Stereoselectivity in Mixed Tris-type Complexes of Cobalt(III) with L-Proline and L- or D-Aspartic Acid[1]

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Mixed complexes with L-proline and L- or D-aspartic acid, $[Co(L\text{-pro})_{3-n}(L\text{-(or D-)asp})_n]^{n-}$ (n=1,2), have been prepared and separated into a number of stereoisomers by means of ion-exchange chromatography. The structures of the isomers have been characterized by various spectral data. As to the $[Co(L\text{-pro})(D\text{-asp})_2]^{2-}$ and $[Co(L\text{-pro})_2(D\text{-asp})]^-$ complexes, all of three possible *mer*-isomers have been isolated in their Δ-forms. The formation ratios among the isomeric species in the reaction system have been estimated spectrophotometrically. Marked differences in stereoselectivity have been found between the L-aspartato complexes and the corresponding D-aspartato complexes. These selectivities have been qualitatively explained in terms of the interaction between the dangling β-carboxylate group in a chelated aspartate ion and the adjacent ligand.

Through several experiments on the stereoselectivity in mixed-ligand complexes of cobalt(III) containing L-aspartic acid as a bidentate ligand, we have isolated a number of complexes and ascertained their stereoselective formations in various degrees.[2-5] In comparison with these aspartato complexes, the mixed complexes containing L-glutamic acid have also been investigated.[6] On the other hand, Denning and Piper[7] have obtained three of the four possible isomers of tris(L-prolinato)cobalt(III) in different yields; they have said that the absence of one isomer (*i.e.*, *mer*-Λ) is predictable on steric grounds. Yasui *et al.*[8] have obtained only one isomer (*i. e.*, *fac*-Λ), consistent with the consideration of the molecular models.

Thus, in the present work L- or D-aspartic acid and L-proline were chosen as the ligands. That is, two series of complexes, $[Co(L\text{-pro})_{3-n}(L\text{-asp})_n]^{n-}$ and $[Co(L\text{-pro})_{3-n}(D\text{-asp})_n]^{n-}$ (n=1,2), have been prepared, and their diastereoisomers have been isolated. These isomers have been characterized on the basis of the spectral data; the degree of the stereoselectivity has also been evaluated spectrometrically.

Experimental

Preparations. Freshly prepared (7.2 g, 0.02 mol) sodium tricarbonatocobaltate(III) trihydrate[9] and 4.6 g (0.04 mol) of L-proline were dissolved in 50 ml of water; the mixture was then stirred at 60 °C for 2 hr, whereupon the solution became blue-violet in color. Then, 4.0 g (0.03 mol) of L-aspartic acid was added to the above solution. After activated charcoal (1.0 g) had then been added, the reaction mixture was stirred for an additional 3 hr at 60 °C; the solution turned red-violet, and a small amount of a water-insoluble material was precipitated. After the removal of the precipitates and charcoal by filtration, the filtrate was passed through a column containing a cation-exchange resin in hydrogen form (Dowex 50W-X8, 100—200 mesh). By this treatment, the coexisting $[CoCO_3(L\text{-pro})_2]^-$ species was converted to a cationic species, which was adsorbed on the column. The effluent was adjusted to pH ~8.5 with an aqueous solution of sodium hydroxide. The resulting solution was charged on an anion-exchange resin column containing 100—200 mesh Dowex 1-X8 in chloride form (column diameter, 7.0 cm; resin height, 45 cm). The same experiment was then carried out using D-aspartic acid instead of L-aspartic acid.

When water was passed through the column, a non-charged tris(L-prolinato)cobalt(III) complex flowed out. Then, chromatographic separation was carried out with a $CaCl_2$ solution (prepared initially in 0.03 M and finally in 0.05 M) at the rate of *ca.* 0.5 ml/min. Through the prolonged elutions, five bands for the L-aspartato-L-prolinato series complexes and ten bands for the D-aspartato-L-prolinato series complexes were separated. These eluted bands were collected in fractions and labeled from L-1 to L-5 for the L-aspartato complexes and from D-1 to D-10 for the D-aspartato complexes, according to the elution order. The four fractions of L-1, L-3, D-5 and D-10 were colored red, and the other fractions, violet. Except the L-2, L-5 and D-4 fractions, each of the other fraction was concentrated to a small volume under reduced pressure at a temperature below 35 °C. Ethanol was added to the concentrate to precipitate calcium salt of the desired isomer. This crude salt was dissolved in a small amount of water, and then the solution was passed through a column containing Dowex 50W-X8 resin in hydrogen form. By this chromatographic procedure, each salt obtained from the L-3 and D-3 fractions was separated into two bands, alternately colored violet and red. These were again labeled as L-3′ and L-3″, and as D-3′ and D-3″. All the effluents thus obtained were evaporated to dryness at 35 °C, and the following procedures were employed. Each residue of the D-2, D-3′, D-5, D-7, and D-8 fractions was dissolved in a minimum amount of water, and acetone was added. After that, the solution was kept in an ice-box for several days to crystallize a hydrogen compound of each isomer. On the other hand, each residue of the L-1, L-3″, D-1, D-3″, D-6, D-9, and D-10 fractions was dissolved in an aqueous solution slightly alkalined with a Na_2CO_3 solution; the solution was then acidified with aqueous hydrochloric acid to precipitate the desired isomer as the hydrogen compound. Each residue obtained from the L-3′ and L-4 fractions was dissolved in a minimum amount of water, after which the solution was passed again through a Dowex 50W-X8 column in hydrogen form. The effluent was evaporated

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TABLE 1. ELEMENTAL ANALYSES, ABSORPTION[a] AND CD[a] SPECTRAL DATA

Label	Complex	Elemental anal., %[b] C	H	N	Band I $10^{-3}\nu_{max}$ cm^{-1}	ε_{max}	Band II $10^{-3}\nu_{max}$ cm^{-1}	ε_{max}	CD $10^{-3}\nu_{max}$ cm^{-1}	$\Delta\varepsilon_{max}$
L-1	*fac*-*Δ*-[Co(L-pro)$_2$ (L-aspH)]·2H$_2$O	37.03 (36.93)	6.09 (5.76)	8.88 (9.23)	19.19	118	26.52	126	18.08	−1.63
L-2	*mer*-*Δ*-Ca$_{1/2}$[Co(L-pro)$_2$ (L-asp)]·0.5 H$_2$O	37.60 (37.59)	5.46 (4.96)	9.36 (9.39)	*ca.* 19.0	92	26.65	139	17.86	−2.25
L-3′	*mer*-1-*Δ*-[Co(L-pro) (L-aspH)$_2$]·1.5H$_2$O	33.85 (33.63)	4.98 (4.99)	9.25 (9.05)	*ca.* 18.8	105	26.74	157	18.52	−1.89
L-3″	*fac*-*Δ*-[Co(L-pro) (L-aspH)$_2$]·2H$_2$O	33.50 (32.99)	5.33 (5.11)	8.71 (8.88)	19.31	141	26.67	122	18.42	−1.71
L-4	*mer*-2-*Δ*-[Co(L-pro) (L-aspH)$_2$]·H$_2$O	34.42 (34.30)	4.95 (4.87)	9.23 (9.23)	*ca.* 18.9	126	26.80	183	18.28	−2.28
L-5	*mer*-*Λ*-[Co(L-pro) (L-aspH)$_2$]·0.5H$_2$O	35.00 (34.99)	5.16 (4.74)	9.34 (9.42)	*ca.* 18.7	128	26.93	186	19.12	+3.91
D-1	*mer*-*Λ*-[Co(L-pro)$_2$ (D-aspH)]·*n*H$_2$O[c]	—	—	—	*ca.* 18.9	—	26.67	—	19.27	+
D-2	*mer*-1-*Δ*-[Co(L-pro)$_2$ (D-aspH)]·0.5H$_2$O	39.22 (39.26)	5.98 (5.41)	9.92 (9.81)	*ca.* 18.7	115	26.60	175	18.21	−2.73
D-3′	*mer*-2-*Δ*-[Co(L-pro)$_2$ (D-aspH)]·H$_2$O	38.47 (38.45)	5.97 (5.53)	9.52 (9.61)	*ca.* 19.1	109	26.58	171	18.21	−2.97
D-3″	*fac*-*Δ*-[Co(L-pro)$_2$ (D-aspH)]·2H$_2$O	37.29 (36.93)	6.08 (5.76)	9.23 (9.23)	19.16	125	16.53	141	18.18	−1.57
D-4	*mer*-3-*Δ*-Ca$_{1/2}$[Co(L-pro)$_2$ (D-aspH)]·4H$_2$O	33.00 (32.94)	6.18 (5.73)	8.28 (8.23)	*ca.* 18.6	110	26.52	169	17.86	−1.93
D-5	*fac*-*Λ*-[Co(L-pro)$_2$ (D-aspH)]·*n*H$_2$O[c]	—	—	—	18.87	—	26.39	—	18.38	+
D-6	*mer*-1-*Δ*-[Co(L-pro) (D-aspH)$_2$]·0.5H$_2$O	35.51 (34.99)	4.96 (4.74)	9.07 (9.42)	*ca.* 18.5	104	26.81	155	18.98	−2.42
D-7	*mer*-*Λ*-[Co(L-pro) (D-aspH)$_2$]·2H$_2$O	32.95 (32.99)	5.20 (5.11)	9.24 (8.88)	*ca.* 18.9	120	26.88	205	18.98	+4.01
D-8	*mer*-2-*Δ*-[Co(L-pro) (D-aspH)$_2$]·2H$_2$O	33.38 (32.99)	5.54 (5.11)	8.58 (8.88)	*ca.* 18.8	110	26.88	160	18.80	−2.30
D-9	*mer*-3-*Δ*-[Co(L-pro) (D-aspH)$_2$]·1.5H$_2$O	33.54 (33.63)	5.34 (4.99)	8.84 (9.05)	*ca.* 18.8	112	26.67	169	18.48	−3.57
D-10	*fac*-*Λ*-[Co(L-pro) (D-aspH)$_2$]·H$_2$O	34.73 (34.30)	5.14 (4.87)	9.26 (9.23)	19.01	188	26.46	157	18.59	+2.24

a) Measured in 60% perchloric acid. b) ( ): calcd. c) Because of the poor yield, no elemental analyses were carried out.

to dryness at 30 °C. A violet, glassy material was thus obtained.

To the L-2 and D-4 fractions, acetone was added to precipitate calcium salts of the complexes. Attempts to isolate these isomers as hydrogen compounds were unsuccessful. The remaining fraction, L-5, was once concentrated to precipitate crude calcium salt, and the crude material was dissolved in 60% perchloric acid. When an aqueous NaOH solution was added to the solution drop by drop, the hydrogen compound of the complex began to precipitate.

The recrystallizations were repeated with all the compounds except those obtained from the L-3′ and L-4 fractions until their main CD peaks showed constant intensities. The results of the elemental analyses are summarized in Table 1.

Formation Ratios. From the spectral data of the fractions, the formation ratios among the bands separated chromatographically were evaluated. For some isomers not isolated as crystals, we assumed their ε values from the known ε values of the corresponding isomers (that is, 100 for the D-1 and 120 for the D-5).

Measurements. The absorption spectra were measured with a Hitachi Perkin-Elmer Model 139 UV-VIS spectrophotometer. The circular dichroism spectra were recorded on a JASCO Model ORD/UV-5 spectropolarimeter. The proton magnetic resonance spectra were recorded on a JEOL Model C-60H spectrometer at about 25 °C, using deuterium oxide containing an equivalent mole of Na_2CO_3 as the solvent. The values of the chemical shifts were referred to internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS).

Results and Discussion

Characterization of the Isomers. From the results of the elemental analyses and the elution order, it was apparent that the compounds obtained from the L-1 and L-2 fractions were the isomers of the bis(L-prolinato)L-aspartatocobaltate(III) complex, while the compounds obtained from the L-3′, L-3″, L-4, and L-5 fractions were the isomers of the L-prolinatobis(L-aspartato)cobaltate(III) complex. Likewise, for the D-aspartato complexes, it was apparent that the compounds obtained from the D-1∼D-5 fractions were the isomers of the bis(L-prolinato)D-aspartatocobaltate(III) complex, and that the compounds from the D-6∼D-10 fractions were the isomers of L-prolinatobis(D-aspartato)cobaltate(III), although for the compounds from the D-1 and D-5 fractions we have no results of elemental analyses because of their extremely poor yields. The geometrical form (*mer* or *fac*) of each compound could easily be identified on the basis

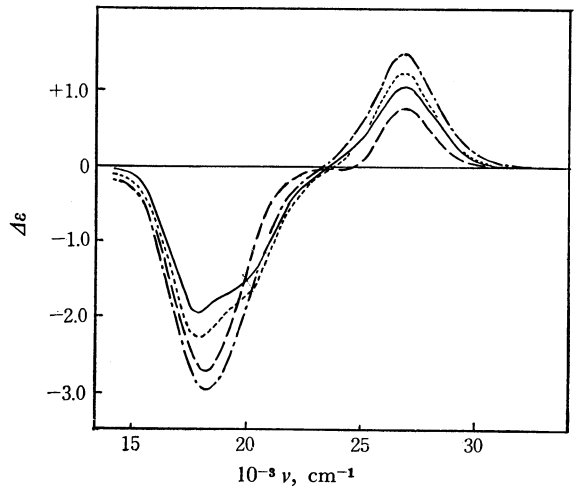


Fig. 1. CD spectra of *mer*-[Co(L-pro)$_2$(aspH)] in 60% $HClO_4$
····· *mer*-*Δ*-$Ca_{1/2}$[Co(L-pro)]$_2$(L-asp)]
---- *mer*-1-*Δ*-[Co(L-pro)$_2$(D-aspH)]
—·— *mer*-2-*Δ*-[Co(L-pro)$_2$(D-aspH)]
—— *mer*-3-*Δ*-$Ca_{1/2}$[Co(L-pro)$_2$(D-asp)]

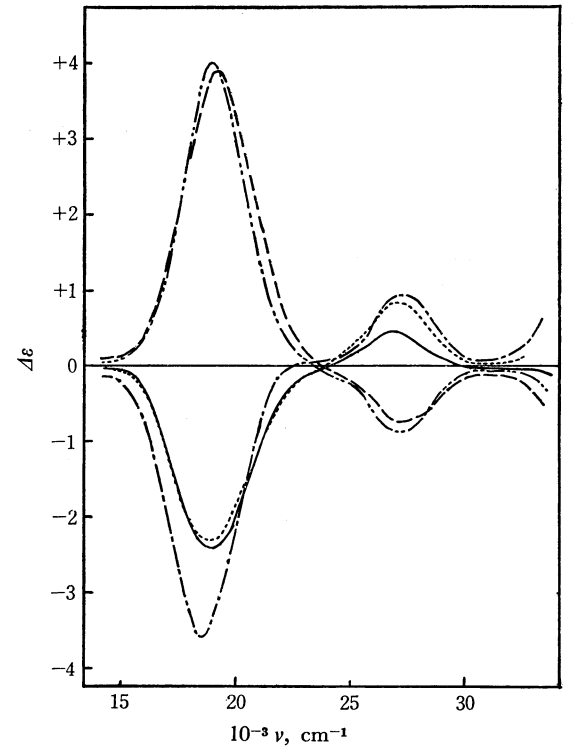


Fig. 2. CD spectra of *mer*-[Co(L-pro)(aspH)$_2$] in 60% $HClO_4$
--- *mer*-*Δ*-[Co(L-pro)(L-aspH)$_2$]
-·-· *mer*-*Δ*-[Co(L-pro)(D-aspH)$_2$]
—— *mer*-1-*Δ*-[Co(L-pro)(D-aspH)$_2$]
····· *mer*-2-*Δ*-[Co(L-pro)(D-aspH)$_2$]
-·-· *mer*-3-*Δ*-[Co(L-pro)(D-aspH)$_2$]

of its absorption spectrum; the violet compounds could be identified as *mer* forms, and the red ones, as *fac* forms. The absorption spectral data in 60% perchloric acid are given in Table 1. The absolute configurations of the isomers were determined from the signs of the main CD peaks in the first absorption band region. The CD spectra of the isolated compounds

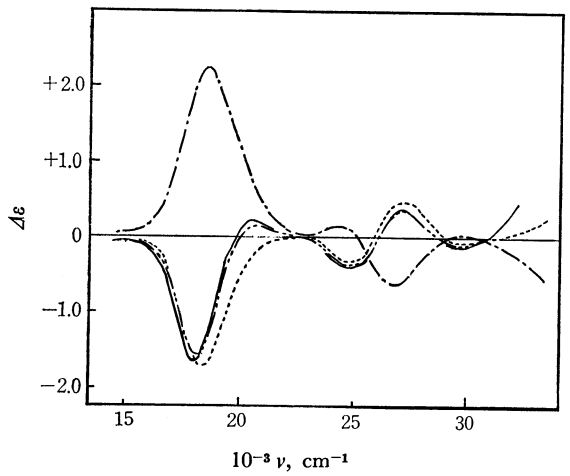


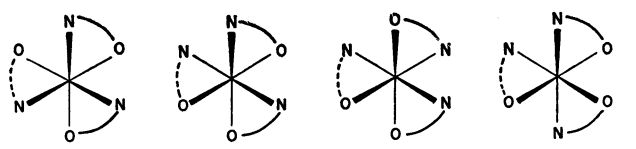
Fig. 3. CD spectra of *fac* isomers in 60% $HClO_4$
—— *fac*-*Δ*-[Co(L-pro)$_2$(L-aspH)]
-·-· *fac*-*Δ*-[Co(L-pro)$_2$(D-aspH)]
····· *fac*-*Δ*-[Co(L-pro)(L-aspH)$_2$]
—·— *fac*-*Δ*-[Co(L-pro)(D-aspH)$_2$]

are shown in Figs. 1—3.

Through the experiments, an interesting fact has been found with regard to the elution order; for the D-aspartato complexes, the *mer* isomers were eluted earlier than the corresponding *fac* ones. This was a general trend in geometrical isomers of a complex. However, for the L-aspartato complexes, the *fac* isomers were eluted earlier than the corresponding *mer* ones.

Structure of mer *Isomers.* In a tris-chelated complex with two kinds of α-aminoacidato ligands, three geometrical isomers are possible for the *mer* form (Fig. 4). In our previous works,[3,6] at least two isomers among the three have been found. In the present work, three isomers were separated for the *mer*-*Δ*-[Co(L-pro)(D-asp)$_2$]$^{2-}$ species. For the sake of convenience, these will be labeled *mer*-1-*Δ*, *mer*-2-*Δ*, and *mer*-3-*Δ*, according to the elution order. The absorption spectra of these isomers are shown in Fig. 5. These spectra, as well as the CD spectra (Fig. 2), exhibit different shapes among the three isomers.

With the *mer*-[Co(L-pro)(L-asp)$_2$]$^{2-}$ complex, only one isomer of the *Δ* form was isolated (see Table 2), and no other two isomers of the same form were detected. The molecular models for the three possible isomers of this *Δ* form indicate that a certain steric interaction exists between a pyrrolidine ring of the chelated L-prolinate ion and a side-chain of a chelated L-aspartate in the geometry of each *cis*(N)*cis*(O) and *trans*(N)*cis*(O), while no such interaction exists in the geometry of *cis*(N)*trans*(O). From these facts, it may



cis(N)*cis*(O) *cis*(N)*trans*(O) *trans*(N)*cis*(O)
fac *mer*

Fig. 4. Possible geometrical isomers.

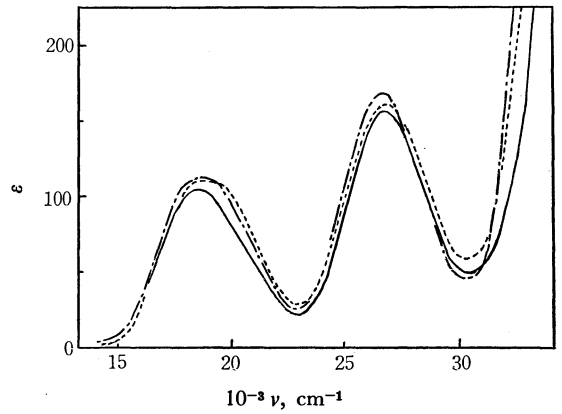


Fig. 5. Absorption spectra of three isomers of *mer*-*Δ*-[Co(L-pro)(D-aspH)$_2$] in 60% $HClO_4$
—— *mer*-1-*Δ* isomer
····· *mer*-2-*Δ* isomer
—·— *mer*-3-*Δ* isomer

be considered that formations of the isomers of both *cis*(N)*cis*(O) and *trans*(N)*cis*(O) will be less favored than that of the isomer of *cis*(N)*trans*(O). This consideration leads to the conclusion that the *mer*-*Λ*-[Co(L-pro)-(L-aspH)$_2$] complex, in which only one *Λ*-isomer is isolated, has the *cis*(N)*trans*(O) structure.

The PMR spectra concerning the methylene proton signals due to the coordinated aspartate ions in the bis(aspartato) complexes are shown in Fig. 6. Each spectrum is characteristic of each isomer. For the CH_2 signal of an aspartate ion, the AB portion of a ABX pattern is expected, and the separation width of the appeared doublet is represented by the expression of $(J_{AX}+J_{BX})/2$.[10] Moreover, since the vicinal coupling constant depends on the dihedral angle,[11] it is considered that the width of the doublet reflects the orientation of the side-chain of the coordinated aspartate. From this point of view, it is considered that two side-chains of the aspartate ions in the *mer*-1-*Δ* isomer are oriented differently, for considerably different widths are observed (Fig. 6(a)). Separately, measurements with the *fac*-[Co(L-asp)$_3$]$^{3-}$ complexes gave different spectra between the *Δ* and *Λ* isomers

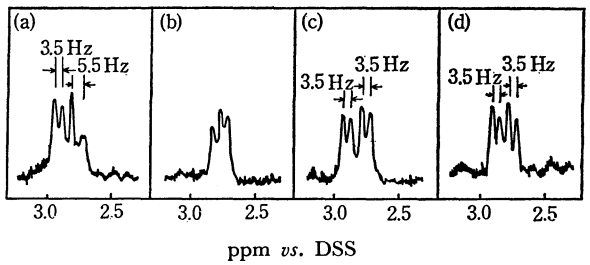


Fig. 6. PMR spectra of [Co(L-pro)(asp)$_2$]$^{2-}$ in D_2O (pD ~7), (methylene proton resonance of aspartate ion)
(a) *mer*-1-*Δ*-[Co(L-pro)(D-asp)$_2$]$^{2-}$
(b) *mer*-2-*Δ*-[Co(L-pro)(D-asp)$_2$]$^{2-}$
(c) *mer*-3-*Δ*-[Co(L-pro)(D-asp)$_2$]$^{2-}$
(d) *mer*-*Λ*-[Co(L-pro)(L-asp)$_2$]$^{2-}$

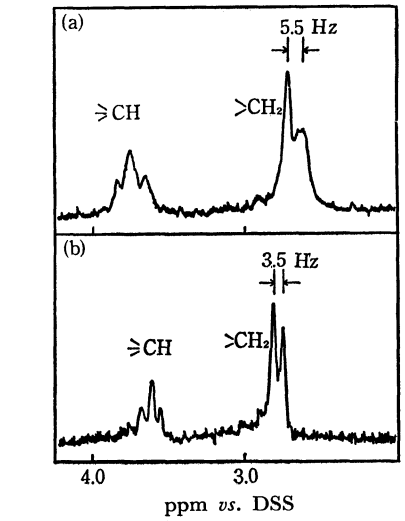


Fig. 7. PMR spectra of *fac*-[Co(L-asp)$_3$]$^{3-}$ in D_2O (pD ~8)
(a) *fac*-*Λ* isomer (b) *fac*-*Δ* isomer

(Fig. 7); the *Λ* isomer exhibits a more separated doublet than the *Δ* isomer. This fact means that the orientations of the aspartate side-chain will be affected by the interactions of the *β*-carboxylate groups with adjacent ligands. Thus, it is considered on the basis of a comparison of the spectra (c) and (d) in Fig. 6 that the *mer*-3-*Δ* isomer of the bis(D-aspartato) complex and the *mer*-*Λ* isomer of the bis(L-aspartato) complex have the same geometry, *cis*(N)*trans*(O). In this geometry, both *β*-carboxylate groups in an isomer are able to interact equally with the adjacent NH_2 groups, while in the other geometries one *β*-carboxylate interacts with the NH_2 group and the other *β*-carboxylate, with adjacent carboxylate group. The structural assignments of the other *mer*-1-*Δ* and *mer*-2-*Δ* complexes are difficult at present. For the [Co(L-pro)$_2$(D-asp)]$^-$ complex, three *mer*-*Δ* isomers have been isolated, but their geometrical assignments are also difficult.

Absorption and CD Spectra. Figure 8 shows the absorption spectra of the *fac*-*Δ*-[Co(L-pro)$_{3-n}$(L-aspH)$_n$]

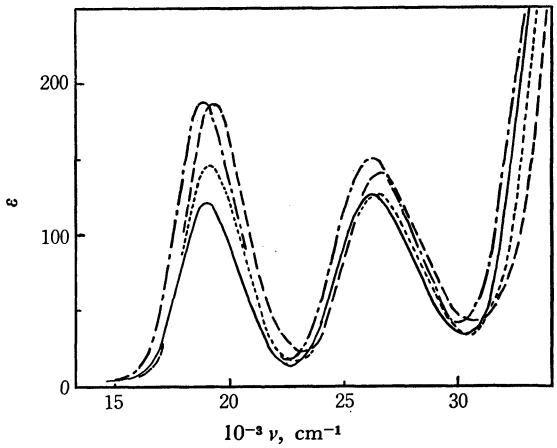


Fig. 8. Absorption spectra of *fac*-[Co(L-pro)$_{3-n}$(aspH)$_n$] in 60% $HClO_4$
---- *fac*-*Δ*-[Co(L-aspH)$_3$]
····· *fac*-*Δ*-[Co(L-pro)(L-aspH)$_2$]
—— *fac*-*Δ*-[Co(L-pro)$_2$(L-aspH)]
=:=: *fac*-*Λ*-[Co(L-pro)(D-aspH)$_2$]

10) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London (1965), p. 357.
11) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

TABLE 2. FORMATION RATIOS

n	Label	Isomer	Ratio
a)	$[Co(L\text{-pro})_{3-n}(L\text{-asp})_n]^{n-}$		
1	L-1	*fac*-Δ	4
	L-2	*mer*-Δ	14
2	L-3′	*mer*-1-Δ	1
	L-3″	*fac*-Δ	5
	L-4	*mer*-2-Δ	1
	L-5	*mer*-Λ	8
b)	$[Co(L\text{-pro})_{3-n}(D\text{-asp})_n]^{n-}$		
1	D-1	(*mer*-Λ)[a]	1
	D-2	*mer*-1-Δ	8
	D-3′	*mer*-2-Δ	52
	D-3″	*fac*-Δ	1
	D-4	*mer*-3-Δ	8
	D-5	(*fac*-Λ)[a]	1
2	D-6	*mer*-1-Δ	3
	D-7	*mer*-Λ	2
	D-8	*mer*-2-Δ	4
	D-9	*mer*-3-Δ	28
	D-10	*fac*-Λ	8

a) No analyses.

(n=1,2,3) and *fac*-Λ-[Co(L-pro)(D-aspH)$_2$] complexes. In the L-aspartato complex species, both the first and second absorption bands show bathochromic shifts with an increase in the number of the chelated proline, as is to be expected from a weaker ligand field of a secondary amine group than that of primary amine. Moreover, the differences in the absorption and CD spectral data (Table 1) among the three *mer*-Δ isomers of the [Co(L-pro)(D-aspH)$_2$] complex seem to be attributable mainly to a weaker ligand field of secondary amine group of proline. It is interesting that the absorption maxima of the *fac*-Λ-[Co(L-pro)(D-aspH)$_2$] (D-10) complex are observed at a lower energy than the maxima of the *fac*-Δ-[Co(L-pro)(L-aspH)$_2$] (L-3″) complex. The former complex differs from the latter merely in the orientation of the pyrrolidine ring of the chelated proline, since the mirror image of the *fac*-Λ-[Co(L-pro)(D-asp)$_2$]$^{2-}$ is the *fac*-Δ-[Co(D-pro)(L-asp)$_2$]$^{2-}$.

Stereoselectivity. Each fraction separated chromatographically showed distinctly a plus or a minus CD sign in the first absorption-band region. With each fraction, the ratio of the observed intensity of the main CD peak to the absorbance at the Band I maximum was estimated. On the other hand, the ratio of the $\Delta\varepsilon_{max}$ to the ε_{max} of Band I was estimated with each complex isolated. When the former ratio was divided by the latter, the quotient was within 0.8$\sim$1 in all the fractions. Since this fact indicated that only one isomer predominated in each fraction, the minor species were ignored in evaluating the formation ratios. The results are given in Table 2.

In the bis(L-aspartato) complex species, the selective formation of the Δ isomer is found for the *fac* form, while the selective formation of the Λ isomer is found for the *mer* form. In the bis(D-aspartato) complex species, the Λ isomer for the *fac* form and the Δ isomer for the *mer* are found preferentially. The *fac*/*mer* ratios have been estimated as *ca.* 1/2 and 1/4.6 for the bis(L-aspartato) and the bis(D-aspartato) complex species respectively.

In the bis(L-prolinato) species, remarkable differences in selectivity occur depending upon the optical form of the chelated aspartate ion (*i.e.*, L or D). The L-aspartato complex species exhibit preferential formations of Δ isomers for both the *fac* and *mer* forms. The *fac*/*mer* ratio is estimated as 1/3.5. On the other hand, the D-aspartato complex species exhibit a preferential formation of the Δ isomer for the *mer* form, while no preferential formation is observed in the *fac* form, and the formation amounts themselves are very poor; the *fac*/*mer* ratio is estimated to be *ca.* 1/35, indicating serious inter-ligand interactions.

Until now, the selectivity in the mixed L-aspartato complexes with other amino acids[2,3] or diamines[4,5] has been interpreted in terms of hydrogen-bonding between the β-carboxylate group of the chelated L-aspartate ion and the amino group in the adjacent ligand. The stereoselectivity observed in this study can also be interpreted in this way. The interactions between the side-chain of an aspartate ion and the adjacent ligand can now be classified into the following four types from the stereo models: (A) a favorable interaction through a hydrogen bond, in which the apical position (a) in Fig. 9 is occupied by an amino group; (B) an electrostatic repulsive interaction between the β-carboxylate group and the chelated oxygen atom occupying the apical position (a); (C) some interactions of the side-chain with the pyrrolidine ring of the chelated proline, in which hydrogen-bonding is not favorable because of the existence of the pyrrolidine ring; (D) a marked steric crowding

TABLE 3. INTERACTION OF THE SIDE-CHAIN OF COORDINATED ASPARTATE

Complex \ Isomer	Config.	*fac*	*mer*		
			cis(N)*cis*(O)	*cis*(N)*trans*(O)	*trans*(N)*cis*(O)
$Co(L\text{-pro})_2(L\text{-asp})^-$	Δ	A	B	B	A
	Λ	B	D	B(X)	D
$Co(L\text{-pro})(L\text{-asp})_2^{2-}$	Δ	A A	A B	A B	B B
	Λ	B B	B D	A A	B D
$Co(L\text{-pro})_2(D\text{-asp})^-$	Δ	B	A	B	A
	Λ	C	B	B(X)	C
$Co(L\text{-pro})(D\text{-asp})_2^{2-}$	Δ	B B	A B	A A	A B
	Λ	A C	A B	B C	B B

A: polar interaction with the amino group in the adjacent ligand. B: polar interaction with the carboxylate group in the adjacent ligand. C: some interaction with the pyrrolidine ring. D: steric interaction with the pyrrolidine ring. X: steric interaction between two pyrrolidine rings.

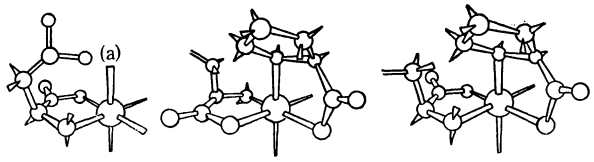


Fig. 9. Interactions of coordinated aspartate.

between the pyrrolidine ring and the side-chain of the chelated aspartate ion. These four types are drawn in Fig. 9. The relation between the types and the geometrical arrangements are given in Table 3. In this table, the symbol X expresses the existence of a steric hindrance between the two pyrrolidine rings.

Thus, the preferential formations of the *Δ* isomer in the *fac*-[Co(L-pro)(L-asp)$_2$]$^{2-}$ and of the *Λ* isomer in the *fac*-[Co(L-pro)(D-asp)$_2$]$^{2-}$ can be explained by the favorable interaction of Type A. The preference of the *Δ* isomers in the *mer*-[Co(L-pro)$_2$(D-asp)]$^-$ can also be explained in this way. The preferential formation of the *Δ* isomers in the *mer*-[Co(L-pro)$_2$(L-asp)]$^-$ can be explained by considering there to be less stability in the opposed *Λ* isomers containing the interactions of Types D and X. Moreover, the poorer formation of the *fac* isomers of the [Co(L-pro)$_2$(D-asp)]$^-$ complex than of the *mer* ones can be interpreted in terms of the lack of a favorable interaction of Type A.

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