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Circular Dichroism Spectra of *fac*(*D*)-[Co(a)(BC)(DDD)]$^{n+}$ Type Complexes with 1,4,7-Triazacyclononane, (2*R*)-2-Methyl-1,4,7-triazacyclononane, and 1,5,9-Triazacyclododecane

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The complexes, $[Co(L\text{-}val)(NH_3)(tacn)]^{2+}$ (tacn=1,4,7-triazacyclononane), $[Co(gly)(NH_3)(Me\text{-}tacn)]^{2+}$ (Me-tacn=(2*R*)-2-methyl-1,4,7-triazacyclononane) have been prepared and separated into diastereomers by column chromatography. Six other complexes, $[Co(a)(\beta\text{-}ala)(tacn)]^{n+}$ (a=CN^-, NO_2^-, or NH_3) and $[Co(a)(gly)(tacdd)]^{n+}$ (a=NO_2^-, NCS^-, or H_2O; tacdd=1,5,9-triazacyclododecane) have also been prepared and resolved into enantiomers. By comparing the CD spectra of the L-valinato and the Me-tacn complexes with that of $[Co(gly)(NH_3)(tacn)]^{2+}$, the optical activities of [Co(a)(gly)(tacn)] $^+$ are considered to be mainly derived from chiral arrangements of four kinds of donor atoms. The change from five-membered chelate ring to a six-membered one has slight influence upon the CD spectral shapes in the β-alaninato complex, but a large influence in the tacdd complexes.

In recent studies on the CD spectra of a series of $[Co(a)(gly)(tacn)]^{n+}$ complexes (a=CN^-, NO_2^-, NH_3, NCS^-, H_2O, OH^-, N_3^-, or Cl^-; tacn=1,4,7-triazacyclononane), it has been concluded that, though two helical ring-pairs exist in the complexes, the optical activities of the complexes are mainly derived from a chiral arrangement of four kinds of donor atoms, each N donor in tacn and gly, O donor in gly, and the donor of a unidentate.[1] In this work, we aimed to confirm the above conclusion by extending the CD spectral studies to various *fac(D)*-$[Co(a)(BC)(DDD)]^{n+}$ complexes which contain tacn, Me-tacn(=(2*R*)-2-methyl-1,4,7-triazacyclononane) or tacdd (=1,5,9-triazacyclododecane) as DDD, and L-val or β-ala as BC. The Me-tacn complex has a preferable conformation due to the orientation of the methyl group. Therefore, the CD spectral comparison between the Me-tacn and tacn complexes will afford information about the conformational contribution to the optical activity in the latter complex. Since the L-valinate ion has a bulky isopropyl group, a large interaction between the substituent and the tacn molecule are anticipated in the $[Co(a)(L\text{-}val)(tacn)]^{n+}$ complex. Six-membered chelate rings exist in the β-alaninato and the tacdd complexes, and the CD spectra of these complexes are interesting to compare with those of $[Co(a)(gly)(tacn)]^{n+}$ which contains five-membered chelate rings.

Experimental

Ligand. 1,4,7-Triazacyclononane trihydrochloride (TACN·3HCl), (2*R*)-2-methyl-1,4,7-triazacyclononane trihydrobromide (Me-TACN·3HBr), and 1,5,9-triazacyclododecane trihydrochloride or trihydrobromide (TACDD·3HCl or TACDD·3HBr) were prepared according to the literatures.[2,3]

Preparation of Complexes. *1) (Ammine)(1,4,7-triazacyclononane)(L-valinato)cobalt(III) Chloride,* $[Co(L\text{-}val)(NH_3)(tacn)]Cl_2$: At first, a $[Co(NCS)(L\text{-}val)(tacn)]^+$ complex was prepared in the same way as a $[Co(NCS)(gly)(tacn)]^+$ complex,[1] by using of *mer(N)-trans(NH$_3$)*-$[Co(CO_3)(L\text{-}val)(NH_3)_2]$[4] (3.5 g, 0.013 mol) and TACN·3HCl (3 g, 0.013 mol). At the second step, the isothiocyanato complex was oxidized with aqueous H_2O_2 (30%) at pH *ca.* 3.[1] The resulting solution was poured onto a column of SP-Sephadex C-25 in Na$^+$ form (3.5 cm×40 cm). The adsorbed band was eluted with a 0.05 mol/dm^3 Na_2SO_4 solution, and an orange band containing aimed bivalent cation was collected in a fraction. The effluent was concentrated at 40 °C and the eluting agent removed.

One fourth of the concentrate was dissolved in a large amount of water, and poured onto a column of SP-Sephadex C-25 in Na$^+$ form (2.5 cm×70 cm). By eluting with 0.075 mol/dm^3 $K_2[Sb_2(d\text{-}tart)_2]$, the adsorbed band was separated into two components which were labelled E1 and E2 in the order of elution (these labels were also used to designate the isomers contained in each band). When the E1 band had descended to the neighborhood of the outlet of the column, the two bands were washed with water and then eluted with a 0.1 mol/dm^3 NaCl solution. The two bands were collected in each fraction. This procedure was repeated for the residual portion of the concentrate. The combined fractions were concentrated, and the eluting agent which precipitated was removed by repeated filtration. To the final filtrate was added a small amount of ethanol, and the whole was kept in a refrigerator. The crude products were recrystallized from warm water. The yield was *ca.* 0.05 g for E1, and 0.1 g for E2. Found for E1: C, 30.64; H, 7.36; N, 16.33%. Calcd for $[Co(L\text{-}val)(NH_3)(tacn)]Cl_2\cdot 2H_2O = C_{11}H_{32}N_5O_4Cl_2Co$: C, 30.85; H, 7.53; N, 16.35%. Found for E2: C, 31.83; H, 7.07; N, 17.16%. Calcd for $[Co(L\text{-}val)(NH_3)(tacn)]Cl_2\cdot H_2O = C_{11}H_{30}N_5O_3Cl_2Co$: C, 32.21; H, 7.37; N, 17.07%.

2) (Ammine)(glycinato)[(2R)-2-methyl-1,4,7-triazacyclononane]cobalt(III) Perchlorate, $[Co(gly)(NH_3)(Me\text{-}tacn)](ClO_4)_2$: This complex was prepared in the same manner as a $[Co(gly)(NH_3)(tacn)]^{2+}$ complex,[1] except for the use of Me-TACN·3HCl in place of TACN·3HCl.

The reaction mixture was poured onto a column of Dowex 50W-X8 in H$^+$ form (5.5 cm×10 cm), and the adsorbed band was eluted by a 0.5 mol/dm^3 H_2SO_4 solution. The descended orange band was collected in a fraction, and the eluate was adjusted to pH 6 by $BaCO_3$. After filtration, the filtrate was concentrated, and small amount of ethanol was added to the concentrate. The whole system was kept in a refrigerator. The yield was about 0.1 g. Found: C, 26.31; H, 6.73; N, 17.28%. Calcd for $[Co(gly)(NH_3)(Me\text{-}tacn)]SO_4\cdot H_2O = C_9H_{26}O_7N_5SCo$: C, 26.53; H, 6.45; N, 17.19%.

The orange crystals obtained were dissolved in water and the solution was subjected to a column chromatography on SP-Sephadex C-25 in Na$^+$ form (2.5 cm×110 cm). By elution with 0.05 mol/dm^3 $K_2[Sb_2(d\text{-}tart)_2]$, the adsorbed band was separated into three bands which were labelled B1, B2, and B3 in the order of elution (these labels were also used to designate the isomers contained in each band). When the B1 band had descended to the neighborhood of the outlet of the column, the band was washed with water and then eluted with a 0.1 mol/dm^3 NaCl solution. The absorption and CD spectra of the effluents were measured and the metal-concentrations were evaluated by atomic absorption spectrophotometry.

3) (β-Alaninato) (nitro) (1,4,7-triazacyclononane) cobalt (III) Chloride Dihydrate, $[Co(NO_2)(\beta\text{-}ala)(tacn)]Cl\cdot 2H_2O$: At the first step, a $[Co(\beta\text{-ala})(H_2O)(tacn)]^{2+}$ complex was prepared similarly to a $[Co(gly)(H_2O)(tacn)]^{2+}$ complex.1) The aqua complex could not be isolated because of the great solubility of the species in water. At the next step, a $[Co(NO_2)(\beta\text{-ala})(tacn)]^+$ complex was derived from the aqua complex, according to the literature method.1) Found: C, 27.41; H, 6.51; N, 17.48%. Calcd for $[Co(NO_2)(\beta\text{-ala})(tacn)]Cl\cdot 2H_2O = C_9H_{25}N_5O_6ClCo$: C, 27.45; H, 6.41; N, 17.79%.

4) (β-Alaninato) (ammine) (1,4,7-triazacyclononane) cobalt (III) Perchlorate Monohydrate, $[Co(\beta\text{-}ala)(NH_3)(tacn)](ClO_4)_2\cdot H_2O$: This complex was derived from the above $[Co(\beta\text{-ala})(H_2O)(tacn)]^{2+}$ complex in the same manner as in the $[Co(gly)(NH_3)(tacn)]^{2+}$ complex.1) Found: C, 21.13; H, 5.18; N, 13.63%. Calcd for $[Co(\beta\text{-ala})(NH_3)(tacn)](ClO_4)_2\cdot H_2O = C_9H_{26}N_5O_{11}Cl_2Co$: C, 21.18; H, 5.15; N, 13.73%.

5) (β-Alaninato) (cyano) (1,4,7-triazacyclononane) cobalt (III) Perchlorate, $[Co(CN)(\beta\text{-}ala)(tacn)]ClO_4$: This complex was also prepared similarly to the $[Co(CN)(gly)(tacn)]^+$ complex,1) starting from the $[Co(\beta\text{-ala})(H_2O)(tacn)]^{2+}$ by way of $[Co(Cl)(\beta\text{-ala})(tacn)](NO_3)$. The complex was isolated by column chromatography (SP-Sephadex C-25, 4.5 cm × 25 cm, Na$^+$ form, by use of 0.05 mol/dm^3 NaClO$_4$ as eluent). Found: C, 29.62; H, 5.28; N, 17.56%. Calcd for $[Co(CN)(\beta\text{-ala})(tacn)]ClO_4 = C_{10}H_{21}N_5O_6ClCo$: C, 29.89; H, 5.28; N, 17.44%.

6) (Glycinato) (isothiocyanato) (1,5,9-triazacyclododecane) cobalt (III) Bromide 1,5-Hydrate, $[Co(NCS)(gly)(tacdd)]Br\cdot 1.5H_2O$: A $[Co(gly)(H_2O)(tacdd)]^{2+}$ complex was first prepared by use of *mer(N)-trnas(NH$_3$)*-$[Co(CO_3)(gly)(NH_3)_2]$5) (0.8 g, 0.0036 mol) and TACDD·3HCl (1 g, 0.0036 mol), by the method similar to that for the $[Co(gly)(H_2O)(tacn)]^{2+}$ complex.1) Crystallization of the aqua complex was unsuccessful because of a great solubility of the complex species in water.

An isothiocyanato complex was then derived from the aqua complex in the same way as the $[Co(NCS)(gly)(tacn)]^+$ complex,1) with slight modifications; an aqueous solution (20 cm^3) containing the aqua complex which had been prepared at 0.01 mol scale was adjusted to pH 2 with 20% HClO$_4$, after which KSCN (1.5 g, 0.015 mol) was added to the solution. The mixture was stirred at *ca.* 50 °C for 2 h. The resulting solution was poured onto a column of SP-Sephadex C-25 in Na$^+$ form (4.5 cm × 30 cm). The adsorbed band was eluted with a 0.03 mol/dm^3 NaBr solution, and a red-violet band which descended was collected in a fraction. The eluate was concentrated by means of a rotary evaporator at 35 °C. After addition of ethanol, the solution was kept in a refrigerator. The crystal deposited was recrystallized from water. The yield was *ca.* 0.3 g. Found: C, 30.44; H, 6.06; N, 15.15%. Calcd for $[Co(NCS)(gly)(tacdd)]Br\cdot 1.5H_2O = C_{12}H_{28}N_5O_{3.5}SBrCo$: C, 30.71; H, 6.01; N, 14.92%.

7) (Glycinato) (nitro) (1,5,9-triazacyclododecane) cobalt (III) Bromide, $[Co(NO_2)(gly)(tacdd)]Br$: This complex was prepared by the same method as a $[Co(NO_2)(gly)(tacn)]^+$ complex,1) except for the use of $[Co(gly)(H_2O)(tacdd)]^{2+}$ which had been prepared at 0.01 mol scale. The yield was *ca.* 0.3 g. Found: C, 30.48; H, 5.76; N, 16.00%. Calcd for $[Co(NO_2)(gly)(tacdd)]Br = C_{11}H_{25}N_5O_4BrCo$: C, 30.71; H, 5.76; N, 16.28%.

8) Trinitro(1,5,9-triazacyclododecane)cobalt(III), $[Co(NO_2)_3(tacdd)]$: This complex was prepared by the same procedure as a $[Co(NO_2)_3(tacn)]$ complex,6) except for the use of TACDD·3HBr in place of TACN·3HBr. The crystals deposited in the course of the reaction were washed with a small amount of water. Starting from 0.1 mol TACDD·3HBr (2.96 g), the yield was *ca.* 0.1 g. Found: C, 29.26; H, 5.68; N, 22.79%. Calcd for $[Co(NO_2)_3(tacdd)] = C_9H_{21}N_6O_6Co$: C, 29.36; H, 5.75; N, 22.82%.

Optical Resolution. The three β-alaninato complexes, $[Co(CN)(\beta\text{-ala})(tacn)]^+$, $[Co(NO_2)(\beta\text{-ala})(tacn)]^+$, and $[Co(\beta\text{-ala})(NH_3)(tacn)]^{2+}$, were resolved into each optical antipodes by means of a column chromatography of SP-Sephadex C-25 (2.5 cm × 110 cm, Na$^+$ form), using 0.05 mol/dm^3 $K_2[Sb_2(d\text{-tart})_2]$ as eluent. Total resolution was attained for the ammine complex, and partial resolutions, for the cyano and nitro complexes.

All of the tacdd complexes were also resolved by means of a column chromatography of SP-Sephadex C-25 in Na$^+$ form (2.5 cm × 110 cm, for the nitro and isothiocyanato complexes; 2.5 cm × 130 cm, for the aqua complex). Total resolutions were attained for the nitro and isothiocyanato complexes, when the elutions were performed with 0.075 mol/dm^3 and 0.15 mol/dm^3 (saturated) $K_2[Sb_2(d\text{-tart})_2]$ solutions, respectively. As to the aqua complex, a 0.15 mol/dm^3 $Na_2[Sb_2(d\text{-tart})_2]$ solution was used as eluent. When each adsorbed band descended to four-fifths of the column height, the band was sufficiently washed with water and eluted with 0.1 mol/dm^3 NaCl or NaClO$_4$. The effluents were concentrated and submitted to the measurement of CD spectra, while the concentrations of the complex species were evaluated from the absorption spectral data.

Derivations from Optically Active Complex. $(+)^{CD}_{500}[Co(NO_2)(gly)(tacdd)]^+$ and $(+)^{CD}_{500}[Co(NCS)(gly)(tacdd)]^+$ could be derived from $(-)^{CD}_{500}[Co(gly)(H_2O)(tacdd)]^{2+}$ in the same way as described in *6)* and *7)*.

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. As to $[Co(gly)(H_2O)(tacdd)]^{2+}$ and $[Co(gly)(NH_3)(Me\text{-tacn})]^{2+}$, a Hitachi 170-50 Atomic Absorption Spectrophotometer was used in order to evaluate the metal-concentration.

Results and Discussion

1) The $[Co(\text{L-}val)(NH_3)(tacn)]^{2+}$ Complex. As described in Experimental, the $[Co(\text{L-val})(NH_3)(tacn)]^{2+}$ complex was prepared by oxidation of a $[Co(\text{L-val})(NCS)(tacn)]^+$ complex. When the reaction mixture of $[Co(\text{L-val})(H_2O)(tacn)]^+$ and ammonia under the conditions of pH > 10 and 60 °C was chromatographed on SP-Sephadex C-25 column, four bands of $[Co(val)(NH_3)(tacn)]^{2+}$ species appeared. The same situation was encountered by use of D-val. These facts showed that racemization of chelating L (or D)-valinate ion took place. On the other hand, aimed two diastereomers were obtained by the reaction of $[Co(\text{L-val})(NCS)(tacn)]^+$ with H_2O_2 in an acidic solution.

The absorption and CD spectra of the diastereomers are shown in Fig. 1, and numerical data are summarized in Table 1. The calculated vicinal and configurational contribution curves of the L-valinato complex are illustrated in Fig. 2. The vicinal contribution curve resembles that of $[Co(L\text{-}val)(NH_3)_4]^{2+}$,[7] and the configurational contribution curve is similar to that of $(-)_{589}[Co(gly)(NH_3)(tacn)]^{2+}$.[1] This fact indicates that the earlier eluted isomer (E1) has the same absolute configurations as the $(-)_{589}[Co(gly)(NH_3)(tacn)]^{2+}$ isomer,[1,8] and that there is slight interaction between the isopropyl group of chelated L-val and the tacn rings. In other words, the orientation of the isopropyl group does not have much influence on the d-electron optical activity of the L-valinato complex. On this basis, it is considered that the interaction between the CH_2 group of glycinato ligand and the tacn chelate rings is small in the $(-)_{589}$-$[Co(gly)(NH_3)(tacn)]^{2+}$ complex.

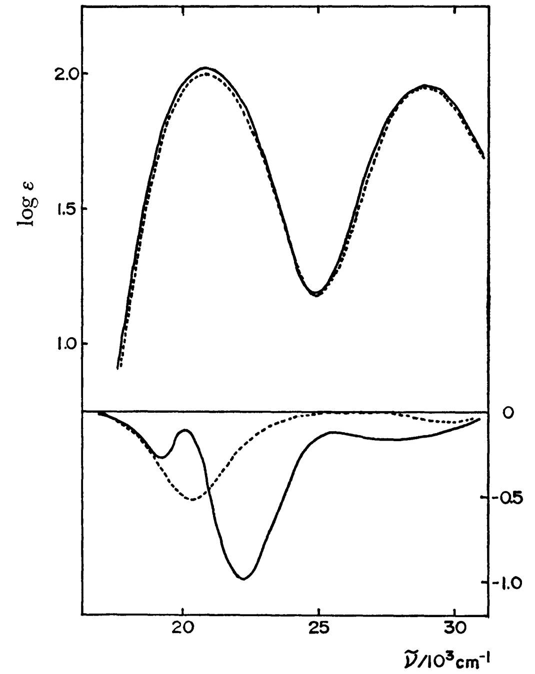

Fig. 1. Absorption and CD spectra of $[Co(L\text{-}val)(NH_3)(tacn)]^{2+}$, E1 (——), E2 (······).

2) The $[Co(gly)(NH_3)(Me\text{-}tacn)]^{2+}$ *Complex.* There are two coordination modes of Me-tacn, as shown in Fig. 3 (I). In the both modes, the C–CH_3

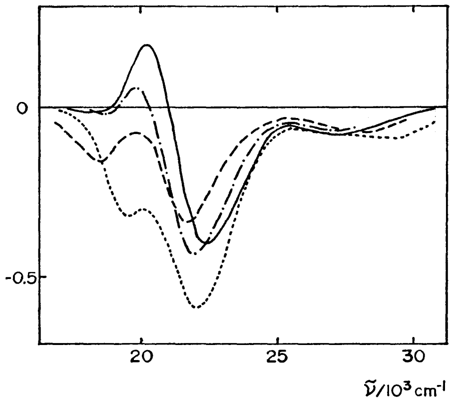

Fig. 2. Calculated configurational and vicinal contribution curves of $[Co(L\text{-}val)(NH_3)(tacn)]^{2+}$, $[\Delta\varepsilon(E1)-\Delta\varepsilon(E2)]/2$; configurational contribution curve (——), $[\Delta\varepsilon(E1)+\Delta\varepsilon(E2)]/2$; vicinal contribution curve (······), $(-)_{589}[Co(gly)(NH_3)(tacn)]^{2+}$ (·—·—), $[Co(L\text{-}val)(NH_3)_4]^{2+}$ (- - -).

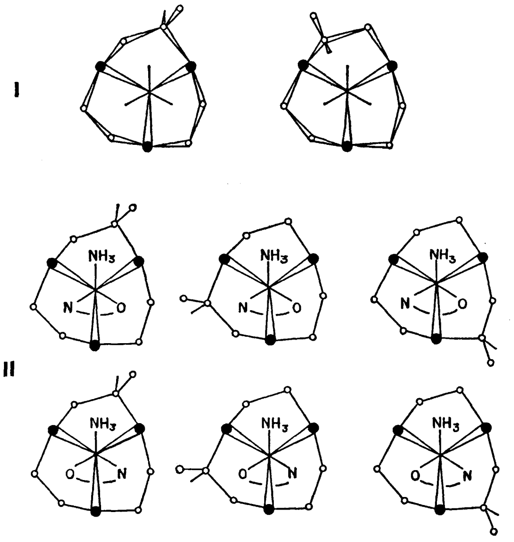

Fig. 3. Possible isomers of $[Co(gly)(NH_3)(Me\text{-}tacn)]^{2+}$.

TABLE 1. ABSORPTION AND CD SPECTRAL DATA OF $[Co(L\text{-}val)(NH_3)(tacn)]^{2+}$ AND $[Co(gly)(NH_3)(Me\text{-}tacn)]^{2+}$ COMPLEXES

Complex	Absorption $\tilde{\nu}/10^3\ cm^{-1}$ (log ε)	CD $\tilde{\nu}/10^3\ cm^{-1}$ (Δε)
$[Co(L\text{-}val)(NH_3)(tacn)]^{2+}$ (E1)	20.8 (2.02)	19.2 (−0.26) 22.2 (−0.98)
	29.0 (1.96)	27.8 (−0.17)
$[Co(L\text{-}val)(NH_3)(tacn)]^{2+}$ (E2)	20.8 (1.99) 29.0 (1.95)	20.2 (−0.51) 29.9 (−0.06)
$[Co(gly)(NH_3)(Me\text{-}tacn)]^{2+}$ (B1)	20.7 (1.95) 29.0 (1.99)	20.6 (1.28) 27.0 (0.05) 29.3 (−0.07)
$[Co(gly)(NH_3)(Me\text{-}tacn)]^{2+}$ (B2)	20.7 (1.95) 29.0 (1.99)	20.5 (1.29) 27.0 (0.07) 29.4 (−0.06)
$[Co(gly)(NH_3)(Me\text{-}tacn)]^{2+}$ (B3)	20.8 (1.97) 29.0 (2.01)	21.6 (1.15) 27.0 (0.16)

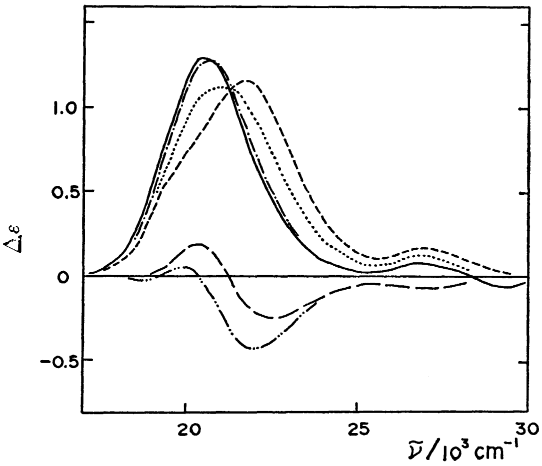

Fig. 4. CD spectra of $[Co(gly)(NH_3)(Me\text{-}tacn)]^{2+}$, B1 (·—·—), B2 (——), B3 (- - -), $[\Delta\varepsilon(B1)+\Delta\varepsilon(B3)]/2$ (······), $[\Delta\varepsilon(B1)-\Delta\varepsilon(B3)]/2$ (— —), $(-)_{589}[Co(NH_3)(gly)(tacn)]^{2+}$ (··—··—).

bond in Me-tacn is directed to the equatorial position with respect to a mean plane of three chelate rings of Me-tacn and the chelate conformations are fixed to λ, but the configuration of the coordinated secondary nitrogen atoms in one mode is opposite to that in another mode. Since six diastereomers are possible for one mode (Fig. 3 (II)), twelve diastereomers may exist in the $[Co(gly)(NH_3)(Me\text{-}tacn)]^{2+}$ complex. The column chromatography separated three isomers of the complex, the distance between bands B1 and B2 being much smaller than that between bands B2 and B3.

The CD spectra of the diastereomers are shown in Fig. 4. The spectrum of B1 is similar to that of B2, but different from that of B3. It is assumed that the isomers with different configuration with respect to the arrangement of donor atoms are easily separable compared with those due to coordination modes or relative positions of the methyl group of Me-tacn. Therefore, the configuration of B1 is considered to be the same as that of B2 and opposite to that of B3. The conformational and vicinal contribution curve of $[Co(gly)(NH_3)(Me\text{-}tacn)]^{2+}$ was tentatively calculated from Eq. 1 and the configurational contribution curve, from Eq. 2.

$$[\Delta\varepsilon(B1\ or\ B2) + \Delta\varepsilon(B3)]/2 \qquad (1)$$

$$[\Delta\varepsilon(B1\ or\ B2) - \Delta\varepsilon(B3)]/2 \qquad (2)$$

As is seen in Fig. 4, the intensity of the resultant curve from Eq. 1 is higher than that of the resultant curve from Eq. 2. This corresponds to the large vicinal and conformational effects in the $[Co(Me\text{-}tacn)_2]^{3+}$ complex, the $\Delta\varepsilon$ values in the first absorption band region being *ca.* 5.[9] The calculated configurational contribution curve resembles the CD spectrum of $(-)_{589}[Co(gly)(NH_3)(tacn)]^{2+}$. However, the weak Cotton peak of the tacn complex observed at the lowest frequency in the first absorption band region disappeares at the calculated curve. From these observations, it is concluded that no fixed chiral conformation of chelated tacn exists in aqueous solution of $[Co(gly)(NH_3)(tacn)]^{2+}$, as described in the previous paper.[1]

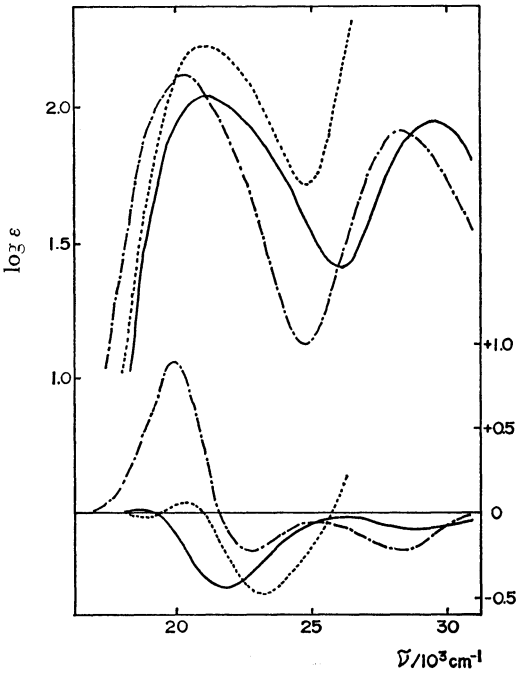

Fig. 5. Absorption and CD spectra of, $(-)^{CD}_{450}[Co(CN)(\beta\text{-}ala)(tacn)]^{+}$ (——), $(-)^{CD}_{450}[Co(NO_2)(\beta\text{-}ala)(tacn)]^{+}$ (······), $(+)_{589}[Co(\beta\text{-}ala)(NH_3)(tacn)]^{2+}$ (·—·—).

3) The $[Co(a)(\beta\text{-}ala)(tacn)]^{n+}$ *Complexes.* The β-alaninato complexes were prepared similarly to the glycinato complexes. By chromatography on SP-Sephadex C-25, total resolution was achieved for the ammine complex, $[Co(\beta\text{-}ala)(NH_3)(tacn)]^{2+}$, and partial resolution for the cyano and nitro complexes. The CD spectra of the earlier eluted isomers of these complexes are shown in Fig. 5, and numerical data are listed in Table 2. The $(+)_{589}[Co(\beta\text{-}ala)(NH_3)(tacn)]^{2+}$ isomer exhibits two Cotton peaks with + and − signs from the lower frequency side in the first absorption band region, the positive peak being dominant. On the other hand, the corresponding $(-)_{589}[Co(gly)(NH_3)(tacn)]^{2+}$ isomer exhibits three Cotton peaks with −, +, and − signs from the lower frequency side, the negative peak at the highest frequency being dominant.[1] For the nitro complexes, both the $(-)_{589}$-glycinato and $(-)^{CD}_{450}$-β-alaninato complexes exhibit −, +, and − peaks in the first absorption band region. The CD spectrum of the $(-)_{589}[Co(CN)(gly)(tacn)]^{+}$ complex shows a negative Cotton peak, and that of the $(-)^{CD}_{450}[Co(CN)(\beta\text{-}ala)(tacn)]^{+}$ shows two peaks with opposite signs, the positive peak at the lower frequency being extremely weak. By comparison with the Cotton sign at the highest frequency, the absolute configurations of the earlier eluted isomers of $[Co(a)(\beta\text{-}ala)(tacn)]^{n+}$ ($a=NH_3$, NO_2^-, or CN^-) are assumed to be the same as those of the corresponding $(-)_{589}[Co(a)(gly)(tacn)]^{n+}$ isomers.[1]

To confirm the above assumption, we attempted to determine the absolute configuration of $(-)_{589}[Co(\beta\text{-}ala)(NH_3)(tacn)](ClO_4)_2\cdot HClO_4$, by an X-ray analysis. This was crystallized from the later eluted band. The absolute configuration found is shown in Fig. 6

TABLE 2. ABSORPTION AND CD SPECTRAL DATA OF THE EARLIER-ELUTED ENANTIOMERS

Complex	Absorption $\tilde{\nu}/10^3$ cm^{-1} (log ε)	CD $\tilde{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$)
$(-)^{CD}_{450}$[Co(NO$_2$)(β-ala)(tacn)]$^+$	21.0 (2.23)	18.6 (−0.01)
		20.3 (0.07)
		23.2 (−0.47)
	30.3 (3.19)	
$(+)_{589}$[Co(β-ala)(NH$_3$)(tacn)]$^{2+}$	20.3 (2.12)	20.0 (0.89)
		22.7 (−0.22)
	28.3 (1.91)	28.1 (−0.21)
$(-)^{CD}_{450}$[Co(CN)(β-ala)(tacn)]$^+$	21.1 (2.05)	18.7 (0.02)
		21.8 (−0.43)
	29.4 (1.94)	29.0 (−0.10)
$(-)^{CD}_{500}$[Co(NCS)(gly)(tacdd)]$^+$	19.1 (2.22)	19.4 (−0.65)
	31.0 (3.23 sh)	25.0 (0.08)
	41.6 (4.31)	
$(-)^{CD}_{500}$[Co(NO$_2$)(gly)(tacdd)]$^+$	20.1 (2.10)	19.5 (−0.30)
	29.4 (3.28)	22.0 (−0.17 sh)
	38.6 (4.35)	
$(-)^{CD}_{500}$[Co(gly)(H$_2$O)(tacdd)]$^{2+}$	19.2 (1.94)	17.6 (0.03)
		20.0 (−0.17)
	27.2 (1.93)	

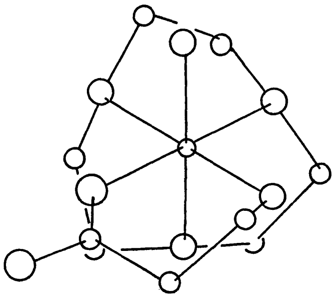

Fig. 6. Absolute configuration of $(-)_{589}$[Co(β-ala)(NH$_3$)(tacn)]$^{2+}$ complex.

(details will be published elsewhere). The structure of the complex closely resembles that of the corresponding glycinato complex.[7] However, the absolute configuration of the β-alaninato complex is opposite to that of the $(-)_{589}$-glycinato complex. In the previous work,[1] the absolute configuration of the [Co(a)(gly)(tacn)]$^{n+}$ complexes was determined on the basis of the Cotton sign of the dominant peak in the first absorption band region. In the present work, the absolute configuration of [Co(a)(amino acidato)(tacn)]$^{n+}$ can be determined not by the Cotton sign of dominant peak, but by the Cotton sign at the highest frequency.

A change from the five-membered glycinate chelate ring to the six-membered β-alaninate one causes the CD spectral shape to vary somewhat, especially, on the lower frequency side of the first absorption band region. It was previously assumed[1] that the optical source of the helical distributions of a NH$_2$–CH$_2$–COO$^-$ chelate and –NH–CH$_2$–CH$_2$–NH– moieties of tacn had a small contribution to the optical activity of [Co(a)(gly)(tacn)]$^{n+}$, since the two helical ring-pairs canceled each other. The CD spectra of the β-alaninato complexes suggest that such cancellation is incomplete, but the spectra also indicate that the contribution of the helical ring-pairs is small. Thus, the main optical activities of the tacn complexes are considered to be derived from chiral arrangements of the donor atoms.

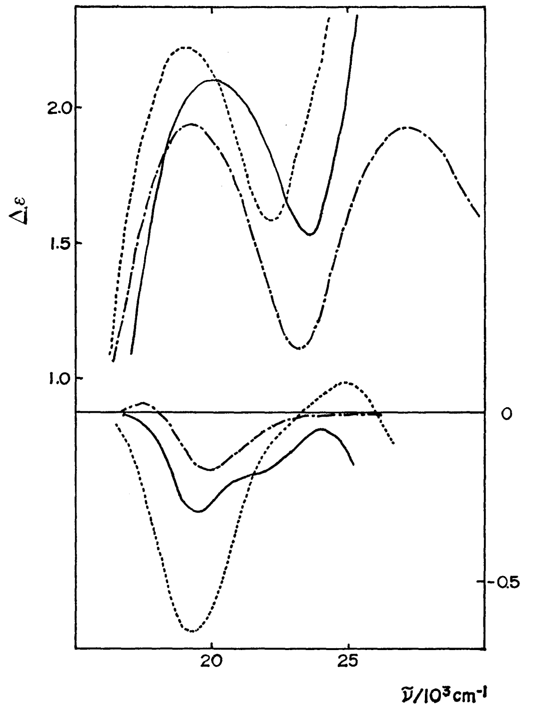

Fig. 7. Absorption and CD spectra of, $(-)^{CD}_{500}$[Co(NO$_2$)(gly)(tacdd)]$^+$ (——), $(-)^{CD}_{500}$[Co(NCS)(gly)(tacdd)]$^+$ (······), $(-)^{CD}_{500}$[Co(gly)(H$_2$O)(tacdd)]$^{2+}$ (·—·—).

4) The [Co(a)(gly)(tacdd)]$^{n+}$ Complexes. Absorption and CD spectra of [Co(NO$_2$)(gly)(tacdd)]$^+$, [Co(NCS)(gly)(tacdd)]$^+$ and [Co(gly)(H$_2$O)(tacdd)]$^{2+}$ are shown in Fig. 7. At present, there are few complexes containing the tacdd ligand,[10 11] and the ligand field strength of this ligand has not been reported. The [Co(NO$_2$)(gly)(tacdd)]$^+$ complex exhibits the first absorption band at 20100 cm^{-1}, and the related [Co(NO$_2$)(gly)(tacn)]$^+$ and *fac(NH$_3$)*-[Co(NO$_2$)(gly)-

$(NH_3)_3]^+$,[12] at 21800 cm^{-1} and 20900 cm^{-1}, respectively. On this basis, it is found that the ligand field strengths decrease in the order, tacn>NH_3>tacdd. To obtain a ligand field parameter of tacdd (Δ(tacdd)$=3e_\sigma$), we prepared trinitro complex, $[Co(NO_2)_3(tacdd)]$, which exhibited an absorption maximum at 21300 cm^{-1} ($\log \varepsilon=2.21$). Since the absorption maximum of $[Co(NO_2)_3(tacn)]$ appears at 22700 cm^{-1}, the following relation of the ligand field parameters can be derived from an angular overlap model;[13]

$$\Delta(\text{tacdd}) = \Delta(\text{tacn}) - 2800\,(\text{cm}^{-1}).$$

The earlier eluted $(-)^{CD}_{500}[Co(NO_2)(gly)(tacdd)]^+$ complex exhibits a negative Cotton peak and a shoulder peak in the first absorption band region. The net rotatory strength of the tacdd complex is negative as well as that of the tacn complex, but the spectral shape is very different from that of the tacn complex. The CD spectra of the earlier eluted isomers, $(-)^{CD}_{500}$-$[Co(NCS)(gly)(tacdd)]^+$ and $(-)^{CD}_{500}[Co(gly)(H_2O)$-$(tacdd)]^{2+}$, show a single peak and two peaks, respectively, which resemble those of the corresponding isomers of the tacn complexes.

In the case of the tacn complexes, the earlier eluted isomers are all of the same absolute configuration.[1] This is not the case for the tacdd complexes, since the later eluted isomers, $(+)^{CD}_{500}[Co(NO_2)(gly)(tacdd)]^+$ and $(+)^{CD}_{500}[Co(NCS)(gly)(tacdd)]^+$, are derived from the earlier eluted $(-)^{CD}_{500}[Co(gly)(H_2O)(tacdd)]^{2+}$ isomer. Therefore, we were unable to determine the absolute configuration of the tacdd complexes, by CD comparison with the tacn complexes.

The reason why the CD spectra of the tacdd complexes are different from those of the corresponding acn complexes seems to be due to a large repulsive interaction between the bulky tacdd chelate and the glycinato chelate. The interaction may induce the presence of a chiral conformation of the tacdd chelate rings. It is interesting that the change from five-membered glycinate to six-membered β-alaninate chelate ring brings about only a slight variation of the CD spectral shapes, while the change from five-membered tacn to six-membered tacdd chelate ring causes a large variation. This suggests that non-ligating atoms of cyclic terdentate ligands somewhat influence the optical activity of the complexes.

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