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Circular Dichroism Spectra and Absolute Configurations of *fac*(*NH*$_3$)-[Co(a)(gly)(NH$_3$)$_3$]$^{n+}$-type Complexes

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Four complexes [Co(a)(gly)(NH$_3$)$_3$]$^+$ (a=CN$^-$, NO$_2$$^-$, NCS$^-$, and N$_3$$^-$) and a related [Co(NO$_2$)($\beta$-ala)(NH$_3$)$_3$]$^+$ complex have been prepared; they were characterized by the absorption spectra in the ultraviolet region. The *fac*(*NH*$_3$) isomers of these complexes have been optically resolved by column chromatography. The CD spectra of *fac*(*NH*$_3$)-[Co(H$_2$O)(gly)(NH$_3$)$_3$]$^{2+}$ and *fac*(*NH*$_3$)-[Co(H$_2$O)(β-ala)(NH$_3$)$_3$]$^{2+}$ have also been measured. The absolute configurations of the *fac*(*NH*$_3$) isomers have been determined by referring to the CD spectrum of *fac*(*NH*$_3$)-($-$)$_{589}$[Co(NO$_2$)(gly)(NH$_3$)$_3$]ClO$_4$ which had been subjected to an X-ray analysis. Each isomer has exhibited a dominant Cotton peak at *ca.* 20000 cm^{-1} in the first absorption band region. The peak has been assigned to the electronic transition component which arises in the plane containing the glycinate chelate. The CD spectra of *fac*(*NH*$_3$)-[Co(a)(gly)(NH$_3$)$_3$]$^+$ have been compared with those of the corresponding [Co(a)(gly)(1,4,7-triazacyclononane)]$^+$ complexes, and the sources of the optical activities in these complexes have been investigated.

We are interested in the optically active complexes whose chiralities are due to the arrangements of donor atoms around a central metal ion. In the previous papers,[1,2] the circular dichroism (CD) spectra of *fac*(*D*)-[Co(a)(BC)(DDD)]$^{n+}$ complexes have been reported. Here a represents several kinds of unidentate ligands; DDD represents a cyclic terdentate ligand: 1,4,7-triazacyclononane(=tacn), (2*R*)-2-methyl-1,4,7-triazacyclononane (Me-tacn), or 1,5,9-triazacyclododecane(=tacdd); BC denotes an amino carboxylate ion; glycinate, β-alaninate, or L-valinate. Though two helical ring-pairs exist in the complexes, the optical activities of the complexes have been mainly attributed to a chiral arrangement of four kinds of donor atoms around the central metal ion.

The *fac*(*NH*$_3$)-($-$)$_{589}$[Co(NO$_2$)(gly)(NH$_3$)$_3$]$^+$ complex[3] has a chiral arrangement of donor atoms similar to the [Co(NO$_2$)(gly)(tacn)]$^+$ and no ring-pair is contained in the complex. The absolute configuration of the complex has been determined by X-ray analysis.[4] This paper will deal with further syntheses and optical resolutions of the *fac*(*NH*$_3$)-[Co(a)(gly)(NH$_3$)$_3$]$^{n+}$ (a=CN$^-$, NO$_2$$^-$, NCS$^-$, N$_3$$^-$, or H$_2$O) and *fac*(*NH*$_3$)-[Co(b)($\beta$-ala)(NH$_3$)$_3$]$^{n+}$ (b=NO$_2$$^-$ or H$_2$O) complexes. The CD spectra of the *fac*(*NH*$_3$) complexes will be compared with those of the corresponding tacn complexes, and the contribution of the chelate ring to the optical activities will be reported.

Experimental

Synthesis and Optical Resolution. *1)* fac(NH$_3$)-*Triammineglycinatonitrocobalt(III) Chloride*, fac(NH$_3$)-[*Co(NO$_2$)(gly)(NH$_3$)$_3$*]*Cl*: This complex was prepared from [Co(NO$_2$)(NH$_3$)$_5$]$^{2+}$, and optically resolved according to the literature.[3]

2) fac(NH$_3$)-*Triammineglycinatoisothiocyanatocobalt(III) Bromide 0.5-Hydrate*, fac(NH$_3$)-[*Co(NCS)(gly)(NH$_3$)$_3$*]*Br·0.5H$_2$O*: To an aqueous solution of [Co(NCS)(NH$_3$)$_5$]SO$_4$ (15 g in 150 cm^3 H$_2$O) were added glycine (3.3 g), Na$_2$CO$_3$ (2.0 g) and activated charcoal (1.0 g), and the solution was stirred for a day at room temperature. After filtering off the activated charcoal, the filtrate was adjusted to pH 7 with perchloric acid and diluted to 3 dm^3 with water. The solution was poured onto a column of Dowex 50W-X8 (Na$^+$ form, 100—200 mesh, ϕ4.0 cm × 40 cm). By elution with a 0.1 mol/dm^3 NaCl solution, four bands of univalent cations were discharged; they were labelled A1, A2, A3, and A4 in the order of elution. The labels are also used to designate the complex species in each band. The A3 fraction was rechromatographed with a short column of the same resin (ϕ2 cm × 10 cm) in order to convert the counter ion to bromide. The adsorbed band was eluted with 0.1 mol/dm^3 NaBr, and collected in a fraction (A3′). Each fraction was concentrated by means of a rotary evaporator with simultaneous removal of precipitated eluent. To a final filtrate was added a small amount of ethanol, and the whole was kept in a refrigerator. The crude product which precipitated was recrystallized from a minimum amount of warm water. A2 and A4 were identified to be the isomers of a known complex, [Co(gly)$_2$(NH$_3$)$_2$]$^+$.[5] From elemental analyses, absorption and IR spectra, A1 and A3′ were assigned to the isomers of the [Co(NCS)(gly)(NH$_3$)$_3$]$^+$ complex. The yields of A1 and A3′ were 0.3 g and 0.2 g respectively. Found for A1: C, 13.00; H, 4.76; N, 25.22%. Calcd for [Co(NCS)(gly)(NH$_3$)$_3$]Cl: C, 12.98; H, 4.72; N, 25.23%. Found for A3′: C, 11.17; H, 3.90; N, 21.02%. Calcd for [Co(NCS)(gly)(NH$_3$)$_3$]Br·0.5H$_2$O: C, 10.88; H, 4.22; N, 21.15%.

The A3′ isomer was resolved into optical antipodes by using a column of Dowex 50W-X8 (Na$^+$ form, 200—400 mesh, ϕ2.5 cm × 70 cm) and 0.05 mol/dm^3 Na$_2$[Sb$_2$(*d*-tart)$_2$] as eluent. This fact indicates that A3′ is a *fac*(*NH*$_3$) isomer and A1 is a *mer*(*NH*$_3$) one. When the adsorbed band descended in the neighborhood of the outlet of the column, the band was washed sufficiently with water, and collected in several fractions by eluting with 0.1 mol/dm^3 NaCl. Each fraction was concentrated and submitted to the measurement of CD spectrum, while the concentration of the complex species was evaluated from the absorption spectral data.

3) fac(NH$_3$)-*Triammineazidoglycinatocobalt(III) Chloride*, fac(NH$_3$)-[*Co(N$_3$)(gly)(NH$_3$)$_3$*]*Cl*: The complex was prepared in the same manner as the isothiocyanato complex, except for the use of [Co(N$_3$)(NH$_3$)$_5$]Cl$_2$ (13 g, 0.05 mol, in 150 cm^3 H$_2$O) in place of [Co(NCS)(NH$_3$)$_5$]SO$_4$. By elution with a 0.1 mol/dm^3 NaCl solution, four bands of univalent cations were discharged; they were labelled B1, B2, B3, and B4 in the order of elution. B2 and B4 were identified to be the isomers of [Co(gly)$_2$(NH$_3$)$_2$]$^+$.[5] B1 and B3 were assigned to the isomers of [Co(N$_3$)(gly)(NH$_3$)$_3$]$^+$. The yields of B1 and B3 were *ca.* 0.3 g. Found for B1: C, 9.48; H, 4.87; N, 37.73%. Found for B3: C, 9.41; H, 5.24; N, 37.57%. Calcd for [Co(N$_3$)(gly)(NH$_3$)$_3$]Cl: C, 9.18; H, 5.01; N, 37.49%.

The B3 isomer was optically resolved by a method similar to that described in 2). Therefore, B3 was assigned to a *fac*(*NH*$_3$)

isomer, and B1 was a *mer(NH$_3$)* one.

4) fac(NH$_3$)-*Triamminecyanoglycinatocobalt(III) Chloride 0.75-* fac(NH$_3$)-*[Co(CN)(gly)(NH$_3$)$_3$]Cl·0.75H$_2$O*: To a cold green solution of tricarbonatocobaltate(III) (0.042 mol scale),[6] potassium cyanide (4.1 g, 0.063 mol) was added by portions, and the mixture was stirred vigorously at room temperature for 20 min. A deep red solution was obtained. After addition of glycine (3.75 g, 0.05 mol), the solution was carefully adjusted to pH 8 with 30% perchloric acid, and stirred at room temperature for two days. The resulting red-violet solution was adjusted to pH 3 with 60% perchloric acid under an iced conditions, and stirred for 30 min. Concentrated aqueous ammonia (20 cm^3, 0.28 mol) and activated charcoal (1 g) were added to the solution and the whole was stirred at room temperature for two days. After filtration, the filtrate was neutralized with 30% perchloric acid under an iced conditions, and the precipitate was filtered out. The filtrate was diluted to 3 dm^3 with water and charged on a column of Dowex 50W-X8 (Na$^+$ form, 200—400 mesh, ϕ4 cm × 30 cm). By elution with a 0.1 mol/dm^3 NaCl solution, five bands of univalent cations were discharged; they were labelled C1, C2, C3, C4, and C5 in the order of elution. Each fraction was concentrated to a small volume by a rotary evaporator, with simultaneous removal of deposited NaCl. A small amount of ethanol was added to the concentrate, and the whole was kept in a refrigerator. Cl was identified to be [Co(CN)$_2$(NH$_3$)$_4$]$^+$,[7] and C5, to be the isomers of [Co(gly)$_2$(NH$_3$)$_2$]$^+$.[5] The yellow crystals obtained from C2 and the orange crystals from C3 were assigned to isomers of [Co(CN)(gly)(NH$_3$)$_3$]$^+$. Each yield was *ca.* 0.3 g. Found for C2: C, 13.04; H, 5.86; N, 25.68%. Calcd for [Co(CN)(gly)(NH$_3$)$_3$]Cl·1.5H$_2$O: C, 13.22; H, 5.92; N, 25.69%. Found for C3: C, 13.66; H, 5.76; N, 27.29%. Calcd for [Co(CN)(gly)(NH$_3$)$_3$]Cl·0.75H$_2$O: C, 13.91; H, 5.64; N, 27.03%.

The C3 isomer was optically resolved by column chromatography in the same manner as in 2). Therefore, C3 was assigned to a *fac(NH$_3$)* isomer and C2 to a *mer(NH$_3$)* one.

5) fac(NH$_3$)-*Triammineaquaglycinatocobalt(III) Cation,* fac(NH$_3$)-*[Co(H$_2$O)(gly)(NH$_3$)$_3$]$^{2+}$*: This complex was prepared by acid-hydrolysis of the *fac(NH$_3$)*-[Co(NO$_2$)(gly)(NH$_3$)$_3$]$^+$ complex. The nitro complex (1.0 g) was dissolved in hydrobromic acid (47%, 20 cm^3). The solution was stirred at 50—60 °C for 90 min, whereupon the corresponding aqua complex was formed. The solution was diluted to 3 dm^3 with water, and poured onto a column of SP-Sephadex C-25 (Na$^+$ form, ϕ4.0 cm × 30 cm). The adsorbed red band was eluted with 0.1 mol/dm^3 HClO$_4$, and collected in a fraction. The eluate was concentrated to a small volume by a rotary evaporator, and its absorption spectrum was measured. The metal concentration was evaluated from the data of the atomic absorption spectrum. This complex was unable to be crystallized because of the great solubility of the complex species in water. The chromatographic behavior of the species indicates that the species is a bivalent cation. This complex was resolved into enantiomers by using a column of SP-Sephadex C-25 (Na$^+$ form, ϕ2.5 cm × 140 cm) and a 0.05 mol/dm^3 Na$_2$[Sb$_2$(*d*-tart)$_2$] solution as eluent.

1) fac(NH$_3$)-*(β-Alaninato)triamminenitrocobalt(III) Chloride Monohydrate,* fac(NH$_3$)-*[Co(NO$_2$)(β-ala)(NH$_3$)$_3$]Cl·H$_2$O*: This complex was prepared in the same manner as the *fac(NH$_3$)*-[Co(NO$_2$)(gly)(NH$_3$)$_3$]Cl, except for the use of β-alanine in place of glycine. The yield was *ca.* 0.3 g. Found: C, 12.24; H, 5.69; N, 23.37%. Calcd for [Co(NO$_2$)(β-ala)(NH$_3$)$_3$]Cl·H$_2$O: C, 12.11; H, 5.76; N, 23.53%.

The complex was also resolved into the optical antipodes in the same manner as in 2).

7) fac(NH$_3$)-*(β-Alaninato)triammineaquacobalt(III) Cation,* fac(NH$_3$)-*[Co(H$_2$O)(β-ala)(NH$_3$)$_3$]$^{2+}$*: This complex was prepared from *fac(NH$_3$)*-[Co(NO$_2$)(β-ala)(NH$_3$)$_3$]Cl and optically resolved by the method described in 5). The values of ε and $\Delta\varepsilon$ were evaluated from the data of atomic absorption spectra. The complex species could not be isolated because of its great solubility in water.

Derivations from Optically Active Complexes. The optically active complex, *fac(NH$_3$)*-(+)$_{589}$[Co(NCS)(gly)(NH$_3$)$_3$]$^+$, was derived from the *fac(NH$_3$)*-(+)$_{589}$[Co(H$_2$O)(gly)(NH$_3$)$_3$]$^{2+}$ complex by the following procedure. To a solution of the aqua complex was added an excess amount of NaSCN, and the mixture was adjusted to pH 4 with HClO$_4$. The solution was stirred at 50—60 °C for 1 h, and then subjected to Sephadex column chromatography in a similar way to that described in 5). The eluate obtained by elution with 0.05 mol/dm^3 NaCl was concentrated by means of a rotary evaporator, and a small amount of ethanol was added to the concentrate. When the whole kept in a refrigerator, red crystals deposited.

The *fac(NH$_3$)*-(−)$_{589}$[Co(N$_3$)(gly)(NH$_3$)$_3$]$^+$ and *fac(NH$_3$)*-(−)$_{589}$[Co(NO$_2$)(β-ala)(NH$_3$)$_3$]$^+$ were also derived from *fac-(NH$_3$)*-(+)$_{589}$[Co(H$_2$O)(gly)(NH$_3$)$_3$]$^{2+}$ and *fac(NH$_3$)*-(+)$_{589}$-[Co(H$_2$O)(β-ala)(NH$_3$)$_3$]$^{2+}$ respectively, by a similar procedure to that described above. The optically active complex *fac-*, *(NH$_3$)*-(−)$_{589}$ [Co(NO$_2$)(gly)(NH$_3$)$_3$]$^+$, was directly converted to the optically active aqua complex, *fac(NH$_3$)*-(+)$_{589}$ [Co(H$_2$O)(gly)(NH$_3$)$_3$]$^{2+}$, according to the method described in 5). When the *fac(NH$_3$)*-(+)$_{589}$[Co(NCS)(gly)(NH$_3$)$_3$]$^+$ complex was treated with aqueous H$_2$O$_2$ at *ca.* pH 3 in a similar manner to that described in the previous paper,[1] *fac(NH$_3$)*-(−)$_{589}$[Co(CN)(gly)(NH$_3$)$_3$]$^+$, *fac(NH$_3$)*-(+)$_{589}$[Co(H$_2$O)(gly)(NH$_3$)$_3$]$^{2+}$, and optically inactive [Co(gly)(NH$_3$)$_4$]$^{2+}$ [8] were obtained by means of chromatography.

Measurements. The absorption spectra in aqueous solution were recorded with a Hitachi 323 recording spectrophotometer. The CD spectra were measured with a JASCO J-40C automatic recording spectropolarimeter equipped with a JASCO Model J-DPZ data processor for CD. For the measurements of the optical rotation, a JASCO Model DIPSL automatic polarimeter was used. In order to evaluate the metal concentrations from the data of atomic absorption spectra, a Hitachi 170-50 atomic absorption spectrophotometer was used.

Results and Discussion

Preparation and Characterization. Three *fac(NH$_3$)*-[Co(a)(gly)(NH$_3$)$_3$]$^+$ (a=NO$_2^-$, NCS$^-$, and N$_3^-$) complexes and the *fac(NH$_3$)*-[Co(NO$_2$)(β-ala)(NH$_3$)$_3$]$^+$ complex were derived from the corresponding pentaammineanionocobalt(III) complexes. However, the *fac(NH$_3$)*-[Co(CN)(gly)(NH$_3$)$_3$]$^+$ complex could not be derived from a [Co(CN)(NH$_3$)$_5$]$^{2+}$ complex because of the small solubility of the pentaammine complex in water. The desired cyano complex was obtained by substitution reactions starting from [Co(CO$_3$)$_3$]$^{3-}$. The aqua complexes were also not obtained from [Co(H$_2$O)(NH$_3$)$_5$]$^{3+}$.

There are three possible geometrical isomers in the [Co(a)(amino acidato)(NH$_3$)$_3$]$^{n+}$ complex: *mer(NH$_3$)-trans(a,O)*, *mer(NH$_3$)-trans(a,N)*, and *fac(NH$_3$)*, where O and N represent donors of the amino acidato ligand.[3] Two *mer(NH$_3$)* isomers are achiral, while the *fac(NH$_3$)* isomer is chiral and resolvable into the optical antipodes. Except for *fac(NH$_3$)*-[Co(H$_2$O)(β-ala)(NH$_3$)$_3$]$^{2+}$, all the *fac*(*NH*$_3$) isomers were separated completely into the enantiomers on columns of 200—400 mesh cation exchanger. These isomers were only partially resolved on columns of 100—200 mesh exchanger.

Absorption spectra of *fac*(*NH*$_3$)-[Co(a)(gly)(NH$_3$)$_3$]$^{n+}$ complexes are shown in Figs. 1—5 (a=CN$^-$, NO$_2$$^-$, NCS$^-$, N$_3$$^-$, and H$_2$O), along with those of the related [Co(a)(gly)(tacn)]$^{n+}$ complexes. The numerical data are summarized in Table 1. The absorption maxima of the first absorption bands of the *fac*(*NH*$_3$) complexes appear at somewhat lower frequencies than those of the corresponding tacn complexes, and the intensities of the bands of the former are weaker than those of the latter.

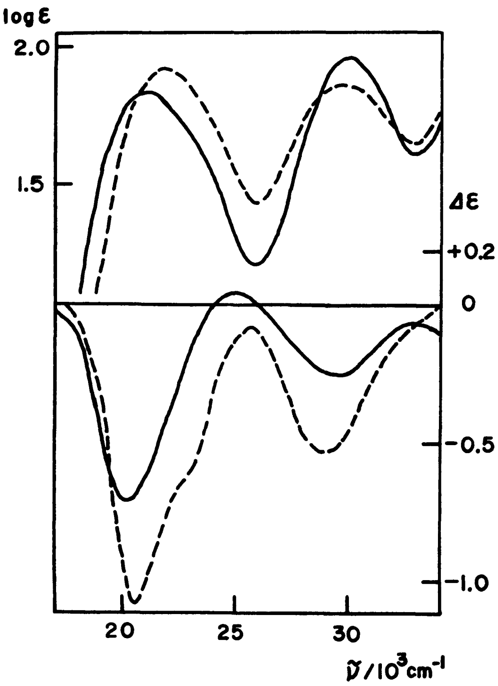

Fig. 1. Absorption and CD spectra of; ——: *fac*(*NH*$_3$)-(−)$_{589}$[Co(CN)(gly)(NH$_3$)$_3$]$^+$, - - -: (−)$_{589}$[Co(CN)-(gly)(tacn)]$^+$.

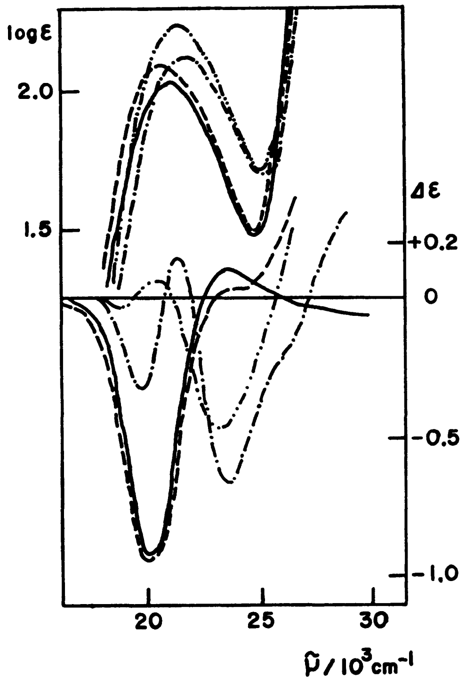

Fig. 2. Absorption and CD spectra of; ——: *fac*(*NH*$_3$)-(−)$_{589}$[Co(NO$_2$)(gly)(NH$_3$)$_3$]$^+$, - - -: *fac*(*NH*$_3$)-(−)$_{589}$-[Co(NO$_2$)(β-ala)(NH$_3$)$_3$]$^+$, ·—·—·: (−)$_{589}$[Co(NO$_2$)(gly)-(tacn)]$^+$, —··—: (−)$_{589}$[Co(NO$_2$)(β-ala)(tacn)]$^+$.

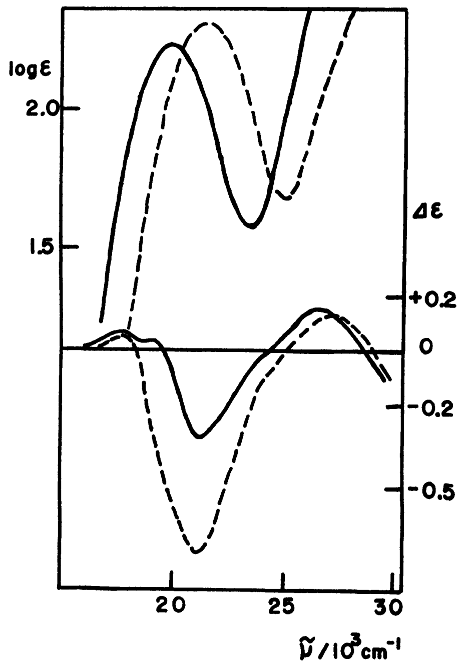

Fig. 3. Absorption and CD spectra of; ——: *fac*(*NH*$_3$)-(+)$_{589}$[Co(NCS)(gly)(NH$_3$)$_3$]$^+$, - - -: (−)$_{589}$[Co(NCS)-(gly)(tacn)]$^+$.

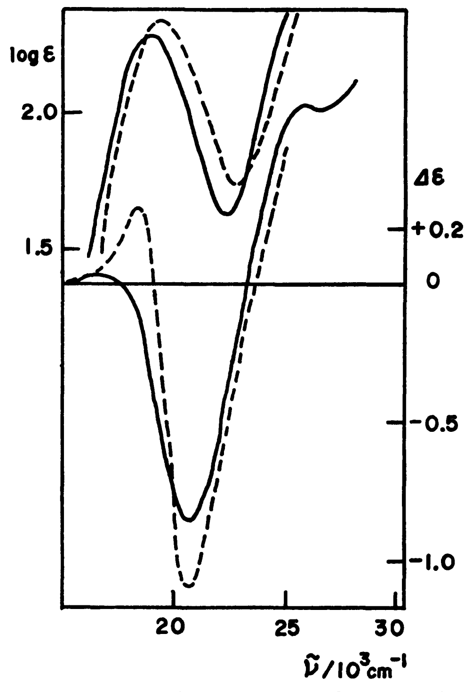

Fig. 4. Absorption and CD spectra of; ——: *fac*(*NH*$_3$)-(−)$_{589}$[Co(N$_3$)(gly)(NH$_3$)$_3$]$^+$, - - -: (+)$_{589}$[Co(N$_3$)-(gly)(tacn)]$^+$.

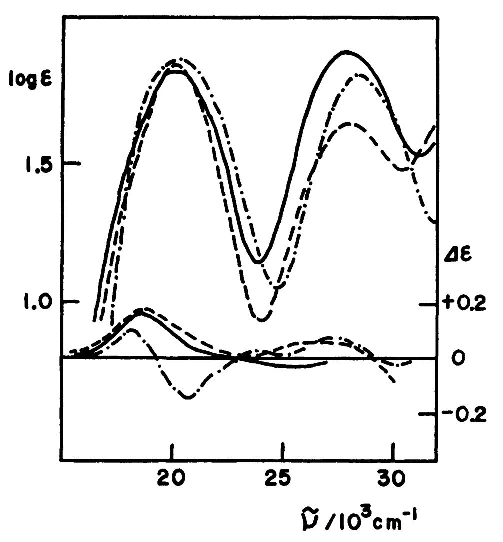

Fig. 5. Absorption and CD spectra of; ——: *fac*(NH_3)-$(+)_{589}[Co(H_2O)(gly)(NH_3)_3]^{2+}$, - - -: *fac*($NH_3$)-$(+)_{589}[Co(H_2O)(\beta\text{-ala})(NH_3)_3]^{2+}$, -·-·-: $(-)_{589}[Co(H_2O)(gly)(tacn)]^{2+}$.

Two *mer*(NH_3) isomers were isolated for the $[Co(NO_2)(gly)(NH_3)_3]^+$ complex, and assigned on the basis of absorption spectra in the ultraviolet region.[3] However only one of two *mer*(NH_3) isomers was obtained for each of the $[Co(CN)(gly)(NH_3)_3]^+$, $[Co(NCS)(gly)(NH_3)_3]^+$, and $[Co(N_3)(gly)(NH_3)_3]^+$ complexes. As to the isothiocyanato complex, the absorption band at *ca.* 32000 cm^{-1} can be assigned to $2\pi(NCS)\rightarrow d(z^2)$.[9] Since the band in the *mer*(NH_3) isomer is observed at a lower frequency than that in the corresponding *fac*(NH_3) isomer, the *mer*(NH_3)-*trans*(*NCS,O*) configuration is assignable for the *mer*(NH_3) complex in the same manner as described in the nitro complex.[3]

The absorption band at *ca.* 47000 cm^{-1} in the cyano complex can be assigned to $d\pi\rightarrow\pi(CN)$.[9] The bands observed at *ca.* 30000 cm^{-1} in the nitro complex are assignable to $d\pi\rightarrow\pi(NO_2)$, and the maximum of the *mer*(NH_3)-*trans*(NO_2,*O*) isomer is observed at a lower frequency than those of the *mer*(NH_3)-*trans*(NO_2,*N*) and *fac*(NH_3) isomers. Since the maximum of the *mer*(NH_3)-cyano isomer is observed at a lower frequency than that of the *fac*(NH_3) isomer, the isomer is considered to have the *mer*(NH_3)-*trans*(*CN,O*) configuration.

CD Spectra and Absolute Configurations. CD spectra of *fac*(NH_3)-$[Co(a)(gly)(NH_3)_3]^{n+}$ isomers, all of which were slow-moving isomers in column chromatography, are shown in Figs. 1—5, together with those of the fast-moving isomers of the corresponding tacn complexes. The $(+)_{589}[Co(H_2O)(gly)(NH_3)_3]^{2+}$ complex exhibits a single Cotton peak in the first absorption band region, and $(-)_{589}[Co(NO_2)(gly)(NH_3)_3]^+$ two peaks in this region, the CD spectra of these complexes being different from those of the corresponding tacn complexes. However, the CD spectra of $(-)_{589}[Co(CN)(gly)(NH_3)_3]^+$, $(+)_{589}[Co(NCS)(gly)(NH_3)_3]^+$, and $(-)_{589}[Co(N_3)(gly)(NH_3)_3]^+$ resemble those of the corresponding tacn complexes.

The *fac*(NH_3)-$(+)_{589}[Co(H_2O)(gly)(NH_3)_3]^{2+}$ complex could be converted to *fac*(NH_3)-$(-)_{589}[Co(NO_2)(gly)(NH_3)_3]^+$, *fac*($NH_3$)-$(+)_{589}[Co(NCS)(gly)(NH_3)_3]^+$, and *fac*($NH_3$)-$(-)_{589}[Co(N_3)(gly)(NH_3)_3]^+$ complexes. Furthermore, the *fac*(NH_3)-$(+)_{589}[Co(NCS)(gly)(NH_3)_3]^+$ complex was converted to *fac*(NH_3)-$(+)_{589}[Co(H_2O)(gly)(NH_3)_3]^{2+}$ and *fac*(NH_3)-$(-)_{589}[Co(CN)(gly)(NH_3)_3]^+$ by treatment with H_2O_2. Therefore, it is concluded that the isomers, *fac*(NH_3)-$[Co(a)(gly)(NH_3)_3]^{n+}$ (a=CN^-, NO_2^-, NCS^-, H_2O, or N_3^-), given in Figs. 1—5 have the same absolute configuration. The absolute configurations of the fast-moving isomers of the tacn complexes have been determined as shown in Fig. 6(a).[1,4] Since the CD spectra of $(-)_{589}[Co(CN)(gly)(NH_3)_3]^+$, $(+)_{589}[Co(NCS)(gly)(NH_3)_3]^+$, and $(-)_{589}[Co(N_3)(gly)(NH_3)_3]^+$ resemble those of the corresponding tacn complexes, all the slow-moving isomers of the triammine complexes are predicted to have the absolute configuration illustrated in Fig. 6(b).

In order to confirm the above prediction, an X-ray analysis of *fac*(NH_3)-$(-)_{589}[Co(NO_2)(gly)(NH_3)_3]ClO_4$ was attempted.[4] The results of the analysis support the prediction. Since the glycinate ligand forms a chelate ring much less puckered than the 1,2-diamine chelate ring, the optical activity of *fac*(NH_3)-$[Co(a)(gly)(NH_3)_3]^{n+}$ is considered to be mainly derived from a chiral arrangement of donor atoms.

Though the aqua complex exhibits a single Cotton peak in the first absorption band region, the remaining complexes exhibit two or three extrema in this region. The dominant peaks are observed at the lower frequency side of this region for the cyano and nitro complexes, and at the higher frequency side of this region for the isothiocyanato and azido complexes. However, the dominant Cotton peak is observed at *ca.* 20000 cm^{-1} in each complex.

Every complex has a rhombic ligand field in which the $A_{1g}\rightarrow T_{1g}$ transition component in octahedral parentage splits into three transition components: $(xy)\rightarrow(x^2-y^2)$, $(yz)\rightarrow(y^2-z^2)$, and $(zx)\rightarrow(z^2-x^2)$. An angular overlap model[10] predicts that the electronic transition at *ca.* 20000 cm^{-1} should be assigned to the transition component which arises in the plane containing the glycinato and two ammine ligands.[11] Therefore, it is suggested that a single chelate ring increases somewhat the rotatory strength of the Cotton peak associated with the electronic transition which arises in the plane containing a chelate ring. This finding is incompatible with the results obtained in the tris or bis(diamine) complexes such as $[Co(en)(tn)(tmd)]^{3+}$ [12] and *cis*-$[Co(NH_3)_2(tn)_2]^{3+}$.[13] In these complexes, the number of asymmetric pairs of

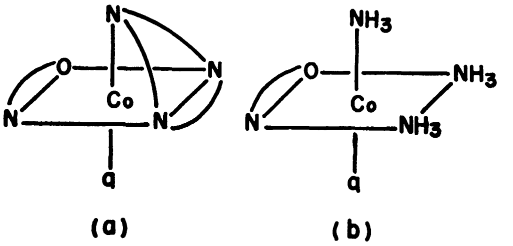

Fig. 6. Absolute configurations of; a) $[Co(a)(gly)(tacn)]^{n+}$, b) *fac*(NH_3)-$[Co(a)(gly)(NH_3)_3]^{n+}$.

TABLE 1. ABSORPTION AND CD SPECTRAL DATA

Complex	Absorption		CD	
	$\tilde{\nu}/10^3\ \mathrm{cm^{-1}}$	$(\log \varepsilon)$	$\tilde{\nu}/10^3\ \mathrm{cm^{-1}}$	$(\Delta\varepsilon)$
$fac(NH_3)$-$(-)_{589}[\mathrm{Co(CN)(gly)(NH_3)_3}]^+$	21.1	(1.83)	20.1	(−0.71)
			24.9	(+0.03)
	30.0	(1.95)	29.6	(−0.27)
	47.6	(4.26)		
$mer(NH_3)$-$trans(CN,O)$-$[\mathrm{Co(CN)(gly)(NH_3)_3}]^+$	22.0	(1.94)		
	29.8	(1.93)		
	46.8	(4.27)		
$fac(NH_3)$-$(-)_{589}[\mathrm{Co(NO_2)(gly)(NH_3)_3}]^+$	20.9	(2.03)	20.0	(−0.92)
			23.4	(+0.09)
	30.5	(3.18)		
	41.6	(4.14)		
$mer(NH_3)$-$trans(NO_2,O)$-$[\mathrm{Co(NO_2)(gly)(NH_3)_3}]^+$	21.4	(2.11)		
	29.6	(3.27)		
	40.7	(4.25)		
$mer(NH_3)$-$trans(NO_2,N)$-$[\mathrm{Co(NO_2)(gly)(NH_3)_3}]^+$	21.2	(2.02)		
	30.3	(3.33)		
	41.7	(4.21)		
$fac(NH_3)$-$(+)_{589}[\mathrm{Co(H_2O)(gly)(NH_3)_3}]^{2+}$	20.0	(1.84)	18.6	(+0.15)
	27.6	(1.91)		
$fac(NH_3)$-$(+)_{589}[\mathrm{Co(NCS)(gly)(NH_3)_3}]^+$	19.9	(2.23)	17.7	(+0.05)
			19.0	(+0.03)
			21.2	(−0.31)
	32.7	(3.24)	26.8	(+0.14)
$mer(NH_3)$-$trans(NCS,O)$-$[\mathrm{Co(NCS)(gly)(NH_3)_3}]^+$	18.9	(2.25)		
	32.0	(3.22)		
$fac(NH_3)$-$(-)_{589}[\mathrm{Co(N_3)(gly)(NH_3)_3}]^+$	18.9	(2.26)	16.3	(+0.02)
			20.8	(−0.86)
	32.8	(3.91)	25.6	(+0.64)
$mer(NH_3)$-$[\mathrm{Co(N_3)(gly)(NH_3)_3}]^+$	18.4	(2.21)		
	32.7	(3.71)		
$fac(NH_3)$-$(-)_{589}[\mathrm{Co(NO_2)}(\beta\text{-ala})\mathrm{(NH_3)_3}]^+$	20.5	(2.09)	20.1	(−0.95)
			24.1	(+0.03)
	30.2	(3.18)		
	41.8	(4.23)		
$mer(NH_3)$-$trans(NO_2,O)$-$[\mathrm{Co(NO_2)}(\beta\text{-ala})\mathrm{(NH_3)_3}]^+$	21.0	(2.18)		
	29.7	(3.25)		
	40.1	(4.28)		
$fac(NH_3)$-$(+)_{589}[\mathrm{Co(H_2O)}(\beta\text{-ala})\mathrm{(NH_3)_3}]^{2+}$	20.1	(1.86)	18.6	(+0.17)
	27.8	(1.63)	27.4	(+0.05)

chelate rings is more important in determining the CD intensity than the number of chelate rings.

The [Co(a)(gly)(tacn)]$^{n+}$ complexes have the same chromophore as the present complexes.$^{1)}$ An intense Cotton peak was characteristically observed at the highest frequency side of the first absorption band region in the tacn complexes. Such an intense peak is not always observed in the present complexes. It is noticeable that when the unidentate ligand a in [Co(a)(gly)(NH$_3$)$_3$]$^{n+}$ is planar, the CD spectrum of the complex is somewhat different from that of the corresponding [Co(a)(gly)(tacn)]$^{n+}$ complex. On the other hand, when the unidentate is a linear ligator, the CD spectrum of the complex is similar to that of the tacn complex. Since the CD spectral patterns of the [Co(a)(gly)(NH$_3$)$_3$]$^{n+}$ complexes, on the whole, resemble those of the corresponding [Co(a)(gly)(tacn)]$^{n+}$ complexes, it is concluded that the chiral arrangement of donor atoms is the main source of the optical activity in [Co(a)(gly)(tacn)]$^{n+}$. This is supported by the fact that the [Co(a)(gly)(tacn)]$^{n+}$ complexes give CD spectra similar to [Co(a)(NH$_3$)(H$_2$O)(tacn)]$^{(n+1)+}$ complexes (a=CN$^-$, NO$_2$$^-$, NCS$^-$, N$_3$$^-$, and Cl$^-$).$^{14)}$

The $fac(NH_3)$-$(-)_{589}$[Co(NO$_2$)(β-ala)(NH$_3$)$_3$]$^+$ complex exhibits a CD spectrum similar to that of the $fac(NH_3)$-$(-)_{589}$[Co(NO$_2$)(gly)(NH$_3$)$_3$]$^+$ complex, namely, a negative dominant peak is observed at *ca.* 20000 cm^{-1} and a positive minor peak at *ca.* 24000 cm^{-1}. The CD spectrum of $fac(NH_3)$-$(+)_{589}$[Co(H$_2$O)(β-ala)(NH$_3$)$_3$]$^{2+}$ also resembles that of $fac(NH_3)$-$(+)_{589}$[Co(H$_2$O)(gly)(NH$_3$)$_3$]$^{2+}$, a positive extremum being observed in the complexes. Therefore, each pair of the glycinato and β-alaninato complexes is considered to have the same absolute configuration, and the change from the five-membered chelate ring to the six-membered one has little effect on the optical activity in the complexes. A similar situation is encountered in the $(-)_{589}$[Co(NO_2)(gly)(tacn)]$^+$ and $(-)_{589}$[Co(NO_2)(β-ala)(tacn)]$^+$ complexes, the same absolute configuration being assigned to these complexes.[2]

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