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Stereoselectivity in Ion-Pair Formation. 4.[1] Stereochemical Consideration about Specific Ion Association between Optically Active (Amino acidato)bis(ethylenediamine)cobalt(III) and Tartrate Ions

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The ion association constants were determined in aqueous solution for the ion pairs consisting of optically active (phenylalaninato)bis(ethylenediamine)cobalt(III) and an L-tartrate anion, by utilizing circular dichroism measurements: $K = 4.3 \pm 0.1$ for Λ-(L-phe), $K = 4.0 \pm 0.1$ for Δ-(D-phe), $K = 2.7 \pm 0.3$ for Λ-(D-phe), and $K = 1.2 \pm 0.6$ for Δ-(L-phe). This difference in association constant was interpreted in terms of the difference in steric repulsion between the phenyl group of the complex ion and the L-tartrate anion in the ion-pair formation. Futhermore, it was noted that the difference in association constant is related to the elution order in column chromatography.

Introduction

In earlier investigations[2–5] of stereoselective ion association of metal complexes, it has been reported that L-tartrate associates with the tris(ethylenediamine)cobalt(III) complex in favor of its Λ form in aqueous solution. Recently we have demonstrated by the study[6] of X-ray analysis of Λ-$[Co(en)_3]Br$-L-tart·$5H_2O$ that L-tartrate approaches $[Co(en)_3]^{3+}$ along the direction of C_3 axis and concluded that this structural feature plays an important role in the stereoselective formation of this diastereomeric salt. In contrast to the solid state, it is difficult to detect the requisite for the stereoselectivity of L-tartrate in solution. Nevertheless, it was proposed[7] on the basis of the above structural information that it is essential for the complex to have three sets of NH hydrogen atoms in the face perpendicular to the C_3 axis (triangular NH face) for the great stereoselective ion association with L-tartrate. This proposal is based on the consideration of the efficiency for optical resolution of *fac*- and *mer*-$[Co(\beta\text{-ala})_3]$ through column chromatography; the *fac* isomer with the triangular NH face is resolved with L-tartrate, but the *mer* isomer with no triangular NH face is not resolved.[7] At present, however, it is not yet known how the stereoselectivity is influenced by the steric interaction. In this paper, we wish to report the investigation of the stereoselective interaction between L-tartrate and the optically active (amino acidato)bis(ethylenediamine)cobalt(III) complex, $[Co(am)(en)_2]^{2+}$ (am = $NH_2CH(R)COO^-$), which has three sets of NH hydrogen atoms in the face perpendicular to the pseudo C_3 axis and an R group related to this axis.

Experimental Section

Preparation and Resolution. Optically active phenylalanine and tartaric acids were reagent grade. The other chemicals were also reagent grade and were used without further purification. The glycinato complex was resolved into the two enantiomers. The L-phenylalaninato complex was resolved into the two configurational isomers. The preparation of the D-phenylalaninato complex was not attempted. The complexes used here were prepared and resolved as described by Liu and Douglas.[8]

Measurements. The circular dichroism (CD) spectra were recorded on a reference solution of the complex ion (0.002 M) and on a sample solution of the complex ion (0.002 M) containing a tartrate anion (0.030 M). To obtain the association constant the CD at 445 nm was measured for the reference solution and for the sample solution containing the tartrate anion ranging in concentration from 0.010 to 0.030 M. The ionic strength (μ) was made 0.1 by the addition of an appropriate amount of sodium perchlorate. A JASCO J-40CS recording spectropolarimeter with a 2-cm cell was used. The cell was kept at 25.0 ± 0.2 °C with a Haake circulator, Model FK. The difference in the CD spectra between the sample and reference solutions was measured by using the data processor (DP) compartment operating at 0.2 nm/step of processor resolution. The D- and L-tartrate salts used here were obtained by neutralizing the corresponding tartaric acids with $LiOH{\cdot}H_2O$. The neutralized tartaric acids showed a pH around 7, and so the hydrogen tartrate content was negligible. The CD and UV spectra do not change throughout the measurement of the CD change, and so racemization or decomposition does not take place in this system.

Cation–Anion Association Constants. The data obtained from CD measurements were analyzed by using the equation

$$C_M(C_X - C_{MX})/(\Delta CD/2) = (C_X - C_{MX})/(\Delta\epsilon_{MX} - \Delta\epsilon_M) + 1/K(\Delta\epsilon_{MX} - \Delta\epsilon_M)$$

where ΔCD refers to the difference in the CD between a sample solution and a reference solution, and $\Delta\epsilon$ refers to the molar CD of the species indicated by the subscript. The association constant, K, is obtained through the similar procedure in the previous paper[1] ($[Co(en)_3]^{3+}$ is replaced by $[Co(am)(en)_2]^{2+}$ in this case).

Results and Discussion

The circular dichroism (CD) spectra of Λ- and Δ-$[Co(L\text{-}phe)(en)_2]^{2+}$, which are diastereomeric to each other, are shown in Figure 1. The CD spectra for the two complexes

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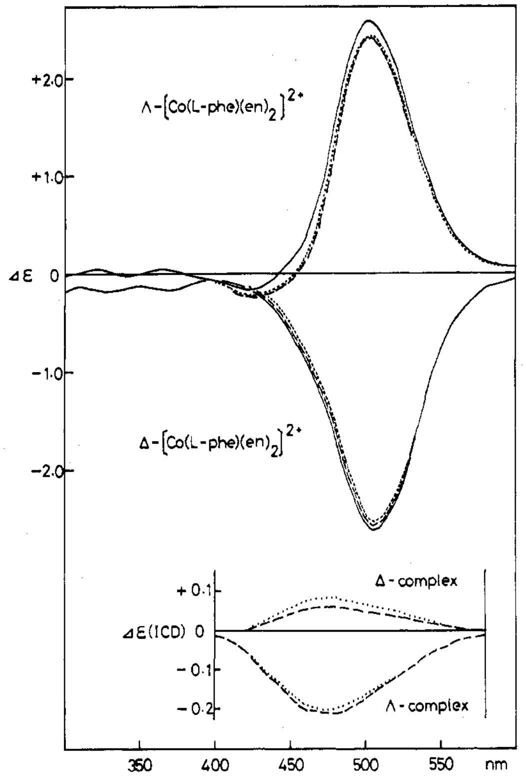


Figure 1. CD spectra of Λ-[Co(L-phe)(en)$_2$]$^{2+}$ and Δ-[Co(L-phe)(en)$_2$]$^{2+}$ (—) and the CD changes upon addition of L (‒‒) and D (- - -) tartrates. The complex and tartrate concentrations were 0.002 and 0.030 M, respectively; $T = 25.0$ °C and $\mu = 0.1$ (NaClO$_4$); Δε(ICD) = $\Delta\epsilon_{\text{sample}} - \Delta\epsilon_{\text{ref.}}$

Table I. Association Constants for Λ- and Δ-[Co(am)(en)$_2$]$^{2+}$ at 25 °C and $\mu = 0.1$

	L-tart^{2-}	D-tart^{2-}
Λ-[Co(gly)(en)$_2$]$^{2+}$	4.3 ± 0.2	
Δ-[Co(gly)(en)$_2$]$^{2+}$	3.9 ± 0.3	
group E$_1$		
(A) Λ-[Co(L-phe)(en)$_2$]$^{2+}$	4.3 ± 0.1	4.0 ± 0.1
(B) Δ-[Co(D-phe)(en)$_2$]$^{2+}$	(4.0 ± 0.1)	
group E$_2$		
(C) Λ-[Co(D-phe)(en)$_2$]$^{2+}$	(2.7 ± 0.3)	
(D) Δ-[Co(L-phe)(en)$_2$]$^{2+}$	1.2 ± 0.6	2.7 ± 0.3
Λ-[Co(en)$_3$]$^{3+}$	13.6 ± 0.2[a]	
Δ-[Co(en)$_3$]$^{3+}$	11.7 ± 0.4[a]	

[a] Reference 5.

change upon addition of L- and D-tartrates in the first absorption region, and the resulting CD changes are different in magnitude. These CD changes can be observed more clearly by recording the difference in CD spectra between the reference and sample solutions, and so the magnitude of the CD change is also represented in Figure 1 by the symbol Δε(ICD). These CD changes are considered to be due to the association between the complex and tartrate ions. The association constants were determined from the analysis of the CD change. These results are summarized in Table I. This table also contains the values for optically active [Co(gly)(en)$_2$]$^{2+}$ complex ions, which have no bulky R group like the phenyl group of phenylalaninato complexes. In this measurement the complexes employed are Λ-[Co(gly)(en)$_2$]$^{2+}$, Δ-[Co(gly)(en)$_2$]$^{2+}$, Λ-[Co(L-phe)(en)$_2$]$^{2+}$, and Δ-[Co(L-phe)(en)$_2$]$^{2+}$. The association constants of D-phenylalaninato complexes with L-tartrate were not obtained. However, these values should be equal to those for their enantiomers, L-phenylalaninato complexes, with D-tartrate. Therefore, the values for L-phenylalaninato complexes with D-tartrate are designated in parentheses in place of the observed data for D-phenylalaninato complexes with L-tartrate. In comparison with the small difference in the association constant of L-tartrate between the enantiomers Λ-(L-phe) and Δ-(D-phe) (group E$_1$) or Λ-(D-phe) and Δ-(L-phe) (group E$_2$), the difference between the diastereomer groups E$_1$ and E$_2$ is large. The values for [Co(gly)(en)$_2$]$^{2+}$ are analogous to those for group E$_1$. According to the electrostatic theory,[9] the values for 2:2 charge type are about $^2/_3$ powers of the association constants for the 3:2 charge type, for example, those between optically active [Co(en)$_3$]$^{3+}$ and L-tartrate, if the ion sizes are similar for the two charge types. This is the case with [Co(gly)(en)$_2$]$^{2+}$ and group E$_1$. (In Table I the values for these complexes are nearly equal to $^2/_3$ powers of the values for [Co(en)$_3$]$^{3+}$). In contrast to group E$_1$, the values for group E$_2$ are smaller than those for [Co(gly)(en)$_2$]$^{2+}$. This result leads to the speculation of interactions other than the electrostatic force for group E$_2$. Such a difference in the interaction between the isomers and L-tartrate seems to be closely related to the structures of the isomers.

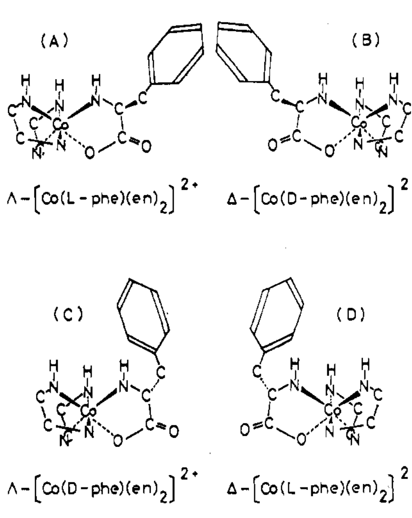
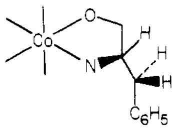


Figure 2. Molecular models for the phenylalaninato complexes.

The phenylalaninato complexes consist of three rotamers with respect to the phenyl group: I–III. Of these rotamers, isomer II is the main rotamer and its population is more than 50%.[10] Figure 2 presents the molecular models of phenylalaninato complexes of this rotamer. These models were depicted by assuming that the amino acidato chelate ring is nearly planar.[11] If L-tartrate approaches the complex ion along the direction of the pseudo C_3 axis and forms hydrogen bonds with NH hydrogen atoms, the interaction between L-tartrate and the complex will be influenced by the steric repulsion between the phenyl group and the approaching L-tartrate. As shown in A and B (group E$_1$) in Figure 2, the phenyl group, being remote from the triangular NH face of the complex, does not interfere with the approach of L-tartrate. In contrast, in C and D (group E$_2$), the phenyl group, which is located near the triangular NH face, interferes with the approach of L-tartrate. The association constants for group E$_1$ are similar to those for the glycinato complex which has no bulky R group like a phenyl group. In contrast to group E$_1$, the association constants for group E$_2$ are relatively small.



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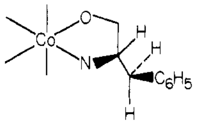

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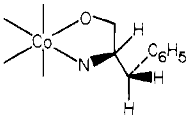

III

One more factor which might control the association between L-tartrate and the diastereomers of the complex is the

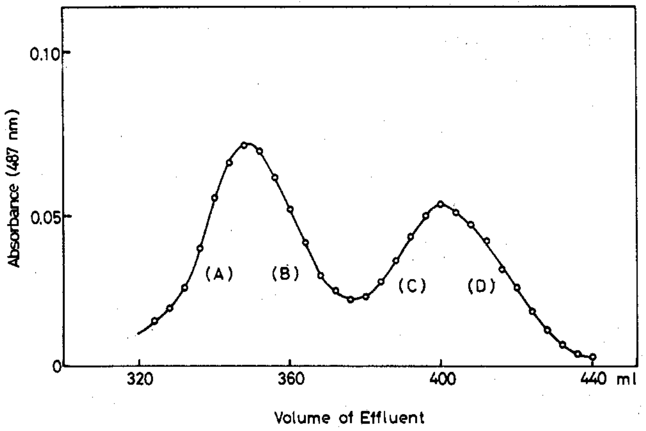

Figure 3. Elution curve of $[Co(DL\text{-}phe)(en)_2]I_2$ (20 mg) with L-tartrate (0.15 M) (resin SP-Sephadex, column 1.1 × 70 cm): A, Λ-$[Co(L\text{-}phe)(en)_2]^{2+}$; B, Δ-$[Co(D\text{-}phe)(en)_2]^{2+}$; C, Λ-$[Co(D\text{-}phe)(en)_2]^{2+}$; D, Δ-$[Co(L\text{-}phe)(en)_2]^{2+}$.

effect of the amino acidato and ethylenediamine ring conformations. Ogino[12] suggested that L-tartrate associates more with Λ-$[Co(d\text{-}pn)_3]^{3+}$ than with Δ-$[Co(d\text{-}pn)_3]^{3+}$, which are diastereomeric to each other, and concluded that this difference in ion association should be attributed to the difference in the orientation of the N–H bonds depending on the conformational preference of the propylenediamine ligand. However, in our case, one amino acidato chelate ring is nearly planar in both diastereomers, and conformational preference for ethylenediamine rings is expected to be much smaller.[8,13]

The preferential association in this system is confirmed by the consideration of chromatographic data. In previous papers[5,14] we reported that the difference in the association constant is related to the elution order in column chromatography. Figure 3 shows the elution curve of the complex $[Co(DL\text{-}phe)(en)_2]I_2$ eluted with the L-tartrate solution. It is noted that the complex is separated into two bands. The components of these bands are identified on the basis of the CD spectra. The assignment is as follows: A, Λ-$[Co(L\text{-}phe)(en)_2]^{2+}$; B, Δ-$[Co(D\text{-}phe)(en)_2]^{2+}$; C, Λ-$[Co(D\text{-}phe)(en)_2]^{2+}$; D, Δ-$[Co(L\text{-}phe)(en)_2]^{2+}$.

This elution order is consistent with the data on association constants if the elution of the complex is caused by strong association with the eluent. That is, the isomer A, which associates to a greater extent with L-tartrate (Table I), is eluted fastest with the L-tartrate solution. The other three isomers are eluted in the order B, C, and D.

Furthermore, the racemic complex is not completely separated into the enantiomers A and B (group E_1) or C and D (group E_2) which have similar association constants with L-tartrate, while it is clearly separated into the diastereomer groups E_1 and E_2 which have rather different association constants.

The corresponding leucinato and alaninato complexes are not completely separated into two bands under the same conditions as those for the phenylalaninato complex. The elution order for the leucinato complex is as follows: Λ-(L-leu) > Λ-(D-leu) > Δ-(D-leu) > Δ-(L-leu). These results are reasonable where there is a lack of a bulky R group like a phenyl group which affects the steric interaction between the complex and L-tartrate in the ion-pair formation.

Thus it is concluded that the position of the R group of amino acidato ligand markedly influences the association between the complex and L-tartrate ions. That is, though the influence of the R group on the difference in the stereoselective interaction with L-tartrate between the enantiomers was not so large, the influence between the diastereomers was serious for the phenylalaninato complexes.

Registry No. Λ-$[Co(gly)(en)_2]^{2+}$, 19657-80-8; Δ-$[Co(gly)(en)_2]^{2+}$, 19657-79-5; Λ-$[Co(L\text{-}phe)(en)_2]^{2+}$, 67576-69-6; Δ-$[Co(D\text{-}phe)(en)_2]^{2+}$, 67576-68-5; Λ-$[Co(D\text{-}phe)(en)_2]^{2+}$, 67529-71-9; Δ-$[Co(L\text{-}phe)(en)_2]^{2+}$, 47101-62-2; $[Co(DL\text{-}phe)(en)_2]I_2$, 67505-75-3; L-$tart^{2-}$, 3715-17-1; D-$tart^{2-}$, 5976-86-3.

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