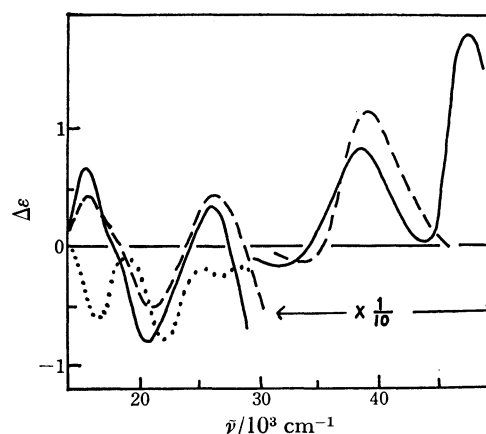


Fig. 3. CD spectra of $\text{trans}[\text{CoCl}_2\text{L}_2]^+$ in methanol, $\text{L}=(\text{S},\text{S})\text{-dppn}$ (—), $(\text{R},\text{R})\text{-ptn}$ (---), and $(\text{S},\text{S})\text{-stien}$ (.....).

Assignment of Absolute Configuration of dppn. The CD spectra of the complexes, $\text{trans}[\text{CoCl}_2\text{L}_2]^+$ in methanol are shown in Fig. 3, where L represents $(\text{S},\text{S})\text{-dppn}$, $(\text{R},\text{R})\text{-ptn}$ or $(\text{S},\text{S})\text{-stien}$. The absolute configuration of $(\text{S},\text{S})\text{-dppn}$ can be assigned by comparing the CD spectrum of the $(\text{S},\text{S})\text{-dppn}$ complex with that of the $(\text{R},\text{R})\text{-ptn}$ complex. Both spectral patterns are similar to each other in the region of 14 to $45 \times 10^3 \text{ cm}^{-1}$. It has been recognized that the optical activity of $\text{trans}[\text{CoCl}_2(\text{diamine})_2]^+$ complexes is affected strongly by the conformational contribution of the diamine and weakly by the vicinal effect of asymmetric carbons.¹⁵⁾ Hence, the conformation of the dppn seems to be the same

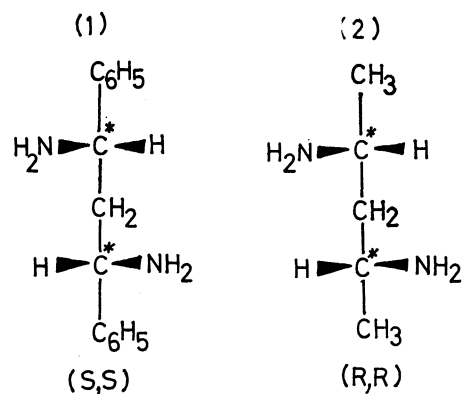


Fig. 4. Absolute configurations of $(\text{S},\text{S})\text{-dppn}$ (1) and $(\text{R},\text{R})\text{-ptn}$ (2).

λ -skew form as that of the ptn ligand, in which the two substituent groups on the asymmetric carbons adopt equatorial orientation. The λ -skew form of (*R,R*)-ptn chelate has been confirmed on (+)₅₄₆-[Co(*R,R*-ptn)₃]Cl₃·H₂O by an X-ray diffraction method.⁶⁾ According to the sequence rule,¹⁶⁾ the designation (*S,S*) of the dppn is opposite to that of the ptn to form the same λ -skew form (Fig. 4).

Circular Dichroism Spectra. Yano *et al.*¹⁵⁾ studied the CD spectra of various complexes of the type, *trans*-[CoCl₂(1,2-diamine)₂]⁺ in methanol. In the Ib(¹A_{2g}←¹A_{1g}, D_{4h}) region, cobalt(III) complexes of (*R*)-1-phenyl-1,2-ethanediamine and (*R,R*)-stien which form five-membered λ -gauche chelate rings gave a CD peak with the opposite sign to that of the corresponding (*R*)-1-alkyl- or (*R,R*)-1,2-dialkyl-1,2-diamine complexes. However, all these complexes show similar CD patterns in the charge transfer region. They ascribed the difference to the vicinal effect of the phenyl groups on the chelate. Such a discussion is not applicable to the dppn complex. The pattern of the CD spectrum of *trans*-[CoCl₂(*S,S*-dppn)₂]⁺ differs from that of the corresponding (*S,S*)-stien complex, while it resembles that of the corresponding (*R,R*)-ptn complex. The CD spectra of cobalt(III) complexes containing six-membered chelate diamines may not be appreciably affected by the presence of phenyl groups on the asymmetric carbons.

Figure 5 shows the absorption and CD spectra of the two diastereomers (named I and II) of [Co(*S,S*-dppn)₃]Cl₃ in DMSO. The CD spectrum of the isomer II which is eluted later from an SE-Cellulose column gives a weak minus peak at $18.2 \times 10^3 \text{ cm}^{-1}$ ($\Delta\epsilon = -0.58$) and a strong plus peak at $20.2 \times 10^3 \text{ cm}^{-1}$ ($\Delta\epsilon = +2.75$) in the first absorption band region. This pattern is similar to that of Δ -[Co(*R,R*-ptn)₃](ClO₄)₃ in DMSO (Fig. 6).⁹⁾ The CD spectrum of the isomer I which is eluted earlier from an SE-Cellulose column is similar to that of Δ -[Co(*R,R*-ptn)₃](ClO₄)₃ in water. Thus, we assigned

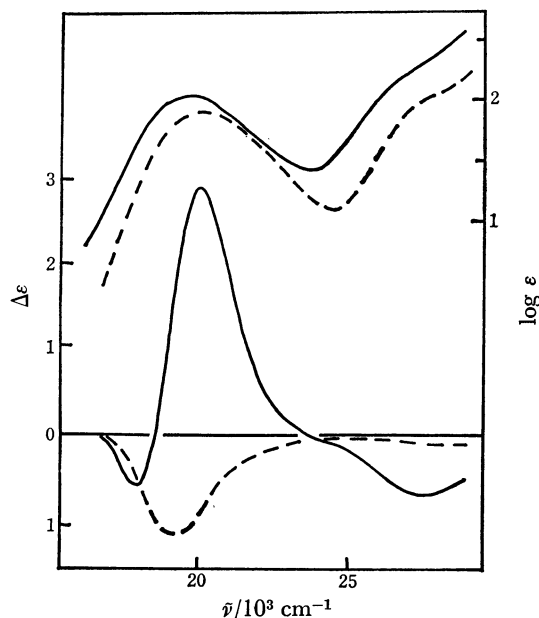


Fig. 5. Absorption and CD spectra of the diastereomers of [Co(*S,S*-dppn)₃]Cl₃ in DMSO, I(—) and II(---).

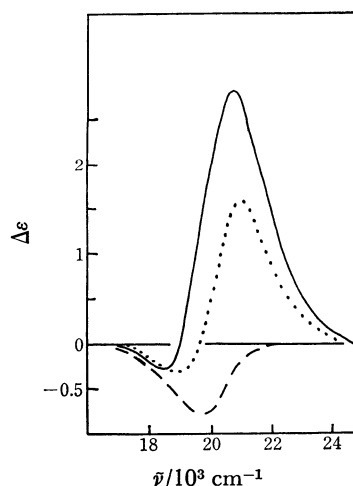


Fig. 6. CD spectra of Δ -[Co(*R,R*-ptn)₃](ClO₄)₃ in DMSO (—), Δ -[Co(*R,R*-ptn)₃](ClO₄)₃·3H₂O in water(---) and Δ -[Co(*R,R*-ptn)₃]Br₃ in DMSO (.....).⁹⁾

II to Δ and I to Δ isomer. However, the spectrum of I is very different from that of Δ -[Co(*R,R*-ptn)₃]Br₃ in DMSO (Fig. 6). In a previous paper,⁹⁾ we have shown that the CD spectrum of Δ -[Co(*R,R*-ptn)₃]³⁺ shows a remarkable variation in the first absorption band region in the presence of various electrolytes and in various solvents. There must be similar variations for the corresponding dppn complexes because of the flexible six-membered chelate rings. Detailed discussion for this system cannot be made unless the solvent effect is investigated. However, the solubility restriction of [Co(*S,S*-dppn)₃]Cl₃ makes us difficult to investigate the solvent effect.

The assignment of the absolute configuration of the [Co(*S,S*-dppn)₃]Cl₃ complex will be also supported by the formation ratio of the diastereomers. When the (*S,S*)-dppn takes a λ -skew form upon coordination, a tris complex can give two diastereomers, $\Delta(\lambda\lambda\lambda)$ and $\Delta(\lambda\lambda\lambda)$. It has been known that the former complex in which the two asymmetric carbons of (*S,S*)-dppn lie oblique to the C₃ axis of the complex ion is less stable than the latter. The reason is believed to be due to large steric interactions among chelate rings in the former complex.^{5,17)} In fact, the formation ratio of the *lel*₃- $\Delta(\lambda\lambda\lambda)$ isomer to the *ob*₃- $\Delta(\lambda\lambda\lambda)$ isomer is *ca.* 10 for tris(*R,R*-ptn)cobalt(III) complexes.¹⁾ The tris(*S,S*-dppn)cobalt(III) complex gives always a large amount of the $\Delta(\lambda\lambda\lambda)$ isomer as described in the Experimental section.

Figure 7 shows the configurational and the vicinal effect curves derived from the CD spectra of Δ - and Δ -[Co(*S,S*-dppn)₃]Cl₃ in DMSO. The CD spectrum of [Co(NH₃)₄(*S,S*-dppn)]Br₃¹⁸⁾ in water is also shown. Although the additivity on CD curves is only an empirical rule, it may be useful to compare the difference between six-membered and five-membered chelate ligands. The additivity of the vicinal (conformational) contribution holds satisfactorily for a variety of five-membered chelate ring systems.^{14,19)} This is not the case for the present dppn system. The spectral pattern of the calculated vicinal effect curve of (*S,S*)-dppn in

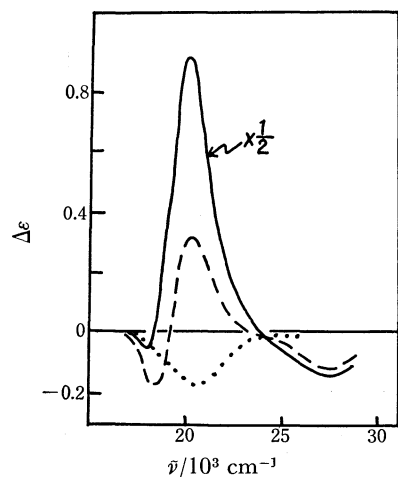


Fig. 7. The configurational (—) and the vicinal(---) contribution in the CD calculated from the spectra of the two diastereomers of $[\text{Co}(\text{S},\text{S-dppn})_3]\text{Cl}_3$ in DMSO, and the CD spectra of $[\text{Co}(\text{NH}_3)_4(\text{S},\text{S-dppn})]\text{Br}_3$ in water(.....).

$[\text{Co}(\text{S},\text{S-dppn})_3]^{3+}$ resembles that derived from the two diastereomers of $[\text{Co}(\text{S},\text{S-dppn})(\text{en})_2]^{3+}$ in water,¹⁸⁾ but differs completely from that of $[\text{Co}(\text{NH}_3)_4(\text{S},\text{S-dppn})]^{3+}$ in water. Interligand steric interactions in $[\text{Co}(\text{S},\text{S-dppn})_3]^{3+}$ must be larger than those in the tetraammine complex of dppn. The most stable conformation of each bulky and flexible six-membered chelate ring in these complexes might be somewhat different from each other.

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