Appendix

Derivation of the Rate Expression for the Slow Reaction. The rate of decomposition of I_{1b}

$$\text{rate} = k_3[I_{1b}] \qquad (1)$$

must be rewritten in terms of B_{tot}, B, and I_a (*vide infra*) since

$$[I_{1b}] = [B_{tot}] - [B] - [I_{1a}]$$

and

$$K_{1a} = [I_{1a}]/[A_a][B]$$

The substitution can be made as in

$$[I_{1b}] = [B_{tot}] - [B]\{(1 + K_{1a}[A_a])\} \qquad (2)$$

Then since

$$K_{1b} = [I_{1b}]/[A_b][B]$$

one can solve for [B] and make this substitution in (2)

$$[I_{1b}] = [B_{tot}] - \frac{[I_{1b}](1 + K_{1a}[A_a])}{K_{1b}[A_b]}$$

Gathering like terms, it can be seen that

$$[I_{1b}] = \frac{[B_{tot}]}{1 + \dfrac{1 + K_{1a}[A_a]}{K_{1b}[A_b]}} \qquad (3)$$

Sustituting (3) into the rate expression 1 gives

$$\text{rate} = \frac{k_3}{1 + \dfrac{1 + K_{1a}[A_a]}{K_{1b}[A_b]}}[B_{tot}] = k_{3app}[B_{tot}] \qquad (4)$$

Expressing the concentrations of A_a and A_b in terms of A_{tot} and the equilibrium constant K_{ab}, one obtains an expression for the desired rate law

$$\frac{1}{k_{3app}} = \frac{1}{k_3} + \frac{1 + [H^+]/K_{ab}}{k_3K_{1b}[A_{tot}]} + \frac{K_{1a}[H^+]}{k_3K_{1b}K_{ab}} \qquad (5)$$

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Stereoisomers of the Bis(L-hydrogen aspartato)ethylenediamine- and L-Aspartatobis(ethylenediamine)cobalt(III) Complexes

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The bis(L-hydrogen aspartato)ethylenediamine- and L-aspartatobis(ethylenediamine)cobalt(III) complexes have been prepared from the reaction of the *trans*-$CoCl_2(en)_2^+$ complex with L-aspartic acid. The stereoisomers of these complexes have been separated by an ion-exchange chromatographic method. For the bis(L-hydrogen aspartato)ethylenediamine complexes, the six stereoisomers have newly been isolated; they are Λ- and Δ-trans(O), Λ- and Δ-cis(O),cis(N), and Λ- and Δ-trans(N) isomers. On the other hand, two known diastereoisomers have been isolated for the bis(ethylenediamine) complexes. All of the complexes isolated 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 formation ratios of the isomers. The pmr studies have been carried out with regard to the signals of the NH_2 protons.

Introduction

There have been a few papers concerning the stereoselectivity in the mixed diamine complexes of cobalt(III) with L-glutamic acid or L-aspartic acid; Gillard and his coworkers[1] have reported that the reaction of L-glutamic acid with the $CoCO_3(en)_2^+$ complex results in kinetically controlled stereoselective formation of the Λ-Co(L-glu)$(en)_2^+$ isomer (D(+) isomer in the paper). Very recently, he and his coworkers[2] reinvestigated the same reaction in detail, and they have found that the end products in this reaction are not only the paired isomers (Λ and Δ) of that bis(ethylenediamine) complex but also a racemic mixture of another type of bis(ethylenediamine) complex. They believed the latter to be the complex with the L-glutamate ligand bound through two carboxyl groups. Legg and Steele[3] have isolated several pairs of the Co(L-aa)$(en)_2^+$ and Co(L-Haa)$(en)_2^{2+}$ complexes (aa = aspartate and glutamate, Haa = protonated aspartate and glutamate) from the reaction of the amino acid with the $CoCO_3(en)_2^+$ in the presence of activated charcoal. They have found a 70:30 distribution between the Λ and Δ isomers for the L-glutamato complex, and a 60:40 distribution for the L-aspartato complex. The present authors[4] have also isolated a number of stereoisomers of the Co(L-Hasp)$_2$(*l*-pn)$^+$ and Co(L-asp)(*l*-pn)$_2^+$ complexes and have discussed the stereoselectivity found in terms of the dangling β-carboxylate group in the chelated L-aspartate and the fixed conformation of the chelated *l*-propylenediamine.

The present work has been undertaken in connection with that previous work in order to confirm the stereoselective effect caused by the chelated L-aspartate, since the conformational effect caused by a chelated diamine may well be ignored in the complexes of the ethylenediamine-L-aspartato series. The isolated complexes have been characterized by electronic absorption, circular dichroism (CD), and proton magnetic resonance (pmr) spectra. The description of the work concerning the bis(ethylenediamine) complex will be minimized, since similar work has been published.[3]

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[1] J. H. Dunlop, R. D. Gillard, and N. C. Payne, *J. Chem. Soc. A*, 1469 (1967); J. H. Dunlop, R. D. Gillard, N. C. Payne, and G. B. Robertson, *Chem. Commun.*, 874 (1967).

[2] R. D. Gillard, R. Maskill, and A. Pasini, *J. Chem. Soc. A*, 2268 (1971).

[3] J. I. Legg and J. Steele, *Inorg. Chem.*, **10**, 2177 (1971).

[4] Y. Kojima and M. Shibata, *Inorg. Chem.*, **10**, 2382 (1971).

Table I. Elemental Analyses of the Complexes Prepared

Fraction no.	Complex	% C		% H		% N	
		Calcd	Found	Calcd	Found	Calcd	Found
1	Λ-(+)-[Co(L-Hasp)$_2$(en)]ClO_4	24.88	24.78	4.18	4.33	11.61	11.70
2	Δ-(−)-[Co(L-Hasp)$_2$(en)]$ClO_4 \cdot 0.5H_2O \cdot C_2H_5OH$[a]	26.80	27.02	5.06	5.00	10.42	10.00
3	Δ-(−)-[Co(L-Hasp)$_2$(en)]I$\cdot 3.5H_2O$[b]	20.96	21.09	4.75	4.67	9.78	9.30
	Λ-(+)-[Co(L-Hasp)$_2$(en)]I$\cdot 0.5H_2O$[c]	23.14	23.39	4.08	4.19	10.82	10.40
4	Λ-(+)-[Co(L-Hasp)$_2$(en)]Cl$\cdot 0.5H_2O$	28.08	28.03	4.95	5.22	13.10	13.08
5	Δ-(−)-[Co(L-Hasp)$_2$(en)]$ClO_4 \cdot nH_2O$[d]						
6	Λ-(+)-[Co(L-asp)(en)$_2$]I$\cdot H_2O$	21.11	21.41	5.09	5.14	15.39	15.43
7	Δ-(−)-[Co(L-asp)(en)$_2$]I$\cdot 1.5H_2O$	20.70	20.99	5.21	5.26	15.09	14.99
	[Co(L-Hasp)$(NH_3)_4$]$(ClO_4)_2$	10.49	10.43	3.96	4.08	15.29	15.38

[a] Ethanol of crystallization. [b] More soluble isomer. [c] Less soluble isomer. [d] No elemental analyses were carried out because of no isolation of this isomer.

Experimental Section

Preparation. The preparative reaction for the present complexes and the procedure for the chromatographic separation of the isomers were essentially the same as those in the previous work.[4] The complex *trans*-[$CoCl_2$(en)$_2$]Cl$\cdot$HCl$\cdot 2H_2O$ (9 g, 0.025 mol) and L-aspartic acid (8.5 g, 0.064 mol) were allowed to react, in the presence of activated charcoal, under an alkaline condition (pH ~10). For the chromatographic separation, a column (diameter 7.5 cm, height of resin 23 cm) containing 100–200 mesh Dowex 50W-X8 resin in the H form was used. Upon elution with a 0.1 *M* aqueous solution of $NaClO_4$, five bands colored red or red-violet eluted with complete separation (fraction no. 1–5). Then, by eluting with 0.3 *M* $NaClO_4$, two more bands colored red-brown eluted with complete separation (fraction no. 6–7).

The isolations of the compounds from these fractions were carried out as follows. Fraction no. 1 was concentrated at 40° until crystallization of a red material occurred and was then allowed to stand in a refrigerator for 1 day. The compound thus obtained was recrystallized from water by adding ethanol.

Fraction no. 2 was once evaporated to near dryness at 40° along with the simultaneous removal of the perchlorate used for the elution. A large amount of an ethanol–ether mixture (1:1) was introduced into the residue to precipitate pink material. This precipitate was collected by means of a centrifuge and washed with ethanol. The crude material was dissolved in a minimum amount of water, and a large amount of ethanol was added to the solution, which was then kept in a refrigerator for several days. The compound thus obtained was recrystallized from water by adding an ethanol–ether mixture (1:1).

Since the band corresponding to fraction no. 3 actually consisted of two overlapping bands exhibiting different Cotton effects (the first band had a negative sign in the main peak; the second, a positive sign), the treatment of the fraction was more difficult. The treatment to obtain the crude product of a less soluble isomer was the same as that in fraction no. 2; the filtrate was saved. The product was dissolved in a minimum amount of water containing excess sodium iodide, and ethanol and then ether were added to the solution which was kept in a refrigerator to complete precipitation. The precipitate was filtered and then recrystallized from water by adding ethanol and then ether. The recrystallization was repeated until a constant $\Delta\epsilon$ value in the dominant peak of the CD spectrum was obtained. Since the sign of the peak was positive, the less soluble isomer corresponds to the second band.

To the filtrate which was obtained from the isolation of the first isomer an additional amount of ether was added until the solution began to cloud over. By means of a centrifuge, a small amount of precipitate was collected and discarded because it contained the less soluble compound mentioned above. Ether was then added to the filtrate to precipitate the more soluble compound. It was collected by means of a centrifuge and recrystallized from water by adding an ethanol–ether mixture (1:1). This recrystallization was repeated until a constant $\Delta\epsilon$ value was obtained. This more soluble isomer thus isolated corresponds to the first band.

Fraction no. 4 was treated in the same fashion as no. 2 in order to obtain the crude complex, after which the product was dissolved in a minimum amount of water containing excess calcium chloride. Upon standing the solution in a refrigerator after addition of ethanol and then ether, red crystals were deposited. They were recrystallized from water by adding ethanol. Crystallization of a compound from fraction no. 5 could not be carried out because of the small amount of this species present.

Fractions 6 and 7 were concentrated to a few milliliters at 40° along with the simultaneous removal of the sodium perchlorate, and a large amount of an acetone–ether mixture (1:4) was added to the concentrates, whereupon the desired complexes separated as oils. A large amount of acetone was added to the oils to precipitate the complexes. The precipitates were dissolved in a little water containing excess sodium iodide. A large amount of ethanol was added to the solutions, which were then kept in a refrigerator for 1 day. The compounds thus obtained were recrystallized from water by adding ethanol.

A related complex, [Co(L-Hasp)$(NH_3)_4$]$(ClO_4)_2$, was prepared by the following method. The [$Co(NH_3)_6$]Cl_3 complex (34 g) was dissolved in aqueous ammonia (20 ml of concentrated NH_3 in 100 ml of H_2O), and L-aspartic acid (13 g) was then added to the solution. After activated charcoal (1 g) was added, the mixture was stirred at 50° for about 1 hr; the solution became red-brown. After the removal of charcoal by hot filtration, concentrated HCl (16 ml) was added to the filtrate. The resulting solution was added to a column containing 100–200 mesh Dowex 50W-X8 resin in the Na form (diameter 6 cm, height of resin 30 cm). Upon elution with 0.5 *M* $NaClO_4$, a red-brown band after a red-violet one eluted. From this second band, the complex was obtained. The yield was about 55% based on aspartic acid used. Legg and Steele[3] have prepared the same complex from the [$Co(H_2O)(NH_3)_5$]$^{3+}$ complex.

Results of the elemental analyses for all the compounds obtained are given in Table I.

Formation Ratios of Isomers. The concentrations of the complex species in the fractions were spectrophotometrically estimated by the same method as described in the previous paper,[4] and the formation ratios among the isomers were calculated from the results.

Measurements. The electronic, CD, and pmr spectra were measured with the same instruments as were used for the previous works.[4,5]

Results and Discussion

Characterization of Isomers. The isolated complexes are now labeled as E-1, E-2, E-3, E-3′, E-4, E-5, E-6, and E-7 corresponding to the numbers of the fractions, of which E-3 and E-3′ correspond to the less soluble and more soluble complexes obtained from fraction no. 3. From the analytical results summarized in Table I, it is obvious that the complexes from E-1 to E-4 are the isomers of bis(L-hydrogen aspartato)-ethylenediaminecobalt(III) and the complexes E-6 and E-7 are those of L-aspartatobis(ethylenediamine)cobalt(III). The elemental analysis for E-5 was not obtained because no crystal was isolated from this fraction.

Some typical electronic spectra are shown in Figure 1, and the numerical data for the all compounds obtained are given in Table II. The spectra of E-1 and E-2 are essentially the same and showed a characteristic splitting[6] in their first absorption bands. From these, it is clear that both complexes have trans(O),cis(N) geometry with respect to the coordinated N and O atoms of the two L-aspartate ions. For the remaining E-3, E-3′, and E-4 complexes, the values of ϵ_2/ϵ_1 are calculated as 1.32, 1.05, and 1.07, respectively. For the known Λ- and Δ-*cis(O),cis(N)*-Co(gly)$_2$(*l*-pn)$^+$ complex,[5] the value is calculated to be 1.10, and this value is considerably smaller than that (1.23) for the corresponding cis(O),trans(N) isomer. In applying this empirical relation to the present

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(5) Y. Kojima and M. Shibata, *Inorg. Chem.*, 9, 238 (1970).

(6) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, 4, 1576 (1965).

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

		Band I		Band II		CD	
Label	Complex ion	$10^{-3}\tilde{\nu}_{max}$, 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	*trans*(*O*),*cis*(*N*)-Λ-(+)-[Co(L-Hasp)$_2$(en)]$^+$	18.8 21.6 sh	94	27.6	144	18.6	+3.17
E-2	*trans*(*O*),*cis*(*N*)-Δ-(−)-[Co(L-Hasp)$_2$(en)]$^+$	18.8 21.6 sh	78	27.6	120	18.4 21.7	−2.08 −1.43
E-3	*cis*(*O*),*trans*(*N*)-Λ-(+)-[Co(L-Hasp)$_2$(en)]$^+$	19.9	128	27.9	169	19.5 22.2	+4.83 −1.18
E-3′	*cis*(*O*),*cis*(*N*)-Δ-(−)-[Co(L-Hasp)$_2$(en)]$^+$	20.0	127	27.7	133	19.5	−2.24
E-4	*cis*(*O*),*cis*(*N*)-Λ-(+)-[Co(L-Hasp)$_2$(en)]$^+$	19.9	144	27.8	154	19.6	+2.64
E-5	*cis*(*O*),*trans*(*N*)-Δ-(−)-[Co(L-Hasp)$_2$(en)]$^+$	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
	[Co(L-Hasp)(NH$_3$)$_4$]$^{2+}$	20.2	79	28.7	87	19.6 21.7	+0.32 −0.33

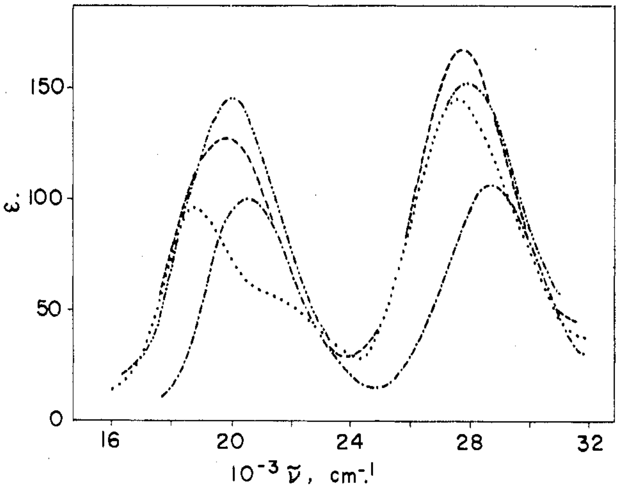

Figure 1. The electronic absorption spectra of *trans*(*O*),*cis*(*N*)-Λ-Co(L-Hasp)$_2$(en)$^+$ (· · · · ·), *cis*(*O*),*cis*(*N*)-Λ-Co(L-Hasp)$_2$(en)$^+$ (— · · — · · —), *cis*(*O*),*trans*(*N*)-Λ-Co(L-Hasp)$_2$(en)$^+$ (— — — — —), and Λ-Co(L-asp)(en)$_2$$^+$ (— · — · —).

complexes, it is appears that the E-3′ and E-4 are isomers of cis(O),cis(N) geometry, and E-3 is one of cis(O),trans(N) geometry. Since the maximum positions for E-5 coincide with those for E-3, the remaining E-5 should be the other isomer of cis(O),trans(N) geometry. These absorption spectral assignments agree with those made by pmr spectra, which will be mentioned later.

No difference is observed between the spectra of E-6 and E-7, and the numerical data are well in accord with other bis(diamine)(α-amino acidato) complexes.[4,5,7,8]

The CD spectra are shown in Figures 2-4, and the numerical data are included in Table II. For E-5, the CD curve is drawn by assuming the ε values in the absorption spectrum to be the same as the values of E-3. Legg and his coworkers[9] have shown that the (+)$_{589}$ isomer of *trans*(*O*)-[Co(en)(EDDA)]$^+$, which has dominant positive peak at the lowest energy band, should have the same absolute configuration as Λ-[Co(en)$_3$]$^{3+}$.[10] Dabrowiak and Cooke[11] have reported use of nmr data for the assignments of absolute configuration of complexes such as *trans*(*O*)-[Co(en)(EDDA)]$^+$ and *trans*(*O*)-[Co(en)(L-ala)$_2$]$^+$, and they have found that the assignments are consistent with the work of Mason,[12] who assigned the Δ configuration to that isomer which has a negative CD band for the A → E transition in the first absorption band region. Matsuoka and his coworkers[13] have determined absolute configurations of all isomers of the oxalatobis(L-amino acidato)cobaltate(III) complex based on the major CD band in the first absorption band region. Applying these results to the present isomers, it is tentatively assumed that the E-1, E-3, and E-4 complexes have the Λ configuration, while the E-2, E-3′, and E-5 have the Δ configuration.

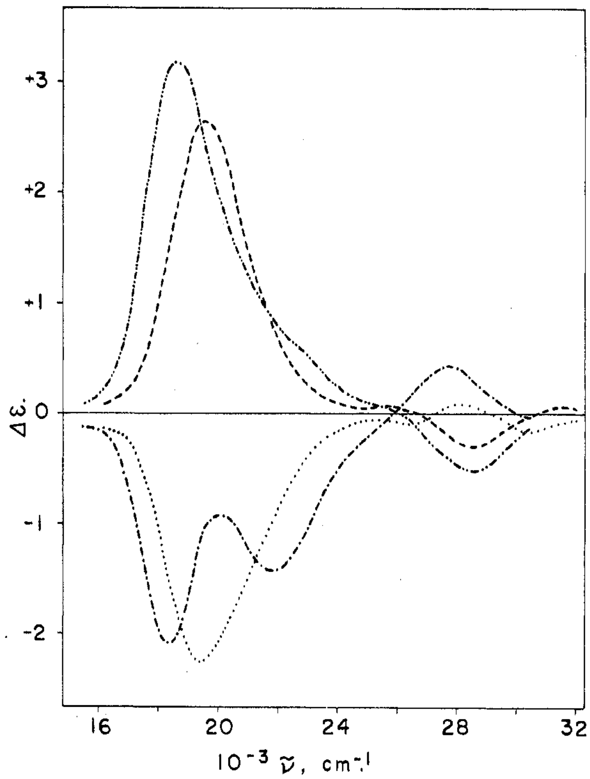

Figure 2. The CD spectra for *trans*(*O*),*cis*(*N*)-Λ-(+)-[Co(L-Hasp)$_2$(en)]ClO$_4$ (E-1) (— · · — · · —), *trans*(*O*),*cis*(*N*)-Δ-(−)-[Co(L-Hasp)$_2$(en)]ClO$_4$ (E-2) (— · — · —), *cis*(*O*),*cis*(*N*)-Λ-(+)-[Co(L-Hasp)$_2$(en)]Cl (E-4) (— — — — —), and *cis*(*O*),*cis*(*N*)-Δ-(−)-[Co(L-Hasp)$_2$(en)]I (E-3′) (· · · · ·).

The diastereoisomers of the Co(L-asp)(en)$_2$$^+$ complex have been characterized from the CD spectral data by Legg and Steele.[3] They have reported that the vicinal effect curve calculated from the data on Λ- and Δ-Co(L-Hasp)(en)$_2$$^{2+}$ is more

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(7) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, 3, 1356 (1964).

(8) S. K. Hall and B. E. Douglas, *Inorg. Chem.*, 8, 372 (1969).

(9) J. I. Legg, D. W. Cooke, and B. E. Douglas, *Inorg. Chem.*, 6, 700 (1967).

(10) The symbols Δ and Λ are based upon the convention proposed by the IUPAC in *Inorg. Chem.*, 9, 1 (1970).

(11) J. C. Dabrowiak and D. W. Cooke, *J. Amer. Chem. Soc.*, 92, 1097 (1970).

(12) S. F. Mason, *Quart Rev., Chem. Soc.*, 17, 20 (1963).

(13) N. Matsuoka, J. Hidaka, and Y. Shimura, *Inorg. Chem.*, 9, 719 (1970).

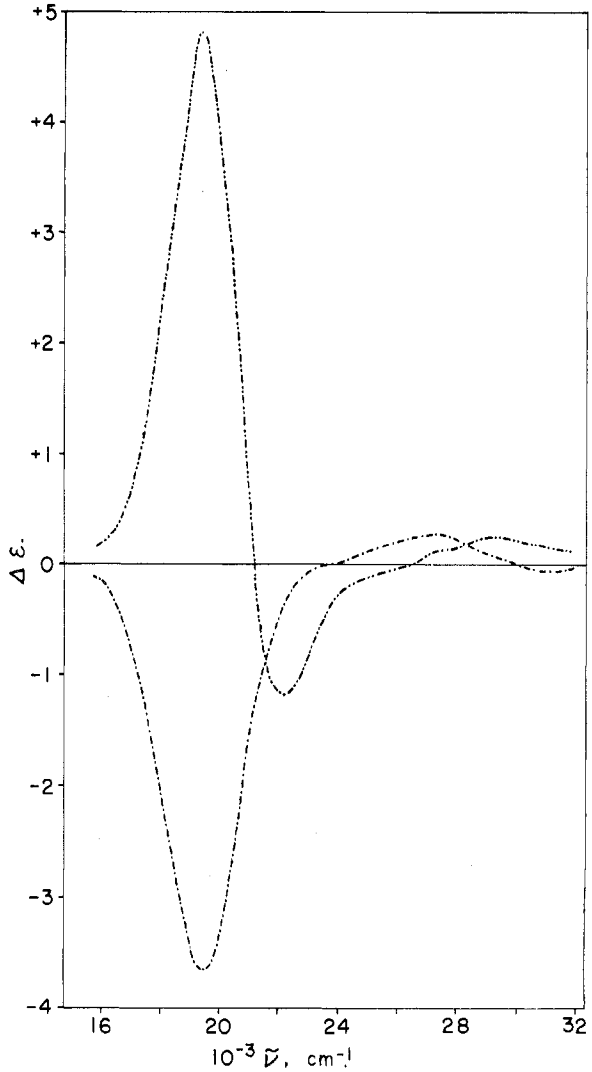

Figure 3. The CD spectra for *cis(O),trans(N)*-Λ-(+)-[Co(L-Hasp)$_2$(en)]I (E-3) (– · · · – · · · –) and *cis(O),trans(N)*-Δ-(–)-[Co(L-Hasp)$_2$(en)]ClO$_4$ (E-5) (– · – · –).

intense than the spectrum of Co(L-Hasp)(NH$_3$)$_4$$^{2+}$. In the present work, the vicinal curve calculated from the data on E-6 and E-7 isomers by Douglas' relationship[7,14] is less intense than the spectrum of the referred tetraammine complex (Figure 4). On the other hand, when aqueous solutions of the present complexes are adjusted to pH ~2.5 with an acid solution, the vicinal curves calculated from the spectra in the acidified solutions coincide well with the spectrum for the referred complex.

In the pmr studies, the signals of the CH$_2$ groups of the coordinated aspartates were used for the characterization. The pmr spectra of the bis(L-hydrogen aspartato) complexes were measured in D$_2$O solution, and the signal of the methylene protons of the β carbon in the chelated aspartate as well as that of the ethylene protons of the chelated ethylenediamine is shown in Figure 5. The signal of the CH$_2$ protons was detected as a doublet, and the chemical shifts are given as the center of the doublet. The results indicate that E-1, E-2, E-3, and E-5 belong to C_2, and E-3′ and E-4, to C_1 symmetry.

Thus, we can now conclude that E-1 and E-2 are the Λ and Δ isomers of the trans(O),cis(N) complex, E-3′ and E-4 are the Δ and Λ isomers of the cis(O),cis(N) complex, and E-3 and E-5 are the Λ and Δ isomers of the cis(O),trans(N) complex. In the present work, cationic species other than the above-mentioned complex species were not detected during the chromatographic separation.

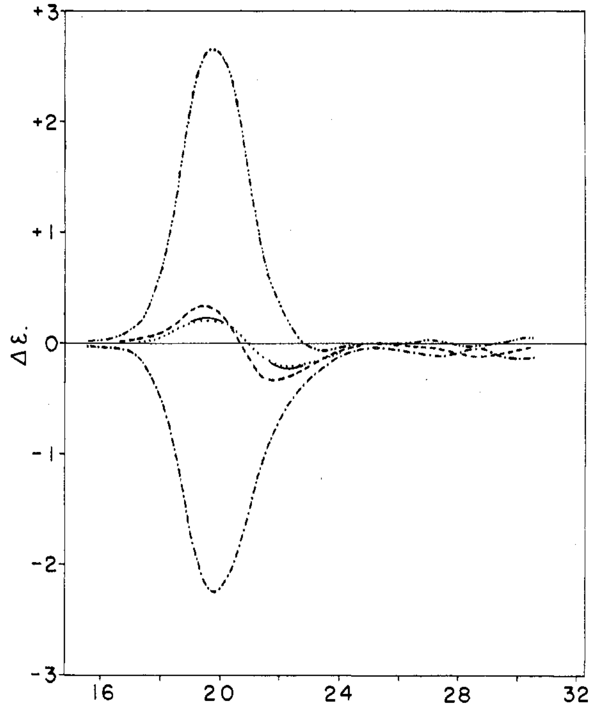

Figure 4. The CD spectra for Λ-(+)-[Co(L-asp)(en)$_2$]I (E-6) (– · · – · · –), Δ-(–)-[Co(L-asp)(en)$_2$]I (E-7) (– · – · –), the vicinal curve (· · · · ·), [Co(L-Hasp)(NH$_3$)$_4$](ClO$_4$)$_2$ (– – – – – –), and [Co(L-Hasp)(NH$_3$)$_4$](ClO$_4$)$_2$ at pH ~7 (———).

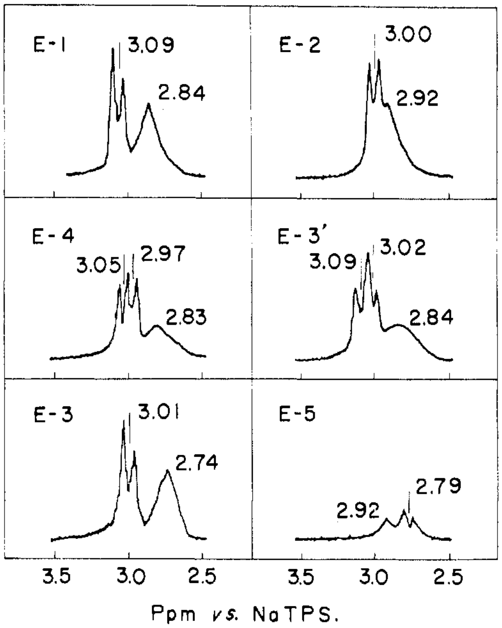

Figure 5. The pmr spectra of the CH$_2$ protons for (E-1) *trans(O),cis(N)*-Λ-(+)-Co(L-Hasp)$_2$(en)$^+$, (E-2) *trans(O),cis(N)*-Δ-(–)-Co(L-Hasp)$_2$(en)$^+$, (E-4) *cis(O),cis(N)*-Λ-(+)-Co(L-Hasp)$_2$(en)$^+$, (E-3′) *cis(O),cis(N)*-Δ-(–)-Co(L-Hasp)$_2$(en)$^+$, (E-3) *cis(O),trans(N)*-Λ-(+)-Co(L-Hasp)$_2$(en)$^+$, and (E-5) *cis(O),trans(N)*-Δ-(–)-Co(L-Hasp)$_2$(en)$^+$.

Our attention was also given to the resonance signals of the NH$_2$ protons of the chelated diamine and aspartate. Each spectrum was measured in a D$_2$O solution and also in a D$_2$O-D$_2$SO$_4$ (~25 wt %) solution. When the bis(ethylenediamine) complexes were dissolved in D$_2$O, the resulting solu-

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(14) B. E. Douglas and S. Yamada, *Inorg. Chem.*, 4, 1561 (1965).

tion was neutral, while the corresponding solution of the bis(L-hydrogen aspartato) complexes was acid (pH ~1.5). In the spectra of the D_2O solutions for the bis(ethylenediamine) complexes, the Λ isomer shows two broad signals due to the NH_2 groups (Figure 6(A)), while the Δ isomer shows one broad signal (Figure 6(C)). The intensities of these peaks decreased to some extent after 3 days' standing. On the other hand, in the spectra of the related complexes Λ-Co(gly)$(en)_2{}^{2+}$, and Λ- and Δ-Co(gly)(*l*-pn)$_2{}^{2+}$, such signals due to the NH_2 groups were not observed after 1 hr of standing. Buckingham and his coworkers[15] have reported that in the spectra for the Co(aa)$(en)_2{}^{2+}$ complexes (aa = gly, val, ala, phe, and leu) measured in a DCl acidic solution, the NH_2 protons of the coordinated ethylenediamine show one broad signal at 5.2 ppm, and those of the coordinated amino acidate show another broad signal at 4.4 ppm. In the spectra of the present bis(ethylenediamine) complexes in D_2O–D_2SO_4 solution, new signals due to the NH_2 protons are observed overlapping partly with the signals observed in D_2O (Figure 6). With reference to the work cited above and considering the relative intensities observed, the broad signals at 4.1 ppm in Figure 6(B) and 6(D) are to be assigned to the NH_2 protons plus CH proton of the aspartato ligand, and the signals observed downfield of those peaks are to be assigned to the NH_2 protons of the ethylenediamine ligand. Based on these assignments, the NH_2 signals observed in D_2O solution for the present complexes may be understood as evidence for the existence of an NH_2 group which hydrogen bonds with the β-carboxylate of the chelated aspartate. In other words, it is assumed that the deuterium exchange is considerably suppressed by hydrogen bonding of this kind.

The Δ isomer of the related Co(L-asp)(*l*-pn)$_2{}^+$ complex shows a broad absorption at 5.6 ppm (Figure 6), similar to the Δ-Co(L-asp)$(en)_2{}^+$ complex. From this fact the same mode of hydrogen bonding is considered between these complexes.

The spectrum of the Λ isomer of the *l*-pn complex differs from that of the corresponding ethylenediamine complex; the former shows a broad signal at 5.8 ppm in contrast to two absorptions of the latter isomer (Figure 6). This fact suggests different modes of hydrogen bonding in the isomers.

The spectrum for the trans(O),cis(N)-Λ isomer of the ethylenediamine complex in D_2O showed two broad resonance signals due to the NH_2 groups at 5.4 and 6.3 ppm. Moreover, the spectrum was the same as that in D_2O-D_2SO_4 and as that for the corresponding *l*-pn complex.

The spectrum for the trans(O),cis(N)-Δ isomer in D_2O showed three broad peaks at 5.3, 5.75, and 5.9 ppm, and that pattern was the same as that in D_2O-D_2SO_4. On the other hand, the spectrum for the corresponding *l*-pn complex also showed three broad peaks at 5.5, 5.75, and 5.9 ppm.

The spectra for the *cis(O),cis(N)*-Λ and -Δ-Co(L-Hasp)$_2$(en)$^+$ complexes were also measured in D_2O and in D_2O–D_2SO_4 with regard to the signals of NH_2 protons. However, any suggestive information concerning hydrogen bonding was not obtained. The situation was the same in the case of the cis(O),-trans(N)-Λ isomer.

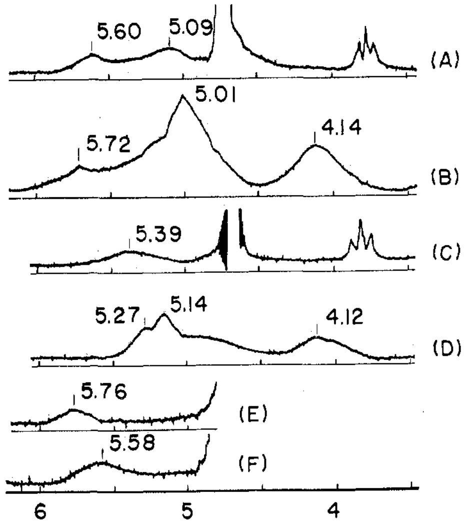

Figure 6. The pmr spectra of the NH_2 protons for (A) Λ-(+)-Co(L-asp)$(en)_2{}^+$ in D_2O, (B) Λ-(+)-Co(L-asp)$(en)_2{}^+$ in D_2O–D_2SO_4, (C) Δ-(−)-Co(L-asp)$(en)_2{}^+$ in D_2O, (D) Δ-(−)-Co(L-asp)$(en)_2{}^+$ in D_2O–D_2SO_4, (E) Λ-(+)-Co(L-asp)(*l*-pn)$_2{}^+$ in D_2O, and (F) Δ-(−)-Co(L-asp)(*l*-pn)$_2{}^+$ in D_2O.

Table III. Formation Ratios of Co(L-Hasp)$_2$(en)$^+$ Isomers

trans(O),cis(N)		cis(O),cis(N)		cis(O),trans(N)	
Λ E-1	Δ E-2	Λ E-4	Δ E-3′	Λ E-3	Δ E-5
12.2	3.4	1	8.6	3.1	Trace
Λ:Δ = 3.6:1 $\Delta G_{\mathrm{obsd}}(25°)$ = −0.76 kcal mol^{-1}		Λ:Δ = 1:8.6 $\Delta G_{\mathrm{obsd}}(25°)$ = 1.3 kcal mol^{-1}			

Stereoselectivity. The formation ratios among the six isomers of the bis(L-hydrogen aspartato) complexes are summarized in Table III with the standard free energy difference between the Λ and Δ pairs (calculated by assuming equibrium in the adopted reaction system). The amount formed in the present reaction decreases in the order of trans(O),cis(N)-Λ > cis(O),cis(N)-Δ > trans(O),cis(N)-Δ ≃ cis(O),trans(N)-Λ > cis(O),cis(N)-Λ ≫ cis(O),trans(N)-Δ. This order agrees with that found for the corresponding propylenediamine complex: trans(O),cis(N)-Λ > cis(O),cis(N)-Δ > trans(O),cis(N)-Δ > cis(O),trans(N)-Λ = cis(O),cis(N)-Λ ≫ cis(O),trans(N)-Δ. Therefore, the stereoselectivity in the present complex is explained in the same way as mentioned in the *l*-pn complex.[4]

The formation ratio of the Δ and Λ isomers of the bis(ethylenediamine) complex is estimated to be 1:1.5 ($\Delta G(25°)$ = 0.24 kcal mol^{-1}). As is mentioned in the Introduction, the same ratio (40:60[3]) has been reported from the experiment by a reaction system different from the present one. This agreement in the ratio indicates the same effects upon the different reactions. In the previous paper,[5] the stereoselective formation of the Δ-Co(gly)(*l*-pn)$_2{}^{2+}$ complex was interpreted by the stable "lel" conformation of the chelated *l*-pn ligand, and the nearly equal amounts found for the Λ- and Δ-Co(L-asp)(*l*-pn)$_2{}^+$ complexes[4] have been explained by putting the effects of the chelated *l*-pn and the chelated L-aspartate together. In the present ethylenediamine complex, the slightly greater formation of the Λ isomer is qualitatively explained by considering the same modes of hydrogen bonding previously proposed for the *l*-propylenediamine complex, hydrogen bonding between the dangling β-carboxylate and an NH_2 group of a chelated ethylenediamine.

Registry No. Λ-(+)-[Co(L-Hasp)$_2$(en)]ClO_4, 37988-65-1; Δ-(−)-[Co(L-Hasp)$_2$(en)]ClO_4, 37988-66-2; Δ-(−)-[Co(L-Hasp)$_2$(en)]I, 38078-18-1; Λ-(+)-[Co(L-Hasp)$_2$(en)]I, 37988-67-3; Λ-(+)-[Co(L-Hasp)$_2$(en)]Cl, 38078-19-2; Δ-(−)-[Co(L-Hasp)$_2$(en)]ClO_4, 37988-68-4; Λ-(+)-[Co(L-asp)$(en)_2$]I, 37988-69-5; Δ-(−)-[Co(L-asp)$(en)_2$]I, 37988-70-8; [Co(L-Hasp)$(NH_3)_4$]$(ClO_4)_2$, 33864-68-5.

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[15] D. A. Buckingham, L. Durham, and A. M. Sargeson, *Aust. J. Chem.*, 20, 257 (1967).