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Metal Complexes Containing Six-membered Chelate Rings. III. Preparation and Structure of Mono- and Bis(2,4-Pentanediamine)cobalt(III) Complexes Containing Acetylacetonate or Oxalate Ion[1]

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New cobalt(III) complexes $[Co(acac)_2(2,4\text{-}ptn)]^+$, $[Co(acac)(2,4\text{-}ptn)_2]^{2+}$ and $[Co(ox)(2,4\text{-}ptn)_2]^+$ have been synthesized, resolved into optical isomers and their structures determined; 2,4-ptn=optically active (*RR* and *SS*) and *meso* (*RS*) 2,4-pentanediamine, acac=acetylacetonate ion, ox=oxalate ion. The patterns of circular dichroism spectra of these complexes in the first absorption band region are very similar to those of the corresponding α-diamine cobalt(III) complexes.

Kawaguchi *et al.*[2] recently determined the absolute configuration of $(-)_{589}$-$[Co(acac)(tn)_2]^{2+}$ (tn=trimethylenediamine) as Δ. This complex shows a main circular dichroism (CD) band with positive sign in the first absorption band region. The result agrees with that of a number of chiral complexes of cobalt(III) containing such five-membered chelate rings as ethylenediamine (en). The CD curve of Λ-$[Co(tn)_3]^{3+}$ is known to differ greatly from that of Λ-$[Co(en)_3]^{3+}$ in the first absorption band region.[3] Mason[4] proposed a new regional rule for a metal complex to account for such a difference. We have reported[1] that the *tris*-cobalt(III) complexes of *meso*(*RS*)- and optically active (*RR* or *SS*)-2,4-pentanediamine showed CD curves differing from those of both $[Co(en)_3]^{3+}$ and $[Co(tn)_3]^{3+}$, while the optically active 2,4-pentanediamine chelate gave vicinal contribution to the CD similar to that of the optically active propylenediamine (pn) chelate. In order to elucidate the optical activity of metal complexes, therefore, it is desirable to accumulate CD data on those complexes containing six-membered chelates.

This paper deals with preparation of optically active cobalt(III) complexes containing 2,4-pentanediamine and acetylacetonate or oxalate ion and their stereochemistry on the basis of CD and pmr spectra.

Experimental

Optically active-(*RR* and *SS*) and *meso*-(*RS*) 2,4-pentanediamine were synthesized according to the method reported previously.[5]

Δ-$(-)_{546}$-$[Co(acac)_2(RR\text{-}2,4\text{-}ptn)](ClO_4)$. This was synthesized according to a method similar to that for the cor-

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[1] Part II of this series, F. Mizukami, H. Ito, J. Fujita, and K. Saito, This Bulletin, **45**, 2129 (1972).

[2] H. Kawaguchi, K. Matsumoto, H. Kuroya, and S. Kawaguchi, *Chem. Lett.*, **1972**, 125.

[3] F. Woldbye, *Rec. Chem. Progr.*, **24**, 197 (1963). P. G. Beddoe and S. F. Mason, *Inorg. Nucl. Chem. Lett.*, **4**, 433 (1968). J. R. Gollogly and C. J. Hawkins, *Chem. Commun.*, **1968**, 689. R. R. Judkins and D. J. Royer, *Inorg. Nucl. Chem. Lett.*, **6**, 305 (1970). P. G. Beddoe, M. J. Hardings, S. F. Mason, and B. J. Peart, *Chem. Commun.*, **1971**, 1283.

[4] S. F. Mason, *J. Chem. Soc.*, *A*, **1971**, 667.

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

responding ethylenediamine complex.[6] Charcoal (1.5 g) and *RR*-2,4-pentanediamine (0.66 g) were added to a 20% aqueous methanol solution (80 ml) of $Na[Co(acac)_2(NO_2)_2]\cdot 5H_2O$[7] (3 g) with stirring at room temperature. After 20 min, the charcoal was filtered off and washed with 10 ml of water. The filtrate and washings were combined, and then evaporated to about 35 ml at about 50 °C under reduced pressure. The solution was passed through a column containing cation exchanger Dowex 1-X4 in sodium form. The column was washed with water to remove tris(acetylacetonato)cobalt(III). At this stage the column gave two separated bands, violet and red ([Co(acac)(*RR*-2,4-ptn)$_2$]$^{2+}$). The violet band was eluted with 0.3 M sodium perchlorate solution, but the two diastereoisomers did not separate in the column. Thus, each fraction was checked by its CD and absorption spectrum. Fractions showing similar spectral data were collected, and evaporated under reduced pressure. Crystals thus obtained were recrystallized fractionally from water until the CD exhibited a constant curve. Less soluble crystals seemed to be a pseudo-racemate of Δ and Λ isomers, and only the more soluble $(-)_{546}$-isomer was obtained as pure optically active diastereoisomer, its yield appearing to be greater (>60%) than that of the other.

Found: C, 39.01; H, 6.14; N, 5.95%. Calcd for $C_{15}H_{28}N_2O_8CoCl$: C, 39.27; H, 6.15; N, 6.11%.

*Δ-$(-)_{589}$-[Co(acac)(*RR*-2,4-ptn)$_2$](ClO$_4$)$_2$.* To an aqueous solution (25 ml) of *trans*-[CoCl$_2$(*RR*-2,4-ptn)$_2$]ClO$_4$[1] (1 g) was added sodium acetylacetonate (0.28 g). The solution was stirred for half an hour at 60 °C, and cooled to room temperature. A red powder was precipitated by addition of sodium perchlorate (5 g) in 3 ml of water, filtered off and air dried. More complex was obtained by evaporating the filtrate in a desiccator over diphosphorus pentoxide under reduced pressure. Total yield: 1.2 g (93%). The crude complex was a mixture of Δ and Λ diastereoisomers, and separated into optical isomers by fractional recrystallization from water. Pure $(-)_{589}$-isomer (0.7 g) was obtained, but $(+)_{589}$-isomer was always accompanied by a small amount of $(-)_{589}$-isomer. The pmr spectrum of the crude complex showed that the $(-)_{589}$-isomer was obtained in much greater yield (>75%) than the $(+)_{589}$-isomer.

Found: C, 31.98; H, 6.28; N, 9.94%. Calcd for $C_{15}H_{35}N_4O_{10}CoCl_2$: C, 32.10; H, 6.29; N, 9.98%.

*Δ,Λ-[Co(acac)$_2$(*RS*-2,4-ptn)](ClO$_4$).* To a 20% aqueous ethanol solution (125 ml) of $Na[Co(acac)_2(NO_2)_2]\cdot 5H_2O$ (5 g) were added 2.5 g of charcoal and 1 g of *RS*-2,4-pentanediamine. The solution was stirred for 15 min at room temperature, and the charcoal was then filtered off and washed with 30 ml of water. The filtrate and washings were combined, and 35 g of sodium perchlorate in 30 ml of water was added. After a while, a red powder ([Co(acac)(*RS*-2,4-ptn)$_2$](ClO$_4$)$_2$) precipitated was filtered off. To the filtrate was added more sodium perchlorate (35 g). On cooling the solution at 0 °C for 1.5 hr, more [Co(acac)(*RS*-2,4-ptn)$_2$](ClO$_4$)$_2$ was precipitated almost completely, and then filtered off. The filtrate was cooled again at 0 °C for 5 hr. Purple crystals thus formed were filtered off, and recrystallized from hot ethanol. Yield: 1.3 g.

Found: C, 39.01; H, 6.34; N, 6.40%. Calcd for $C_{15}H_{28}N_2O_8CoCl$: C, 39.27; H, 6.15; N, 6.11%.

*Λ-$(+)_{546}$-[Co(acac)$_2$(*RS*-2,4-ptn)]$^+$.* Δ,Λ-[Co(acac)$_2$(*RS*-2,4-ptn)](ClO$_4$) (1 g) and sodium hydrogendibenzoyltartrate (0.45 g) (2 : 1 mole ratio) were dissolved in 100 ml of water with stirring at about 80 °C. The solution was cooled gradually to room temperature. A purple powder was precipitated, filtered off, washed with a small amount of water and air dried. (0.7 g). This was dissolved in an appropriate amount of ethanol containing an excess mole of silver perchlorate. The silver hydrogen dibenzoyltartrate was filtered off, and the filtrate was evaporated to dryness. The residue was dissolved again in a small amount of water, and filtered. The filtrate was gradually evaporated to remove less soluble racemic perchlorate which was filtered off occasionally. Evaporation was continued until the ratio of $\Delta\varepsilon$ and ε values of the filtrate became constant. From the final filtrate, more soluble optically active perchlorate was obtained crystalline but it was contaminated with silver perchlorate which could not be removed completely. Thus the quantitative CD curve of this isomer was determined with the aid of the ε values of the racemate.

*Δ,Λ-[Co(acac)(*RS*-2,4-ptn)$_2$](ClO$_4$)$_2$·H$_2$O.* To a suspension of *trans*-[CoCl$_2$(*RS*-2,4-ptn)$_2$]Cl (5 g) in 50 ml of water was added an aqueous solution (50 ml) of sodium acetylacetonate (2 g), and this was warmed at 70 °C for 2 hr. After cooling, the solution was filtered and excess sodium perchlorate was added to the filtrate. Red crystals were precipitated, filtered off and recrystallized from water (75 °C). The complex thus obtained was assigned tentatively to *cis-cis* isomer of three possible geometrical isomers. Attempts to resolve this complex into optical isomers with sodium hydrogendibenzoyltartrate were only partially successful.

Found: C, 31.02; H, 6.91; N, 9.36%. Calcd for $C_{15}H_{37}N_4O_{13}CoCl_2$: C, 31.10; H, 6.44; N, 9.67%.

trans-cis-*Δ,Λ-[Co(ox)(*RS*-2,4-ptn)$_2$]Cl·2H$_2$O (less soluble isomer in water).* A solution of [Co(NO$_2$)$_2$(*RS*-2,4-ptn)$_2$]NO$_2$[8] (2.2 g) and oxalic acid (2 g) in 70 ml of water was warmed at 60—70 °C for 1 hr. To this was added 10 ml of concentrated hydrochloric acid dropwise over a period of 2 hr with warming at 60—70 °C, which was then cooled to room temperature. Pink flakes were filtered off, washed with a small amount of water and ethanol, and air dried. Yield: 1 g. This complex is hardly soluble in water.
The other geometrical isomer, *cis-cis*-[Co(ox)(*RS*-2,4-ptn)$_2$]Cl was highly soluble in water and was obtained from the filtrate.

Found: C, 33.75; H, 7.62; N, 13.25%. Calcd for $C_{12}H_{32}N_4O_6CoCl$: C, 34.09; H, 7.63; N, 13.25%.

*Δ-$(-)_{510}$- and Λ-$(+)_{510}$-*trans-cis-*[Co(ox)(*RS*-2,4-ptn)$_2$]ClO$_4$·2H$_2$O.* To a suspension of *Δ,Λ-trans-cis*-[Co(ox)(*RS*-2,4-ptn)$_2$]Cl·2H$_2$O (0.8 g) in 50 ml of water was added silver nitrate (0.3 g) with stirring. After 30 min, silver chloride was filtered off, and washed with 50 ml of water. The filtrate and washings were combined, and stirred with sodium hydrogendibenzoyltartrate (0.38 g) for 2 hr at 60 °C. A pink powder was precipitated upon cooling at room temperature and filtered off to give crude dibenzoyltartrate salt of $(-)_{510}$-isomer (0.6 g). The filtrate was stored to obtain $(+)_{510}$-isomer. The crude dibenzoyltartrate was converted into perchlorate by treating with 99% acetic acid saturated with magnesium perchlorate. The crude perchlorate of $(-)_{510}$-isomer was recrystallized from water fractionally until the CD showed a constant curve. The pure optically active perchlorate is much more soluble in water than the racemate. The filtrate free of pink powder was stirred with an excess of anion exchanger Dowex 1-X4 in

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[6] L. J. Boucher and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.* **27**, 1093 (1965). L. J. Boucher, *Inorg. Chem.*, **6**, 2162 (1967).

[7] A. Rosenheim and A. Garfunkel, *Ber.*, **44**, 1865 (1911).

[8] C. J. Dippel and F. M. Jaeger, *Rec. Trav. Chim.*, **50**, 525 (1931).

perchlorate form for 4 hr at room temperature. The anion exchanger was filtered off, and washed with a small amount of water. The filtrate and washings were combined, evaporated to 40 ml at 55 °C under reduced pressure and filtered to remove less soluble racemate. Crystals were obtained fractionally from the filtrate by evaporation in a vacuum desiccator over diphosphorus pentoxide. Each fraction was checked by its CD, and pure perchlorate salt of $(+)_{510}$-isomer was obtained by repeating such fractional recrystallization.

Found: C, 29.85; H, 6.47; N, 11.78%. Calcd for $C_{12}H_{32}N_4O_{10}CoCl$: C, 29.61; H, 6.59; N, 11.51%.

cis-cis-Δ,Λ-[Co(ox)(RS-2,4-ptn)$_2$]Cl·6H$_2$O (more soluble isomer in water). A suspension of *trans*-[CoCl$_2$(*RS*-2,4-ptn)$_2$]Cl (6 g) and oxalic acid (2.1 g) in 110 ml of water was warmed at 70 °C for 2.5 hr and cooled to room temperature. A mixture of *cis-cis-* and *trans-cis-*isomer was obtained, and separated by recrystallization from 50 ml of hot water. More soluble *cis-cis*-isomer was condensed in the filtrate, and crystallized by evaporation in a vacuum desiccator over diphosphorus pentoxide. A pure complex was obtained by recrystallizing from hot water. Yield: *cis-cis*-isomer 7.2 g. *trans-cis*-isomer 0.3 g.

Found: C, 29.14; H, 7.48; N, 11.39%. Calcd for $C_{12}H_{40}N_4O_{10}CoCl$: C, 29.13; H, 8.15; N, 11.32%.

Δ-$(+)_{510}$- and Λ-$(-)_{510}$-cis-cis-[Co(ox)(RS-2,4-ptn)$_2$]-ClO$_4$·4H$_2$O. To a solution of Δ,Λ-*cis-cis*-[Co(ox)(*RS*-2,4-ptn)$_2$]Cl·6H$_2$O (1 g) in 50 ml of water was added sodium hydrogendibenzoyltartrate (0.44 g) in 20 ml of water. The solution was stirred for 2 hr at 60 °C. A red powder was precipitated upon cooling at room temperature and filtered off. The powder was crude dibenzoyltartrate of $(+)_{510}$-isomer, and converted into perchlorate as in the case for the *trans-cis*-isomer. The filtrate was stirred with anion exchanger Dowex 1-X4 in perchlorate form (3 g) for 4 hr at room temperature. The anion exchanger was filtered off and washed with a small amount of water. The filtrate and washings were combined, and crystallized fractionally by evaporation of the solution in a vacuum desiccator over diphosphorus pentoxide. Fractions which exhibited similar CD were combined and recrystallized from water until the CD of $(-)_{510}$-isomer became constant.

Found: C, 27.99; H, 6.86; N, 10.50%. Calcd for $C_{12}H_{36}N_4O_{12}CoCl$: C, 27.57; H, 6.94; N, 10.72%.

Λ-$(+)_{546}$-[Co(ox)(SS-2,4-ptn)$_2$]ClO$_4$. A solution of *trans*-[CoCl$_2$(*SS*-2,4-ptn)$_2$]ClO$_4$ (1 g) and oxalic acid (0.5 g) in 30 ml of water was warmed at 65 °C for 2 hr, and evaporated to dryness at 50 °C under reduced pressure. The residue, a mixture of Δ and Λ isomer, was separated into diastereoisomers by fractional recrystallization from water. Both isomers were very soluble in water, only less soluble Λ-isomer with a constant CD being obtained crystalline.

Found: C, 30.55; H, 6.14; N, 12.19%. Calcd for $C_{12}H_{30}N_4O_9CoCl$: C, 30.75; H, 6.45; N, 11.95%.

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 JASCO with its CD attachment. PMR spectra in D_2O and in a mixed solvent of D_2O and pyridine were obtained with a Varian T-60 spectrometer using Na-TMS as internal standard. All the measurements were carried out at room temperature.

Results and Discussion

Structure of the Complexes. A pair of diastereoisomers Δ and Λ are possible for the complexes [Co(acac)$_2$(*RR*-2,4-ptn)]$^+$ and [Co(acac)(*RR*-2,4-ptn)$_2$]$^{2+}$. However, only one pure isomer was obtained for each complex. Purity can be checked by pmr spectra, since the pairs of isomers are not enantiomeric with each other and the stereochemical environments of the protons on the chelate rings may differ for the two diastereoisomers.

Figure 1a shows the pmr spectrum of $(-)_{546}$-[Co(acac)$_2$(*RR*-2,4-ptn)]$^+$ in D_2O. A sharp doublet at 1.2 ppm, a doublet at 2.2 ppm and a singlet at 5.8 ppm are assigned to the methyl signal of the diamine chelate,[1] two kinds of methyl signals Me_1 and Me_2 (Fig. 2b) and the methylene signal of the acetylacetonato chelate,[9] respectively. The appearance of a single doublet of the methyl signal on the diamine chelate may indicate that the complex ion has C_2 symmetry, and that the diamine chelate takes a λ-skew boat conformation with two equatorial methyl groups (Fig. 2b). The pmr spectrum of unresolved [Co(acac)$_2$(*RR*-2,4-ptn)]$^+$ is more complex than that of the $(-)_{546}$-isomer, and reveals itself as a mixture of the two diastereoisomers (Fig. 1b).

A similar difference is seen between $(-)_{546}$-[Co(acac)(*RR*-2,4-ptn)$_2$]$^{2+}$ and a mixture of the two diastereoisomers. Each diastereoisomer should have two kinds of methyl groups Me_1 and Me_2 in the diamine chelate, whenever the chelates are in a λ-skew boat conformation (Fig. 2g). However, the spectrum of the $(-)_{546}$-isomer at 60 MHz shows no such presence (Fig. 3a). This might be due to the small difference in chemical shift between Me_1 and Me_2. A mixture of the two diastereoisomers gives a quartet signal due to the methyl groups of the diamine chelates. The mole ratio of the two isomers can be determined by the intensity of each peak (Fig. 3b).

[Co(acac)$_2$(*RS*-2,4-ptn)]$^+$ has no symmetry element except C_1, even thought the *RS*-2,4-pentanediamine chelate takes a fixed chair conformation with two equa-

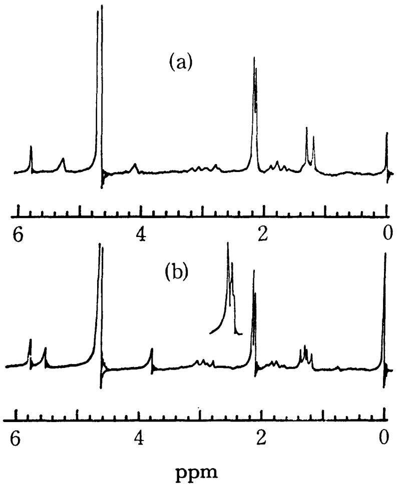

Fig. 1. a) PMR spectra of $\Delta(-)_{546}$-[Co(acac)$_2$(*RR*-2,4-ptn)]$^+$, b) Δ,Λ-[Co(acac)$_2$(*RR*-2,4-ptn)]$^+$ in D_2O.

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[9] R. J. York, W. D. Bonds, Jr., B. P. Cotsoradis, and R. D. Archer, *Inorg. Chem.*, **8**, 789 (1969). S. H. Laurie, *J. Chem. Soc. Dalton*, **1972**, 573.

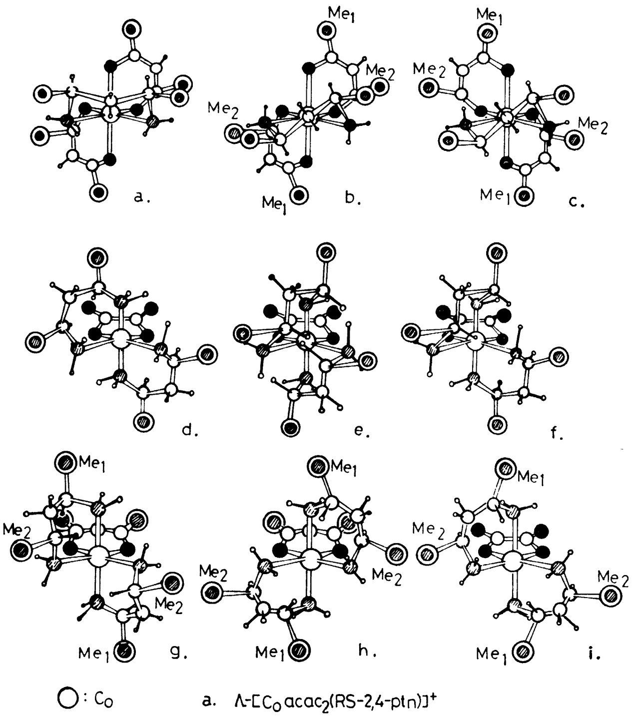

Fig. 2. Schematic structures of $[Co(AA)_{2,1}(2,4\text{-ptn})_{1,2}]$ (AA $=$acac$^-$, ox^{2-}).

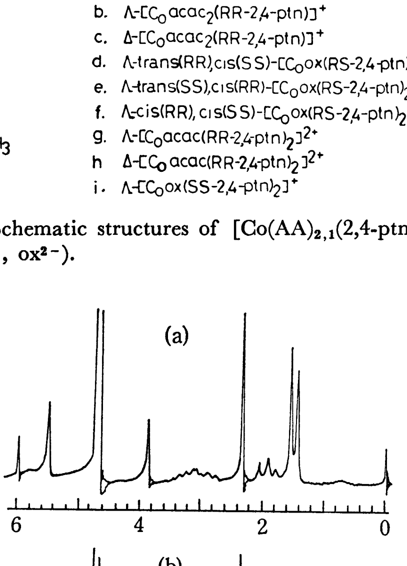

Fig. 3. PMR spectra of a) $\Delta(-)_{589}$-[Co(acac)(*RR*-2,4-ptn)$_2$]$^{2+}$, b) Δ,Λ-[Co(acac)(*RR*-2,4-ptn)$_2$]$^{2+}$ in D_2O.

torial methyl groups.[10] Therefore, the two methyl groups of the diamine chelate and the four methyl and the two methyne groups of the acetylacetonato chelates should all be in different environments. However, the pmr spectrum of the complex shows such a clear difference only on the methyne signal (Fig. 4a).

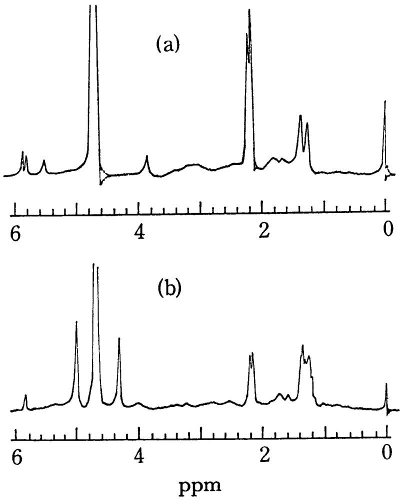

Fig. 4. PMR spectra of a) $\Delta\Lambda$-[Co(acac)$_2$(*RS*-2,4-ptn)]$^+$, b) Δ,Λ-[Co(acac)(*RS*-2,4-ptn)$_2$]$^{2+}$ in D_2O.

For the complexes of the type [Co(AA)(*RS*-2,4-ptn)$_2$] (AA$=$acac$^-$, ox^{2-}), three geometrical isomers can exist with respect to the location of the asymmetric carbon atoms of the diamine. These isomers are designated as *cis(RR)cis(SS)*, *trans(RR)cis(SS)* and *trans(SS)cis(RR)* (Fig. 2d, e, f). Each geometrical isomer has two optical isomers Δ and Λ, Of these six isomers, an enantiomeric pair, Λ-*trans(SS)cis(RR)* and Δ-*trans(RR)cis(SS)*, seems to have steric hindrance between the diamine chelates (Fig. 2e). Accordingly, two enantiomeric pairs, Λ-*cis(RR)cis(SS)* and Δ-*cis(SS)cis(RR)*, and Λ-*trans(RR)cis(SS)* and Δ-*trans(SS)cis(RR)*, may be formed.

We have obtained two geometrical isomers of racemic [Co(ox)(*RS*-2,4-ptn)$_2$]$^+$, *cis-cis*(more soluble isomer in water) and *trans-cis*(less soluble isomer in water) isomer, and resolved them into optical isomers.

For [Co(acac)(*RS*-2,4-ptn)$_2$]$^{2+}$, only a *cis-cis* geometrical isomer has been obtained, its optical resolution being only partially successful (see Experimental).

Since the *RS*-2,4-pentanediamine chelate would be in a chair conformation, the symmetries of *cis-cis* and *trans-cis* isomers are C_1 and C_2, respectively (Fig. 2). Thus the former has four unequivalent methyl groups and the latter two kinds of methyl groups on the diamine chelate. We see from Fig. 5b that the pmr spectrum of Λ-$(+)_{510}$-*cis(RR)cis(SS)*-[Co(ox)(*RS*-2,4-ptn)$_2$]$^+$ in a mixed solvent of pyridine and D_2O (1 : 4 in volume) clearly exhibits an octet signal due to the methyl groups of the diamine, although the Λ-$(+)_{510}$-*trans(RR)cis(SS)*-[Co(ox)(*RS*-2,4-ptn)$_2$]$^+$ gives a triplet signal which seems to be an accidental overlapping of two doublet signals (Fig. 5a). Thus we can determine the geometrical structure of the isomers by pmr spectra. A mixed solvent of pyridine and D_2O is more effective for the present complexes than D_2O, since it makes the difference in chemical shifts of the unequivalent methyl groups greater. The pmr spectrum of Λ-$(+)_{510}$-*trans(RR)cis(SS)*-[Co(ox)(*RS*-2,4-ptn)$_2$]$^+$ in D_2O shows only a doublet methyl signal (Fig. 5c).

The only isomer of [Co(acac)(*RS*-2,4-ptn)$_2$]$^{2+}$ we obtained can be assigned to the *cis-cis* structure, since its pmr spectrum shows two kinds of methyl signals for

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

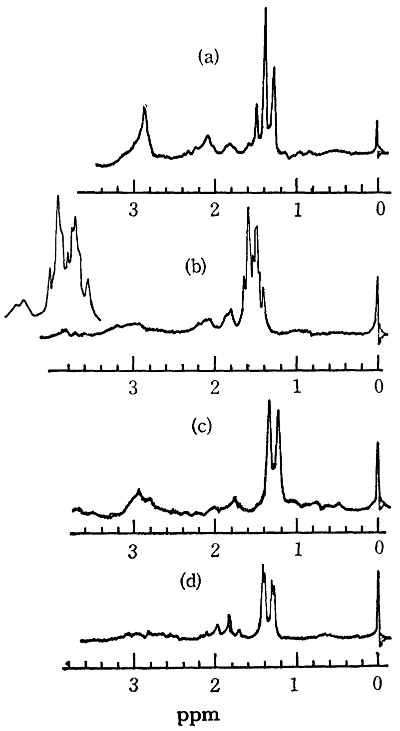

Fig. 5. PMR spectra of a) $\Lambda(+)_{510}$-*trans*(*RR*)*cis*(*SS*)-[Co-(ox)(*RS*-2,4-ptn)$_2$]$^+$ in D_2O-pyridine mixed solvent, b) $\Lambda(+)_{510}$-*cis*(*RR*)*cis*(*SS*)-[Co(ox)2,4-ptn)$_2$]$^+$ in D_2O-pyridine mixed solvent, c) $\Lambda(+)_{510}$-*trans*(*RR*)*cis*(*SS*)-[Co(ox)(*RS*-2,4-ptn)$_2$]$^+$ in D_2O, d) $\Lambda(+)_{546}$- or Δ,Λ-[Co(ox)(*SS*-2,4-ptn)$_2$[$^+$ in D_2O.

the acetylacetonato chelate (Fig. 4b).

[Co(ox)(*SS*-2,4-ptn)$_2$]$^+$ gives a pair of diastereoisomers, Δ and Λ. However, the pmr spectrum of Λ-isomer at 60 MHz is almost the same as that of a diastereoisomeric mixture Δ and Λ, no detectable chemical shift difference being observed in the methyl signals (Fig. 5d).

CD Spectra. The absorption and CD spectra of the optical isomers we prepared are shown in Figs. 6—9 and their numerical data in Table 1. Assignment of the absolute configurations of the complexes was made by comparison of their CD patterns in the first absorption band region with those of the related complexes of known absolute configuration.

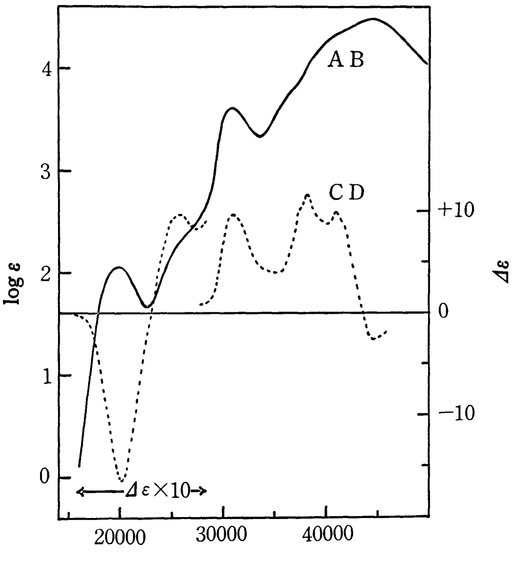

Fig. 6. Absorption (AB) and CD spectra of $\Delta(-)_{589}$-[Co-(acac)(*RR*-2,4-ptn)$_2$]$^{2+}$ in water.

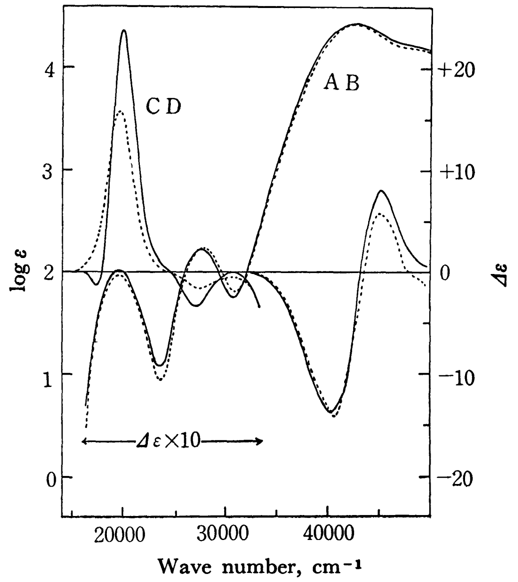

Fig. 7. Absorption (AB) and CD spectra of (——) $\Lambda(+)_{510}$-*trans*(*RR*)*cis*(*SS*)-[Co(ox)(*RS*-2,4-ptn)$_2$]$^+$, (······) $\Lambda(+)_{510}$-*cis*(*RR*)*cis*(*SS*)-[Co(ox)(*RS*-2,4-ptn)$_2$]$^+$ in water.

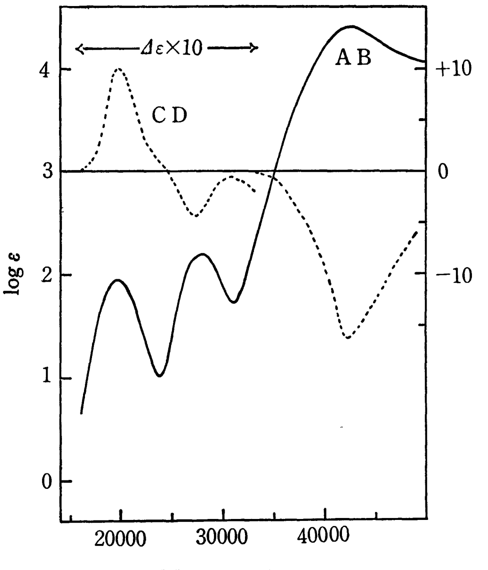

Fig. 8. Absorption (AB) and CD spectra of $\Lambda(+)_{546}$-[Co-(ox)(*SS*-2,4-ptn)$_2$]$^+$ in water.

The CD curve of Λ-[Co(en)$_3$]$^{3+}$ 11) (five-membered chelate) differs greatly from that of Λ-[Co(tn)$_3$]$^{3+}$ 12) (six-membered chelate) in the first absorption band region.3) The main CD band of the former is strong and has positive sign (+1.89), while that of the latter is very weak and has negative sign (−0.14). On the

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11) Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, This Bulletin, **30**, 795 (1957).

12) Y. Saito, T. Nomura, and F. Marumo, *ibid.*, **41**, 530 (1968).

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

Complex	AB	CD
$\Lambda(+)_{546}$-[Co(acac)$_2$(*RS*-2,4-ptn)]ClO$_4$	18.62 (2.08)	17.30 (−1.41)
		19.42 (+3.66)
	ca. 25.3 (*ca.* 2.4)	25.00 (−3.03)
	31.00 (3.81)	30.30(−51.79)
$\Lambda(-)_{546}$-[Co(acac)$_2$(*RR*-2,4-ptn)]ClO$_4$	18.52 (2.08)	17.33 (+1.28)
		19.42 (−2.78)
	ca. 25.3 (*ca.* 2.5)	25.13 (+2.15)
	30.96 (3.82)	30.58(+30.63)
		35.97 (+3.50)
	ca. 40.7 (*ca.* 4.4)	39.37(−44.50)
	44.05 (4.49)	46.30(+12.00)
$\Lambda(-)_{589}$-[Co(acac)(*RR*-2,4-pin)$_2$](ClO$_4$)$_2$	19.80 (2.06)	20.08 (−1.64)
	ca. 26.0 (*ca.* 2.3)	25.84 (+0.96)
	30.86 (3.61)	30.96 (+9·63)
		38.17(+11.72)
	ca. 41.0 (*ca.* 4.3)	40.98 (+9.98)
	44.44 (4.48)	44.64 (−2.74)
$\Lambda(+)_{510}$-*trans*(*RR*)*cis*(*SS*)[Co(ox)(*RS*-2,4-ptn)$_2$]ClO$_4\cdot$2H$_2$O	19.61 (2.01)	17.39 (−0.13)
		19.88 (+2.36)
	27.62 (2.22)	27.03 (−0.34)
	42.55 (4.43)	40.32(−13.75)
		45.05 (+8.13)
$\Lambda(+)_{510}$-*cis*(*RR*)*cis*(*SS*)[Co(ox)*RS*-2,4-ptn)$_2$]ClO$_4$-4H$_2$O	19.61 (1.96)	19.65 (+1.57)
	27.86 (2.23)	27.40 (−0.16)
	42.55 (4.42)	40.65(−14.13)
		45.05 (+5.78)
$\Lambda(+)_{546}$-[Co(ox)(*SS*-2,4-ptn)$_2$]ClO$_4$	19.72 (1.94)	19.84 (+1.00)
	27.93 (2.19)	27.17 (−0.44)
	42.74 (4.40)	42.37(−16.16)

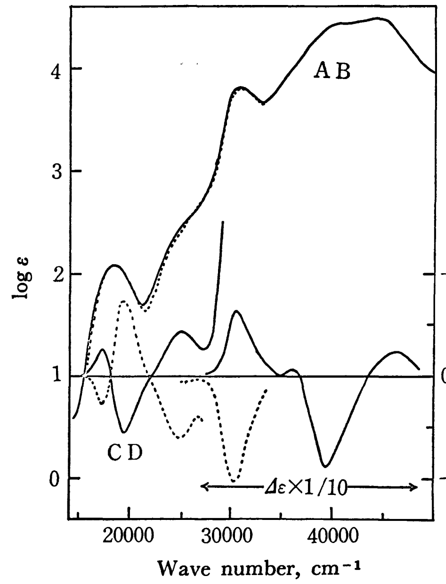

Fig. 9. Absorption (AB) and CD spectra of (——) $\Delta(-)_{546}$-[Co(acac)$_2$(*RR*-2,4-ptn)]$^+$, (······) $\Lambda(+)_{546}$-[Co(acac)$_2$(*RS*-2,4-ptn)]$^+$ in water.

other hand, Λ-[Co(*RR*-2,4-ptn)$_3$]$^{3+}$ 13) and Δ-[Co(*RR*-2,4-ptn)$_3$]$^{3+}$ 14) give a single CD band with positive and negative signs, respectively,1) in agreement with the sign of the main CD band of [Co(en)$_3$]$^{3+}$. However, the CD magnitudes of these two diastereoisomers differ greatly (Λ-isomer: +2.69; Δ-isomer: −0.55), even when the vicinal contribution of the optically active *RR*-2,4-pentanediamine chelate is taken into account.1) Thus, the CD spectra of tris-β-diamine complexes differ more or less from those of tris-α-diamine complexes.

On the other hand, the CD spectrum of Δ-(b)$_{589}$-[Co(acac)(tn)$_2$]$^{2+}$ whose absolute configuration was determined by the X-ray method2) is very similar to that of the corresponding ethylenediamine complex, [Co(acac)(en)$_2$]$^{2+}$. Although the absolute configuration of the latter is assigned on the basis of its CD sign in the first absorption band region,15) such a similarity suggests that a difference in the CD between six-membered and five-membered diamine complexes is not so marked for the present bis-type complex as in the tris-type complex. $(-)_{589}$-[Co(acac)(*RR*-2,4-ptn)$_2$]$^{2+}$ gives a CD curve very similar to that of Δ-[Co-

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

14) A. Kobayashi, F. Marumo, and Y. Saito, presented at the 22nd Symposium on Coordination Chemistry, Osaka, Japan (1972).

15) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, **1965**, 5094.

(acac)(tn)$_2$]$^{2+}$ in the entire region, and can be safely assigned to Δ configuration (Fig. 6). For [Co(acac)-(*RS*-2,4-ptn)$_2$]$^{2+}$, complete optical resolution was not achieved, but the complex shows a CD pattern similar to that of the corresponding RR-2,4-pentanediamine complex.

No report has been published on the absolute configuration of any oxalato-bis-α-diamine complex by the X-ray method.[16] However, such a configuration may be assigned without ambiguity on the basis of the CD sign in the first absorption band region, since the CD is usually very similar to that of [Co(en)$_3$]$^{3+}$. Stereospecifically formed Λ-oxalato-bis-diamine type complexes give a main CD band with the positive sign in this region.[17] The main CD bands of both $(+)_{510}$-*cis-cis* and $(+)_{510}$-*trans-cis* isomers of [Co(ox)(*RS*-2,4-ptn)$_2$]$^+$ are positive and almost enantiomeric with those of Δ-[Co(ox)(α-diamine)$_2$]$^+$ (α-diamine=en, R-pn) (Fig. 7).[15] Therefore, the $(+)_{510}$- and $(+)_{510}$-isomers can be assigned to Λ-*cis(RR)cis(SS)* and Λ-*trans(RR)-cis(SS)* structure, respectively. The Λ-*cis(RR)cis(SS)* isomer has one positive CD band, while the Λ-*trans-(RR)cis(SS)* isomer has one very weak negative and one strong positive band from longer to shorter wave length, but the origin of this difference is unknown.

In a similar way, less soluble $(+)_{546}$-isomer of [Co-(ox)(*SS*-2,4-ptn)$_2$]$^+$ is assigned to Λ configuration (Fig. 8). The CD spectrum of $(-)_{546}$-[Co(acac)$_2$(*RR*-2,4-ptn)]$^+$ is shown in Fig. 9. It is almost enantiomeric with the spectra of $(+)_{546}$-[Co(acac)$_2$(en)]$^+$ [18] and $(+)_{546}$-[Co(acac)$_2$(NH$_3$)$_2$]$^+$ [18] which are assigned to Λ configuration from the sign of their CD in the first absorption band region.[19] Therefore, $(-)_{546}$-[Co-(acac)$_2$(*RR*-2,4-ptn)]$^+$ can be assigned to Δ configuration. $(+)_{546}$-[Co(acac)$_2$(*RS*-2,4-ptn)]$^+$ gives a CD curve enantiomeric with that of $(-)_{546}$-[Co(acac)$_2$-(*RR*-2,4-ptn)]$^+$, and is assigned to Λ configuration (Fig. 9). Thus, the CD spectra of bis-acetylacetonato-β-diamine cobalt(III) complexes are essentially the same as those of the corresponding ethylenediamine complexes.

All the results lead to the conclusion that the mono- and bis-β-diamine complexes of the types given in this paper show CD spectra similar to those of the corresponding α-diamine complexes, and their absolute configuration may be assigned on the basis of their CD sign in the first absorption band region as well as the α-diamine complexes.

It is to be noted that the assignment of structures for the present bis-diamine complexes on the basis of pmr and CD spectra is consistent with that deduced from the studies with molecular models; the smaller the steric interaction among chelate rings in a complex, the greater the formation of a diastereoisomer. For example, the steric interaction for the Δ-$(-)_{589}$-isomer of [Co(acac)(*RR*-2,4-ptn)$_2$]$^{2+}$ seems to be smaller than that for the Λ-isomer, and the former is always formed to a much greater extent than the latter.

We are grateful to the Ministry of Education for a Grant-in-aid for studies on optically active complexes.

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[16] $(-)_D$ -[Co(ox)(en)$_2$]$^+$ has been assigned to Δ configuration by the X-ray analysis. T. Aoki, K. Matsumoto, S. Ooi, and H. Kuroya, This Bulletin, **46**, 159 (1973).

[17] T. Hattori, M. Saburi, and S. Yoshikawa, presented at the 21st Symposium on Coordination Chemistry, Nagoya, Japan (1971). F. Mizukami, to be published.

[18] L. J. Boucher, *Inorg. Chem.*, **9**, 1202 (1970); *Inorg. Chim. Acta*, **6**, 29 (1972).

[19] The absolute configuration of these two complexes seems to be Δ from comparison of the CD spectra of some [CoN$_2$O$_4$] type complexes. However, the absolute configuration is not discussed here.