Four Isomers of the Bis(ethylenediamine)sarcosinatocobalt(III) Ion: Separation, Identification, and Characterization

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All four possible isomers of the bis(ethylenediamine)sarcosinatocobalt(III) ion, [Co(sar) $(en)_2]^{2+}$, were separated chromatographically on the column of an SP-Sephadex cation exchanger, and their absorption, circular dichroism, and ^{13}C NMR spectra were measured. The more stable pair of isomers were identified as Δ-[Co(*S*-sar) $(en)_2]^{2+}$ and Λ-[Co(*R*-sar) $(en)_2]^{2+}$, while the less stable pair were Δ-[Co(*R*-sar) $(en)_2]^{2+}$ and Λ-[Co(*S*-sar) $(en)_2]^{2+}$. The Δ-[Co(*S*-sar) $(en)_2]^{2+}$ isomer in an aqueous solution showed mutarotation which can be ascribed to a change in configuration (epimerization) about the sarcosinato nitrogen atom. In equiribrium at 25 °C, the mixture consisted of 84.8% of the $\Delta(S)$ isomer and 15.2% of the $\Delta(R)$ isomer. From this result, the free-energy difference between the isomers was estimated to be 4.2_6 kJ mol^{-1}. The presence of the less stable isomers, which were not found by Buckingham *et al.*, was also confirmed by the ^{13}C NMR measurements.

The bis(ethylenediamine)sarcosinatocobalt(III) ion possesses four possible isomers arising from two asymmetric centers, one at the cobalt and the other at the sarcosinato nitrogen atom. Figure 1 shows two of the isomers, $\Delta(S)$ and $\Delta(R)$, which are different from each other only with respect to their configurations about the nitrogen atom. The $\Delta(R)$ configuration appears to be less stable than $\Delta(S)$ due to nonbonded repulsive interactions between the hydrogen atoms on the methyl group and those on the adjacent ethylenediamine chelate ring.

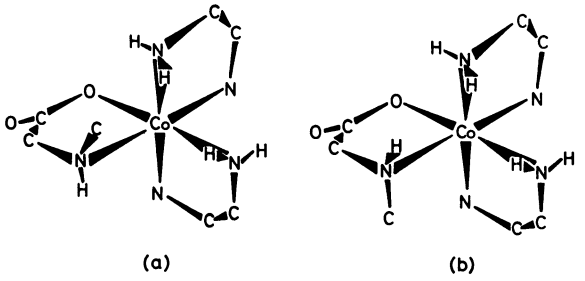

Fig. 1. Structures of Δ-[Co(*S*-sar)$(en)_2]^{2+}$ (a) and Δ-[Co(*R*-sar)$(en)_2]^{2+}$ (b) viewed along the pseudo-C_3 axis. Some of hydrogen atoms attached to carbon and nitrogen atoms are omitted.

The first attempt to separate the four isomers was made by Meisenheimer *et al.*,[1] who claimed to have obtained one isomer having high positive rotatory power in the pure state and two having lower rotatory powers of positive and negative signs, at least in an impure state. However, their results have not been reproduced by other investigators.[2]

In a previous paper,[3] the present authors briefly reported that the four isomers were present as a mixture in an aqueous solution and that their less stable enantiomers were completely resolved into optical isomers by a chromatographic technique using an SP-Sephadex column.

The present study was undertaken to obtain all four isomers of the complex in optically pure form, and to characterize them from measurements of the absorption, circular dichroism (CD), and ^{13}C NMR spectra, the mutarotation rate, and the isomer distribution. The results will be discussed from the structural point of view with reference to the available data on X-ray structural analysis[6] and conformational analysis.[9]

Experimental

Synthesis of the Racemic Complex. Bis(ethylenediamine)-sarcosinatocobalt(III) iodide was prepared from *trans*-$[CoCl_2(en)_2]Cl$ and sarcosine according to the procedure described by Liu and Douglas.[4] The iodide obtained was recrystallized twice from slightly alcoholic water and was dried under reduced pressure. Found: C, 16.14; H, 4.26; N, 13.44%. Calcd for $[Co(CH_3NHCH_2COO)(C_2H_8N_2)_2]I_2$: C, 16.55; H, 4.18; N, 13.52%.

Resolution. The method of Buckingham *et al.*[5] for the resolution of [Co(sar) $(en)_2]I_2$ was used with slight modification. A very slight excess of silver (+)-bromocamphorsulfonate,† Ag (+)-BCS, suspended in water was added to a solution of the complex at about 40 °C. After stirring of the mixture for 30 min, the precipitated silver iodide was filtered off and washed with water. The filtrate and washings were combined and evaporated to dryness on a water bath. The resulting (+)-bromocamphorsulfonate, [Co(sar) $(en)_2]\{(+)\text{-BCS}\}_2$, was recrystallized from aqueous ethanol. The crystals showed a negative CD peak in the vicinity of 518 nm and the filtrate showed a positive CD peak in the same region. After repeated fractional recrystallizations, the least soluble fraction gave a $\Delta\varepsilon_{518}/\varepsilon_{495}$ value of -0.014 and the most soluble fraction a value of $+0.015$. The isomers of the complex showing CD signs of $\{-\}_{518}$ and $\{+\}_{518}$ will hereafter be represented by M and P, respectively (see Table 1).

Chromatographic Separation. An aqueous solution containing about 0.2 g of the (+)-bromocamphorsulfonate of the M-complex was poured onto a small column of SP-Sephadex (volume of 5 cm^3) to collect the complex ions. The SP-Sephadex carrying the complex was transferred to the top of another SP-Sephadex column (2.7 diam × 137 cm). Chromatographic elution with 0.12 M (=mol dm^{-3}) sodium (+)-tartratoantimonate(III), $Na_2[Sb_2((+)\text{-}C_4H_2O_6)_2]$, (pH 3.5) gave two bands, denoted by M-I and M-II in order of effluence (Fig. 2). Similar experiments were also made on the P-complex, which gave two bands, P-I and P-II, and,

† In the present paper, (+)-bromocamphorsulfonate denotes (+)-3-bromocamphor-8-sulfonate.

Table 1. Assignments and abbreviations of the isomers

Isomer	Assignment	CD sign[a)]	Abbrev.	Relative stability
P-I	$\Lambda(+)_{589}$[Co(*S*-sar)$(en)_2$]$^{2+}$	$\{+\}_{518}$	$\Lambda(S)$	less stable
P-II	$\Lambda(+)_{589}$[Co(*R*-sar)$(en)_2$]$^{2+}$	$\{+\}_{518}$	$\Lambda(R)$	stable
M-I	$\Delta(-)_{589}$[Co(*R*-sar)$(en)_2$]$^{2+}$	$\{-\}_{518}$	$\Delta(R)$	less stable
M-II	$\Delta(-)_{589}$[Co(*S*-sar)$(en)_2$]$^{2+}$	$\{-\}_{518}$	$\Delta(S)$	stable

a)The $\{+\}_\lambda$ and $\{-\}_\lambda$ symbols represent the CD sign at λ nm.[7)]

on the racemic complex, which gave three bands, A, B, and C (Fig. 2). The notations, M-I, M-II, P-I, and P-II, will hereafter also be used to designate the isomer contained in each band.

Conversion to the Chloride. The combined eluate of the M-I bands from several elutions was diluted twenty times with water, acidified by a small amount of HCl (pH≈3), to prevent isomerization.†† The complex in the diluted eluate from the M-I band was again collected on a separate SP-Sephadex column. After washing the column with 0.005 M HCl to remove sodium ions, if any, the M-I isomer sorbed was eluted with 0.5 M HCl. The eluate containing the chloride of the M-I isomer was evaporated almost to dryness under reduced pressure. Ethanol, and subsequently ether, were added to precipitate the chloride. The chloride of the M-I isomer obtained was dried under reduced pressure. The chlorides of the M-II, P-I, and P-II isomers were also obtained from the eluates of the corresponding bands by means of similar procedures. M-I (P-I). Found: C, 20.47 (20.51); H, 6.55 (6.33); N, 16.57 (16.57)%. Calcd for [Co(CH_3-$NHCH_2COO$)$(C_2H_8N_2)_2$]$Cl_2\cdot 2H_2O\cdot HCl$: C, 20.47; H, 6.63; N, 17.06%. M-II (P-II). Found: C, 22.24 (22.40); H, 6.33 (5.88); N, 18.15 (18.38)%. Calcd for [Co(CH_3NHCH_2COO) $(C_2H_8N_2)_2$]$Cl_2\cdot 2H_2O$: C, 22.47; H, 5.93; N, 18.72%.

Physical Measurements. Absorption spectra were recorded on a Shimadzu UV 200S spectrophotometer equipped with a 1-cm quartz cell at room temperature. The sample solutions contained complex ions at approximately 4×10^{-3} M in 0.5 M HCl. CD curves were measured for a *ca.* 10^{-3} M solution of each isomer in 0.5 M HCl with a JASCO J-20 CD recorder using a 1-cm cell. The ^{13}C NMR spectra were obtained with a JEOL JNM FX-60 spectrometer at a probe temperature of 35 °C. Dioxane in D_2O in a coaxial inner tube was used as an external reference for all samples. The concentrations of the samples were approximately 0.1 M. Usually, 40000—50000 pulses were accumulated to produce a very clear spectrum.

Equilibration. About 0.02 g of each isomer was dissolved in 10 cm^3 of each solution listed in the first column of Table 4. The slightly alkaline or neutral solution (with added NaOH, if necessary) was allowed to stand at 25 °C for three days and then acidified with 0.5 M HCl. The complex was collected from the solution on a small amount of SP-Sephadex. The collected equilibrium mixture of the complex was subjected to chromatographic separation on an SP-Sephadex column (1.5 diam×87 cm) using 0.12 M $Na_2[Sb_2((+)\text{-}C_4H_2O_6)_2]$ as the eluent. The isomer ratio was obtained from the ratio of the areas of the bands in the elution curve.

Mutarotation. The rate of CD change was measured for a 0.1 M acetate buffer solution (pH 5.66) of each isomer (3.0×10^{-3} M) at 30.0 °C. The change in the CD intensity was observed at 465 nm, the wavelength at which the CD spectra showed a marked difference between the I and II isomers. The reaction was followed for at least three half-lives.

†† Although the elutions were carried out at room temperature (15—20 °C), the eluates were stored in a refrigerator (≈5 °C) to inhibit isomerization.

Results and Discussion

Chromatographic Behavior and Identification. Figure 2 shows the results of chromatographic elutions of the M-, P-, and racemic complexes with 0.12 M sodium (+)-tartratoantimonate(III). The ratios of the areas under the peaks are approximately 1 : 4.5 for (a) and (b), and 1 : 1 : 9 for (c) in Fig. 2. Comparisons of the band positions identified the A, B, and C bands of the racemic complex as the M-I, P-I, and combined P-II and M-II bands, respectively. For the C band, the CD sign at 518 nm was positive at the head of the band and negative at the tail, in agreement with the observation that the P-II isomer was eluted slightly faster than M-II.

The CD spectrum of the M-II isomer (Fig. 4) closely resembles that of $(-)_{589}$[Co(sar)$(en)_2$]$^{2+}$ obtained by Buckingham *et al.*[5)] On the basis of an X-ray analysis of $(-)_{589}$[Co(sar)$(en)_2$]$I_2\cdot 2H_2O$,[6)] the M-II isomer is identified as Δ-[Co(*S*-sar)$(en)_2$]$^{2+}$ (Fig. 1(a)). The P-II isomer can be identified as Λ-[Co(*R*-sar)$(en)_2$]$^{2+}$ from its enantiomeric relationship to the M-II isomer. Taking account of the isomerization behavior, which is described below, the M-I and P-I isomers are identified as the less stable isomers, Δ-[Co(*R*-sar)$(en)_2$]$^{2+}$ (Fig.

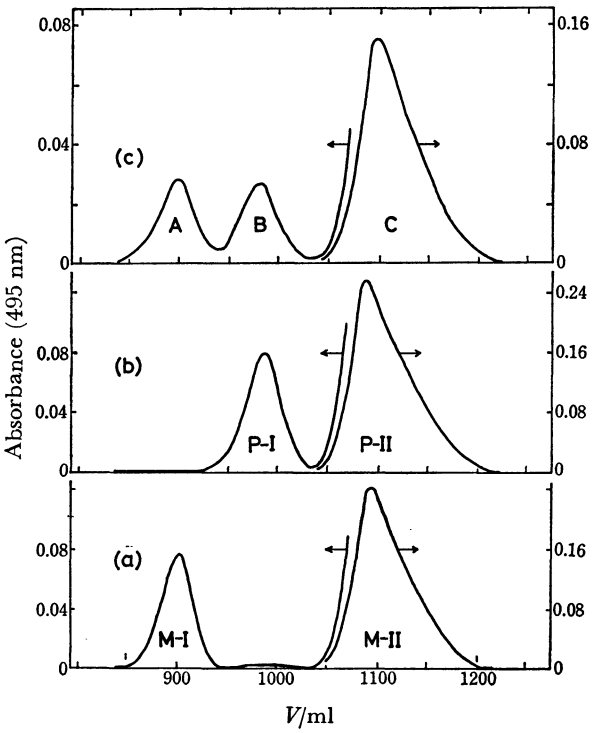

Fig. 2. Elution curves for $\{-\}_{518}$[Co(sar)$(en)_2$]$^{2+}$ (a), $\{+\}_{518}$[Co(sar)$(en)_2$]$^{2+}$ (b), and *rac*-[Co(sar)$(en)_2$]$^{2+}$(c).

1(b)) and *Λ*-$[Co(S\text{-sar})(en)_2]^{2+}$, respectively. The assignments are summarized in Table 1.

The P-I isomer showed no measurable CD change either in 0.12 M $Na_2[Sb_2((+)\text{-}C_4H_2O_6)_2]$ or in acidified water at room temperature over one week. This indicates that epimerization (configuration change) at the nitrogen center of the sarcosinato ligand is very slow in acidic solutions. The (+)-bromocamphorsulfonate of M-complex was dissolved in acidified water (pH≈3), and was subjected to chromatographic separation, as described in the experimental section. The elution curve showed a very small peak corresponding to M-I and a large peak corresponding to M-II, with the area ratio being 1 : 23. This suggests that the recrystallized (+)-bromocamphorsulfonate of the M-complex consists almost solely of the M-II isomer. On the other hand, in a neutral or alkaline solution, epimerization at the nitrogen center occurred to give an equilibrium mixture of M-I and M-II (Fig. 2(a)).

The fact that the less stable isomers, M-I and P-I, are eluted faster than the more stable M-II and P-II (Fig. 2) can be taken as an indication of the former being favored in the interaction with the eluting agent, sodium (+)-tartratoantimonate(III). The stereoselectivity is ascribed to the structural feature of the less stable isomers that each has a set of three N–H hydrogens directed nearly parallel to the pseudo-C_3 axis of the complex (Fig. 1). Further discussion in this connection can be found below.

Absorption (AB) and Circular Dichroism (CD) Spectra. Figures 3 and 4 show the AB and CD spectra of the four isomers, and Table 2 summarizes the numerical data for the M-I and M-II isomers. For the less stable isomer, M-I, both the first and second absorption bands appeared at slightly lower wave numbers than for the more stable isomer, M-II, indicating a slightly weaker ligand field in the M-I isomer. The CD spectra of M-I and P-I (Fig. 3) were mirror images of each other, confirming the enantiomeric relationship deduced from their chromatographic behavior. A similar relationship was observed between M-II and P-II (Fig. 4). The CD spectra of M-I and M-II are similar in that they have a main CD band of negative sign in the $^1T_{1g} \leftarrow {}^1A_{1g}$ (O_h) region, but are different from each other in other respects, as depicted in Figs. 3 and 4.

In Fig. 5, the halved sum of CD curves for P-I and P-II, showing the contribution of the *Λ*-configuration about the cobalt center, is compared with the CD curve for $\Lambda(+)_{546}[Co(gly)(en)_2]I_2$;[4] the latter has a configura-

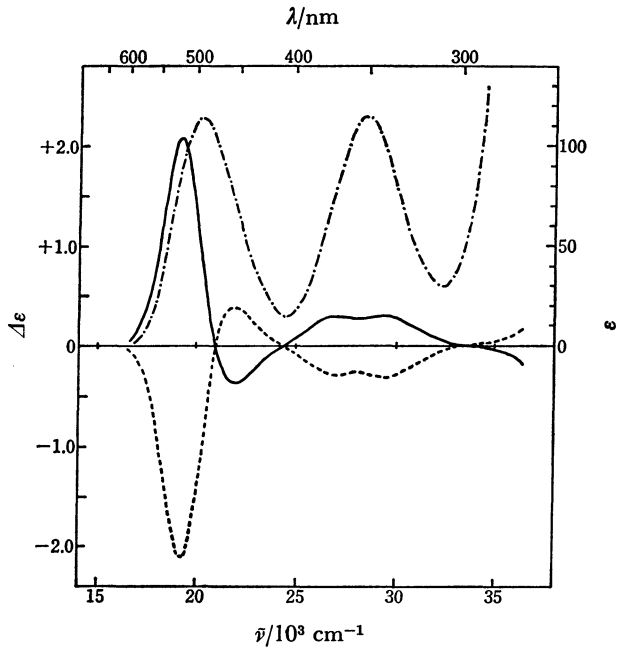

Fig. 3. Absorption spectrum (– · –) of P-I and circular dichroism spectra of P-I (——) and M-I (------) in 0.5 M HCl solutions.

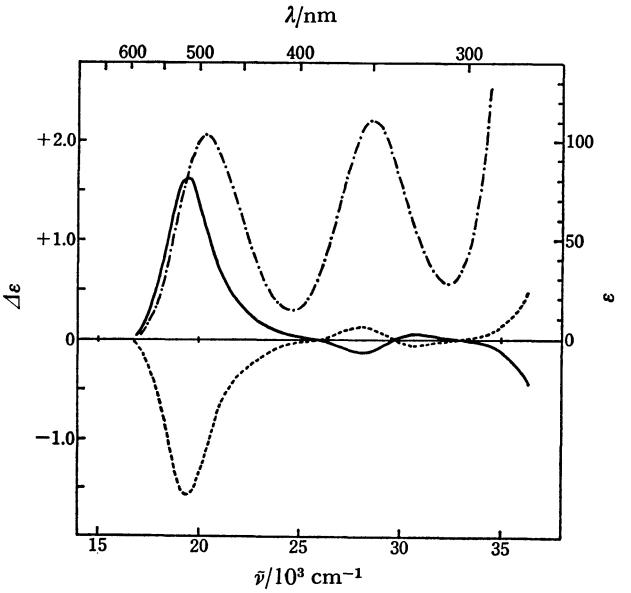

Fig. 4. Absorption spectrum (– · –) of P-II and circular dichroism spectra of P-II (——) and M-II (------) in 0.5 M HCl solutions.

Table 2. Absorption (AB) and circular dichroism (CD) spectral data

Complex		AB peak		CD peak	
		$\bar{\nu}/10^3$ cm^{-1}	ε	$\bar{\nu}/10^3$ cm^{-1}	$\Delta\varepsilon$
$\Lambda\{-\}_{518}[Co(R\text{-sar})(en)_2]Cl_2\cdot 2H_2O\cdot HCl$ (M-I)	1st band	20.3	114	19.2	−2.10
				21.9	+0.38
	2nd band	28.4	115	27.1	−0.29
				29.4	−0.31
$\Lambda\{-\}_{518}[Co(S\text{-sar})(en)_2]Cl_2\cdot 2H_2O$ (M-II)	1st band	20.4	103	19.5	−1.59
	2nd band	28.6	111	28.1	+0.13
				30.8	−0.04

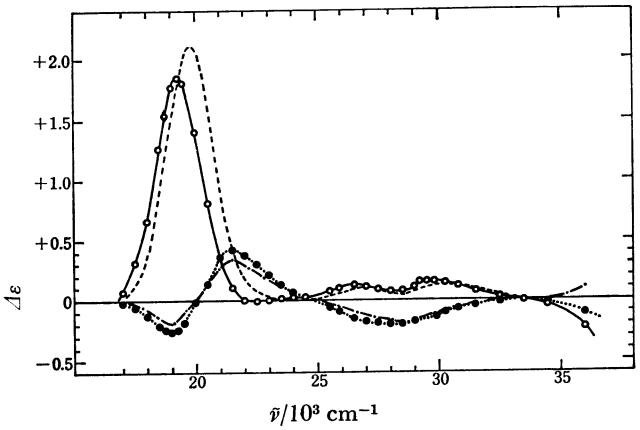

Fig. 5. Configurational and vicinal CD curves of $[Co(sar)(en)_2]^{2+}$: $1/2\times\{(P\text{-}I)+(P\text{-}II)\}$ (-○-) and $1/2\times\{(M\text{-}I)-(M\text{-}II)\}$ (···●···), respectively, compared with the CD spectra of Λ-$[Co(gly)(en)_2]^{2+}$ (------) and $(-)_{436}$-$[Co(R\text{-}sar)(NH_3)_4]^{2+}$ (- · -).

tion similar to that of the P-isomers, but has no asymmetric center at the aminoacidato nitrogen. Figure 5 also shows the halved difference of the CD spectra for M-I and M-II, showing *R*-vicinal contribution of the asymmetric nitrogen. This difference was compared with the CD spectrum for $(-)_{436}[Co(R\text{-}sar)(NH_3)_4](NO_3)_2$,[8] which makes only a vicinal contribution of the sarcosinato nitrogen to the CD spectrum. The similarity of the halved-sum and -difference spectra to those of the reference complexes can be taken as additional evidence for our assignment of the absolute configurations of the isomers; the small difference in the position of the main peak between the halved-sum CD spectrum and the reference spectrum may result from some conformational effect of the ethylenediamine rings.

In an X-ray study of the Λ-$[Co(S\text{-}sar)(en)_2]I_2\cdot 2H_2O$ crystal, the conformation of the ethylenediamine rings was found to be $\delta\lambda$.[6] On the other hand, Buckingham and his coworkers[9] have shown in their strain-energy

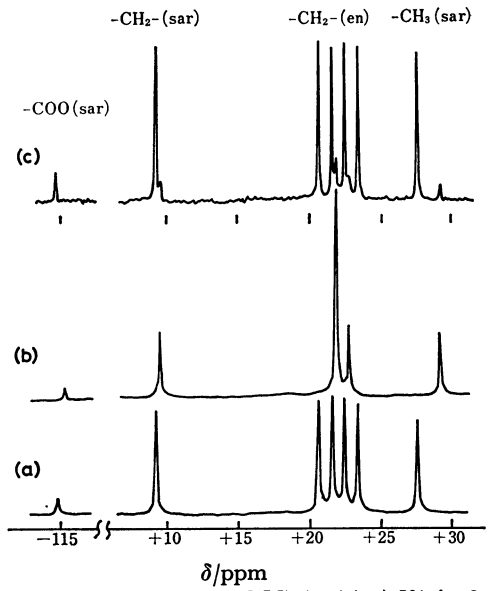

Fig. 6. ^{13}C NMR spectra of $[Co(sar)(en)_2]^{2+}$ in 0.5 M HCl solutions using dioxane as an external standard: P-II, (a); P-I, (b); racemic complex, (c).

calculations that the $\delta\lambda$ and $\lambda\lambda$ conformations would have the same minimum energy for the $\Lambda(S)$ ion and that the $\lambda\lambda$ conformation is most stable for the $\Lambda(R)$ ion. Thus, it is very probable that the $\Lambda(S)$ and $\Lambda(R)$ ions have different ring conformations and, therefore, that the halved-sum spectrum of these ions shows a conformational effect in addition to the Λ-configurational effect.

Carbon-13 NMR Spectra. Figure 6 shows the ^{13}C NMR spectra (^1H "noise" decoupled) of P-II, P-I, and the racemic mixture, which was equilibrated in an aqueous solution. All measurements were made in 0.5 M hydrochloric acid solutions to prevent isomerization. A comparison of the spectra shows that the racemic mixture contains II isomers as the major component and I isomers as the minor component.

The $[Co(sar)(en)_2]^{2+}$ ion has seven carbon atoms:

Table 3. Carbon-13 NMR Spectral data

Compound	Chemical shifts, δ[a]							
	$-CH_3$(sar)		$-CH_2$-(en)		$-CH_2$-(sar)		-COO (sar)	
$[Co(sar)(en)_2]^{2+}$ P-II		+27.3		+23.2 (1)[b]		+9.14		−116.4
				+22.3 (1)				
				+21.4 (1)				
				+20.4 (1)				
P-I	+28.9		+22.6 (1)[b]		+9.40		−116.0	
			+21.7 (3)					
Racemic	+28.7	+27.2	+22.5[c]	+23.2	+9.33[c]	+9.06	—[d]	−116.4
			+21.7	+22.3				
				+21.4				
				+20.4				
$[Co(gly)(en)_2]^{2+}$			+22.9		+20.5[e]		−118.4[f]	
			+21.8					
			+21.6					
			+21.0					

a) Shifts in ppm from dioxane: positive values, upfield; negative values, downfield. b) Figures in parentheses are relative intensities. c) Shoulders. d) Peak not detected. e) Glycinato methylene carbon. f) Glycinato carboxyl carbon.

four methylene carbon atoms in the two ethylenediamine ligands, and single methyl, methylene, and carboxyl carbon atoms in the sarcosinato ligand. Correspondingly, the spectrum for P-II shows seven resonance peaks of nearly equal intensity except for the lowest-field peak of low intensity (Fig. 6(a)). The latter was assigned to the carboxyl carbon, which is known to relax slowly and to show a weak resonance peak.[10] Further information was obtained by allowing the ^{13}C nuclei to couple with protons. The resonance peak at the highest field split into a quartet and was readily assigned to the methyl carbon atom of the sarcosinato ligand. The signal of the methylene carbon atom in the sarcosinato ligand was distinguished from those of the methylene carbon atoms in the ethylenediamine ligands, because each of the triplet signals of the latter carbon atoms was broadened due to long-range coupling with the protons of the adjacent methylene and amino groups. However, the resonances of the ethylenediamine carbon atoms were difficult to assign to the individual atoms. The chemical shift data and assignments are summarized in Table 3. The table also gives the data for *rac*-$[Co(gly)(en)_2]Cl_2$ measured under the same conditions.

All the resonance peaks for the carbon atoms in the sarcosinato ligand appeared at a higher field for P-I than P-II. Since the chemical shift difference was the greatest between the methyl carbon signals of the two isomers, the high-field shifts observed for P-I can be ascribed to a distortion of the chelate ring brought about by an increase in the nonbonded repulsive interactions of the methyl group with an adjacent ethylenediamine ring. Such a distortion was also inferred from the low wave-number shift of the absorption spectrum of P-I relative to that of P-II. Concerning the resonance pattern of the four carbon atoms in ethylenediamine ligands, a marked difference was observed between P-I and P-II. Whereas P-II gave four nearly equally spaced peaks (Fig. 6(a)), P-I resulted in a pattern in which three of the four carbon atoms were apparently equivalent (Fig. 6(b)). The reasons for the incidental degeneracy in this nonsymmetric complex are not immediately evident. The ethylenediamine carbon atoms of the corresponding glycinato complex gave four distinct resonance peaks similar to those of P-II, although slight chemical-shift differences were observed among them. Therefore, nonbonded repulsive interactions of methyl group are responsible for the incidental degeneracy of the ethylenediamine carbon signals of P-I.

Mutarotation Rate (Rate of Epimerization at the Nitrogen Center). Figure 7 shows a typical set of CD spectra (480—380 nm) obtained at intervals after the P-I isomer had been dissolved in the acetate buffer solution at 28 °C. The spectra gave an isosbestic point at 403 nm and showed the greatest intensity change at 465 nm. From these observations, it is inferred that the CD change resulted from only one reaction which is epimerization at the nitrogen center yielding the P-II isomer.

The CD change measurements were carried out starting from the P-I and P-II isomers. In each kinetic run, the plot of $\ln|(\Delta\varepsilon)_t-(\Delta\varepsilon)_\infty|$ *vs.* time gave a straight line for at least three half-lives, where $(\Delta\varepsilon)_t$ and $(\Delta\varepsilon)_\infty$ represent the CD intensities at time t and at infinite

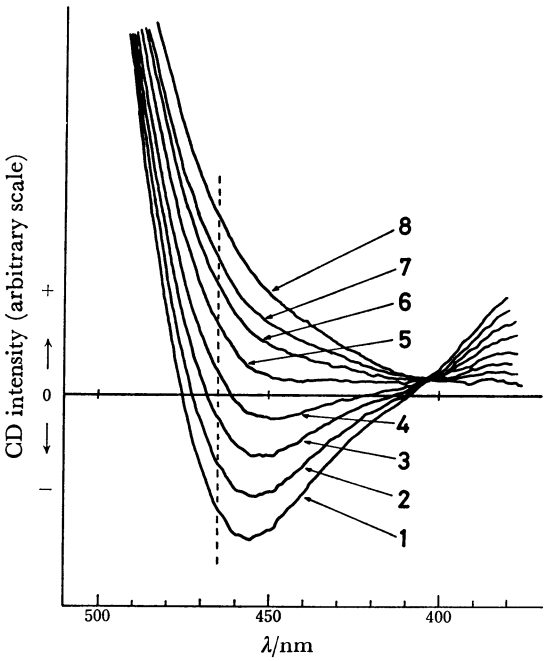

Fig. 7. Change of the CD spectrum with time for the P-I isomer in a 0.1 M acetate buffer at 28 °C. The curves 1—8 show the spectra measured at 5, 30, 60, 90, 130, 170, 215, and >1400 minutes, respectively.

time, respectively, at 465 nm. The slope gave the pseudo first-order rate constant, k_{obsd}. The runs using P-I and P-II as the starting isomers in a 0.1 M acetate buffer solution (pH 5.66) at 30.0 °C gave k_{obsd} values of 3.32×10^{-4} and 3.37×10^{-4} s^{-1}, respectively. They are in good agreement with each other.

For reversible isomerization (epimerization):

$$\text{P-II}\,(\Lambda(R)) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{P-I}\,(\Lambda(S))$$

the forward and reverse rate constants, k_f, and k_r, are related to the observed rate constant, k_{obsd}, and to the equilibrium constant, K, as follows:

$$k_{obsd} = k_f + k_r$$
$$K = k_f/k_r.$$

The K values was found to be 0.177 in chromatographic experiments on the equilibrium mixture (Table 4). This leads to k_f and k_r values of 0.50×10^{-4} and 2.85×10^{-4} s^{-1}, respectively. The rate of epimerization is known to be proportional to the hydroxide ion concentration,[8] and the second-order rate constants, k, k_1, and k_2, can be obtained from the corresponding first-order rate constants, k_{obsd}, k_f, and k_r, in terms of the equations:

$k = k_{obsd}/[OH^-]$, $k_1 = k_f/[OH^-]$, and $k_2 = k_r/[OH^-]$.

The resulting values are 7.32×10^4, 1.1×10^4, and 6.2×10^4 M^{-1} s^{-1}, respectively. On the other hand, Halpern *et al.*[8] obtained a corresponding rate constant, $k=1.9\times10^4$ M^{-1} s^{-1}, for the racemization of $[Co(sar)(NH_3)_4](NO_3)_2$ dissolved in a 0.1 M acetate buffer at 30.0 °C. This gives $k_1=k_2=1.0\times10^4$ M^{-1} s^{-1}, which can be compared with the k_1 value for $[Co(sar)(en)_2]^{2+}$ of the present study. The several times greater value of k_2 for $[Co(sar)(en)_2]^{2+}$ suggests that some steric

TABLE 4. EQUILIBRIUM ISOMER DISTRIBUTIONS FOR $[Co(sar)(en)_2]^{+2}$ IN VARIOUS SOLUTIONS AT 25.0 °C

Solution	Isomer[a]	Isomer proportion(%)		Isomer ratio I/II
		I	II	
H_2O	M-I	15.4	84.6	0.182
	M-II	15.1	84.9	0.177
	P-II	15.1	84.9	0.178
0.1 M $NaCH_3COO$[b]	P-II	15.1	84.9	0.177
0.3 M $NaCH_3COO$	M-II	15.3	84.7	0.181
	P-II	15.7	84.3	0.187
	racemic	7.90+7.61	84.5	0.184
0.1 M Na_2SO_4	M-II	18.1	81.9	0.221
	P-II	17.7	82.3	0.215
0.1 M $Na_2(+)$-$C_4H_4O_6$	M-II	16.3	83.7	0.195
	P-II	16.3	83.7	0.195
0.3 M $Na_2(+)$-$C_4H_4O_6$	M-II	17.0	83.0	0.205
	P-II	17.8	82.2	0.217

a) Starting substance for equilibration. b) Kinetic run in an acetate buffer at 30.0 °C (see text).

repulsion exists in the $\Lambda(S)$ isomer to result in the acceleration of the $\Lambda(S)$ to $\Lambda(R)$ epimerization.

Equilibrium Isomer Distribution. The complex was equilibrated in various solutions at 25 °C and chromatographically analyzed for the isomer distribution. The results are given in Table 4. No indication was observed of the formation of other isomers and decomposition products in the column-chromatographic procedure.

The runs starting from M-I and from M-II in water gave essentially the same I to II ratios within the experimental error ($\approx\pm3\%$), consistent with the mutarotation experiments. Therefore, other runs were performed with either of the stable isomers (M-II and P-II) as the starting substance. At equilibrium in an aqueous solution, the I to II ratio was 15.2: 84.8 on the average, which gave the equilibrium constant, $K=0.177$, and the free energy difference, $\Delta G=4.2_6$ kJ mol^{-1}, between the I and II isomers. This ΔG value is close to the strain energy difference of 0.9 kcal mol^{-1} (=3.8 kJ mol^{-1}) calculated by Buckingham and his coworkers,[9] who gave minimized strain energies of 3.8 kcal mol^{-1} for the $\delta\lambda$-*S* and $\lambda\lambda$-*S* isomers of the Δ-complex and 4.7 kcal mol^{-1} for the $\lambda\lambda$-*R* isomer of the Δ-complex.†††

The addition of oxo anions effected an increase in the proportion of I isomer. Whereas, in 0.3 M CH_3COONa, this effect was not clearly observable due to the experimental error, a marked effect was found in 0.1 M Na_2SO_4. Sodium (+)-tartrate also showed the effect of increasing the proportion of I isomer, although the abundance of I isomer in 0.1 M $Na_2((+)$-$C_4H_4O_6)$ was not as high as that in 0.1 M Na_2SO_4 (Table 4). It is to be noted that, in 0.3 M $Na_2((+)$-$C_4H_4O_6)$, the M-and P-isomers showed different I/II ratios (Table 4), which is suggestive of stereoselective interactions of the isomers with the (+)-tartrate ion.

Such stereoselectivity was confirmed by the following chromatographic experiment. A slightly acidic (with HCl) aqueous solution of the P-I and M-I isomers mixed in equal amounts was allowed to flow through an SP-Sephadex column (1.5 dia. × 90 cm) and the complex sorbed by the column was eluted with 0.24 M $NaH((+)$-$C_4H_4O_6)$ (pH 3.4). Although the elution curve showed only one band, CD measurements revealed partial resolution of the enantiomers with an elution order P-I ($\Lambda(S)$) and M-I ($\Delta(R)$). This order can be compared with the Λ-Δ order of $[Co(en)_3]^{3+}$ when eluted with a sodium (+)-tartrate solution[11] and also when eluted with a sodium hydrogen-(+)-tartrate solution,[12] although the stereoselectivity was much higher in the $[Co(en)_3]^{3+}$ cases.

The behavior of the I isomer is understandable from the structural point of view. Both P-I and M-I isomers have a set of three N–H bonds (one sarcosinato and two ethylenediamine N–H bonds) aligned approximately parallel to the pseudo-C_3 axis of the complex, if the ethylenediamine ligands assume the *lel* conformation (Fig. 1). In the P-II and M-II isomers, on the other hand, the N–CH_3 bond of the sarcosinato ligand is nearly parallel to the pseudo-C_3 axis. Therefore, I isomers will more favorably interact with sulfate, (+)-tartrate, and hydrogen-(+)-tartrate ions than will II isomers and, thus, the proportion of I isomers in the equilibrated mixture will increase. The greatest effect shown by sulfate ions (Table 4) can be taken as suggesting that sulfate ions have the greatest tendency to form ion pairs with I isomers. This is consistent with the fact that the formation constant for the $[Co(en)_3]^{3+}$–SO_4^{2-} ion pair is approximately twice as large as that for the ion pair with the (+)-tartrate.[13]

The stereoselectivity of the (+)-tartrate ion for the P-I and M-I isomers can be explained in a manner similar to that for the case of stereoselective ion-pair formation between the (+)-tartrate ion and the $[Co(en)_3]^{3+}$ isomers.[14] The lower stereoselectivity for the $[Co(sar)(en)_2]^{2+}$ isomers appears to result mainly from the lower charge of this complex than for $[Co(en)_3]^{3+}$. For $[Co(gly)(en)_2]^{2+}$, (+)-tartrate ions showed little stereoselectivity.

The stereoselectivity shown by (+)-tartratoanti-

††† However, they assumed that the actual ΔG value probably exceeds $\approx$2 kcal mol^{-1}, since their careful ion-exchange chromatographic studies failed to show any isomeric separation.

monate(III) ions is very different from that of (+)-tartrate ions. As illustrated in Fig. 2(c), (+)-tartratoantimonate(III) ions show a high stereoselectivity for $[Co(sar)(en)_2]^{2+}$; however, this selectivity is the reverse of that shown by (+)-tartrate ions. This is in contrast to the case of $[Co(en)_3]^{3+}$, for which (+)-tartratoantimonate(III) ions show a stereoselectivity of the same preference as that shown by (+)-tartrate ions. The formation of the $[Co(sar)(en)_2]^{2+}$–$[Sb_2((+)\text{-}C_4H_2O_6)_2]^{2-}$ ion pair may occur through a mechanism different from that in the ion-pair formation involving (+)- tartrate or hydrogen-(+)-tartrate ions, since the tartrato hydroxyl groups in the (+)-tartratoantimonate(III) ion are bound to antimon(III) ions[15] and not readily available for ion pairing.

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