

Figure 3.—Variation in the quadrupole coupling constant,  $eQq_{zz}$ , at  $^{59}\text{Co}$ , as a function of the highest infrared CO stretching frequency measured in hexane solution, for compounds of the form  $\text{X}_n\text{Sn}[\text{Co}(\text{CO})_4]_{4-n}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{or } \text{CH}_3; n = 0, 1, 2, \text{ or } 3$ ).

of any  $\pi$ -bonding interaction between halogen and tin, this should be difficult to explain. Since bromine is a less electronegative element than chlorine, one would expect the changes upon bromine substitution to be smaller. A  $\pi$ -bonding interaction between chlorine and tin would have the effect of making the tin atom a better  $\sigma$  donor and poorer  $\pi$  acceptor toward the remaining  $-\text{Co}(\text{CO})_4$  groups.<sup>8</sup> We conclude that

(8) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

chlorine is a relatively stronger  $\pi$ -bonded atom toward tin in these compounds than bromine, thus compensating for its somewhat greater  $\sigma$ -electron withdrawal.

Substitution of  $\text{CH}_3$  for  $\text{Co}(\text{CO})_4$  groups has the effect of lowering  $eQq_{zz}$  at the remaining cobalts. This effect is shown also in Figure 2. The  $-\text{Co}(\text{CO})_4$  group is considerably more electron withdrawing than methyl and is roughly intermediate between methyl and chlorine or bromine in effective electron withdrawal toward the tin atom.

It is of interest to relate observed values of  $eQq_{zz}$  at cobalt to properties of the CO groups. The factors which tend to lower  $eQq_{zz}$ , e.g., donation from L, should tend also to lower the CO stretching force constants and, *ipso facto*, the CO stretching frequencies. Similarly,  $\pi$ -electron withdrawal from cobalt by L, which raises  $eQq_{zz}$ , should also raise the CO force constants and frequencies. The most reliable index of the relative Co-CO interaction obtainable from the vibrational spectrum, short of a detailed vibrational analysis, is the high-frequency, totally symmetric CO stretch. Figure 3 shows a graph of the  $A_1^2$  stretching mode for all of the tin-substituted compounds studied, measured in solution, *vs.*  $eQq_{zz}$ . (The range of  $eQq_{zz}$  values observed is shown where multiple resonances were observed.) The correlation is reasonably good considering the diverse character of the two observables involved. It suggests that  $^{59}\text{Co}$  nqr data on compounds of this type should be of value as a guide to the interpretation of CO vibrational data and that they might serve to test certain conclusions based on simplified force field analyses of the CO stretching modes.

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## The Stereoisomers of the Bis(glycinato)-*l*-propylenediamine- and Glycinatobis(*l*-propylenediamine)cobalt(III) Complexes

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The reaction of the *trans*- $\text{CoCl}_2(\text{l-pn})_2^+$  complex with glycine in an alkaline solution led to the formation of the  $\text{Co}(\text{gly})_2(\text{l-pn})^+$  and  $\text{Co}(\text{gly})(\text{l-pn})_2^{2+}$  complexes. By means of ion-exchange chromatography and solubility difference, a series of geometrical-optical isomers has been separated and characterized by the order of the chromatographic elution, the uv spectra, the CD spectra, and the pmr spectra. The isomers obtained are *trans*(O),*cis*(N)- $\Delta[\text{Co}(\text{gly})_2(\text{l-pn})]\text{Cl}\cdot 6\text{H}_2\text{O}$ , *trans*(O),*cis*(N)- $\Delta[\text{Co}(\text{gly})_2(\text{l-pn})]\text{Cl}\cdot 2\text{H}_2\text{O}$ , *cis*(O),*cis*(N)- $[\text{Co}(\text{gly})_2(\text{l-pn})]\text{Cl}\cdot \text{H}_2\text{O}$  (less soluble), *cis*(O),*cis*(N)- $[\text{Co}(\text{gly})_2(\text{l-pn})]\text{Cl}$  (more soluble), *cis*(O),*trans*(N)- $\Delta[\text{Co}(\text{gly})_2(\text{l-pn})]\text{Cl}\cdot n\text{H}_2\text{O}$ , *cis*(O),*trans*(N)- $\Delta[\text{Co}(\text{gly})_2(\text{l-pn})]\text{Cl}\cdot 2.5\text{H}_2\text{O}$ ,  $\Delta[\text{Co}(\text{gly})(\text{l-pn})_2]\text{Cl}_2\cdot 2\text{H}_2\text{O}$ , and  $\Delta[\text{Co}(\text{gly})(\text{l-pn})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ .

### Introduction

Liu and Douglas<sup>1</sup> prepared complexes of the type  $\text{Co}(\text{aa})(\text{en})_2^{2+}$  (aa = the anion of the optically active alanine, leucine, or phenylalanine) and reported on the circular dichroism spectral characterization of the complexes. Recently, Hall and Douglas<sup>2</sup> extended

their study on the same line by using optically active serine, threonine, and proline. In these studies, the complexes have been prepared by the reaction of *trans*- $\text{CoCl}_2(\text{en})_2^+$  with the desired amino acids. Matsuoka and her coworkers<sup>3</sup> prepared the complex  $\text{Co}(\text{gly})_2\text{en}^+$  by means of a direct synthesis from the

(1) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1350 (1964).

(2) S. K. Hall and B. E. Douglas, *ibid.*, **8**, 372 (1969).

(3) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, **40**, 1868 (1967).

components and separated its geometrical isomers by ion-exchange chromatography. Bailar and his co-workers<sup>4</sup> made the complex  $\text{Co}(\text{ala})(l\text{-pn})_2^{2+}$  from the reaction of  $\text{trans-CoCl}_2(l\text{-pn})_2^+$  with racemic  $\alpha$ -alanine, but they did not attempt to separate any isomeric form. Later, Murakami, *et al.*,<sup>5</sup> also prepared some complexes of the same type using racemic propylenediamine and glycine, alanine, or phenylalanine.

We have found that when glycine reacts with  $\text{trans-CoCl}_2(l\text{-pn})_2^+$  in an alkaline aqueous solution, both of the complexes  $\text{Co}(\text{gly})_2(l\text{-pn})^+$  and  $\text{Co}(\text{gly})(l\text{-pn})_2^{2+}$  are formed. In this paper, the preparations of these complexes in some isomeric forms and the visible, circular dichroism (CD), and proton magnetic resonance (pmr) spectral characterizations of their isomers are described.

### Experimental Section

**Reagent.**—Optically active *l*-propylenediamine (*l*-pn) was obtained by resolving its commercial racemate according to the method described in the literature.<sup>6</sup> The specific rotation  $[\alpha]^{25\text{D}}$  in dry benzene was  $-34.7^\circ$  (lit.<sup>6</sup> value  $-34.8 \pm 0.4^\circ$ ).

**Measurements.**—Electronic absorption spectra were measured with a Hitachi Perkin-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-60 H spectrometer (60 Mc/sec) at about  $25^\circ$ . The values of the chemical shifts were measured in relation to sodium 3-(trimethylsilyl)-1-propanesulfonate (NaTPS) as an internal reference. All spectra were run in deuterium oxide.

**Preparations.**—The complex  $\text{trans}[\text{CoCl}_2(l\text{-pn})_2]\text{Cl} \cdot \text{H}_2\text{O}$ ,<sup>4</sup> 16 g (0.048 mol), was dissolved in 90 ml of water, and the solution was adjusted to pH  $\sim 8$  with an aqueous NaOH solution. The solution of 3.8 g (0.05 mol) of glycine (glyH) in 60 ml of water was added dropwise at room temperature with stirring. The mixed solution was stirred for about 3 hr and then evaporated to dryness at about  $70^\circ$ . The red-brown product was obtained.

The product was dissolved in about 50 ml of water, and the solution was added to an ion-exchange column [diameter ( $\phi$ ) = 8 cm, height of resin ( $h$ ) = 14.5 cm] containing 100–200 mesh Dowex 50WX8 resin in the sodium form. The absorbed complexes formed a compact band at the top of the column. After the column had been swept with water, the absorbed band was eluted with a 0.5 M aqueous solution of NaCl at a rate about 0.6 ml/min. Through elution over a period of about 24 days, four bands colored red-violet were completely separated, while a red-brown band remained at the top of the column. The four eluted bands were collected in fractions, and these fractions were numbered according to the order of the eluted bands (no. 1–4). The red-brown band remaining in the column was then eluted with a 2 M NaCl solution over a period of about 36 days. Two closely spaced red-brown bands separated from a yellow band. The latter still remained at the top of the column and was the +3-charged  $(l\text{-pn})_3$  complex. The former bands were collected in fractions (no. 5 and 6).

Each fraction of no. 1–4 was evaporated to a few milliliters below  $40^\circ$  with the simultaneous removal of a large amount of NaCl. After that, each concentrated solution was added to a small column (Dowex 50WX8, 100–200 mesh,  $\phi = 5$  cm,  $h = 3$  cm) in the calcium form. The solution eluted with a 0.1 M  $\text{CaCl}_2$  aqueous solution was evaporated to dryness at about  $40^\circ$ . The solid material thus obtained was suspended in a few milliliters

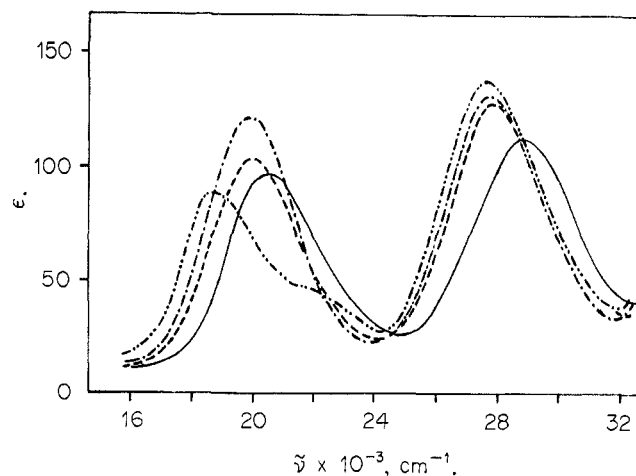


Figure 1.—The electronic absorption spectra of  $\text{trans}(\text{O}), \text{cis}(\text{N})\text{-Co}(\text{gly})_2(l\text{-pn})^+$  (— · — · —),  $\text{cis}(\text{O}), \text{cis}(\text{N})\text{-Co}(\text{gly})_2(l\text{-pn})^+$  (— · — · —),  $\text{cis}(\text{O}), \text{trans}(\text{N})\text{-Co}(\text{gly})_2(l\text{-pn})^+$  (— — —), and  $\text{Co}(\text{gly})(l\text{-pn})_2^{2+}$  (—).

of water, and to it a large amount of an ethanol-acetone mixture (1:1) was added. After standing as a suspension overnight, the desired complex was found as an oil at the bottom, while calcium chloride remained in suspension. After this treatment was repeated once more, the resulting oil was dissolved in a minimum amount of water, and an ethanol-acetone mixture (1:1) was added to the solution to crystallize the desired complex. As a result, one isomer of the bis(glycinato)-*l*-propylenediamine-cobalt(III) complex was obtained from either of the fractions no. 1 and no. 2, and two isomers were obtained from either of the fractions no. 3 and no. 4. These isomers are conveniently labeled as E-1, E-2, E-3 (less soluble), E-3' (more soluble), E-4 (less soluble), and E-4' (more soluble).

Each fraction of no. 5 and no. 6 was evaporated almost to dryness at about  $40^\circ$  with the simultaneous removal of NaCl. The resulting solid material was treated with methanol. After removal of the undissolved substance, the methanol solution was diluted with a small amount of water, and ether was added to the aqueous-alcohol solution in order to crystallize the product. Two isomers of the glycinatobis(*l*-propylenediamine)cobalt(III) complex obtained from the fractions no. 5 and no. 6 are labeled as E-5 and E-6, respectively.

Results of the elemental analyses for these isomers will be given in the Results and Discussion.

**Isomer Ratios.**—In order to determine the ratio of the equilibrium concentrations of the isomers of the bis-glycinato and bis-*l*-propylenediamine complexes, a reaction mixture prepared according to the above-mentioned procedure was chromatographed on a smaller column of the Dowex 50WX8 resin ( $\phi = 3$  cm,  $h = 14.5$  cm). Six bands were collected as fractions, and their relative concentrations were determined spectrophotometrically using estimated  $\epsilon$  values at the first absorption band. The results were: no. 1: no. 2: no. 3: no. 4 =  $\sim 1:1:4:2$  and no. 5: no. 6 =  $\sim 1:7$ .

### Results and Discussion

Results of the elemental analyses on the complexes are summarized in Table I, in which no result was cited for one isomer (E-4'), because the yield was too poor. From the results, it is considered that the isomers from E-1 to E-4 are those corresponding to the bis(glycinato)-*l*-propylenediamine complex, and the other two isomers (E-5 and E-6) are those corresponding to the glycinatobis(*l*-propylenediamine) complex.

The electronic absorption spectra are shown in Figure 1 and the numerical data are summarized in Ta-

(4) J. C. Bailar, Jr., C. A. Stiegman, J. H. Balthis, Jr., and E. H. Huffman, *J. Am. Chem. Soc.*, **61**, 2402 (1939).

(5) M. Murakami, S. Senoo, T. Matsuzato, H. Itatani, and M. Yo, *Nippon Kagaku Zasshi*, **83**, 734 (1962).

(6) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

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

Label	Complex	Elemental anal, %			Band I		Band II		CD		
		C	H	N	$\bar{\nu}_{\max}^c$	$\epsilon_{\max}$	$\bar{\nu}_{\max}^c$	$\epsilon_{\max}$	$\bar{\nu}$	$\Delta\epsilon_{\max}$	
E-1	<i>trans</i> (O), <i>cis</i> (N)-(+) [Co(gly) <sub>2</sub> ( <i>l</i> -pn)]Cl·6H <sub>2</sub> O	Calcd	19.80	7.12	13.19	18.8	90	27.6	138	18.5	+2.14
		Found	20.15	7.18	13.14	21.4	...			21.4	+0.63
E-2	<i>trans</i> (O), <i>cis</i> (N)-(-) [Co(gly) <sub>2</sub> ( <i>l</i> -pn)]Cl·2H <sub>2</sub> O	Calcd	23.84	6.29	15.89					18.4	-2.14
		Found	24.17	6.44	15.43					21.6	-0.76
E-3	<i>cis</i> (O), <i>cis</i> (N)-[Co(gly) <sub>2</sub> ( <i>l</i> -pn)]Cl·H <sub>2</sub> O (less soluble)	Calcd	25.12	6.02	16.74	19.9	117	27.7	129	19.7	+0.74
		Found	25.55	5.64	16.79						
E-3'	<i>cis</i> (O), <i>cis</i> (N)-[Co(gly) <sub>2</sub> ( <i>l</i> -pn)]Cl (more soluble)	Calcd	26.55	5.73	17.69					20.8	+0.20
		Found <sup>a</sup>	26.17	5.69	17.14					19.1	-0.15
E-4	<i>cis</i> (O), <i>trans</i> (N)-(-) [Co(gly) <sub>2</sub> ( <i>l</i> -pn)]Cl·2.5H <sub>2</sub> O (less soluble)	Calcd	23.25	6.41	15.49	20.0	104	27.9	128	19.3	-1.94
		Found	23.14	5.99	15.14						
E-4'	<i>cis</i> (O), <i>trans</i> (N)-(+) [Co(gly) <sub>2</sub> ( <i>l</i> -pn)]Cl (more soluble)	Calcd	...	...	...					19.8	+ (...)
		Found <sup>b</sup>	...	...	...						
E-5	(+) [Co(gly)( <i>l</i> -pn) <sub>2</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O	Calcd	24.75	7.27	18.04	20.5	96	28.8	113	20.1	+2.33
		Found	24.86	7.16	17.69						
E-6	(-) [Co(gly)( <i>l</i> -pn) <sub>2</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O	Calcd	24.75	7.27	18.04					19.5	-2.20
		Found	25.27	7.24	17.64						

<sup>a</sup> For substantially pure. <sup>b</sup> Because of the poor yield, no elemental analyses were carried out. <sup>c</sup> All  $\bar{\nu}$  in  $\text{cm}^{-1} \times 10^{-3}$ .

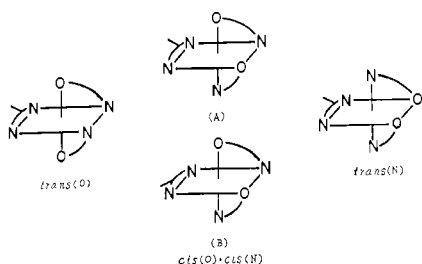


Figure 2.—The possible geometrical isomers of  $\text{Co}(\text{gly})_2(\textit{l}\text{-pn})^+$ .

ble I. For the bis-glycinato complex, three geometrical isomers are possible to exist with respect to the coordinated N and O atoms of the glycinate ions: (a) *trans*(O),*cis*(N), (b) *cis*(O),*cis*(N), and (c) *cis*(O),*trans*(N). The absorption curves are essentially the same with the isomers E-1 and E-2, and the same splitting is found in the first absorption band of both curves. This indicates that both E-1 and E-2 have *trans*(O),*cis*(N) geometry, because it is well known that the first band of a *trans*(O)- $\text{Co}^{\text{III}}(\text{O})_2(\text{N})_4$  type of complex shows a more remarkable splitting than is found in the corresponding *cis*(O) isomer.<sup>7-9</sup> It is impossible to determine the *cis*(O) geometries of the isomers E-3 and E-4 from their absorption spectra (the spectra of E-3' and E-4' are essentially the same as those of E-3 and E-4, respectively). Matsuoka and her coworkers,<sup>8</sup> however, have found in their study of the complex  $\text{Co}(\text{gly})_2\text{en}^+$  that the earlier eluted *cis* species is the *cis*(O),*cis*(N) isomer and the later eluted *cis* species is the *cis*(O),*trans*(N) isomer. Corresponding to this order of elution, the species obtained from fraction no. 3 are regarded as the *cis*(O),*cis*(N) isomer, and those from fraction no. 4, as the *cis*(O),*trans*(N) isomer. The absorption curves for the bis-*l*-propylenediamine complex are also the same with the species E-5 and E-6, and only one of the curves is given in Figure 1.

It is well known that the coordinating *l*-propylenediamine can exist predominantly in the more stable

$\lambda$  conformation<sup>10</sup> with an equatorial methyl group.<sup>11,12</sup> When such  $\lambda$  conformation is considered concerning the above-mentioned three geometrical isomers of the bis-glycinato complex, one of the three produces new geometrical isomerism with respect to the equatorial methyl group (Figure 2). In addition, if the right and left spirals of the chelate rings are considered, eight optical isomers are possible. The configuration of such an isomer can be designated as  $\Delta$  or  $\Lambda$ .<sup>10</sup>

It is well known that in the  $\Delta$  absolute configuration of the 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  $\Lambda$  configuration, the C-C bond axis is oblique to the  $C_3$  axis.

In order to assign the above-mentioned possible structures to the isolated isomers, the data from the CD and pmr spectra were used. The CD spectra for both isomers of *trans*(O)- $\text{Co}(\text{gly})_2(\textit{l}\text{-pn})^+$  are shown in Figure 3. It is apparent from the spectra that the complexes have opposite spiral configurations. The glycinatodiamine complexes can be figuratively related to  $\text{Co}(\text{en})_3^{3+}$  by replacing two oxygen atoms by nitrogen atoms in  $\text{Co}(\text{gly})_2(\textit{l}\text{-pn})^+$  and one oxygen atom by a nitrogen atom in  $\text{Co}(\text{gly})(\textit{l}\text{-pn})_2^{2+}$ . Mason and his coworkers<sup>13</sup> have shown that the dominant lower energy CD peak in the first absorption band region can be related to the  ${}^1A_1 \rightarrow E_a$  transition of  $\text{Co}(\text{en})_3^{3+}$  which is positive in the  $\Lambda$  isomer and negative in the  $\Delta$  isomer. On this basis, the absolute configurations of the present complexes with a dominant positive peak in the first absorption band region should be related to  $\Lambda$ - $\text{Co}(\text{en})_3^{3+}$ ; the  $\Lambda$  configuration may be assigned to the earlier eluted complex (E-1), whose dominant CD band is positive. The CD spectra for the *cis*(O),*cis*(N) isomers (E-3 and E-3') are not the mirror images of each other but differ in their shapes (Figure 4). The CD curve of the E-3 complex

(10) A chelate ring conformation is designated as  $\lambda$  if the C-C bond defines a left spiral about the edge of the octahedron spanned by that ring. The symbols  $\Delta$  and  $\Lambda$  are based upon the convention proposed by T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

(11) E. J. Corey and J. C. Bailar, Jr., *ibid.*, **81**, 2620 (1959).

(12) S. T. Speer, Jr., L. J. Durham, and A. M. Sargeson, *Inorg. Chem.*, **5**, 2103 (1966).

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

(7) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **264**, 321 (1951).

(8) M. Ogawa, Y. Shimura, and R. Tsuchida, *Nippon Kagaku Zasshi*, **81**, 72 (1960).

(9) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, **39**, 1257 (1966).

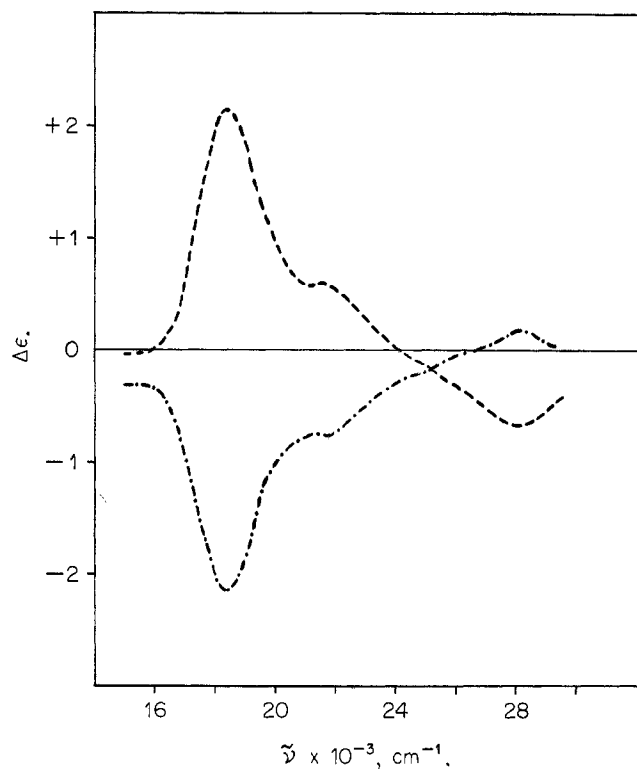


Figure 3.—The CD spectra for *trans*(O),*cis*(N)-(+) [ $\text{Co}(\text{gly})_2(l\text{-pn})\text{Cl}$ ] (---) and *trans*(O),*cis*(N)-(-) [ $\text{Co}(\text{gly})_2(l\text{-pn})\text{Cl}$ ] (-·-·-).

shows a positive peak in the first band region, but the intensity is weak. The CD curve of the E-3' complex shows two peaks in the same region, and the shape seems a kind of vicinal-effect curve. This difference may be attributed to the isomerism with respect to the methyl group of the *l*-pn ligand. The experimental results for the isomer ratios, which are given in the Experimental Section, are also suggestive; the formation ratio of the *cis*(O),*cis*(N) species to the *trans*(O) or *cis*(O),*trans*(N) species has been determined as about 2:1. Although the CD curve for the more soluble isomer of the *cis*(O),*trans*(N) complex (E-4') is drawn assuming the anhydrate [ $\text{Co}(\text{gly})_2(l\text{-pn})\text{Cl}_2$ ] by lack of the elemental analyses, its Cotton effect in the first-band region is opposite to that of the less soluble isomer (E-4) (Figure 4). Therefore, these isomers are in the  $\Delta$  and  $\Lambda$  configurations.

In the case of the bis-*l*-propylenediamine complex, there were two compounds isolated (E-5 and E-6) and their CD spectra are of opposite signs at the dominant peak. This fact indicates that they are diastereoisomeric. Applying Douglas' relationship<sup>1,14</sup> to these CD data, the vicinal effect curve is calculated and shown in Figure 5. When this curve is subtracted from the CD curves for E-5 and E-6, the resultant curves are almost mirror images and similar to the CD curve for  $\Lambda$  [ $\text{Co}(\text{gly})(\text{en})_2\text{I}_2$ ].<sup>1</sup> Based on these CD data, the configuration of the present complex can be assigned as  $\Lambda$  for the earlier eluted isomer (E-5) and as  $\Delta$  for the later eluted one (E-6). The

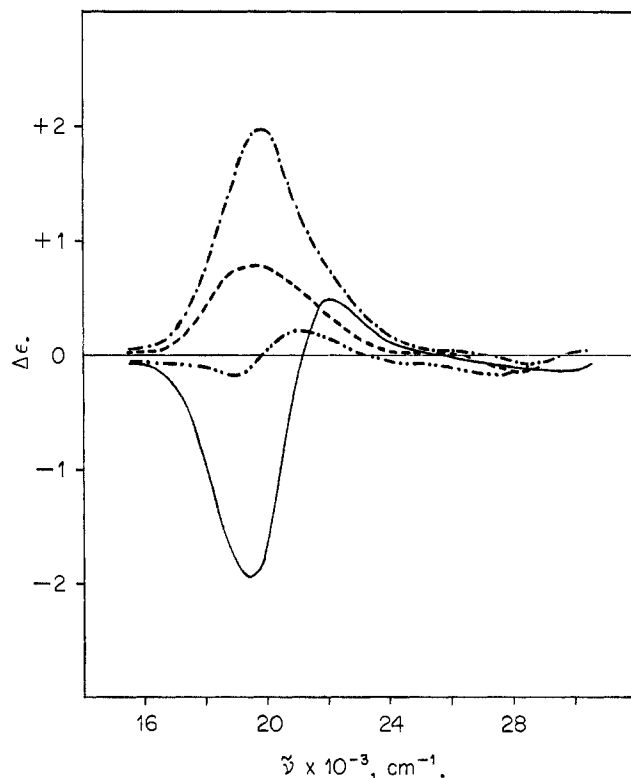


Figure 4.—The CD spectra for *cis*(O),*cis*(N)-[ $\text{Co}(\text{gly})_2(l\text{-pn})\text{Cl}$ ] (less soluble) (---), *cis*(O),*cis*(N)-[ $\text{Co}(\text{gly})_2(l\text{-pn})\text{Cl}$ ] (more soluble) (-·-·-), *cis*(O),*trans*(N)-(+)[ $\text{Co}(\text{gly})_2(l\text{-pn})\text{Cl}$ ] (more soluble) (-·-·-·-), and *cis*(O),*trans*(N)-(-)[ $\text{Co}(\text{gly})_2(l\text{-pn})\text{Cl}$ ] (less soluble) (-).

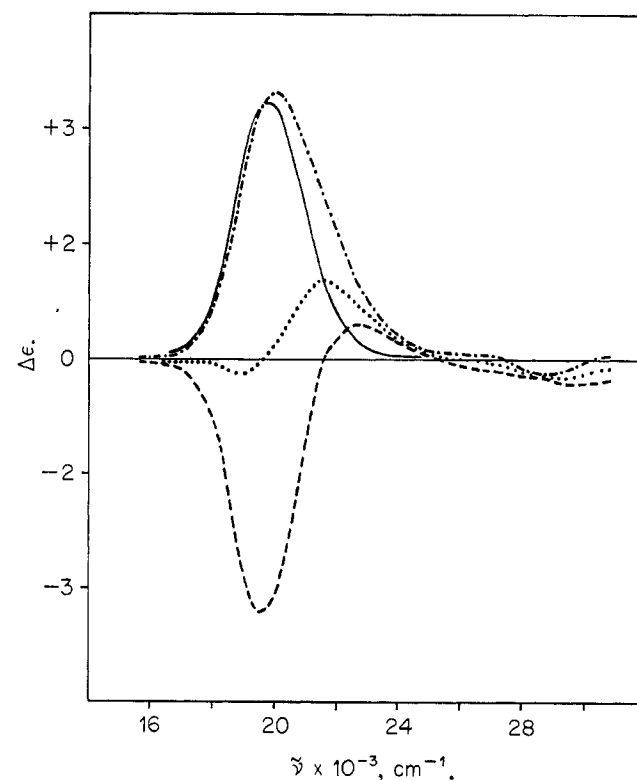


Figure 5.—The CD spectra for (+) [ $\text{Co}(\text{gly})(l\text{-pn})_2\text{Cl}_2$ ] (-·-·-), (-) [ $\text{Co}(\text{gly})(l\text{-pn})_2\text{Cl}_2$ ] (---), the vicinal effect (· · · ·), and (+) [ $\text{Co}(\text{gly})(l\text{-pn})_2\text{Cl}_2$ ] from which the vicinal-effect curve was subtracted (-).

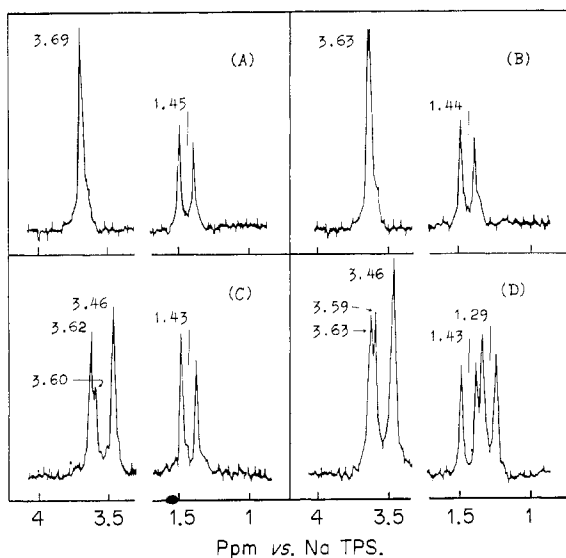


Figure 6.—The pmr spectra of: (A) *trans*(O),*cis*(N)-(+)-Co(gly)<sub>2</sub>(*l*-pn)<sup>+</sup>; (B) *trans*(O),*cis*(N)-(−)Co(gly)<sub>2</sub>(*l*-pn)<sup>+</sup>; (C) *cis*(O),*cis*(N)-Co(gly)<sub>2</sub>(*l*-pn)<sup>+</sup> (less soluble); (D) *cis*(O),*cis*(N)-Co(gly)<sub>2</sub>(*l*-pn)<sup>+</sup> (more soluble).

experimental result that the isomer ratio is 1:7 may indicate the specificity due to the difference of the conformations with respect to the C-C bond of *l*-pn ("ob" or "lel").

Figure 6 shows portions of the pmr spectra of the two *trans*(O) isomers of the Co(gly)<sub>2</sub>(*l*-pn)<sup>+</sup> complex; the (+) isomer exhibits a doublet ( $J = 6$  cps) due to the CH<sub>3</sub> group of the coordinated *l*-pn at 1.45 ppm and a singlet due to the CH<sub>2</sub> groups of the coordinated glycinate rings at 3.69 ppm, while the (−) isomer exhibits a similar doublet at 1.44 ppm and a slightly split line at 3.63 ppm. The fact that the chemical shift of the CH<sub>3</sub> resonance signal in the (−) isomer is slightly less than that of the CH<sub>3</sub> signal in the (+) isomer is also observed in the pmr spectra for the  $\Delta(-)_{889}$ - and  $\Lambda(+)_889$ Na[Co(*l*-pn)(ox)<sub>2</sub>] complexes.<sup>15</sup> The less soluble form of the *cis*(O),*cis*(N) isomer shows a doublet at 1.43 ppm and three resonance

lines at 3.62, 3.60, and 3.46 ppm, while the more soluble form shows the same kind of two doublets at 1.29 and 1.43 ppm. The doublet at 1.43 ppm may be considered to be the CH<sub>3</sub> resonance signals of *l*-pn of the less soluble form which could not be separated even by repeated recrystallizations. The CH and CH<sub>2</sub> resonance signals of *l*-pn for the less soluble isomer were observed at higher field than that of the more soluble isomer: for the former, at 2.24–2.79 ppm; for the latter, at 2.55–3.08 ppm (this latter value agreed with that of the *trans*(O)-Co(gly)<sub>2</sub>en<sup>+</sup> complex). By the construction of the molecular models, it is shown that the CH and CH<sub>2</sub> protons of *l*-pn in the isomer shown in Figure 2B are farther away from the NH<sub>2</sub> groups of two glycinate ligands than the CH and CH<sub>2</sub> protons of *l*-pn in the isomer shown in Figure 2A. Accordingly, the CH and CH<sub>2</sub> protons of *l*-pn of the complex shown in Figure 2A should have the different chemical environment as compared with that of the complex shown in Figure 2B. Based on this consideration, the geometry of the more soluble form is assigned as B in Figure 2. In consequence, the less soluble one is A. The pmr spectra for the *cis*(O),*trans*(N) species are not obtained, because of the shortage of samples.

In the cation-exchange chromatography of the Co(gly)<sub>2</sub>(*l*-pn)<sup>+</sup> ion, the order of elution of the three geometrical isomers with respect to the coordinated N and O atoms of the glycinate ions agrees with the order that is estimated from the dipole moments and also with Matsuoka and coworkers'<sup>3</sup> experimental results.

The elution order of the present optical isomers *trans*(O),*cis*(N)-Co(gly)<sub>2</sub>(*l*-pn)<sup>+</sup> and Co(gly)(*l*-pn)<sub>2</sub><sup>2+</sup> could be explained based on the statement by Liu, *et al.*<sup>16</sup> Namely, the methyl group of coordinated *l*-pn in the  $\Lambda$  isomer is farther away from an adjacent glycinate ligand than that in the  $\Delta$  isomer, and, consequently, the steric interactions of the methyl group in the  $\Lambda$  isomer are weaker than that in the  $\Delta$  one.

(15) J. G. Brushmiller and L. G. Stadtherr, *Inorg. Nucl. Chem. Letters*, **3**, 525 (1967).

(16) L. N. Schoenberg, D. W. Cooke, and C. F. Liu, *Inorg. Chem.*, **7**, 2386 (1968).