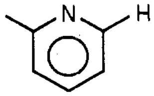
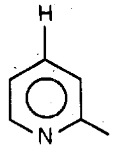
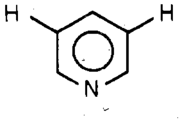
3.0 ppm (multiplet); $-CH_2CH_2S$, 3.0 ppm (multiplet);



8.50 ppm (doublet, $J_{\text{ortho}} = 8.0$ Hz, $J_{\text{meta}} = 2.0$ Hz);



8.04 ppm (triplet, $J_{\text{ortho}} = 8.0$ Hz, $J_{\text{meta}} = 2.0$ Hz);



7.50 ppm (multiplet);

$\mathrm{NH}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{CH_3}$

2.02 ppm (singlet).

Anal. Calcd for $C_{12}H_{16}N_2SO_3$: C, 53.73; H, 5.97; N, 10.45. Found: C, 53.90; H, 6.04; N, 10.41.

Preparation of the Copper(II) Complex of 2-PEC (1:2), 3.[18] **Procedure A.** In a flask was placed 0.9 g (4 mmol) of 2-PEC dissolved in 3 ml of distilled deionized water. To this was added 0.170 g (1 mmol) of copper(II) chloride dihydrate. The blue-green 2:1 complex, **3**, immediately precipitated out of solution and was filtered and dried under vacuum to give 0.5 g in 97% yield.

Anal. Calcd for $C_{20}H_{26}N_4O_4S_2Cu$: C, 46.7; H, 5.05; N, 10.9; Cu, 12.4. Found: C, 46.6; H, 4.93; N, 10.8; Cu, 12.1.

Procedure B. A procedure similar to A was used, except that 2 mmol of 2-PEC was allowed to react with 1 mmol of $CuCl_2 \cdot 2H_2O$. The complex **3** was precipitated out of solution at pH 8 using 0.1 *N* sodium hydroxide. The yield was 95% and the complex was similar to that formed in procedure A.[19]

Registry No. 2-PEC, 29567-83-7; *N*-acetyl-(*S*)-β-(2-pyridylethyl)-L-cysteine, 38402-54-9; 2-vinylpyridine, 100-69-6; *N*-acetylcysteine, 616-91-1; triethylamine, 121-44-8; **3**, 38402-55-0.

[18] We wish to acknowledge G. Secor, M. Long, and E. Ducay for elemental analyses.

[19] Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

Contribution from the Department of Industrial Chemistry, Ehime University, Matsuyama, Japan, and the Department of Chemistry, Osaka University, Osaka, Japan

Stereochemistry and Circular Dichroism of Cobalt(III) Complexes with a Tripod-Like Ligand Having Nonidentical Feet. Geometrical and Optical Isomers of Potassium (*N*,*N*-β-Alaninatediacetato)(α-aminocarboxylato)cobaltate(III)

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Received August 28, 1972

Fourteen new *trans*(*N*)- and *cis*(*N*)-(*N*,*N*-β-alaninatediacetato)(α-aminocarboxylato)cobaltate(III) ions have been prepared and isolated as their potassium salts, where the α-aminocarboxylate is glycinate, *S*-alaninate, or *S*-prolinate. The isomers with respect to the arrangement of three feet of a tripod-like *N*,*N*-β-alaninatediacetate ligand have been separated by optical resolution, fractional crystallization, or ion-exchange column chromatography and characterized by electronic absorption, proton nuclear magnetic resonance, and circular dichroism spectra. The additivity of two kinds of circular dichroism contributions, the one from the arrangement chirality of *N*,*N*-β-alaninatediacetato ligand and the other from the vicinal chirality of optically active α-aminocarboxylato ligand, has been discussed.

Introduction

There have been many studies concerning the circular dichroism (CD) spectra in the region of first and second d-d spin-allowed absorption bands of optically active Co(III) complexes, which have "configurational" contribution due to a chiral configuration of the tris-chelate[1] or bis-chelate[2] type around the central Co(III) ion and which have "vicinal" contribution due to optically active ligands, *i.e.*, unidentate[3] or bidentate[4-6] amino acids or diamines,[7] or which have both the contributions operating additive.[8,9] In a previous paper,[10] we reported the CD spectra of *trans*(*N*)- and *cis*(*N*)-((*S*)- or (*R*)-*N*,*N*-alaninatediacetato)-((*S*)-α-aminocarboxylato)cobaltate(III) ion, which had two kinds of vicinal and no configurational chirality, and recognized a good additivity between the two vicinal CD contributions.

In a similar complex containing a tripod-like quadridentate ligand which has nonidentical feet, *N*,*N*-β-alaninatediacetate ion, three kinds of structure are possible for the arrangement of chelate rings of the tripod-like ligand as shown in Figure 1.

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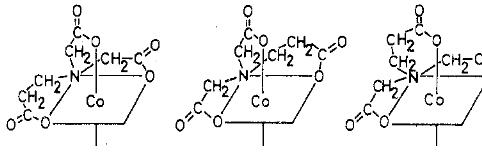
[8] See, *e.g.*, C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964); C. Y. Lin and B. E. Douglas, *Inorg. Chim. Acta*, **4**, 3 (1970).

[9] N. Matsuoka, J. Hidaka, and Y. Shimura, *Inorg. Chem.*, **9**, 719 (1970).

[10] (a) N. Koine, N. Sakota, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jap.*, **43**, 1737 (1970); (b) *ibid.*, **42**, 1779 (1969).



u-1 u-2 s

Figure 1. Three kinds of arrangement of chelate rings in an octahedral β-alada complex.

In the present paper, the preparation and separation of such isomers of *trans(N)*- and *cis(N)*-(*N,N*-β-alaninatediacetato)-(α-aminocarboxylato)cobaltate(III) complex ions are reported. The structural assignments of these complexes are made from their d-d absorption, proton nuclear magnetic resonance (pmr), and CD spectra. The CD spectra are discussed in relation to those of the corresponding *trans(N)*- and *cis(N)*-(nitrilotriacetato)((*S*)-α-aminocarboxylato)-cobaltate(III) complexes.[5] Abbreviations are used for the ligands as follows: β-alada, an *N,N*-β-alaninatediacetate ion; *S*- or *R*-alada, (*S*)- or (*R*)-*N,N*-alaninatediacetate; nta, nitrilotriacetate; gly, glycinate; *S*-ala, (*S*)-alaninate; *S*-pro, (*S*)-prolinate; am, α-aminocarboxylate, in general.

Experimental Section

(1) Ligands. *N,N*-β-Alaninediacetic acid (β-aladaH$_3$) was prepared by the method of Tsuchiya and coworkers.[11] α-Amino acids were obtained from Yoneyama Chemical Industry Co., Ltd.

(2) Preparation of Parent Mixtures. (i) ***trans(N)*-K[Co(β-alada)-(am)].** An isomeric mixture of trans(N) complexes was prepared by a procedure used for the corresponding *N,N*-α-alaninatediacetato complexes,[10a] with some modifications as follows. To 4.1 g (0.02 mol) of β-aladaH$_3$ was added 2 *N* potassium hydroxide (about 23 ml), until the pH reached 6.0, to which was added a solution of 5.0 g (0.02 mol) of cobalt(II) acetate tetrahydrate in 15 ml of water and then 3 g of lead dioxide. After the resulting mixture had been mechanically stirred at 50° for 30 min, an α-amino acid concerned (0.02 mol) and 3 g of lead dioxide were added to it and the mixture obtained was stirred at 50° during the following reaction times: about 10 hr for the glycinato or (*S*)-alaninato complex and about 3 hr for the (*S*)-prolinato complex. The solution became reddish purple. After having been allowed to stand at room temperature, the reaction mixture was filtered a few times repeatedly to remove insoluble substances. The filtrate was evaporated to several milliliters on a vacuum evaporator. After a dark green precipitate was removed by filtration, large amounts of ethanol and ether were added to the filtrate to precipitate almost all of colored complexes. The crude product precipitated was filtered and washed with ethanol and ether and then air-dried. This was dissolved in a minimum amount of water and the solution was poured through a column (35 × 600 mm) containing a strong-base anion-exchange resin (Dowex 1-X8, 200–400 mesh, chloride form). A reddish violet substance was eluted when the column was swept with water. The adsorbed band was eluted with 0.07 *M* aqueous potassium chloride at a rate of 2.5 ml/min. After about 30 hr of operation, two colored bands, a reddish purple one and a violet one, were separately eluted in this order for the glycinato or (*S*)-alaninato complex; on the other hand only one reddish purple band was obtained for the (*S*)-prolinato complex. The reddish purple bands were confirmed to indicate a mixture of the trans(N) isomers and the violet bands cis(N) isomers, by the measurements of their absorption spectra as in the case of the corresponding *N,N*-α-alaninatediacetato complexes.[10a]

Yields of the complexes were estimated spectrophotometrically on the basis of absorptivity of the eluates in the first absorption band maxima as follows: about 60% for the trans(N) isomer of the glycinato or (*S*)-alaninato complex, about 65% for the trans(N) isomer of the (*S*)-prolinato complex, and below 5% for the cis(N) isomer of the glycinato or (*S*)-alaninato complex. The cis(N) isomer was obtained in better yield by the procedure described in section (ii).

(ii) ***cis(N)*-K[Co(β-alada)(am)].** A mixture of the cis(N) and trans(N) complexes was obtained similarly as in section (i) but the reaction time was 1 hr. The crude product was chromatographed, and the trans(N) and cis(N) eluates (yield about 30 and 40%, respectively) were separated for the glycinato and (*S*)-alaninato complexes.

(3) Separation of Isomers. (i) ***trans(N)*-K[Co(β-alada)(gly)].** The trans(N) eluate obtained in section (2-i) was evaporated to several milliliters on a vacuum evaporator below 40° and the potassium chloride deposited was removed by filtration. To the filtrate a small amount of methanol was added and the potassium chloride deposited was removed again. After repeating this procedure, the reddish purple prismatic complex began to crystallize out with a small amount of potassium chloride. After cooling in a refrigerator overnight, the complex was filtered and washed with small amounts of water and methanol and recrystallized twice from hot water by adding methanol; yield 0.1 g. This complex was labeled as trans-g-1.

The filtrate from trans-g-1 was evaporated to dryness below 40°. The resulting solid was contaminated with a small amount of potassium chloride; therefore it was treated as follows. The solid was dissolved in a minimum amount of water and an appropriate amount of silver acetate was added to the solution. The silver chloride precipitated was removed by filtration and to the filtrate a large amount of ethanol was added in order to precipitate almost all of the colored complexes. The product was filtered, washed with methanol and ether, and air-dried; yield 4.3 g. This product was proved to be a racemic complex (trans-g-2 + trans-g-3) by its optical resolution as indicated in section (4). The pmr spectrum of racemic product showed about 3% contamination of trans-g-1, but the product was used in optical resolution experiments without further purification.

(ii) ***trans(N)*-K[Co(β-alada)(*S*-ala)].** The eluate in section (2-i) was evaporated almost to dryness below 40° on a vacuum evaporator. To the residue just enough methanol to dissolve the colored material at 50° was added and the potassium chloride deposited was removed by filtration. The filtrate was cooled to room temperature and then kept in a refrigerator overnight. The crude product deposited was filtered and washed with methanol–water (4:1) and then methanol and air-dried (the filtrate was reserved for the preparation of another isomer). It was recrystallized twice from methanol–water (4:1) by adding ethanol; yield 3.5 g. The pmr spectrum of this product indicated that it was a mixture of two isomers (trans-a-1 and trans-a-2). A solution of 1.5 g of this product in 98% methanol was poured into a column (35 × 800 mm) containing strong-base anion-exchange resin (Dowex 1-X8, 200–400 mesh, chloride form), which was flushed with a 0.05% (w/v) solution of potassium chloride in 98% methanol at a rate of about 1 ml/min. After about 800 hr, two reddish bands, trans-a-1 and trans-a-2 in this order, completely separated from each other. The two eluted bands were collected in fractions, and the CD spectra showed that each band consisted of only one isomer. Each of the eluates was evaporated almost to dryness below 30° on a vacuum evaporator. To the residue a small amount of methanol was added and the potassium chloride deposited was removed by filtration. By repeating this process, potassium chloride was removed as much as possible. An appropriate amount of ethanol was gradually added to the filtrate and the solution was kept in a refrigerator overnight. The needle-shaped complex deposited was gathered by filtration, washed with a small amount of methanol and ether, and air-dried. Each of the complexes was recrystallized twice from methanol–water (2:1) by adding ethanol; yield 0.4 g each for trans-a-1 and -2; $[M]_{589}$ −1150°, $[M]_{546}$ −170° for trans-a-1; $[M]_{589}$ +315°, $[M]_{546}$ −2540° for trans-a-2.

The reserved filtrate from the crude mixture of trans-a-1 and -2 was evaporated to dryness below 40°. In order to remove potassium chloride in the resulting solid, it was treated with silver acetate described in section (3-i). The solid product precipitated by addition of a large amount of ethanol was gathered, washed with ethanol and ether, and air-dried. The product was dissolved in a minimum amount of water. When an appropriate amount of ethanol was gradually added to the solution, a mixture of trans-a-1 and -2 crystallized out and was removed by filtration. By this process the crystalline complex (a mixture of trans-a-1 and -2) was removed from the solution as much as possible. The final filtrate was evaporated to dryness on a vacuum evaporator; yield 0.5 g. The pmr spectrum of this product indicated that it was a mixture of three isomers, trans-a-1 and trans-a-2 (about 40% in total of the two isomers) and new trans-a-3 (about 60%). The separation of the new isomer from the mixture was carried out by the same chromatographic procedure as for the separation of trans-a-1 and -2. By about 600 hr of elution, two reddish purple bands, separated from each other, appeared to be eluted. It was confirmed by CD measurements of the fractionated eluates that the earlier eluted band consists of trans-a-3 and trans-a-1 (eluted in this order, but partly overlapped) and the later eluted band trans-a-2. The former several fractions of the first eluted band,

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[11] A. Uehara, E. Kyuno, and R. Tsuchiya, *Bull. Chem. Soc. Jap.*, **41**, 2385 (1968).

which showed a constant CD, were collected, and the contaminants were removed as in the case of trans-a-1 or trans-a-2. Finally by the recrystallization from methanol–water (10:1) by adding ethanol, the pure complex was obtained in powder; yield 0.05 g; $[M]_{589}$ −330°, $[M]_{546}$ −930°. This complex was labeled as trans-a-3.

(iii) *trans(N)*-K[Co(β-alada)(*S*-pro)]. The trans(N) eluate in section (2-i) was evaporated almost to dryness below 40° on a vacuum evaporator. To the residue just enough methanol to dissolve the colored material at 50° was added and the potassium chloride deposited was removed by filtration. To the filtrate a large amount of ethanol and ether was added to precipitate almost all of the colored complexes. The crude product was filtered, washed with ether, and then dried under vacuum; yield 5.5 g. The separation of isomers was carried out using 1.5 g of the product by the same procedure as for trans-a-1 and trans-a-2. After 1300 hr of elution, three reddish purple bands, trans-p-1, trans-p-2, and trans-p-3, were eluted in this order and completely separated from one another. The trans-p-2 eluate was slightly tinged with violet as compared with the other two.

Each of the three eluates was evaporated to dryness below 30° on a vacuum evaporator. To the residue just enough methanol to dissolve the colored material at 50° was added and the potassium chloride deposited was removed by filtration. An appropriate amount of ethanol was gradually added to the filtrate and the solution was kept in a refrigerator overnight. The complex deposited was gathered by filtration, and washed with a small amount of methanol and ether, and then air-dried. Each of the complexes was recrystallized from methanol–water (20:1) by adding ethanol; yield 0.3 g of needle-shaped crystals, $[M]_{589}$ −445°, $[M]_{546}$ +1185° for trans-p-1; 0.03 g of powder, $[M]_{589}$ +1050°, $[M]_{546}$ +470° for trans-p-2; 0.2 g of needle-shaped crystals, $[M]_{589}$ +1010°, $[M]_{546}$ −2560° for trans-p-3.

(iv) *cis(N)*-K[Co(β-alada)(*S*-ala)]. The cis(N) eluate in section (2-ii) was evaporated to several milliliters below 40° on a vacuum evaporator and the potassium chloride precipitated was removed by filtration. When a small amount of methanol was added to the filtrate, violet prismatic crystals (cis-a-1) began to crystallize. After cooling in a refrigerator overnight, the complex was filtered, washed with a small amount of water and methanol, and then air-dried. It was recrystallized twice from water by adding methanol; yield 1.2 g; $[M]_{589}$ +1585°, $[M]_{546}$ +7460°.

In order to remove potassium chloride in the filtrate from cis-a-1, it was treated with silver acetate as described in section (3-i). The solid product precipitated by adding a large amount of ethanol was gathered, washed with ethanol and ether, and air-dried. This was dissolved in a minimum amount of water and to the solution was gradually added a few milliliters of ethanol. The needle-shaped crystals deposited were gathered, washed with methanol–water (2:1) and ethanol, and air-dried. The compound was recrystallized twice from water by adding ethanol; yield 0.6 g; $[M]_{589}$ −625°, $[M]_{546}$ −2890°. This complex was labeled as cis-a-2.

The filtrate from cis-a-2 was treated by a similar procedure to that for the isolation of trans-a-3 (section (3-ii)). The pmr spectrum of product indicated that it was a mixture of three isomers, cis-a-1 and -2 (about 30% in total of the two isomers) and new cis-a-3 (about 70%). The separation of new isomer from the mixture was carried out chromatographically as in section (2-i). The column, the concentration of eluent, and the elution rate were converted to 17 × 1000 mm, and 0.03 *M*, and 1 ml/min, respectively. In about 700 hr of elution, no separation of the isomers was observed, but it was confirmed by CD measurements of the fractionized eluates that the elution order was cis-a-3, cis-a-2, and cis-a-1. Several fractions eluted first showed a constant CD; they were collected and the contaminant potassium chloride was removed as much as possible (see section (3-ii)). Because attempts to crystallize cis-a-3 from the resulting filtrate were unsuccessful, the filtrate was evaporated to dryness on a vacuum evaporator below 30° and dried in a vacuum desiccator containing calcium chloride. The final product contains a small amount of potassium chloride and is very hygroscopic; therefore no elemental analysis was carried out. Its optical rotation was positive in both 589 and 546 nm. This was labeled as cis-a-3.

(4) Optical Resolution. (i) *u-trans(N)*-K[Co(β-alada)(gly)]. A suspension of 3.9 g (0.01 mol) of $(-)_{546}$-$[Co(ox)(en)_2]I$ in 12 ml of water was stirred with 1.8 g (0.011 mol) of silver acetate at 50° for about 10 min. The silver iodide precipitated was filtered and washed with a small amount of water. In the combined filtrate and washings was dissolved 4.0 g of the racemic complex (trans-g-2 + trans-g-3) obtained in section (3-i). Repeating fractional crystallizations by cooling in a refrigerator or by adding an appropriate amount of methanol, several fractions of the diastereomer were obtained. The less soluble fractions with similar values of optical rotation ($[\alpha]_{546}$ −270 to −350°) were combined and recrystallized several times to constant rotation from hot water by adding methanol; yield 0.8 g; $[\alpha]_{589}$ −532°, $[\alpha]_{546}$ −246°. *Anal.* Calcd for [Co(β-alada)(gly)]-$[Co(ox)(en)_2]\cdot 3H_2O$: C, 27.44; H, 5.23; N, 12.81. Found: C, 27.74; H, 5.37; N, 12.68. The diastereomer (0.6 g) was dissolved in a minimum amount of water and the solution was poured into a column (17 × 50 mm) containing a cation-exchange resin (Dowex 50W-X8, 200–400 mesh, potassium form). By sweeping with water, the desired complex, K[Co(β-alada)(gly)], was eluted as a violet solution, while the resolving agent, $(-)_{546}$-$Co(ox)(en)_2^+$, remained at top of the column. The violet eluate was evaporated to a few milliliters below 40° on a vacuum evaporator. An appropriate amount of ethanol was gradually added to the solution. The needle-shaped crystals deposited were filtered, washed with methanol–water (3:1) and then methanol, and air-dried; yield 0.2 g; $[M]_{589}$ −375°, $[M]_{546}$ +1300°. This complex was labeled as trans-g-2.

The more soluble fractions of the diastereomer with similar rotations ($[\alpha]_{546}$ −500 to −620°) were treated likewise; yield 0.4 g; $[\alpha]_{589}$ −388°, $[\alpha]_{546}$ −690°. *Anal.* Calcd for [Co(β-alada)(gly)]·$[Co(ox)(en)_2]\cdot 2H_2O$: C, 28.22; H, 5.06; N, 13.17. Found: C, 28.13; H, 5.29; N, 12.77. The optically active potassium salt was obtained from the diastereomer (0.3 g) as needle-shaped crystals by the same procedure as that for the enantiomer; yield 0.1 g; $[M]_{589}$ +395°, $[M]_{546}$ −1290°. This complex was labeled as trans-g-3.

(ii) *u-cis(N)*-K[Co(β-alada)(gly)]. The cis(N) eluate in section (2-ii) was evaporated to several milliliters below 40° on a vacuum evaporator and the potassium chloride deposited was removed by filtration. By further addition of methanol to the filtrate, potassium chloride was removed as much as possible. The final filtrate was evaporated to dryness below 40° and the resulting solid was treated as described in section (3-i) for the trans(N) isomer, using silver acetate to remove contaminated potassium chloride. The solid product precipitated by addition of a large amount of ethanol was gathered, washed with ethanol and ether, and air-dried; yield 3.0 g. Although this product was a mixture of three isomers, cis-g-1 and cis-g-2 (antipodal to each other and about 94% of the total of the three isomers) and one more isomer (about 6%; isolation of this isomer was not attempted), it was used for next step without further purification.

The isomeric mixture (2.0 g) was dissolved in the solution containing the acetate of $(-)_{546}$-$Co(ox)(en)_2^+$ which was obtained as in section (4-i) from 2.0 g of $(-)_{546}$-$[Co(ox)(en)_2]I$ and 0.9 g of silver acetate and 8 ml of water. When the solution was cooled in a refrigerator and the vessel was scratched with a glass rod, the crude, less soluble diastereomer began to crystallize out. After cooling in a refrigerator overnight, it was filtered and washed with a small amount of ice water; yield 1.2 g. It was recrystallized a few times to constant rotation from hot water by adding methanol; yield 0.8 g of prismatic crystals, $[\alpha]_{589}$ −300°, $[\alpha]_{546}$ +250°. *Anal.* Calcd for [Co(β-alada)(gly)]$[Co(ox)(en)_2]\cdot 4H_2O$: C, 26.71; H, 5.39; N, 12.46. Found: C, 26.64; H, 5.48; N, 12.26.

To the filtrate from the less soluble diastereomer was added 5 ml of methanol and the solution was allowed to stand for 5 hr at room temperature. The crude, more soluble diastereomer deposited was filtered and washed with a small amount of ice water; yield 0.6 g. Recrystallization was achieved as for the more soluble diastereomer; yield 0.4 g of prismatic crystals, $[\alpha]_{589}$ −505°, $[\alpha]_{546}$ −1130°. *Anal.* Calcd for [Co(β-alada)(gly)]$[Co(ox)(en)_2]\cdot 6H_2O$: C, 25.36; H, 5.69; N, 11.83. Found: C, 25.42; H, 5.79; N, 11.62.

The desired potassium salts of these complexes, cis-g-1 and cis-g-2, were obtained as powders from the less soluble diastereomer (0.6 g) and the more soluble one (0.3 g), respectively, by the same procedure as that for the trans(N) isomer; yield 0.2 g, $[M]_{589}$ +1200°, $[M]_{546}$ +5020° for cis-g-1; 0.1 g, $[M]_{589}$ −1195°, $[M]_{546}$ −5010° for cis-g-2.

Analyses. The analytical data for the complexes obtained are shown in Table I.

Measurements. The electronic absorption spectra were measured with a Shimadzu spectrophotometer, Model QV-50; the absorption curves are shown in Figure 4 and the numerical data are collected in Table III. The CD spectra and optical rotations were recorded with a Jasco Model ORD/UV-5 spectrometer fitted with a CD attachment; the CD curves are shown in Figures 5–10 and the numerical data are collected in Table III. All the measurements were made in aqueous solution at room temperature.

The pmr spectra were measured with a Japan Electron Optics JNM-4H-100 spectrometer operating at 100 MHz, in deuterium oxide solutions at about 27°, the internal temperature of probe. All the signals lie at lower field than that of *tert*-butyl alcohol which was used as an internal standard. Chemical shifts are referred to

Table I. Elemental Analyses (%)

Label	Complex	C Calcd	C Found	H Calcd	H Found	N Calcd	N Found
trans-g-1	*s-trans*(*N*)-K[Co(β-alada)(gly)]·2H$_2$O	26.34	26.57	3.94	3.96	6.82	6.76
trans-g-2	$(-)_{589}$-*u-trans*(*N*)-K[Co(β-alada)(gly)]·3H$_2$O	25.24	25.17	4.24	4.18	6.54	6.44
trans-g-3	$(+)_{589}$-*u-trans*(*N*)-K[Co(β-alada)(gly)]·3H$_2$O	25.24	24.80	4.24	4.10	6.54	6.53
trans-a-1	$(-)_{589}$-*u-trans*(*N*)-K[Co(β-alada)(*S*-ala)]·5H$_2$O	25.11	25.43	5.07	5.18	5.86	5.81
trans-a-2	$(+)_{589}$-*u-trans*(*N*)-K[Co(β-alada)(*S*-ala)]·4H$_2$O	26.09	26.01	4.81	4.81	6.08	5.98
trans-a-3	$(-)_{589}$-*s-trans*(*N*)-K[Co(β-alada)(*S*-ala)]·3H$_2$O	27.15	27.28	4.57	4.36	6.33	6.33
trans-p-1	$(-)_{589}$-*u-trans*(*N*)-K[Co(β-alada)(*S*-pro)]·3H$_2$O	30.77	30.80	4.74	4.68	5.98	5.58
trans-p-2	$(+)_{589}$-*s-trans*(*N*)-K[Co(β-alada)(*S*-pro)]·2.5H$_2$O	31.37	31.44	4.62	4.64	6.10	5.78
trans-p-3	$(+)_{589}$-*u-trans*(*N*)-K[Co(β-alada)(*S*-pro)]·3H$_2$O	30.77	30.73	4.74	4.91	5.98	5.76
cis-g-1	$(+)_{589}$-*u-cis*(*N*)-K[Co(β-alada)(gly)]·2.5H$_2$O	25.78	26.16	4.09	4.35	6.68	6.69
cis-g-2	$(-)_{589}$-*u-cis*(*N*)-K[Co(β-alada)(gly)]·2.5H$_2$O	25.78	25.63	4.09	4.36	6.68	6.44
cis-a-1	$(+)_{589}$-*u-cis*(*N*)-K[Co(β-alada)(*S*-ala)]·2.5H$_2$O·0.5KCl	25.52	25.43	4.08	4.04	5.95	5.94
cis-a-2	$(-)_{589}$-*u-cis*(*N*)-K[Co(β-alada)(*S*-ala)]·4H$_2$O	26.09	26.09	4.81	4.84	6.08	6.03
cis-a-3	$(+)_{589}$-*s-cis*(*N*)-Co(β-alada)(*S*-ala)$^-$ [a]						

[a] Not isolated; see Experimental Section.

Table II. Chemical Shifts[a] and Coupling Constants[b] for Co(β-alada)(am)$^-$ Ions

Part I. Trans(N) Isomer

Assignment	Glycinato complex		(*S*)-Alaninato complex			(*S*)-Prolinato complex	
	s	$(-)_{589}$-*u*	$(-)_{589}$-*u*	$(+)_{589}$-*u*	$(-)_{589}$-*s*	$(-)_{589}$-*u*	$(+)_{589}$-*u*
-CH$_2$- (gly)	3.82	3.85[c]					
-CH$_3$			1.62 (7.5)	1.65 (7.5)	1.62 }(7.5)		
>CH-			4.03[d]	. . .[e]	3.91		
>N-CH$_2$-COO$^-$ (β-alada)							
AB-1		3.95 }(18.7) 4.31	3.95 }(18.5) 4.31	3.95 }(18.4) 4.32		3.93 }(18.2) 4.27	3.88 }(18.2) 4.27
AB-2	4.14 }(16.8) 4.59	4.02 }(16.2) 4.50	4.03 }(15.6) 4.54	4.03 }(15.5) 4.53	4.19 }(*ca.* 17.0)[f] 4.58	4.04 }(15.8) 4.55	3.96 }(16.2) 4.44

Part II. Cis(N) Isomer

Assignment	Glycinato complex	(*S*)-Alaninato complex		
	$(+)_{589}$-*u*	$(+)_{589}$-*u*	$(-)_{589}$-*u*	$(+)_{589}$-*s*
-CH$_2$- (gly)	3.38[c]			
-CH$_3$		1.42 }(7.5)	1.41 }(7.5)	1.42 }(7.5)
>CH-		3.54	3.54	3.46
>N-CH$_2$-COO$^-$ (β-alada)				
AB-1	3.82 }(18.1) 4.13	3.79 }(18.5) 4.13	3.82 }(18.3) 4.10	
AB-2	3.79 }(16.8) 4.27	3.79 }(16.4) 4.38	3.76 }(16.4) 4.18	3.90 }(17.1) 4.34 3.89 }(17.3) 4.58

[a] Values in ppm from DSS (DSS = 0). [b] Values in Hz, in parentheses. [c] Observed as a sharp singlet although the two protons are theoretically in different environments. [d] Assignment is tentative because of overlapping with other signals. [e] Ambiguous because of overlapping with other signals. [f] Consists of two AB quartets overlapped practically.

sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as zero; *tert*-butyl alcohol is shifted 1.234 ppm downfield from DSS. The representative pmr spectra are shown in Figures 2 and 3, and the chemical shift and coupling constant data are presented in Table II. Since a trans-p-2 sample containing about 30% (in total) of trans-p-1 and trans-p-3 was used in pmr measurements because of shortage of the isomer, only some characteristic signals near 1.3 ppm are suitable in discussions for trans-p-2. All of the pmr spectra were taken under conditions where the nitrogen protons of aminocarboxylate exchange rapidly with solvent. Most sharp signals made a similar pattern to that of analogous complexes reported earlier,[5,10] and the broad signals for the ethylenic protons of β-alada or for the protons of prolinate ligand are distinguishable from the sharp signals.

Results and Discussion

The tripod-like ligand β-alada spans four coordination sites of an octahedron by its three feet, of which one makes a six-membered chelate ring and another two five-membered rings. Consequently there are three possibilities for arrangement of chelate rings (Figure 1). In two of the three possibilities, the arrangements are unsymmetrical (designated as *u*) and are antipodal to each other, but the dissymmetry does not arise from the distribution of chelate rings, the so-called configurational effect. Another one is symmetrical (designated as *s*) and optically inactive. The optical activity of *u* isomers with glycinato ligand is attributed only to the chirality due to the arrangement of chelate rings of β-alada.[12] In the case of *u* isomers with an optically active α-aminocarboxylato ligand ((*S*)-alaninate or (*S*)-prolinate), the optical activity is attributed partly to the asymmetric bidentate ligand and partly to the arrangement chirality of β-

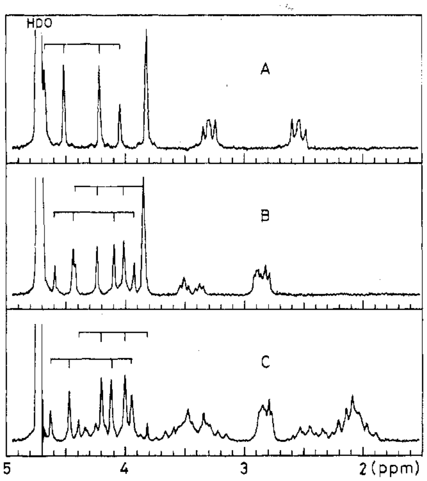

Figure 2. Pmr spectra of (A) *s-trans(N)*-Co(β-alada)(gly)$^-$ (trans-g-1), (B) $(-)_{589}$-*u-trans(N)*-Co(β-alada)(gly)$^-$ (trans-g-2), and (C) $(-)_{589}$-*u-trans(N)*-Co(β-alada)(*S*-pro)$^-$ (trans-p-1), in D_2O at 100 MHz.

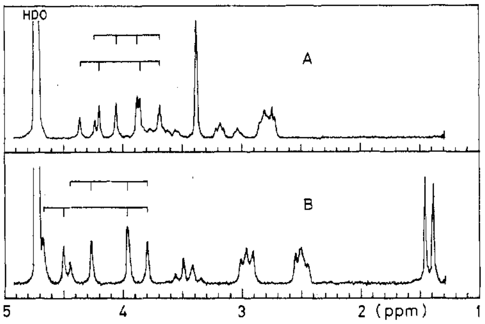

Figure 3. Pmr spectra of (A) $(+)_{589}$-*u-cis(N)*-Co(β-alada)(gly)$^-$ (cis-g-1) and (B) $(+)_{589}$-*s-cis(N)*-Co(β-alada)(*S*-ala)$^-$ (cis-a-3), in D_2O at 100 MHz.

alada, whereas that of the *s* isomer is attributed only to the asymmetric bidentate ligand.

Structural Assignments. It has been well established that trans(N) and cis(N) isomers of a Co^{III}(O)$_4$(N)$_2$ type complex can be identified from the splitting patterns of their first spin-allowed d-d absorption bands.[5,9,10,13] The first absorption bands of nine complexes labeled as trans-g, trans-a, and trans-p exhibit an explicit shoulder at the longer wavelength side of major peak. On the contrary, the absorption curves of five complexes labeled as cis-g and cis-a show a vague shoulder at the shorter wavelength side of major peak (Figure 4 and Table III). From these absorption data it is concluded that the former nine complexes are trans(N) isomers and the latter five cis(N).

In the preparation of the (*S*)-prolinato complex, the cis(N) isomer was not recognized. A similar selective formation was also observed in the case of the complexes containing nta[5] or *S*- or *R*-alada[10] instead of β-alada. These facts may be a consequence from the steric hindrance between the pyrrolidine ring of (*S*)-prolinato ligand and one of the three chelate rings of the quadridentate ligand in the cis(N) isomers.

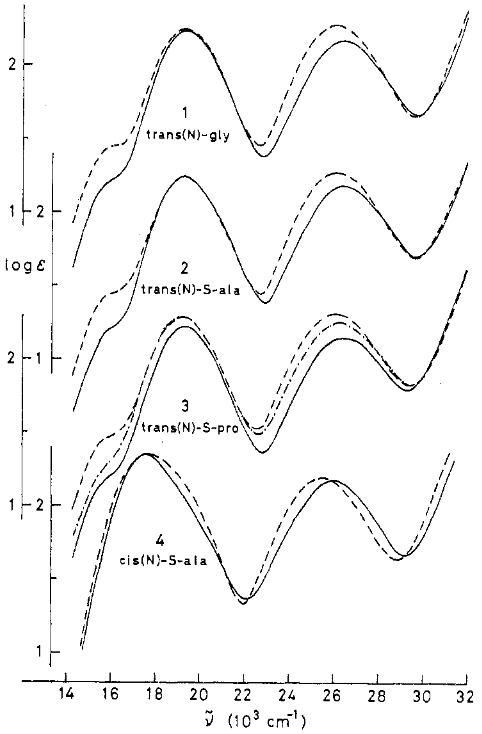

Figure 4. Absorption curves of Co(β-alada)(am)$^-$: (1) ——, $(-)_{589}$-*u* (trans-g-2); – – –, *s* (trans-g-1); (2) ——, $(+)_{589}$-*u* (trans-a-2); – – –, $(-)_{589}$-*s* (trans-a-3); (3) ——, $(-)_{589}$-*u* (trans-p-1); – · –, $(+)_{589}$-*u* (trans-p-3); – – –, $(+)_{589}$-*s* (trans-p-2); (4) ——, $(-)_{589}$-*u* (cis-a-2); – – –, $(+)_{589}$-*s* (cis-a-3) (see footnote *b* of Table III).

As described in Experimental Section, a racemic isomer was obtained and resolved into two optically active isomers for each of the trans(N) and cis(N) glycinato complexes. It is obvious that these isomers, trans-g-2, trans-g-3, cis-g-1, and cis-g-2, are *u* isomers, and hence the remaining unresolvable glycinato isomer, trans-g-1, is an *s* isomer.

From the construction of molecular models of the complexes, it is expected for the *s*-glycinato isomer that the ligand β-alada shows one AB pattern for the four methylenic protons of *N*-acetate feet and one AA′BB′ pattern for the four ethylenic protons of the β-alaninate foot. In the *u*-glycinato complexes, the two AB patterns are expected for four *N*-acetate protons and one ABCD pattern is expected for four β-alaninate protons. The expectation is realized in Figures 2 and 3: the signals of *s*-trans(N) glycinato complex near 2.5 ppm (two protons) and 3.3 ppm (two protons) constitute a typical AA′BB′ pattern which has the midpoint at 2.91 ppm, while the *u*-trans(N) and *u*-cis(N) glycinato complexes show complicated spectra as expected for the ABCD pattern. Judging from intensity integrations, the signals near 2.8, 3.0–3.3, and 3.5–3.65 ppm for the *u*-cis(N) glycinato complex correspond to two, one, and one protons, respectively, and signals resembling these are also observed for the *u*-trans(N) glycinato complex near 2.8, 3.3–3.6, and 3.8–4.1 ppm, although the signals in the last named region are most likely hidden by other intense signals.

The signals for β-alaninate ring in the complexes with optically active α-aminocarboxylates are quite similar in the chemical shifts and splitting patterns to those of the corresponding isomers of glycinato complexes; namely, trans-a-1, trans-a-2, trans-p-1, and trans-p-3 resemble the *u*-trans(N) glycinato complex, trans-a-3 and trans-p-2 resemble the *s*-trans(N) one, and cis-a-1 and cis-a-2 resemble the *u*-cis(N) one, where some signals in the three (*S*)-prolinato complexes partly overlap on the signals of pyrrolidine ring protons. The pyrrolidine proton signals are very similar in the chemical shifts and splitting patterns to those in Co(*S*- or *R*-alada)-

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(12) It may be possible to designate the configurations of two *u* isomers as Δ(5,6)Λ(5,5) for *u*-1 and Λ(5,6)Δ(5,5) for *u*-2 on the basis of relationships between the five- and six-membered chelate rings of β-alada and a five-membered one of the α-aminocarboxylato ligand: IUPAC, "Nomenclature of Inorganic Chemistry," 2nd ed, Butterworths, London, 1971, p 75.

(13) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jap.*, **40**, 1868 (1967).

Table III. Electronic Absorption and CD Spectral Data of Co(β-alada)(am)$^-$ Ions

	Electronic absorption				CD			
	Band I		Band II		Band I		Band II	
Complex ion	ν_{max}, cm^{-1}	ϵ_{max}	ν_{max}, cm^{-1}	ϵ_{max}	ν_{ext}, cm^{-1}	$\Delta\epsilon_{ext}$	ν_{ext}, cm^{-1}	$\Delta\epsilon_{ext}$
s-trans(*N*)-Co(β-alada)(gly)$^-$	~16,000	28	26,040	190				
	19,340	178						
$(-)_{589}$-*u-trans*(*N*)-Co(β-alada)(gly)$^-$	~16,000	16	26,530	147	14,990	−0.05	26,110	−0.58
		(16)[a]		(148)[a]		(+0.05)[a]		(+0.57)[a]
	19,340	171			18,420	−1.02		
		(173)[a]				(+1.00)[a]		
					20.620	+0.65		
						(−0.66)[a]		
$(-)_{589}$-*u-trans*(*N*)-Co(β-alada)(*S*-ala)$^-$	~16,000	16	26,530	154	14,990	−0.05	26,110	−0.45
	19,310	180			18,760	−1.26		
					21,510	+0.05		
$(+)_{589}$-*u-trans*(*N*)-Co(β-alada)(*S*-ala)$^-$	~16,000	16	26,600	158	16,050	−0.10	26,320	+0.88
	19,340	177			18,380	+1.05		
					20,530	−1.46		
$(-)_{589}$-*s-trans*(*N*)-Co(β-alada)(*S*-ala)$^-$	~16,000	28	26,110	187	16,560	−0.08	26,460	+0.25
	19,310	175			19,960	−0.62		
$(-)_{589}$-*u-trans*(*N*)-Co(β-alada)(*S*-pro)$^-$	~16,000	16	26,460	147	16,130	+0.10	25,580	−0.35
	19,190	168			18,450	−0.85		
					20.750	+0.31		
$(+)_{589}$-*s-trans*(*N*)-Co(β-alada)(*S*-pro)$^-$	~16,000	30	25,970	206	15,870	−0.16	26,460	+0.36
	19,120	191			18,550	+0.44		
					20,750	−0.15		
$(+)_{589}$-*u-trans*(*N*)-Co(β-alada)(*S*-pro)$^-$	~16,000	20	26,250	181	16,050	−0.14	26,040	−0.65
	19,050	196			18,180	+1.16		
					20,330	−1.06		
$(+)_{589}$-*u-cis*(*N*)-Co(β-alada)(gly)$^-$	17,610	224	26,110	143	17,210	−1.41	~24,500	−0.15
		(218)[a]		(141)[a]		(+1.38)[a]		(+0.16)[a]
					19,960	+0.50	26,810	−0.21
						(−0.50)[a]		(+0.22)[a]
$(+)_{589}$-*u-cis*(*N*)-Co(β-alada)(*S*-ala)$^-$	17,580	228	26,110	141	17,270	−2.08	~24,200	−0.11
					19,920	+1.00	26,880	−0.34
$(-)_{589}$-*u-cis*(*N*)-Co(β-alada)(*S*-ala)$^-$	17,610	221	26,110	152	17,240	+0.81	~24,400	+0.16
					20,410	−0.15	26,670	+0.21
$(+)_{589}$-*s-cis*(*N*)-Co(β-alada)(*S*-ala)$^-$ [b]	17,670	. . .	25,580	. . .	17,120	−	25,130	−
					19,460	+		

[a] Values in parentheses are for the antipode. [b] The ϵ_{max} and $\Delta\epsilon_{ext}$ values have not been obtained because of the lack of elemental analyses. Electronic absorption and CD curves in Figures 4 and 7 were drawn by assuming the ϵ_{max} value of the first absorption band to be the same as the mean value (ϵ_{max} 225) for those of the corresponding $(+)_{589}$-*u* and $(-)_{589}$-*u* isomers.

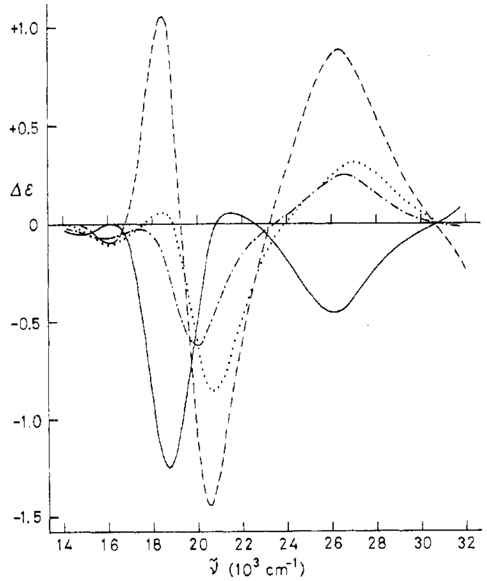

Figure 5. CD curves of *trans*(*N*)-Co(β-alada)(*S*-ala)$^-$: ——, $(-)_{589}$-*u*; – – –, $(+)_{589}$-*u*; – · –, $(-)_{589}$-*s*. CD curve of *trans*(*N*)-Co(nta)-(*S*-ala)$^-$ is reproduced from ref 5 for comparison (· · ·).

(*S*-pro)$^-$ complexes.[10a] Cis-a-3 is quite similar in the splitting pattern to the *s*-trans(N) glycinato complex. From these observations, it is possible to assign the arrangement configurations clearly to all of the present complexes as shown in Table I. These assignments are also supported by another consideration (*vide infra*).

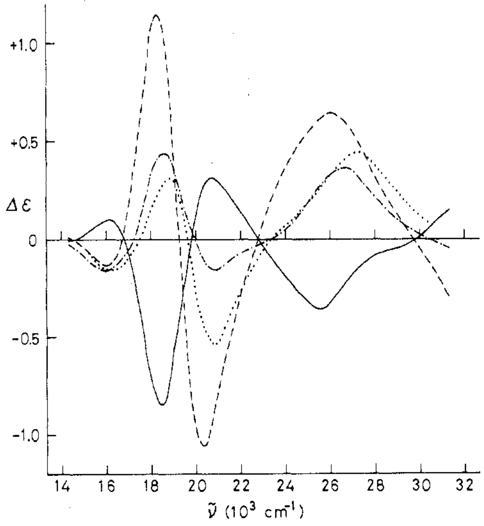

Figure 6. CD curves of *trans*(*N*)-Co(β-alada)(*S*-pro)$^-$: ——, $(-)_{589}$-*u*; – – –, $(+)_{589}$-*u*; – · –, $(+)_{589}$-*s*. CD curve of *trans*(*N*)-Co(nta)-(*S*-pro)$^-$ is reproduced from ref 5 for comparison (· · ·).

As described above, a set of the signals of β-alaninate ring protons of β-alada at the highest magnetic field corresponds to two protons in each of the *u* and *s* isomers. Moreover, the set of signals of *u* isomer is far apart in chemical shift

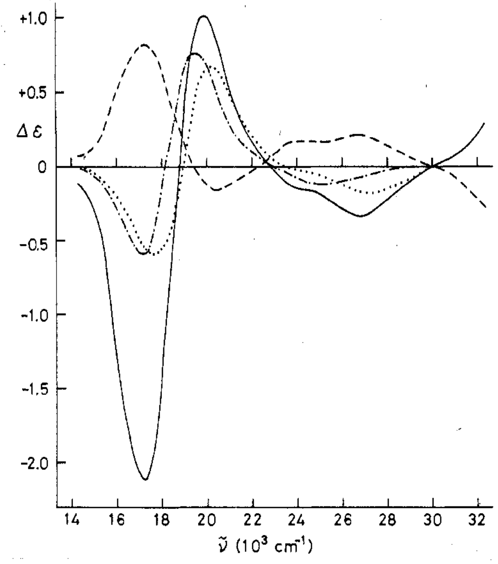

Figure 7. CD curves of *cis*(*N*)-Co(β-alada)(*S*-ala)$^-$: ——, $(+)_{589}$-*u*; – – –, $(-)_{589}$-*u*; – · –, $(+)_{589}$-*s* (see footnote *b* of Table III). CD curve of *cis*(*N*)-Co(nta)(*S*-ala)$^-$ is reproduced from ref 5 for comparison (· · ·).

from that of the *s* isomer; on this basis, it was possible to determine the yield proportion of the *u* and *s* isomers.

The two *N*-acetate rings of coordinated β-alada are identical in their environments for the *s*-trans(N) glycinato complex, but different for the other complexes. As expected, only one AB pattern is observed for the former type of complexes and two AB patterns for the others (Table II). Although the *s*-trans(N) (*S*)-alaninato complex apparently shows one AB pattern, the broadening of each signal of the AB quartet indicates the overlapping of two AB patterns.

Sudmeier and coworkers[14] pointed out that the magnitudes of *N*-acetate geminal proton coupling constants for multidentate aminocarboxylatocobalt(III) complexes fall into two categories, the one of approximately 16.0 Hz for in-plane *N*-acetate rings and the other of 18.0 Hz for out-of-plane *N*-acetate rings. In the present complexes, the AB patterns can be classified into two categories, AB-1 and AB-2, according to the magnitudes of coupling constants as shown in Table II. Sudmeier's rule appears to apply also for the present complexes, because the two *N*-acetate rings of β-alada are in plane and out of plane, one each for the *u* isomer, and both in plane for the *s* isomer (the plane passes through two coordinated oxygen atoms which are trans to each other and a nitrogen atom in Figure 1). On this basis, AB-1 and AB-2 in the *u* isomers can be assigned to the protons on the out-of-plane and in-plane *N*-acetate ring, respectively.

In a previous paper,[5] we pointed out for the *trans*(*N*)-$Co(O)_4(N)_2$ type complexes that the ratio $\epsilon_{max}(sub)/\epsilon_{max}(major)$ of a sub and a major component of the first absorption band is smaller in the complexes with tridentate or quadridentate ligand (0.09–0.28)[5,10,15,16] than in the complexes with bidentate one (0.46–0.58).[9] This situation also stands for the present trans(N) complexes. Between *s* and *u* isomers of the present trans(N) complexes, the following differences are observed in their absorption spectra (Figure 4 and Table III). The ratio mentioned above is about 0.16 and 0.10 for *s* and *u* isomers, respectively. The second absorption band of the *s* isomer is higher in intensity than its first absorption band and shifts to a longer wavelength than the second absorption band of the *u* isomer, which is lower in intensity than its first absorption band. A difference is also observed between the *s* and *u* isomers of cis(N) complexes (Figure 4 and Table III). The assignments of the arrangement configurations from the absorption curves coincide well with those from the pmr spectra.

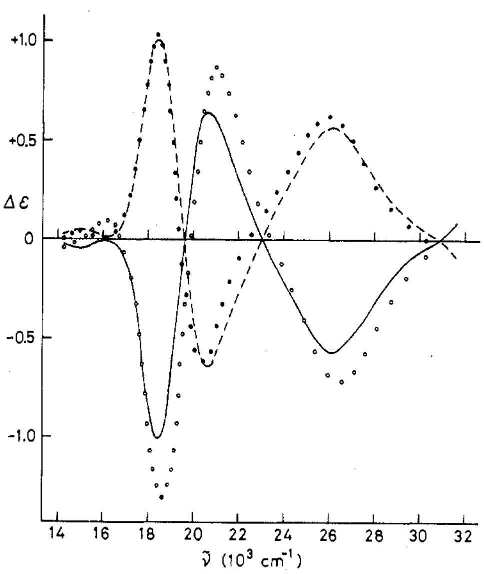

Figure 8. Calculated CD curves: ∘∘∘, $(-)_{589}$-*u-trans*(*N*)-Co(β-alada)-(*S*-ala)$^-$ minus *trans*(*N*)-Co(nta)(*S*-ala)$^-$; •••, $(+)_{589}$-*u-trans*(*N*)-Co(β-alada)(*S*-ala)$^-$ minus *trans*(*N*)-Co(nta)(*S*-ala)$^-$. These are compared with CD curves of *u-trans*(*N*)-Co(β-alada)(gly)$^-$: ——, $(-)_{589}$; – – –, $(+)_{589}$.

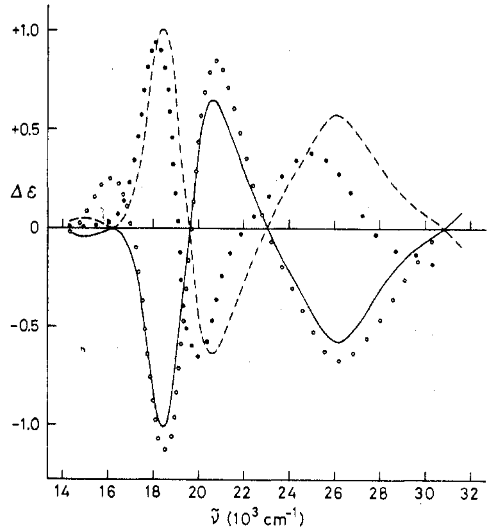

Figure 9. Calculated CD curves: ∘∘∘, $(-)_{589}$-*u-trans*(*N*)-Co(β-alada)-(*S*-pro)$^-$ minus *trans*(*N*)-Co(nta)(*S*-pro)$^-$; •••, $(+)_{589}$-*u-trans*(*N*)-Co-(β-alada)(*S*-pro)$^-$ minus *trans*(*N*)-Co(nta)(*S*-pro)$^-$. These are compared with CD curves of *u-trans*(*N*)-Co(β-alada)(gly)$^-$: ——, $(-)_{589}$; – – –, $(+)_{589}$.

Circular Dichroism Spectra. The CD curves of two *u*-trans(N) (*S*)-alaninato isomers, which are diastereomeric to each other, deviate considerably from that of either of two *u*-trans(N) glycinato isomers, which are antipodal to each other (Figures 5 and 8). The CD curve of the *s*-trans(N) (*S*)-alaninato isomer is very similar to that of *trans*(*N*)-

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[14] J. L. Sudmeier, A. J. Senzel, and G. L. Blackmer, *Inorg. Chem.*, 10, 90 (1971).

[15] K. Okamoto, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jap.*, 44, 1601 (1971).

[16] J. Hidaka, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Jap.*, 35, 567 (1962); D. W. Cooke, *Inorg. Chem.*, 5, 1141 (1966); B. B. Smith and D. T. Sawyer, *ibid.*, 7, 922 (1968); S. Yamada, J. Hidaka, and B. E. Douglas, *ibid.*, 10, 2187 (1971); J. Hidaka, S. Yamada, and B. E. Douglas, *J. Coord. Chem.*, 2, 123 (1972).

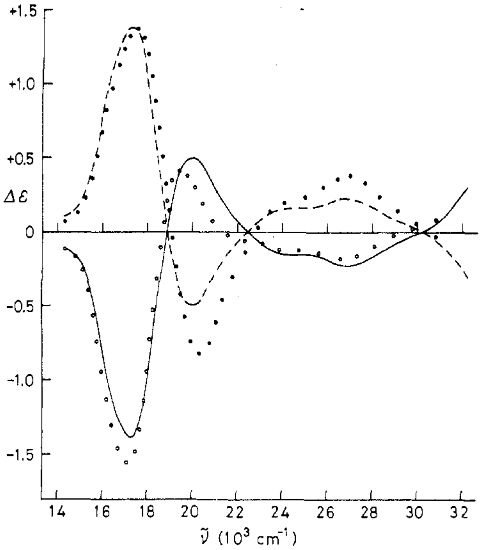

Figure 10. Calculated CD curves ∘∘∘, $(+)_{589}$-*u-cis*(*N*)-Co(β-alada)-(*S*-ala)$^-$ minus *cis*(*N*)-Co(nta)(*S*-ala)$^-$; •••, $(-)_{589}$-*u-cis*(*N*)-Co(β-alada)(*S*-ala)$^-$ minus *cis*(*N*)-Co(nta)(*S*-ala)$^-$. These are compared with CD curves of *u-cis*(*N*)-Co(β-alada)(gly)$^-$: ——, $(+)_{589}$; – – –, $(-)_{589}$.

Co(nta)(*S*-ala)$^-$; the optical activity of the latter complex is contributed only by the optically active α-aminocarboxylato ligand.[5] Similar CD relationships are also recognized for the *s* and *u* isomers of trans(N) (*S*)-prolinato or cis(N) (*S*)-alaninato complexes (Figures 6 and 7).

It has been generally recognized that the vicinal and configurational contributions in a complex are separable and additive on the CD curves in the spin-allowed d–d absorption band region.[8–10,15] For a complex with two kinds of the optically active ligands, it has been confirmed that each of the chiral ligands independently contributed to CD of the complex.[10] The optical activity of *u* isomers with the (*S*)-aminocarboxylato ligand (*S*-am) should be attributed partly to the arrangement chirality due to the arrangement of the β-alada chelate rings and partly to the vicinal one due to the *S*-am. If the additivity rule is also correct here, the following relationship will hold for each the isomers of *u*-trans(N) (*S*)-alaninato, (*S*)-prolinato, and *u*-cis(N) (*S*)-alaninato complexes

$$\Delta\epsilon[\text{arrang}] = \Delta\epsilon[\text{obsd}] - \Delta\epsilon[S]$$

where Δε[obsd] is the observed CD of an isomer, Δε[arrang] is the arrangement contribution, and Δε[*S*] is the vicinal one of *S*-am. If we assume that the Δε[*S*] is equal to the observed CD of the corresponding Co(nta)(*S*-am)$^-$, we can obtain the arrangement contribution Δε[arrang]. As seen in Figures 8 and 9, the calculated arrangement contribution curve for $(-)_{589}$-*u-trans*(*N*)-Co(β-alada)(*S*-ala)$^-$ or $(-)_{589}$-*u-trans*(*N*)-Co(β-alada)(*S*-pro)$^-$ agrees with the observed CD curve of $(-)_{589}$-*u-trans*(*N*)-Co(β-alada)(gly)$^-$, while those for the corresponding $(+)_{589}$ isomers agree with the observed CD curve of $(+)_{589}$-*u-trans*(*N*)-Co(β-alada)(gly)$^-$. Similar agreement is also substantiated for the CD curves of cis(N) isomers (Figure 10). These facts indicate that the additivity rule is maintained also between the vicinal and the arrangement contributions. In consequence, it is possible to point out that the $(-)_{589}$-*u*-trans(N) isomer with *S*-ala or *S*-pro has an absolute configuration of chelate ring arrangement of β-alada, the same as $(-)_{589}$-*u-trans*(*N*)-Co(β-alada)(gly)$^-$, and that $(-)_{589}$-*u-cis*(*N*)-Co(β-alada)(*S*-ala)$^-$ and $(-)_{589}$-*u-cis*(*N*)-Co(β-alada)(gly)$^-$ have the same absolute configuration as β-alada arrangement. X-Ray studies of these new types of complexes are desirable.

Registry No. *s-trans*(*N*)-K[Co(β-alada)(gly)], 37843-49-5; $(-)_{589}$-*u-trans*(*N*)-K[Co(β-alada)(gly)], 37843-50-8; $(+)_{589}$-*u-trans*(*N*)-K[Co(β-alada)(gly)], 37843-51-9; $(-)_{589}$-*u-trans*-(*N*)-K[Co(β-alada)(*s*-ala)], 37843-52-0; $(+)_{589}$-*u-trans*(*N*)-K[Co(β-alada)(*s*-ala)], 37843-53-1; $(-)_{589}$-*s-trans*(*N*)-K[Co-(β-alada)(*s*-ala)], 37861-97-5; $(-)_{589}$-*u-trans*(*N*)-K[Co-(β-alada)(*s*-pro)], 37861-98-6; $(+)_{589}$-*s-trans*(*N*)-K[Co-(β-alada)(*s*-pro)], 37862-00-3; $(+)_{589}$-*u-trans*(*N*)-K[Co-(β-alada)(*s*-pro)], 37861-99-7; $(+)_{589}$-*u-cis*(*N*)-K[Co(β-alada)-(gly)], 37862-01-4; $(-)_{589}$-*u-cis*(*N*)-K[Co(β-alada)(gly)], 37862-02-5; $(+)_{589}$-*u-cis*(*N*)-K[Co(β-alada)(*s*-ala)], 37862-03-6; $(-)_{589}$-*u-cis*(*N*)-K[Co(β-alada)(*s*-ala)], 37862-04-7; $(+)_{589}$-*s-cis*(*N*)-Co(β-alada)(*s*-ala)$^-$, 37862-05-8; [Co(β-alada)(gly)]-[Co(ox)(en)$_2$], 37897-30-6; [Co(β-alada)(gly)][Co(ox)(en)$_2$], 37897-31-7; [Co(β-alada)(gly)][Co(ox)(en)$_2$], 37897-32-8; [Co(β-alada)(gly)][Co(ox)(en)$_2$], 37897-33-9; cobalt, 7440-48-4.