Synthesis, Absorption and CD Spectra of [Co(amino alcohol)$(N)_2(O)_2$]-type Complexes

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Complexes of the [Co(amOH)$(N)_2(O)_2$]-type, where amOH represents 2-aminoethanol or (*S*)-2-amino-1-propanol and $(N)_2(O)_2$ represents $(gly)_2$, $(\beta\text{-ala})_2$, (ox)(en) or $(ox)(NH_3)_2$, have been prepared and characterized on the basis of absorption and PMR spectra. Splitting of the T_{2g} band has been observed in the solution spectra of certain isomers of the [Co$(gly)_2$(eta)], [Co$(gly)_2$(*S*-pra)], or [Co$(\beta\text{-ala})_2$(eta)] complex. Using the crystal spectral data of the isomers of [Co$(gly)_2$(eta)], the σ- and π-antibonding parameters for the ligating alcoholate O atom have been estimated and it has been found that each parameter shows a higher value than the corresponding parameters for the other ligating N and O atoms. The CD spectrum, in the T_{2g} region, of *fac*-[Co$(gly)_2$(eta)] has shown an intense peak at *ca.* 25000 cm^{-1}, and the vicinal effect curve of each isomer of the [Co$(gly)_2$(*S*-pra)] complex has shown an intense peak at the same frequency.

The mixed ligand complex of cobalt(III) containing 2-aminoethanol (Heta) and ethylenediamine, [Co$(en)_2$(Heta)]$^{3+}$, was first prepared by Buckingham *et al.*[1] Later, Ogino *et al.*[2] prepared optically active complexes such as [Co$(en)_2$(*S*-Hpra)]$^{3+}$ (*S*-Hpra denotes (*S*)-2-amino-1-propanol), [Co$(en)_2$(Heta)]$^{3+}$ and [Co$(NH_3)_4$(*S*-Hpra)]$^{3+}$ and reported that dissociation of the hydroxyl protons resulted in changes in the absorption and circular dichroism (CD) spectra; in the spectra of the deprotonated [Co(eta)$(en)_2$]$^{2+}$ and [Co(*S*-pra)$(en)_2$]$^{2+}$ complexes, a shoulder and maximum are observed in the second absorption (T_{2g}) region. In the CD spectra of [Co(*S*-pra)$(en)_2$]$^{2+}$ and [Co(*S*-pra)$(NH_3)_4$]$^{2+}$ complexes, the vicinal effect curve shows of medium intensity peaks not only in the first absorption (T_{1g}) region but also at the shoulder of the split T_{2g} band. These observations are of interest since, in general, splitting of the T_{2g} band and an intense CD peak in the T_{2g} region are both rare. Nishide *et al.*[3] prepared [Co(amOH)$(N)_4$]-type complexes using a variety of amino alcohols (amOH) and studied the vicinal effect due to the chelated amino alcohols. There is however no study of other complexes which differ from the above in chromophore.

The present work was undertaken to prepare mixed ligand complexes of [Co(amOH)$(N)_2(O)_2$]-type, in which amOH denotes 2-aminoethanol or optically active (*S*)-2-amino-1-propanol and the $(N)_2(O)_2$ moiety denotes two glycinate ions, two β-alaninate ions, ethylenediamine and oxalate ion, or two ammonia and oxalate ions. The complexes obtained exhibited remarked different absorption and CD spectra, and splitting of the second absorption band was observed. In order to clarify the splitting of the T_{1g} and T_{2g} bands, polarized crystal spectra were measured, and from the spectral data, the σ- and π-antibonding parameters of the N and O donor atoms of the 2-aminoethanolate ion evaluated using the Angular Overlap Model.[4]

Experimental

Preparation. *a) (2-Aminoethanol)bis(glycinato)cobalt(III) Perchlorate, [Co(gly)$_2$(Heta)]ClO_4*: To a slurry of K[Co$(CO_3)(gly)_2]\cdot H_2O$ (9.7 g, 0.03 mol)[5] in water (25 cm^3) was added sufficient 3 M $HClO_4$ (M=mol dm^{-3}) to acid-hydrolyze the carbonato complex species. After removal of the precipitated $KClO_4$ by filtration, 2-aminoethanol (1.8 g, 0.03 mol) was added to the filtrate. The solution was stirred at 50 °C for 40 min, during which the pH of the solution was maintained at *ca.* 8.5 by the addition of an aqueous KOH solution. The resulting solution was adjusted to pH *ca.* 2, and the precipitated material filtered off. The filtrate was charged on a column containing 100—200 mesh Dowex 50W-X8 resin (Na^+ form, 5×20 cm). The red violet band held on the top of the column was eluted with 0.3 M NaCl solution and the band separated into four bands, the second and third bands being the desired species. Both eluates were concentrated to a small volume below 35 °C under reduced pressure and the concentrate poured into a column of the same resin (5×45 cm). By elution with water, the concentrate from the second band gave a violet band which was the parent species and a dark blue band which was the desired species (labeled A-1). The concentrate from the third band gave three bands, dark violet, red violet and red bands, of the desired species labeled A-2, A-3, and A-4 respectively. Acidification of the eluates with $HClO_4$ to pH *ca.* 3 brought about a change in colour, A-1, A-2, and A-3 to red violet and A-4 to rose. After concentration of the acidified solutions to small volumes, the A-1 and A-4 concentrates were kept in a refrigerator overnight, A-2 being kept in a refrigerator after the addition of a mixture of ethanol and ether (1 : 1). With respect to A-3, red violet crystals deposited during concentration. The yields of A-1, A-2, A-3, and A-4 were approximately 0.1, 0.2, 2.3, and 0.4 g, respectively.

b) (2-Aminoethanol)(ethylenediamine)(oxalato)cobalt(III) Perchlorate, [Co(ox)(en)(Heta)]ClO_4: To a green solution of tricarbonatocobaltate(III) ($Co(NO_3)_2\cdot 6H_2O$, 0.1 mol)[6] was added the solid material (17 g), prepared previously from ethylenediamine and oxalic acid. The mixture was stirred at 40 °C for 1.5 h, the resulting solution carefully acidified with $HClO_4$ under ice-cold conditions and filtered to remove any material precipitated. To this filtrate was added 2-aminoethanol (6 g, 0.1 mol), and the mixture stirred at 60 °C for 1 h, during which time the pH of the mixture was maintained at *ca.* 8.5 by the addition of an aqueous solution of KOH. The resulting solution was acidified to pH *ca.* 6 and concentrated. After the insoluble material had been filtered off, the filtrate was poured into a column of 100—200 mesh Dowex 50W-X8 resin (Na^+ form, 7×20 cm). Elution with water produced two bands, one dark violet and the other red (B-1 and B-2). Both eluates were adjusted to pH *ca.* 3 and concentrated. The crystals formed were recrystallized several times from aque-

ous solution (pH 2 adjusted with $HClO_4$).

c) (2-Aminoethanol)diamine(oxalato)cobalt(III) Perchlorate and Bis(2-aminoethanol)ammine(oxalato)cobalt(III) Bromide, [Co(ox)-$(NH_3)_2$(Heta)]ClO_4 and [Co(ox)(NH_3)(Heta)$_2$]Br: In the same manner as in a), $K[Co(CO_3)(ox)(NH_3)_2]\cdot H_2O$ (12 g, 0.04 mol)[7] was acid-hydrolyzed with 3 M $HClO_4$ and 2-aminoethanol (2.4 g, 0.04 mol) and ammonium oxalate (0.7 g) added to the solution. After the mixture had been stirred for 40 min at 60 °C, the pH being maintained at 8.5, the solution was acidified to pH *ca.* 6 and concentrated. The material precipitated was filtered off and the filtrate charged on a column of the same resin (Na^+ form, 7×20 cm). Elution with water produced three bands consisting of an anionic species, non-charged dark violet species and a red species. The final eluate (C-1) was further acidified to pH *ca.* 3 with aqueous $HClO_4$, concentrated and kept in a refrigerator overnight. The dark-violet eluate was made pH 2, whereupon the color turned violet. This solution was charged on a column of the same cation exchanger (4.5×12 cm). Elution with a 0.3 M $NaClO_4$ solution, produced two violet bands (C-2 and C-3). The eluates were adjusted to pH *ca.* 2 and concentrated under reduced pressure, whereby pure violet crystals were obtained with respect to C-3. Crystals of C-2 were obtained as follows; to the concentrate was added a mixture of ethanol and ether (1 : 3), whereby a tarry material separated out. This material was dissolved in a small amount of water and an ethanol–HBr (47%) mixture (4 : 1) and ether added to the solution. The violet crystals (C-2) thus obtained were recrystallized from water by adding the same mixture of ethanol–HBr as above.

d) Bis(β-alaninato)(2-aminoethanol)cobalt(III) Perchlorate and Iodide, [Co(β-ala)$_2$(Heta)]X (X=ClO_4 or I): To a solution of tricarbonatocobaltate(III) ($Co(NO_3)_2\cdot 6H_2O$, 0.05 mol scale)[6] was added β-alanine (10.7 g, 0.12 mol), and the mixture stirred at 50 °C for 3 h. To the resulting solution 2-aminoethanol (3.5 g, 0.05 mol) neutralized previously with aqueous $HClO_4$ and activated charcoal (4 g) were added, and the solution stirred at 50 °C for 30 min. After the activated charcoal had been removed, the solution was neutralized and concentrated. The concentrate was poured into a column of the same resin as above (Na^+ form, 7×20 cm), and eluted with water. A violet band and some overlapped bands descended after some bands of the anionic species had been eluted. For the sake of convenience, the violet band eluate has been named E-1, and the overlapped ones combined and named E-2. Each fraction was brought to pH 2 and charged on a column containing the same resin as above (5×22 cm). Elution with a 0.3 M $NaClO_4$ solution at pH 2, enabled each band held at the top of the column to be separated into four bands colored red or violet, numbered Nos. 1—4 according to the order of elution. The eluates No. 1 and No. 2 of the E-1 and No. 2 of the E-2, were subsequently concentrated. After the addition of a mixture of ethanol and ether (2 : 1), the concentrates were kept in a refrigerator overnight and the deposited crystals were recrystallized from water. With respect to eluate No. 4 of E-1, the addition of an ethanol–ether mixture (1 : 3) to the concentrate induced immediate crystallization. The crystals thus obtained sparingly recrystallized from aqueous solution due to the ready isomerized to an other species identical to No. 1 of E-1. The No. 1 eluate of E-2 was concentrated until red crystals were found and the crystals recrystallized from aqueous $HClO_4$. The addition of ethanol–ether mixture (1 : 5) to No. 3 of E-2, resulted in a red tarry material separating from the aqueous phase, this being dissolved in a minimum amount of water. To this solution a small amount of NaI and followed by an ethanol–ether mixture were added. On standing in the refrigerator overnight, red crystals deposited. No recrystallization was conducted due to the poor yield of product. The eluates of No. 3 of E-1 and No. 4 of E-2 were too small in quantity for crystals to be obtained.

e) (S)-2-Amino-1-propanolbis(glycinato)cobalt(III) Perchlorate, [Co(gly)$_2$(S-Hpra)]ClO_4: Four fractions were obtained in the same way as in a), except that (*S*)-2-amino-1-propanol (1.5 g, 0.02 mol) was used instead of 2-aminoethanol and that a longer time was necessary for reaction (1 h). The fractions were conveniently named A-1—A-4. The following description concerns the separation of the diastereoisomers for each geometrical isomer: Eluate A-1, adjusted to pH 2 with aqueous $HClO_4$ was charged on a column of the same cation exchanger (3×35 cm). The red violet band held at the top of the column was eluted first with a 0.2 M aqueous solution of sodium $(+)_{589}$-bis(tartrato)diantimonate(III), the pH being controlled to 3.5 with aqueous $HClO_4$, until the band clearly separated into two, and secondly eluted with a 0.3 M aqueous solution of $NaClO_4$. A-2 gave two bands in chromatographic elution conducted in a similar manner to that in A-1, using a 0.3 M $NaClO_4$ solution as the eluent. The effluents were concentrated and ethanol added. The products of the diastereoisomeric pairs were recrystallized from water by the addition of ethanol. The diastereoisomers for A-3 were isolated in the following manner; the eluate containing non-charged species was concentrated and charged on a column of the same resin (5×45 cm). Elution was conducted with water by means of a fraction collector. Frontal fractions, where the intensity ratios of the $\Delta\varepsilon$ values at 530 nm and the ε values at 550 nm were smaller than −0.033 and the rear fractions where the intensity ratios of the $\Delta\varepsilon$ values at 581 nm and the ε values at 550 nm were larger than 0.015 were collected and labeled A-3(−) and A-3(+), respectively. The collected eluates were adjusted to pH *ca.* 3 and evaporated. The violet crystals of A-3(−) separated out during concentration and the crystals of A-3(+) were obtained by adding an ethanol–ether mixture (1 : 1). Recrystallization was repeated until the $\Delta\varepsilon$ of the main CD peak attained a constant value. One of the diastereoisomers of A-4 was obtained as red crystals from the concentrate adjusted to pH *ca.* 3; the crystals were recrystallized repeatedly until the $\Delta\varepsilon$ value remained constant. The solution containing the other diastereoisomer was charged on a column containing the same resin (3×35 cm) and the band held at the top of the column eluted with a 0.3 M $NaClO_4$ solution. The rear fractions exhibiting a (−) CD sign were collected together and concentrated. A mixture of ethanol and ether (1 : 1) was added and the solution kept in a refrigerator until crystals separated. The crystals thus obtained were recrystallized until the $\Delta\varepsilon$ value remained constant.

The elemental analyses are summarized in Table 1.

Resolution. The A-1 and A-3 Isomers of [Co(gly)$_2$-(Heta)]$^+$: In an aqueous, warm solution (*ca.* 40 °C) of the perchlorate (0.76 g, 0.002 mol) was dissolved $(-)_{589}Na[Co(ox)_2(en)]$ (0.34 g, 0.001 mol),[8] whereupon the less soluble diastereoisomeric salt crystallized. The crystals were dissolved in water (100 cm^3) containing some $NaHCO_3$ in order to assist dissolution. The resulting alkaline solution was adjusted to pH 2 with aqueous $HClO_4$ and concentrated until crystallization, after which recrystallization was repeated.

The A-4 Isomer of [Co(gly)$_2$(Heta)]$^+$: The chloride which is more soluble than the perchlorate was prepared in the following manner; the red effluent (A-4) described in a) was acidified with an aqueous HCl solution and concentrated and methanol added to precipitate the chloride. The chlo-

Table 1. Elemental analyses of the prepared complexes

Label	Complex	C%	H%	N%
A-1	$[Co(gly)_2(Heta)]ClO_4 \cdot 0.5\ H_2O$	19.10 (19.13)	4.41 (4.29)	10.82 (11.16)
A-2	$[Co(gly)_2(Heta)]ClO_4 \cdot 0.5\ H_2O$	19.16 (19.13)	4.44 (4.29)	10.91 (11.16)
A-3	$[Co(gly)_2(Heta)]ClO_4$	19.90 (19.60)	4.13 (4.12)	11.45 (11.43)
A-4	$[Co(gly)_2(Heta)]ClO_4 \cdot H_2O$	18.71 (18.69)	4.47 (4.45)	10.92 (10.90)
B-1	$[Co(ox)(en)(Heta)]ClO_4$	19.57 (19.60)	4.14 (4.12)	11.44 (11.43)
B-2	$[Co(ox)(en)(Heta)]ClO_4 \cdot 0.5\ H_2O$	18.95 (19.13)	4.22 (4.29)	11.14 (11.16)
C-1	$[Co(ox)(NH_3)_2(Heta)]ClO_4 \cdot H_2O$	13.39 (13.36)	4.19 (4.21)	11.63 (11.69)
C-2	$[Co(ox)(NH_3)(Heta)_2]Br \cdot H_2O$	19.24 (19.21)	4.80 (5.11)	11.55 (11.20)
C-3	$[Co(ox)(NH_3)_2(Heta)]ClO_4 \cdot H_2O$	13.60 (13.36)	4.10 (4.21)	11.65 (11.69)
No. 1 (E-1)	$[Co(\beta\text{-ala})_2(Heta)]ClO_4$	24.27 (24.29)	4.85 (4.84)	10.52 (10.62)
No. 2 (E-1)	$[Co(\beta\text{-ala})_2(Heta)]ClO_4 \cdot H_2O$	23.30 (23.23)	5.38 (5.12)	10.00 (10.16)
No. 1 (E-2)	$[Co(\beta\text{-ala})_3] \cdot (HClO_4)_2 \cdot 0.5\ H_2O$	20.50 (20.28)	4.08 (3.97)	7.93 (7.88)
No. 2 (E-2)	$[Co(\beta\text{-ala})_2(Heta)]ClO_4 \cdot 0.5\ H_2O$	23.79 (23.75)	4.87 (4.98)	10.03 (10.38)
A-1(+)	$[Co(gly)_2(S\text{-Hpra})]ClO_4 \cdot 0.5\ H_2O$	21.88 (21.58)	4.46 (4.40)	10.76 (10.79)
A-1(−)	$[Co(gly)_2(S\text{-Hpra})]ClO_4 \cdot 0.5\ H_2O$	22.00 (21.58)	4.42 (4.40)	10.61 (10.79)
A-2(+)	$[Co(gly)_2(S\text{-Hpra})]ClO_4 \cdot H_2O$	21.08 (21.09)	4.87 (4.55)	10.58 (10.54)
A-2(−)	$[Co(gly)_2(S\text{-Hpra})]ClO_4 \cdot 1.5\ H_2O$	20.61 (20.63)	4.70 (4.70)	10.37 (10.31)
A-3(+)	$[Co(gly)_2(S\text{-Hpra})]ClO_4 \cdot 1.5\ H_2O$	20.68 (20.63)	4.68 (4.70)	10.44 (10.31)
A-3(−)	$[Co(gly)_2(S\text{-Hpra})]ClO_4 \cdot 0.5\ H_2O$	21.60 (21.58)	4.44 (4.40)	10.85 (10.79)
A-4(+)	$[Co(gly)_2(S\text{-Hpra})]ClO_4 \cdot 1.5\ H_2O$	20.81 (20.63)	4.86 (4.70)	10.28 (10.31)
A-4(−)	$[Co(gly)_2(S\text{-Hpra})]ClO_4 \cdot H_2O$	21.07 (21.09)	4.91 (4.55)	10.49 (10.54)
A-1	$[Co(gly)_2(Heta)][Co(ox)_2(en)] \cdot 2.5\ H_2O$	23.84 (23.70)	4.51 (4.64)	11.55 (11.51)
A-3	$[Co(gly)_2(Heta)][Co(ox)_2(en)] \cdot 0.5\ H_2O$	25.26 (25.19)	4.00 (4.23)	12.26 (12.24)
A-4	$[Co(gly)_2(Heta)][Co(ox)_2(en)] \cdot 3.5\ H_2O$	22.93 (23.01)	4.65 (4.83)	11.15 (11.18)

( ): Calcd.

ride (2 g, 0.0065 mol) was dissolved in warm water (*ca.* 15 cm^3, *ca.* 40 °C), and $(-)_{589}Na[Co(ox)_2(en)]$ (1 g, 0.003 mol)[8] added. The addition of ethanol gave red, needle-like crystals. Which was followed by recrystallization from warm water (*ca.* 40 °C).

The elemental analyses are summarized in Table 1.

Measurements. The absorption spectra were measured with a Hitachi 323 recording spectrophotometer, the absorption spectra of single crystals being measured by a micro-spectrophotometer constructed in this laboratory.[9] The CD spectra were recorded with a JASCO Model ORD/UV-5 spectrometer with CD attachments. Proton magnetic resonance (PMR) spectra were conducted with JEOL Model JNM-PS-100 spectrometer (100 MHz) at *ca.* 24 °C. The values of the chemical shifts were measured in relation to sodium 2,2,3,3-tetradeuterio-3-(trimethylsilyl)propionate (TMSP) as the internal reference. The acid dissociation constants of the complexes were determined by pH titration at 25 °C and the ionic strength 0.1 adjusted by $NaClO_4$.

The absorption and CD spectra were measured in acid (pH 2) or alkaline solutions (pH 8). For the PMR spectra, all of the protons of $-NH_2$ of the isomeric complexes of $[Co(gly)_2(Heta)]^+$ were deuterized in alkaline D_2O solution and the chlorides of the isomers used for the samples in acid solutions (DCl). The PMR spectra of the C-2 and C-3 were measured in D_2O–D_2SO_4 (30%) solutions.

Results and Discussion

Characterization of Complexes. The possible geometrical isomers of a $[Co(Heta)(N)_2(O)_2]$-type complex are illustrated in Fig. 1, where *trans(O)*, *cis·cis*, and *trans(N)* isomers are *mer* isomers with respect to the three N donor atoms. Assuming the $(N)_2(O)_2$ moiety consists of two glycinate or two β-alaninate ions, *i.e.* $(N)_2(O)_2=(gly)_2$ or $(\beta\text{-ala})_2$, then the four isomers are possible. When the moiety consists of (ox)(en), two isomers, *cis·cis* and *fac*, are possible; $(ox)(NH_3)_2$ as the moiety gives, *cis·cis*, *trans(N)* and *fac* isomers.

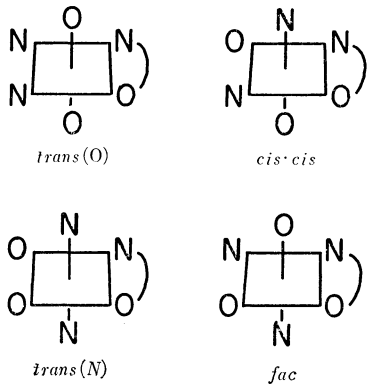

Fig. 1. Possible geometrical isomers of $[Co(Heta)(N)_2(O)_2]$. N–O denotes Heta.

From the absorption spectra of whole complexes, some of which are shown in Figs. 2 and 3, a *fac* isomer is readily distinguishable from the corresponding *mer* isomer, but the *mer* isomers cannot be distinguished from each other despite the fact that there are remarkable differences in the spectra for deprotonated isomers.

Yoneda *et al.*[10] explained theoretically the "through-cobalt effect" which had been found experimentally,[11] and on this basis assigned the signals of a number of complexes in the PMR spectra. The "through-cobalt effect" has been applied to the PMR data of the *mer*-$[Co(gly)_2(eta)]$ isomers and to the C-2 and C-3 isomers for characterization.

The PMR spectra, in alkaline solutions, of the $[Co(gly)_2(eta)]$ isomers are shown in Fig. 4, in which the signals of the methylene groups of the glycinate ions may be distinguished from the multiplets due to the methylene groups of the chelated eta, since the glycinate protons undoubtedly exhibit either a singlet or a doublet. No significant difference in chemical

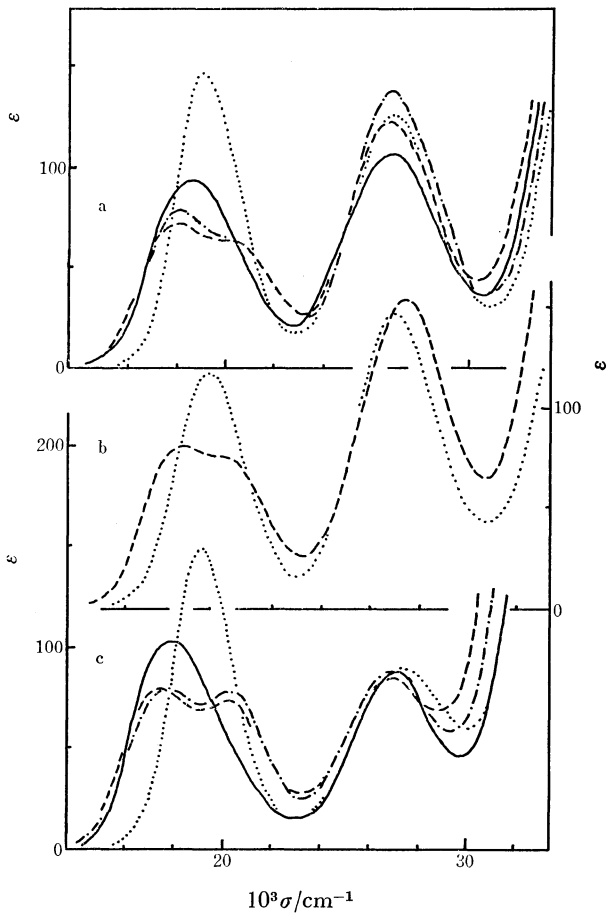

Fig. 2. Absorption spectra of protonated complexes, a) $[Co(gly)_2(Heta)]^+$, b) $[Co(ox)(en)(Heta)]^+$, and c) $[Co(\beta\text{-ala})_2(Heta)]^+$; —— *trans(O)*, —— *cis·cis*, —·— *trans(N)*, and ····· *fac*.
The ε values of *cis·cis*-, *fac*-$[Co(\beta\text{-ala})_2(Heta)]^+$ are taken arbitrarily.

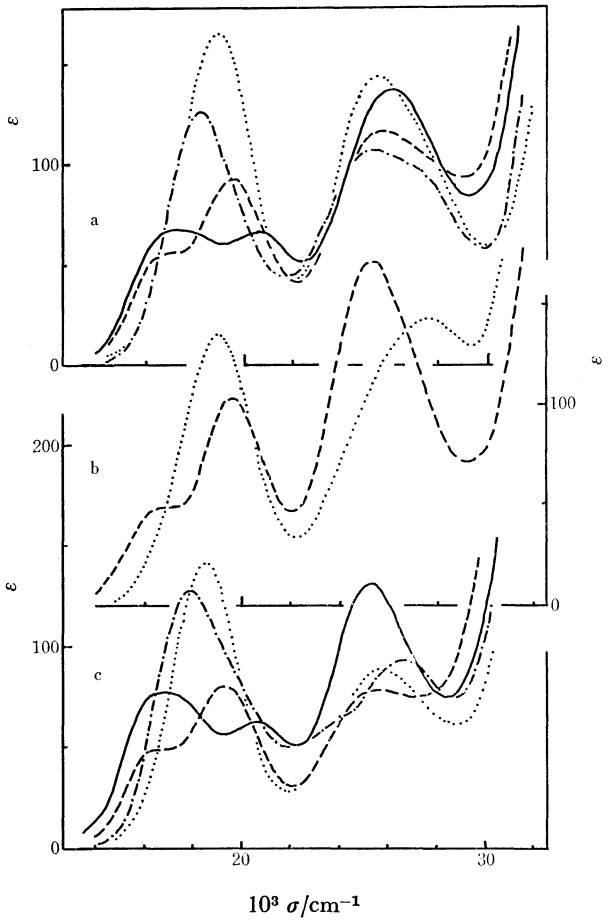

Fig. 3. Absorption spectra of deprotonated complexes, a) $[Co(gly)_2(eta)]$, b) [Co(ox)(eta)(en)], and c) $[Co(\beta\text{-ala})_2(eta)]$; —— *trans(O)*, —— *cis·cis*, —·— *trans(N)*, and ····· *fac*.
The ε values of *cis·cis*-, *fac*-$[Co(\beta\text{-ala})_2(eta)]$ are taken arbitrarily.

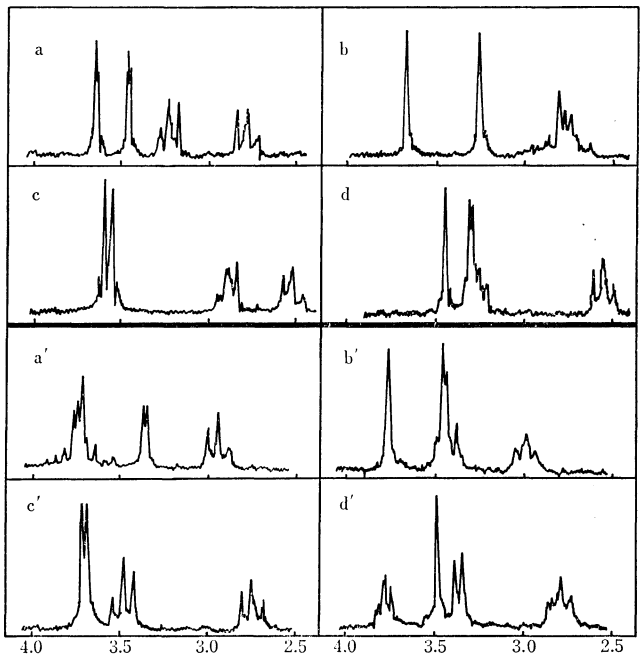

Fig. 4. PMR spectra of; a—d) $[Co(gly)_2(eta)]$ (deprotonated form), a'—d') $[Co(gly)_2(Heta)]^+$ (protonated form), a, a') *trans(O)* (A-1), b, b') *cis·cis* (A-2), c, c') *trans(N)* (A-3), d, d') *fac* (A-4).

shift between the two glycinate groups of the *trans(N)* isomer is expected because of the symmetric situations of the two N atoms in the glycinate ions. Thus the spectrum of A-3, which possesses two singlets around 3.6 ppm, has been assumed to be the *trans(N)* isomer. Concerning the signals eminating from the chelated 2-aminoethanol, the multiplet of the CH_2 protons adjacent to the oxygen is thought to appear at lower field than that of the CH_2 protons adjacent to the nitrogen because of the stronger electron-withdrawing effect due to oxygen. The spectrum of the A-1 isomer shows two multiplets at approximately 3.2 and 2.8 ppm, whereas the spectrum of A-2 shows a multiplet around 2.8 ppm, the integrated intensity of which corresponds to the four hydrogens of the 2-aminoethanol, *i.e.*, the protons adjacent to the oxygen induce the signals at approximately 3.2 ppm in the A-1 isomer and at approximately 2.8 ppm in the A-2 isomer. Thus the A-1 isomer may be identified as the *trans(O)*, and the A-2 as the *cis·cis*. The results[12] of X-ray analysis of a crystal of the A-2 isomer supports this.

The PMR spectra of the protonated $[Co(gly)_2(Heta)]^+$ isomers are also shown in Fig. 4. The resonance signals of the protonated and deprotonated forms of the $[Co(gly)_2(Heta)]^+$ isomers may be assigned in the same manner as above, the results of which are summarized in Table 2.

With respect to the C-2 and C-3 isomers, the PMR spectra measured in D_2O–D_2SO_4 (30%) solution are shown in Fig. 5. There are five signals in the C-3 spectrum; the signal at 5.94 ppm is due to the NH_2 protons of the chelated 2-aminoethanol (Deta), where the hydroxyl group is deuterated, and the signals due to the two NH_3 groups are at 4.40 and 3.72 ppm. The other two signals due to the methylene groups of the Deta are at *ca.* 3.6 and 2.9 ppm as multiplets. Since the spectrum indicates the existence of two non-equivalent NH_3 groups, the C-3 isomer is regarded as the *cis·cis* form. Furthermore, from the "through-cobalt effect" the NH_3 proton signal at low field is due to the NH_3 trans to the N atom of the chelated Deta. From elemental analysis and PMR data it is thought that the C-2 isomer is $[Co(ox)(NH_3)(Heta)_2]^+$, in which one of the Heta molecules acts as a bidentate ligand and another as a unidentate ligand. The PMR spectrum of the C-2 isomer is more intricate than C-3; there are two broad signals at 5.9 and 4.4 ppm and multiplets around 3.7 and 2.8 ppm, the integrated ratio

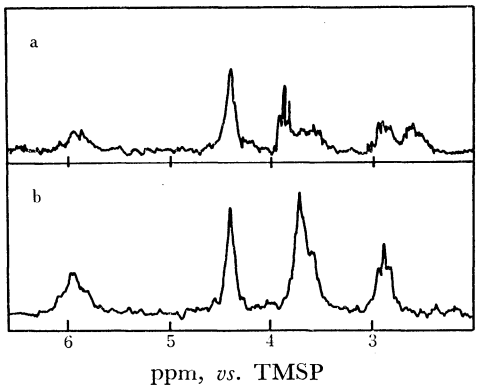

Fig. 5. PMR spectra of; a) *cis·cis*-$[Co(ox)(NH_3)(Heta)_2]^+$ (C-2) and b) *cis·cis*-$[Co(ox)(NH_3)_2(Heta)]^+$ (C-3).

Table 2. Assignment of PMR signals[a] of the $[Co(gly)_2(Heta)]^+$ and $[Co(gly)_2(eta)]$ complexes

Complex	Glycine		2-Aminoethanol	
	CH_2	CH_2	O-CH_2	N-CH_2
trans(O)-$[Co(gly)_2(Deta)]^+$	3.75 (o)	3.36 (d)	3.75 (m)	2.95 (m)
trans(O)-$[Co(gly)_2(eta)]$	3.64 (d)	3.45 (d)	3.21 (m)	2.80 (m)
cis·cis-$[Co(gly)_2(Deta)]^+$	3.77 (s)	3.46 (s)	3.43 (m)	2.99 (m)
cis·cis-$[Co(gly)_2(eta)]$	3.68 (s)	3.26 (s)	2.78 (m)	2.78 (m)
trans(N)-$[Co(gly)_2(Deta)]^+$	3.72 (s)	3.69 (s)	3.48 (m)	2.76 (m)
trans(N)-$[Co(gly)_2(eta)]$	3.58 (s)	3.54 (s)	2.88 (m)	2.53 (m)
fac-$[Co(gly)_2(Deta)]^+$	3.36 (d)	3.48 (s)	3.78 (m)	2.78 (m)
fac-$[Co(gly)_2(eta)]$	3.45 (s)	3.31 (o)	3.26 (m)	2.56 (m)

a) Values in ppm from TMSP. (s): Singlet. (d): Doublet. (m): Multiplet. (o): Overlap.

Table 3. Results of the assignment and absorption spectral data

Label	Complex	I band		II band	
		$\tilde{\nu}/10^3$ cm^{-1}	ε	$\tilde{\nu}/10^3$ cm^{-1}	ε
A-1	*trans*(*O*)-[Co(gly)$_2$(Heta)]$^+$	18.6	92.5	26.8	106
	trans(*O*)-[Co(gly)$_2$(eta)]	17.2	66.9	26.0	137
		20.4	65.9		
A-2	*cis*·*cis*-[Co(gly)$_2$(Heta)]$^+$	18.0	72.2	26.8	123
		sh. 19.8	63.0		
	cis·*cis*-[Co(gly)$_2$(eta)]	sh. 17.0	54.6	25.6	117
		19.6	92.9		
A-3	*trans*(*N*)-[Co(gly)$_2$(Heta)]$^+$	18.2	78.0	26.8	138
		sh. 20.2	69.4		
	trans(*N*)-[Co(gly)$_2$(eta)]	18.2	124	25.2	108
A-4	*fac*-[Co(gly)$_2$(Heta)]$^+$	19.2	147	26.8	125
	fac-[Co(gly)$_2$(eta)]	18.8	166	25.4	144
B-1	*cis*·*cis*-[Co(ox)(en)(Heta)]$^+$	18.4	79.5	27.4	156
		sh. 19.8	75.2		
	cis·*cis*-[Co(ox)(en)(eta)]	16.6	48.7	25.2	171
		19.4	103		
B-2	*fac*-[Co(ox)(en)(Heta)]$^+$	19.3	117	26.8	147
	fac-[Co(ox)(en)(eta)]	19.0	134	27.6	143
C-1	*fac*-[Co(ox)(NH$_3$)$_2$(Heta)]$^+$	19.2	94.2	27.0	134
	fac-[Co(ox)(NH$_3$)$_2$(eta)]	19.0	115	27.2	137
C-2	*cis*·*cis*-[Co(ox)(NH$_3$)(Heta)$_2$]$^+$	17.6	82.5	27.0	163
	cis·*cis*-[Co(ox)(NH$_3$)(Heta)(eta)]	sh. 16.6	45.1	24.6	148
		19.0	81.0		
C-3	*cis*·*cis*-[Co(ox)(NH$_3$)$_2$(Heta)]$^+$	18.0	77.7	27.4	155
	cis·*cis*-[Co(ox)(NH$_3$)$_2$(eta)]	sh. 16.6	45.7	25.0	158
		19.2	89.0		
No. 1 (E-1)	*trans*(*O*)-[Co(*β*-ala)$_2$(Heta)]$^+$	18.0	104	27.2	88
	trans(*O*)-[Co(*β*-ala)$_2$(eta)]	16.8	77.2	25.2	133
		20.6	63.4		
No. 2 (E-1)	*trans*(*N*)-[Co(*β*-ala)$_2$(Heta)]$^+$	17.7	79.4	26.8	87.7
		20.4	77.9		
	trans(*N*)-[Co(*β*-ala)$_2$(eta)]	17.8	128	sh. 24.0	64.9
				26.4	94.2
No. 4 (E-1)	*cis*·*cis*-[Co(*β*-ala)$_2$(Heta)]$^+$ [a]	17.4	—	27.0	—
		20.2	—		
	cis·*cis*-[Co(*β*-ala)$_2$(eta)][a]	sh. 16.8	—	25.6	—
		19.2	—		
No. 3 (E-2)	*fac*-[Co(*β*-ala)$_2$(Heta)]$^+$ [a]	19.0	—	27.3	—
	fac-[Co(*β*-ala)$_2$(eta)][a]	18.4	—	25.6	—
A-1	*trans*(*O*)-*Δ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	18.6	89.8	27.1	108
	trans(*O*)-*Δ*-[Co(gly)$_2$(*S*-pra)]	17.2	62.7	26.2	130
		20.6	67.8		
	trans(*O*)-*Λ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	18.7	98.5	26.8	119
	trans(*O*)-*Λ*-[Co(gly)$_2$(*S*-pra)]	17.2	72.7	25.6	159
		20.5	74.2		
A-2	*cis*·*cis*-*Δ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	17.8	71.4	26.7	122
		sh. 20.0	62.9		
	cis·*cis*-*Δ*-[Co(gly)$_2$(*S*-pra)]	sh. 17.0	48.5	25.6	104
		19.6	87.4		
	cis·*cis*-*Λ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	18.0	74.0	26.6	133
		sh. 20.0	62.2		
	cis·*cis*-*Λ*-[Co(gly)$_2$(*S*-pra)]	16.5	65.5	25.4	128
		19.4	105		
A-3	*trans*(*N*)-*Δ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	18.1	70.4	26.7	131
		sh. 20.0	62.0		

TABLE 3. (Continued)

Label	Complex	I band		II band	
		$\tilde{\nu}/10^3$ cm^{-1}	ε	$\tilde{\nu}/10^3$ cm^{-1}	ε
	trans(*N*)-*Λ*-[Co(gly)$_2$(*S*-pra)]	18.1	123	26.0	96.3
	trans(*N*)-*Λ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	18.2	84.4	26.8	146
		sh. 20.0	69.6		
	trans(*N*)-*Λ*-[Co(gly)$_2$(*S*-pra)]	18.2	141	24.8	127
A-4	*fac*-*Λ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	19.2	149	26.8	118
	fac-*Λ*-[Co(gly)$_2$(*S*-pra)]	18.9	183	25.7	132
	fac-*Λ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	19.3	153	26.8	133
	fac-*Λ*-[Co(gly)$_2$(*S*-pra)]	18.9	180	25.2	170

a) The ε values were not obtained because of a lack of elemental analyses.

of the four signals being estimated as 2 : 5 : 4 : 4 (from lower to higher field). The multiplets are due to the methylene groups of the two Deta, while one of the broad signals at 5.9 ppm is assignable to the NH_2 protons of the chelated Deta from a comparison with the spectrum of the C-3 isomer. With respect to the broad signal at 4.4 ppm, it is considered from the integrated ratio that the two types of signal due to the NH_3 and the NH_2 of the unidentately bound amino alcohol overlap. Comparing the signals due to NH_3 and NH_2 in the C-2 isomer spectrum (4.4 and 5.9 ppm) with those in the C-3, *cis*·*cis* configuration with NH_3 in the trans position of the N of the chelated Deta is assumed to this isomer. The remaining isomer for the [Co(ox)$(NH_3)_2$(Heta)]$^+$ complex should be *trans*(*N*), but no band corresponding to such a species has been observed in the chromatographic separation.

The absorption spectra in alkaline solutions for the *cis*·*cis* isomers (A-2, B-1, C-2, and C-3) are similar. The No. 4 isomer of E-1 which exhibits a similar spectrum to those of the *cis*·*cis* isomers has been assigned *cis*·*cis*. On the basis of the similarity of spectra, the No. 1 isomer of E-1 and the No. 2 isomer of E-2 have been assigned *trans*(*O*) and the No. 2 isomer of E-1 *trans*(*N*).

The crystals of the No. 1 isomer of E-2 have been identified as *fac*-[Co(*β*-ala)$_3$]·$(HClO_4)_2$·0.5H_2O from elemental analysis, the absorption spectrum,[13] and the acid-base titration (see below). The complex species in acidified aqueous solution was adsorbed on the cation exchanger and the crystals contained perchloric acid of crystallization, both of which are of interest.

The No. 1 isomer of E-1 and the No. 2 isomer of E-2 have been identified as the same isomer since both species exhibit identical absorption spectra in acidic and basic solution and possess the same pK_a values as seen from Table 4.

Ogino *et al.*[2] assigned the absolute configurations of the [Co(en)$_2$(Heta)]$^{3+}$ and [Co(en)$_2$(*S*-Hpra)]$^{3+}$ complexes by a comparison of the CD spectra with those of the [Co(gly)(en)$_2$]$^{2+}$ and [Co(L-ala)(en)$_2$]$^{2+}$ complexes. Each CD spectrum of the *mer* and *fac* isomers of the present [Co(gly)$_2$(amOH)]$^+$ (amOH=Heta, *S*-Hpra) complexes exhibits a major CD peak in the T_{1g} region, similarly to those of the *mer* and *fac* isomers of [Co(am)$_3$] (am=gly, L-ala)[14,15] complexes, respectively. Thus, the sbaolute configuration of an isomer of [Co(gly)$_2$(amOH)]$^+$, which exhibits (+) CD sign at *ca.* 19000 cm^{-1}, is assignable to *Λ*, and hence, the other isomer to *Δ*. The structures thus assigned are summarized in Table 3.

pK_a *Values.* Nishide *et al.*[3] have reported that the pK_a values of the [Co$(NH_3)_4$(amOH)]$^{3+}$, [Co(en)$_2$-(amOH)]$^{3+}$ and [Co(*R*-chxn)$_2$(amOH)]$^{3+}$ complexes are *ca.* 3.6, 3.2, and 3.2, respectively. From the pK_a values of the present complexes summarized in Table 4, it is seen that the *cis*·*cis* and *trans*(*N*) isomers exhibit lowerer pK_a values (*ca.* 4.2) compare to the *trans*(*O*) and *fac* isomers (*ca.* 5.2). This indicates that the pK_a value of amOH, where the O atom is situated trans to the other O atom, shows *ca.* 4.2, while the value of amOH, where the O atom is situated trans to the N atom, shows *ca.* 5.2. This difference may be due to reduced electron density on the former hydroxyl O atom.

The No. 1 isomer of E-2, which has been assigned as [Co(*β*-ala)$_3$] from the absorption spectrum,[13] behaves as a strong and dibasic acid in titration, this being additional evidence that the chemical formula is [Co(*β*-ala)$_3$]·$(HClO_4)_2$.

Absorption Spectra. A spectra of [Co(gly)$_2$(*S*-Hpra)]$^+$ isomers show great similarity to the spectrum of the corresponding [Co(gly)$_2$(Heta)]$^+$ isomer. The numerical data for all the absorption spectra for the protonated and deprotonated isomers are summarized in Table 3. The spectrum of the *fac*-[Co(gly)$_2$(Heta)]$^+$

TABLE 4. pK_a VALUES

Complex	pK_a
cis·*cis*-[Co(gly)$_2$(Heta)]$^+$	4.1
trans(*N*)-[Co(gly)$_2$(Heta)]$^+$	4.2
cis·*cis*-[Co(ox)(en)(Heta)]$^+$	4.4
cis·*cis*-[Co(ox)$(NH_3)_2$(Heta)]$^+$	4.3
cis·*cis*-[Co(ox)(NH_3)(Heta)$_2$]$^+$	4.4
trans(*N*)-[Co(*β*-ala)$_2$(Heta)]$^+$	4.4
trans(*O*)-[Co(gly)$_2$(Heta)]$^+$	5.1
fac-[Co(gly)$_2$(Heta)]$^+$	5.3
fac-[Co(ox)(en)(Heta)]$^+$	5.2
fac-[Co(ox)$(NH_3)_2$(Heta)]$^+$	5.2
trans(*O*)-[Co(*β*-ala)$_2$(Heta)]$^+$ [a]	5.9

a) No. 1 (E-1) and No. 2 (E-2) complexes.

complex is similar to that of *fac*-[Co(gly)$_3$],[16] suggesting that amino alcohol in the protonated form and the glycinate ion are situated in close positions in the spectrochemical series.[17] For the *mer* isomers of [Co(*β*-ala)$_2$(Hpta)]$^+$, having two six-membered chelate rings, the spectra of the *cis·cis* and *trans*(*N*) isomers exhibit a remarkable degree of splitting in the T_{1g} region, while no splitting has been observed in the spectrum of the *trans*(*O*) isomer. Among the *cis·cis* and *trans*(*N*) isomers of the [Co(gly)$_2$(Heta)]$^+$, [Co(gly)$_2$(*S*-Hpra)]$^+$ and [Co(ox)(Heta)(N)$_2$]$^+$-type complexes, the spectra are similar and show a little splitting; however, no splittings have been observed in the spectra of the *trans*(*O*) isomers in the T_{1g} region.

Each of the deprotonated complexes exhibits quite a different spectrum from the corresponding protonated complex. The *trans*(*O*), *cis·cis*, *trans*(*N*) and *fac* isomers exhibit remarkedly different spectra. The T_{1g} band for each *trans*(*O*) isomer is clearly split into two and the separation between the maxima is in the range 3200—3800 cm^{-1}; the T_{2g} band for each *trans*(*O*) isomer shows a sharp band. For the *cis·cis* isomers, the T_{1g} bands are not split as clearly as the *trans*(*O*) isomers, but each has a noticeable shoulder at lower wave-number, the T_{2g} band exhibiting a broad maximum generally splitting. The exceptions are the *cis·cis* isomers of B-1, C-2, and C-3, which contain no N–O chelate rings beyond eta, which show only sharp bands in the T_{2g} region. For the *trans*(*N*) isomers, recognizable splittings in the T_{2g} region and sharp bands in the T_{1g} region have been observed in contrast to the *trans*(*O*) isomers. The remaining isomers of *fac* give sharp and red-shifted bands in both the T_{1g} and T_{2g} regions. The complexes are, however, shifted to the blue end.

As seen in Fig. 3, there is a remarkable difference between the shapes of the T_{2g} bands for the *trans*(*N*) isomers of the [Co(gly)$_2$(eta)] and [Co(*β*-ala)$_2$(eta)] complexes, both of which have an identical chromophore *trans*(*N*)-[Co(eta)(N)$_2$(O)$_2$]. The same differences in the T_{2g} bands have been observed between the *cis·cis*-[Co(ox)(eta)(N)$_2$] isomer and each *cis·cis* isomer of the [Co(gly)$_2$(eta)] and [Co(*β*-ala)$_2$(eta)] complexes as well as between the *fac* isomers of the [Co(ox)(eta)(N)$_2$] complex and the [Co(gly)$_2$(eta)] and [Co(*β*-ala)$_2$(eta)] complexes. These differences may be related to the manner of chelation of the ligands forming the (N)$_2$(O)$_2$ moiety.

Three possible transitions for the T_{1g} band have been revealed in the polarized crystal spectra of the *trans*(*O*) and *cis·cis* isomers of the [Co(gly)$_2$(eta)] complex, and the polarized crystal spectra of the *cis·cis* and *trans*(*N*) isomers provides clearer splitting of the T_{2g} band (Fig. 6). The *trans*(*O*) isomer shows a large splitting of the T_{1g} band and this together with the X-ray analysis of the *cis·cis* isomer[12] allows assignment of the three bands. The paths of the polarized light are schematically shown in Fig. 7. In the ∥ polarized spectra, a maximum at 15900 cm^{-1} for the *trans*(*O*) isomer and two maxima at 20200 and 16400 cm^{-1} for the *cis·cis* isomer have been assigned to the transitions from the d_{zx} orbital for the *trans*(*O*) and from the d_{yz} and d_{zx} orbitals for the *cis·cis* isomer,

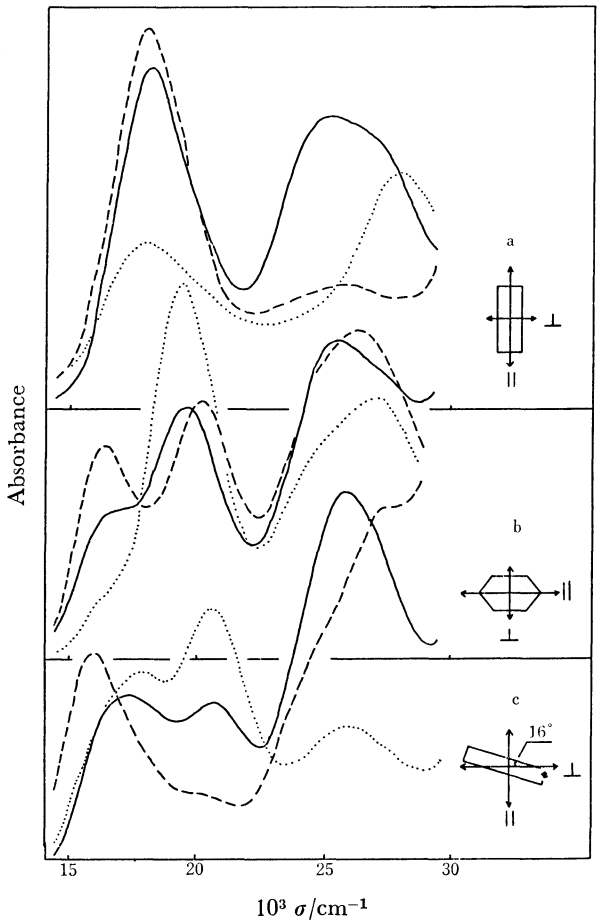

Fig. 6. Absorption spectra of [Co(gly)$_2$(eta)]; a) *trans*(*N*), b) *cis·cis*, and c) *trans*(*O*) (—— solution, —— ∥, ····· ⊥).

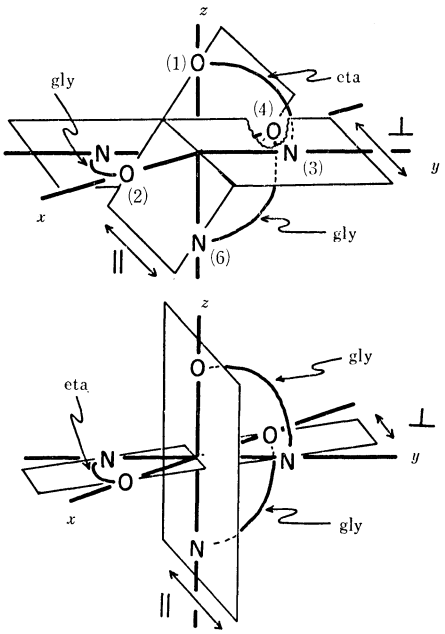

Fig. 7. The arrangements of the donor atoms and the paths of the polarized lights; *trans*(*O*)-[Co(gly)$_2$(eta)] (upper) and *cis·cis*-[Co(gly)$_2$(eta)] (lower).

respectively (Fig. 7). In the spectra with ⊥ polarization two maxima at 20600 and 17800 cm^{-1} for the *trans(O)* and a maximum at 19500 cm^{-1} for the *cis·cis* isomer have been assigned to the transitions from d_{yz} and d_{xy} for the former and from d_{xy} for the latter isomer, respectively. Using the Angular Overlap Model[4] (Appendix), the antibonding parameters, e_σ and e_π, may be obtained from the above data assuming that the $e_\sigma(N)$ parameters of the amino alcoholate and glycinate ions are equal. Assuming $C=4B$ and $B=450$ cm^{-1} (C and B denote the Racah parameters), the most reasonable values are shown in Table 5. Both the e_σ and the e_π values for the alcoholate O atom are large which are comparable with those for the OH^- ligand. The e_σ and e_π values for the OH^- ligand have been reported as 8500 and 2100 cm^{-1}, respectively, for the *trans*-$[Cr(OH)_2(NH_3)_4]^+$ isomer.[18]

CD Spectra. The CD spectra of the protonated and deprotonated forms of the resolved three isomers of the $[Co(gly)_2(Heta)]^+$ complex are shown in Fig. 8, and the configurational and vicinal effect curves, calculated from the CD spectra of the protonated and deprotonated isomers of the $[Co(gly)_2(S\text{-Hpra})]^+$ complex are shown in Fig. 9. The configurational curves show striking resemblances to the CD spectra, in both acidic and basic solutions of the corresponding isomers of the $[Co(gly)_2(Heta)]^+$ complex indicating the additivity of the configurational and vicinal effects in both the $[Co(gly)_2(S\text{-Hpra})]^+$ and $[Co(gly)_2(S\text{-pra})]$

Table 5. The σ- and π-antibonding parameters for the N and O donor atoms of the glycinate and 2-aminoethanolate ions

gly	eta	Value (cm^{-1})
$e_\sigma(N)$	$e_\sigma(N)$	7700
$e_\sigma(O)$		5800
	$e_\sigma(O')$	8100
$e_\pi(O)$		325
	$e_{\pi 1}(O')$[a]	2300
	$e_{\pi 2}(O')$[a]	700

a) Appendix.

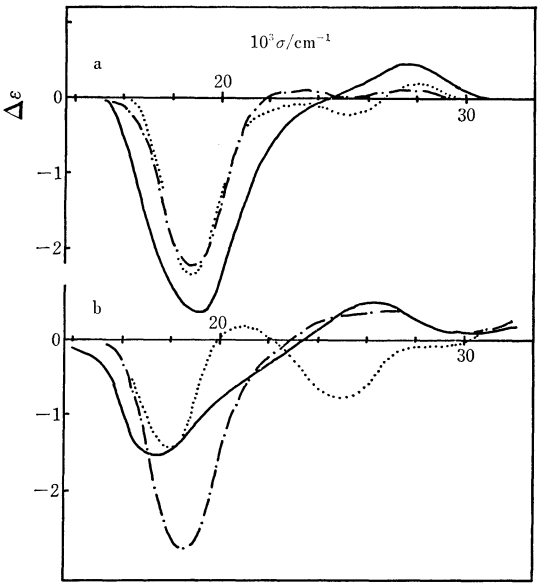

Fig. 8. CD spectra of $[Co(gly)_2(Heta)]^+$ (upper) and $[Co(gly)_2(eta)]$ (lower); —— *trans(O)*, —·— *trans(N)*, and ····· *fac*.

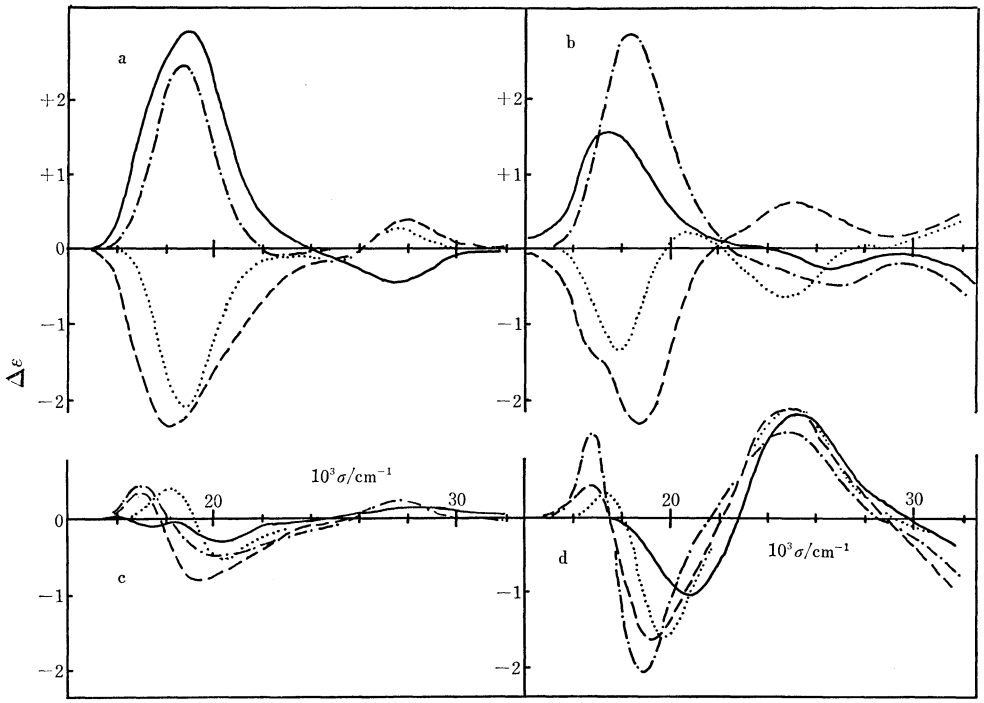

Fig. 9. Configurational and vicinal effect curves of $[Co(gly)_2(S\text{-Hpra})]^+$ (a,c) and $[Co(gly)_2(S\text{-pra})]$ (b, d); upper, configurational effect curves; lower, vicinal effect curves (—— *trans(O)*, —— *cis·cis*, —·— *trans(N)*, and ····· *fac*).

Table 6. CD spectral data

Label	Complex	I band		II band	
		$\tilde{\nu}/10^3$ cm^{-1}	$\Delta\varepsilon$	$\tilde{\nu}/10^3$ cm^{-1}	$\Delta\varepsilon$
A-1	*trans*(*O*)-*Δ*-[Co(gly)$_2$(Heta)]$^+$	19.2	−2.81	27.8	+0.45
	trans(*O*)-*Δ*-[Co(gly)$_2$(eta)]	17.4	−1.51	26.2	+0.48
A-3	*trans*(*N*)-*Δ*-[Co(gly)$_2$(Heta)]$^+$	18.8	−2.21		
	trans(*N*)-*Δ*-[Co(gly)$_2$(eta)]	18.4	−2.76	27.0	+0.40
A-4	*fac*-*Δ*-[Co(gly)$_2$(Heta)]$^+$	18.8	−2.31	25.2	−0.19
				28.0	+0.19
	fac-*Δ*-[Co(gly)$_2$(eta)]	18.0	−1.44	25.0	−0.75
		20.8	+0.16		
A-1	*trans*(*O*)-*Δ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	19.2	−2.99	27.6	+0.56
	trans(*O*)-*Δ*-[Co(gly)$_2$(*S*-pra)]	18.0	−1.55	25.6	+1.57
		sh. 19.8	−1.41		
	trans(*O*)-*Λ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	18.9	+2.77	27.4	−0.33
	trans(*O*)-*Λ*-[Co(gly)$_2$(*S*-pra)]	17.4	+1.49	25.2	+1.21
		21.0	−0.74		
A-2	*cis*·*cis*-*Δ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	18.8	−2.96	28.2	+0.50
	cis·*cis*-*Δ*-[Co(gly)$_2$(*S*-pra)]	18.9	−3.85	24.8	+2.02
	cis·*cis*-*Λ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	17.6	+2.29	27.8	−0.22
	cis·*cis*-*Λ*-[Co(gly)$_2$(*S*-pra)]	17.0	+1.86	24.4	+0.85
		21.2	−0.29		
A-3	*trans*(*N*)-*Δ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	19.1	−2.69	27.6	+0.23
	trans(*N*)-*Δ*-[Co(gly)$_2$(*S*-pra)]	18.7	−4.71	25.4	+1.45
	trans(*N*)-*Λ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	18.6	+2.24	27.4	+0.22
		22.6	−0.32		
	trans(*N*)-*Λ*-[Co(gly)$_2$(*S*-pra)]	17.2	+2.50	24.4	+0.83
		sh. 19.8	+0.44		
A-4	*fac*-*Δ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	19.4	−1.97	27.8	+0.39
	fac-*Δ*-[Co(gly)$_2$(*S*-pra)]	19.2	−1.73	25.6	+0.79
	fac-*Λ*-[Co(gly)$_2$(*S*-Hpra)]$^+$	18.6	+2.38		
	fac-*Λ*-[Co(gly)$_2$(*S*-pra)]	17.8	+1.54	25.0	+2.07
		20.0	−1.58		

complexes. The T_{2g} transitions are magnetic-dipole-forbidden, but nevertheless the configurational effect curve for the *fac*-[Co(gly)$_2$(eta)] isomer exhibits a sharp peak at *ca.* 25000 cm^{-1}.

With respect to the [Co(N)$_5$(O)]-type complexes, Nishide *et al.*[3] reported that all vicinal effect curves for the deprotonated [Co(*S*-pra)(en)$_2$]$^{2+}$ and [Co(*S*-pra)(NH$_3$)$_4$]$^{2+}$ complexes showed a weak positive and an intense negative CD peak in the T_{1g} region and a moderately intense positive CD peak in the T_{2g} region (*ca.* 25000 cm^{-1}). In the [Co(N)$_3$(O)$_3$]-type complexes, all the vicinal effect curves of the deprotonated isomers exhibit a strong negative CD band on the high-frequency-side in the T_{1g} region and a strong positive CD band at *ca.* 25000 cm^{-1} in the T_{2g} region. It is interesting that the strong positive CD peaks in the T_{2g} region for both the [Co(N)$_5$(O)]- and [Co(N)$_3$(O)$_3$]-type have been observed at the same frequency of 25000 cm^{-1}. Among the *mer* isomers the half-width of each T_{1g} band decreases in the order: *trans*(*O*), *cis*·*cis* and *trans*(*N*). In this order each major peak in the vicinal effect shifts to the lower-energy-side, while the minor (+) peak at a lower-energy gradually enhances in intensity.

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Appendix

Energy Matrices. For the *trans*(*O*) isomer, the arrangement of gly$^-$ and eta$^-$ is defined as in Fig. 7; all the ligating atoms are placed on the x, y, and z axes, and the lone pairs of the alcoholate ion interact with only the d_{xz} and d_{yz} orbitals. The π orbitals of the chelating carboxylate ions at (2) and (4) in Fig. 7 interact with only d_{xz} and d_{xy}, respectively. Based on these assumptions, the antibonding parameters have been defined as follows:

σ_N=a σ-antibonding parameter for the N donor atom of gly$^-$ or eta$^-$=e_σ(N)

σ=a σ-antibonding parameter for the O donor atom of gly$^-$=e_σ(O)

σ'=a σ-antibonding parameter for the O donor atom of eta$^-$=e_σ(O′)

π=a π-antibonding parameter for the O donor atom of gly$^-$=e_π(O)

π'=a π-antibonding parameter for the O donor atom of eta$^-$ related with the d_{xz} orbital=$e_{\pi 1}$(O′)

π''=a π-antibonding parameter for the O donor atom of

eta⁻ related with the d_{yz} orbital=$e_{\pi 2}(O')$.
The antibonding energies with non-vanishing values are;

$$\langle z^2|\mathbf{A}|z^2\rangle = \frac{3}{2}\sigma_N + \frac{1}{2}\sigma + \sigma'$$
$$\langle yz|\mathbf{A}|yz\rangle = \pi''$$
$$\langle zx|\mathbf{A}|zx\rangle = \pi + \pi'$$
$$\langle xy|\mathbf{A}|xy\rangle = \pi$$
$$\langle x^2-y^2|\mathbf{A}|x^2-y^2\rangle = \frac{3}{2}\sigma_N + \frac{3}{2}\sigma$$
$$\langle x^2-y^2|\mathbf{A}|z^2\rangle = \frac{\sqrt{3}}{2}[\sigma_N-\sigma].$$

Using the above relations, the energy matrix for the *trans(O)* isomer may be obtained.

On the assumption that the N and O donor atoms for the *cis·cis* isomer are arranged as in Fig. 7, the energy matrix can be obtained similarly to that for the *trans(O)* isomer.

Evaluation of Parameters. The three transitions assigned are for the *trans(O)* isomer,

$$E(d_{y^2-z^2} \longleftarrow d_{yz}) = 20600\ cm^{-1}$$
$$E(d_{z^2-x^2} \longleftarrow d_{zx}) = 15900\ cm^{-1}$$
$$E(d_{x^2-y^2} \longleftarrow d_{xy}) = 17800\ cm^{-1},$$

and for the *cis·cis* isomer,

$$E(d_{y^2-z^2} \longleftarrow d_{yz}) = 20200\ cm^{-1}$$
$$E(d_{z^2-x^2} \longleftarrow d_{zx}) = 16400\ cm^{-1}$$
$$E(d_{x^2-y^2} \longleftarrow d_{xy}) = 19500\ cm^{-1}.$$

Assuming the energy differences originating from the off-diagonal elements are negligibly small; the above relations may be rewritten in terms of the diagonal elements of T_{1g} transitions

$$\frac{3}{4}(3\sigma_N+\sigma') - \pi'' - C = 20600 \quad (1)$$
$$\frac{3}{4}(\sigma_N+2\sigma+\sigma') - \pi - \pi' - C = 15900 \quad (2)$$
$$\frac{3}{4}(\sigma_N+\sigma) - \pi - C = 17800 \quad (3)$$
$$\frac{3}{4}(3\sigma_N+\sigma) - C = 20200 \quad (4)$$
$$\frac{3}{4}(\sigma_N+2\sigma+\sigma') - \pi - \pi' - C = 16400 \quad (5)$$
$$\frac{3}{4}(2\sigma_N+\sigma+\sigma') - \pi - \pi'' - C = 19500 \quad (6)$$

The left-hand-sides of the equations are related as follows;
(1)+(3)=(4)+(6)
(2)=(5),
and t us the six equations may be reduced to four. Assuming $C=4B$, the value of B may be estimated for the [Co(gly)$_2$(eta)] complex (450 cm^{-1}), since the values of B for the *fac*-[Co(gly)$_3$] and *fac*-[Co(eta)$_3$] isomers are equal to 470 and 430 cm^{-1}, respectively. Furthermore, the value of σ_N has been estimated as 7700 cm^{-1}, which is identical with the value of σ_N for the [Co(en)$_3$] complex.

Using these values of B and σ_N, the four independent equations, which have been arbitrarily chosen from the six equations, may be solved and eight groups of $\sigma,\sigma'-4\pi''/3$, π, and $\pi'-\pi''$ values obtained. The average values of each $\sigma,\sigma'-4\pi''/3$, π, and $\pi'-\pi''$ are 5800, 7200, 325, and 1600 cm^{-1}, respectively.

From the above relations, the energies of the diagonal elements of the T_{2g} transitions are expressed by the use of the parameters. By comparing the absorption spectra with the calculated energies of the T_{2g} transitions, the most reasonable value of π'' is 700 cm^{-1}. Consequently, the parameters of σ_N, σ, σ', π, π', and π'' have been evaluated as 7700, 5800, 8100, 325, 2300 and 700 cm^{-1}, respectively.

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