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The PMR Studies of Tris-Type Mixed Complexes of Cobalt(III) with Amino Acid and Diamine

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Abstract For the mixed ligand complexes of Co(III) with (a) glycine and *l*-propylenediamine, (b) L-aspartic acid and *l*-propylenediamine, and (c) L-aspartic acid and ethylenediamine, 16, 8, and 16 stereoisomers are possible to exist, respectively. The greater part of the stereoisomers has been separated by ion-exchange column chromatography. The proton magnetic resonance spectra of the isolated isomers have been measured and investigated with respect to the structures of the isomers. The results have shown the following facts; the methyl protons of the chelated *l*-propylenediamine ring in the *trans*-(O)*cis*(N)-bis(L- α -amino-acidato)-*l*-propylenediamine complex resonate at lower magnetic field than those of the *cis*(O)*trans*(N) complex, and the β -proton of the chelated L- α -amino-acidate ring of the Λ L- α -amino-acidato-diamine complex resonates at lower field than that of the Δ complex.

1. Introduction

Recently, a number of reports¹⁻¹⁰⁾, including our studies, have been presented for the stereochemistry of the mixed ligand cobalt(III) complexes with ethylenediamine (or *l*-propylenediamine) and α -amino-acidato ligand. In those studies, the characterizations of the stereoisomers have mainly been based on the absorption and circular dichroism (CD) spectra. And the proton magnetic resonance (PMR) spectra have been used for an additional characterization in a few reports⁶⁻⁷⁾.

MATSUOKA *et al*⁶⁾ measured the PMR spectra of three geometrical isomers of the Co(gly)₂(en)⁺ complex and assigned them to the structure of C₁-*cis*(O) and C₂-*cis*(O) isomer on the basis of the splitting of the methylene resonance peaks of the chelated glycinate ring. KOJIMA and SHIBATA¹⁰⁾ have applied the same assignment to the Co(L-aspH)₂(en)⁺ complex; the *cis*(O)*cis*(N) isomer could be distinguished from other two isomers on the basis of the splitting signals of the methylene protons of the chelated L-aspartate. DABROVICK and COOKE¹¹⁾ measured the PMR spectra of several isomers of the mixed complexes of ethylenediamine and L- α -amino acid, and found that the α -proton of the chelated α -amino-acidate of the Λ isomer resonates at lower field than that of the corresponding Δ isomer. These assignments made use of the steric compressions of

the α -protons of L- α -amino acids with the amino groups of the neighboring chelates. The consideration of the structures based upon the different electronic environments of certain protons has been made to the cobalt(III) complexes of ethylenediamine-N, N'-diacetic acid¹²⁾ or ethylenediamine-N, N'-di-L(or D)- α -propionic acid¹³⁾ with ethylenediamine or *l*-propylenediamine.

KOJIMA and SHIBATA^{7, 8)} have measured the PMR spectra of a series of the stereoisomers with *l*-propylenediamine and L-aspartic acid or glycine, and characterized the isomers on the basis of the signals of the methylene protons in glycine and L-aspartic acid and the methyl protons in *l*-propylenediamine. However, no detailed investigation concerning the structures and spectra has been undertaken by them. On the relation of the absolute configuration of diastereomers with *l*-propylenediamine to the PMR spectra, only a study of the $\text{Co}(\text{ox})_2(\textit{l-pn})^+$ complexes¹⁴⁾ have so far been reported.

In this paper, the PMR spectra of the various stereoisomers of the mixed complexes of diamine and amino acid will be reported and the relation of their structures and PMR spectra will be discussed.

2. Experimental

2-1. Reagents

Optically active *l*-propylenediamine (*l*-pn) was obtained by resolving its commercial racemate with *d*-tartaric acid according to the method described in the literature¹⁵⁾. The specific rotation in dry benzene $[\alpha]_{\text{D}}^{25}$ was -34.7° (lit.¹⁵⁾ value $-34.8 \pm 0.4^\circ$). For glycine (glyH), L-aspartic acid (L-aspH₂), and ethylenediamine (en), the chemical grade reagents were used.

2-2. Preparation

Trans-dichlorobis (*l*-propylenediamine) cobalt (III) chloride Monohydrate, *trans*- $[\text{CoCl}_2(\textit{l-pn})_2]\text{Cl} \cdot \text{H}_2\text{O}$.—0.42 mol of cobalt chloride hexahydrate was dissolved in about 2 l of water containing 0.55 mol of *l*-pn, and air was bubbled through the solution for 33 hours. After that, 800 ml of conc. HCl was added, and the solution was concentrated to 400 ml on a water-bath at 60°C. On standing at room temperature for a day, the green crystals of *trans*- $[\text{CoCl}_2(\textit{l-pn})_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ ¹⁶⁾ were obtained. After dissolving the solid in ethanol, ether was added to the solution to crystallize gray-green crystals of the *trans*- $[\text{CoCl}_2(\textit{l-pn})_2]\text{Cl} \cdot \text{H}_2\text{O}$ complex. This treatment was repeated several times in order to purify the complex. Anal. Calcd for $[\text{CoC}_3\text{H}_{10}\text{N}_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$: C, 21.68; H, 6.72; N, 16.74%. Found: C, 21.74; H, 6.69; N, 16.90%.

Trans-dichlorobis(ethylenediamine)cobalt(III)chloride Hydrochloric Acid Dihydrate, *trans*- $[\text{CoCl}_2(\text{en})_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$.—This complex¹⁷⁾ was prepared by the same procedure as the *trans*- $[\text{CoCl}_2(\textit{l-pn})_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ complex.

Bis (L - hydrogenaspartato) - *l* - propylenediaminecobalt (III) and L - aspartatobis-

(*l*-propylenediamine)cobalt(III),⁸⁾ $[\text{Co}(\text{L-aspH})_2(\textit{l-pn})]^+$ and $[\text{Co}(\text{L-asp})(\textit{l-pn})_2]^+$. — The complex *trans*- $[\text{CoCl}_2(\textit{l-pn})_2]\text{Cl} \cdot \text{H}_2\text{O}$, 9g (0.027 mol), was dissolved in 20 ml of water, and L-aspartic acid, 7.4g (0.055mol), was dissolved in the solution, adding simultaneously an aqueous NaOH solution. After that, the resulting solution was adjusted to pH~10 with the alkaline solution. After adding active charcoal (1.2 g), the mixture was stirred at 55°C for 15 min; then the color of the solution became red-brown. After the removal of the charcoal by hot filtration, the filtrate was adjusted to pH~8 with aqueous hydrochloric acid. The solution was added to an ion-exchange column (diameter, 6 cm; height of resin, 40cm) containing 100–200 mesh Dowex 50W X 8 resin in the hydrogen form. At this stage, the absorbed complexes formed two bands at the top of the column (a red-brown and a red band, up and down). After the column was thoroughly swept with water, the bands were eluted with successive, a 0.1M, 0.4M, and 1M aqueous solution of sodium perchlorate at a rate of about 0.2ml/min. As the result, six bands colored red or red-violet, four bands colored red-brown, and two bands colored red-brown eluted with complete separation corresponding to concentrations of sodium perchlorate solution. The fractions of these bands were collected, and then the complexes were isolated from each fractions.

The last fraction was rechromatographed using a smaller column and 0.5M NaClO₄ at a slower rate (0.1ml/min). Three overlapped bands were obtained and these were collected in fractions. A yellow band still remained at the top of the original column and it was the tris(*l*-propylenediamine)cobalt(III) species.

Each fraction was evaporated to about dryness at 40°C 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 kept in a refrigerator for several days to crystallize the desired complex as the perchlorate salt.

Bis(L-hydrogenaspartato)ethylenediaminecobalt(III) and L-aspartatobis(ethylenediamine)cobalt(III), $[\text{Co}(\text{L-aspH})_2(\text{en})]^+$ and $[\text{Co}(\text{L-asp})(\text{en})_2]^+$. — A series of the stereoisomers of these complexes were prepared according to the method described in the literature¹⁰⁾. The preparative reaction for the present complexes and the procedure for the chromatographic separation of the isomers were essentially the same as those of the *l*-propylenediamine complexes above-mentioned. The *trans*- $[\text{CoCl}_2(\text{en})_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ (19g, 0.025mol) complex and L-aspartic acid (8.5g, 0.04mol) were allowed to react, in the presence of active charcoal, under an alkaline condition (pH~10). For the chromatographic separation, a column (7.5cm X 23cm) containing

100–200 mesh Dowex 50W X 8 resin in the hydrogen form was used. Two absorbed bands were eluted with a 0.1M and 0.3M aqueous solution of NaClO₄. By treating each fraction of seven bands, six possible isomers of the [Co(L-aspH)₂(en)]⁺ complex and the diastereoisomers of [Co(L-asp)(en)₂]⁺ complex were isolated.

Bis(glycinato)-*l*-propylenediaminecobalt(III) and glycinatobis(*l*-propylenediamine)cobalt(III), [Co(gly)₂(*l*-pn)]⁺ and [Co(gly)(*l*-pn)₂]²⁺. — The geometrical optical isomers of these complexes were prepared according to the method described in the literature⁷). An aqueous solution containing *trans*-[CoCl₂(*l*-pn)₂]Cl · H₂O (16g, 0.048mol) and glycine (3.8g, 0.05mol) was adjusted to pH~8 with an aqueous NaOH solution. The solution was stirred for about 3 hrs at room temperature, and then evaporated to dryness at about 70°C. The red-brown product was obtained.

This product was dissolved in water, and the solution was added to an ion-exchange column (8cm X 14.5cm) containing 100–200 mesh Dowex 50W X 8 resin in the sodium form. The band of the complex observed at the top of the column was successively eluted with 0.5M and 2M aqueous solution of NaCl at a rate about 0.6ml/min. As the result, four band colored red or red-violet were completely separated for a 0.5M NaCl solution, and four eluted bands were collected in fractions. On the other hand, for 2M NaCl solution, two red-brown bands were collected in two fractions. By treating these fractions, six isomers of the [Co(gly)₂(*l*-pn)]⁺ complex and two optical isomers of [Co(gly)(*l*-pn)₂]²⁺ were isolated.

2-3. Measurements

Electronic absorption spectra were measured with a Hitachi Parkin-Elmer Model 139 UV-visible spectrophotometer. Circular dichroism spectra were recorded on a JASCO Model ORD/UV-5 spectrophotometer with CD attachment. Proton magnetic resonance spectra were recorded on a JEOL Model C-60H spectrometer (60 MHz) or a JEOL Model JNM-MH-60II spectrometer (60 MHz) at about 25°.

The values of the chemical shift were measured in relation to DSS (sodium 2, 2-dimethyl-2-silapentane-5-sulfonate) as an internal reference and corrected by the mixed reference sample. All spectra were run with deuterium oxide solutions.

3. Results and Discussions

3-1. Possible Isomers

Both of the aspartate ion and the *l*-propylenediamine molecule contain one asymmetric carbon, and it is well-known that the absolute configurations of L-aspartic acid¹⁸⁾ and *l*-propylenediamine¹⁹⁾ are of the structures shown in Figure 1. The chelated α-amino-acidate ion as a bidentate ligand forms a planar five-membered ring with slight distortion²⁰⁾. On the other hand, it is well-known generally that the *l*-pn chelate as well as the en one is not mere planar structure but two amino groups exist in *gauche* form^{21–23)}. Two *gauche* conformations of the *l*-pn rings are shown in Figure 2. As

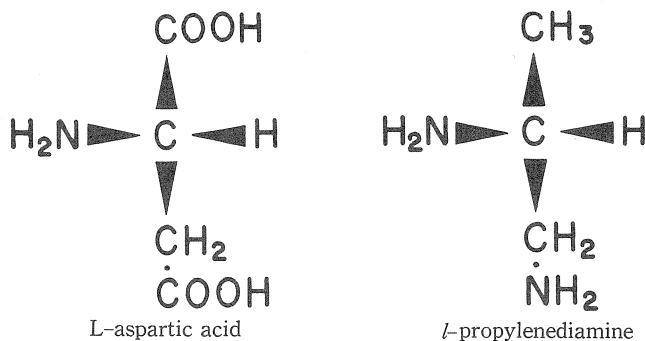
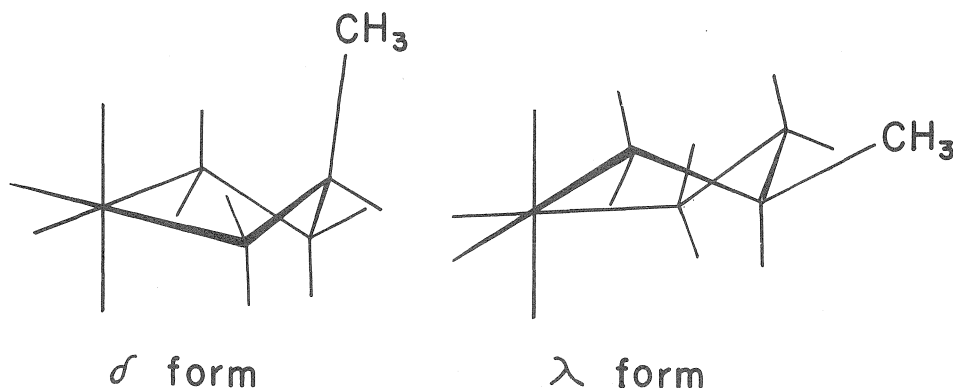


Figure 1. The absolute configuration of L-aspartic acid and l-propylenediamine.

Figure 2. The conformation of the M-*l*-pn chelate ring.

shown in Figure 2, when the conformation of the chelated *l*-pn ring is λ form²⁴), a methyl group occupies the axial position to the chelate ring, and when the conformation is δ form, the methyl group occupies the equatorial position (the ring conformation of the ligand and the absolute configuration of the complex are designated according to IUPAC rule²⁵). The energy difference between the conformers with the axial and equatorial methyl groups was estimated to be about 2 Kcal/mol by BAILAR and COREY²²). Recently, it has been substantiated, on the basis of the PMR spectra of the $[\text{Co}(\text{CN})_4(\textit{l-pn})]^-$ complex²⁶) and the X-ray structural analysis of the $(-)\text{CD}-[\text{Co}(\textit{l-pn})_3]\text{Br}_3$ complex²³), that the *l*-pn ligand has the rigid *gauche* structure of the λ conformation. From these facts, it has been established that the five-membered ring formed by the metal ion and the coordinating *l*-pn is λ conformation in which the methyl group of *l*-pn occupies an equatorial direction to the chelate ring.

When the right or left spiral of the chelate ring is considered to exist in such a complex, the diastereoisomers exist, and the structures of those isomers are distinguished as the symbols Λ and Δ ²⁵). In the Λ absolute configuration of the complex, the C-C bond axis of the backbone of *l*-pn with the λ conformation is oblique (*ob*) to the pseudo C_3 axis of the complex ion, while in the Δ absolute configuration, the C-C bond

axis is parallel (*lel*) to the pseudo C_3 axis. These relations have become apparent by referring to the construction of the molecular models. However, the energy difference between the *lel* and *ob* forms was estimated to be 0.6 Kcal/mol \cdot ring²²⁾, and it has been found on the basis of the X-ray structural analysis that in the crystals of the various complexes with the Λ and Δ absolute configurations of the en ligand, the C-C bond axis of the chelating en is parallel to the C_3 axis in both of the Λ and Δ ²¹⁾. But it is known that the conversion between the λ and δ conformations takes place rapidly in

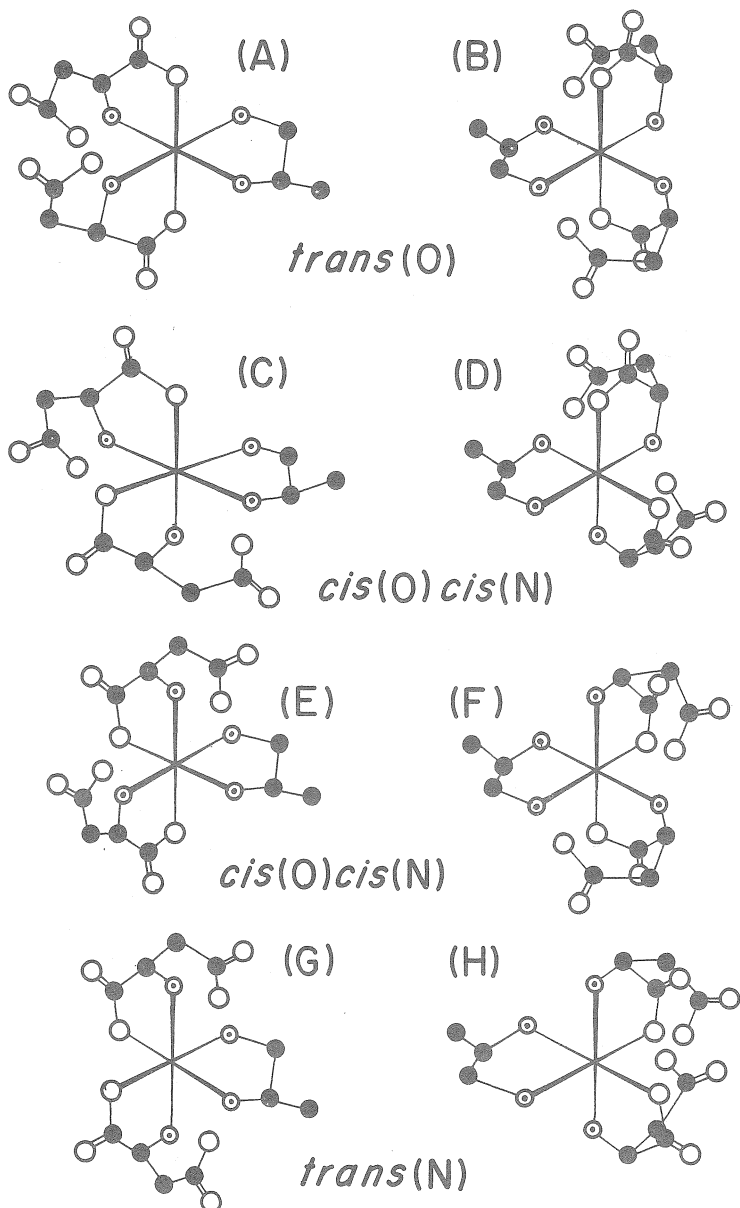


Figure 3. The possible stereoisomers of $\text{Co}(\text{L-aspH})_2(\text{l-pn})^+$.

solution at room temperature²⁷).

For the bis(α -amino-acidato) complex, three geometrical isomers are possible to exist with respect to the coordinated N and O atoms of the α -amino-acidate ions; trans(O)cis(N), cis(O)cis(N), and cis(O)trans(N). The spiral of the chelate ring (Λ and Δ) must be considered for these all isomers. Consequently, six stereoisomers are to exist for the bis(L-hydrogenaspartato)ethylenediamine complex. On the other hand, for the complex containing *l*-pn instead of en, cis(O)cis(N) isomer produces two stereoisomers with respect to the equatorial methyl groups as shown in Figure 3. Consequently, eight stereoisomers are possible to exist for the α -aminoacidatobis(*l*-propylenediamine) complex.

For the $[\text{Co}(\text{N})_5(\text{O})]$ -type complex with one α -amino-acidate ion and two diamine molecules, when the diamine is en, only one pair of the Λ and Δ isomers can exist. However, when the diamine is *l*-pn, four isomers can exist with respect to the orientation of the equatorial methyl groups of the *l*-pn. Consequently, when the spiral of the chelate ring is taken into consideration, eight possible stereoisomers exist for the bis(*l*-propylenediamine) complex (Figure 4).

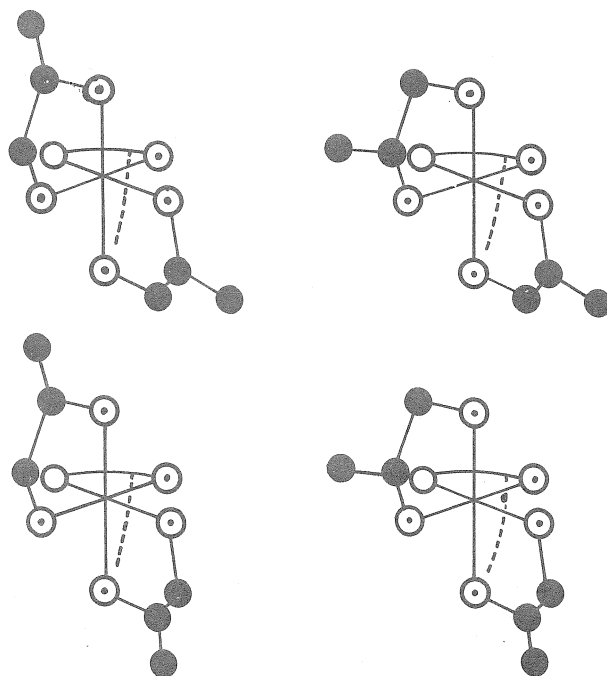


Figure 4. The possible stereoisomers of $\Lambda\text{-Co}(\text{L-asp})(\textit{l}\text{-pn})_2^+$.

3-2. Characterization by Absorption and CD Spectra

The numerical data of the electronic absorption spectra of all compounds isolated

Table I. Electronic Absorption Spectra and CD Spectra of the Complexes.

Label ^a	Complex ion	Band I		Band II		CD	
		$10^{-3}\tilde{\nu}_{max}$, cm ⁻¹	ϵ_1	$10^{-3}\tilde{\nu}_{max}$, cm ⁻¹	ϵ_2	$10^{-3}\tilde{\nu}_{max}$, cm ⁻¹	$\Delta\epsilon_{max}$
E-1	<i>trans(O)cis(N)</i> - Λ -(+)-[Co(L-aspH) ₂ (en)] ⁺	18.8 21.6 sh	94	27.6	144	18.6	+3.17
E-2	<i>trans(O)cis(N)</i> - Δ -(-)-[Co(L-aspH) ₂ (en)] ⁺	18.6 21.6 sh	78	27.6	120	18.4 21.7	-2.08 -1.43
E-4	<i>cis(O)cis(N)</i> - Λ -(+)-[Co(L-aspH) ₂ (en)] ⁺	19.9	144	27.8	154	19.6	+2.64
E-3'	<i>cis(O)cis(N)</i> - Δ -(-)-[Co(L-aspH) ₂ (en)] ⁺ ^c	20.0	127	27.7	133	19.5	-2.24
E-3	<i>cis(O)trans(N)</i> - Λ -(+)-[Co(L-aspH) ₂ (en)] ⁺ ^b	19.9	128	27.9	169	19.5 22.2	+4.83 -1.18
E-5	<i>cis(O)trans(N)</i> - Δ -(-)-[Co(L-aspH) ₂ (en)] ⁺ ^d	19.9		27.9		19.5	-
E-6	Λ -(+)-[Co(L-asp)(en) ₂] ⁺	20.5	102	28.7	109	19.8	+2.66
E-7	Δ -(-)-[Co(L-asp)(en) ₂] ⁺	20.5	100	28.7	104	19.7	-2.25
E-1	<i>trans(O)cis(N)</i> - Λ -(+)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺	18.9 21.6 sh	97	27.7	145	18.7	+2.20
E-2	<i>trans(O)cis(N)</i> - Λ -(+)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺	18.9 21.6 sh	98	27.7	146	18.8	+2.35
E-3	<i>trans(O)cis(N)</i> - Δ -(-)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺	18.9 21.6 sh	96	27.6	146	18.4 21.9	-1.55 -0.98
E-4	<i>cis(O)cis(N)</i> - Λ -(+)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺ ^e	20.0	135	27.9	155	20.0	+1.35
E-5	<i>cis(O)cis(N)</i> - Δ -(-)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺ ^e	20.0	135	27.9	154	19.2	-0.82
E-6	<i>cis(O)trans(N)</i> - Λ -(+)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺ ^d					19.7	+
E-8	Λ -(+)-[Co(L-asp)(<i>l</i> -pn) ₂] ⁺	20.5	99	29.0	115	20.2	+1.92
E-9	Λ -(+)-[Co(L-asp)(<i>l</i> -pn) ₂] ⁺	20.5	99	29.0	115	20.2	+1.92
E-10	Λ -(+)-[Co(L-asp)(<i>l</i> -pn) ₂] ⁺	20.6	99	29.0	115	20.2	+1.88
E-11	Λ -(+)-[Co(L-asp)(<i>l</i> -pn) ₂] ⁺	20.5	99	29.0	115	20.2	+1.87
E-12	Δ -(-)-[Co(L-asp)(<i>l</i> -pn) ₂] ⁺	20.6	99	28.7	115	19.6	-1.80
E-13	Δ -(-)-[Co(L-asp)(<i>l</i> -pn) ₂] ⁺ ^e	20.5	99	28.7	115	19.6	-1.80
E-1	<i>trans(O)cis(N)</i> - Λ -(+)-[Co(gly) ₂ (<i>l</i> -pn)] ⁺	18.8 21.4 sh	90	27.6	138	18.5 21.4	+2.14 +0.63
E-2	<i>trans(O)cis(N)</i> - Δ -(-)-[Co(gly) ₂ (<i>l</i> -pn)] ⁺	18.8 21.4 sh	90	27.6	138	18.4 21.6	-2.14 -0.76
E-3	<i>cis(O)cis(N)</i> -[Co(gly) ₂ (<i>l</i> -pn)] ⁺ ^b	19.9	117	27.7	129	19.7	+0.74
E-3'	<i>cis(O)cis(N)</i> -[Co(gly) ₂ (<i>l</i> -pn)] ⁺ ^{c, e}	19.9	117	27.7	129	20.8 19.1	+0.20 -0.15
E-4'	<i>cis(O)trans(N)</i> - Λ -(+)-[Co(gly) ₂ (<i>l</i> -pn)] ⁺ ^{c, d}					19.8	+
E-4	<i>cis(O)trans(N)</i> - Δ -(-)-[Co(gly) ₂ (<i>l</i> -pn)] ⁺ ^b	20.0	104	27.9	128	19.3	-1.94
E-5	Λ -(+)-[Co(gly)(<i>l</i> -pn) ₂] ²⁺	20.5	96	28.8	113	20.1	+2.33
E-6	Δ -(-)-[Co(gly)(<i>l</i> -pn) ₂] ²⁺	20.5	96	28.8	113	19.5	-2.20

a Fraction order.

b Less soluble isomer.

c More soluble isomer.

d No elemental analyses were carried out because of the poor yield.

e For substantially pure compounds.

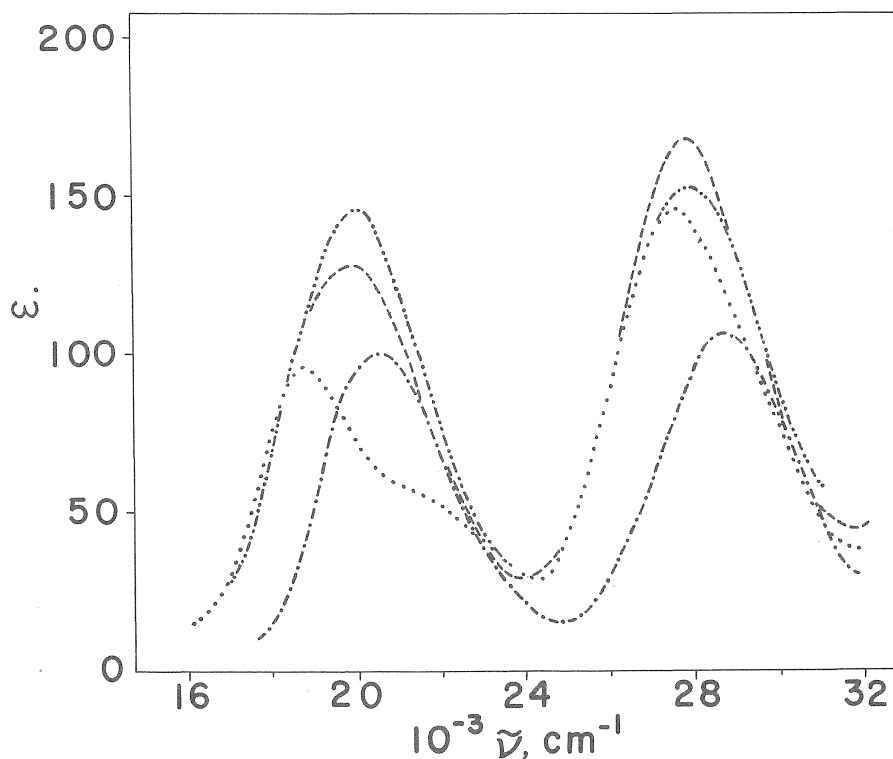


Figure 5. The electronic absorption spectra of *trans(O)cis(N)*- Λ -Co(L-aspH)₂(en)⁺ (.....), *cis(O)cis(N)*- Λ -Co(L-aspH)₂(en)⁺ (-·-·-·-·-), *cis(O)trans(N)*- Λ -Co(L-aspH)₂(en)⁺ (-·-·-·-·-), and Λ -Co(L-asp)(en)₂⁺ (- - - -) in D₂O.

are summarized in Table I, and some typical electronic spectra of the L-aspartato-bis(ethylenediamine) and bis(L-hydrogenaspartato)ethylene diamine complexes are shown in Figure 5. The shapes of the electronic spectra for the bis(glycinato)-*l*-propylenediamine and bis(L-hydrogenaspartato)-*l*-propylenediamine complexes were the same as those of the corresponding ethylenediamine complexes. For the bis(amino-acidato) complex, three stereoisomers exist with respect to the coordinated N and O atoms of the amino-acidato ligand as mentioned before. The first absorption band of the *trans(O)cis(N)* isomer shows a more remarkable splitting than is found in two corresponding *cis(O)* isomers as is seen in Figure 5. The same fact is found for the *trans(O)* isomer of the Co(en)(aa)₂⁺ (aa = gly⁶, ala²⁸), Co(X)(EDDA)⁺ (X = en, *l*-pn)¹², Co(X)(EDDP)⁺ (X = en, *l*-pn)¹³, and Co(NH₃)₂(EDDA)⁺ complexes²⁹, and it is generally recognized that the splitting of the absorption curve of the [Co(N)₄(O)₂]-type complex is characteristic to the *trans(O)* isomer. On the other hand, shapes of the *cis(O)* isomers have nothing to show for the characteristic difference. Consequently, it is necessary to assign on the basis of PMR spectra, which will be mentioned latter. Nevertheless, it is found that the values of ϵ_2/ϵ_1 calculated from the molar extinction coefficients (ϵ_1) of

the first absorption band and those (ϵ_2) of the second absorption band for three isomers are small in order of *trans*(O)*cis*(N), *cis*(O)*trans*(N), and *cis*(O)*cis*(N) for the

Table II. Values of ϵ_2/ϵ_1 for Co(aa)₂(diamine) Complexes.

complex ion	<i>trans</i> (O) <i>cis</i> (N)	<i>cis</i> (O) <i>cis</i> (N)	<i>cis</i> (O) <i>trans</i> (N)	ref.
[Co(L-aspH) ₂ (en)] ⁺ ^a	1.32	1.05	1.07	
[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺ ^a	1.50	1.15		
[Co(gly) ₂ (<i>l</i> -pn)] ⁺ ^a	1.53	1.10	1.23	
[Co(gly) ₂ (en)] ⁺ ^{b, d}	1.52	1.09	1.17	5
[Co(L-ser) ₂ (en)] ⁺ ^{c, d}	1.52	1.07	1.24	5

a Value of Λ isomer is equal to that of Δ isomer.

b No resolved complex.

c Average values of Λ and Δ isomers.

d ϵ was converted from log ϵ .

Co(L-aspH)₂(en)⁺, Co(L-aspH)₂(*l*-pn)⁺, and Co(gly)₂(*l*-pn)⁺ complexes (Table II). This relation in ϵ values has also been found in the Co(L-ser)₂(en)⁺ complex⁵⁾. From these, it is considered that the above-mentioned empirical relation can be used to identify three isomers of the bis(amino-acidato) complex.

MASON *et al.*³⁰⁾ have shown that the dominant lower energy CD peak in the first absorption band region can be related to the ¹A₁ → E_a transition of the Co(en)₃³⁺ complex. That is, positive sign indicates the Λ isomer and negative sign, the Δ isomer. MASON³¹⁾ has assigned the Δ configuration to the *trans*(O)-Co(en)(EDDA)⁺ and *trans*(O)-Co(en)(L-ala)₂⁺ isomers which have a negative CD band due to the ¹A₁ → E_a transition in the first absorption band region. These assignments have been supported by the PMR data¹¹⁾. MATSUOKA *et al.*³²⁾ have determined the absolute configurations of all isomers for the Co(ox)(L-ser)₂ complex on the basis of the major CD band in the first absorption band region. In the same manner, the present isomers having dominant positive peak in the first absorption band region were to be assigned to the Λ configuration, and corresponding isomers having a negative peak, to the Δ configuration^{7,8,10)}. The numerical data of the isolated isomers are summarized in Table I.

3-3. PMR Spectra

3-3-A. Assignment of the Signal

In the PMR spectrum of the Co(L-aspH)(NH₃)₄²⁺ complex¹¹⁾ in deuterium oxide, only the ABX portion of the chelated aspartate is detected. The spectrum shows a triplet at 3.74 ppm (one proton from integration) with a splitting between the outer peaks of 3 Hz and a doublet centering at 2.85 ppm (two protons). It follows then that the triplet belongs to the methine proton (X of ABX) of the α carbon, and the doublet, to the methylene protons (AB of ABX) of the β carbon. The PMR spectrum of the Co(en)₃³⁺ complex in deuterium oxide shows a singlet at 2.84 ppm. This singlet must belong to the methylene protons of the chelated en. On the other hand, the PMR spectrum of the Λ -Co(gly)(en)₂²⁺

complex¹⁾ in deuterium oxide exhibits two peaks at 2.81 and 3.57 ppm, and the integrated intensities of the observed peaks are in 4:1. This ratio corresponds to eight protons of the four methylene groups of the two ethylenediamine and to two protons of a methylene group of the chelated glycinate. Furthermore, the peak at the higher field is the chemical shift close to that of the peak of the tris(ethylenediamine) complex. Judging from these facts, the singlet at 3.57 ppm is assignable to the methylene protons of the glycinate. Moreover, in the spectrum of $\Lambda(+)$ ₅₈₉-Na[Co(ox)₂(*l*-pn)] in D₂O, one doublet (J=6Hz) at 81 Hz (60 MHz, from NaTPS) had been assigned to the methyl protons of *l*-pn¹⁴⁾. On the basis of these facts and the intensities of the signals, the assignments of the signals in the spectra of the various isomers of the present complexes, L-aspartato-ethylenediamine, L-aspartato-*l*-propylenediamine, and glycinate-*l*-propylenediamine, have easily been achieved^{7,8,10)}. The numerical data of the PMR spectra are summarized in Table III~IV.

Table III. Assignments of PMR Signals^a of [Co(aa)₂(diamine)] Complexes.

Complex ion	<i>l</i> -pn ^b CH ₃	en CH ₂ · CH ₂	L-aspH ^b CH ₂	L-aspH ^b CH	gly CH ₂
<i>trans</i> (O) <i>cis</i> (N)- Λ -(+)-[Co(L-aspH) ₂ (en)] ⁺		2.84	3.09	3.81	
<i>trans</i> (O) <i>cis</i> (N)- Δ -(-)-[Co(L-aspH) ₂ (en)] ⁺		2.92	3.00	4.02	
<i>cis</i> (O) <i>cis</i> (N)- Λ -(+)-[Co(L-aspH) ₂ (en)] ⁺		2.83	2.97, 3.05	d	
<i>cis</i> (O) <i>cis</i> (N)- Δ -(-)-[Co(L-aspH) ₂ (en)] ⁺		? ^c	2.77, 2.88	3.65, 3.78	
<i>cis</i> (O) <i>trans</i> (N)- Λ -(+)-[Co(L-aspH) ₂ (en)] ⁺		2.74	3.01	3.94	
<i>cis</i> (O) <i>trans</i> (N)- Δ -(-)-[Co(L-aspH) ₂ (en)] ⁺		2.92	2.79	4.13	
<i>trans</i> (O) <i>cis</i> (N)- Λ -(+)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺	1.44		3.11	3.85	
<i>trans</i> (O) <i>cis</i> (N)- Δ -(-)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺	1.41		3.06	3.98	
<i>cis</i> (O) <i>cis</i> (N)- Λ -(+)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺ f	1.35, 1.45		2.95 ^e	3.84 ^e	
<i>cis</i> (O) <i>cis</i> (N)- Δ -(-)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺ f	1.28, 1.38		2.73, 2.81	3.58, 3.60	
<i>cis</i> (O) <i>trans</i> (N)- Λ -(+)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺	1.25		2.90	ca.3.7 ^e	
<i>cis</i> (O) <i>trans</i> (N)- Δ -(-)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺ g					
<i>trans</i> (O) <i>cis</i> (N)- Λ -(+)-[Co(gly) ₂ (<i>l</i> -pn)] ⁺	1.45				3.69
<i>trans</i> (O) <i>cis</i> (N)- Δ -(-)-[Co(gly) ₂ (<i>l</i> -pn)] ⁺	1.44				3.63
<i>cis</i> (O) <i>cis</i> (N)- Λ -(+)-[Co(gly) ₂ (<i>l</i> -pn)] ⁺	1.43				3.46, 3.62
<i>cis</i> (O) <i>cis</i> (N)- Δ -(-)-[Co(gly) ₂ (<i>l</i> -pn)] ⁺	1.29				3.46, 3.59
<i>cis</i> (O) <i>trans</i> (N)- Λ -(+)-[Co(gly) ₂ (<i>l</i> -pn)] ⁺	1.35				3.67
<i>cis</i> (O) <i>trans</i> (N)- Δ -(-)-[Co(gly) ₂ (<i>l</i> -pn)] ⁺	1.31				3.64

a Values in ppm from DSS.

b Chemical shifts of *l*-pn:CH₃, L-aspH:CH₂, and L-aspH:CH are shown at the centers of doublet, doublet, and triplet, respectively.

c This peak is covered due to the methylene peaks of L-aspartate.

d Because of the poor solubility, no peak was detected.

e Broad peak.

f Mixture of two Λ (or Δ) isomers.

g Because of the poor yield, no measurement was carried out.

Table IV. Assignments of PMR Signals^a of [Co(aa)(diamine)₂] Complexes.

complex ion		Λ				Δ			
[Co(L-asp)(en) ₂] ⁺	en:CH ₂ ·CH ₂	2.90				2.83			
	L-asp:CH ₂ ^b	2.81				2.76			
	L-asp:CH ^b	3.78				3.82			
[Co(L-asp)(l-pn) ₂] ⁺	l-pn:CH ₃ ^b	1.35, 1.39	1.35	1.25, 1.35	1.24, 1.40	1.33, 1.38	1.33, 1.27, 1.33	1.29, 1.39	
	L-asp:CH ₂ ^b	2.82	2.83	2.84	2.83	2.81	2.80 ^c	2.78	
	L-asp:CH ^b	3.75	3.81	3.82	3.77	3.65	3.73 ^c	3.75	
[Co(gly)(l-pn) ₂] ²⁺	l-pn:CH ₃ ^b	1.23, 1.27, 1.41				1.31, 1.37, 1.43			
	gly:CH ₂	3.63 ^d				3.59 ^d			

a Values in ppm from DSS.

b Chemical shifts of l-pn:CH₃, L-asp:CH₂, and L-asp:CH are shown at the centers of doublet, doublet, and triplet, respectively.

c Mixture of two isomers.

d Mixture of four isomers.

3-3-B. Geometrical Isomers Concerning Donor Atom

For the mixed complex with two amino acids and a ethylenediamine, three geometrical isomers are possible to exist, and the trans(O)cis(N) and cis(O)trans(N) isomers belong to C₂ symmetry, and cis(O)cis(N) isomer, to C₁ symmetry. Accordingly, the chemical environment of the protons of two α-amino-acidato ligand in the former C₂ complex are equivalent each other. Therefore, one resonance peak is expected. On the other hand, the protons in the latter C₁ complex are nonequivalent, and two splitting resonance peaks with equal intensities are expected. The spectra, which are shown in Figure 6 (A)~(F), are obtained for the Co(L-aspH)₂(en)⁺ complex, and (C) and (D) in Figure 6 are assigned to the cis(O)cis(N) isomer on the basis of the above-mentioned considerations. Such assignments had been used in the cases of the Co(ox)(gly)₂⁻ and Co(en)(gly)₂⁺ complexes⁹, too. On the other hand, for the complex with l-pn, the chemical environments of the protons of two α-amino-acidato ligand in the trans(O) and trans(N) isomers are not equivalent. Accordingly, splittings of the peak are expected. However, the methylene protons of the chelated L-aspartato ligand in the spectra of the trans(O)cis(N)-Λ- and Δ-Co(L-aspH)₂(l-pn)⁺ complexes show a simple doublet similarly to the corresponding ethylenediamine complexes. This observation suggests a little difference of the chemical environment of the methylene groups of L-aspartato ligand. From the facts, the structure of the cis(O)cis(N)-Co(L-aspH)₂(l-pn)⁺ complex can be characterized by using the signal of the methylene protons of the chelated L-aspartate. The signal of the methylene protons of the glycinate in trans(O)cis(N)-Co(gly)₂(l-pn)⁺ complex shows no splittings. Accordingly, the cis(O)cis(N) isomers of this complex are characterized from the peak of the glycinate ligand.

The methyl protons signals of the chelated L-aspartate and ethylenediamine in the PMR spectra of the cis(O)cis(N)-Δ-Co(L-aspH)₂(en)⁺ complex are shown in Figure 7. For the sake of convenience, we call the complexes A, B, and C according to spectra (a), (b), and (c), respectively. The complex A and C were of those prepared separately by the

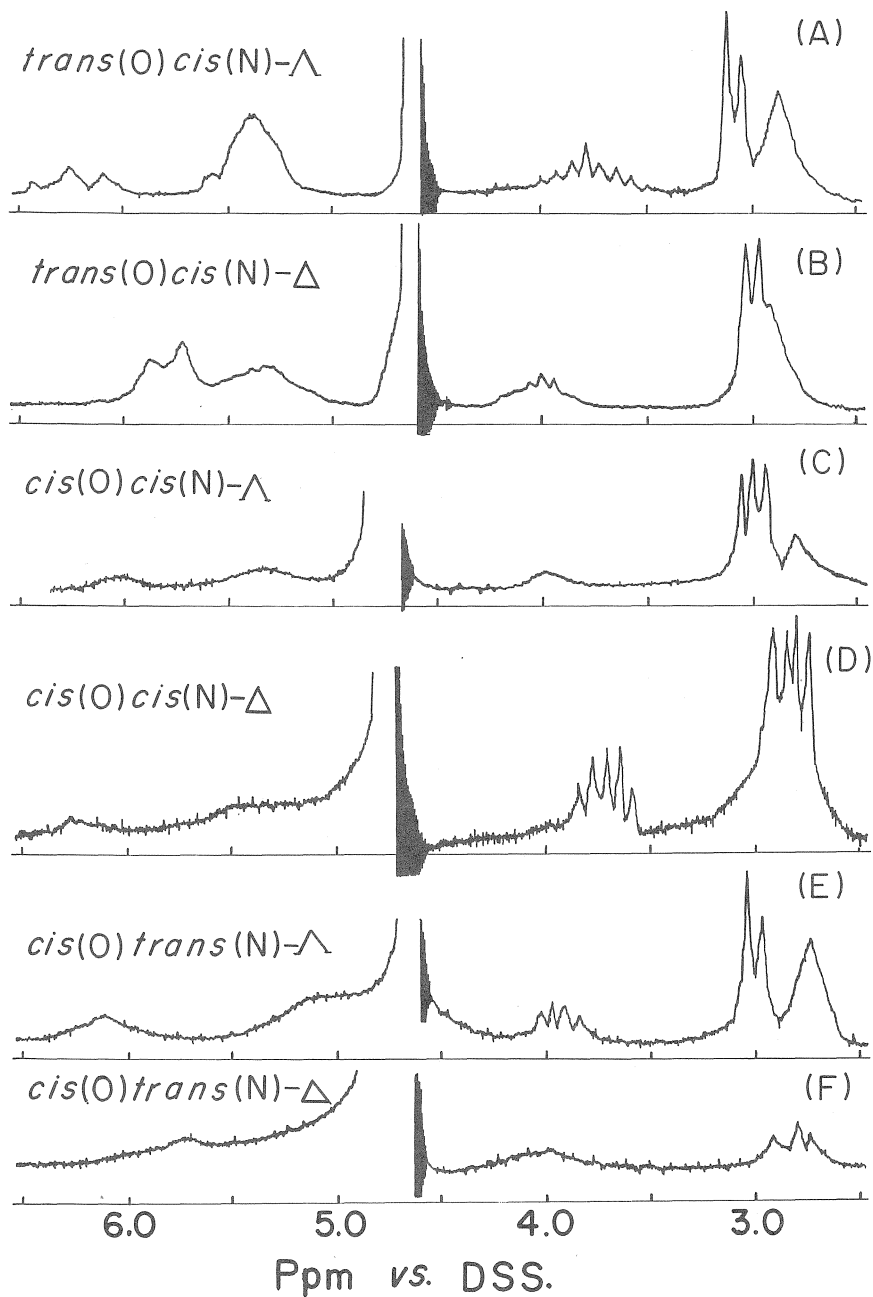


Figure 6. The PMR spectra of $\text{Co(L-aspH)}_2(\text{en})^+$.

same procedure. The complex B is what is converted from A to the nitrate by means of ion-exchange resin. The spectrum (b) is similar to the spectrum (c). The complex A, B, and C are assigned to the cis(O)cis(N) isomers because those exhibit the same two

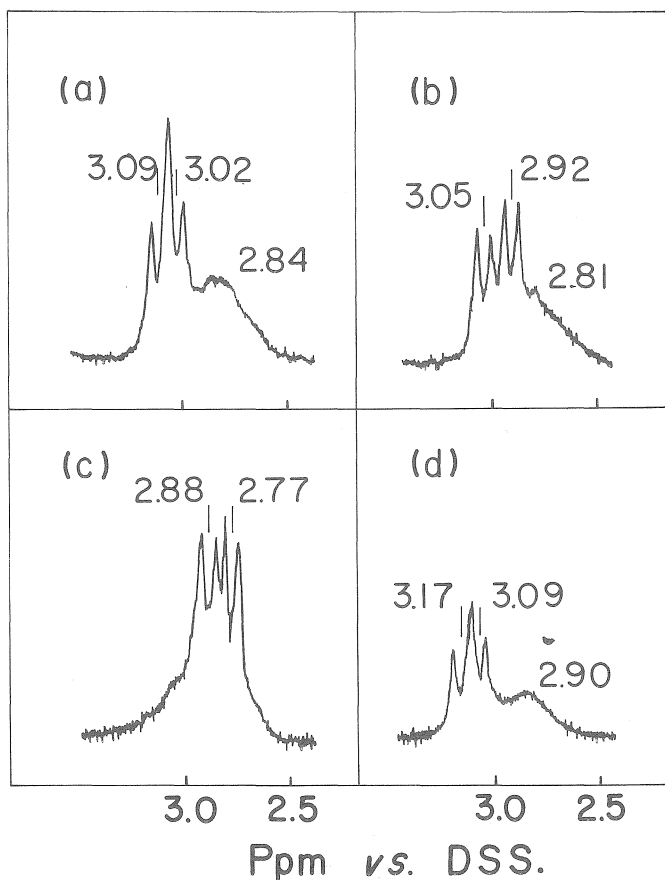


Figure 7. The PMR spectra of the CH_2 protons for $\text{cis}(\text{O})\text{cis}(\text{N})-\Delta\text{-Co}(\text{L-aspH})_2(\text{en})^+$.

doublets. The signal of the methylene protons of L-aspartic acid in the complex A shows a triplet, while the complexes B and C show completely separated two doublets. These facts suggest that the difference of the chemical environments in two methylene protons of the complex A is less than those of the complexes B and C. The signal due to the en ligand of the complex C moves slightly to the lower field (0.05 ppm) compared to the complex A, but the corresponding peaks of the methylene protons of the chelated L-aspartate shift to the higher field with 0.25 and 0.21 ppm. The difference of the chemical shifts in the methyl protons of the ligand EDDP of the $\Lambda\text{-Co}(\text{l-pn})(\text{LL-EDDP})^+$ and $\Lambda\text{-Co}(\text{d-pn})(\text{LL-EDDP})^+$ complexes, and that of the $\Lambda\text{-Co}(\text{l-pn})(\text{DD-EDDP})^+$ and $\Lambda\text{-Co}(\text{d-pn})(\text{DD-EDDP})^+$ complexes are 0.08 and 0.02 ppm^{11,13)}, respectively. Judging from these data, it is difficult to consider that such a large difference of the chemical shifts of the methylene protons is due to the difference of their chemical environments induced by fixing the conformation of the en ligand to the λ and δ form. The complexes A, B, and C show the same spectra in $\text{D}_2\text{O}-\text{D}_2\text{SO}_4$ (~25wt%) solution (Figure 7(d)), and the signals of the methylene protons of L-aspartic acid of the complexes A, B, and C shift to

lower field. The shift of the complex C is rather distinctive. Judging from the facts, it is considered that such a shift of the methylene protons is caused the protonation of the β -carboxylate group. Considering from the above-mentioned facts, it is understood that the degree of the protonation of the complex A is greater than that of the complex C. The construction of the molecular models indicates that for the *cis(O)cis(N)*- Δ -Co(L-aspH)₂(en)⁺ complex, the β -carboxylate group of an L-aspartate ligand directs to an amino group of the other aspartate ligand, and the β -carboxylate group of the second ligand locates at an amino group of the en ligand. In addition, the molecular models show that hydrogen-bonding is possible between the β -carboxylate groups and the amino groups. It is considered that the β -COO⁻ group can easily form hydrogen-bonding compared with β -COOH group. Accordingly, it is understood that the degree of the hydrogen-bonding of the complex C is greater than the complex A. Furthermore, judging from the fact that the complex A converts to the complex B, the complex C should be more stable than the complex A. Moreover, no difference was observed in the absorption or CD spectra between the A and C complexes. The above-mentioned result was examined for other isomers of the bis(L-aspartato)ethylenediamine complex, but the different PMR spectra were not observed, contrast to the spectra observed for the *cis(O)cis(N)*- Δ isomer.

Table V. Methyl Proton Chemical Shifts^a of *trans(O)* and *trans(N)* Isomers.

Complex ion	<i>trans(O)cis(N)</i>	<i>cis(O)trans(N)</i>	ref.
Λ -(+)-[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺	1.44	1.25	
Λ -(+)-[Co(gly) ₂ (<i>l</i> -pn)] ⁺	1.45	1.35	
Δ -(-)-[Co(gly) ₂ (<i>l</i> -pn)] ⁺	1.44	1.31	
Δ -(-)-[Co(L-ser) ₂ (<i>l</i> -pn)] ⁺	1.33	1.31	33

a values in ppm from DSS.

The PMR data of the various *trans(O)cis(N)* and *cis(O)trans(N)* isomers are shown in Table V. For the isomers with the same configuration, the signals of the methyl protons of *l*-pn in the *trans(O)cis(N)* isomers are always observed at lower magnetic field than those in the corresponding *cis(O)trans(N)* isomers. It is understood that such a difference in the chemical shifts is attributed to the characteristic chemical environments of the *trans(O)* and *trans(N)* isomers, and the PMR spectra give a useful measure to distinguish the *trans(O)* from *trans(N)* stereoisomers. The influence of the magnetic anisotropic effect of the carbonyl group being located at the methyl group of *l*-pn, and influence of the electrophilic effects of the coordinated groups (NH₂ and COO⁻) of the amino acid must be considered for the difference of the chemical shift. But the reason can not been made clear.

3-3-C. Absolute Configuration

BRUSHMILLER and STADTHERR¹⁴⁾ have found that the protons of the methyl group of *l*-pn in the Λ (+)₅₈₉-Na[Co(ox)₂(*l*-pn)] complex resonate at lower field than those in

the corresponding Δ isomer, and they assumed such phenomenon to be attributed to the differences in orientation of the C-C bond axis of the diamine in the isomers. In fact, the relation holds for the $\text{Co}(\text{L-asphH})_2(l\text{-pn})^+$ and $\text{Co}(\text{gly})_2(l\text{-pn})^+$ complexes (Table III). However, for the $\text{trans-Co}(l\text{-pn})(\text{LL-EDDP})^+$ ¹³⁾(1.38 for Λ , and 1.42 for Δ , ppm from DSS) and $\text{trans-Co}(l\text{-pn})(\text{DD-EDDP})^+$ complex¹³⁾ (1.33 for Λ , and 1.42 for Δ), the methyl protons signals of the $l\text{-pn}$ in the Δ isomer resonate at lower magnetic field than those in the Λ isomer. This reversed relation is also found in the $\text{Co}(l\text{-pn})_2(\text{aa})$ ($\text{aa}=\text{L-asph}$, gly) complexes.

Recently, DABROVICK and COOKE¹¹⁾ investigated the PMR spectra of the diastereomer of the $\text{trans}(O)\text{-Co}(\text{en})(\text{L-ala})_2^+$, $\text{trans}(O)\text{-Co}(\text{en})(\text{gly})(\text{aa})^+$ ($\text{aa}=\text{L-thr}$, L-ser), $\text{Co}(\text{en})_2(\text{aa})^{2+}$ ($\text{aa}=\text{L-ala}$, L-val), and $\text{Co}(\text{LL-dimethyltrien})(\text{L-ala})^{2+}$ complexes, and found that the methine proton of the L- α -amino-acidato ligand in their Λ isomers resonates at higher magnetic field than those in the corresponding Δ isomers. This assignment was made on the basis of the steric compression between the α -proton and the amino proton of the neighboring ligand. Such relation holds for the present diastereoisomers of the $\text{trans}(O)\text{-Co}(\text{L-asphH})_2(\text{en})^+$ and $\text{Co}(\text{L-asph})(\text{en})_2^+$ complexes (Table III).

The methine proton of L-aspartic acid in the $\text{trans}(N)\text{cis}(O)\text{-}\Lambda\text{-Co}(\text{L-asphH})_2(\text{en})^+$ isomer resonates at higher field than that in the Δ isomer, too. This assignment may also be explained in terms of steric compression. Namely, the α -protons of the chelated two L-aspartate direct to the chelated O atom of the neighboring L-aspartate in the Λ isomer, and to a H atom of the neighboring amino groups of en in the Δ isomer. Accordingly, certain steric compression is found in the Δ isomer.

However, for the mixed complexes of a L- α -amino acid and l -propylenediamine, the C-C bond axis of the $l\text{-pn}$ chelate ring is oblique to the pseudo-C₃ axis in the Λ isomer. So, the l -propylenediamine complexes differ from the ethylenediamine complexes in this manner. For the $\text{trans}(O)\text{cis}(N)\text{-Co}(\text{L-asphH})_2(l\text{-pn})^+$ complex, the α -protons of the L-aspartato ligands in the Λ isomer resonate at higher field than those in the Δ isomer similarly to the corresponding ethylenediamine complex. However, the molecular models show that the steric compression is equal between the Λ and Δ isomers. Moreover, the signal of the α -proton of the L-aspartato ligand in the $\Lambda\text{-Co}(\text{L-asph})(l\text{-pn})_2^+$ complex is found at lower field than that in the Δ isomer.

The PMR data of the β -protons of the L- α -amino-acidato ligand in the various complexes containing diamines together acid are summarized in Table VI. By comparing the chemical shifts of a Λ isomer and corresponding Δ isomer, it is found that the β -protons of the L- α -amino-acidato ligand in the Λ isomer resonate at lower field than those in the Δ isomer. This facts suggest that the signal of the β -proton of the L- α -amino-acidato ligand is useful for the assignment of the absolute configuration of a complex mixed with diamine and α -amino acid.

Table VI. Chemical Shifts^a of β -Proton of Chelated L- α -Amino-acidate Ring.

complex ion	Λ	Δ	ref.
<i>trans(O)cis(N)</i> -[Co(L-aspH) ₂ (en)] ⁺	3.09	3.00	
<i>trans(O)cis(N)</i> -[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺	3.11	3.00	
<i>trans(O)cis(N)</i> -[Co(L-ser) ₂ (<i>l</i> -pn)] ⁺	3.97	3.91	33
<i>trans(O)cis(N)</i> -[Co(L-ala) ₂ (en)] ⁺	1.55	1.53	11
<i>cis(O)cis(N)</i> -[Co(L-aspH) ₂ (en)] ⁺	2.97, 3.05	2.77, 2.88	
<i>cis(O)cis(N)</i> -[Co(L-aspH) ₂ (<i>l</i> -pn)] ⁺	2.95 ^b	2.73, 2.81	
<i>cis(O)trans(N)</i> -[Co(L-aspH) ₂ (en)] ⁺	3.01	2.79	
[Co(L-asp)(en) ₂] ⁺	2.81	2.76	
[Co(L-asp)(<i>l</i> -pn) ₂] ⁺	2.82~2.84 ^c	2.78~2.81 ^c	
[Co(L-ala)(en) ₂] ²⁺	1.5	1.48	11

a Values in ppm from DSS.

b A overlapped peak of two CH₂ protons.

c Maximum and minimum values.

3-3-D. Geometrical Isomers due to Methyl Groups of the Ligand

It has already been mentioned that for the *cis(O)cis(N)*-bis(α -amino-acidato)-*l*-propylenediamine complex, there are two stereoisomers with respect to the orientation of the methyl group in *l*-pn, and there are four stereoisomers for bis(*l*-propylenediamine). Of course, these isomers are doubled when a pair of Δ and Λ configurations is considered. The stereoisomers with the same absolute configuration (Δ and Λ) are difficult to distinguish the structures on the basis of the absorption and CD spectra. The PMR spectra are a useful means. KOJIMA and SHIBATA⁸⁾ confirmed the existence of eight stereoisomers of the Co(L-asp)(*l*-pn)₂⁺ complex on the basis of the PMR data. However, the identification of the Co(gly)(*l*-pn)₂²⁺ complex was unsuccessful for the four isomeric forms with respect to the methyl groups of the *l*-pn.

This complex was chromatographically separated into two bands, and the earlier eluted band consisting of only a (+) isomer and the later eluted band consisting of only a (-) isomer are to be assigned to the Λ and Δ configuration, respectively. The PMR spectra of these two isomers are shown in Figure 8. The signal of the methyl protons of *l*-pn in the Δ shows very complicated pattern. However, considering the fact that the methyl protons of *l*-pn show a doublet with the coupling constant of 6 Hz, the complicated signals are assorted to three peaks of 1.31, 1.37, and 1.43 ppm. From the heights of the peaks, the ratio of the intensity is estimated to be 1:2:1. The signals of four isomers of the Δ -Co(L-asp)(*l*-pn)₂⁺ complex are observed at 1.27~1.29, 1.33, and 1.38~1.39 ppm as is shown in Table IV. The numbers of the methyl groups that resonate at the same chemical shift are two, four, and two, respectively. And, this ratio agrees with the intensity ratio of the Δ -Co(gly)(*l*-pn)₂²⁺ complex. The same fact is recognized for the Λ -Co(L-asp)(*l*-pn)₂⁺ complex, too. Considering the above-mentioned facts, the signals of the methyl groups of the Δ -Co(gly)(*l*-pn)₂²⁺ complex are assigned to

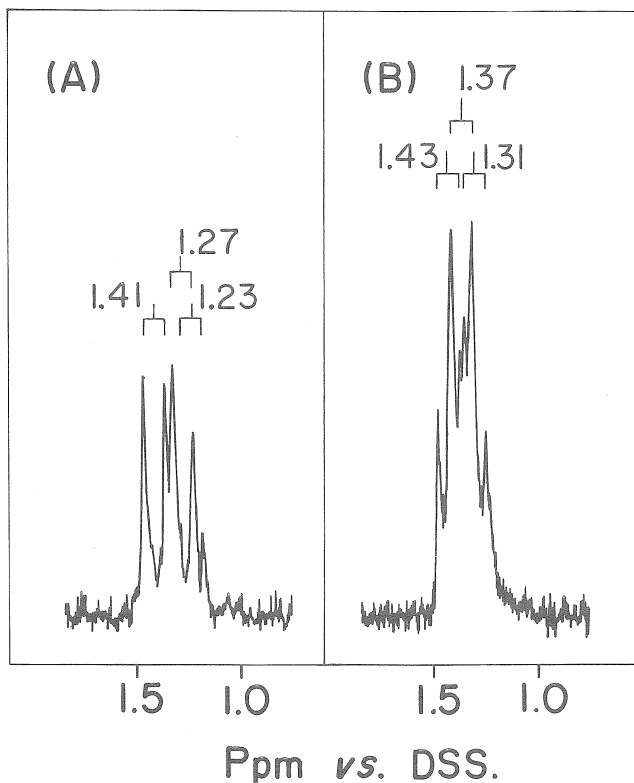


Figure 8. The PMR spectra of the CH_3 protons for (A) $\Lambda\text{-Co(gly)(l-pn)}_2^{2+}$ and (B) $\Delta\text{-Co(gly)(l-pn)}_2^{2+}$ in D_2O .

the four stereoisomers that resonate at (1.43, 1.37 ppm), (1.37 ppm), (1.31, 1.37 ppm), and (1.31, 1.43 ppm), respectively.

For the $\Lambda\text{-Co(gly)(l-pn)}_2^{2+}$ complex (Fig. 8(A)), the signals of the methyl protons are observed at 1.23, 1.27, and 1.41 ppm. However, the intensity ratio of the peaks is not consistent with that of the Δ complex. The consideration of the stereoselectivity have assumed existence of four stereoisomers⁷⁾. The disagreement of the intensity ratio is now can be attributed to the different solubilities of the four isomers obtained. Considering the chemical shift of the methyl groups of the Λ - and $\Delta\text{-Co(L-asp)(l-pn)}_2^+$ and $\Delta\text{-Co(gly)(l-pn)}_2^{2+}$ complexes, the signals of the complex concerned (1.41, 1.27 ppm), (1.27 ppm), (1.32, 1.41 ppm), and (1.23, 1.27 ppm) are assorted to four isomers.

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