position within close distance to the departing aquo ligand. X-Ray structural determinations would be be most enlightening in this regard.

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The Stereoisomers of the Bis(L-hydrogen aspartato)-*l*-propylenediamine- and L-Aspartatobis(*l*-propylenediamine)cobalt(III) Complexes

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The bis(L-hydrogen aspartato)-*l*-propylenediamine- and L-aspartatobis(*l*-propylenediamine)cobalt(III) complexes have been prepared from the reaction of the *trans*-$CoCl_2(l\text{-pn})_2^+$ complex with L-aspartic acid. The stereoisomers of these complexes have been separated by an ion-exchange chromatographic method. The isolated complexes are Λ- and Δ-trans(O), Λ- and Δ-cis(O),cis(N), and Λ-trans(N) isomers for the bis(L-hydrogen aspartato)-*l*-propylenediamine complexes. On the other hand, for the bis(*l*-propylenediamine) complexes eight possible stereoisomers have been separated and the four Λ isomers and one Δ isomer have been crystallized. All of the complexes isolated as crystals have been characterized by their electronic absorption, circular dichroism, and proton magnetic resonance spectra. The stereoselectivity in these complexes has also been discussed based on the results of the formation ratios of the isomers.

Introduction

We reported, in the previous paper, the isolation of a series of stereoisomers of the glycinato-*l*-propylenediaminecobalt(III) complexes.[1] Recently, the preparation of tris-type mixed complexes of cobalt(III) with glycinato and L-aspartato ligands was also reported from our laboratory.[2] The present work has been undertaken in connection with those studies and in order to isolate the mixed complexes with L-aspartato and *l*-propylenediamine ligands and investigate their stereoselectivity.

Experimental Section

Preparations.—The complex *trans*-$[CoCl_2(l\text{-pn})_2]Cl\cdot H_2O$,[3] 9 g (0.027 mol), was dissolved in 20 ml of water, and L-aspartic acid, 7.4 g (0.055 mol), was dissolved in the solution, adding simultaneously an aqueous sodium hydroxide solution. After that, the resulting solution was adjusted to pH ~10 with the alkali solution. After adding active charcoal (1.2 g), the mixture was stirred at 55° for 15 min; then the color of the solution became red-brown. After the removal of the active charcoal by hot filtration, the filtrate was adjusted to pH ~8 with aqueous hydrochloric acid. A portion of the solution was added to an ion-exchange column (diameter, 6 cm; height of resin, 40 cm) containing 100–200 mesh Dowex 50W-X8 resin in the sodium form. At this stage, the absorbed complexes formed two bands at the top of the column (a red-brown band and a red band, up and down). After the column was swept with water, the bands were eluted with a 0.1 *M* aqueous solution of sodium perchlorate at a rate about 0.2 ml/min. Through elution over a period of about 2 months, the red band was completely separated into seven bands colored red or red-violet. These eluted bands were collected in seven fractions and numbered according to the order of the eluted bands (no. 1–7). The other red-brown band remaining in the column was then eluted with a 0.4 *M* sodium perchlorate solution over a period of about 3 months. At this stage, four bands colored red-brown were separated from the original band, and these eluted bands were collected in fractions (no. 8–11). When the rest of the red-brown band still remaining in the column was eluted with a 1 *M* sodium perchlorate solution, two bands came down and collected in fractions (no. 12–13). The last fraction (no. 13) was rechromatographed using a smaller column and 0.5 *M* $NaClO_4$ at a slower rate (0.1 ml/min). Three overlapped bands were obtained and these were collected in fractions (no. 13′, 13″, and 13‴). A yellow band still remained at the top of the original column and it was the tris(*l*-propylenediamine)cobalt(III) species. The chromatographic separation was repeated over and over again from the beginning in order to store up the same fractions.

Each fraction was evaporated to about dryness at 40° along with the simultaneous removal of a large amount of the perchlorate. After that, the residue was dissolved in a few milliliters of water, and to it a large amount of an acetone–ether mixture (1:4) was added. After the solution had stood for some time, the desired complex was separated as an oil from the organic solvent. After this treatment was repeated several times, a large amount of acetone was added to the resulting oil to precipitate the product. The precipitates were collected by means of the centrifuge and washed with acetone. The precipitates were again dissolved in a minimum amount of water and the solution was allowed to stand for several days at room temperature to crystallize the desired complex. Results of the elemental analyses for the isolated complexes will be given in the Results and Discussion.

Formation Ratios of Isomers.—The relative concentrations and the formation ratios of the eluted bands were spectrophotometrically determined using the ε values of the first absorption band of each of the isomers obtained from no. 1–13, but the ε values of the isomers from no. 6 and 7 were assumed to be the same as that of the isomer from no. 5.

Reagents.—Optically active *l*-propylenediamine (*l*-pn) used in the above experiment was obtained by resolving its commercial racemate according to the usual method.[4] The observed $[\alpha]^{25}D$ in dry benzene was −34.6°. L-Aspartic acid (L-aspH_2) used was reagent grade and the observed $[\alpha]^{25}D$ was +25.3°.

Measurements.—The electronic absorption, circular dichroism (CD), and proton magnetic resonance (pmr) spectra were measured with the same instruments as were used in the previous investigation.[1]

Results and Discussion

Results of the elemental analyses are summarized in Table I. For the sake of convenience, the isolated complexes are numbered as E-1, E-2, ..., E-13 corresponding to the numbers of the fractions. No results

(1) Y. Kojima and M. Shibata, *Inorg. Chem.*, **9**, 238 (1970).
(2) K. Kawasaki, J. Yoshii, and M. Shibata, *Bull. Chem. Soc. Jap.*, **40**, 3819 (1970).
(3) J. C. Bailar, Jr., C. A. Stiegman, J. H. Balthis, Jr., and E. H. Huffman, *J. Amer. Chem. Soc.*, **61**, 2402 (1939).
(4) F. P. Dwyer, F. L. Garvan, and A. Shulman, *ibid.*, **81**, 290 (1959).

TABLE I
ELEMENTAL ANALYSES, ELECTRONIC ABSORPTION SPECTRA, AND CD SPECTRA OF THE COMPLEXES PREPARED

Label	Complex		Elemental analyses, % C	H	N	Band I $10^{-3}\bar{\nu}_{max}$, cm^{-1}	ϵ_{max}	Band II $10^{-3}\bar{\nu}_{max}$, cm^{-1}	ϵ_{max}	CD $10^{-3}\bar{\nu}_{max}$, cm^{-1}	$\Delta\epsilon_{max}$
E-1	*trans*(*O*),*cis*(*N*)-Λ-[Co(L-aspH)$_2$(*l*-pn)]ClO_4	Calcd	26.62	4.47	11.29	18.9	97	27.7	145	18.7	+2.20
		Found	26.77	4.70	10.92	21.6	sh				
E-2	*trans*(*O*),*cis*(*N*)-Λ-[Co(L-aspH)$_2$(*l*-pn)]$ClO_4\cdot 1.5H_2O$	Calcd	25.24	4.82	10.71	18.9	98	27.7	146	18.8	+2.35
		Found	25.29	4.65	10.37	21.6	sh				
E-3	*trans*(*O*),*cis*(*N*)-Δ-[Co(L-aspH)$_2$(*l*-pn)]$ClO_4\cdot 1.5H_2O$	Calcd	25.24	4.82	10.71	18.9	96	27.6	146	18.4	−1.55
		Found	25.36	4.66	10.46	21.6	sh			21.9	−0.98
E-4	*cis*(*O*),*cis*(*N*)-Λ-[Co(L-aspH)$_2$(*l*-pn)]$ClO_4\cdot H_2O$[a]	Calcd	25.69	4.70	10.89	20.0	135	27.9	155	20.0	+1.35
		Found	25.83	4.72	10.68						
E-5	*cis*(*O*),*cis*(*N*)-Δ-[Co(L-aspH)$_2$(*l*-pn)]ClO_4[a]	Calcd	26.62	4.47	11.29	20.0	135	27.9	154	19.2	−0.82
		Found	26.65	4.81	11.45						
E-6	*cis*(*O*),*trans*(*N*)-Λ-[Co(L-aspH)$_2$(*l*-pn)]$ClO_4\cdot nH_2O$	Calcd	...	...	...	...	...	...	...	19.7	+
		Found[b]									
E-7	*cis*(*O*),*trans*(*N*)-Λ-[Co(L-aspH)$_2$(*l*-pn)]$ClO_4\cdot nH_2O$	Calcd	...	...	...	...	...	...	...	19.7	+
		Found[b]									
E-8	Λ-[Co(L-asp)(*l*-pn)$_2$]$ClO_4\cdot 0.5H_2O$	Calcd	26.91	5.81	15.69	20.5	99	29.0	115	20.2	+1.92
		Found	27.13	5.81	15.35						
E-9	Λ-[Co(L-asp)(*l*-pn)$_2$]$ClO_4\cdot 2.5H_2O$	Calcd	24.90	6.27	14.52	20.5	99	29.0	115	20.2	+1.92
		Found	25.27	6.20	14.20						
E-10	Λ-[Co(L-asp)(*l*-pn)$_2$]$ClO_4\cdot 2H_2O$	Calcd	25.37	6.18	14.80	20.6	99	29.0	115	20.2	+1.88
		Found	25.48	5.84	14.50						
E-11	Λ-[Co(L-asp)(*l*-pn)$_2$]$ClO_4\cdot 0.5H_2O$	Calcd	26.91	5.81	15.69	20.5	99	29.0	115	20.2	+1.87
		Found	27.21	5.96	15.10						
E-12	Δ-[Co(L-asp)(*l*-pn)$_2$]ClO_4	Calcd	27.47	5.76	16.01	20.6	99	28.7	115	19.6	−1.80
		Found	27.45	6.42	15.82						
E-13	Δ-[Co(L-asp)(*l*-pn)$_2$]$ClO_4\cdot 1.5H_2O$[a]	Calcd	25.30	6.28	15.58	20.5	99	28.7	115	19.6	−1.80
		Found	25.76	6.08	15.08						

[a] For substantially pure compounds. Mixture of two Λ isomers for E-4, of two Δ isomers for E-5, and of three Δ isomers for E-13. [b] Because of the poor yield, no elemental analyses were carried out.

for the E-6 or E-7 are obtained on account of the poorest yield. From these analytical results, it is concluded that the complexes from E-1 to E-7 are the isomers of bis(L-hydrogenaspartato)-*l*-propylenediaminecobalt(III), and the complexes from E-8 to E-13 are those of the L-aspartatobis(*l*-propylenediamine)cobalt(III) complex.

Electronic Spectra.—The typical spectra are shown in Figure 1 and the numerical data are summarized in Table I. The spectra of the E-1, E-2, and E-3 complexes are essentially the same and show a splitting in the first absorption band. From this, it is assumed that these complexes are isomers of trans(O),cis(N) geometry with respect to the coordinated N and O atoms of the L-aspartate ions.[1,5-7] No fundamental difference can be recognized between the spectrum of the E-4 complex and that of the E-5 complex. The E-7 complex exhibits the same spectrum as that of the E-6.

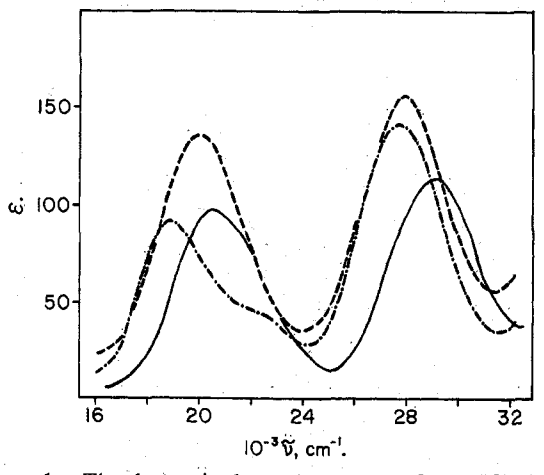

Figure 1.—The electronic absorption spectra of *trans*(*O*),*cis*(*N*)-Co(L-aspH)$_2$(*l*-pn)$^+$ (-·-·-), *cis*(*O*),*cis*(*N*)-Co(L-aspH)$_2$(*l*-pn)$^+$ (- - - -), and Co(L-asp)(*l*-pn)$_2^+$ (———).

No difference was found among the spectra of the complexes from E-8 to E-13, and the numerical data on the positions of the absorption maxima agree almost exactly with those of the Co(gly)(*l*-pn)$_2^{2+}$ complex.[1]

Geometry.—It is well-known that the coordinated *l*-propylenediamine exists predominantly in the λ conformation[8,9] with an equatorial CH_3 group.[10-12] It is also known that the coordinated α-amino acidate ion as a bidentate ligand forms a nearly planar five-membered ring.[13] When the relative positions of the donor atoms of the complexed L-hydrogen aspartate ions (L-aspH), the λ conformation of the complexed *l*-propylenediamine, and the spirals of the chelate rings (Λ and Δ) are all taken into consideration, a total of eight possible stereoisomers exists for the bis(L-hydrogen aspartato) complex (Figure 2). On the other hand, four diastereoisomers with respect to the orientation of the coordinating diamines are possible for the bis(*l*-propylenediamine) complex (Figure 3). Therefore, eight isomers are possible when the spirals are considered. It is well known that in the Δ absolute configuration[8,9] of a complex containing *l*-propylenediamine, the C–C bond axis of the *l*-pn chelate ring is parallel to the pseudo-C_3 axis, while in the Λ configuration, the C–C bond axis is oblique to the C_3 axis.

CD Spectra.—In order to assign the above-men-

(5) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **264**, 321 (1951).
(6) M. Ogawa, Y. Shimura, and R. Tsuchida, *Nippon Kagaku Zasshi*, **81**, 72 (1960).
(7) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jap.*, **39**, 1257 (1966); *Inorg. Chem.*, **9**, 719 (1970).
(8) A chelate ring conformation is designated as λ if the C–C bond defines a left spiral about the edge of the octahedron spanned by that ring. The symbols Δ and Λ are based upon the convention proposed by T. S. Piper, *J. Amer. Chem. Soc.*, **83**, 3908 (1961).
(9) The symbols are according to *Inorg. Chem.*, **9**, 1 (1970).
(10) E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).
(11) S. T. Spees, Jr., U. T. Durham, and A. M. Sargeson, *Inorg. Chem.*, **5**, 2103 (1966).
(12) S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42**, 3184 (1969).
(13) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).

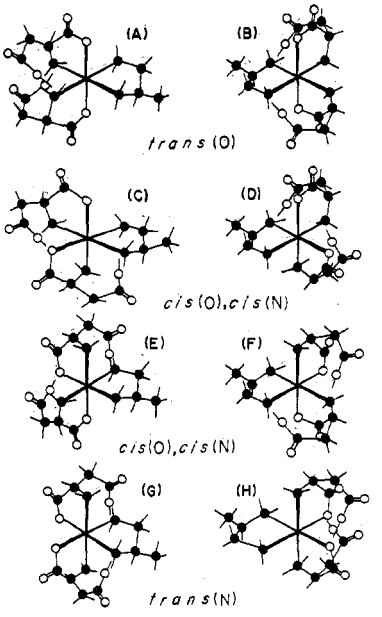

Figure 2.—The possible stereoisomers of $Co(L\text{-}aspH)_2(l\text{-}pn)^+$.

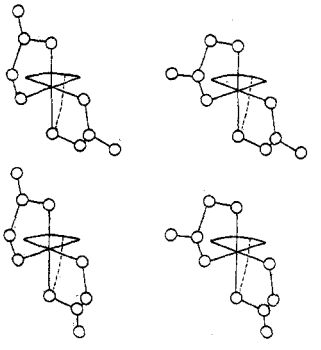

Figure 3.—The possible diastereoisomers of $\Lambda\text{-}Co(L\text{-}asp)(l\text{-}pn)_2^+$.

tioned possible structures to the isolated complexes, the CD (and pmr) spectral data were used. Figures 4–6 show the CD spectra. The absolute configuration assigned to a complex was determined by relating the sign of the dominant peak in the first absorption band region to that for the $\Lambda\text{-}Co(en)_3^{3+}$ complex.[14] The CD spectra of the E-1 and E-2 complexes were identical and showed a dominant positive peak, while the spectrum of the E-3 complex showed a dominant negative peak (Figure 4). From these, the Λ configuration can be assigned to the E-1 and E-2 complexes, and the Δ configuration, to the E-3 complex. The identity of the E-2 complex with the E-1 complex was confirmed by comparing the infrared spectra, including the far-infrared region, of the two complexes. In addition, the pmr spectra also showed the same patterns for both complexes. From these, it is concluded that both are the same compounds even though they have been crystallized from the two different fractions (no. 1 and 2). No difference was observed between the absorption spectra of no. 1 and 2 fractions, but a difference was observed between the CD spectra of the two fractions: the spectrum for no. 2 showed a characteristic shoulder on the high-energy side of the dominant positive peak

(14) R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc., London*, 331 (1962); A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).

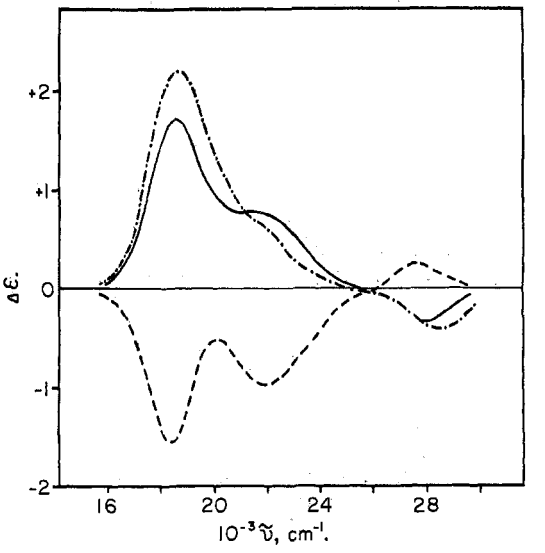

Figure 4.—The CD spectra for *trans(O),cis(N)*-(+)[$Co(L\text{-}aspH)_2(l\text{-}pn)$]$ClO_4$ (E-1) (—·—·—), *trans(O),cis(N)*-(−)[$Co(L\text{-}aspH)_2(l\text{-}pn)$]$ClO_4$ (E-3) (- - - - -), and the no. 2 fraction (———).

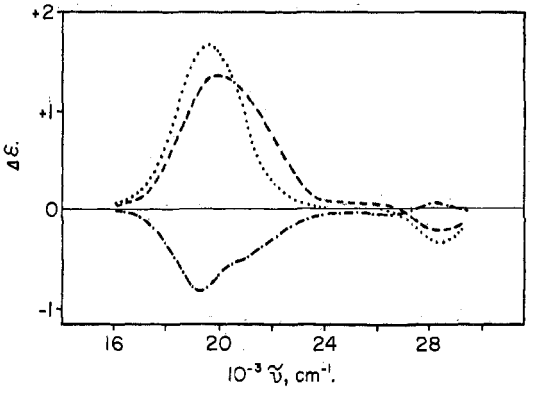

Figure 5.—The CD spectra for *cis(O),cis(N)*-(+)[$Co(L\text{-}aspH)_2(l\text{-}pn)$]$ClO_4$ (E-4) (- - - - -), *cis(O),cis(N)*-(−)[$Co(L\text{-}aspH)_2(l\text{-}pn)$]$ClO_4$ (E-5) (—·—·—), and *cis(O),trans (N)*-(+)[$Co(L\text{-}aspH)_2(l\text{-}pn)$]$ClO_4$(E-6) (· · · · ·).

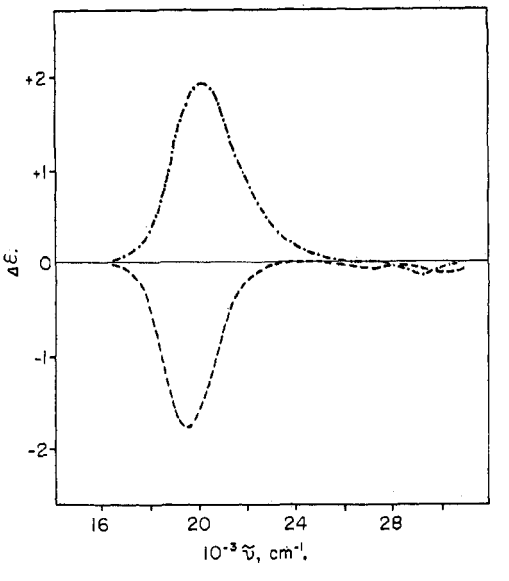

Figure 6.—The CD spectra for (+)[$Co(L\text{-}asp)(l\text{-}pn)_2$]$ClO_4$ (—·—·—) and (−)[$Co(L\text{-}asp)(l\text{-}pn)_2$]$ClO_4$ (- - - - -).

in the first absorption band region, while the spectrum for no. 1 showed the similar peak with a less noticeable shoulder and accorded with that of the E-1 (or E-2) complex. The differences in the chromatographic and CD spectral behaviors between the two fractions show that the existing complex species in no. 2 takes a different form from that in no. 1. These different forms may arise from different kinds of hydrogen bonding of the dangling β-carboxylic acid group: the molecular models indicated the possible hydrogen bonding with the coordinated NH_2, coordinated carboxylic OH, or carbonyl oxygen of the same amino acid anion or with the coordinated NH_2, the dangling carboxylic OH, or carboxyl oxygen of the other L-aspartate anion.

The CD spectra for the E-4 and E-5 complexes are of opposite signs at their dominant peaks, and consequently these complexes are regarded as the isomers in the Λ and Δ configurations. The CD spectrum of the E-6 complex shows a positive peak (the $\Delta\epsilon$ value has not been estimated because of the lack of the elemental analyses, but the CD curve was drawn by assuming the ϵ values to be the same as the values of E-5). The CD spectrum of E-7 also showed the same positive peak. From the signs it is assumed that both the E-6 and E-7 complexes have the Λ configurations.

In the case of the bis(*l*-propylenediamine) complex, the compounds from E-8 to E-11 showed a positive peak indicating the Λ configurations, while the other compounds, E-12 and E-13, each showing a negative peak, are regarded as the isomers of the Δ configuration (Figure 6).

Pmr Spectra.—The pmr spectra of the bis(L-hydrogen aspartato) and bis(*l*-propylenediamine) complexes are partially shown in Figures 7 and 8. In these spectra, the resonance signals in the higher field region are due to the CH_3 groups of the coordinated *l*-pn molecules, and the signals in the lower field region are due to the CH_2 groups of the coordinated L-aspartate ions. The data of the CH_2 resonance signals for the E-6 and E-7 complexes are not shown in Figure 7 because of the shortage of the samples. The spectra of E-1 and E-2 (Λ) exhibit the same patterns, each having a doublet (J = 6 cps) due to the CH_3 group of the *l*-pn at -1.44 ppm, while the spectrum of E-3 (Δ) shows a similar doublet signal at -1.41 ppm. Such a slight difference in chemical shift between the Λ and Δ isomers is also observed when we compare the complexes in $Na[Co(l\text{-pn})(C_2O_4)_2]$[15] and those in $[Co(gly)_2(l\text{-pn})]Cl$.[1]

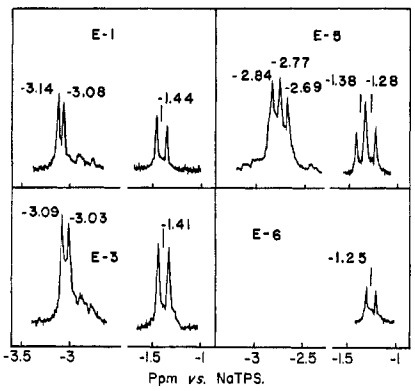

Figure 7.—The pmr spectra of (E-1) *trans*(*O*),*cis*(*N*)-(+)Co(L-aspH)$_2$(*l*-pn)$^+$, (E-3) *trans*(*O*),*cis*(*N*)-(−)Co(L-aspH)$_2$(*l*-pn)$^+$, (E-5) *cis*(*O*),*cis*(*N*)-(−)Co(L-aspH)$_2$(*l*-pn)$^+$, and (E-6) *cis*(*O*), *trans*(*N*)-(+)Co(L-aspH)$_2$(*l*-pn)$^+$.

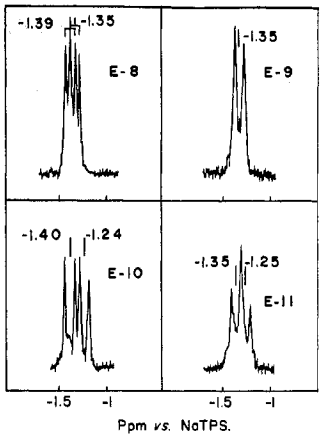

Figure 8.—The pmr spectra of (+)Co(L-asp)(*l*-pn)$_2^+$.

The spectrum of the E-4 complex shows two overlapping doublets due to the CH_3 group at -1.45 and -1.35 ppm, and the integrated intensities of the observed three peaks are in the ratio 1:2:1. The spectrum of E-5 shows the same kind of two overlapping doublets at -1.38 and -1.28 ppm, and the observed three peaks have the intensity ratio 1:2:1. From these data, it is concluded that both E-4 and E-5 are equimolar mixtures of two isomers which differ from each other in the chemical environments of the CH_3 of the *l*-pn. Furthermore the fact that the difference in chemical shift between the two doublets is 0.10 ppm in either E-4 or E-5 suggests that the equimolar mixtures in both complexes differ in the orientation of the coordinated *l*-pn. Judging from these facts and the facts from the CD data, E-4 is regarded as the mixture of the cis(O),-cis(N)-Λ isomers (Figure 2 (C) and (E)), and E-5 is regarded as the mixture of the corresponding Δ isomers (Figure 2 (D) and (F)). Considering the fact that the pmr spectrum of the E-6 complex exhibits a doublet at -1.25 ppm and that the spectrum of E-7 is the same as that of E-6 and considering the CD data, it is concluded that the both complexes are identical, being the trans(N),cis(O)-Λ isomer (Figure 2 (G)). The difference in the chromatographic behavior between no. 6 and 7 fractions indicates different forms of the existing complex species, and the reason for this fact may be due to different kinds of hydrogen bonding. The reason that the same complexes crystallized from the different fractions is attributed to the change from one form to the other form in the process of the crystallization procedure.

As is shown in Figure 8, a doublet due to the CH_3 group of the *l*-pn is observed at -1.35 and -1.39 ppm for E-8, -1.35 ppm for E-9, -1.24 and -1.40 ppm for E-10, and -1.25 and -1.35 ppm for E-11. From these data, the four complexes are regarded as the geometrical isomers with respect to the CH_3 groups of the *l*-pn molecules (Figure 3). On the other hand, the same kind of doublet is observed for the remaining complexes: at -1.33 and -1.38 ppm for E-12, at -1.33 ppm for E-13′, at -1.27 and -1.33 ppm for E-13″, and at -1.29 and -1.39 ppm for E-13‴. These data lead to the same conclusion about the geometries of the

(15) J. C. Brushmillar and L. G. Stadther, *Inorg. Nucl. Chem. Lett.*, **3**, 525 (1967).

complexes. However, the assignment of these complexes to the structures, as shown in Figure 3, is difficult at the present stage because of the lack of a method of correlating the chemical shift of the CH_3 group to its chemical environment.

Stereoselectivity.—Among the possible eight isomers of the bis(L-hydrogen aspartato) complex, seven, trans(O),cis(N)-Λ and -Δ, cis(O),cis(N)-Λ (two kinds) and -Δ (two kinds), and cis(O),trans(N)-Λ, have been found in the present study. The formation ratios of the isomers of the bis(L-hydrogen aspartato) complex are summarized in Table II. Ratios between the Λ and Δ

TABLE II
FORMATION RATIOS OF Co(L-aspH)$_2$(*l*-pn)$^+$ ISOMERS

Trans(O),cis(N) (A)[a] Λ	Trans(O),cis(N) (B)[a] Δ	Cis(O),cis(N) (C) + (E)[a] Λ	Cis(O),cis(N) (D) + (F)[a] Δ	Cis(O),trans(N) (G)[a] Λ
E-1 + E-2	E-3	E-4	E-5	E-6 + E-7
16.5 + 3.3	4.7	2	12	1 + 1
Λ:Δ = 4.2:1		Λ:Δ = 1:6		
$\Delta G_{obsd}(25°)$ = −0.85 kcal mol^{-1}		$\Delta G_{obsd}(25°)$ = 1.1 kcal mol^{-1}		

[a] The letters in parentheses signify the isomers in Figure 2.

pairs are also given as standard free energy differences.

For the trans(O),cis(N) isomers, the ratio of Λ:Δ is about 4.2:1 and the stereoselective formation of the Λ diastereoisomer is found. For the cis(O),cis(N) isomers, the ratio of Λ:Δ is about 1:6 and the stereoselective formation of the Δ isomer is found. For the remaining cis(O),trans(N) isomers, only the Λ form is found in about the same yield as that of the cis(O),cis(N)-Λ isomer. These stereoselective formations can be explained in the following ways. Since the preparative reaction of the *trans*-$CoCl_2$(*l*-pn)$_2^+$ complex with L-aspartic acid has been carried out under the alkaline condition (pH ~10), it is considered that the interactions of the β-carboxylate groups with the neighboring groups play an important role in the selective formations. When the molecular model for the Λ form of the trans(O),cis(N) isomers is constructed, the β-carboxylate group of the first chelated L-aspartate ligand is seen to be able to approach an H atom of the NH_2 group of the second aspartate ligand, and hydrogen bonding is expected in this case. On the other hand, in the Δ form of the corresponding complex, the β-carboxylate groups of the two L-aspartate groups locate at the middle of the two H atoms of the amino groups of the diamine ligand as the most probable form. Thus, stronger hydrogen bonding is expected of the Λ form than for the corresponding Δ form. For the cis(O),cis(N)-Δ isomer, the β-carboxylate group of an L-aspartate ligand can take the direction of an H atom of the NH_2 of the other aspartate, and the β-carboxylate group of the latter ligand locates at the middle of the two H atoms of an NH_2 of the diamine as the most probable form. On the other hand, in the corresponding Λ isomer, the β-carboxylate group of an L-aspartate ligand points to an H atom of an NH_2 of the diamine, but the β-carboxylate group of the other aspartate is most probable to point to the coordinated carboxylate of the first aspartate ligand and will cause a certain repulsion against the latter. The poorer formation of the Λ isomer than of the Δ form is concluded to have arisen from this kind of repulsion. In fact, the model for the Δ form of the cis(O),trans(N) isomer shows that the β-carboxylate group from either aspartate ligand points to the complexed carboxylate group of the opposite ligand, and the corresponding complex has not been isolated in the present work.

The formation ratio of the Λ and Δ isomers of the bis(*l*-propylenediamine) complex is estimated as about 5.4:5.6 (Table III). By way of comparison, the result on the Co(gly)(*l*-pn)$_2^{2+}$ complex was Λ:Δ = 1:7.[1] If only the stereospecific effect of the coordinated *l*-pn is considered in application to the selective formation of the present complex, the Δ form is to be formed predominantly because of the stable "lel" conformation of the *l*-pn ligand.[8,9] However, the experimental result gives nearly the same amount of the Λ form as of the Δ one (1:1.03). This fact will be attributed to the β-carboxylate group of the coordinated L-aspartate. Namely, in the Λ form, the β-carboxylate group can take the direction of an H atom of an NH_2 of the neighboring diamine. On the other hand, in the Δ isomer, the β-carboxylate group locates at the middle of the two

TABLE III
FORMATION RATIOS OF Co(L-asp)(*l*-pn)$_2^+$ ISOMERS

Λ	Δ
E-8 + E-9 + E-10 + E-11	E-12 + E-13
1 + 1 + 1.7 + 1.7	0.6 + 5
Λ:Δ = 1:1.03	
$\Delta G_{obsd}(25°)$ = 0.017 kcal mol^{-1}	

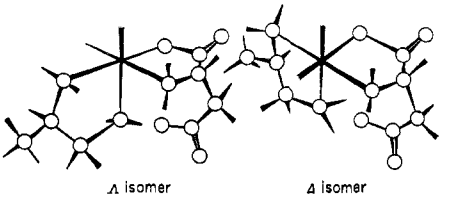

Figure 9.—Orientation of the β-COO^- of complexed aspartate ion.

H atoms of an NH_2 of the neighboring diamine (Figure 9). It is expected that there are stronger hydrogen bondings in the Λ isomer than in the Δ isomer.