Cobalt(III) Complexes with Tripodlike Quadridentate Ligands. III.[1,2) Absorption and Circular Dichroism Spectra of Cobalt(III) Complexes Containing *N*-(2-Aminoethyl)iminodiacetate and Amino Carboxylate or 1,2-Diamine

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Glycinato, L-alaninato, ethylenediamine, *N,N*-dimethylethylenediamine, (*R*)-propylenediamine, (*R,R*)-1,2-cyclohexanediamine and meso-2,3-butanediamine cobalt(III) complexes of a tripodlike ligand, *N*-(2-aminoethyl)-iminodiacetate have been prepared. The geometrical configurations are assigned on the basis of their absorption, circular dichroism, and ^{1}H-NMR spectra. The *trans*(*O*) isomer of *meso*-2,3-butanediamine complex is optically resolved and the relationship between the absolute configurations of the chiral 1,2-diamine complexes and their circular dichroism is discussed.

The aeida[3) ligand is a tripodlike quadridentate ligand with two nitrogen and two oxygen atoms as donors and, as well as *i*-dtma, can take two different configurations in the six-coordinate metal complex (s-type and u-type in Fig. 1). The s-type configuration with a plane of symmetry is achiral, while the u-type, for lack of it, chiral. The isomerism of the u-type [Co(tripod)-(bidentate)] complexes was mainly argued in the previous paper[2) concerning the *i*-dtma complexes.

Two different kinds of isomerism occur in the s-type [Co(tripod)(bidentate)] complexes: the geometrical isomerism in the glycinato complexes and the optical isomerism in the *meso*-2,3-butanediamine complexes, where both bidentate ligands, gly and *meso*-2,3-bn, are achiral (Fig. 2). When bidentate ligands are chiral (such as L-ala and (*R*)-pn), the two kinds of isomerism (geometrical and optical) arise at the same time.[1)

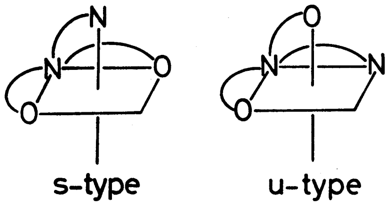

Fig. 1. Two different coordination modes of aeida ligand.

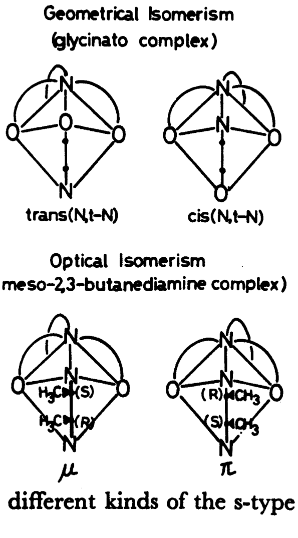

Fig. 2. Two different kinds of the s-type isomerism.

In the present paper the u- and s-types of isomersim in the aeida cobalt(III) complexes with an amino carboxylate or 1,2-diamine are reported.

Experimental

Preparations. *1) [Co(gly)(aeida)]*: One gram of Na-[Co(NO$_2$)$_2$(aeida)]·2H$_2$O[4) was treated with 10 cm^3 of acetic acid and 2 cm^3 of water on a steam bath for 1 h. The resulting red-violet solution was concentrated almost to dryness and to the residue was added 30 cm^3 of acetone to precipitate a pale violet powder, which contained the complex anion, [Co(CH$_3$-CO$_2$)$_2$(aeida)]$^-$. The powder was filtered with suction and washed with a small amount of acetone several times and then with ether and dried in a desiccator. The dry powder was dissolved in 10 cm^3 of water and to this red-violet solution was added a solution of glycine (0.5 g) neutralized with an equimolar amount of NaOH. The solution was mechanically stirred for 2 h at 60 °C. The resulting deep red solution was poured into a cation-exchanger column (Dowex 50w-x2, H$^+$ form, 200—400 mesh) and the product was eluted with water. The adsorbed band separated into seven bands. The first and second bands were found to contain complex anions and the seventh band seemed to contain [Co(aeida)(H$_2$O)$_2$]$^+$ because it was not eluted with water. Fractions from the third to the sixth band contained neutral complexes. The fourth and the sixth turned out to contain *mer*- and *fac*-[Co-(gly)$_3$], respectively, from their absorption spectra and elemental analyses. The third (red; G-3) and the fifth (purple; G-5) contained the desired complexes. Each of them was evaporated almost to dryness and a small amount of methanol was added to the residue to precipitate the complex as a powder, which was recrystallized from warm water, washed with methanol and ether and dried in air. Found for G-3: C, 28.00; H, 5.27; N, 12.26%. Calcd for [Co(gly)(aeida)]·2H$_2$O: C, 27.99; H, 5.30; N, 12.25%. Found for G-5: C, 31.06; H, 4.65; N, 13.57%. Calcd for [Co(gly)(aeida)]: C, 31.28; H, 4.60; N, 13.68%.

2) [Co(L-ala)(aeida)]: This complex was prepared in the same way as that for the glycinato complex in *1)* using L-alanine instead of glycine. Sparingly soluble isomers of [Co-(L-ala)$_3$] deposited during the substitution reaction were filtered off and the filtrate was loaded on a cation-exchanger column. On elution with water, seven bands appeared, the desired bands being A-3 (red) and A-5 (purple). The other fractions turned out to be complex anions (A-1 and -2) and *mer*- and *fac*-[Co(L-ala)$_3$] (A-4 and -6) from their absorption and circular dichroism spectra. Found for A-3: C, 29.86; H, 5.66; N, 11.65%. Calcd for [Co(L-ala)(aeida)]·$2H_2O$: C, 30.26; H, 5.65; N, 11.76%. Found for A-5: C, 30.85; H, 5.37; N, 11.76%. Calcd for [Co(L-ala)(aeida)]·$1.5H_2O$: C, 31.04; H, 5.51; N, 12.07%.

3) [Co(aeida)(en)]ClO_4: A reaction mixture containing this complex was prepared by the same method as described in the literature.[4] Two isomers, called E-1 and E-2 in the elution order, were obtained by a column chromatographic method, using a Sephadex C-25 column and 0.05 M $NaClO_4$ as an eluting solvent (1 M = 1 mol dm^{-3}). Found for E-1: C, 24.50; H, 4.66; N, 14.39%. E-2: C, 24.33; H, 4.62; N, 14.15%. Calcd for [Co(aeida)(en)]ClO_4: C, 24.47; H, 4.63; N, 14.27%.

4) Other 1,2-Diamine Complexes with Aeida: (*R*)-Propylenediamine, (*R,R*)-1,2-cyclohexanediamine and *N,N*-dimethylethylenediamine complexes were prepared in the same way as that for the ethylenediamine complex using the relevant 1,2-diamine instead of en. Two isomers (M-1, blue-violet, and M-2, red-violet, in the elution order) were isolated for *N,N*-Me_2-en and only one isomer (*trans*(*O*)) for (*R*)-pn and (*R,R*)-chxn. Found for the (*R*)-pn complex: C, 26.46; H, 5.07; N, 13.88%. Calcd for [Co(aeida){(*R*)-pn}]ClO_4: C, 26.58; H, 4.97; N, 13.78%. Found for the (*R,R*)-chxn complex: C, 30.15; H, 5.90; N, 11.74%. Calcd for [Co(aeida){(*R,R*)-chxn}]ClO_4·$2H_2O$: C, 29.85; H, 5.89; N, 11.61%. Found for M-1: C, 27.96; H, 5.22; N, 13.07%. Calcd for [Co(aeida)(*N,N*-Me_2-en)]ClO_4·$0.5H_2O$: C, 27.95; H, 5.41; N, 13.04%. Found for M-2: C, 28.40; H, 5.32; N, 13.13%. Calcd for [Co(aeida)(*N,N*-Me_2-en)]ClO_4: C, 28.54; H, 5.28; N, 13.32%.

*5) Preparation and Optical Resolution of [Co(aeida)(*meso*-2,3-bn)]Cl·H_2O:* A red-violet solution prepared from Na[Co$(NO_2)_2$(aeida)]·$2H_2O$ (1 g), acetic acid (10 cm^3) and water (2 cm^3) was evaporated to about one tenth of the initial volume. To the syrupy material was added a small amount of water and the solution was evaporated again on a steam bath. To the residue were added 5 cm^3 of water and a solution (3 cm^3) of *meso*-2,3-butanediamine dihydrochloride[5] (0.8 g) neutralized with an equimolar amount of NaOH. The mixture was heated on a steam bath for 30 min. The resulting deep red solution was poured into a Sephadex C-25 column (Na^+ form) as is described in *1)* and the adsorbed band was eluted with a 0.05 M NaCl aqueous solution. Two bands appeared; the first band was overwhelmingly larger than the second. The first eluted band (B-1) was evaporated on a rotary evaporator almost to dryness below 40 °C and to the residue was added 50 cm^3 of methanol to extract the complex. The extract containing the desired chloride was evaporated and the red-violet powder deposited was collected on a glass filter and recrystallized from a small amount of warm water by adding methanol. The second band (B-2) was also treated with the same method as that for B-1 and pale pink powder was isolated. Found for B-1: C, 32.21; H, 6.34; N, 15.00%. For B-2: C, 32.00; H, 6.27; N, 14.84%. Calcd for [Co(aeida)(*meso*-2,3-bn)]Cl·H_2O: C, 32.05; H, 6.47; N, 14.95%.

The racemate, B-1, [Co(aeida)(*meso*-2,3-bn)]Cl·H_2O, (0.68 g; 1.8×10^{-3} mol) was dissolved in 10 cm^3 of water and to the solution was added a solution of $(+)_{546}$-Ag[Co(edta)][6] (0.87 g; 1.9×10^{-3} mol) in 10 cm^3 of water and the mixture was mechanically stirred for 10 min at 40 °C. Silver chroide deposited was filtered off, 20 cm^3 of methanol was added to the filtrate, and the solution was kept standing overnight in a refrigerator. Pale red-violet crystals deposited were collected with suction and recrystallized from a small amount of water by adding methanol. Found: C, 32.29; H, 5.45; N, 11.28%. Calcd for [Co(aeida)(*meso*-2,3-bn)][Co(edta)]·$4H_2O$: C, 32.44; H, 5.73; N, 11.35%.

The less-soluble diastereomer was dissolved in a small amount of water and converted into $(+)_{589}$-chloride by passing through an anion-exchanger column (Cl^- form) and evaporating the eluate on a rotary evaporator. Found: C, 32.70; H, 6.36; N, 15.13%. Calcd for $(+)_{589}$-[Co(aeida)(*meso*-2,3-bn)]Cl·$0.5H_2O$: C, 32.84; H, 6.35; N, 15.32%.

Measurements. The visible and ultraviolet absorption spectra were measured by a Shimadzu UV-200 spectrophotometer in aqueous solutions. The CD spectra were recorded on a Jasco MOE-1 spectropolarimeter in aqueous solutions and the ^1H-NMR spectra were obtained in deuterium oxide (D_2O) on a Varian XL-100-15 spectrometer using DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as an internal standard.

Results and Discussion

a) Aeida Complexes with Amino Carboxylates. As an aeida ligand can take both s- and u-type configurations, four geometrical isomers are possible for the (amino carboxylato) complex (Fig. 3). In Fig. 3 the upper two are s-type and the lower two u-type with respect to the tripodlike ligand, and only one isomer, u-*β*, of the four is a *fac*(*O*)-isomer and the others (s-*α* and -*β*, and u-*α*) are *mer*(*O*)-isomers. Two isomers were isolated for each of the glycinato and the L-alaninato complexes: G-3 and -5 for gly; A-3 and -5 for L-ala. The fact that G-3 and A-3 show splitting of the first d-d absorption band (see Fig. 5) implies that A-3 and G-3 are *mer*-isomers, of structure s-*α*, s-*β*, or u-*α*. The absorption spectrum of A-5 corresponds well to that of G-5 showing a *fac* pattern, while the splitting of the first d-d band for A-3 is quite different from that for G-3. Thus G-3 and A-3 should have different geometrical structures in spite of their resemblance both in the column chromatographic behavior and in their formation ratio to the corresponding *fac*-isomer (G-5 or A-5).

^1H-NMR spectra lead one to more explicit distinction between the isomers. Figure 4 shows the ^1H-NMR spectra of four isomers obtained for the glycinato and L-alaninato complexes. For the gly complex, G-3 and -5 show an AB quartet pattern (4.42, 4.27, 4.08, and 3.94 ppm for G-3; 4.22, 4.06, 3.88, and 3.72 ppm for G-5) and a singlet peak due to the acetate methylene protons of aeida (G-3, 4.08; G-5, 3.92 ppm). Thus they are suggested to have the u-type structure (u-*α* or -*β*). Because G-5 is assigned to have the structure *mer*(u-*β*)

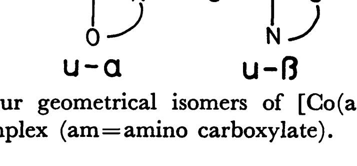

Fig. 3. Four geometrical isomers of [Co(am)(aeida)]-type complex (am = amino carboxylate).

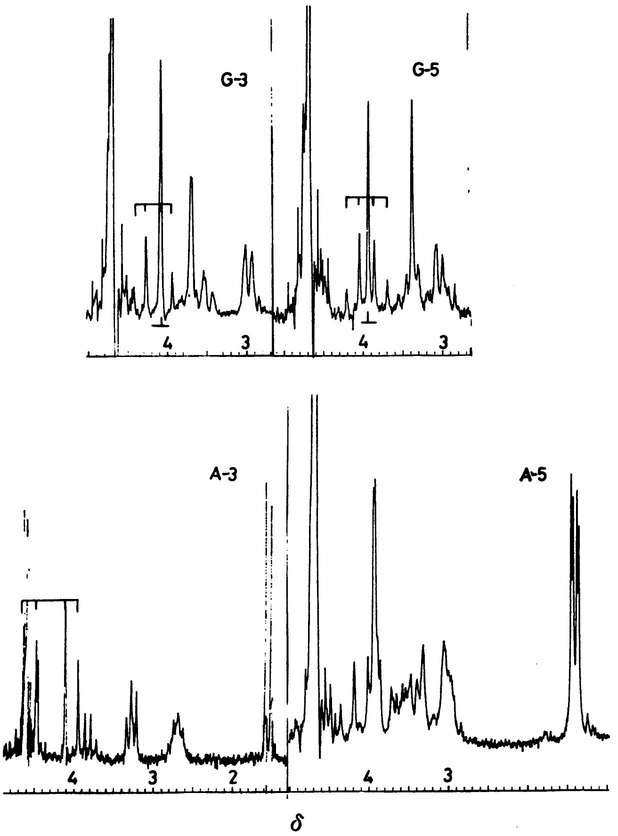

Fig. 4. ^{1}H-NMR spectra of isomers of [Co(am)(aeida)] (am=gly or L-ala).

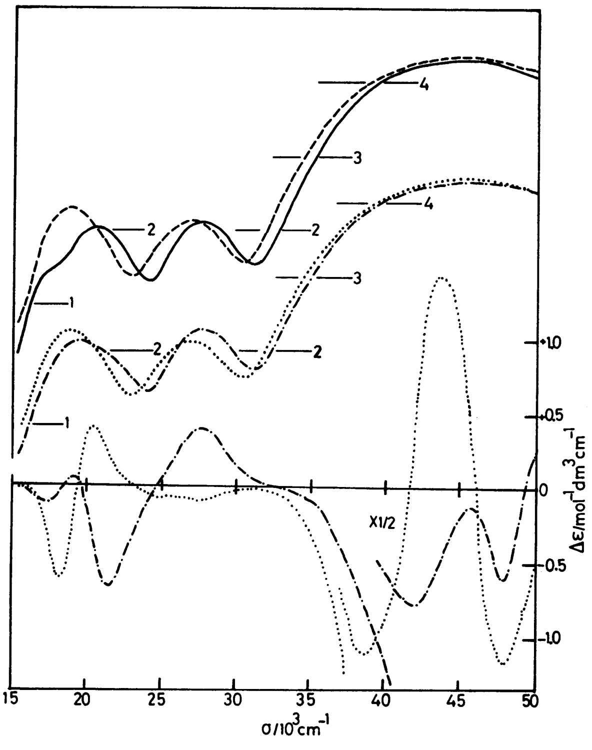

Fig. 5. Absorption and CD curves of [Co(am)(aeida)] (am=gly or L-ala): G-3 (——), G-5 (------), A-3 (–·–·–), and A-5 (······).

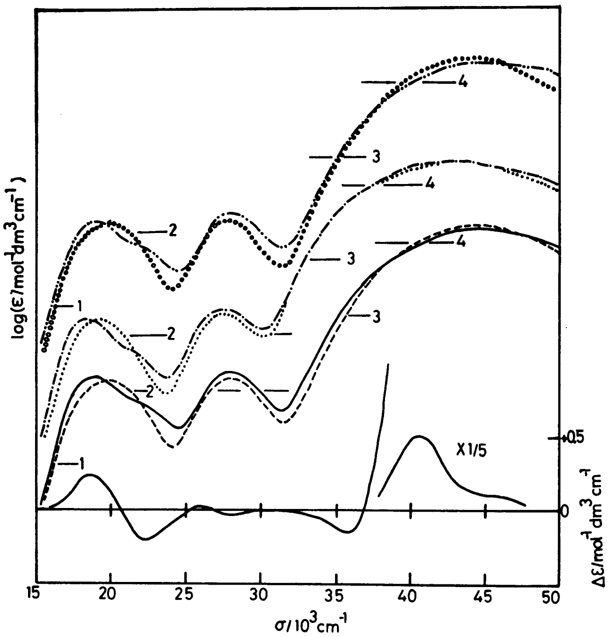

Fig. 6. Absorption and CD curves of [Co(aeida)(da)]$^+$ (da=en, N,N-Me$_2$-en, and *meso*-2,3-bn): E-1 (–··–··–), E-2 (oooooo), M-1 (–·–·–), M-2 (······), B-1 (——), and B-2 (------).

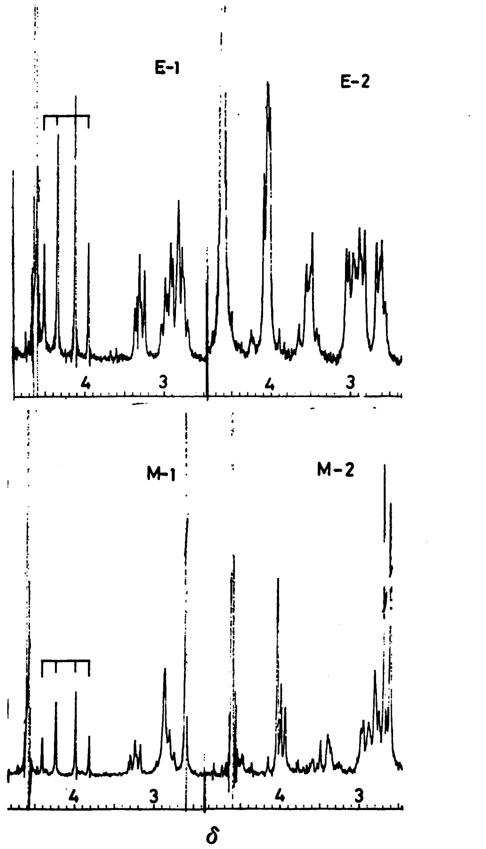

Fig. 7. ^{1}H-NMR spectra of isomers of [Co(aeida)(da)]$^+$ (da=en and N,N-Me$_2$-en).

from the absorption spectrum, G-3 should be of the structure u-α. The L-ala complex A-3 exhibiting an AB quartet (4.64, 4.48, 4.11, and 3.95 ppm) due to the aeida methylene protons and a methyl doublet (1.58 and

TABLE 1. ABSORPTION DATA OF [Co(A-B)(aeida)]-TYPE COMPLEXES (A-B=gly, L-ala,en,*N*,*N*-Me$_2$-en, *meso*-2,3-bn, (*R*)-pn, AND (*R*,*R*)-chxn)
Wave numbers and log ε values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1}, respectively.

Complex	d-d transition band 1st	2nd	UV band
(G-3)-[Co(gly)(aeida)]	≈18.5 (sh 1.5) 20.55 (2.04)	27.66 (2.12)	45.15 (4.29)
(G-5)-[Co(gly)(aeida)]	18.87 (2.30)	26.88 (2.14)	44.84 (4.34)
(A-3)-[Co(L-ala)(aeida)]	19.47 (2.14) ≈22 (sh 1.8)	27.70 (2.29)	45.46 (4.28)
(A-5)-[Co(L-ala)(aeida)]	18.87 (2.27)	26.92 (2.13)	45.05 (4.33)
(E-1)-[Co(aeida)(en)]$^+$	19.05 (2.16) ≈22 (sh 1.8)	28.25 (2.26)	44.84 (4.26)
(E-2)-[Co(aeida)(en)]$^+$	20.06 (2.12)	27.93 (2.16)	44.15 (4.30)
(M-1)-[Co(aeida)(*N*,*N*-Me$_2$-en)]$^+$	18.47 (2.20) ≈21.5 (sh 1.8)	27.55 (2.33)	≈37 (sh) 43.01 (4.31) ≈48 (sh)
(M-2)-[Co(aeida)(*N*,*N*-Me$_2$-en)]$^+$	19.18 (2.20)	27.66 (2.28)	≈37 (sh) 43.10 (4.30) ≈48 (sh)
(B-1)-[Co(aeida)(*meso*-2,3-bn)]$^+$	18.94 (2.18) ≈22 (sh 1.8)	28.13 (2.26)	44.64 (4.25)
(B-2)-[Co(aeida)(*meso*-2,3-bn)]$^+$	19.96 (2.13)	28.03 (2.17)	44.44 (4.30)
[Co(aeida){(*R*)-pn}]$^+$	19.01 (2.18) ≈22 (sh 1.8)	28.13 (2.26)	44.94 (4.31)
[Co(aeida){(*R*,*R*)-chxn}]$^+$	18.94 (2.18) ≈22 (sh 1.8)	28.05 (2.33)	44.44 (4.33)

1.51 ppm) due to L-alaninate was assigned to have the s-type structure (s-α or s-β), while A-5 isomer which was assigned to the *fac*-isomer exhibits two methyl doublets (1.45 and 1.38; 1.43 and 1.36 ppm) with about the same intensity, and thus was assigned to a mixture of two diastereomers of the structure u-β.

Figure 5 shows the absorption and CD spectra of the gly and the L-ala complexes. The first absorption band of G-3 shows a large splitting: $\tilde{\nu}_{max}/10^3$ cm^{-1} (log (ε_{max}/cm^{-1} mol^{-1} dm^3)), ≈18.5 (sh 1.5), 20.55 (2.04); while G-5 a narrow and simple peak 18.87 (2.30). For the L-ala complex, A-3 shows a broad peak 19.47 (2.14) with an ambiguous shoulder at higher energy $\approx 22\times 10^3$ cm^{-1}, while A-5 a simple peak. The CD pattern of A-3 resembles that of *trans*(*N*)-[Co(ata)(L-ala)]$^-$ complex;[1] three (−, + and −) for the first and one (+) component for the second d-d band. This suggests that A-3 has the structure s-α. The CD of A-5 (about 1 : 1 mixture of the diastereomers of the structure u-β) shows a pattern similar to those of the [Co(ata)(L-ala)]$^-$ and [Co(tren)(L-ala)]$^{2+}$ complexes of *cis*(*N*,*t*-*N*)-structure;[1] two (− and +) for the first and two (− and −) components for the second d-d band. These observations suggest that the relationship between the CD patterns in the d-d absorption band region and the coordination geometry of L-amino carboxylato complexes found for the ata and tren complexes also holds for the aeida complex, because structures s-α and s-β correspond to the structure *trans*(*N*,*t*-*N*) and *cis*(*N*,*t*-*N*), respectively. An equimolar mixing of the diastereomers of the structure u-β will cancel the chiralities of u-type aeida and leave only those of L-amino carboxylates to give a CD pattern corresponding to the structure *cis*(*N*,*t*-*N*).

Though four isomers are possible (Fig. 3) for each of the glycinato and the L-alaninato complexes, only two were isolated. It is difficult to explain why the main products isolated have different structures (s-α for the L-ala complex; u-α for the gly complex).

b) Aeida Complexes with 1,2-Diamines. Two isomers are possible for the en complex; *trans*(*O*) s-type and *cis*(*O*) u-type, and they can be distinguished by means of their absorption and ^{1}H-NMR spectra.[7] Though the *N*,*N*-Me$_2$-en complex has four possible isomers (two s-type and two u-type isomers similar to those in Fig. 3), only two were isolated. They can also be assigned to *trans*(*O*) and *cis*(*O*) by the same method as used for the en complex. Both E-1 and M-1 show a large splitting of the first d-d band: 19.05 (2.16), ≈22 (sh) for E-1; 18.47 (2.20), ≈21.5 (sh) for M-1), while E-2 and M-2 only a simple broad peak (Fig. 6 and Table 1). E-1 and M-1 show an AB quartet pattern (4.49, 4.32, 4.09, and 3.93 ppm for E-1; 4.41, 4.24, 3.99, and 3.82 ppm for M-1) due to the acetate methylene protons of aeida (Fig. 7). Though E-2 and M-2 show complicated acetate signals, two AB quartets are observed for E-2 (4.26, 4.10, 4.06, and 3.90; 4.23, 4.04, 4.02; and 3.84 ppm). The *N*-methyl signals (two singlets at 2.66 and 2.59 ppm) are more useful in the structural assignment than AB quartets for M-2. These results imply that E-1 and M-1 have s-type and E-2 and M-2 u-type structures, respectively, though the optical resolution of the u-type isomers was not successful. It is found that the two more-stable isomers the for the *N*,*N*-Me$_2$-en complex should have such structures that the two tertiary amine groups occupy *trans* positions each other by examining molecular models. The absorption spectra of the *N*,*N*-Me$_2$-en complex showed an absorp-

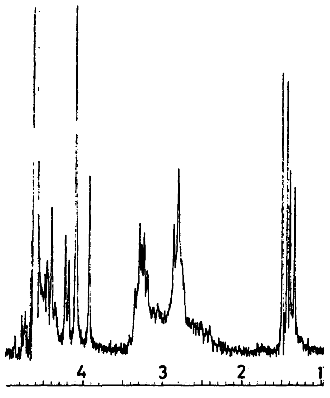

Fig. 8. ^{1}H-NMR spectrum of [Co(aeida){(*R*)-pn}]$^+$.

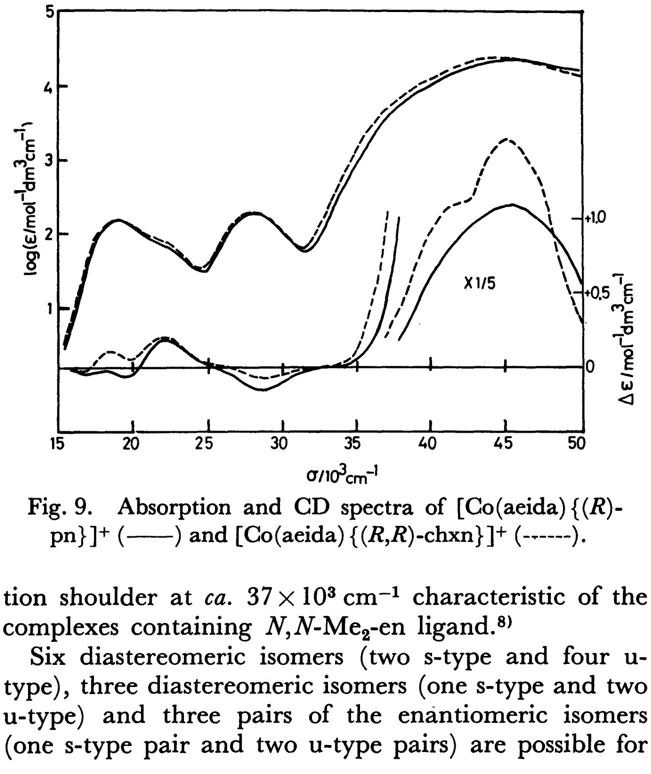

Fig. 9. Absorption and CD spectra of [Co(aeida){(*R*)-pn}]$^+$ (——) and [Co(aeida){(*R*,*R*)-chxn}]$^+$ (------).

tion shoulder at *ca.* 37×10^3 cm^{-1} characteristic of the complexes containing *N*,*N*-Me$_2$-en ligand.[8)]

Six diastereomeric isomers (two s-type and four u-type), three diastereomeric isomers (one s-type and two u-type) and three pairs of the enantiomeric isomers (one s-type pair and two u-type pairs) are possible for the (*R*)-pn, (*R*,*R*)-chxn, and *meso*-2,3-bn complexes, respectively. Only one complex isolated for the (*R*)-pn or (*R*,*R*)-chxn was assigned to *trans*(*O*) s-type structure and two complexes B-1 and -2 of *meso*-2,3-bn to *trans*(*O*) and *cis*(*O*), respectively, from their absorption spectra (Table 1). The ^{1}H-NMR spectrum of the (*R*)-pn complex (Fig. 8) showed two methyl doublets (1.40 and 1.34; 1.30 and 1.24 ppm), indicating that the complex is composed of about 3 : 2 mixture of the two s-type isomers.

All possible two isomers of the s-type complexes with a chiral amino carboxylate have been isolated for the ata, tren and *i*-dtma, except for the aeida. The CD intensities in the d-d transition band region have been explained by assuming two contributions from the "intrinsic vicinal effect" of the asymmetric carbons and from the "quasi-enantiomeric effect" of the substituents. Meanwhile, the separation of the s-type isomers of the (*R*)-pn complexes for ata,[1)] *i*-dtma[2)] and aeida was unsuccessful and the only one isomer of the two for the tren complex was isolated.[1)]

The (*R*)-pn complex has two sources of the optical activity, similar to those of the L-ala complex, one is the "intrinsic vicinal effect," and the other is the "quasi-enantiomeric effect," while the (*R*,*R*)-chxn complex has only one source of the optical activity from the "intrinsic vicinal effect" because the coordination of (*R*,*R*)-chxn produces no quasi-enantiomeric isomerism. The CD spectrum of the (*R*)-pn complex (a mixture of two diastereomers) exhibited three (−, −, and +), one (−) and one (+) component, while that of the (*R*,*R*)-chxn three (−, + and +), one (−) and one (+) component in the first, second d-d, and charge-transfer band region, respectively (Fig. 9 and Table 2). Their CD intensities and patterns in the d-d transition band region are similar to those of the complexes which have no "quasi-enantiomeric effect."

In the previous paper[1)] it was pointed out that the (*R*)-pn complex with tren, which contains only one isomer, showed larger CD than the other (*R*)-pn complexes with ata and *i*-dtma, which contain two isomers. The large CD intensity of the (*R*)-pn tren complex is due to the "quasi-enantiomeric effect."

Table 2. CD Data of [Co(A-B)(aeida)]-type complexes (A-B=L-ala,(*R*)-pn, (*R*,*R*)-chxn, and *meso*-2,3-bn)
Wave numbers and Δε values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1}, respectively.

Complex	d-d transition band		UV band
	1st	2nd	
(A-3)-[Co(L-ala)(aeida)]	17.24(−0.116) 19.14(+0.057) 21.53(−0.685)	27.55(+0.375)	42.02(−1.59) 47.85(−1.24)
(A-5)-[Co(L-ala)(aeida)]	18.25(−0.632) 20.35(+0.389)	≈25(−0.08) 27.40(−0.094)	38.76(−2.23) 43.86(+3.06) 47.85(−2.35)
[Co(aeida){(*R*)-pn}]$^+$	16.95(−0.045) 19.35(−0.064) 22.12(+0.190)	28.53(−0.150)	45.46(+5.48)
[Co(aeida)(*R*,*R*)-chxn]$^+$	16.53(−0.020) 18.52(+0.111) 21.98(+0.208)	28.99(−0.071)	≈41.5(sh+5.6) 44.84(+7.75)
(+)$_{589}$-[Co(aeida)(*meso*-2,3-bn)]$^+$ (B-1)	18.66(+0.232) 22.32(−0.208)	26.11(+0.009) 28.09(−0.035)	35.71(−0.17) 40.65(+2.53)

The *trans*(*O*) isomer of the *meso*-2,3-bn complex has the optical isomers which is "enantiomeric," and the CD pattern will be a measure of the "quasi-enantiomeric effect" for the (*R*)-pn complexes. The CD pattern of the $(+)_{589}$-[Co(aeida)(*meso*-2,3-bn)]$^+$ (B-1) showed two (+ and −), two (+ and −) and two (− and +) components in the first, second d-d transition and charge-transfer band region, respectively (Fig. 6 and Table 2) and the intensity in the d-d transition band region was similar to those of the "intrinsic vicinal effect" for the (*R*)-pn complexes with ata, *i*-dtma and aeida. The absolute configuration of the $(+)_{589}$-[Co(aeida)(*meso*-2,3-bn)]$^+$ complex can be assigned to π structure in Fig. 2 from the CD pattern in the d-d transition band region, if the relationship between the CD patterns of the "quasi-enantiomeric effect" and the absolute configurations for the [Co(tripod)(L-ala)] complexes is supposed to be applied to the *meso*-2,3-bn complex; The s-type *trans*(*N*,*t*-*N*) isomers of the L-ala complexes with ata, tren[1)] and *i*-dtma,[2)] which have π structure with regard to the methyl substituents, show two (+ and −) and one (+) component in the first and second d-d band region, respectively.

References

1) Part I of this series: K. Akamatsu, T. Komorita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **54**, 3000 (1981).

2) Part II of this series: K. Akamatsu, T. Komorita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **55**, 140 (1982).

3) Abbreviations of ligands: aeida = *N*-(2-aminoethyl)-iminodiacetate, L-ala = L-alaninate, ata = nitrilotriacetate, *meso*-2,3-bn = *meso*-2,3-butanediamine, (*R*,*R*)-chxn = (*R*,*R*)-1,2-cyclohexanediamine, en = ethylenediamine, gly = glycinate, *i*-dtma = *N*,*N*-bis(2-aminoethyl)glycinate, *N*,*N*-Me_2-en = *N*,*N*-dimethylethylenediamine, (*R*)-pn = (*R*)-propylenediamine, and tren = tris(2-aminoethyl)amine.

4) K. Kuroda, S. Ohtsuka, and N. Matsumoto, *Bull. Chem. Soc. Jpn.*, **48**, 1055 (1975).

5) F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Am. Chem. Soc.*, **81**, 4185 (1959).

6) C. W. Maricondi and B. E. Douglas, *Inorg. Chem.*, **11**, 688 (1972).

7) M. W. S. Chu, D. W. Cooke, and C. F. Liu, *Inorg. Chem.*, **7**, 2435 (1968).

8) K. Akamatsu and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **51**, 2586 (1978).