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Metal Complexes Containing Six-Membered Chelate Rings. II. Preparation and Structure of 2,4-Pentanediamine Complexes of Cobalt(III)

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New cobalt(III) complexes containing optically active (*RR* and *SS*) and *meso*(*RS*) 2,4-pentanediamine (2,4-ptn) have been synthesized. $[Co(RR\text{-}2,4\text{-ptn})_3]^{3+}$ gives two diastereoisomers, prismatic crystals with $(-)_{546}$ rotation and needle-like crystals with $(+)_{546}$ rotation. The former is produced much more than the latter. The conformations of the *RR*- (or *SS*-) and *RS*-2,4-pentanediamine chelate of the complexes were assigned to λ- (or δ-) twist and chair form, respectively, from comparison of their PMR spectra with those of the corresponding tetraacetato complexes. $[Co(RS\text{-}2,4\text{-ptn})_3]^{3+}$ seems to have *fac* structure with respect to the coordination of the amino groups adjacent to the *R*- and *S*-carbon atoms. The circular dichroism spectra of mono and *trans*-bis-(*RR*-2,4-ptn) complexes in the first band region are essentially the same as those of the corresponding *R*-propylenediamine complexes. The circular dichroism spectra of $(+)_{546}$- and $(-)_{546}$-$[Co(RR\text{-}2,4\text{-ptn})_3]^{3+}$ and $(-)_{546}$-$[Co(RS\text{-}2,4\text{-ptn})_3]^{3+}$ are very different from those of the triscobalt(III) complexes of *R*-propylenediamine and trimethylenediamine. Such differences have been discussed with reference to the stereochemistry of six-membered chelate complexes.

The stereospecificity of complex formation from metal ions and ligands has been elucidated mostly in terms of a specific conformation of the ligand and the repulsive interaction between non-bonded atoms of the coordinated ligands. Most of such studies, however, have been made on metal complexes containing five-membered chelates such as α-diamines or α-aminoacids. It is, therefore, of great interest to investigate whether a similar specificity is seen in metal complexes containing six-membered chelates. In the previous paper,[1] we reported that the formation of cobalt(III) complexes of *RR*- (or *SS*-) and *RS*-2,4-pentanediaminetetraacetate was stereospecific to give a sexadentate Δ-type (or Λ-type) and a quinquedentate complex, respectively. The tendency of the methyl groups on the carbon atoms to take equatorial orientation was thus demonstrated to be very strong in these puckered six-membered rings as well as in the five-membered rings. This paper deals with preparation and stereochemistry of cobalt(III) complexes containing six-membered β-diamines, optically active and *meso*-2,4-pentanediamine (2,4-ptn), which are expected to have a preferred, non-convertible conformation upon coordination.

Circular dichroism (CD) study provides useful information on the absolute configuration of metal complex and the conformation of chelated ligands. However, the work on metal complexes of β-diamines is limited to those of trimethylenediamine(tn),[2-6] in contrast to the extensive work on α-diamine complexes. Furthermore, these trimethylenediamine complexes are known to exhibit CD curves considerably different from those of the corresponding α-diamine complexes in the region of the first absorption band. Thus, the CD data reported in this paper on 2,4-pentanediamine complexes of cobalt(III) will give valuable information for elucidating the origin of optical activity of metal complexes as well as the conformation of six-membered chelate rings.

Experimental

RR-, SS-, *and* RS-*2,4-pentanediamine.* These isomers of 2,4-pentanediamine were obtained by the method reported previouly.[1]

trans-Dinitro- and -dichloro-bis(2,4-pentanediamine)cobalt(III) complexes were prepared by modifying the method of

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[1] F. Mizukami, H. Ito, J. Fujita, and K. Saito, This Bulletin, **44**, 3051 (1971).

[2] F. Woldbye, *Record of Chemical Progress*, **24**, 197 (1963).

[3] P. G. Beddoe and S. F. Mason, *Inorg. Nucl. Chem. Lett.*, **4**, 433 (1968).

[4] J. R. Gollogly and C. J. Hawkins, *Chem. Commun.*, **1968**, 689.

[5] R. R. Judkins and D. J. Royer, *Inorg. Nucl. Chem. Lett.*, **6**, 305 (1970).

[6] H. Kawaguchi and S. Kawaguchi, This Bulletin, **43**, 2103 (1970).

Dippel.(7)

trans-$[Co(NO_2)_2($*RR- or SS-ptn*$)_2]ClO_4$. An aqueous solution containing 11.5 g of $Na_3[Co(NO_2)_6]$(8) and 5.8 g of *RR-* or *SS-*2,4-pentanediamine in 40 m*l* of water was heated at 60—70°C for 5 hr, and filtered. To the filtrate was added a large excess of sodium perchlorate. Yellow flakes were precipitated, filtered off, washed with a small amount of cold water and dried over phosphorus pentoxide under reduced pressure.

Found: C, 26.55; H, 6.26; N, 18.58%. Calcd for $C_{10}H_{28}N_6O_8CoCl$: C, 26.41; H, 6.21; N, 18.48%.

trans-$[CoCl_2($*RR- or SS-2,4-ptn*$)_2]ClO_4$. Twelve grams of *trans*-$[Co(NO_2)_2($*RR-* or *SS-*ptn$)_2]ClO_4$ was dissolved in 100 m*l* of 6N hydrochloric acid by heating at 65—70°C for 10 hr with occasional stirring. To the resultant green solution was added 100 m*l* of 60% perchloric acid. Upon cooling at 5°C, green crystals were precipitated, filtered off, washed with a small amount of cold water and dried over phosphorus pentoxide under reduced pressure.

Found: C, 27.70; H, 6.56; N, 13.24%. Calcd for $C_{10}H_{28}N_4O_4CoCl_3$: C, 27.70; H, 6.51; N, 12.92%.

trans-$[CoCl_2($*RS-2,4-ptn*$)_2]Cl$. This complex was prepared from cobalt(II) chloride-hexahydrate and *RS*-2,4-pentanediamine by air oxidation according to Dippel's method.(7)

Found: C, 32.16; H, 7.70; N, 14.97%. Calcd for $C_{10}H_{28}N_4CoCl_3$: C, 32.49; H, 7.64; N, 15.16%.

trans-$[CoBr_2($*RR- or SS-2,4-ptn*$)_2]ClO_4$. To an aqueous solution of 1 g of *trans*-$[CoCl_2($*RR-* or *SS-*2,4-ptn$)_2]ClO_4$ in 25 m*l* of water was added 1 g of silver perchlorate. The solution was stirred for 3 hr at room temperature, and then filtered to remove the silver chloride. The filtrate was treated with 10 m*l* of 47% hydrobromic acid and evaporated to about 8 m*l* in a vacuum desiccator over potassium hydroxide. Yellowish green crystals were filtered off, washed with cold ethanol and recrystallized from hot ethanol.

Found: C, 23.48; H, 5.56; N, 10.78%. Calcd for $C_{10}H_{28}N_4O_4Br_2CoCl$: C, 22.98; H, 5.40; N, 10.72%.

trans(Br-Br)-$[CoBr_2(NH_3)_2($*RR- or SS-2,4-ptn*$)]Br\cdot H_2O$. A suspension of $NH_4[Co(SO_3)_2(NH_3)_4]$(9) in 10% aqueous solution of *RR-* or *SS-*2,4-pentanediamine (1: 1 mole ratio) was heated at 80°C for 2 hr with stirring and cooled to room temperature. To the dark brown solution was added a large amount of methanol. After a while, the solution was filtered. An oily product was precipitated by adding ether to the filtrate and separated from the supernatant. A yellow complex was obtained as powder by treating the oily product with an appropriate amount of ethanol, filtering off, washing with ethanol and air-drying. This complex which was believed to be crude $NH_4[Co(SO_3)_2(NH_3)_2($*RR-* or *SS-*2,4-ptn$)]$, was dissolved in a small amount of 47% hydrobromic acid and the solution was warmed at 35—40°C for 2 hr to give yellowish green crystals. After a while, the crystals were filtered off, washed with ethanol and recrystallized from methanol by adding ether.

Found: C, 12.86; H, 4.74; N, 12.47%. Calcd for $C_5H_{22}N_4OCoBr_3$: C, 13.26; H, 4.90; N, 12.37%.

$[Co(NH_3)_4($*RR- or SS-2,4-ptn*$)](ClO_4)_3$. This complex was synthesized according to a similar method to that for the corresponding *R*-propylenediamine complex by Hawkins *et al.*(10)

Liquid ammonia was poured onto *trans*(Br-Br)-$[CoBr_2(NH_3)_2($*RR-* or *SS-*ptn$)]Br\cdot H_2O$ to give an orange solution. Orange powder which remained after the ammonia had evaporated, was dissolved in a minimum amount of hot water, and the solution was cooled to room temperature and filtered. To the filtrate was added an appropriate amount of 60% perchloric acid. Upon cooling at 0°C, orange crystals were precipitated and filtered off. The crystals were dissolved in a minimum amount of water and concentrated in a vacuum desiccator over sodium hydroxide. Deposited orange crystals were filtered off, washed with ethanol and air-dried.

Found: C, 11.11; H, 5.20; N, 15.72%. Calcd for $C_5H_{26}N_6O_{12}CoCl_3$: C, 11.38; H, 4.97; N, 15.93%.

$[Co(NH_3)_4($*RS-2,4-ptn*$)](ClO_4)_3\cdot H_2O$, $[Co(NH_3)_4(tn)]Br\cdot H_2O$ *and* $[Co(NH_3)_4($*d,l-1,3-btn*$)]Br_3$.(11) These complexes were prepared from $NH_4[Co(SO_3)_2(NH_3)_4]$ and *RS*-2,4-ptn, tn, or *d,l*-1,3-btn by a similar method to that for the corresponding *RR-* or *SS-*2,4-ptn complex described above. The complexes of tn and *d,l*-1,3-btn were obtained as bromide by use of 47% hydrobromic acid instead of 60% perchloric acid.

Found: C, 11.10; H, 5.01; N, 15.36%. Calcd for $C_5H_{28}N_6O_{13}CoCl_3$: C, 11.01; H, 5.17; N, 15.40%.

Found: C, 7.80; H, 4.86; N, 17.89%. Calcd for $C_3H_{24}N_6O_{13}Br_3Co$: C, 7.85; H, 5.27; N, 18.31%.

Found: C, 10.84; H, 5.44; N, 18.17%. Calcd for $C_4H_{24}N_6Br_3Co$: C, 10.56; H, 5.32; N, 18.47%.

$(-)_{546}$-$[Co($*RR-2,4-ptn*$)_3](ClO_4)_3\cdot H_2O$. An aqueous solution containing 1 g of *trans*-$[CoCl_2($*RR*-2,4-ptn$)_2]ClO_4$, 0.5 g of *RR*-2,4-pentanediamine and 1 g of activated charcoal in 20 m*l* of water was warmed at 60°C. After about 2 hr, prismatic crystals began to appear. CD study showed that each of these single crystals was composed of about 90% $(-)_{546}$-isomer and 10% $(+)_{546}$-isomer of tris-diamine complex. Without separating these crystals, the reaction was still caused to proceed for 8—10 hr, and then the reaction mixture was cooled to room temperature. The precipitate containing activated charcoal was filtered off and washed with 60 m*l* of hot water (70°C). To the filtrate was added 34 m*l* of 60% perchloric acid. Upon cooling at 0°C for half an hour, first fraction of orange needle crystals was precipitated. They were filtered off, washed with a small amount of cold water, and recrystallized by evaporating the aqueous solution in a vacuum desiccator over potassium hydroxide. All the filtrates and washings were combined, concentrated to 30 m*l* at 50°C under reduced pressure and cooled to room temperature. The second fraction was obtained and recrystallized from water according to the method described above. The species remained in the final fraction on the above procedure seemed to be mostly bis-diamine complexes, since the filtrate changed its color to green on warming with hydrochloric acid and green dichloro complex was precipitated. Yield: Total 0.78 g.

Found: 26.35; H, 6.51; N, 12.07%. Calcd for $C_{15}H_{44}N_6O_{13}Cl_3Co$: C, 26.42; H, 6.50; N, 12.33%.

$(+)_{546}$-$[Co($*RR-2,4-ptn*$)_3]Cl_3\cdot 2H_2O$. Two grams of *trans*-$[CoCl_2($*RR*-2,4-ptn$)_2]ClO_4$ was converted into chloride by use of the anion exchanger Dowex 1-X4. This chloride was dissolved in 60 m*l* of 50% aqueous ethanol, and 0.5 g of *RR*-2,4-pentanediamine was added. The solution was warmed at 55—60°C for 8—10 hr. Deposited orange needle crystals were filtered off in hot, and recrystallized from water in a similar way as for $(-)_{546}$-isomer. Yield: 0.09 g.

Found: C, 35.74; H, 9.40; N, 16.61%. Calcd for $C_{15}H_{46}N_6Cl_3CoO_2$: C, 35.47; H, 9.13; N, 16.55%.

Orange prismatic crystals were obtained by evaporating

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7) C. J. Dippel, *Rec. Trav. Chim.*, **50**, 525 (1931).

8) E. Billman, *Z. Anal. Chem.*, **39**, 284 (1900).

9) A. Werner and H. Gruger, *ibid.*, **16**, 398 (1898).

10) C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

11) 1,3-btn. 1,3-diaminobutane. Details on 1,3-btn complexes will be published later.

the filtrate to almost dryness in a vacuum desiccator. The crystals recrystallized from water in a similar way gave the chemical composition $[\mathrm{Co}(RR\text{-}2,4\text{-ptn})_3]\mathrm{Cl}_3\cdot 2\mathrm{H}_2\mathrm{O}$. Yield: 0.48 g.

Found: C, 35.32; H, 9.34; N, 16.55%. Calcd for $\mathrm{C}_{15}\mathrm{H}_{46}\mathrm{N}_6\mathrm{Cl}_3\mathrm{CoO}_2$: C, 35.47; H, 9.13; N, 16.55%.

However, the CD spectra of each of these single crystals in water coincided with that of a mixed sample consisting of 93% $(-)_{546}$-isomer and 7% $(+)_{546}$-isomer.

Racemic-$[Co(\mathrm{RS}\text{-}2,4\text{-}ptn)_3](ClO_4)_3\cdot 3H_2O$. An aqueous solution containing 5 g of *trans*-$[\mathrm{CoCl}_2(RS\text{-}2,4\text{-ptn})_2]\mathrm{Cl}$ and 2 g of *RS*-2,4-pentanediamine and 1.5 g of activated charcoal was warmed at 60°C for a day, and filtered. Orange crystals were precipitated by the addition of sodium perchlorate to the filtrate, filtered off and recrystallized by evaporating an aqueous solution in a desiccator over phosphorus pentoxide under reduced pressure. Yield: 5 g.

Found: C, 25.49; H, 6.34; N, 11.29%. Calcd for $\mathrm{C}_{15}\mathrm{H}_{48}\mathrm{N}_6\mathrm{O}_{15}\mathrm{CoCl}_3$: C, 25.10; H, 6.34; N, 11.29%.

$(-)_{546}$-$[Co(\mathrm{RS}\text{-}2,4\text{-}ptn)_3](ClO_4)_3\cdot 3H_2O$. Five grams of *racemic*-$[\mathrm{Co}(RS\text{-}2,4\text{-ptn})_3](\mathrm{ClO}_4)_3\cdot 3\mathrm{H}_2\mathrm{O}$ was converted into chloride by use of the anion exchanger Dowex 1-X4. To the aqueous chloride solution was added 4 g of silver tartrate with stirring. After half an hour, silver chloride was filtered off and the filtrate was concentrated to about 15 m*l* in a desiccator over phosphorus pentoxide under reduced pressure. Reddish orange powder (0.5 g) was obtained by filtration, and recrystallized by concentrating its aqueous solution in a similar way. This procedure was repeated to give a constant CD curve. Pure sample was dissolved in a small amount of water and sodium perchlorate was added. The perchlorate salt was recrystallized from water.

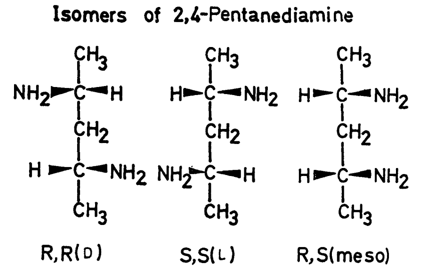
Found: C, 25.31; H, 6.30; N, 11.72%. Calcd for $\mathrm{C}_{15}\mathrm{H}_{48}\mathrm{N}_6\mathrm{O}_{15}\mathrm{CoCl}_3$: C, 25.10; H, 6.74; N, 11.71%.

Measurements. Visible and ultraviolet absorption spectra were recorded with a Hitachi 124 recording spectrophotometer. The CD curves were recorded with a Model ORD/UV-5 spectrophotometer of Japan Spectroscopic Co. with its CD attachment. PMR spectra were obtained with a Varian T-60 spectrometer using HOD signal as an internal standard. The complexes prepared here were hardly soluble in deuterium oxide containing Na-TMS. All the measurements were made at room temperature.

Results and Discussion

Conformation of Chelate Rings and Geometrical Isomerism. As shown in Part I, four conformations, chair, boat, and a pair of twist (skew boat) forms are possible in β-diamine chelate rings. The boat form is generally unstable and not formed in octahedral complexes such as those of cobalt(III), because big steric hindrance is involved between apical ligands and the central methylene group of the equatorial ligand. Hence chair and a pair of twist forms are the more probable conformations. A pair of twist forms are mirror images to each other, and they are designated as δ and λ, as shown in Part I.

It is generally understood that substituting groups on carbon atoms in puckered chelate rings always tend to take equatorial positions. Therefore, *RR*-, *SS*-, and *RS*-2,4-pentanediamine are expected to give λ- and δ-twist and chair conformation, respectively in six-membered chelate rings (Figs. 1 and 2). Such conformations of 2,4-pentanediamine were demonstrated by the structural study of 2,4-pentanediaminetetraacetato(2,4-ptnta)cobalt(III) complexes in Part 1.



Ligand	Conformation		
	chair	δ-twist	λ-twist
R,R-2,4-ptn	a,e	a,a	e,e
S,S-2,4-ptn	a.e	e,e	a,a
R,S-2,4-ptn	a,a e,e	a,e	a,e

e: methyl equatorial a: methyl axial

Fig. 1. Isomers of 2,4-pentanediamine and their conformations in the chelate.

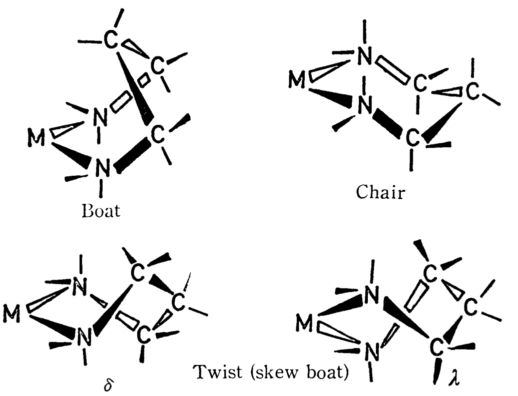


Fig. 2. Possible conformations of six-membered 1,3-diamine chelate.

The interconversion between δ- and λ-twist and between twist and chair form is not likely because of the steric hindrance among the chelate rings and the preference of equatorial orientation of the methyl groups. Appleton and Hall[12] studied the PMR spectra of a number of complexes of platinum(II) and palladium(II) with trimethylenediamine and its methyl-substituted derivatives including 2,4-pentanediamine. They suggested that the 2,4-pentanediamine chelates in these complexes might take stable conformations with equatorial orientation of the methyl groups.

As Fig. 3 shows, the PMR spectrum of $[\mathrm{Co}(\mathrm{NH}_3)_4(RR\text{-}2,4\text{-ptn})]^{3+}$ in deuterium oxide gives a sharp doublet of the methyl signal and a sharp triplet of the central methylene signal. The pattern of these multiplets is very similar to that of the diamine part of $[\mathrm{Co}(RR\text{-}2,4\text{-ptnta})]^-$.[1] Since the diamine part of the tetraacetato complex should have fixed λ-twist form, the *RR*-2,4-pentanediamine chelate of the tetrammine complex should take λ-twist form, and the interconversion among conformers would not take place in an aqueous solution at room temperature. The PMR spectrum of $[\mathrm{Co}(\mathrm{NH}_3)_4(RS\text{-}2,4\text{-ptn})]^{3+}$ in deuterium oxide gives a sharp doublet and a broad triplet corre-

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[12] T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **9**, 1807 (1970).

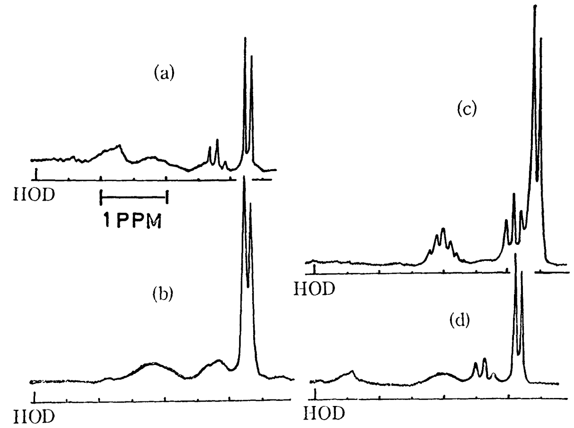

Fig. 3. PMR spectra of a) $[Co(NH_3)_4(RR\text{-}2,4\text{-}ptn)]^{3+}$, b) $[Co(RR\text{-}2,4\text{-}ptn)_3]^{3+}$, c) *trans*-$[Co(NO_2)_2(SS\text{-}2,4\text{-}ptn)_2]^+$, d) $(-)_{546}$-$[Co(RR\text{-}2,4\text{-}ptn)_3]^{3+}$ in D_2O. (Relative shifts in ppm from the HOD signal.)

sponding to the signals of the methyl and the central methylene protons, respectively. Such a signal of methyl protons indicates that the two methyl groups are equivalent in the chelate. Therefore, the conformation of the *RS*-2,4-pentanediamine of $[Co(NH_3)_4(RS\text{-}2,4\text{-}ptn)]^{3+}$ was assigned to chair form with equatorial methyl groups.

The spectral pattern in a lower field region is complicated because of the overlapping of the signals of –CH, $-NH_2$, and –NHD, and depends sensitively on the other ligands. Hence it is not useful for discussing the conformation of 2,4-pentanediamine chelates.

Figure 3 shows also the PMR spectra of $[Co(NO_2)_2(SS\text{-}2,4\text{-}ptn)_2]^+$ and $(-)_{546}$-$[Co(RR\text{-}2,4\text{-}ptn)_3]^{3+}$. These spectra are also similar to that of $[Co(NH_3)_4(RR\text{-}2,4\text{-}ptn)]^{3+}$ in the region of the methyl and the central methylene signals, indicating that the chelate rings have also twist form. Furthermore, each spectrum of these complexes seems to consist of the signals due to one kind of chelate ring. These facts suggest that the dinitro complex is in trans form and the tris complex has D_3 symmetry. The diastereoisomer, $(+)_{546}$-$[Co(RR\text{-}2,4\text{-}ptn)_3]^{3+}$ gives the same PMR spectrum as that of $(-)_{546}$-$[Co(RR\text{-}2,4\text{-}ptn)_3]^{3+}$ at 60 MHz. The *trans* structure of the dinitro complex may also be supported from comparison of *cis* and *trans* isomers of the corresponding trimethylenediamine complex, $[Co(NO_2)_2(tn)_2]^+$. Kawaguchi and Kawaguchi[6] obtained the *cis* isomer by treating the *trans* isomer with a warm aqueous nitrite solution, and found that the former gives the first absorption band at a lower wavelength than does the latter. When the present dinitro complex was treated similarly with an aqueous nitrite solution, the resultant solution gave the first absorption band at lower wavelength by 11 nm as compared with that of the original complex. The CD spectrum also changed substantially. An attempt to isolate the product was unsuccessful because of its high solubility in water.

As Fig. 3 shows, the PMR spectrum of $[Co(RS\text{-}2,4\text{-}ptn)_3]^{3+}$ exhibits a broader methyl signal than that of $[Co(RR\text{-}2,4\text{-}ptn)_3]^{3+}$. This complex can have two geometrical isomers with respect to *mer* and *fac* coordination of the amino groups adjacent to the *R*- and *S*-carbon atoms. However, studies with molecular models disclose that only the *fac* isomer is formed without big steric hindrance among the chelate rings. Therefore, the broad methyl signal may not be due to the presence of two geometrical isomers, but will be due to C_3 symmetry of the *fac* isomer. The two methyl groups on *R*- and *S*-carbon atom are in a different environment from each other in this complex.

The dichloro and dibromo complexes prepared here were assigned to *trans* (Cl-Cl, or Br-Br) structure from their characteristic green color.

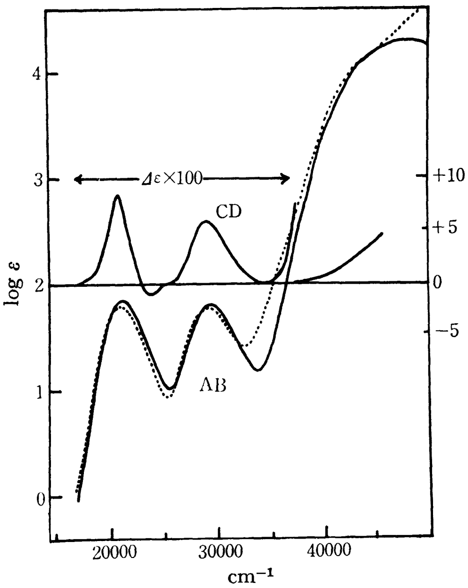

Fig. 4. Absorption (AB) and CD sepectra of (——) $[Co(NH_3)_4(RR\text{-}2,4\text{-}ptn)]^{3+}$, (······) $[Co(NH_3)_4(tn)]^{3+}$ in water.

Absorption Spectra. Table 1 and Fig. 4 compare the absorption spectra of four tetrammine-β-diamine cobalt(III) complexes. The absorption bands including the first, the second and the charge transfer band are shifted from longer to shorter wavelength with increase in the number of methyl group, *i.e.* in the order $[Co(NH_3)_4tn]^{3+}$, $[Co(NH_3)_4(1,3\text{-}btn)]^{3+}$, and $[Co(NH_3)_4(2,4\text{-}ptn)]^{3+}$. The absorption spectra of $[Co(NH_3)_4(RR\text{-}2,4\text{-}ptn)]^{3+}$ and $[Co(NH_3)_4(RS\text{-}2,4\text{-}ptn)]^{3+}$ are almost identical with each other, regardless of the different conformation of the chelate rings. A similar relationship also holds between *trans*-$[CoCl_2(RR\text{-}2,4\text{-}ptn)_2]^+$ and *trans*-$[CoCl_2(RS\text{-}2,4\text{-}ptn)_2]^+$ as shown in Fig. 5. On the other hand, the absorption bands of the four tris complexes are shifted to shorter wavelength in the sequence $[Co(RS\text{-}2,4\text{-}ptn)_3]^{3+}$, $[Co(tn)_3]^{3+}$, $(+)_{546}$-$[Co(RR\text{-}2,4\text{-}ptn)_3]^{3+}$, and $(-)_{546}$-$[Co(RR\text{-}2,4\text{-}ptn)_3]^{3+}$, as shown in Fig. 6 and Table 1. Such a sequence is not in accord with that of tetrammine complexes given above. The differences in the absorption maxima of the first bands amount to 380 cm^{-1} between $[Co(RS\text{-}2,4\text{-}ptn)_3]^{3+}$ and $(-)_{546}$-$[Co(RR\text{-}2,4\text{-}ptn)_3]^{3+}$ and 220 cm^{-1} between $(+)_{546}$-$[Co(RR\text{-}2,4\text{-}ptn)_3]^{3+}$ and $(-)_{546}$-$[Co(RR\text{-}2,4\text{-}ptn)_3]^{3+}$. It is not possible to discuss these results in detail at present. However, they seem to be related to the steric interaction among chelate rings. Such an inter-

TABLE 1. NUMERICAL DATA OF ABSORPTION (AB) AND CIRCULAR DICHROISM (CD) $\tilde{\nu}$ IN $10^3\,\text{cm}^{-1}$, $(\log\varepsilon)$ AND $(\varepsilon_l-\varepsilon_r)$

Complex	AB	CD
$[Co(NH_3)_4tn]Br_3\cdot H_2O$	20.90 (1.79)	
	29.20 (1.78)	
$[Co(NH_3)_4(1,3\text{-btn})]Br_3$	20.94 (1.82)	
	29.24 (1.79)	
$[Co(NH_3)_4(RS\text{-}2,4\text{-ptn})](ClO_4)_3\cdot H_2O$	20.96 (1.83)	
	29.24 (1.78)	
	47.62 (4.30)	
$[Co(NH_3)_4(RR\text{-}2,4\text{-ptn})](ClO_4)_3$	20.96 (1.84)	20.62 (+0.085)
		23.53 (−0.010)
	29.24 (1.80)	28.82 (+0.059)
	47.62 (4.29)	
trans-$[Co(NO_2)_2(RR\text{-}2,4\text{-ptn})_2]ClO_4$	22.37 (2.23)	21.51 (−0.695)
		24.27 (+0.245)
	28.90 (3.44)	28.57 (+0.325)
		34.25 (−1.300)
	39.84 (4.34)	42.74 (+6.250)
trans-$[CoCl_2(RS\text{-}2,4\text{-ptn})_2]Cl$	15.75 (1.59)	
	21.37 (1.48)	
	25.32 (1.85)	
	38.76 (4.35)	
	45.05 (4.02)	
trans-$[CoCl_2(RR\text{-}2,4\text{-ptn})_2]ClO_4$	15.75 (1.63)	16.00 (+0.475)
	21.37 (1.57)	20.92 (−0.575)
	25.32 (1.81)	26.46 (+0.470)
	ca. 32.0 (3.14)	34.01 (−2.000)
	38.76 (4.37)	38.76 (+10.625)
	46.08 (4.06)	
trans-$[CoBr_2(NH_3)_2(SS\text{-}2,4\text{-ptn})]Br\cdot H_2O$	14.90 (1.76)	15.15 (−0.162)
		20.62 (+0.202)
	ca. 27.8 (3.22)	25.32 (−0.550)
trans-$[CoBr_2(SS\text{-}2,4\text{-ptn})_2]ClO_4$	14.79 (1.78)	15.11 (−0.275)
		20.70 (+0.424)
	27.79 (3.28)	25.97 (−0.369)
$(-)_D\text{-}[Co(tn)_3]Br_3\cdot H_2O$	20.49 (1.90)	18.80 (+0.067)
		21.10 (−0.140)
	28.57 (1.88)	27.80 (−0.015)
$(-)_{546}\text{-}[Co(RR\text{-}2,4\text{-ptn})_3](ClO_4)_3\cdot H_2O$	20.75 (1.88)	19.61 (−0.586)
	28.82 (1.87)	28.57 (+0.066)
	43.48 (4.43)	43.48 (+18.337)
$(+)_{546}\text{-}[Co(RR\text{-}2,4\text{-ptn})_3]Cl_3\cdot 2H_2O$	20.53 (1.99)	20.83 (+2.690)
	28.65 (1.96)	28.41 (−0.283)
	42.92 (4.43)	43.86 (+7.164)
$(-)_{546}\text{-}[Co(RS\text{-}2,4\text{-ptn})_3](ClO_4)_3\cdot 3H_2O$	20.37 (1.96)	19.69 (−0.548)
	28.41 (1.95)	28.17 (−0.013)
	42.37 (4.40)	39.37 (+6.543)
		44.64 (−9.347)
$[Co(NH_3)_6]Cl_3$	21.10 (1.76)	
	29.50 (1.67)	

action may affect more or less the strength of coordination bonds, when a large and bulky ligand such as 2,4-pentanediamine forms a tris type complex. Molecular models indicate that the steric interaction among twist chelate rings in the tris complexes is much smaller than that among chair chelate rings, and that $\Delta(\lambda\lambda\lambda)$ form involves less congestion of ligand atoms than $\Lambda(\lambda\lambda\lambda)$ form. As shown later, the $(-)_{546}$- and $(+)_{546}$-isomer of $[Co(RR\text{-}2,4\text{-ptn})_3]^{3+}$ have $\Delta(\lambda\lambda\lambda)$ and $\Lambda(\lambda\lambda\lambda)$ absolute configuration, respectively. The diamine chelate rings in $[Co(tn)_3]^{3+}$ can take both twist and chair form in solution without involving big mutual interaction, although they have chair form in crystals.[13] The fact that the absorption bands of $[Co(tn)_3]^{3+}$ are at shorter wavelengths than those of $[Co(RS\text{-}2,4\text{-ptn})_3]^{3+}$ may be caused by conformational interconversion of the trimethylenediamine chelate rings in solution. Thus, it seems that the complexes involving less steric

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[13] T. Nomura, F. Marumo, and Y. Saito, This Bulletin, **42**, 1016 (1969).

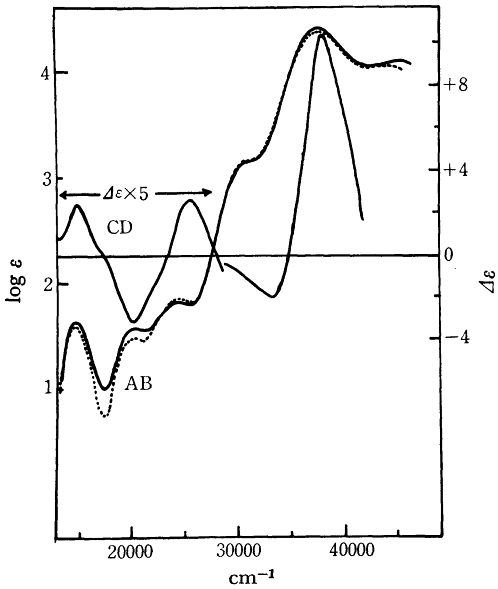

Fig. 5. Absorption (AB) and CD spectra of
(——) *trans*-[CoCl$_2$(*RR*-2,4-ptn)$_2$]$^+$,
(······) *trans*-[CoCl$_2$(*RS*-2,4-ptn)$_2$]$^+$ in ethanol.

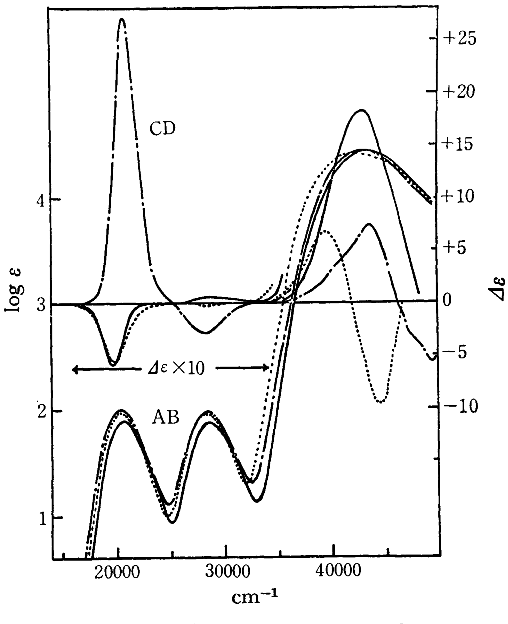

Fig. 6. Absorption (AB) and CD spectra of
(——) (−)$_{546}$-[Co(*RR*-2,4-tpn)]$^{3+}$,
(-·-·-) (+)$_{546}$-[Co(*RR*-2,4-ptn)$_3$]$^{3+}$,
(······) (−)$_{546}$-[Co(*RS*-2,4-ptn)$_3$]$^{3+}$ in water.

interaction cause the absorption peaks to shift to shorter wavelength. It is worth noticing that such a shift has not been observed clearly for the complexes with five-membered chelates. For example, the absorption peaks of two diastereoisomers, $\Delta(\lambda\lambda\lambda)$(*lel*)- and $\Lambda(\lambda\lambda\lambda)$-(*ob*)-[Co(*R*-pn)$_3$]$^{3+}$(*R*-pn=*R*-propylenediamine) are at almost identical wavelengths with each other.[14] The mono and *trans*-bis diamine complexes studied here should involve smaller steric interactions among ligands, and in fact give their absorption peaks at the wavelengths expected from the spectrochemical series.

Circular Dichroism and Absolute Configuration. So far as the methyl group on the carbon atoms tends to take equatorial orientation to the chelate ring, *RR*-2,4-pentanediamine and *R*-propylenediamine should give λ-twist and λ-gauche conformation, respectively. Since these two belong to the chirality λ, it seems interesting to compare the CD spectra of their cobalt(III) complexes with one another.

(1) Mono- and bis-2,4-Pentanediamine Cobalt(III) Complexes: As shown in Figs. 7 and 8, the CD pattern of *trans*-[Co(NO$_2$)$_2$(*RR*-2,4-ptn)$_2$]$^+$ is very similar to that

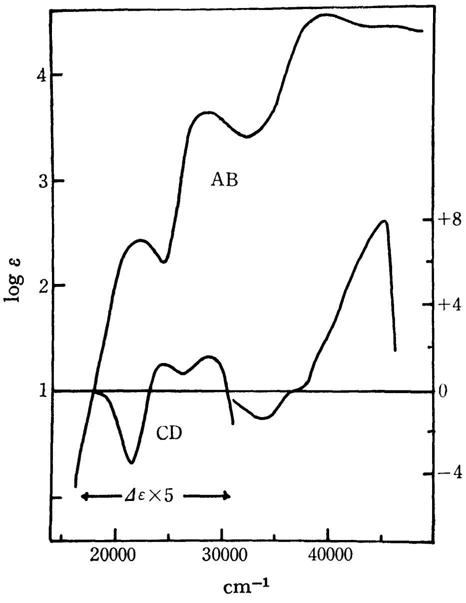

Fig. 7. Absorption (AB) and CD spectra of *trans*-[Co(NO$_2$)$_2$-(*RR*-2,4-ptn)$_2$]$^+$ in water.

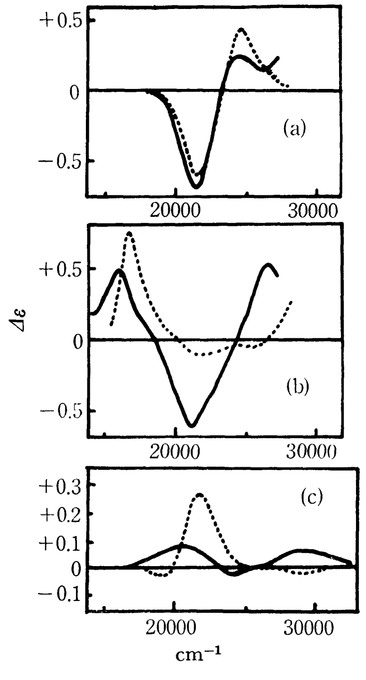

Fig. 8. Comparison of the CD spectra of *RR*-2,4-pentanediamine (——) and *R*-propylenediamine (······) complexes. a) *trans*-dinitro complexes, b) *trans*-dichloro complexes, c) tetrammine complexes.

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[14] K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1968).

of *trans*-$[Co(NO_2)_2(R\text{-pn})_2]^+$.[15] The CD curve of *trans*-$[CoCl_2(RR\text{-}2,4\text{-ptn})_2]^+$ shown in Figs. 5 and 8 is also similar to that of *trans*-$[CoCl_2(R\text{-pn})_2]^+$[16] essentially, but the CD band with minus sign of the former in the Ib band region (A_2) is much stronger than that of the latter. The CD curves of the tetrammine complexes of *RR*-2,4-pentanediamine and *R*-propylenediamine are different from each other. In the first band region, the former gives a plus and a small minus peak at 20620 and 23530 cm^{-1}, respectively, whereas the latter a small minus and a plus peak at 19300 and 21580 cm^{-1}, respectively.[10] (Fig. 8)

Such a difference could be explained if the location for propylenediamine and 2,4-pentanediamine in the spectrochemical series were taken into consideration. The first absorption bands of $[Co(NH_3)_4(R\text{-pn})]^{3+}$, $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_4(RR\text{-}2,4\text{-ptn})]^{3+}$ are at 21500,[10] 21100, and 20960 cm^{-1}, respectively. Thus, the order of these ligands in the spectrochemical series may be determined as $R\text{-pn} > NH_3 > RR\text{-}2,4\text{-ptn}$. Since the complex, $[Co(NH_3)_4AA]^{3+}$ (AA=diamine) can be approximated as C_{2v} symmetry, the first absorption band would consist of two components, Ia(B_1) and Ib(A_2, B_2; accidentaly degenerate) as predicted by Yamatera's theory.[17] These components may be arranged in the order Ia and Ib, and Ib and Ia from longer to shorter wave length in $[Co(NH_3)_4(R\text{-pn})]^{3+}$ and $[Co(NH_3)_4(RR\text{-}2,4\text{-ptn})]^{3+}$, respectively, on the basis of the spectrochemical series of the ligands given above. Hence the CD patterns of the tetrammine complexes of *R*-propylenediamine and *RR*-2,4-pentanediamine are understood as due to such a different arrangement of the two components, Ia and Ib.

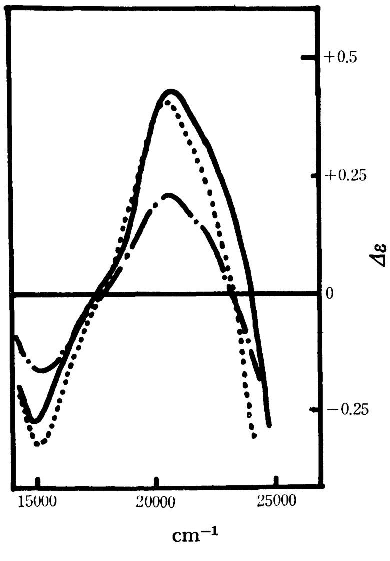

Fig. 9. CD spectra in the first absorption band region.
(——) *trans*-$[CoBr_2(SS\text{-}2,4\text{-ptn})_2]^+$
(–·–·) *trans*(Br-Br)-$[CoBr_2(NH_3)_2(SS\text{-}2,4\text{-ptn})]^+$
(······) *trans*(Br-Br)-$[CoBr_2(NH_3)_2(SS\text{-}2,4\text{-ptn})]^+$ with doubled $\Delta\varepsilon$ value, in a mixture of methanol and 47% hydrobromic acid (9:1, v/v).

The CD of $[Co(NH_3)_4(RR\text{-}2,4\text{-ptn})]^{3+}$ in the region of the second absorption band is entirely different from that of $[Co(NH_3)_4(R\text{-pn})]^{3+}$; the sign is reversed, and the magnitude is almost the same as in the region of the first absorption band. However, the reasons are unknown.

Figure 9 shows the absorption and CD spectra of *trans*(Br-Br)$[CoBr_2(NH_3)_2(SS\text{-}2,4\text{-ptn})]^+$ and *trans*-$[CoBr_2(SS\text{-}2,4\text{-ptn})_2]^+$ in a mixture of methanol and 47% hydrobromic acid (9:1, v/v). The absorption spectra are essentially equal, and the CD curves have the same pattern. The dotted line in Fig. 9 shows the CD curve of the former complex with doubled $\Delta\varepsilon$ value. This curve coincides well with the CD curve of the latter complex. Thus the magnitude of CD due to the vicinal effect is proportional to the number of optically active ligand. The same relation was observed between *trans*(Cl-Cl)-$[CoCl_2(NH_3)_2(R\text{-pn})]^+$ and *trans*-$[CoCl_2(R\text{-pn})_2]^+$ by Hawkins *et al.*[10] It is, thus, suggested that the six-membered chelate rings in the two dibromo complexes have almost the same state in the given solution and there seems to be no substantial interaction between the chelate rings in the *trans*-bis-complex.

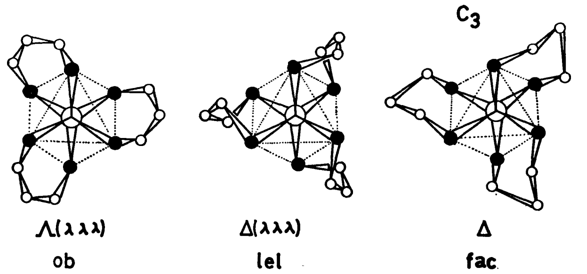

Fig. 10. Schematic structures of tris(1,3-diamine) complexes.

(2) Tris-RR-*2,4-pentanediamine Complexes*: Tris-*RR*-2,4-pentanediamine cobalt(III) complex gives two diastereoisomers, prismatic crystals with $(-)_{546}$ rotation and needle-like crystals with $(+)_{546}$ rotation. The CD and absorption spectra are shown in Fig. 6. We tentatively assigned that the former and the latter have Δ and Λ configuration, respectively, on the basis of the sign of CD bands in the region of the first absorption band.[18] Lately two of us, together with colaborators, examined the absolute configuration of $(+)_{546}$-isomer by X-ray diffraction method and found that it has Λ configuration and the three chelate rings have λ-twist conformation.[19] The line connecting two asymmetric carbon atoms of *RR*-2,4-pentanediamine chelate is oblique to the C_3 axis of the complex ion. Hence this isomer is written as $\Lambda(\lambda\lambda\lambda)(ob)$. Thus, the other $(-)_{546}$-isomer should have unequivocally $\Delta(\lambda\lambda\lambda)(lel)$ form. (Fig. 10) Therefore, the empirical rule that the diastereoisomer with plus main CD sign in the region of the first absorption band has Λ configuration, seems to hold in the two diastereoisomers, $(+)_{546}$- and $(-)_{546}$-$[Co(RR\text{-}2,4\text{-ptn})_3]^{3+}$. However, the magnitudes of the CD are very different from each other, even if the vicinal

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[15] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 202 (1965).

[16] H. Ito, J. Fujita, and K. Saito, This Bulletin, **42**, 1286 (1969).

[17] H. Yamatera, *ibid.*, **31**, 95 (1958).

[18] F. Mizukami, H. Ito, J. Fujita, and K. Saito, *ibid.*, **43**, 3973 (1970).

[19] A. Kobayashi, F. Marumo, Y. Saito, J. Fujita, and F. Mizukami, *Inorg. Nucl. Chem. Lett.*, **7**, 777 (1971).

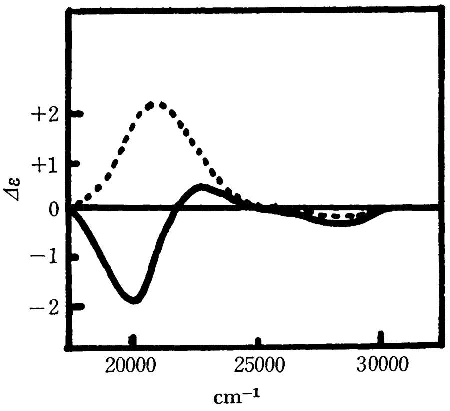

Fig. 11. CD spectra of (——) Δ $(\lambda\lambda\lambda)(lel)$-$[\mathrm{Co}(R\text{-pn})_3]^{3+}$, (······) $\Lambda(\lambda\lambda\lambda)(ob)$-$[\mathrm{Co}(R\text{-pn})_3]^{3+}$. (Ref. 13)

contribution of the *RR*-2,4-pentanediamine is taken into account.

In general, the optical activity of a metal complex is understood as a superposition of configurational and conformational (vicinal effect of optically active ligand) chirality. In other words, both chiralities contribute to the CD of a metal complex additively. The CD spectra of $\Delta(\lambda\lambda\lambda)(lel)$- and $\Lambda(\lambda\lambda\lambda)(ob)$-$[\mathrm{Co}(R\text{-pn})_3]^{3+}$ shown in Fig. 11 was interpreted satisfactorily by such an additive law.[14,20] However, this law does not hold in the present two diastereoisomers as stated above. There should be some kinds of factors affecting the optical activity of these complexes. Although the factors are not clear at present, they seem to be characteristic of the six-membered tris-complexes, since the CD spectra of mono and *trans*-bis-(*RR*-2,4-ptn) complexes given before are rather normal as compared with those of the corresponding *R*-propylenediamine complexes.

It was stated previously that the $\Lambda(\lambda\lambda\lambda)(ob)$ isomer might involve larger steric interaction among chelate rings than the $\Delta(\lambda\lambda\lambda)(lel)$ isomer, and such an interaction seemed to correlate with the frequency difference of absorption bands between the two diastereoisomers. The same interpretation may be useful for the CD spectra. The interaction among chelate rings may produce a somewhat different field from that expected from a superposition of configurational and conformational chirality. A large interaction of such kind may also induce delicate change in conformation or configuration of the complex. These factors may be reflected sensitively on the CD spectra, although the PMR spectra of the two diastereoisomers are almost identical with each other at 60 MHz. The CD of $\Lambda(\lambda\lambda\lambda)(ob)$ isomer which involves larger steric interaction seems to be exceptionally strong as compared with those of other tris-β-diamine complexes shown in Figs. 6 and 13. However, further studies on such anomalous CD will be needed.

Both $(+)_{546}$ and $(-)_{546}$ isomers of $[\mathrm{Co}(RR\text{-}2,4\text{-ptn})_3]^{3+}$ give plus CD bands in the charge transfer region. This fact may be attributed to the vicinal contribution of the optically active ligand, *RR*-2,4-pentanediamine.[14] Details on the CD in the charge transfer region will be discussed later.

The $\Delta(\lambda\lambda\lambda)(lel)$ isomer may be more stable thermodynamically than the $\Lambda(\lambda\lambda\lambda)(ob)$ isomer because of smaller steric interaction. The yield of diastereoisomers is governed by various factors including kinetics and solubility, and does not necessarily reflect the relative stability of the isomers. However, it should be pointed out that the $\Delta(\lambda\lambda\lambda)(lel)$ isomer was produced much more than the $\Lambda(\lambda\lambda\lambda)(ob)$ isomer as stated in the Experimental part.

As also stated in the Experimental part, $[\mathrm{Co}(RR\text{-}2,4\text{-ptn})_3]^{3+}$ gives large single crystals of pseudo-racemate with different moles of the two diastereoisomers. The CD spectrum of the single crystal dissolved in water indicates the composition, 93% $\Delta(\lambda\lambda\lambda)(lel)$ and 7% $\Lambda(\lambda\lambda\lambda)(ob)$ (Fig. 12).

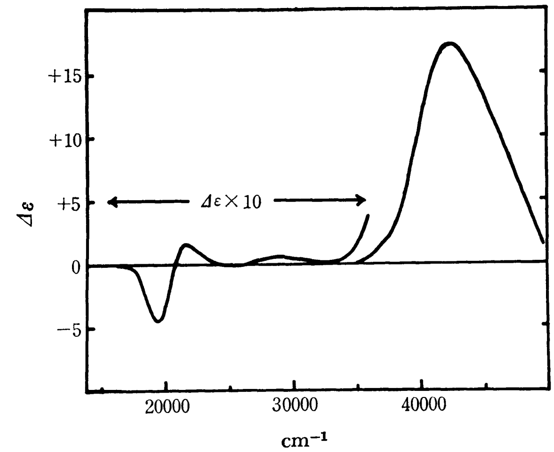

Fig. 12. CD spectra of pseudo-racemate, $(\Delta(93)+\Lambda(7))$-$[\mathrm{Co}(RR\text{-}2,4\text{-ptn})]^{3+}$ in water.

*(3) Tris-*RS*-2,4-pentanediamine Complex*: Figure 6 shows the CD spectrum of $(-)_{546}$-$[\mathrm{Co}(RS\text{-}2,4\text{-ptn})_3]^{3+}$ in water. As stated before, $[\mathrm{Co}(RS\text{-}2,4\text{-ptn})_3]^{3+}$ can give two geometrical isomers. We assigned the $(-)_{546}$-isomer as *fac*, and the conformation of the chelated ligands as chair form, on the basis of the PMR spectrum. The absolute configuration of this isomer, however, can be assigned with difficulty from the CD spectrum. When the empirical rule that the main CD of Δ-isomer in the region of the first absorption band has minus sign, is applied, the $(-)_{546}$-isomer seems to have Δ configuration. This assignment seems to be in good harmony with the CD sign of $(+)_{546}$- and $(-)_{546}$-$[\mathrm{Co}(RR\text{-}2,4\text{-ptn})_3]^{3+}$ given before, but contradicts the fact that the major CD peak of Λ-$(-)_{\mathrm{D}}$-$[\mathrm{Co}(\mathrm{tn})_3]^{3+}$ has minus sign[3] (Fig. 13). The trimethylenediamine chelates in this complex have chair conformation in crystals.[12] Gollogly and Hawkins[4] reported that the major CD component (A_2) of Δ-$(+)_{\mathrm{D}}$-$[\mathrm{Co}(\mathrm{tn})_3]^{3+}$ was increased while the minor CD component (E) decreased in 0.05M-selenite or 0.05M-phosphate solution. The resultant CD pattern seems to be enantiomeric with that of $(-)_{546}$-$[\mathrm{Co}(RS\text{-}2,4\text{-ptn})_3]^{3+}$ as shown in Fig. 14. A similar CD change was also observed by Beddoe and Mason[3] with Λ-$(-)_{\mathrm{D}}$-$[\mathrm{Co}(\mathrm{tn})_3]^{3+}$ in 0.01M sodium selenite. Very recently Beddoe *et al.*[21] observed that

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20) B. E. Douglas, *Inorg. Chem.*, **4**, 1813 (1965).

21) P. G. Beddoe, M. J. Harding, S. F. Mason, and B. J. Peart, Private communication.

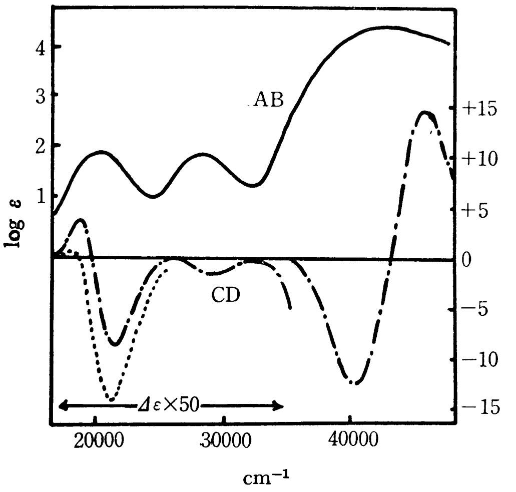

Fig. 13. Absorption (AB) and CD spectra of Λ-(−)$_D$-]Co-(tn)$_3$]$^{3+}$. (——) AB in water, (—·—·) CD in water, (······) CD in 0.01M sodium selenite. (Ref. 3)

the CD spectrum of Δ-(+)$_D$-[Co(tn)$_3$]$^{3+}$ in 0.05M oxy-anion solutions are almost identical with that in the solid state. They suggested that the [Co(tn)$_3$]$^{3+}$ in water exists in an equilibrium between a tris-chair and a tris-skew boat form, and that the CD change on the addition of oxy-anions can be attributed to the stabilization of the tris-chair form by ion-association. The solid-state CD spectrum of Δ-(+)$_D$-[Co(tn)$_3$]Br$_3$·H$_2$O (tris-chair form[13]) are almost enantiomeric with the solution CD spectrum of (−)$_{546}$-[Co(*RS*-2,4-ptn)$_3$]$^{3+}$ which is constrained to the tris-chair conformation by the equatorial preference of the methyl groups in the chelate rings. Thus, these experiments seem to support strongly that the (−)$_{546}$-[Co(*RS*-2,4-ptn)$_3$]$^{3+}$ has Λ configuration.

On the other hand, the CD pattern of (−)$_{546}$-[Co(*RS*-2,4-ptn)]$^{3+}$ in the charge transfer region is enantiomeric with that of Λ-(−)$_D$-[Co(tn)$_3$]$^{3+}$ as shown in Fig. 13. Previously, one of the authors[14] suggested that the sign of the CD bands of a tris(diamine)cobalt-(III) complex in the charge transfer region seemed to depend on the absolute configuration of the complex; Λ-isomer gives a CD band with minus sign at longer wavelength side. The CD pattern of Λ-(−)$_D$-[Co(tn)$_3$]$^{3+}$ in the charge transfer region is in good accord with this rule. When this rule is applied, the (−)$_{546}$-[Co(*RS*-2,4-ptn)$_3$]$^{3+}$ seems to have Δ configuration.

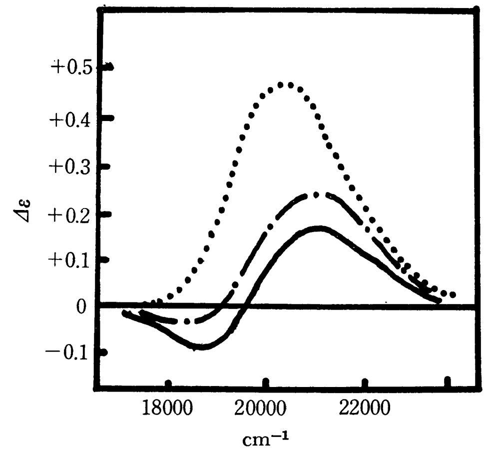

Fig. 14. CD spectra of Δ-(+)$_D$-[Co(tn)$_3$]$^{3+}$. (——) in water, (—·—·) in 0.01M-sulfate, (······) in 0.05M-selenite. (Ref. 4)

These conflicting results discourage us to give any plausible assignment of the absolute configuration of this complex on the basis of the CD spectrum. Further studies including an X-ray analysis will be needed.

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