Metal Complexes of Amino Acids. X.[1] The Preparation and Characterization of Cobalt(III) Complexes of the Type $[Co(N)_2(O)_4]$ Containing β-Alanine

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Three geometrical isomers of the bis(β-alaninato)(oxalato)cobaltate(III) and of the (β-alaninato)(glycinato)-(oxalato)cobaltate(III) complexes have been prepared and resolved into their optical isomers. Their structures were assigned on the basis of the electronic absorption, ^1H NMR and ^{13}C NMR spectra. The circular dichroism spectra of these complexes have been measured and compared with those of the bis(glycinato)(oxalato)cobaltate(III) complexes.

Optically active cobalt(III) complexes containing amino acids are important for clarifying the relationships between their electronic absorption and circular dichroism (CD) spectra and the structures of the complexes. A number of investigators have studied α-amino acid-cobalt(III) complexes.[1-8] However, only a few cobalt(III) complexes containing β-alanine have been reported and further investigation is necessary.

β-Alanine can coordinate to a cobalt(III) ion with both carboxyl and amino groups as in the case of α-amino acids. Consequently, in complexes of the type bis(amino acidato)(oxalato)cobaltate(III) anion, β-alanine complexes provide the same geometrical isomers as α-amino acid complexes. However, β-alanine forms a six-membered chelate ring, unlike α-amino acids. It has been pointed out that the difference in size of chelate rings affects the CD spectra.[9,10] Thus, it would be interesting to compare the CD spectra of the complexes which contain β-alanine with those of the complexes containing α-amino acids.

The present paper deals with the separation and optical resolution of the isomers of bis(β-alaninato)-(oxalato)cobaltate(III) and (β-alaninato)(glycinato)-(oxalato)cobaltate(III) complexes and with their electronic absorption and CD spectra. Their spectra are compared with those of optically active bis(glycinato)-(oxalato)cobaltate(III) complexes.

Experimental

Preparation of Complexes. Isomers of Potassium Bis(β-alaninato)-(oxalato)cobaltate(III): A solution of 20 g of cobalt(II) chloride hexahydrate in 20 ml of hot water was added to a solution containing 18.5 g of potassium oxalate monohydrate and 15 g of β-alanine in 80 ml of water. The resulting dark red solution was oxidized with 20 g of lead dioxide at 60 °C for about 22 h. After the mixture had been cooled to room temperature, a large amount of insoluble material was removed by filtration. The filtrate was poured into a column (30 mm × 600 mm) containing an anion exchange resin (Dowex 1×8, 200—400 mesh, acetate form). A small quantity of non-electrolyte complexes was eluted when the column was flushed with water. The adsorbed band was eluted with a 0.05 M aqueous solution of potassium acetate, giving three colored bands. The bands, in the order of elution, were blue-violet, purple and blue. Another blue band remained at the top of the column. The second and third eluted bands were determined from their electronic absorption spectra and column chromatographic behavior to be C_1-*cis*(N)- and C_2-*cis*(N)-$[Co(\beta\text{-ala})_2(ox)]^-$ ions, respectively. The first eluted band was confirmed to be *trans*(N)-$[Co(\beta\text{-ala})_2(ox)]^-$ ion from its absorption spectrum. Each eluted solution was evaporated to a few milliliters in a vacuum evaporator. To each concentrated solution was added a large amount of ethanol. The complex precipitated was washed with methanol. Each complex was recrystallized from hot water by addition of methanol. The yields were 5.0 g for the C_1-*cis*(N) isomer and 1.5 g for the C_2-*cis*(N) isomer. Found: C, 22.77; H, 4.48; N, 6.55%. Calcd for C_1-*cis*(N)-$K[Co(\beta\text{-ala})_2(ox)]\cdot 3.5H_2O$: C, 22.59; H, 4.50; N, 6.59%. Found: C, 23.18; H, 4.22; N, 6.67%. Calcd for C_2-*cis*(N)-$K[Co(\beta\text{-ala})_2(ox)]\cdot 3H_2O$: C, 23.08; H, 4.35; N, 6.73%.

Isomers of Potassium (β-Alaninato)(glycinato)(oxalato)cobaltate-(III): A solution containing 4.5 g of potassium oxalate monohydrate, 1.6 g of glycine and 3.5 g of β-alanine in 20 ml of water (50 °C) was added to a solution containing 4.5 g of cobalt(II) sulfate heptahydrate in 10 ml of water (50 °C). The solution was oxidized with 3 g of lead dioxide. The resulting mixture was stirred at 50 °C for about 30 min. After the mixture had been cooled in an ice bath for about 3 h, a large amount of insoluble material was removed by filtration. The filtrate was poured into a column (35 mm × 900 mm) containing an anion exchange resin (Dowex 1×8, 200—400 mesh, acetate form). After the column had been swept with four liters of water, the adsorbed band was eluted with a 0.04 M aqueous solution of potassium acetate. Ten colored bands were separated: (i) blue-violet, (ii) blue-violet, (iii) violet, (iv) purple, (v) blue, (vi) violet-red, (vii) red-violet, (viii) pale violet, (ix) red-violet and (x) pale blue-violet. The symbols (i)—(x) represent the fractions eluted from each band. The complex/or isomer obtained from each fraction is abbreviated as **1**—**10**. Thus, (i) represents the fraction from the first band and **1** denotes the complex/or isomer from fraction (i), and so on. Each fraction was concentrated in a vacuum evaporator at 35—40 °C. A mixture of a small amount of methanol and a large amount of acetone was added to each concentrated solution to give two liquid layers, a cloudy colorless layer and a clear colored layer. After the cloudy layer was removed by decantation, a mixture of a small amount of methanol and a large amount of acetone was added to the clear layer, and the resulting new cloudy layer was discarded. This procedure was repeated several times, and finally a large amount of ethanol was added to the residual solution. The crude product deposited was filtered and washed with ethanol. Purification of the complex was carried out by addition of ethanol to a concentrated aqueous solution.

The visible absorption and NMR spectra of the isolated complexes indicate that the complexes **1**, **4**, and **5** are three

geometrical isomers of $[Co(\beta\text{-ala})_2(ox)]^-$ and the complexes **3**, **9**, and **10** are those of $[Co(gly)_2(ox)]^-$. The complexes obtained from the (ii), (vi), (vii), and (viii) fractions are the isomers of $[Co(\beta\text{-ala})(gly)(ox)]^-$. The yield of the complex from the band (viii) was so small that we could not isolate complex **8** in pure form. The yields of **2**, **6**, and **7** were 0.15, 0.2, and 0.1 g, respectively. Found for complex **2**: C, 23.31; H, 3.04; N, 7.86%. Calcd for $K[Co(\beta\text{-ala})(gly)(ox)]\cdot 0.5H_2O$: C, 23.54; H,3.10; N, 7.80%. Found for complex **6**: C, 21.85; H, 3.65; N, 7.22%. Calcd for $K[Co(\beta\text{-ala})(gly)(ox)]\cdot 2H_2O$: C, 21.88; H, 3.67; N, 7.29%. Found for complex **7**: C, 22.34; H, 3.50; N, 7.32%. Calcd for $K[Co(\beta\text{-ala})(gly)(ox)]\cdot 1.5H_2O$: C, 22.41; H, 3.49; N, 7.47%.

Optical Resolution of the Complexes. The Second Eluted Isomer of Potassium Bis(β-alaninato)(oxalato)cobaltate(III): A suspension of 2 g of $(+)_{546}$-$[Co(en)_2(ox)]I$ in 14 ml of water was stirred with 0.9 g of silver acetate at 50 °C for about 10 min. The silver iodide precipitated was filtered and washed with a small amount of ice water. To the combined filtrate and washings was added 2 g of C_1-*cis*(N)-$K[Co(\beta\text{-ala})_2(ox)]\cdot 3.5H_2O$ (the second eluted isomer), and the solution was chilled in an ice bath for about 4 h. The red-brown diastereomer which deposited, $(+)_{546}$-$[Co(en)_2(ox)](+)_{546}$-$[Co(\beta\text{-ala})_2(ox)]\cdot 7H_2O$, was filtered, washed with a small amount of ice water, methanol and then ether, and dried in the air. The diastereomer was recrystallized repeatedly from hot water by addition of methanol until no further increase in optical rotation was observed. $[\alpha]_{546}+1490°$. Found: C, 23.38; H, 6.07; N, 11.57%. Calcd for $(+)_{546}$-$[Co(en)_2(ox)](+)_{546}$-$[Co(\beta\text{-ala})_2(ox)]\cdot 7H_2O$: C, 23.47; H, 5.92; N, 11.73%.

A solution containing 0.7 g of the $(+)_{546}$ diastereomer in a small amount of water was passed through a column (20 mm ×200 mm) containing a cation exchange resin (Dowex 50W ×8, 200—400 mesh, potassium form). The complex anion, $(+)_{546}$-$[Co(\beta\text{-ala})_2(ox)]^-$, was eluted when the column was flushed with water, while the resolving agent, $(+)_{546}$-$[Co(en)_2(ox)]^+$, was adsorbed on the top of the column. The eluate (solution) was evaporated to a few milliliters in a vacuum evaporator, methanol being added to the residue. The complex which precipitated was filtered, washed with a water–methanol mixture and then methanol, and dried in the air. The complex was recrystallized from hot water by addition of methanol. $[\alpha]_{546}+1710°$. Found: C, 23.62; H, 4.34; N, 6.80%. Calcd for $(+)_{546}$-$K[Co(\beta\text{-ala})_2(ox)]\cdot 2.5H_2O$: C, 23.59; H, 4.21; N, 6.88%.

The Third Eluted Isomers of Potassium Bis(β-alaninato)(oxalato)cobaltate(III): A suspension containing 1.1 g of $(+)_{546}$-$[Co(en)_2(ox)]I$ in 10 ml of water was stirred with 0.5 g of silver acetate at 50 °C for about 10 min. The silver iodide which precipitated was filtered and washed with a small amount of water. To the combined filtrate and washings was added 1.1 g of C_2-*cis*(N)-$K[Co(\beta\text{-ala})_2(ox)]\cdot 3H_2O$ (the third eluted isomer). A red-brown diastereomer which deposited immediately, $(+)_{546}$-$[Co(en)_2(ox)](+)_{546}$-$[Co(\beta\text{-ala})_2(ox)]\cdot 4H_2O$, was filtered, washed with a small amount of ice water, methanol and then ether, and dried in the air. The diastereomer was recrystallzed repeatedly from hot water by addition of methanol until no further increase in optical rotation was observed. $[\alpha]_{546}+840°$. Found: C, 25.39; H, 5.57; N, 12.61%. Calcd for $(+)_{546}$-$[Co(en)_2(ox)](+)_{546}$-$[Co(\beta\text{-ala})_2(ox)]\cdot 4H_2O$: C, 25.38; H, 5.49; N, 12.69%.

Separation of $(+)_{546}$-$K[Co(\beta\text{-ala})_2(ox)]$ from the diastereomer was carried out by the same method as described for the separation of $(+)_{546}$ isomer from the second eluted band. The complex obtained was recrystallized from hot water by addition of methanol. $[\alpha]_{546}+590°$. Found: C, 24.87; H, 4.16; N, 6.93%. Calcd for $(+)_{546}$-$K[Co(\beta\text{-ala})_2(ox)]\cdot 1.5H_2O$: C, 24.69; H, 3.88; N, 7.19%.

The Potassium Salt of Complex 3: The recemate, (±)-*trans*-(N)-$K[Co(\beta\text{-ala})(gly)(ox)]\cdot 0.5H_2O$ (0.51 g), was dissolved in 70 ml of water, and the solution was treated with a cation exchange resin (Dowex 50W×8, 200—400 mesh, lithium form). The resolving agent, $(+)_{546}$-$[Co(en)_2(ox)]Br\cdot H_2O$ (0.25 g) was dissolved in 200 ml of water, and the solution was treated with an anion exchange resin (Dowex 1×8, 200—400 mesh, acetate form). The two solutions were mixed, the mixture was evaporated to 50 ml, and then 15 ml of ethanol was added to the concentrated solution. The less soluble diastereomer deposited was filtered and washed with warm water. It is sparingly soluble in water. $[\alpha]_{546}+940°$. Found: C, 25.90; H, 4.72; N, 13.94%. Calcd for $(+)_{546}$-$[Co(en)_2(ox)](+)_{546}$-$[Co(\beta\text{-ala})(gly)(ox)]\cdot 1.5H_2O$: C, 25.88; H, 4.85; N, 13.93%.

The cation exchange resin (Dowex 50W×8, 200—400mesh, potassium form) was added to a suspension of the $(+)_{546}$ diastereomer in water. The mixture was stirred for about 1 h and the resin was removed by filtration. The filtrate containing $(+)_{546}$-$K[Co(\beta\text{-ala})(gly)(ox)]$ was concentrated in a vacuum evaporator, ethanol being added to the concentrated solution. The $(+)_{546}$ isomer obtained was reprecipitated repeadedly from aqueous solution by addition of ethanol until optical rotation attained a constant value. The isomer was gelatinous. $[M]_{546}+2040°$ (concentration of the solution was determined from its absorption spectrum).

The Potassium Salt of Complex 6: A 50 ml of aqueous solution of $K[Co(\beta\text{-ala})(gly)(ox)]\cdot 2H_2O$ (obtained from the eluted band (vi), 0.8 g) was treated with a cation exhange resin (lithium form). An aqueous solution of $(+)_{546}$-$[Co(en)_2(ox)]Br\cdot H_2O$ (0.5 g) was passed through an anion exchange resin (acetate form). These two solutions were mixed, the mixture was evaporated to 50 ml in a vacuum evaporator, and then 50 ml of ethanol was added to the concentrated solution. On cooling the solution in an ice bath for 2 h, the less soluble diastereomer precipitated as a red-violet powder. The precipitate was filtered and washed with ethanol. The diastereomer was recrystallized repeatedly from hot water by addition of ethanol until no further increase in optical rotation was observed. $[\alpha]_{546}$ −940°. Found: C, 25.36; H, 4.99; N, 13.57%. Calcd for $(+)_{546}$-$[Co(en)_2(ox)](-)_{546}$-$[Co(\beta\text{-ala})(gly)(ox)]\cdot 2H_2O$: C, 25.50; H, 4.94; N, 13.73%.

The $(-)_{546}$ diastereomer, $(+)_{546}$-$[Co(en)_2(ox)](-)_{546}$-$[Co(\beta\text{-ala})(gly)(ox)]\cdot 2H_2O$, was dissolved in water and the solution was passed through a small column of cation exchange resin (Dowex 50W×8, 200—400 mesh, potassium form). The solution was evaporated to a few milliliters. Violet-red flakes were deposited by adding ethanol to the concentrated solution. The complex was recrystallized from water by addition of ethanol. $[\alpha]_{546}-1830°$. Found: C, 22.25; H, 3.70; N, 7.25%. Calcd for $(-)_{546}$-$K[Co(\beta\text{-ala})(gly)(ox)]\cdot 2H_2O$: C, 21.88; H, 3.67; N, 7.29%.

The Potassium Salt of Complex 7. The complex was resolved in the same way as described for complex **6**. The racemate, $(\pm)$-$K[Co(\beta\text{-ala})(gly)(ox)]\cdot 1.5H_2O$ (obtained from the eluted band (vii), 1.10 g), was dissolved in 50 ml of water, and the solution was treated with a cation exchange resin (Dowex 50W×8, 200—400 mesh, lithium form). The resolving agent, $(+)_{546}$-$[Co(en)_2(ox)]Br\cdot H_2O$ (0.69 g), was dissolved in 60 ml of water at 60 °C, and the solution was treated with an anion exchange resin (Dowex 1×8, 200—400 mesh, acetate form). The two solutions were mixed. The mixture was evaporated to 75 ml in a vacuum evaporator, and then 25 ml of ethanol was added to the concentrated solution. After 1 h, red-violet crystals deposited were filtered and washed with water–ethanol mixture. They were recrystallized from water by addition of

ethanol. $[\alpha]_{546}+980°$. Found: C, 24.48; H, 5.07; N, 13.55%. Calcd for $(+)_{546}$-$[Co(en)_2(ox)](+)_{546}$-$[Co(\beta\text{-ala})(gly)(ox)]\cdot 3H_2O$: C, 24.77; H, 5.11; N, 13.33%.

The $(+)_{546}$ diastereomer was dissolved in water, and the solution was passed through a column of a cation exchange resin (Dowex 50W×8, 200—400 mesh, potassium form) in order to remove the resolving agent. The resulting solution was evaporated to a few milliliters, and then ethanol was added to the concentrated solution. After the solution had been allowed to stand for about 30 min at room temperature, crystalline powder deposited was filtered. It was recrystallized from a mixture of water and ethanol. $[\alpha]_{546}+1210°$. Found: C, 22.81; H, 3.30; N, 7.58%. Calcd for $(+)_{546}$-K-$[Co(\beta\text{-ala})(gly)(ox)]\cdot H_2O$: C, 22.96; H, 3.30; N, 7.65%.

Measurements. The electronic absorption spectra of the complexes were measured with a Hitachi Model EPS-3T spectrophotometer in aqueous solution. The CD spectra were recorded on a JASCO Model MOE-1 spectropolarimeter, the ^1H NMR spectra on a JEOL Model MH-100 spectrometer with DSS as an internal standard, and the ^{13}C NMR spectra on a JEOL Model MFT-100 spectrometer in pulse Fourier transform/proton noise decoupling mode at 25.15 MHz. The ^{13}C chemical shifts were measured relative to external benzene and converted into the chemical shifts from TMS using the relation $\delta_{TMS}=\delta_{benzene}-128.5$ ppm.

Results and Discussion

Both $[Co(gly)_2(ox)]^-$ and $[Co(\beta\text{-ala})_2(ox)]^-$ ions provide three geometrical isomers, *trans*(N), C_1-*cis*(N) and C_2-*cis*(N). On the other hand, the mixed complex ion, $[Co(\beta\text{-ala})(gly)(ox)]^-$, exists in four geometrical isomers of *trans*(N), *cis*(N)*trans*(O_β,N) (O_β represents the coordinating oxygen atom in β-alanine), *cis*(N)*trans*-(O_g,N) (O_g represents the coordinating oxygen atom in glycine) and *cis*(N)*trans*(O_β,O_g) (this isomer has a pseudo C_2 axis, the glycine being regarded as β-alanine; it is therefore referred to as C_2-*cis*(N) in this paper) (Fig. 1).

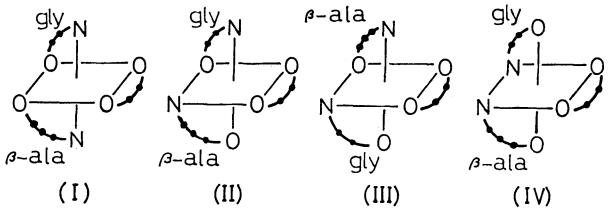

Fig. 1. The geometrical structures of four isomers in the mixed complex ion, $[Co(\beta\text{-ala})(gly)(ox)]^-$.
(I), *trans*(N); (II), *cis*(N)*trans*(O_β,N); (III), *cis*(N)*trans*-(O_g,N); (IV), *cis*(N)*trans*(O_β,O_g) (pseudo C_2 symmetry).

Structural Assignments of the Isomer $[Co(\beta\text{-ala})_2(ox)]^-$. It is generally recognized that the visible absorption band at lower energy side (the so-called first absorption band) of the *trans*(N) isomer of $[Co(N)_2(O)_4]$ type complex shows a more marked split as compared with that of the corresponding *cis*(N) isomer.[12] The $[Co(\beta\text{-ala})_2(ox)]^-$ complex prepared by Hidaka and Shimura[13] has been assigned to *trans*(N) isomer on the basis of the above. A marked split of the first absorption band was also observed for the complex obtained from the first eluted band in the process of separation of $[Co(\beta\text{-ala})_2(ox)]^-$ ion. Thus we conclude that the isomer obtained from the first eluted band has the *trans*(N) configuration. On the other hand, the other two isomers obtained from the second and third eluted bands showed no such marked split in the first absorption band, so that their configurations can be assigned to *cis*(N).

The assignments of the C_1- and C_2-*cis*(N) isomers can be verified by their ^{13}C NMR spectra. Since the chemical environments of the ethylene-carbons of the two β-alanine ligands are equivalent in the C_2-*cis*(N) isomer but not in the C_1-*cis*(N) isomer, two and four resonance lines resulting from ethylene-carbons are expected for the former and the latter, respectively. In addition, one resonance line due to the carboxyl-carbons in the coordinated β-alanines is expected for the C_2-*cis*(N) isomer, and two lines for the C_1-*cis*(N) isomer. The second eluted isomer showed four resonance lines resulting from ethylene-carbons and two resonance lines from carboxyl-carbons (Table 1). On the other hand, the third eluted isomer showed only two resonance lines and one for these carbons. Thus the structures of the second and third eluted isomers can be assigned to C_1-*cis*(N) and C_2-*cis*(N), respectively.

Table 1. ^{13}C CHEMICAL SHIFTS OF THE COORDINATED β-ALANINE

Complex ion	Ethylene-carbons		Carboxyl-carbon
trans(N)-$[Co(\beta\text{-ala})_2(ox)]^-$	33.9 ppm	38.6 ppm	184.4 ppm
C_1-*cis*(N)-$[Co(\beta\text{-ala})_2(ox)]^-$	33.7 (slightly split)	38.0	183.1
		38.6	184.2
C_2-*cis*(N)-$[Co(\beta\text{-ala})_2(ox)]^-$	33.6	38.0	183.3

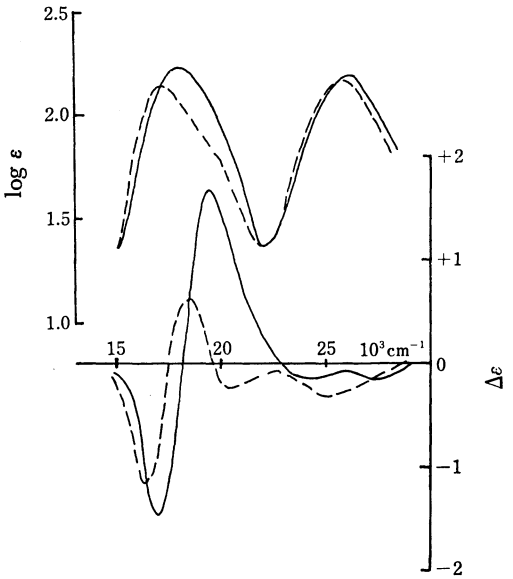

Fig. 2. The absorption and CD spectra of C_1- and C_2-*cis*(N) isomers of $[Co(\beta\text{-ala})_2(ox)]^-$ ion.
—— $(+)_{546}$-C_1-*cis*(N)-$[Co(\beta\text{-ala})_2(ox)]^-$, and
------ $(+)_{546}$-C_2-*cis*(N)-$[Co(\beta\text{-ala})_2(ox)]^-$.

The assignments of the C_1-*cis*(N) and C_2-*cis*(N) isomers can be made also on the basis of the energy difference in the first absorption bands. Matsuoka *et al.*[12] reported three geometrical isomers of a bis(amino acidato)-(oxalato)cobaltate(III) complex, and pointed out that the first absorption maxima of the C_2-*cis*(N) isomers are located in a lower energy region than those of the C_1-*cis*(N) isomers. As shown in Fig. 2, the first absorption maximum (18070 cm^{-1}) of the second eluted isomer was observed in a higher energy region as compared with that (17300 cm^{-1}) of the third eluted isomer. It can be concluded that the second and third eluted isomers take C_1-*cis*(N) and C_2-*cis*(N) structures, respectively. These assignments are in line with those from the ^{13}C NMR data.

Structural Assignments of Four Isomers in [Co(β-ala)(gly)-(ox)]⁻ Ion. Ten chromatographic bands ((i)—(x)) appeared on separation of [Co(β-ala)(gly)(ox)]⁻ (see Experimental). For complexes **3**, **9**, and **10**, the ^1H NMR resonance lines due to only the methylene-protons of the coordinated glycine were observed in the region 3.37—3.67 ppm. On the other hand, for complexes **1**, **4**, and **5**, the resonance lines due to only the ethylene-protons of the coordinated β-alanine were observed in the region 2—3 ppm. However, for complexes **2**, **6**, **7**, and **8**, both signals of the coordinated glycine and β-alanine were observed. The absorption spectra of complexes **1**, **3**, **4**, **5**, **9**, and **10** agree well with those of *trans*(N)-[Co(β-ala)$_2$(ox)]⁻, *trans*(N)-[Co(gly)$_2$(ox)]⁻, C_1-*cis*(N)-[Co(β-ala)$_2$(ox)]⁻, C_2-*cis*(N)-[Co(β-ala)$_2$(ox)]⁻, C_1-*cis*(N)-[Co(gly)$_2$(ox)]⁻, and C_2-*cis*(N)-[Co(gly)$_2$-(ox)]⁻, respectively. It is therefore expected that the remaining complexes, **2**, **6**, **7**, and **8**, are four isomers of the [Co(β-ala)(gly)(ox)]⁻ ion.

Of four isomers of the (β-alaninato)(glycinato)-(oxalato)cobaltate(III) complex, the structure of isomer **2** can be assigned to *trans*(N) since a marked split was observed in the first absorption band, which is characteristic of the complexes of *trans*(N)-[Co(N)$_2$(O)$_4$] type. The other three isomers, **6**, **7**, and **8**, exhibited no such marked split in the first absorption band, and thus would have the *cis*(N) configuration. Of these three *cis*(N) isomers, isomer **8** showed the first absorption band maximum (17670 cm^{-1}) in the lowest energy region (Table 2 and Fig. 3). The absorption maximum of C_2-*cis*(N) isomer was observed in a lower energy region than for the C_1-*cis*(N) isomer in bis(amino acidato)-(oxalato)cobaltate(III) complexes. Isomer **8** is thus expected to take C_2-*cis*(N) structure, as shown in Fig. 1 (IV). The structures of the remaining two isomers **6** and **7** can be assigned to either *cis*(N)*trans*(O_β,N) (Fig. 1 (II)) or *cis*(N)*trans*(O_g,N) (Fig. 1 (III)).

^1H NMR Spectra. The ^1H NMR spectra of the complexes are shown in Fig. 4. The methylene-proton

Table 2. Absorption and CD data of bis(amino acidato)cobaltate(III) complexes

Elution order		Complex ion	Band I		Band II	
			AB_{max} 10^3 cm^{-1} (log ε)	CD_{ext} 10^3 cm^{-1} (Δε)	AB_{max} 10^3 cm^{-1} (log ε)	CD_{ext} 10^3 cm^{-1} (Δε)
(iii)	**3**	(+)$_{546}$-*trans*(N)-[Co(gly)$_2$(ox)]⁻ [a]	*ca.* 16.7 (1.7) 18.87 (2.00)	*ca.* 16.7 (−1.4) 18.88 (−2.07)	25.83 (2.23)	26.17 (+0.69)
(ii)	**2**	(+)$_{546}$-*trans*(N)-[Co(β-ala)(gly)(ox)]⁻	16.30 (1.75) 18.81 (2.01)	*ca.* 16.3 (−1.1) 18.55 (−1.46)	25.97 (2.19)	23.70 (−0.13) 26.11 (+0.54)
(i)	**1**	(+)$_{546}$-*trans*(N)-[Co(β-ala)$_2$(ox)]⁻ [a]	16.00 (1.76) 18.83 (2.00)	15.70 (−0.43) *ca.* 16.7 (−0.3) 19.53 (−0.57)	26.30 (2.12)	23.80 (−0.13) 26.53 (+0.71)
(ix)	**9**	(−)$_{546}$-C_1-*cis*(N)-[Co(gly)$_2$(ox)]⁻ [a]	18.33 (2.15)	17.70 (+2.48) *ca.* 22.3 (+0.04)	25.77 (2.24)	23.93 (+0.09) 26.30 (−0.32) 29.00 (+0.10)
(vi)	**6**	(−)$_{546}$-*cis*(N)*trans*(O_β,N)-[Co(β-ala)(gly)(ox)]⁻	18.52 (2.19)	17.09 (+3.81) 19.49 (−1.88)	25.84 (2.24)	24.27 (+0.49) 26.11 (−0.09) 28.17 (+0.17)
(vii)	**7**	(+)$_{546}$-*cis*(N)*trans*(O_g,N)-[Co(β-ala)(gly)(ox)]⁻	18.02 (2.20)	17.15 (−1.50) 19.80 (+0.24)	26.04 (2.24)	23.98 (−0.10) 26.11 (+0.20) 28.74 (−0.04)
(iv)	**4**	(+)$_{546}$-C_1-*cis*(N)-[Co(β-ala)$_2$(ox)]⁻	18.07 (2.24)	17.00 (−1.45) 19.43 (+1.71)	25.90 (2.18)	24.57 (−0.13) 27.23 (−0.12)
(x)	**10**	(+)$_{546}$-C_2-*cis*(N)-[Co(gly)$_2$(ox)]⁻ [a]	17.83 (2.08)	18.03 (−3.39) *ca.* 22.5 (+0.04)	25.90 (2.20)	25.97 (+0.52)
(viii)	**8**	*cis*(N)*trans*(O_β,O_g)-[Co(β-ala)(gly)(ox)]⁻ (pseudo C_2 symmetry)	17.67 (qualitative)		26.14 (qualitative)	
(v)	**5**	(+)$_{546}$-C_2-*cis*(N)-[Co(β-ala)$_2$(ox)]⁻	17.30 (2.12)	16.47 (−1.19) 18.47 (+0.62) 20.83 (−0.24)	25.77 (2.17)	25.30 (−0.29)

a) Refs. 11 and 13.

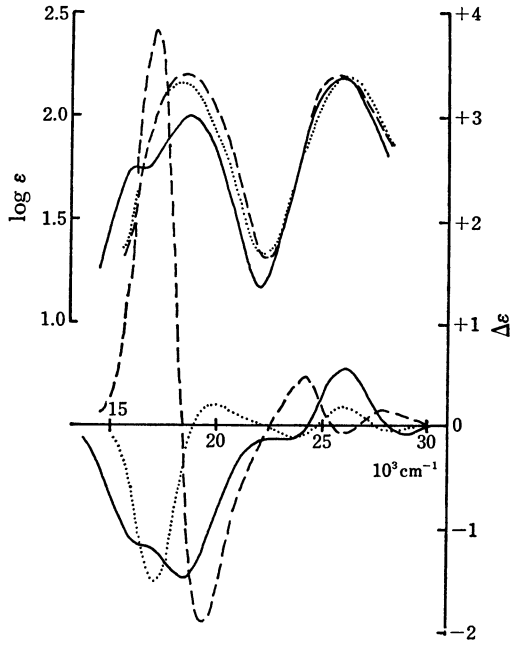

Fig. 3. The absorption and CD spectra of the isomers in $[Co(\beta\text{-ala})(gly)(ox)]^-$ complex ion.
—— $(+)_{546}$-*trans*(N)-$[Co(\beta\text{-ala})(gly)(ox)]^-$,
------ $(-)_{546}$-*cis*(N)*trans*(O_β,N)-$[Co(\beta\text{-ala})(gly)(ox)]^-$,
····· $(+)_{546}$-*cis*(N)*trans*(O_g,N)-$[Co(\beta\text{-ala})(gly)(ox)]^-$.

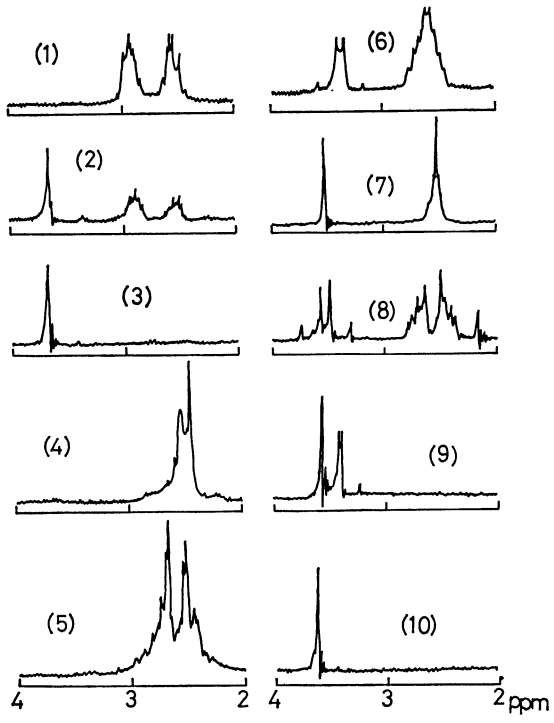

Fig. 4. The ^1H NMR spectra of $[Co(\beta\text{-ala})_{2-x}(gly)_x(ox)]^-$ (x=0—2) ions.
(1), *trans*(N)-$[Co(\beta\text{-ala})_2(ox)]^-$; (2), *trans*(N)-$[Co(\beta\text{-ala})(gly)(ox)]^-$; (3), *trans*(N)-$[Co(gly)_2(ox)]^-$; (4), C_1-*cis*(N)-$[Co(\beta\text{-ala})_2(ox)]^-$; (5), C_2-*cis*(N)-$[Co(\beta\text{-ala})_2(ox)]^-$; (6), *cis*(N)*trans*($O_\beta$,N)-$[Co(\beta\text{-ala})(gly)(ox)]^-$; (7), *cis*(N)-*trans*($O_g$,N)-$[Co(\beta\text{-ala})(gly)(ox)]^-$; (8), *cis*(N)*trans*($O_\beta$, O_g)-$[Co(\beta\text{-ala})(gly)(ox)]^-$ (pseudo C_2 symmetry, containing some contamination); (9), C_1-*cis*(N)-$[Co(gly)_2(ox)]^-$; and (10) C_2-*cis*(N)-$[Co(gly_2(ox)]^-$.

signals of the chelated glycine appear in the region 3.3—3.7 ppm. The *trans*(N) isomer **3** of the bis(glycinato)(oxalato)cobaltate(III) complex showed a single resonance at 3.67 ppm, and the C_2-*cis*(N) isomer **10** one at 3.52 ppm. However, two different resonance signals (a singlet at 3.52 ppm and a quartet at 3.37 ppm) were observed in the C_1-*cis*(N) isomer **9**. This suggests that the methylene-protons of the two glycines in isomer **9** are present in different chemical environments. Sakaguchi *et al.* pointed out the importance of the effect of magnetic anisotropy which is induced on the central Co(III) chromophore. They applied the anisotropy to the assignments of protons in ethylenediamine-Co(III) complexes[14] and amino acidato-Co(III) complexes.[15] They suggested that, in C_1-*cis*(N)-$[Co(gly)_2(ox)]^-$, the methylene-protons of the chelated glycine located in the plane including N-Co(III)-N would be observed in a lower field than the other methylene-protons of the chelated glycine which is not located in the plane. Thus the singlet at 3.52 ppm can be assigned to H_b and H_b', and the quartet at 3.37 ppm to H_a and H_a' (Fig. 5 (I)).

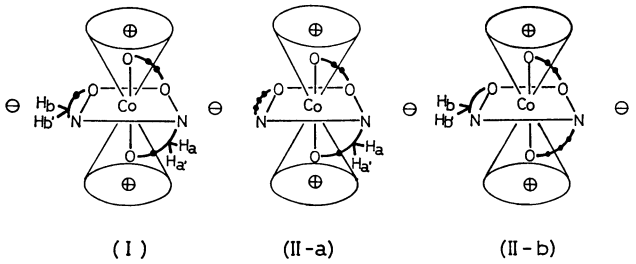

Fig. 5. The magnetic anisotropy induced on cobalt(III) chromophore.
(I); C_1-*cis*(N)-$[Co(gly)_2(ox)]^-$, (II-a); *cis*(N)*trans*(O_β, N)-$[Co(\beta\text{-ala})(gly)(ox)]^-$, and (II-b); *cis*(N)*trans*(O_g,N)-$[Co(\beta\text{-ala})(gly)(ox)]^-$.
+: Shift to up field, −: shift to down field.

The ^1H NMR data of isomer **6** gave a quartet signal due to the methylene-protons of glycine, at 3.38 ppm (Fig. 4). From the chemical shift and splitting pattern, it seems that these methylene-protons are in similar chemical environments to the higher field methylene-protons (H_a and H_a') of the C_1-*cis*(N) isomer of bis(glycinato)(oxalato)cobaltate(III) complex. The resonance line due to the methylene-protons of the glycinato chelate in isomer **7** (a singlet at 3.54 ppm) corresponds to that of the lower field methylene-protons (H_b and H_b') of C_1-*cis*(N)-$[Co(gly)_2(ox)]^-$. The correspondence leads to the conclusion that the structure of isomer **6** is *cis*(N)*trans*(O_β,N) and that of isomer **7** is *cis*(N)*trans*-(O_g,N) (Fig. 5, (II-a) and (II-b)).

The signals in the region 2—3 ppm should be assigned to the ethylene-protons of the β-alaninato chelate.

Electronic Absorption and CD Spectra. Electronic absorption and CD data of *trans*(N) complexes are given in Table 2. The absorption spectra of these complexes are very similar to each other. The intensity ratio of sub- and major-band of the first absorption band, (ε_{max}(sub)/ε_{max} (major)), for the *trans*(N)-$[Co(\beta\text{-ala})_2(ox)]^-$ is 0.58 and that for the *trans*(N)-$[Co(gly)_2(ox)]^-$ is

0.50. The ratio of the *trans*(N)-[Co(β-ala)(gly)(ox)]$^-$ is 0.55, greater than that of *trans*(N) bis(glycinato) and smaller than that of the *trans*(N) bis(β-alaninato) complex. The maximum of the second absorption band of the *trans*(N) (β-alaninato)(glycinato) complex was observed in a higher energy region than that of the bis(glycinato) complex, but in a lower energy region than that of the bis(β-alaninato) complex. For the second absorption bands of these three *trans*(N) complexes, the bis(β-alaninato) complex shows the lowest intensity (log ε_{max}) and the bis(glycinato) complex the highest intensity.

The CD curve of the $(+)_{546}$-*trans*(N) bis(glycinato) complex shows two negative bands in the first absorption band region and a positive band in the second absorption band region (Table 2). The CD curve of the $(+)_{546}$-*trans*(N) bis(β-alaninato) complex shows three negative bands in the first absorption band region, their intensities being significantly smaller compared with those of the bis(glycinato) complex.[13] However, the positive CD band of the bis(β-alaninato) complex observed in the second absorption band region is nearly equal to that of the bis(glycinato) complex. The CD curve of the $(+)_{546}$-*trans*(N)-[Co(β-ala)(gly)(ox)]$^-$ in the first absorption band region shows two negative bands which have somewhat smaller intensities than those of the $(+)_{546}$-*trans*(N) bis(glycinato) complex. The positive CD band of the mixed *trans*(N) complex in the second absorption band region is nearly equal in intensity to those of the other two *trans*(N) complexes. From the CD spectrum of the $(+)_{546}$-*trans*(N)-[Co(β-ala)$_2$(ox)]$^-$ in the first absorption band region, it is possible to assign its absolute configuration to Δ, as in the case of the $(+)_{546}$-*trans*(N) bis(glycinato) complex.[11]

For the four C_1-*cis*(N) complexes (**9**, **6**, **7**, and **4**) in Table 2, the first absorption maximum of the *cis*(N)*trans*-(O_β,N) (β-alaninato)(glycinato) complex **6** was observed in the highest energy region and that of the *cis*(N)*trans*-(O_g,N) (β-alaninato)(glycinato) complex **7** in the lowest energy region. However, the first absorption maximum of the *cis*(N)*trans*(O_β,O_g) (β-alaninato)(glycinato) complex **8** (pseudo C_2 symmetry) is located in a lower energy region than that of the C_2-*cis*(N) bis(glycinato) complex **10**, but in a higher energy region than that of the C_2-*cis*(N) bis(β-alaninato) complex **5**. The maxima of the first absorption band of the C_2-*cis*(N) complexes were observed in a lower energy region than those of the C_1-*cis*(N) complexes.

The *cis*(N)-[Co(α-am)$_2$(ox)]$^-$ type complexes containing glycine or L-serine show only one CD band in the first absorption band region. On the other hand, *cis*(N)-[Co(ida)$_2$]$^-$,[16] [Co(edta)]$^-$ [16,17] and *cis*(N)-[Co(L-alama)$_2$]$^-$ (L-alama: L-alanine-monoacetic acid)[18] have two CD bands of the opposite signs with comparable intensities. The *cis*(N)*trans*(O_β,N) (β-alaninato)(glycinato) complex **6** and the C_1-*cis*(N) bis(β-alaninato) complex **4** belong to the latter group, revealing two CD bands of the opposite signs and of nearly comparable intensities. The CD curves of the *cis*(N)*trans*(O_g,N) (β-alaninato)(glycinato) complex **7** and C_2-*cis*(N) bis(β-alaninato) complex **5** show different patterns from those of C_1-*cis*(N) bis(β-alaninato) and *cis*(N)*trans*(O_β,N) (β-alaninato)(glycinato) complexes in the first absorption band region. Namely, complex **5** shows three CD bands in the first absorption band region, while complex **7** shows two CD bands of opposite signs in the first absorption band region, but the CD intensity at 19800 cm^{-1} is significantly smaller than that of the opposite sign at 17150 cm^{-1}. The differences in the CD spectra would be caused by the difference in ligand field strength between O_g and O_β, and the difference in size of the chelate ring between the glycinato and β-alaninato chelates. However, the dominant factor is unknown.

The absolute configuration of the *cis*(N)-[Co(ida)$_2$]$^-$ isomer for which the CD bands in the first absorption band region show positive and negative signs listing from the lower energy side, was assigned to Λ by Van Saun and Douglas.[16] The Λ $(-)_{546}$-isomer of [Co(edta)]$^-$ shows a similar CD pattern in this region. From a comparison of CD patterns, it is concluded that the $(+)_{546}$-C_1- and $(+)_{546}$-C_2-*cis*(N) isomers of the bis(β-alaninato) complex and $(+)_{546}$-*cis*(N)*trans*(O_g,N) isomer of the (β-alaninato)(glycinato) complex take Δ configuration and the $(-)_{546}$-*cis*(N)*trans*(O_β,N) isomer of the (β-alaninato)(glycinato) complex takes Λ configuration.

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