Stereoisomers of the Bis(L-hydrogenaspartato)-trimethylenediaminecobalt(III) Complex

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(Received October 14, 1974)

The bis(L-hydrogenaspartato)trimethylenediaminecobalt(III) complex has been prepared by the reaction of the *trans*-$[CoCl_2(tn)_2]^+$ complex with L-aspartic acid, and its eight stereoisomers have been separated by an ion-exchange chromatographic method. The six isomers are *trans*(*O*)-*Λ* and -*Δ*, *cis*(*O*)*cis*(*N*)-*Λ* and -*Δ* and *trans*(*N*)-*Λ* and -*Δ* isomers, in which either aspartate ion forms the five-membered chelate ring through an N atom of the amino group and an O atom of the α-carboxylate group. The remaining isomers are *Λ*- and *Δ*-*trans*(*O*) ones containing a five-membered chelate ring and a six-membered ring of L-aspartate ions. On the other hand, stereoselective formations have been found in the *Λ*, *Δ*, and *Λ* isomers for the *trans*(*O*), *cis*(*O*)*cis*(*N*), and *trans*(*N*) isomers respectively. It has become apparent that these stereoselectivities agree with those found for the corresponding *l*-pn and en complexes, while the orders of the formation amounts for the three geometrical isomers disagree.

In order to study stereochemistry and stereoselectivity, we previously examined the mixed L-aspartato complexes with *l*-propylenediamine[1] and ethylenediamine;[2] all of the stereoisomers isolated were characterized by their electronic absorption, circular dichroism (CD), and proton magnetic resonance (PMR) spectra. It was also found that the order of the formation amounts of the isomers agrees well between the *l*-propylenediamine and the ethylenediamine complexes.

In the present work, the stereoisomers of a mixed bis(L-hydrogenaspartato)trimethylenediamine complex ion were chosen in order to examine the influence of the six-membered chelate ring of the γ-diamine on the stereochemistry and stereoselectivity. Through this work, all the diastereoisomers corresponding to the six isomers which had been obtained in the previous work[2] were isolated. In addition, a novel pair of diastereoisomers containing an usual five-membered ring of a chelating L-aspartate ion and a six-membered ring formed by NH_2 and β-COO^- of another aspartate ion have been isolated.

Experimental

Preparation. 1) *Carbonatobis(trimethylenediamine)cobalt(III) Chloride*, $[Co(CO_3)(tn)_2]Cl \cdot 1.5H_2O$: Boyle and Harris[3] synthesized this complex by allowing silver carbonate to react on an aqueous solution of the *trans*-dichlorotrimethylenediamine complex. We prepared this complex easily by allowing trimethylenediamine(tn) to react on a solution of potassium tricarbonatocobaltate(III).[4] Trimethylenediamine (8.8 g, 0.12 mol) was added to a cold solution of tricarbonatocobaltate(III) ($CoCl_2 \cdot 6H_2O$, 10 g (0.042 mol) scale), and the mixture was stirred continuously at about 50 °C for 1.5 hr; the solution turned red-violet. After that, the resulting solution was concentrated on a water-bath until its surface was covered with crystals. The concentrated solution was then kept in a refrigerator overnight. The yield of the crude crystals was 13 g. This was subsequently dissolved in the least possible amount of water. After ethanol had been added to the solution until fine crystals began to deposit, the solution was kept in a refrigerator. The desired complex thus obtained was washed successively with ethanol and ether, and then dried in air.

2) trans-*dichlorobis(trimethylenediamine)cobalt(III) Chloride*, trans-$[CoCl_2(tn)_2]Cl$: Bailar and Work[5] synthesized this complex by allowing trimethylenediamine to react on anhydrous cobalt(II) chloride in ethanol with bubbling air. We prepared the complex easily by allowing concd HCl to react on the $[Co(CO_3)(tn)_2]^+$ complex. The complex obtained in 1) (5 g, 0.016 mol) was dissolved in a small amount of water, and then concd HCl (100 ml) was stirred in, little by little. Then the mixture was evaporated to a small volume (~30 ml) on a water-bath at about 60 °C and allowed to stand for a day to give bright green crystals. They were collected, washed successively with cold concd HCl and ethanol, and finally dried in air. The yield was 3.5 g. The crude crystals were dissolved in the minimum amount of hot concd HCl and then an ethanol–ether mixture (1 : 1) was added to the solution. By keeping the whole in a refrigerator, pure crystals of the desired complex were deposited.

3) *Bis(L-hydrogenaspartato)trimethylenediaminecobalt(III) Perchlorate*, $[Co(L\text{-}Hasp)_2(tn)]ClO_4$: The preparative reaction for this complex and the procedure for the chromatographic separation of the stereoisomers were essentially the same as those in the previous work:[1] The complex obtained in 2) (3.1 g, 0.01 mol) and L-aspartic acid (2.7 g, 0.02 mol) were allowed to react at 50 °C for 1 hr in the presence of active charcoal (1 g) and under alkaline conditions (pH~10). For the chromatographic separation, a cation-exchange column containing 100—200 mesh Dowex 50W-X8 resin in the H-form (5.5×35 cm) was used. By eluting a red-violet band at the top of the column with a 0.05 M $NaClO_4$ aqueous solution, five bands colored red or red-violet were completely separated. After the first band had been collected in a fraction, the remaining bands were again eluted with a 0.1 M $NaClO_4$ solution. The fractions collected from the bands were numbered according to the order of elution (No. 1—5). The red-brown band remaining at the top of the column was of the bis(trimethylenediamine) complex. The chromatographic separation was repeated in order to store the same fractions.

The first eluted band actually consisted of two overlapping bands differing in their sign of the main CD peak; the first band showed (+), and the second band, (−). As to the remaining bands, no such phenomenon was observed.

The isolation of the isomeric compounds from the fractions was carried out as follows. Fraction No. 1 was concentrated at 35 °C until red-violet crystals began to deposit, and then it was allowed to stand in a refrigerator for a day. The less soluble isomer thus obtained was recrystallized from water until the $\Delta\varepsilon$ of the main CD peak with the (+) sign reached a constant value. For the sake of convenience, this isomer was labeled E-1. The filtrate obtained after isolating the E-1 isomer was stored in order to isolate the other isomers.

The No. 2 fraction was evaporated to a small volume at 35

°C along with the simultaneous removal of the perchlorate used for the elution, and then a large amount of an ethanol–ether mixture (1:3) was added to the solution in order to precipitate the red material. After the solution had stood in a refrigerator for a day, the precipitated material was collected by means of a centrifuge and then dissolved in a small amount of water. After ethanol had been added to the solution, the whole was kept in a refrigerator for several days. The red isomer (E-2) thus obtained was recrystallized from water by adding ethanol.

The No. 3 fraction was first evaporated to near dryness at 35 °C, and simultaneously the perchlorate was removed. The residue was dissolved in the minimum amount of water, and to the solution a large amount of an ethanol–ether mixture (1:5) was added. After the solution had been allowed to stand for some time, the desired isomer was separated as an oil. After the solvent had been eliminated, a large amount of ethanol was added to the oil to precipitate the isomer. The precipitates were then collected by means of the centrifuge and washed with ethanol. They were again dissolved in the minimum amount of water, and then ethanol was added until the solution began to cloud over. The turbid solution was clarified by warming and then the solution was kept in a refrigerator for several days. The red isomer (E-3) thus obtained was recrystallized from water by adding ethanol.

The No. 4 fraction was concentrated to a small volume at 35 °C and then kept in a refrigerator for a day to give red crystals. This isomer (E-4) was recrystallized from water.

The No. 5 fraction was treated in the same way as the No. 3. The desired red isomer (E-5) was recrystallized from water by adding ethanol.

The filtrate preserved after the E-1 had been isolated was rechromatographed using a small column (Dowex 50W-X8, 100—200 mesh, 2×40 cm, H-form) and 0.05 M $NaClO_4$. Three bands were separated and collected in fractions. Judging from the sign of the main CD peak, it was recognized that the first band was formed by overlapping two bands: the band showing (+) was first eluted, and then the band showing (−) was eluted, overlapping the (+) band. The second band uniformly showed the (+) sign, and the third band, the (−) sign. The first fraction was treated in the same fashion as No. 3. The crude material thus obtained was dissolved in the minimum amount of water, and ethanol (a 3-fold volume) was then added to the solution. By keeping the solution in a refrigerator, red-violet crystals exhibiting the (−) sign of the main CD peak were deposited. The recrystallization was repeated until the $\Delta\varepsilon$ of the CD peak became constant. This isomer was labeled E-1′. The other isomer, with the (+) sign, was isolated from the filtrate of E-1′. Judging from the spectral data and the chromatographic behavior, this isomer was exactly the same as E-1. The second fraction, containing a very small amount of isomeric species, was concentrated to a small volume at 35 °C and then kept in a refrigerator. The red-violet isomer thus obtained was labeled S-1. Its CD spectrum exhibited the (+) sign at the main peak. The third fraction was treated in the same fashion as No. 3. The crude material thus obtained was dissolved in the minimum amount of water. After alcohol had been added, the solution was kept in a refrigerator for several days. The red-violet isomer thus obtained was recrystallized from water by adding ethanol and was labeled S-2.

Formation Ratios of the Isomers. The relative concentrations of the isomers in the fractions were spectrophotometrically estimated by the method described in previous papers,[1,2] and the formation ratios among the isomers were calculated from the results.

Measurements. The electronic absorption spectra were measured with a Hitachi Recording spectrophotometer, Model 323. The circular dichroism spectra were recorded on JASCO Model ORD/UV-5 spectrophotometer with a CD attachment. The proton magnetic resonance (PMR) spectra were recorded on JEOL Model JNM-PS-100 spectrometer (100 MHz) at 23 °C. The values of the chemical shifts were measured in relation to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the internal reference. All the spectra were run in deuterium oxide. The E-1, E-1′, and E-4 isomers for the PMR samples were converted into chloride using an anion-exchange resin (Dowex 1-X8, 100—200 mesh) because of the poor solubility of the perchlorates.

Results and Discussion

From the results of elemental analysis (Table 1), it is obvious that all the compounds isolated are stereoisomers of the bis(L-hydrogenaspartato)trimethylenediaminecobalt(III) complex. However, elemental analysis was not performed for S-1 and S-2 because of their poor yields.

TABLE 1. ELEMENTAL ANALYSES OF THE COMPLEXES PREPARED

Label	Complex	C%	H%	N%
E-1	(+)-[Co(L-Hasp)$_2$(tn)]ClO_4	26.70 (26.62	4.72 4.47	11.32 11.29)
E-1′	(−)-[Co(L-Hasp)$_2$(tn)]ClO_4	26.52 (26.62	4.88 4.47	11.31 11.29)
E-2	(+)-[Co(L-Hasp)$_2$(tn)]ClO_4	27.01 (26.62	4.92 4.47	11.28 11.29)
E-3	(−)-[Co(L-Hasp)$_2$(tn)]ClO_4	26.47 (26.62	4.68 4.47	11.30 11.29)
E-4	(+)-[Co(L-Hasp)$_2$(tn)]$ClO_4\cdot 0.5H_2O$	26.06 (26.13	4.69 4.58	10.99 11.03)
E-5	(−)-[Co(L-Hasp)$_2$(tn)]$ClO_4\cdot 2.5H_2O$	24.29 (24.38	5.02 5.02	10.02 10.34)

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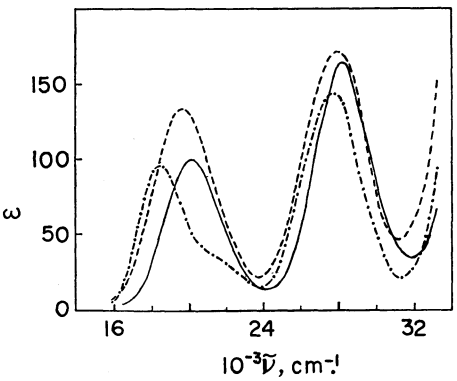

Fig. 1. The electronic absorption spectra of *trans*(*O*)-*cis*(*N*)-*Λ*-[Co(L-Hasp)$_2$(tn)]$^+$ (-·-·-), *cis*(*O*)*cis*(*N*)-*Λ*-[Co(L-Hasp)$_2$(tn)]$^+$ (----), and *cis*(*O*)*trans*(*N*)-*Λ*-[Co(L-Hasp)$_2$(tn)]$^+$ (——).

Characterization of Isomers. Some representative absorption spectra are shown in Fig. 1, while the numerical data are summarized in Table 2. The spectra of E-1, E-1′, S-1, and S-2 are essentially the same and showed a characteristic splitting in their first absorption bands. This fact indicates that these four isomers have *trans*(*O*)*cis*(*N*) geometry, because it is well known that the first band of a *trans*(*O*)-Co^{III}-

TABLE 2. ELECTRONIC ABSORPTION SPECTRA AND CD SPECTRA OF THE COMPLEXES

Label	Complex ion	Band I		Band II		CD	
		$10^{-3}\tilde{\nu}_{max}$ cm^{-1}	ε_I [a]	$10^{-3}\tilde{\nu}_{max}$ cm^{-1}	ε_{II} [a]	$10^{-3}\tilde{\nu}_{max}$ cm^{-1}	$\Delta\varepsilon$ [a]
E-1	*trans(O)cis(N)*-*Λ*-(+)-[Co(L-Hasp)$_2$(tn)]$^+$	18.6	95	27.8	144	18.9	+3.38
		ca. 21.7 sh				22.7	−0.44
E-1′	*trans(O)cis(N)*-*Δ*-(−)-[Co(L-Hasp)$_2$(tn)]$^+$	18.5	94	27.5	146	18.7	−2.15
		ca. 21.7 sh					
E-4	*cis(O)cis(N)*-*Λ*-(+)-[Co(L-Hasp)$_2$(tn)]$^+$	19.6	133	27.9	172	19.5	+1.52
E-3	*cis(O)cis(N)*-*Δ*-(−)-[Co(L-Hasp)$_2$(tn)]$^+$	19.8	114	28.0	148	19.8	−1.64
E-2	*cis(O)trans(N)*-*Λ* -(+)-[Co(L-Hasp)$_2$(tn)]$^+$	20.1	99	28.2	165	19.6	+2.37
						22.2	−0.48
E-5	*cis(O)trans(N)*-*Δ*-(−)-[Co(L-Hasp)$_2$(tn)$^+$	20.0	112	28.2	181	20.5	−2.24
S-1	*trans(O)cis(N)*-*Λ*-(+)-[Co(L-Hasp)$_2$(tn)]$^+$ [b]	18.6	(95)	27.6	(148)	19.0	(+3.17)
		ca. 21.7 sh				22.7	(−0.41)
S-2	*trans(O)cis(N)*-*Δ*-(−)-[Co(L-Hasp)$_2$(tn)]$^+$ [b]	18.7	(94)	27.7	(146)	18.8	(−2.02)
		ca. 21.7 sh					

a) mol^{-1} cm^{-1}. b) The ε and $\Delta\varepsilon$ values of S-1 and S-2 were estimated using the ε values of E-1 and E-1′, respectively, because the lack of the elemental analyses.

$(O)_2(N)_4$ type of complex shows a remarkable splitting.[1,2,6] On the other hand, the spectra of E-2, E-3, E-4, and E-5 reveal symmetrical patterns in their first bands. In addition, the values of $\varepsilon_{II}/\varepsilon_I$ for E-2, E-5, E-3, and E-4 have been calculated as 1.67, 1.62, 1.30, and 1.29 respectively. It has been found experimentally that the value of $\varepsilon_{II}/\varepsilon_I$ for the *cis(O)trans(N)* isomer is larger than that for the *cis(O)cis(N)* isomer.[2,6] These facts suggest that E-2 and E-5 have the *cis(O)trans(N)* geometry, while E-3 and E-4 have the *cis(O)cis(N)* structure. These absorption spectral assignments agree with those made by means of the PMR spectra, which will be discussed later.

The CD spectra are shown in Figs. 2—4, while the numerical data are summarized in Table 2. The spectrum of E-1 (*trans(O)*) shows a dominant (+) peak on the lower-energy-side in the first absorption band

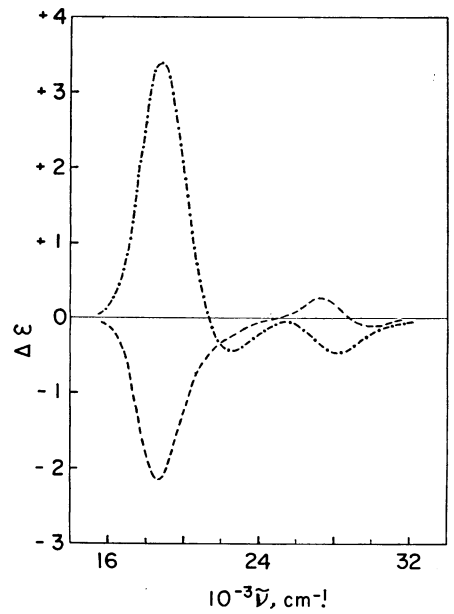

Fig. 2. The CD spectra for *trans(O)cis(N)*-*Λ*-(+)-[Co(L-Hasp)$_2$(tn)]ClO_4 (E-1) (-·-·-) and *trans(O)cis(N)*-*Δ*-(−)-[Co(L-Hasp)$_2$(tn)]ClO_4 (E-1′) (——).

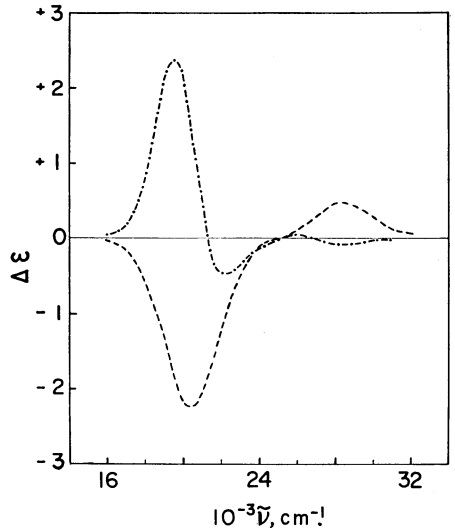

Fig. 3. The CD spectra for *cis(O)trans(N)*-*Λ*-(+)-[Co(L-Hasp)$_2$(tn)]ClO_4 (E-2) (-·-·-) and *cis(O)trans(N)*-*Δ*-(−)-[Co(L-Hasp)$_2$(tn)]ClO_4 (E-5) (——).

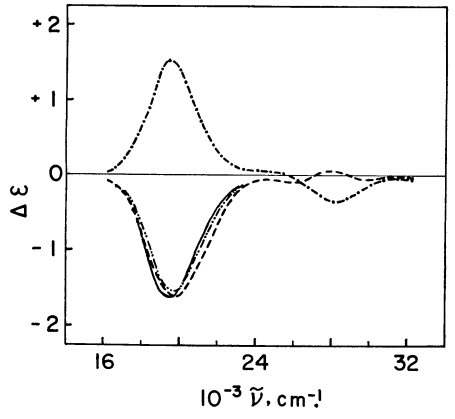

Fig. 4. The CD spectra for *cis(O)cis(N)*-*Λ*-(+)-[Co(L-Hasp)$_2$(tn)]ClO_4 (E-4) (-·-·-) and *cis(O)cis(N)*-*Δ*-(−)-[Co(L-Hasp)$_2$(tn)]ClO_4 (E-3) (——), and the configurational effect curves of *cis(O)cis(N)*-*Δ*-(−)-[Co(L-Hasp)$_2$(tn)]$^+$ (-·-·-·-) and *cis(O)cis(N)*-*Δ*-(−)-[Co(L-ala)$_2$(tn)]$^+$ (——).

region, while only one (−) peak is observed in the spectrum of E-1′ (*trans*(*O*)). E-2 and E-5 have a dominant (+) peak and only one (−) peak respectively in their CD spectra. E-3 shows a spectrum with a (−) peak, and E-4 shows a spectrum with a form nearly symmetrical to that of E-3.

The CD spectrum of the $(-)_{589}$-$[Co(tn)_3]^{3+}$ complex shows a minor (+) peak (E component) at a longer wave length and a major (−) peak (A_2 component) at a shorter wave length in the first band region.[7] The absolute configuration of this complex is determined to be *Λ*,[8,9] which is the same as that of the $(+)_{589}$-$[Co(en)_3]^{3+}$ complex.[10] As to the bis(diamine)-type complexes, the absolute configuration of the $(-)_{589}$-$[Co(acac)(tn)_2]^{2+}$ complex has been determined;[11] its CD spectrum shows only one (−) peak, and the *Λ* configuration is assigned to the complex. The corresponding ethylenediamine complex, $(-)_{589}$-$[Co(acac)(en)_2]^{2+}$, shows a similar spectrum.[12] This similarity suggests that, in the bis(diamine)-type complexes, the difference in tn and en has little influence upon the CD spectra. Accordingly, the absolute configuration of each isomer of the present complex, a bis(aminoacidato)diamine-type complex, was confidently determined by relating the sign of the dominant CD peak in the first absorption band region to that for the $[Co(L\text{-}Hasp)_2(en)]^+$ complex.[2] That is, the E-1, E-2, and E-4 isomers have the *Λ* configuration, and the E-1′, E-3, and E-5 isomers have the *Δ* configuration.

Applying Douglas' relationship,[13] the vicinal curves due to two L-aspartate chelates are calculated for the $[Co(L\text{-}Hasp)_2(tn)]^+$ and $[Co(L\text{-}Hasp)_2(en)]^+$ complexes. The results are shown in Fig. 5. The curves of the complexes resemble each other. This lends support

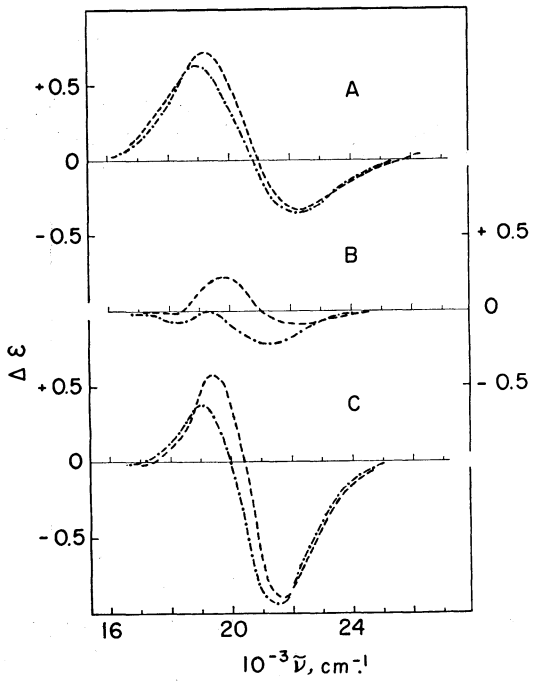

Fig. 5. The vicinal curves of $[Co(L\text{-}Hasp)_2(tn)]^+$ (-·-·-) and $[Co(L\text{-}Hasp)_2(en)]^+$ (——) complexes, A; *trans*(*O*)-*cis*(*N*), B; *cis*(*O*)*cis*(*N*), and C; *cis*(*O*)*trans*(*N*) isomers.

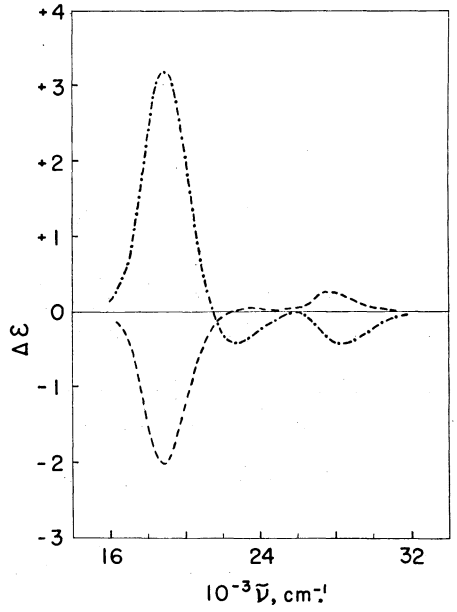

Fig. 6. The CD spectra for *trans*(*O*)*cis*(*N*)-*Λ*-(+)-$[Co(L\text{-}Hasp)_2(tn)]^+$ (S-1) (-·-·-) and *trans*(*O*)*cis*(*N*)-*Δ*-(−) $[Co(L\text{-}Hasp)_2(tn)]^+$ (S-2) (——).

to the previous assignment.

Figure 6 shows the CD curves of S-1 and S-2 drawn by assuming their ε values to be the same as those of E-1 and E-1′ respectively. The curve of S-1 is similar to that of E-1, while the curve of S-2 differs a little from that of E-1′. The absolute configurations of these isomers can also be determined tentatively from the sign of the main CD peak, similarly to the E isomers; S-1 has the *Λ* configuration, and S-2 has the *Δ* configuration. Accordingly, it may be concluded that the E-1 and S-1 isomers are of *trans*(*O*)*cis*(*N*)-*Λ*, while E-1′ and S-2 are *trans*(*O*)*cis*(*N*)-*Δ*.

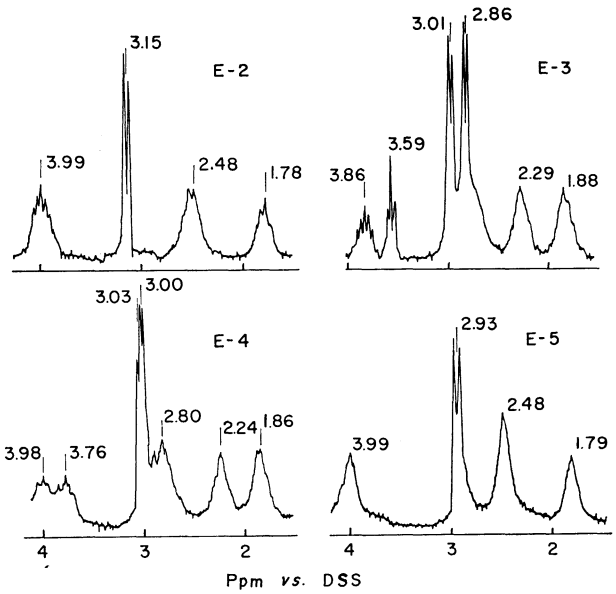

Fig. 7. The PMR spectra for *cis*(*O*)*trans*(*N*)-*Λ*-(+)-$[Co(L\text{-}Hasp)_2(tn)]^+$ (E-2), *cis*(*O*)*cis*(*N*)-*Δ*-(−)-$[Co(L\text{-}Hasp)_2(tn)]^+$ (E-3), *cis*(*O*)*cis*(*N*)-*Λ*-(+)-$[Co(L\text{-}Hasp)_2(tn)]^+$ (E-4), and *cis*(*O*)*trans*(*N*)-*Δ*-(−)-$[Co(L\text{-}Hasp)_2(tn)]^+$ (E-5).

The PMR spectra of the E-2, E-3, E-4, and E-5 isomers are shown in Fig. 7, with the signals of the NH_2 group and HDO eliminated. The resonance signals could be assigned on the basis of the signals of the $[Co(L\text{-Hasp})_2(en)]^+$ [2] and $[Co(CO_3)(tn)_2]^+$ complexes. The signal of the CH_2 protons (AB of ABX) of the β-carbon of the chelated aspartate ion was detected as a doublet, and its chemical shift is given as the center of the doublet. The signals due to the CH_2 and CH groups of the two aspartate ions are observed at 3.15 and 3.99 for E-2, and at 2.93 and 3.99 ppm for E-5. On the other hand, E-3 shows the CH_2 signals at 2.86 and 3.01 ppm and the CH signals at 3.59 and 3.86 ppm. Similarly, E-4 shows the CH_2 signals at 3.00 and 3.03 ppm and the CH signals at 3.76 and 3.98 ppm. Moreover, the signals of three CH_2 groups of the chelated diamine were observed as two peaks in the intensity ratio of 1 : 2 for E-2 and E-5, while the corresponding signals were observed as three peaks of equal intensities for the E-3 and E-4 isomers (a peak at the lowest-magnetic-field for E-3 overlaps with a CH_2 peak of the L-aspartate ion). These results indicate that the E-2 and E-5 isomers have a chemical environment of C_2 symmetry, while E-3 and E-4 have one of C_1 symmetry. Accordingly, it may be concluded that E-2 and E-5 are a pair of diastereoisomers of *cis(O)trans(N)*, while E-3 and E-4 are one of *cis(O)cis(N)*.

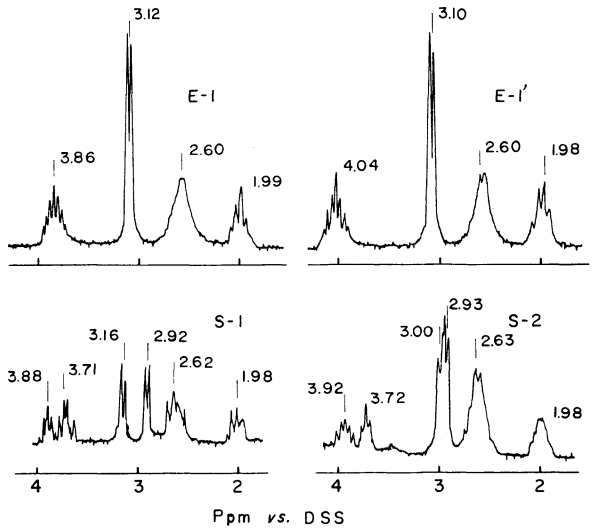

Fig. 8. The PMR spectra for *trans(O)cis(N)*-*Δ*-(+)-$[Co(L\text{-Hasp})_2(tn)]^+$ (E-1), *trans(O)cis(N)*-*Δ*-(−)-$[Co(L\text{-Hasp})_2(tn)]^+$ (E-1'), *trans(O)cis(N)*-*Λ*-(+)-$[Co(L\text{-Hasp})_2(tn)]^+$ (S-1), and *trans(O)cis(N)*-*Δ*-(−)-$[Co(L\text{-Hasp})_2(tn)]^+$ (S-2).

Figure 8 shows the PMR spectra for the E-1, E-1', S-1, and S-2 isomers, whose structure has been determined as *trans(O)cis(N)*. The CH and CH_2 protons of the chelated L-aspartate ions resonate at 3.86 and 3.12 ppm for E-1 and at 4.04 and 3.10 ppm for E-1'. These values are almost equal to those for a pair of diastereoisomers of the corresponding *l*-propylenediamine complex[1] and of the ethylenediamine complex[2] (Table 3). From these correspondences it may be assumed that the E-1 and E-1' isomers are a pair of diastereoisomers with *trans*(O_α)*cis(N)* geometry in respect

Table 3. Assignment of PMR signals[a] of *trans(O)*-*cis(N)*-$[Co(L\text{-Hasp})_2(diamine)]^+$ complexes

(A)

Diamine		*Δ* isomer asp CH_2	*Δ* isomer asp CH	*Δ* isomer tn CH_2	Ref.
tn	(E-1)	3.12	3.86	2.60, 1.99	
	(S-1)	3.16, 2.92	3.88, 3.71	2.62, 1.98	
		(2 : 2	: 1 : 1	: 2 : 1)[b]	
en		3.09	3.81		2
l-pn		3.11	3.85		1

(B)

Diamine		*Δ* isomer asp CH_2	*Δ* isomer asp CH	*Δ* isomer tn CH_2	Ref.
tn	(E-1')	3.10	4.04	2.60, 1.98	
	(S-2)	3.00, 2.93	3.92, 3.72	2.63, 1.98	
		(2 : 2	: 1 : 1	: 2 : 1)[b]	
en		3.00	4.02		2
l-pn		3.06	3.98		1

a) Values in ppm from DSS. b) Ratio of the integrated intensities of peaks.

to the donor O_α and N atoms of the glycinate backbone. As an alternative configuration of C_2 symmetry, the *trans*(O_β)*cis(N)* geometry due to the β-carboxylate ions of the chelated aspartate ions is possible. As may be seen in Fig. 3, the configurational effect curve of the E-3 (or *cis(O)cis(N)*-*Δ*) isomer is in close agreement with the curve of the *cis(O)cis(N)*-*Δ*-$[Co(L\text{-ala})_2(tn)]^+$ complex.[14] An agreement of the same kind is also observed for the other isomers labeled E. From these comparisons, it can be concluded that in every isomer labeled E two L-aspartate ions chelate to the central cobalt(III) ion, thus forming the five-membered rings.

Now let us characterize the S-1 and S-2 isomers. As compared with E-1 and E-1', the yields of these isomers were extremely poor. The ratios of the integrated intensities of all the signals for these isomers (Table 3) support the idea that both are complexes of the bis(L-aspartato)-type. Moreover, from the facts that the absorption spectra of the isomers show remarkable splittings of the first absorption band and that the $\Delta\varepsilon$ in the CD spectra estimated for S-1 and S-2 are almost equal to those for E-1 and E-1' respectively, it may be concluded that the S-1 and S-2 isomers are the stereoisomers of the *trans(O)cis(N)*-$[Co(L\text{-Hasp})_2(tn)]^+$ complex. The PMR spectra of these *trans(O)cis*(N) isomers differ from those of the other *trans(O)cis(N)* isomers (E-1 and E-1'); the CH protons of the two aspartate ions for S-1 resonate at 3.71 and 3.88 ppm, while those for S-2 resonate at 3.72 and 3.92 ppm. The splittings of the signals due to the CH_2 protons are also observed for the isomers labeled S. The chemical shifts of the CH signals and that of the CH_2 signals at the lower magnetic field for S-1 are in close agreement with the corresponding chemical shifts for E-1. The same relation helds for S-2 and E-1'. These

agreements in chemical shifts suggest that S-1 (or S-2) also has a chelate ring such as the E-1 (or E-1') isomer. Since the actual spectra differ between S-1 and E-1 (or S-2 and E-1'), the alternative coordination mode of the L-aspartate ion must be taken into consideration. The pK values of the S-1 and E-1 isomers, which have been calculated from the concentration of the solution and its pH value, were roughly 11.0 and 7.0 respectively. These facts suggest that the S-1 isomer differs in its dangling carboxylate group from the E-1 isomer. Thus, the S-1 and S-2 isomers can now be characterized as a pair of diastereoisomers containing a five-membered ring and a six-membered ring, the latter due to the β-carboxylate of the L-aspartate ion. As far as we know, this is the first time that a complex with a six-membered chelate ring of the aspartate ion has been isolated.

TABLE 4. FORMATION RATIOS OF $[Co(L\text{-}Hasp)_2(tn)]^+$ ISOMERS

trans(O)cis(N)		*cis(O)cis(N)*		*cis(O)trans(N)*	
Λ	Δ	Λ	Δ	Λ	Δ
13	2.2	5.1	20	12	1
$\Lambda:\Delta=5.9:1$		$\Lambda:\Delta=1:3.9$		$\Lambda:\Delta=12:1$	

Stereoselectivity. The formation ratios among three geometrical isomers are summarized in Table 4. The stereoselective formations are found in the Λ, Δ, and Λ isomers for the *trans(O)cis(N)*, *cis(O)cis(N)*, and *cis(O)trans(N)* isomers respectively. This tendency agrees with those for the corresponding *l*-propylenediamine[1] and ethylenediamine complexes.[2] The amount formed in the present reaction decreased in this order: *cis(O)-cis(N)-*Δ > *trans(O)cis(N)-*$\Lambda \cong$ *cis(O)trans(N)-*Λ > *cis(O)-cis(N)-*Λ > *trans(O)cis(N)-*Δ > *cis(O)trans(N)-*Δ; this order differs from those of the *l*-pn and the en complexes.[2] The formation ratio of the *trans(O)cis(N)*: *cis(O)cis(N)*: *cis(O)trans(N)* isomer is about 29: 47: 24. On the other hand, the ratio of these three geometrical isomers in the *l*-pn complex is 61: 34: 5, and that in the en complex is 55: 34: 11. These facts show that the *trans(O)* isomer in the present complex is harder to form than the *cis(O)* isomers, compared with the *trans(O)* isomer in the *l*-pn and the en complexes. The orders in the *l*-pn and the en complexes have been explained on the basis of the consideration of the formation of hydrogen bonding between the β-carboxylate group and the amino group.[1,2] However, the order in the present complex can not be understood from the hydrogen bonding alone.

The author wishes to thank Professor M. Shibata for his kind instruction and continuous encouragement during this work.

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