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Synthesis and Circular Dichroism Spectra of [Co(a)(gly)(1,4,7-triazacyclononane)]-type Complexes

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Complexes of the [Co(a)(gly)(tacn)]-type, where tacn represents 1,4,7-triazacyclononane and a is CN^-, NO_2^-, NH_3, NCS^-, H_2O, OH^-, N_3^-, or Cl^-, have been prepared and resolved. The CD spectra of these complexes have been measured. On the basis of the X-ray analysis of $(-)_{589}$[Co(gly)(NH_3)(tacn)]$I_2\cdot H_2O$, the absolute configurations of the other complexes have been assigned by referring to the CD spectra. These complexes have exhibited a common CD pattern in the T_{1g}-band region, and from this fact a criterion for the assignments of the absolute configurations for the complexes of the *fac*(D)-[Co(a)(BC)(DDD)]-type has been established.

Most circular dichroism (CD) spectral studies of cobalt(III) complexes have been undertaken to investigate various sources of optical activity, such as the distribution of chelate rings, the conformation of chelate rings, the vicinal effect due to asymmetric carbon in an optically active ligand, and the vicinal effect due to an asymmetric donor atom.[1] In contrast to those investigations, little work has been reported on complexes whose optical activity arises from the arrangement of unidentate ligands. The paucity of research on such complexes seems mainly a result of the lack of preparative methods. In our laboratory some complexes of *cis-cis*-[Co(a)$_2$(b)$_2$(CC)]- and *all-cis*-[Co(a)$_2$(b)$_2$(c)$_2$]-types have been prepared through a few steps of ligand substitution, and then resolved into enantiomeric isomers.[2] Shimura *et al.*[3,4] prepared and resolved complexes of the *fac*(D)-[Co(a)(BC)(DDD)]-type, using 2-aminomethyl-2-methyl-1,3-propanediamine (1,1,1-tris(aminomethyl)ethane, TAME) or $Nb_6O_{19}^{8-}$ as the DDD ligand and glycinate as the BC ligand. However, the absolute configurations of these complexes have not been established. Very recently, we reported a complex of the *fac*(D)-[Co(a)(b)(c)(DDD)]-type, where DDD was 1,4,7-triazacyclononane (=TACN) and where a, b, and c were CN^-, Br^-, and NH_3 respectively.[5]

This paper will deal with the syntheses and optical resolution of a series of $[Co(a)(gly)(tacn)]^{n+}$ complexes (a=CN^-, NO_2^-, NH_3, NCS^-, H_2O, OH^-, N_3^-, Cl^-, or I^-). Since TACN coordinates facially in an octahedral complex, the chirality of these complexes is derived from the arrangement of the complexed gly and unidentate ligands, as is shown in Fig. 1. The absolute configurations of these complexes are assigned by referring to the CD spectra, on the basis of the results of the X-ray analysis of $(-)_{589}$[Co(gly)(NH_3)(tacn)]$I_2\cdot H_2O$.[6]

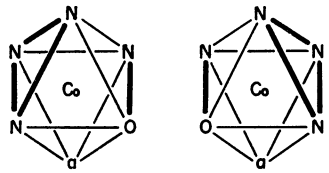

Fig. 1. Enantiomers of [Co(a)(gly)(tacn)]-type complex.

Experimental

Ligand. 1,4,7-Triazacyclononane trihydrochloride (TACN·3HCl) was prepared by the literature method.[7]

Preparation of Complexes. *1) Aquaglycinato-1,4,7-triazacyclononanecobalt(III) Perchlorate Dihydrate, [Co(gly)(tacn)-(H_2O)]$(ClO_4)_2\cdot 2H_2O$*: The *mer*(N)-*trans*(NH_3)-[Co(CO_3)-(gly)$(NH_3)_2$] complex (5.0 g, 0.022 mol)[8] was dissolved in water (20 cm^3), and then the ligand, TACN·3HCl (5.0 g, 0.022 mol), was added to this solution in portions, with care taken to the evolution of carbon dioxide. After the compounds had been dissolved, the solution was adjusted to pH 2 with $HClO_4$ (60%), whereupon the diaqua complex, $[Co(gly)(NH_3)_2(H_2O)_2]^{2+}$, was formed. The solution was alkalized with 5 M (1 M=1 mol dm^{-3}) KOH until pH 9, stirred for 15 min, and then acidified with $HClO_4$ until pH 6. The resulting solution was filtered once and diluted to 2 dm^3 with water. This solution was poured into a column containing SP-Sephadex C-25 (4.5×25.0 cm, Na^+ form). The adsorbed band was eluted with 0.1 M $HClO_4$, and a red band corresponding to the bivalent cation of the desired complex was collected. The eluate was concentrated to a small volume by means of a rotary evaporator, after which a small amount of ethanol and a large amount of ether were added to the concentrate successively. This solution was kept in a refrigerator until the red material of the desired complex was deposited. The crude product was recrystallized from warm water (*ca.* 60 °C). The yield was about 2.0 g. Found: C, 18.55; H, 4.95; N, 10.62%. Calcd for $[Co(gly)(tacn)(H_2O)](ClO_4)_2\cdot 2H_2O = C_8H_{25}O_{13}N_4Cl_2Co$: C, 18.65; H, 4.90; N, 10.88%. This aqua complex was used as the starting material for the following syntheses (*2)—7)*).

2) Glycinatonitro-1,4,7-triazacyclononanecobalt(III) Chloride Monohydrate, [Co(NO_2)(gly)(tacn)]Cl·H_2O: To a solution of the aqua complex (1.5 g in 20 cm^3 H_2O) we added $NaNO_2$ (1 g, 0.014 mol), and then the solution was adjusted to pH 4 with $HClO_4$. The solution was stirred at 50—60 °C until its color changed from red to yellow. The resulting solution was subjected to Sephadex column chromatography in a way similar to that in *1)*. The eluate obtained by elution with 0.05 M NaCl was concentrated to a small volume by means of a rotary evaporator, with the simultaneous removal of the NaCl deposited; a large amount of ethanol was then added to the concentrate. The ethanolic solution was kept in a refrigerator to obtain yellow crystals. The crystals were recrystallized from warm water (*ca.* 50 °C). The yield was *ca.* 0.8 g. Found: C, 26.25; H, 5.69; N, 19.47%. Calcd for $[Co(NO_2)(gly)(tacn)]Cl\cdot H_2O = C_8H_{21}O_5N_5ClCo$: C, 26.56; H, 5.89; N, 19.37%.

3) Ammineglycinato-1,4,7-triazacyclononanecobalt(III) Iodide Monohydrate, [Co(gly)(NH_3)(tacn)]$I_2\cdot H_2O$: The aqua complex (1.5 g) was dissolved in aqueous ammonia (28%,

100 cm³), after which the solution was allowed to stand in a flask with a stopcock at 60 °C until it turned orange (several hours). The resulting solution was poured into a column of Dowex 50W-X8 (4.5×10.0 cm, Na^+ form). The eluate obtained by subsequent elution with 0.3 M NaI was treated in a way similar to that in *2)*. When the concentrated solution was kept in a refrigerator, orange crystals were deposited; they were recrystallized from warm water (60 °C). The yield was *ca.* 1.0 g. Found: C, 17.37; H, 4.26; N, 12.52%. Calcd for $[Co(gly)(NH_3)(tacn)]I_2 \cdot H_2O = C_8H_{24}O_3N_5I_2Co$: C, 17.31; H, 4.37; N, 12.62%.

4) Glycinatoisothiocyanato-1,4,7-triazacyclononanecobalt(III) Bromide, [Co(NCS)(gly)(tacn)]Br: An aqueous solution (20 cm³) containing starting aqua complex (1.5 g) and KSCN (1.5 g, 0.015 mol) was adjusted to pH 4 with $HClO_4$ and then stirred at 50—60 °C for 2—3 h. The resulting red solution was chromatographed in the same manner as *3)*. The elution was carried out with 0.1 M NaBr. The yield of the desired complex was *ca.* 0.8 g. Found: C, 26.91; H, 4.81; N, 17.31%. Calcd for $[Co(NCS)(gly)(tacn)]Br = C_9H_{19}O_2N_5SBrCo$: C, 27.01; H, 4.79; N, 17.50%.

5) Azidoglycinato-1,4,7-triazacyclononanecobalt(III) Iodide Monohydrate, [Co(N₃)(gly)(tacn)]I·H₂O: This complex was prepared in the same manner as the isothiocyanato complex, except for the use of NaN_3 (1.0 g, 0.015 mol) in place of KSCN. The elution was carried out with 0.1 M NaI. Red-violet crystals were obtained in a yield of *ca.* 0.8 g. Found: C, 21.23; H, 4.33; N, 21.42%. Calcd for $[Co(N_3)(gly)(tacn)]I \cdot H_2O = C_8H_{21}O_3N_7ICo$: C, 21.29; H, 4.70; N, 21.73%.

6) Chloroglycinato-1,4,7-triazacyclononanecobalt(III) Chloride 1.5-hydrate, [Co(Cl)(gly)(tacn)]Cl·1.5H₂O: Starting aqua complex (1.5 g) was dissolved in 6 M HCl (20 cm³), after which the solution was stirred at 60 °C for 2—3 h. The resulting solution was poured into a column of Dowex 50W-X8 (5.5×10.0 cm, H^+ form). The eluate obtained by elution with 0.1 M NaCl was treated by the same way as *3)*. The yield of violet crystals was *ca.* 0.5 g. Found: C, 26.66; H, 5.77; N, 15.31%. Calcd for $[Co(Cl)(gly)(tacn)]Cl \cdot 1.5H_2O = C_8H_{22}O_{3.5}N_4Cl_2Co$: C, 26.68; H, 6.17; N, 15.56%.

7) Glycinatoiodo-1,4,7-triazacyclononanecobalt(III) Iodide, [Co(I)(gly)(tacn)]I: When, in the preparation of the aqua complex, elution was carried out with 0.1 M NaI and the eluate was concentrated to a small volume, the solution turned green. From the solution, powdery green crystals of the iodo complex separated out. The yield was *ca.* 1.0 g. Found: C, 18.53; H, 3.54; N, 10.92%. Calcd for $[Co(I)(gly)(tacn)]I = C_8H_{19}O_2N_4I_2Co$: C, 18.48; H, 3.69; N, 10.78%.

8) Cyanoglycinato-1,4,7-triazacyclononanecobalt(III) Chloride Dihydrate, [Co(CN)(gly)(tacn)]Cl·2H₂O: So far as this cyano complex was concerned, attempts at derivation from the aqua complex in an aqueous medium were unsuccessful. Instead, the desired complex was obtained by means of a reaction in dimethyl sulfoxide (DMSO); the chloro complex, $[Co(Cl)(gly)(tacn)]Cl \cdot 1.5H_2O$ (2.0 g, 0.0056 mol), was carefully dissolved in a minimum amount of conc. HNO_3; after the evolution of Cl_2 and NO_2 gases had ceased, ethanol (15 cm³) was added to the solution to precipitate the nitrate of the complex, $[Co(Cl)(gly)(tacn)]NO_3$. The nitrate was dissolved in DMSO (300 cm³) containing KCN (1.0 g, 0.015 mol), after which the solution was heated at 85—90 °C for 2—3 h. The resulting yellow solution was poured into a column of SP-Sephadex C-25 (4.5×25.0 cm, Na^+ form). Elution was carried out with 0.05 M NaCl to collect a portion of the desired species. When the concentrate of the fraction was kept in a refrigerator, yellow crystals separated out; yield, *ca.* 0.6 g. Found: C, 29.92; H, 6.05; N, 19.45%. Calcd for $[Co(CN)(gly)(tacn)]Cl \cdot 2H_2O = C_9H_{23}O_4N_5ClCo$: C, 30.05; H, 6.46; N, 19.47%.

Optical Resolution. Each of the cyano, nitro, and ammine complexes was resolved into two optically active forms by the column chromatography of SP-Sephadex C-25 (2.5×110.0 cm, Na^+ form), using 0.05 M $K_2[Sb_2(d\text{-tart})_2]$ as the eluent. The remaining isothiocyanato, aqua, azido, and chloro complexes were all resolved into two forms each using columns of Dowex 50W-X8 (200—400 mesh, 2.5×34.5 cm, Na^+ form) and a 0.3 M $Na_2[Sb_2(d\text{-tart})_2]$ solution as the eluent. When the adsorbed band had descended to four-fifths of the column height, the band was washed with water and eluted with 0.1 M NaCl or 0.3 M $NaClO_4$. The eluate thus concentrated was submitted to the measurement of the CD spectra, while the concentration of the complex species was evaluated from the absorption spectral data.

Derivations from Optically Active Complexes. Several optically active complexes, $(-)_{589}[Co(NO_2)(gly)(tacn)]^+$, $(-)_{589}[Co(NCS)(gly)(tacn)]^+$, $(+)_{589}[Co(N_3)(gly)(tacn)]^+$, and $(-)_{589}[Co(Cl)(gly)(tacn)]^+$, could be directly derived from the optically active aqua complex, $(-)_{589}[Co(gly)(tacn)(H_2O)](ClO_4)_2 \cdot 2H_2O$, according to the methods described in *2)*, *4)*, *5)*, and *6)* respectively. The reaction of aqueous ammonia of the $(-)_{589}[Co(gly)(tacn)(H_2O)]^{2+}$ complex resulted in the formation of the racemic $[Co(gly)(NH_3)(tacn)]^{2+}$ complex. On the other hand, the oxidation of the $(-)_{589}[Co(NCS)(gly)(tacn)]^+$ complex by aqueous H_2O_2 at *ca.* pH 3 produced the $(-)_{589}[Co(gly)(NH_3)(tacn)]^{2+}$, $(-)_{589}[Co(CN)(gly)(tacn)]^+$ and $(-)_{589}[Co(gly)(tacn)(H_2O)]^{2+}$ complexes, which were separated chromatographically.

Measurements. The absorption spectra in aqueous solutions 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 measurement of the optical rotation, a JASCO Model DIP-SL automatic polarimeter was used. The absorption and CD spectra of hydroxo complex species were measured with an alkalized solution (pH 9) of the aqua complex with 5 M NaOH. The hydroxo complex species was chromatographically pure, and its absorption and CD spectra were changed into the original spectra of the parent aqua complex when the solution was again acidified with $HClO_4$. This fact suggests that the base-hydrolysis proceeds with retention of the configuration.

The CD measurement was carried out for an aqueous solution of bis(1,4,7-triazacyclononane)cobalt(III), $[Co(tacn)_2]^{3+}$,[9] in the presence of $[Sb_2(d\text{-tart})_2]^{2-}$ ($[Co(tacn)_2]Cl_3$ 4.0×10^{-3} M; $K_2[Sb_2(d\text{-tart})_2] \cdot H_2O$ 8.0×10^{-2} M).

Results and Discussion

Preparation and Resolution. A feature of the present method of preparation is that a series of complexes with various unidentates, a, $[Co(a)(gly)(tacn)]^{n+}$, could be derived from one complex, $[Co(gly)(tacn)(H_2O)]^{2+}$. An exception was the case of the cyano complex; the reaction of potassium cyanide on an aqueous solution of the aqua complex resulted in the formation of a hydroxo complex, $[Co(OH)(gly)(tacn)]^+$, which was not isolated because of its great solubility. Instead, the reaction of the chloro complex, $[Co(Cl)(gly)(tacn)]^+$, with potassium cyanide in DMSO yield-

ed the desired complex.

For the optical resolution of the complexes, column chromatography using an ion-exchanger and *d*-tartratoantimonate(III) was useful. It is worth noting that a complete resolution was attained by using a Dowex cation exchanger for the complexes containing unidentates whose ligand-field-strengths are weaker than that of ammonia. On the other hand, the chromatographic resolutions of the same complexes on Sephadex columns were partial. The attempted resolution of the iodo complex was unsuccessful becasue of the great lability of the complexed iodide ion.

Absorption and CD Spectra. The absorption spectrum of the racemic $[Co(gly)(NH_3)(tacn)]^{2+}$ complex and the CD spectra of the two resolved isomers are illustrated in Fig. 2, the CD curves being mirror images of each other. Since the same situation was encountered in the resolved pairs of the other complexes, the CD spectra for only the isomers obtained from the earlier eluates are illustrated, together with the absorption spectra, in Figs. 3—5. The numerical data are summarized in Table 1. Every complex has a rhombic ligand field in which there are three electronic transition components for each of the first absorption (T_{1g}) and second absorption (T_{2g}) bands. However, no appreciable splittings are observed even in the T_{1g} bands of the cyano and chloro complexes. The maximum positions of the first absorption bands ($\tilde{\nu}_{Imax}$) shift to a higher-frequency side in accord with the spectrochemical series[10], $I^- < Cl^- < N_3^- < OH^- < H_2O < NCS^- < NH_3 < NO_2^- < CN^-$, with respect to the unidentates used.

The observed CD spectra are classified into three groups on the basis of the patterns in the T_{1g} band region: 1) one negative broad peak, 2) a positive and a negative peak from a lower frequency, and 3) a negative, a positive, and a negative peak from a lower frequency. The $(-)_{589}[Co(CN)(gly)(tacn)]^+$ complex belongs to Group 1. The extremum is located at a lower frequency compared with the corresponding absorption maximum ($\tilde{\nu}_{Imax}$), and a shoulder is observed at a higher frequency. The

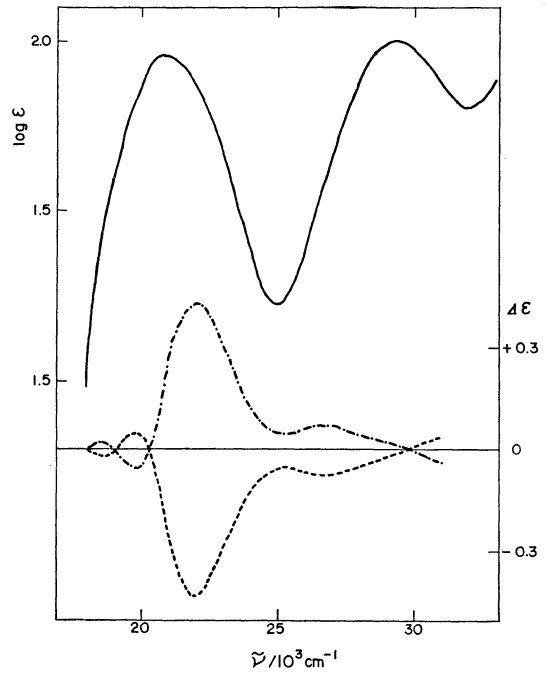

Fig. 2. Absorption spectrum of $[Co(gly)(NH_3)(tacn)]^{2+}$ (——), and CD spectra of $(-)_{589}[Co(gly)(NH_3)(tacn)]^{2+}$ (earlier eluate) (----), $(+)_{589}[Co(gly)(NH_3)(tacn)]^{2+}$ (—·—·—).

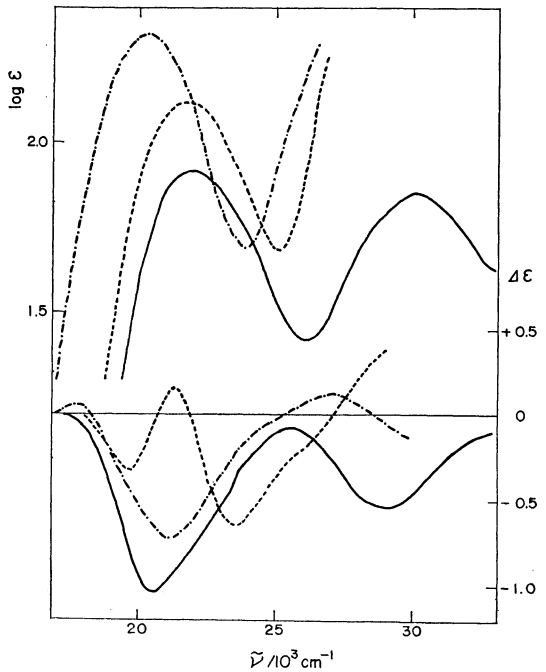

Fig. 3. Absorption and CD spectra of $(-)_{589}[Co(CN)(gly)(tacn)]^+$ (——), $(-)_{589}[Co(NO_2)(gly)(tacn)]^+$ (----), $(-)_{589}[Co(NCS)(gly)(tacn)]^+$ (—·—·—).

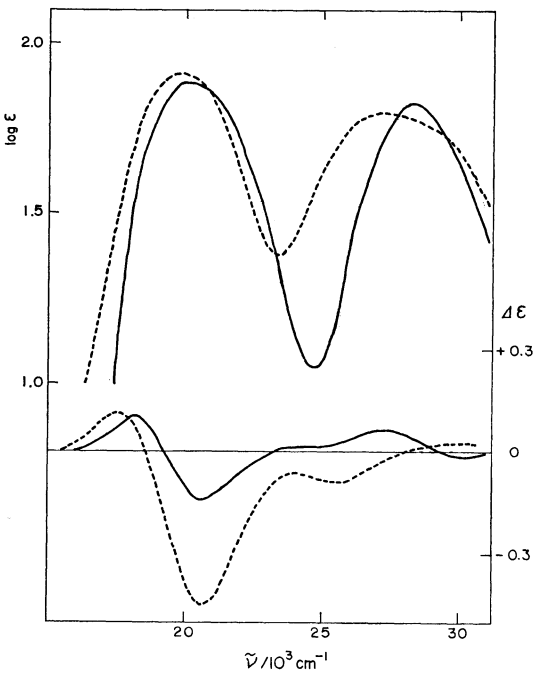

Fig. 4. Absorption and CD spectra of $(-)_{589}[Co(gly)(tacn)(H_2O)]^{2+}$ (——), $(-)_{589}[Co(OH)(gly)(tacn)]^+$ (----).

$(-)_{589}$[Co(NCS)(gly)(tacn)]$^+$, $(-)_{589}$[Co(gly)(tacn)-(H_2O)]$^{2+}$, $(-)_{589}$[Co(OH)(gly)(tacn)]$^+$, $(+)_{589}$[Co-(N_3)(gly)(tacn)]$^+$, and $(-)_{589}$[CoCl(gly)(tacn)]$^+$ complexes exhibit the pattern of Group 2. Two complexes, $(-)_{589}$[Co(NO_2)(gly)(tacn)]$^+$ and $(-)_{589}$[Co-(gly)(NH_3)(tacn)]$^{2+}$, show the pattern of Group 3. However, the negative extremum observed at the lowest frequency in the spectrum of the $(-)_{589}$[Co-(gly)(NH_3)(tacn)]$^{2+}$ complex is extremely weak. A striking characteristic in the CD spectra for the earlier-eluted enantiomers is that a major CD peak of a negative sign is observed at a higher frequency in the T_{1g}-band region, except for the case of the cyano complex, where a negative shoulder appears at a higher frequency. Another characteristic is that the intensity is very weak in comparison with that of bis- or tris-diamine complexes.

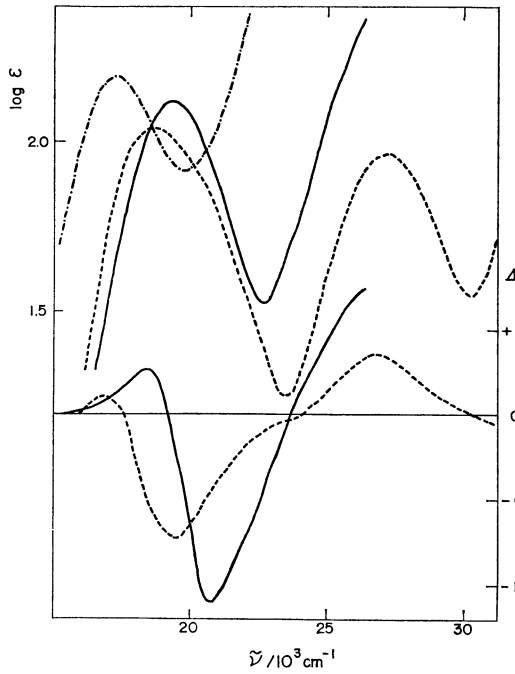

Fig. 5. Absorption and CD spectra of $(+)_{589}$[Co(N_3)-(gly)(tacn)]$^+$ (——), $(-)_{589}$[Co(Cl)(gly)(tacn)]$^+$ (----), [Co(I)(gly)(tacn)]$^+$ (—·—·—).

For the present chiral complexes, three sources of d-electron optical activity can be considered; the helical distribution of a H_2N–CH_2–COO^- chelate and the –NH–CH_2–CH_2–NH– moiety of tacn, the conformations of the three chelate rings of the tacn or glycinate ring, and the arrangement of the three donors of the glycinate and unidentate ligands. Recently, the absolute configuration of the $(-)_{589}$[Co(gly)(NH_3)-(tacn)]$I_2\cdot H_2O$ was determined by X-ray analysis.[6] It was thereby found that the glycinate chelate ring was nearly planar (that is, it was achiral), and the five-membered chelate rings of the tacn ligand had all a δ-conformation. However, it is thought that the conformations of the tacn chelate rings are not fixed in a solution, judging from the following fact. When a solution CD spectrum of the $[Co(tacn)_2]^{3+}$ complex was measured in the presence of $[Sb_2(d$-tart$)_2]^{2-}$, a negative peak ($\Delta\varepsilon=-0.40$) was observed

Table 1. Absorption and CD spectral data of the earlier-eluted enantiomers

Complex	Absorption		CD	
	$\bar{\nu}/10^3$ cm^{-1}	(log ε)	$\bar{\nu}/10^3$ cm^{-1}	($\Delta\varepsilon$)
$(-)_{589}$[Co(CN)(gly)(tacn)]$^+$	21.9	(1.9)	20.7	(−1.05)
			ca. 23.0	(*ca.* −0.5 sh)
	30.0	(1.85)	29.0	(−0.53)
$(-)_{589}$[Co(NO_2)(gly)(tacn)]$^+$	21.8	(2.12)	19.8	(−0.32)
			21.3	(+0.15)
			23.6	(−0.66)
$(-)_{589}$[Co(gly)(NH_3)(tacn)]$^{2+}$	20.8	(1.96)	18.6	(−0.02)
			19.8	(+0.06)
			22.0	(−0.42)
	29.1	(2.00)	26.4	(−0.07)
$(-)_{589}$[Co(NCS)(gly)(tacn)]$^+$	20.3	(2.31)	17.8	(+0.04)
			21.2	(−0.73)
	—	—	27.0	(+0.12)
$(-)_{589}$[Co(gly)(tacn)(H_2O)]$^{2+}$	20.0	(1.88)	18.2	(+0.10)
			20.6	(−0.14)
	28.0	(1.82)	27.1	(+0.06)
			30.3	(−0.01)
$(-)_{589}$[Co(OH)(gly)(tacn)]$^+$	19.7	(1.91)	17.6	(+0.11)
			20.6	(−0.45)
	27.1	(1.80)	25.4	(−0.09)
$(+)_{589}$[Co(N_3)(gly)(tacn)]$^+$	19.4	(2.32)	18.4	(+0.27)
			20.8	(−1.10)
$(-)_{589}$[Co(Cl)(gly)(tacn)]$^+$	18.6	(2.04)	16.9	(+0.10)
			19.6	(−0.71)
	27.0	(1.97)	26.7	(+0.36)
[Co(I)(gly)(tacn)]$^+$	17.2	(2.20)		

at 21200 cm^{-1} in the T_{1g}-band region, indicating the preferential formation of a fixed conformation (probably δ) of the chelate rings. A similar CD spectrum was observed for $[Co\{(2R\text{-Me})\text{-tacn}\}_2]^{3+}$;[11-13] it shows a very strong positive peak in the T_{1g}-band region, probably as a result of the chiral puckering of the chelate rings with the λ-conformation.[14] This experimental result indicates a small contribution from a fixed conformation to the solution CD spectrum of the present $[Co(a)(gly)(tacn)]^{n+}$ complex. There are two kinds of helical distributions in the $[Co(a)(gly)(tacn)]^{n+}$ complex, however, one is designated Δ, and the other, Λ. Therefore, the optical activity due to the helical distribution is probably very small in the complex.

On the other hand, the CD spectra of $(-)_{589}[Co(gly)(NH_3)(tacn)]^{2+}$ and $(-)_{589}[Co(gly)(NH_3)(tame)]^{2+}$, where tame is a tripod ligand, resemble each other well in both shape and peak intensity; *i.e.*, the $\Delta\varepsilon$ value for the dominant peak of $(-)_{589}[Co(gly)(NH_3)(tacn)]^{2+}$, $\Delta\varepsilon=-0.42$, corresponds well with that of $(-)_{589}[Co(gly)(NH_3)(tame)]^{2+}$, $\Delta\varepsilon=-0.44$. These facts also support the idea that the first and second sources make little contribution to optical activity. Therefore, it may be concluded that the optical activity of $[Co(a)(gly)(tacn)]^{n+}$ is due to the arrangement of the three donors of the glycinate and unidentate ligands.

Absolute Configuration. In order to investigate the relation between the Cotton signs and the absolute configuration on the $[Co(a)(gly)(tacn)]^{n+}$ complexes, we tried to obtain optically active complexes directly from the $(-)_{589}[Co(gly)(tacn)(H_2O)]^{2+}$ complex. The conversions were successful in giving the corresponding $(-)_{589}[Co(NO_2)(gly)(tacn)]^{+}$, $(-)_{589}[Co(NCS)(gly)(tacn)]^{+}$, $(+)_{589}[Co(N_3)(gly)(tacn)]^{+}$, and $(-)_{589}[Co(Cl)(gly)(tacn)]^{+}$ complexes. This fact indicates that the configurations of the gly and tacn ligands are retained in the course of the reaction. The oxidation of the $(-)_{589}[Co(NCS)(gly)(tacn)]^{+}$ complex with aqueous H_2O_2 at *ca.* pH 3 produced $(-)_{589}[Co(gly)(NH_3)(tacn)]^{2+}$, $(-)_{589}[Co(CN)(gly)(tacn)]^{+}$ and $(-)_{589}[Co(gly)(tacn)(H_2O)]^{2+}$ complexes. Similar oxidative degradation reactions have been reported by Gillard and Maskill[15]; $(-)_{589}[Co(NCS)_2(en)_2]^{+}$ was converted into $(-)_{589}[Co(NH_3)_2(en)_2]^{3+}$ and $(-)_{589}[Co(CN)_2(en)_2]^{+}$, and these three complexes have the same absolute configuration. Therefore, the four tacn complexes also have the same absolute configuration.

On the basis of the above results, it is concluded that the earlier-eluted enantiomers, whose major CD peaks have a negative sign, have the same arrangement with respect to the donors of gly and the unidentates (CN^-, NO_2^-, NH_3, NCS^-, H_2O, OH^-, N_3^-, and Cl^-), as is shown in Fig. 6. We can now assign the absolute configurations of $(-)_{589}[Co(gly)(NH_3)(tame)]^{2+}$, $(-)^{CD}_{546}[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$, and $(-)^{CD}_{546}[Co(Nb_6O_{19})(gly)(H_2O)]^{6-}$ complexes,[3,4] which belong to the *fac*(D)-[Co(a)(BC)(DDD)]-type, by comparing the sign of the CD peak in the T_{1g}-band region with that of the $(-)_{589}[Co(gly)(NH_3)(tacn)]^{2+}$ or $(-)_{589}[Co(gly)(tacn)(H_2O)]^{2+}$ complex. Thus, the three complexes, $(-)_{589}[Co(gly)(NH_3)(tame)]^{2+}$, $(-)^{CD}_{546}[Co(Nb_6O_{19})(gly)(NH_3)]^{6-}$ and $(-)^{CD}_{546}[Co(Nb_6O_{19})(gly)(H_2O)]^{6-}$, have the same arrangement with respect to the donors of the glycinate and unidentate ligands, as is shown in Fig. 6.

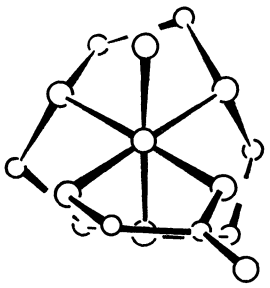

Fig. 6. Absolute configuration of the earlier eluted enantiomer of $[Co(a)(gly)(tacn)]^{n+}$ Complex.

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