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Stereoselective Ion Pair Formation between the Tris(ethylenediamine)cobalt(III) Ion and the (Glycinato)bis(oxalato)cobaltate(III) Ion

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There have been some studies on the stereoselective ion pair formation of coordination compounds.[1-5] However, most of these studies are concerned with stereoselectivity between metal complexes and organic ions such as L-tartrate ion. Although it is well-known that the resolution of racemic complexes can be achieved by using suitable optically active complexes as counterions to form the less soluble diastereomeric salts,[6] few studies have been reported on the stereoselective interactions between cationic and anionic complexes. Conductance measurements can be expected to serve as an effective means for this purpose. In order to determine the ion pair formation constants between chiral metal complexes, the conductance behavior of mixtures has been investigated for Λ-$[Co(en)_3]I_3$–K_2-Δ-$[Co(ox)_2(gly)]$ (system I) and Δ-$[Co(en)_3]I_3$–K_2-Δ-$[Co(ox)_2(gly)]$ (system II) in aqueous solutions of ionic strength $\mu = 0.01$ at 25 °C according to the procedure of Katayama et al.,[7] which was used to obtain the ion pair formation constants of the $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ ions with sulfate ions.

A significant difference between the mobilities of systems I and II was detected and was attributed to the difference in ion pair formation constants between the Λ- and Δ-$[Co(en)_3]^{3+}$ ions with Δ-$[Co(ox)_2(gly)]^{2-}$ ion. We believe this to be only one case of a distinct stereoselectivity between the cationic and anionic Co(III) complexes in ion pair formation.

On the other hand, many cationic complexes have been resolved into their optical isomers in column chromatography by using sodium L-tartrate or sodium antimony L-tartrate, $Na_2[Sb_2(L\text{-}tart)_2]$, as the eluent.[8] However, no complete chromatographic resolution of anionic complexes has yet been achieved because of the lack of effective eluting agents. The above result by conductance suggests the possibility of chromatographic resolution of the anionic complex, $[Co(ox)_2(gly)]^{2-}$. Thus, an attempt was made to resolve $[Co(ox)_2(gly)]^{2-}$ by the chromatographic technique, and a complete resolution was achieved through a DEAE-Sephadex A-25 column using Λ-$[Co(en)_3]Cl_3$–30% aqueous ethanol solution as the eluent.

The Λ-$(+)_D$- and Δ-$(-)_D$-$[Co(en)_3]I_3 \cdot H_2O$ complexes were prepared by the method of Dwyer et al.[9] and were purified by two recrystallizations from their aqueous solutions. The specific rotations at 589 nm were +89.6° and -89.3°, respectively, in good agreement with those reported in the literature.[9] Δ-$(+)_{546}$-$Ba[Co(ox)_2(gly)] \cdot 2H_2O$ was prepared by the method of Shimura et al.[10] The barium salt was converted to the more soluble potassium salt from the barium salt and potassium sulfate by removal of insoluble barium sulfate, and the potassium salt was purified by two recrystallizations from water by the addition of ethanol. The molecular rotation at 546 nm of the sample was +7810° for the potassium salt. The reported value was +8100° for the barium salt.[10]

Aqueous solutions of Λ-$[Co(en)_3]I_3$, Δ-$[Co(en)_3]I_3$, and K_2-Δ-$[Co(ox)_2(gly)]$ of ionic strength $\mu = 0.01$ were carefully prepared by using conductivity water. The electric conductivities of mixtures prepared by mixing the solutions at various volume fractions were measured at 25 ± 0.01 °C with a conductometer (Type MY-7, Yanagimoto Mfg. Co. Ltd.) with a Wheatstone bridge at a frequency of 800 Hz. For both systems I and II, large deviations of the measured conductivity from additivity were observed to be a function of volume fraction, x, of K_2-Δ-$[Co(ox)_2(gly)]$ (Figure 1). The deviation, $\Delta\kappa$, of the mixture, consisting of a C_M molar solution of $[Co(en)_3]I_3$ (abbreviated as MI_3) and a C_B molar solution of K_2B ($B = [Co(ox)_2(gly)]^{2-}$) at volume fractions $1-x$ and x, respectively, is given by

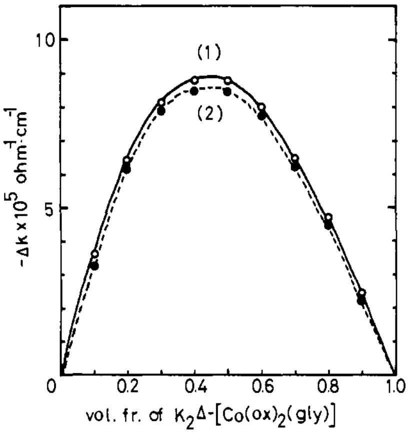

Figure 1. Deviation of the observed conductivity from additivity, $\Delta\kappa$, as a function of the volume fraction, x, of K_2-Δ-$[Co(ox)_2(gly)]$ at 25 °C: (1) Λ-$[Co(en)_3]I_3$–K_2-Δ-$[Co(ox)_2(gly)]$ (system I); (2) Δ-$[Co(en)_3]I_3$–K_2-Δ-$[Co(ox)_2(gly)]$ (system II).

$$10^3\Delta\kappa = 10^3\kappa - C_M(1-x)\Lambda_m(MI_3) - C_Bx\Lambda_m(K_2B) \qquad (1)$$

where κ is the specific conductivity of the mixture and Λ_m is the molar conductivity of the species specified in parentheses at an ionic strength of 0.01. If only a 1:1 ion pair, $M^{3+} \cdot B^{2-}$, is assumed, the deviation $\Delta\kappa$ can be related to the molar concentration of the ion pair $M^{3+} \cdot B^{2-}$ by

$$[M^{3+} \cdot B^{2-}] = 10^3\Delta\kappa/\alpha \qquad (2)$$

$$\alpha = \lambda(M^{3+} \cdot B^{2-}) - 3\lambda(M^{3+}) - 2\lambda(B^{2-}) \qquad (3)$$

where λ is the ionic equivalent conductance at an ionic strength of 0.01 of $M^{3+} \cdot B^{2-}$, M^{3+}, and B^{2-}, respectively.

The ion pair formation constants (K) of $M^{3+} \cdot B^{2-}$ were obtained by analyzing the $\Delta\kappa$ values according to the procedure in the literature.[7] As shown in Figure 1, the $\Delta\kappa$ values of system I were always larger than those of system II, and the deviation reached a maximum at $x = 0.4$–0.5 in each case. The ion pair formation constants $K(\Lambda$–$\Delta)$ and $K(\Delta$–$\Delta)$ and their ratio $K(\Lambda$–$\Delta)/K(\Delta$–$\Delta)$ are given in Table I. These results indicate that Δ-$[Co(ox)_2(gly)]^{2-}$ ion, like L-tartrate ion and $[Sb_2(L\text{-}tart)_2]^{2-}$ ion, unambiguously discriminates Λ- from Δ-$[Co(en)_3]^{3+}$ ion in solution. The stereoselectivity of the L-tartrate and $[Sb_2(L\text{-}tart)_2]^{2-}$ ions for optically active $[Co(en)_3]^{3+}$ ions has been extensively studied.[2-5,12-14] The ratios of the ion pair formation constants for Λ- and Δ-$[Co(en)_3]^{3+}$ ions, $K(\Lambda)/K(\Delta)$, as a measure of this discrimination are given in Table II. For the ion pair of Λ-[Co-

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(1) Parkhurst, L. J.; Kunze, R. W. *J. Am. Chem. Soc.* **1964**, *86*, 300-301.
(2) Ogino, K.; Saito, U. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 826-829.
(3) Norden, B. *Acta Chem. Scand.* **1972**, *26*, 111-126.
(4) Yoneda, H.; Miyoshi, K.; Suzuki, S.; Taura, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1661-1664.
(5) Fujita, M.; Yamatera, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1301-1303.
(6) Dwyer, F. P.; Mellor, D. P. "Chelating Agents and Metal Chelates"; Academic Press: New York, 1964; pp 193-195.
(7) Katayama, S.; Tamamushi, R. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2354-2359.
(8) Yoshikawa, Y.; Yamasaki, K. *Coord. Chem. Rev.* **1979**, *28*, 205-229.
(9) Broomhead, J. A.; Dwyer, F. P.; Hogarth, F. W. *Inorg. Synth.* **1960**, *6*, 183-186.
(10) Yamasaki, K.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 119-126.
(11) Jenkins, I. L.; Monk, C. B. *J. Chem. Soc.* **1951**, 68-73.
(12) Yoneda, H.; Taura, T. *Chem. Lett.* **1977**, 63-66.
(13) Kushi, Y.; Kuramoto, M.; Yoneda, H. *Chem. Lett.* **1976**, 135-136.
(14) Taura, T.; Nakazawa, H.; Yoneda, H. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 603-606.

0002-7863/81/1503-7391$01.25/0

Table I. Ion Pair Formation Constants $K(\Lambda\text{–}\Delta)$ and $K(\Delta\text{–}\Delta)$ for Λ-$[Co(en)_3]^{3+}$–Δ-$[Co(ox)_2(gly)]^{2-}$ and Δ-$[Co(en)_3]^{3+}$–Δ-$[Co(ox)_2(gly)]^{2-}$ at Varying Volume Fractions, x, of $K_2\Delta$-$[Co(ox)_2(gly)]$ at 25 °C ($\mu = 0.01$).

x	$K(\Lambda\text{–}\Delta)$	$K(\Delta\text{–}\Delta)$	$K(\Lambda\text{–}\Delta)/K(\Delta\text{–}\Delta)$
0.1	495	423	1.17
0.2	516	483	1.07
0.3	504	485	1.04
0.4	490	464	1.06
0.5	489	462	1.06
0.6	481	454	1.06
0.7	446	423	1.05
0.8	448	422	1.06
0.9	412	374	1.10
	482 ± 26[a]	456 ± 26[a]	1.06[a]

[a] Average values of $K(A\text{–}\Delta)$, $K(\Delta\text{–}\Delta)$, and the ratio $K(A\text{–}\Delta)/K(\Delta\text{–}\Delta)$. Values of $K(A\text{–}\Delta)$, $K(\Delta\text{–}\Delta)$, and $K(A\text{–}\Delta)/K(\Delta\text{–}\Delta)$ for the top and end volume fractions ($x = 0.1$ and 0.9), which involve very dilute solutions of one of the component complexes and are thus subject to considerable experimental unreliability, have not been included in the averages.

Table II. Discrimination factor $K(A)/K(\Delta)$ for A- and Δ-$[Co(en)_3]^{3+}$ Ions in Water at 25 °C

$K(A)/K(\Delta)$		
L-tartrate	$[Sb_2(\text{L-tart})_2]^{2-}$	Δ-$[Co(ox)_2(gly)]^{2-}$
1.24,[a] 1.18,[b] 1.11,[c] 1.16,[d] 1.16,[e] 1.08[f]	1.76[d]	1.06[g]

[a] UV absorption ($\mu = 0.1$), ref 2. [b] UV absorption ($\mu = 0.1$), ref 3. [c] UV absorption ($\mu = 0.033$), ref 4. [d] CD spectra ($\mu = 0.1$), ref 14. [e] Conductivity ($\mu = 0.1$), ref 15. [f] Conductivity ($\mu = 0.01$), ref 15. [g] Conductivity ($\mu = 0.01$), present work.

$(en)_3]^{3+}$ with L-tartrate ion in solution, a model in which one carboxylate and two hydroxyl groups form hydrogen bonds with three NH groups of $[Co(en)_3]^{3+}$ along the direction of the C_3 axis has been proposed,[5,12] being parallel to the result of an X-ray analysis for Λ-$[Co(en)_3]Br(\text{L-tart})\cdot 5H_2O$.[13] On the other hand, in the case of $[Sb_2(\text{L-tart})_2]^{2-}$ ion, a stereoselective ion pair model of $[Sb_2(\text{L-tart})_2]^{2-}$ with an "L-shaped channel" (the space formed between the three ethylenediamine ligands) of Λ-$[Co(en)_3]^{3+}$ has recently been proposed.[14,16] As can be seen in Table II, the discrimination factor $K(\Lambda)/K(\Delta)$ effected by $[Sb_2(\text{L-tart})_2]^{2-}$ ion with the utilization of the L-shaped channel is considerably greater than that effected by the L-tartrate or Δ-$[Co(ox)_2(gly)]^{2-}$ ions. Since the Δ-$[Co(ox)_2(gly)]^{2-}$ ion seems to utilize the L-shaped channel of Λ-$[Co(en)_3]^{3+}$ with difficulty and seems to be comparable to L-tartrate ion in stereoselectivity for the optically active $[Co(en)_3]^{3+}$ ions (Table II), the structure of the ion pair of Δ-$[Co(ox)_2(gly)]^{2-}$ with Λ-$[Co(en)_3]^{3+}$ may be expected to be similar to that of the L-tartrate type rather than that of the $[Sb_2(\text{L-tart})_2]^{2-}$ type. Furthermore, in analogy with the L-tartrate ion, the $[Co(ox)_2(gly)]^{2-}$ ion has a triangular face composed of three oxygen atoms capable of forming hydrogen bonds with the NH hydrogen atoms of $[Co(en)_3]^{3+}$.

A molecular model shows that the three oxygen atoms at the corners of the triangular face in Δ-$[Co(ox)_2(gly)]^{2-}$ assume the direction of the lone-pair electrons which is more favorable to hydrogen bonding with the three NH hydrogen atoms in Λ-$[Co(en)_3]^{3+}$ than with those in Δ-$[Co(en)_3]^{3+}$. Thus, we propose a model of the ion pair Λ-$[Co(en)_3]^{3+}$–Δ-$[Co(ox)_2(gly)]^{2-}$ in which the Δ-$[Co(ox)_2(gly)]^{2-}$ ion is attached closely to the Λ-$[Co(en)_3]^{3+}$ ion in the direction of its threefold axis and which makes a face-to-face close contact with the Λ-$[Co(en)_3]^{3+}$ ion through hydrogen bonds (Figure 2).

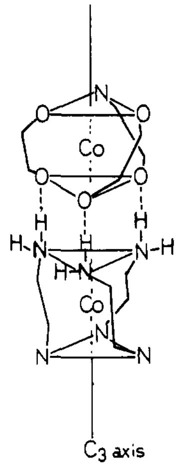

Figure 2. Proposed model of the ion pair between Λ-$[Co(en)_3]^{3+}$ and Δ-$[Co(ox)_2(gly)]^{2-}$.

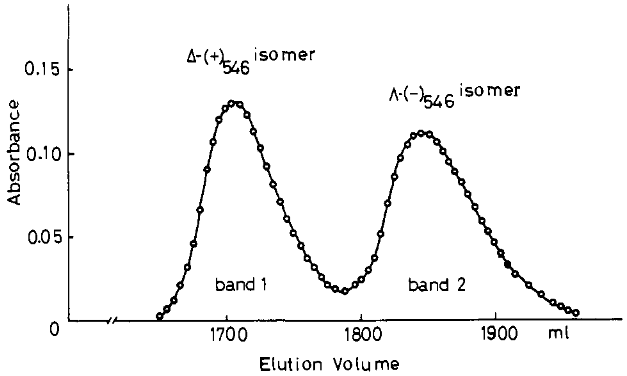

Figure 3. Elution curve of $[Co(ox)_2(gly)]^{2-}$ eluted with 0.1 M Λ-$[Co(en)_3]Cl_3$–30% aqueous ethanol solution.

On the basis of the stereoselectivity in ion pair formation of the Δ-$[Co(ox)_2(gly)]^{2-}$ ion with the Λ- and Δ-$[Co(en)_3]^{3+}$ ions in solution, we can reasonably expect a complete chromatographic resolution of the anionic complex $[Co(ox)_2(gly)]^{2-}$ under appropriate conditions. Thus, we tried to resolve $[Co(ox)_2(gly)]^{2-}$ through a DEAE-Sephadex A-25 column (1.8-cm i.d. × 130 cm). The column was charged with 60 mg of racemic $K_2[Co(ox)_2(gly)]$ in 10 mL of water and was eluted with 0.1 M Λ-$[Co(en)_3]Cl_3$ in 30% aqueous ethanol solution. In order to obtain the elution curve, the absorbance of each fraction (5 mL) collected by the fraction collector was measured at the maximum wavelength (565 nm) of the first absorption band of $[Co(ox)_2(gly)]^{2-}$, with 0.1 M Λ-$[Co(en)_3]Cl_3$–30% aqueous ethanol solution as a reference solution. As shown in Figure 3, the curve has two completely separate bands. The first eluted band was the Δ-$(+)_{546}$ isomer and the second one the Λ-$(-)_{546}$ isomer. This elution order is self-consistent with the result of the stereoselectivity in ion pair formation by conductance. Thus, this is the first case of a complete chromatographic resolution of an anionic Co(III) complex.

During extensions of chromatographic resolution of anionic complexes, preliminary experiments reveal that only the C_1-cis(N) isomer of the three geometric isomers, trans(N), C_2-cis(N), and C_1-cis(N), of $[Co(ox)(gly)_2]^-$ can be resolved by column chromatography with Λ-$[Co(en)_3]Cl_3$ as eluent. Only the C_1-cis(N) isomer has a triangular face composed of three oxygen atoms capable of forming hydrogen bonds along the direction of C_3 axis. This also provides support for our model described above. Further studies in this area are in progress.

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(15) Tatehata, A.; Watanabe, M.; Kotsuji, K., unpublished results. Reference 1 deals with stereoselective ion pair formation of L-tartrate and D-tartrate ions with Λ- or Δ-$[Co(en)_3]^{3+}$ ion as studied by conductance, but the ion pair formation constants were not determined. Therefore, for comparison with the values obtained by other methods, we determined the ion pair formation constants at ionic strengths $\mu = 0.1$ and 0.01, according to a method similar to that used in the present work.

(16) Nakazawa, H.; Yoneda, H. *J. Chromatogr.* **1978**, *160*, 89–99.