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Geometrical Isomers of Anionic Complexes Favorable to Chiral Discriminatory Ion-Pairing with Λ-[Co(en)$_3$]$^{3+}$ Ion and the Diastereomeric Ion-Pair Formation Constants in Solution[1)]

Akira TATEHATA* and Yasuyuki ASABA
Department of Chemistry, Faculty of Science, Shizuoka University, Ohya, Shizuoka 422

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The stereoselectivities in the ion pairing of the geometrical isomers of anionic complexes, [Co(ox)(gly)$_2$]$^-$ and [Co(ox)(edda)]$^-$ (ox=oxalate dianion, gly=glycinate anion, and edda=ethylenediamine-*N*,*N'*-diacetate dianion) with [Co(en)$_3$]$^{3+}$ have been investigated by a chromatographic method. Only the C$_1$-*cis*(*N*) isomer of three geometrical isomers of [Co(ox)(gly)$_2$]$^-$ and the β-*cis* isomer of two of [Co(ox)(edda)]$^-$, in which three coordinated oxygen atoms are disposed triangularly along the pseudo C$_3$ axis, have been observed to interact more strongly with [Co(en)$_3$]$^{3+}$ than the other geometrical isomers. The diastereomeric ion-pair formation constants of C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ and β-*cis*-[Co(ox)(edda)]$^-$ with [Co(en)$_3$]$^{3+}$ in solution have been determined by a conductance method at 25 °C. The results were consistent with those of the chromatographic studies. An enhancement of the circular dichroism (CD) intensity of the A$_2$ component at the first d-d transition region of [Co(en)$_3$]$^{3+}$ has been observed upon the formation of ion pairing between the complex ions. Therefore, a favorable ion pair is considered to involve the hydrogen bonds between the coordinated oxygen atoms of the anionic complexes and the three N-H protons of [Co(en)$_3$]$^{3+}$ along the C$_3$ axis.

It is well-known that chromatography is an extremely valuable technique for the optical resolution of metal complexes.[2,3)] However, examples of a complete chromatographic resolution of anionic complexes are much fewer than those of cationic complexes because of a lack of effective eluting agents. We reported that the optically active [Co(en)$_3$]$^{3+}$ cation is an effective chiral discriminator for various complex anions and, hence, can serve as the highly promising eluting agent for the chromatographic resolution of many anionic complexes.[4,5)] It is thought that [Co(en)$_3$]$^{3+}$ can discriminate the chirality of anionic complexes by two different means: Λ-[Co(en)$_3$]$^{3+}$ prefers the Λ to the Δ isomer of [Co(ox)$_2$(en)]$^-$, whereas it prefers the Δ to the Λ isomer of [Co(ox)$_2$(gly)]$^{2-}$.[6-8)] The discrimination efficiency was shown to be largely different between the above two systems, though there is a difference in the electric charge on the anionic complexes. In order to explain why the absolute configurations of the favorable pairs of [Co(ox)$_2$(en)]$^-$ and [Co(ox)$_2$(gly)]$^{2-}$ with Λ-[Co(en)$_3$]$^{3+}$ are opposite to each other, our attention from an early stage was focused on the structural characteristics of the anionic complexes, especially on the difference in the spatial disposition of the coordinated oxygen atoms.[5,6)] It was therefore noted that [Co(ox)$_2$(gly)]$^{2-}$ has a triangular face comprising three coordinated oxygen atoms capable of forming three hydrogen bonds with N-H protons of Λ-[Co(en)$_3$]$^{3+}$ along its C$_3$ axis;[4)] however, [Co(ox)$_2$(en)]$^-$ has no such triangular face. It was then pointed out that the direction of the lone-pair electrons of coordinated oxygen atoms in Δ-[Co(ox)$_2$(gly)]$^{2-}$ is more favorable to the three hydrogen bonds with Λ-[Co(en)$_3$]$^{3+}$ than that in the antipode.[4,5)]

Subsequently, Miyoshi et al. investigated in detail the mechanism of chiral discrimination between metal complexes using a chromatographic method and proposed association models for the favorable pairs;[8,10)] chiral discrimination is effected along either the (pseudo) C$_3$ axis or the (pseudo) C$_2$ axis of the respective complexes. Thus, a homochiral (Λ-Λ or Δ-Δ) combination is favored when the cationic complex uses its C$_3$ axis, whereas a heterochiral (Λ-Δ or Δ-Λ) combination is favored when the cationic complex uses its C$_2$ axis, regardless of which axis (C$_3$ or C$_2$) of the anionic complex is directed to the cationic complex. Their proposal may explain the difference in the favorable association modes of [Co(ox)$_2$(en)]$^-$ and [Co(ox)$_2$(gly)]$^{2-}$. On the other hand, a crystal structure analysis of Δ-[Co(*l*-pn)$_3$] Λ-[Cr(mal)$_3$]·3H$_2$O (*l*-pn=(R)-1,2-propanediamine, mal=malonate dianion) revealed that the cationic complex approaches the triangular face of Λ-[Cr(mal)$_3$]$^{3-}$ along the C$_3$ axis and makes face-to-face close contact through three hydrogen bonds.[9)] This indicates that the heterochiral combination mode can contribute effectively to chiral discrimination, even if the cationic complexes use the C$_3$ axis. Thus, their proposal may need to be tested further regarding many other metal complex systems.

In this paper the importance of the spatial disposition of coordinated atoms and the arrangement of chelate rings of anionic complexes are discussed in systems which involve the geometrical isomers of anionic complexes, [Co(ox)(gly)$_2$]$^-$ and [Co(ox)(edda)]$^-$. In order to obtain a measure of the discriminatory effect for strongly interacting ion pairs, the diastereomeric ion-pair formation constants are determined for [Co(en)$_3$]$^{3+}$-C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ and [Co(en)$_3$]$^{3+}$-β-*cis*-[Co(ox)(edda)]$^-$ systems. The favorable pair of these systems is Λ-Δ. It is then deduced from the CD change of Λ-[Co(en)$_3$]$^{3+}$ that the cationic complex uses its C$_3$ axis to discriminate the chirality of the anionic complexes, in disagreement with the proposal of Miyoshi et al. for the favorable pair containing the heterochiral combination.

Experimental

Preparation of Complexes. The optically active $[Co(en)_3]I_3\cdot H_2O$ was prepared by a method described in the literature[13] and converted to the chloride using an SP-Sephadex C-25 ion exchanger. Three geometrical isomers (*trans(N)*, C_1-*cis(N)*, and C_2-*cis(N)*) of $[Co(ox)(gly)_2]^-$ were prepared as described by Shimura and co-workers.[14] The C_1-*cis(N)* isomer for conductance measurements was resolved by a method described in the literature[15] (with a little modification) for obtaining the potassium salt.[16] Found for Δ-$(-)_{546}$ isomer ($[M]_{546}=-5530°$): C, 20.90; H, 2.64; N, 8.14%. Found for Δ-$(+)_{546}$ isomer ($[M]_{546}=+5540°$): C, 20.92; H, 2.63; N, 8.06%. Calcd for C_1-*cis(N)*-$K[Co(ox)(gly)_2]\cdot 0.5H_2O=C_6H_9N_2O_{8.5}KCo$: C, 21.00; H, 2.64; N, 8.16%. Two geometrical isomers (α-*cis* and β-*cis*) of $[Co(ox)(edda)]^-$ were prepared and separated by the method of Coleman et al.[17] Δ-$(-)_{589}$-β-*cis*-$K[Co(ox)(edda)]\cdot 2H_2O$ for conductance measurements was prepared according to the method of Jordan and Legg,[18] which was obtained as the dihydrate ($[M]_{589}=-3470°$, $\Delta\varepsilon_{544}=-2.22\ mol^{-1}\ dm^3\ cm^{-1}$) in this study though had been obtained as the monohydrate in Ref. 18 (The value of $\Delta\varepsilon_{544}$ reported for $(+)_{589}$ isomer was +2.05). Found: C, 24.35; H, 3.51; N, 7.04%. Calcd for β-*cis*-$K[Co(ox)(edda)]\cdot 2H_2O=C_8H_{14}N_2O_{10}KCo$: C, 24.25; H, 3.56; N, 7.07%.

Chromatographic Experiments. (*a*) Each sample of the racemic geometrical isomers of $[Co(ox)(gly)_2]^-$ and $[Co(ox)(edda)]^-$ was adsorbed on a column (1.9×60 cm) of DEAE-Sephadex A-25 anion exchanger and was eluted with an aqueous solution of NaCl ($0.3\ mol\cdot dm^{-3}$) or *rac*-$[Co(en)_3]Cl_3$ ($0.1\ mol\cdot dm^{-3}$) at a rate of 0.3—$0.5\ cm^3 min^{-1}$. The eluate was divided into fractions of 3-cm^3 portions and the concentration of the eluted isomer in each fraction was measured spectrophotometrically to obtain an elution curve.

(*b*) Each racemic isomer of the above anionic complexes was chromatographed in a similar manner as mentioned above, except for the length of the column (1.9×150 cm) and the use of an aqueous solution ($0.05\ mol\cdot dm^{-3}$) or 30% aqueous ethanol solution ($0.05\ mol\cdot dm^{-3}$) of Δ-$[Co(en)_3]Cl_3$ as the eluent.

(*c*) A column (1.9×60 cm) of SP-Sephadex C-25 cation exchanger which was converted completely to the Δ-$[Co(en)_3]^{3+}$ form was prepared. The bottom of the column was loaded with the cation exchanger in Na^+ form (10 cm long) in order to remove a small amount of Δ-$[Co(en)_3]^{3+}$ eluted from the upper part of the column. Each racemic anionic complex (5 ml of 20—30 mM; $1\ M=1\ mol\ dm^{-3}$) was placed on the top of the column and eluted with water at a rate of $0.3\ cm^3\ min^{-1}$. The concentration and the optical rotation of the partially resolved complex in each fraction ($2.5\ cm^3$) were measured in order to determine percentage resolution.

Conductance Measurements. The complex anions of C_1-*cis(N)*-$[Co(ox)(gly)_2]^-$ and β-*cis*-$[Co(ox)(edda)]^-$, which were found to interact strongly with $[Co(en)_3]^{3+}$ by chromatographic studies, were selected for conductance measurements. The conductance of the mixed solutions containing various volume ratios of the chiral $[Co(en)_3]^{3+}$ and the chiral anionic complex (ionic strength, $I=0.01\ mol\ dm^{-3}$) was measured at 25±0.01 °C using a conductometer (Type MY-8, Yanagimoto Mfg. Co. Ltd.) at a frequency of 800 Hz. The diastereomeric ion-pair formation constants were estimated according to the procedure described in various previous studies.[4,5,19]

CD Measurements. The CD spectra were measured on a Jasco J-500 spectropolarimeter using a 1-mm cell at room temperature. To an aqueous solution of Δ-$[Co(en)_3]I_3\cdot H_2O$ ($0.025\ mol\ dm^{-3}$) Δ- or *rac*-C_1-*cis(N)*-$K[Co(ox)(gly)_2]$ or *rac*-β-*cis*-$Na[Co(ox)(edda)]\cdot 2H_2O$ was added so as to prepare the solution of 0.025 (for Δ-complex) or $0.05\ mol\ dm^{-3}$ (for *rac*-complex) with respect to the concentration of the anionic complex. Absorption spectra, absorbances of chromatographic fractions, and optical rotations were obtained on a Shimadzu MPS-50L recording spectrophotometer, a Jasco Uvidec-320 spectrophotometer, and a Union automatic polarimeter PM-101, respectively with 1 or 5 cm cells.

Results and Discussion

Chromatography of Geometrical Isomers of $[Co(ox)(gly)_2]^-$ and $[Co(ox)(edda)]^-$. Elution curves of geometrical isomers of $[Co(ox)(gly)_2]^-$ by anion-exchange chromatography are shown in Fig. 1. It can be seen that the C_1-*cis(N)*-isomer is eluted markedly faster when *rac*-$[Co(en)_3]Cl_3$ is used as an eluent than when sodium chloride is used, compared with *trans(N)*- and C_2-*cis(N)*-isomers.

By combining the ion-exchange equilibrium with the ion-pair formation equilibrium, the net retention volume, *V*, of the adsorbed anionic complex in the present anion-exchange chromatography can be

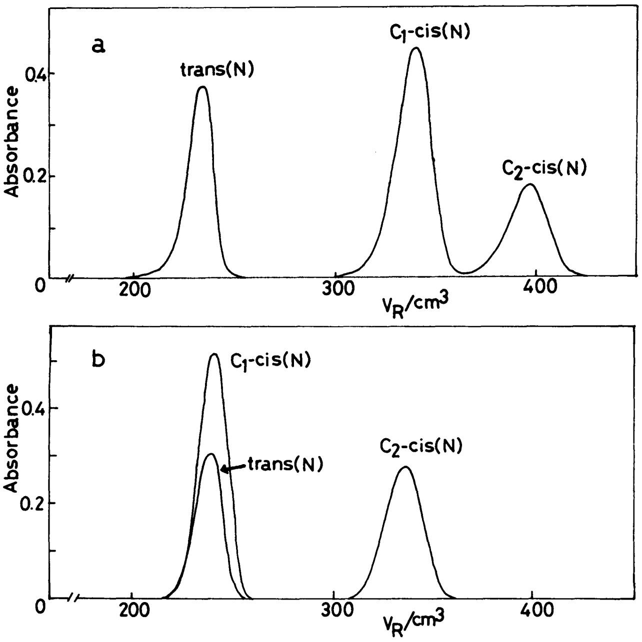


Fig. 1. Elution curves for geometrical isomers of $[Co(ox)(gly)_2]^-$ by chromatography using a column (1.9×60 cm) of DEAE-Sephadex A-25 and an aqueous solution of $0.3\ mol\ dm^{-3}$ NaCl (a) and $0.1\ mol\ dm^{-3}$ *rac*-$[Co(en)_3]Cl_3$ (b) as the eluent.

expressed by Eq. 1,[20)]

$$V = V_s KQ/[\mathrm{Cl}^-]\{1 + \beta[\mathrm{cation}]\}, \qquad (1)$$

where V_s is the volume of ion-exchange resin in the column, K the ion-exchange equilibrium constant for the reaction, $\mathrm{B}^- + \mathrm{R{-}Cl} \rightleftarrows \mathrm{Cl}^- + \mathrm{R{-}B}$ (B=anionic complex, R=ion-exchange group), Q the capacity of the ion-exchange resin, and β the ion-pair formation constant of the anionic complex with the cation contained in an eluting solution. We now consider the difference in the retention volumes of a certain anionic complex between elutions with sodium chloride and $[\mathrm{Co(en)_3}]\mathrm{Cl_3}$. The term $V_sKQ/[\mathrm{Cl}^-]$ for a certain anionic complex is virtually identical in the two cases under the experimental conditions and the term β[cation] is expected to be negligibly small when the cation is sodium ion. Therefore, the ratio of the retention volumes is given by

$$V(\mathrm{Co(en)_3}^{3+})/V(\mathrm{Na}^+) = 1/\{1 + \beta[\mathrm{Co(en)_3}^{3+}]\}, \qquad (2)$$

where $V(\mathrm{Na}^+)$ and $V(\mathrm{Co(en)_3}^{3+})$ are the retention volumes observed when sodium chloride and $[\mathrm{Co(en)_3}]\mathrm{Cl_3}$ are used as an eluent, respectively. According to Eq. 2, the ratios of the retention volumes decrease with an increase in the value of the ion-pair formation constants between the anionic complexes and $[\mathrm{Co(en)_3}]^{3+}$. This leads to the prediction that the anionic complex which forms a strong ion pair with $[\mathrm{Co(en)_3}]^{3+}$ has a small value of the ratio, $V(\mathrm{Co(en)_3}^{3+})/V(\mathrm{Na}^+)$. Figure 1 indicates the decreasing order of the ratio for the three geometrical isomers of $[\mathrm{Co(ox)(gly)_2}]^-$ to be *trans*(*N*)>C$_2$-*cis*(*N*)>C$_1$-*cis*(*N*)-isomer. Thus, it should be noted that C$_1$-*cis*(*N*)-$[\mathrm{Co(ox)(gly)_2}]^-$ forms a stronger ion pair with $[\mathrm{Co(en)_3}]^{3+}$ than do *trans*(*N*)- and C$_2$-*cis*(*N*)-isomers. This may be related to the observation that only a C$_1$-*cis*(*N*)-isomer is resolvable by usual anion-exchange chromatography using Λ-$[\mathrm{Co(en)_3}]\mathrm{Cl_3}$ as an eluent, as shown in Fig. 2. Figure 3 shows elution curves and percentage resolutions of three geometrical isomers in chromatography of which a column of SP-Sephadex C-25 in Λ-$[\mathrm{Co(en)_3}]^{3+}$ form were employed (water: eluent). The complex anion of C$_1$-*cis*(*N*)-isomer was the last to be eluted, and a great degree of resolution was attained, being consistent with the results from the above-mentioned usual anion-exchange chromatography that C$_1$-*cis*(*N*)-isomer tends to form a strong ion pair with $[\mathrm{Co(en)_3}]^{3+}$. The percentage resolution curve shows that the ion pair of Λ-$[\mathrm{Co(en)_3}]^{3+}$-Δ-C$_1$-*cis*(*N*)-$[\mathrm{Co(ox)(gly)_2}]^-$ is more favorable than Λ-$[\mathrm{Co(en)_3}]^{3+}$-Λ-C$_1$-*cis*(*N*)-$[\mathrm{Co(ox)(gly)_2}]^-$. Despite of the presence of an additional chelate ring between the coordinated nitrogen atoms in edda ligand, α-*cis* and β-*cis* isomers of $[\mathrm{Co(ox)(edda)}]^-$ are the same as C$_2$-*cis*(*N*) and C$_1$-*cis*(*N*) isomers of $[\mathrm{Co(ox)(gly)_2}]^-$, respectively, with respect to the spatial disposition of coordinated atoms around Co(III) (Scheme 1). Chromatograms of the geometrical isomers of $[\mathrm{Co(ox)(edda)}]^-$ are shown in Fig.4.

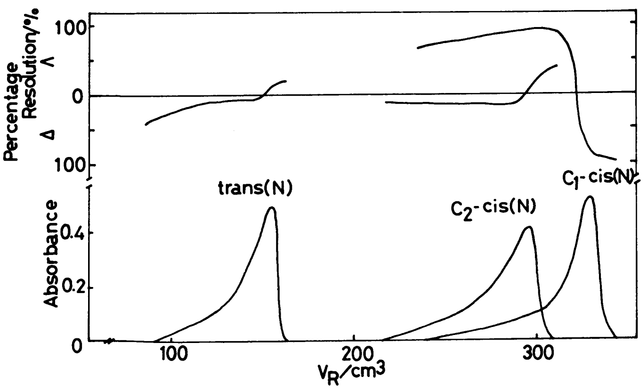


Fig. 3. Elution curves and percentage resolutions for geometrical isomers of $[\mathrm{Co(ox)(gly)_2}]^-$ by chromatography using a column (1.9×60 cm) of SP-Sephadex C-25 in Λ-$[\mathrm{Co(en)_3}]^{3+}$ form and water as an eluent.

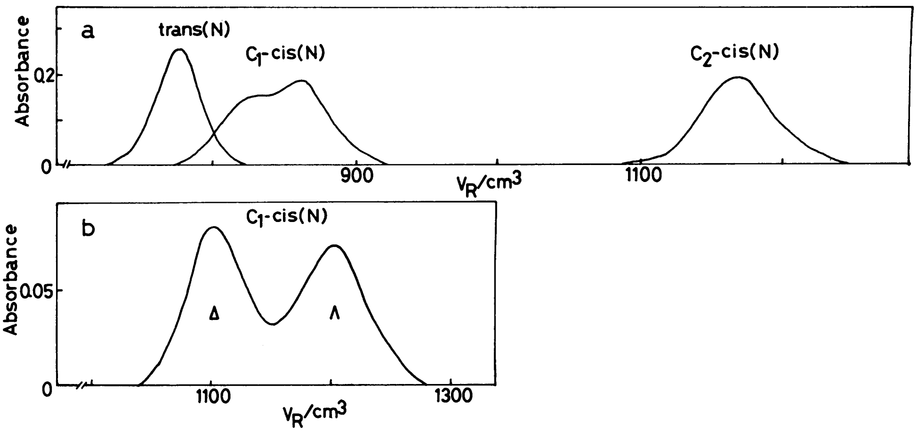
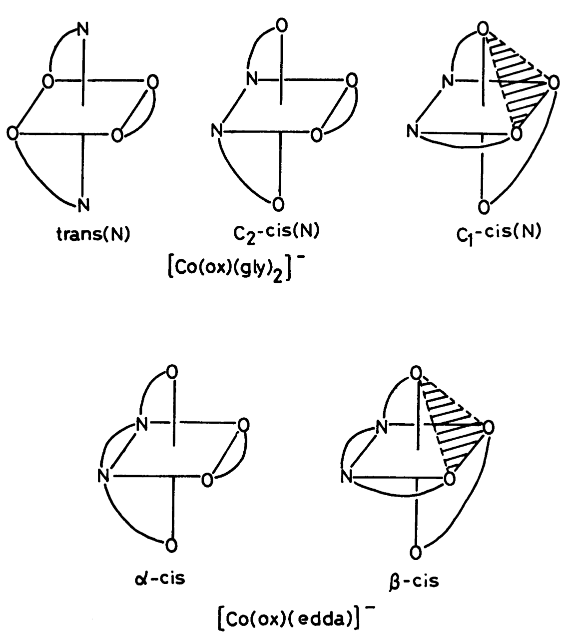


Fig. 2. Elution curves for geometrical isomers of $[\mathrm{Co(ox)(gly)_2}]^-$ by chromatography using a column (1.9×150 cm) of DEAE-Sephadex A-25 and an aqueous solution (a) and a 30% ethanolic aqueous solution (b) of 0.05 mol dm^{-3} Λ-$[\mathrm{Co(en)_3}]\mathrm{Cl_3}$ as the eluent.



Scheme 1.

It can be seen that each chromatographic behavior of α-*cis* and β-*cis*-$[Co(ox)(edda)]^-$ is very similar to that of the corresponding geometrical isomer of $[Co(ox)(gly)_2]^-$. The present observation suggests that the spatial disposition of the oxygen atoms in the complexes is important regarding both the ion pair formation and stereoselectivity. That is, β-*cis*-$[Co(ox)(edda)]^-$ and C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$ are able to form a strong ion pair with $[Co(en)_3]^{3+}$ and to give a great degree of ion-pairing stereoselectivity since these isomers have a highly anionic triangular face consisting of three coordinated oxygen atoms (as shown by the shaded parts in Scheme 1). In order to obtain information about the structure of ion pair, especially about the direction of access of the complex anion to the complex cation, the CD changes of $[Co(en)_3]^{3+}$ in the first absorption band region were measured upon addition of C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$ or β-*cis*-$[Co(ox)(edda)]^-$.

CD Changes and Ion Pair Structure. It is well-known that the addition of a chiral anion such as *d*-tartrate ion to such complexes as $[Co(en)_3]^{3+}$ and $[Co(chxn)_3]^{3+}$, which can form hydrogen bonds with the axial N–H protons along the C_3 axis, enhances the CD intensity of the A_2 component.[11,23)] Yoneda and co-workers have shown by the CD studies of $[Co(sep)]^{3+}$ (sep=1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]-icosane) and the related complexes that when the hydrogen bonds are formed by using equatorial N–H protons directed nearly along the C_2 axis, the effect leads to an enhancement of the E_a rotational strength.[10–12)] Therefore, we can determine the ion pair structure by observing which component (A_2 or E_a) of $[Co(en)_3]^{3+}$ is enhanced upon the addition of a chiral complex anion. Figure 5 shows the CD spectra

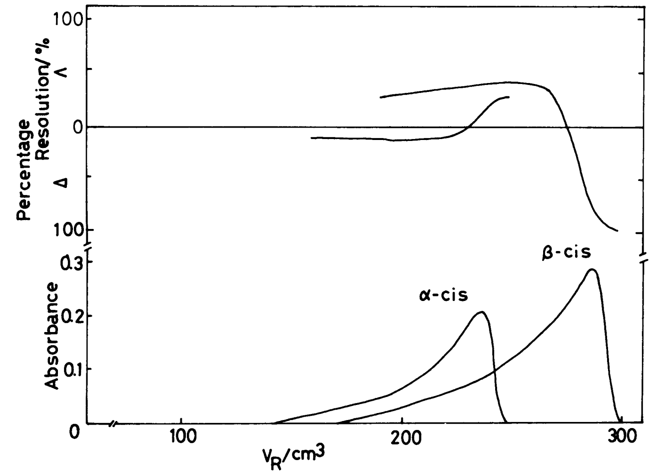


Fig. 4. Elution curves and percentage resolutions for geometrical isomers of $[Co(ox)(edda)]^-$ by chromatography using a column (1.9×60 cm) of SP-Sephadex C-25 in Λ-$[Co(en)_3]^{3+}$ form and water as an eluent.

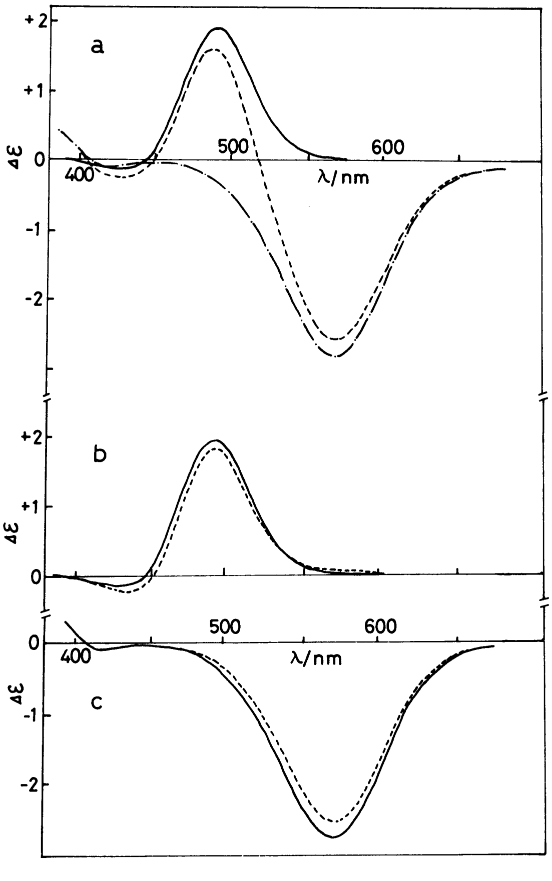


Fig. 5. (a) CD spectra of 0.025 mol dm^{-3} Λ-$[Co(en)_3]^{3+}$ (——), 0.025 mol dm^{-3} Δ-C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$ (—·—), and the mixture (----). (b) CD spectra of 0.025 mol dm^{-3} Λ-$[Co(en)_3]^{3+}$ in the absence (——) and the presence (----) of 0.05 mol dm^{-3} *rac*-C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$. (c) CD spectra of 0.025 mol dm^{-3} Δ-C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$ in the absence (——) and the presence (----) of 0.05 mol dm^{-3} *rac*-$[Co(en)_3]^{3+}$. All the samples were measured using a 1 mm cell.

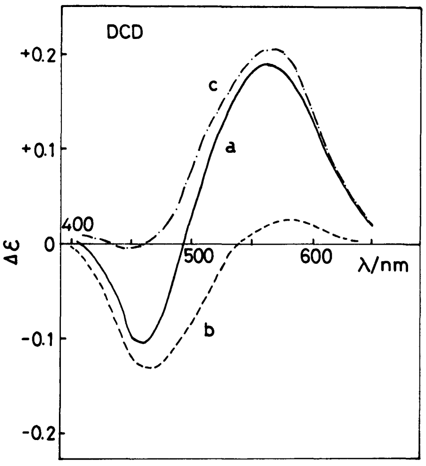


Fig. 6. The DCD spectra in the presence of Λ-[Co(en)$_3$]$^{3+}$ and Δ-C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ (a), Λ-[Co(en)$_3$]$^{3+}$ and *rac*-C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ (b), and *rac*-[Co(en)$_3$]$^{3+}$ and Δ-C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ (c), respectively.

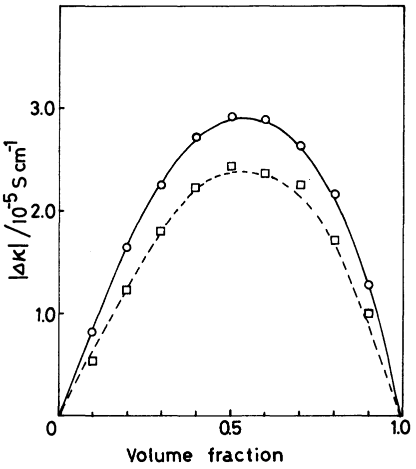


Fig. 7. The deviations, |Δκ|, of the measured conductivity from additivity as a function of the volume fraction, *x*, of Λ-[Co(en)$_3$]I$_3$ for the Λ-Δ (-O-) and the Λ-Λ (-□-) pairs in the [Co(en)$_3$]$^{3+}$-C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ system at 25 °C, *I*=0.01 mol dm^{-3}.

of aqueous Λ-[Co(en)$_3$]$^{3+}$ in the absence and the presence of Δ- or *rac*-C$_1$-*cis*(*N*)-K[Co(ox)(gly)$_2$]$^-$ ion and the CD spectra of aqueous Δ-C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ in the absence and the presence of *rac*-[Co(en)$_3$]$^{3+}$ ion. The difference CD (DCD) spectra, which are defined as the observed CD in the presence of both cationic and anionic complexes minus the simple sums of the component solution spectra, are shown in Fig. 6 in order to clarify the CD spectral changes due to ion pairing between these complex ions. The addition of Δ-C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ to Λ-[Co(en)$_3$]$^{3+}$ not only enhances the CD intensity of the A$_2$ component at the first absorption band region of [Co(en)$_3$]$^{3+}$, but also produces a rather large decrease in the CD intensity of C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ in the first d–d transition region ((*a*) in Figs. 5 and 6). Fortunately, the observed CD changes of [Co(en)$_3$]$^{3+}$ are not seriously disturbed by that of the anionic complex since the CD peaks of both the complex ions are very far apart from each other (at 430 nm(A$_2$) and 490 nm(E$_a$) for the cation, at 569 nm for the anion). The changes in the CD spectrum of Λ-[Co(en)$_3$]$^{3+}$ on addition of Δ- or *rac*-C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ are remarkably similar to the case in which phosphate and *d*-tartrate ions are added. It has been established that three oxygen atoms of the phosphate21,22) and *d*-tartrate ions23,24) form hydrogen bonds with three N–H protons of the [Co(en)$_3$]$^{3+}$ along its C$_3$ axis, in solution as well as in crystal. The similarity in CD change detected in the present study suggests that the hydrogen bonds along the C$_3$ axis of the cation are formed between the three axial N–H protons of the [Co(en)$_3$]$^{3+}$ and the three coordinated oxygen atoms of the C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$. A similar existence of three N–H···O hydrogen bonds along the C$_3$ axis was reported for the diastereoisomer Δ-[Co(*l*-pn)$_3$]Λ-[Cr(mal)$_3$]·3H$_2$O in crystal.9) The DCD spectrum for the solution involving Λ-[Co(en)$_3$]$^{3+}$ and *rac*-C$_1$-*cis*-(*N*)-[Co(ox)(gly)$_2$]$^-$ has a small positive peak in the first d–d transition region of the complex anion ((*b*) in Fig.6). Since the ion-pairing interaction of the Λ-cation with the Δ-anion produces a large decrease in the CD intensity in the spectral region of the anion (a large positive DCD peak) ((*a*) in Figs. 5 and 6), the small positive DCD peak produced by the Λ-cation and the rac-anion indicates that the Λ–Δ interaction is stronger than the Λ–Λ; in other words, the favorable ion pair between [Co(en)$_3$]$^{3+}$ and C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ is Λ–Δ.

Miyoshi et al. have reported that when the cationic complex uses its C$_3$ axis for hydrogen bonding to the anionic complex, a homochiral combination (Λ–Λ or Δ–Δ) is favored, whereas when the cationic complex uses its C$_2$ axis, a heterochiral combination (Λ–Δ or Δ–Λ) is favored.8,10) However, in the present [Co(en)$_3$]$^{3+}$-C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ system, it is strongly suggested from the CD spectral change (an enhancement of the A$_2$ component of [Co(en)$_3$]$^{3+}$) that the favorable pair is a heterochiral combination in which the cation uses its C$_3$ axis for hydrogen bonding. This is inconsistent with the discrimination mechanism proposed above by Miyoshi et al.

Diastereomeric Ion-Pair Formation Constants. We previously showed that the conductance method is useful for a determination of the diastereomeric ion-pair formation constants between chiral complex ions.4,5) The conductance measurements were carried out for [Co(en)$_3$]$^{3+}$–C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ and [Co(en)$_3$]$^{3+}$–β-*cis*-[Co(ox)(edda)]$^-$ systems. In Fig. 7 are shown the deviations (Δκ) of the measured conductivity from the additivity of the component conductivities at various volume fractions (*x*) of [Co(en)$_3$]-

$I_3 \cdot H_2O$ for the Λ-Δ and Λ-Λ pairs in the $[Co(en)_3]^{3+}$–C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$ system at 25 °C, ionic strength I=0.01 mol dm^{-3}. The $\Delta\kappa$ value of the mixture, consisting of a solution of C_M mol dm^{-3} $[Co(en)_3]I_3 \cdot H_2O$ and a solution of C_B mol dm^{-3} K-C_1-*cis*(*N*)-$[Co(ox)(gly)_2] \cdot 0.5H_2O$ at volume fractions of x and 1-x, respectively, is given by

$$10^3\,\Delta\kappa = 10^3\kappa - C_M x \Lambda_m(MI_3) - C_B(1-x)\Lambda_m(KB), \quad (3)$$

where κ is the specific conductivity (S cm^{-1}) of the mixture and Λ_m is the molar conductivity (S cm^2 mol^{-1}) of the species specified in parentheses {M=$[Co(en)_3]^{3+}$, B=C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$} at an ionic strength of 0.01 mol dm^{-3}. If a 1:1 ion pair, $M^{3+} \cdot B^-$, is assumed, $\Delta\kappa$ can be related to the molar concentration of the ion-pair by

$$[M^{3+} \cdot B^-] = 10^3\,\Delta\kappa/\alpha \quad (4)$$

and

$$\alpha = 2\lambda(M^{3+} \cdot B^-) - 3\lambda(M^{3+}) - \lambda(B^-), \quad (5)$$

where λ is the ionic equivalent conductance at 25 °C, I=0.01 mol dm^{-3} of $M^{3+} \cdot B^-$, M^{3+}, and B^-, respectively. It can been seen in Fig. 7 that there exists a significant difference in the $|\Delta\kappa|$ values between the Λ-Δ and Λ-Λ pairs; that is, the $|\Delta\kappa|$ values for the Λ-Δ pair are invariably larger than those for the Λ-Λ pair at every volume fractions. The diastereomeric ion-pair formation constants, $K(\Lambda\text{-}\Delta)$ and $K(\Lambda\text{-}\Lambda)$, obtained by analyzing the $\Delta\kappa$ values according to procedures described in the literature[4,5,19] are given in Table 1 along with the relative formation constants (discrimination factors), $K(\Lambda\text{-}\Delta)/K(\Lambda\text{-}\Lambda)$, which is considered to be a measure of the stereoselectivity in ion pairing determined directly by conductance. The diastereomeric ion-pair formation constants and the discrimination factors for the $[Co(en)_3]^{3+}$–β-cis-$[Co(ox)(edda)]^-$ system are presented in Table 2. As can already be expected from the similarity of the chromatographic behavior to that of C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$, the preference of the Λ-Δ combination was again observed in this system. However, it may be noteworthy that the discrimination factor for the $[Co(en)_3]^{3+}$–β-*cis*-$[Co(ox)(edda)]^-$ system is smaller than that for the $[Co(en)_3]^{3+}$–C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$ system. In β-*cis*-$[Co(ox)(edda)]^-$ complex, the meridional acetate ring of the edda ligand is strained because of the presence of the "ethylenediamine" part of the edda, compared with the strain-free glycinate rings in C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$. Consequently, both the anionic complexes are subtly different in the direction of the lone pair electrons on the coordinated oxygen atoms. Thus, as can be seen in Tables 1 and 2, this effect upon the ion-pair formation constants is more prominent for the favorable pairs ($K(\Lambda\text{-}\Delta)$=83.1 and 69.8 mol^{-1} dm^3 for $[Co(en)_3]^{3+}$–C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$ and $[Co(en)_3]^{3+}$–β-*cis*-$[Co(ox)(edda)]^-$ systems, respectively) than for the unfavorable pairs ($K(\Lambda\text{-}\Lambda)$= 63.8 and $K(\Delta\text{-}\Delta)$=60.0 mol^{-1}dm^3 for the former and the latter systems, respectively) since the stabilization

Table 1. Ion-Pair Formation Constants and Discrimination Factors for $[Co(en)_3]^{3+}$–C_1-*cis*(*N*)-$[Co(ox)(gly)_2]^-$ System at 25 °C, I=0.01 mol dm^{-3}

Volume fraction x	Ion-pair formation constant/mol^{-1} dm^3 $K(\Lambda\text{-}\Delta)$	$K(\Lambda\text{-}\Lambda)$	Discrimination factor $K(\Lambda\text{-}\Delta)/K(\Lambda\text{-}\Lambda)$
0.2	85.9	58.7	1.46
0.3	83.9	62.0	1.35
0.4	85.6	66.2	1.29
0.5	82.0	66.3	1.24
0.6	80.8	64.3	1.26
0.7	80.7	67.8	1.19
0.8	82.6	61.4	1.35
	83.1±2.1[a]	63.8±3.2[a]	1.31±0.09[a]

a) Average and standard deviation.

Table 2. Ion-Pair Formation Constants and Discrimination Factors for $[Co(en)_3]^{3+}$–β-*cis*-$[Co(ox)(edda)]^-$ System at 25 °C, I=0.01 mol dm^{-3}

Volume fraction x	Ion-pair formation constant/mol^{-1} dm^3 $K(\Lambda\text{-}\Delta)$	$K(\Delta\text{-}\Delta)$	Discrimination factor $K(\Lambda\text{-}\Delta)/K(\Delta\text{-}\Delta)$
0.2	70.4	61.6	1.14
0.3	74.9	64.2	1.17
0.4	70.5	62.3	1.13
0.5	68.9	60.8	1.13
0.6	70.3	58.4	1.20
0.7	66.6	56.0	1.19
0.8	66.8	57.0	1.17
	69.8±2.8[a]	60.0±3.0[a]	1.16±0.03[a]

a) Average and standard deviation.

of a favorable pair should greatly depend on the fitness of the hydrogen bonding. The importance of the direction of lone pair electrons on the oxygen atom employed for hydrogen bonding was also observed in chromatographic ion-pairing investigations of C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ and C$_1$-*cis*(*N*)-[Co(ox)(β-ala)$_2$]$^-$ with Λ-[Co(en)$_3$]$^{3+}$5); that is, the separation factor for C$_1$-*cis*(*N*)-[Co(ox)(β-ala)$_2$]$^-$ with six-membered chelate rings has been shown to be slightly greater than that for C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ with five-membered chelate rings, where the separation factor is defined as the value of the retention volume of the later eluted enantiomer devided by that of the faster eluted one. This enhanced stereoselectivity for C$_1$-*cis*(*N*)-[Co(ox)(β-ala)$_2$]$^-$ suggests that the direction of lone pair electrons on the carboxyl oxygen atom in the six-membered chelate ring is more favorable to hydrogen bonding along the C$_3$ axis with the N–H groups on the Λ-[Co(en)$_3$]$^{3+}$ than that in the five-membered chelate ring. The stereoselectivity was observed to increase for chelate rings of the related anionic complexes in the following order: strained five-membered chelate ring<less strained five-membered chelate ring<six-membered chelate ring. Thus, β-*cis*-[Co(ox)(edda)]$^-$ with the strained meridional acetate ring can be understood to show reduced ion-pairing stereoselectivity. The observation that the CD change of Λ-[Co(en)$_3$]$^{3+}$ on addition of β-*cis*-[Co(ox)(edda)]$^-$ is quite similar to that on addition of C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ but is slightly smaller in magnitude also supports the reduced stereoselectivity in [Co(en)$_3$]$^{3+}$–β-*cis*-[Co(ox)(edda)]$^-$ system.

Concluding Remarks

It has been shown that C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ and β-*cis*-[Co(ox)(edda)]$^-$ associate more strongly with [Co(en)$_3$]$^{3+}$ than the respective other geometrical isomers. An important structural characteristic of the anionic complexes is that they have a triangular face consisting of three coordinated oxygen atoms along the pseudo C$_3$ axis. In both [Co(en)$_3$]$^{3+}$-C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ and [Co(en)$_3$]$^{3+}$–β-cis-[Co(ox)(edda)]$^-$ systems a Λ–Δ combination was preferred over a Λ–Λ combination. This has also been confirmed by the diastereomeric ion-pair formation constants determined by the conductance method. The effect of C$_1$-*cis*(*N*)-[Co(ox)(gly)$_2$]$^-$ and β-*cis*-[Co(ox)(edda)]$^-$ on the CD spectra of [Co(en)$_3$]$^{3+}$ was very similar to that of phosphate and *d*-tartrate ions; that is, the A$_2$ rotational strength of [Co(en)$_3$]$^{3+}$ was enhanced upon the formation of ion pairing. This result strongly suggests that the hydrogen bondings formed between the cationic and the anionic complexes play an important role in the ion-pairing stereoselectivity and, further, that the anionic complex approaches a triangular face of [Co(en)$_3$]$^{3+}$ along the C$_3$ axis and makes a face-to-face close contact through three hydrogen bonds. The ion-pair structure is disagreement with the discrimination mechanism proposed by Miyoshi et al.

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