The Isomerism of the (Ethylenediamine-*N*,*N*′-dipropionato)(ethylenediamine)-cobalt(III) Ion and Its Stereoselective Isomerization Reaction

Hiroshi Kawaguchi,* Noboru Maruyama, Tomoharu Ama, and Takaji Yasui
Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780

(Received September 2, 1991)

Three isomers (one α and two β) of $[Co(eddp)(en)]^+$ were prepared and optically resolved. The stereochemistry was studied on the basis of absorption, CD, and ^{13}C NMR spectral data. Two β isomers, β(e-1) and β(e-2), were conformational diastereomers arising from a difference of the chirality around one of the asymmetric N atoms in a coordinated eddp ligand. The $\beta(\text{e-1}) \rightleftharpoons \beta(\text{e-2})$ change was an inversion reaction at the asymmetric sec-N atom in the in-plane β-alaninate ring of the coordinated eddp, and the rate was slow. The $\alpha \rightleftharpoons \beta(\text{e-1})$ or β(e-2) change (coordination-site exchange reaction) was stereoselective and could be explained by the Co–O bond rupture mechanism proposed for Co(III)–edda complexes.

The complex ion in the title, $[Co(eddp)(en)]^+$ (H_2eddp : ethylenediamine-*N*,*N*′-dipropionic acid), provides two possible geometrical isomers, α and β, as shown in Fig. 1. The secondary nitrogen (sec-N) atoms of the coordinated eddp ligand are chiral centers. In the α isomer, the chiralities around two sec-N atoms are restricted by the absolute configuration around the Co(III) ion. Accordingly, the possible configurations for the α isomer are $\Delta(S,S)$ and $\Lambda(R,R)$, where *R* and *S* denote the chiralities around the asymmetric nitrogen. In the β isomer, the two sec-N atoms of the coordinated eddp ligand are in different situations: one is in the in-plane β-alaninate ring (with respect to the ethylenediamine ring of eddp), and the other is in the out-of-plane β-alaninate ring. The sec-N atom of the out-of-plane β-alaninate ring is in the same situation as that in the α isomer; the chirality around the sec-N atom is restricted by the absolute configuration around the Co(III) ion. The sec-N atom of the in-plane β-alaninate ring, however, can adopt either of two possible chiralities (*R* or *S*). Therefore, the β isomer has four possible isomers: $\Delta(R,R^*)$-β, $\Delta(R,S^*)$-β, $\Lambda(S,R^*)$-β, and $\Lambda(S,S^*)$-β, where *S* and *R* denote the chiralities of the sec-N atom in the out-of-plane β-alaninate ring and *S** and *R** denote those in the in-plane β-alaninate ring.

Ethylenediamine-*N*,*N*′-diacetate (edda) is an O–N–N–O type ligand similar to eddp, except that edda can form five-membered (glycinate) chelate rings. Co(III) complexes with edda have been studied both stereochemically[1)] and kinetically.[2)] We recently studied the isomerization reaction of the $[Co(edda)(en)]^+$ system and found that the $\Lambda(R)$-β isomer isomerized to $\Lambda(S,S)$- and $\Delta(R,R)$-α with a constant ratio of 73 : 27.[3,4)] For the stereoselective isomerization of $\Lambda(R)$-β-$[Co(edda)(en)]^+$, we proposed a Co–O bond-rupture mechanism. (See Scheme 1 described below. Path 1 was the major one for $[Co(edda)(en)]^+$.) It is interesting to study whether such a mechanism can also be applied to the isomerization reaction of $[Co(eddp)(en)]^+$, which has six-membered (β-alaninate) chelate rings. We have already presented preliminary results concerning the structure and reactivity of $[Co(eddp)(en)]^+$.[5)] In this paper we describe the isolation and characterization of all possible isomers in $[Co(eddp)(en)]^+$ as well as their isomerization reactions.

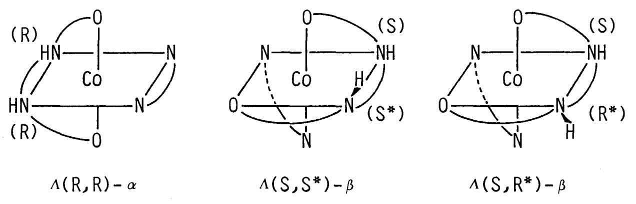


Fig. 1. Structures of possible isomers for Λ-[Co-(eddp)(en)]$^+$.

Experimental

Preparation of [Co(eddp)(en)]Cl. To a solution containing 5.82 g (0.02 mol) of $Co(NO_3)_2 \cdot 6H_2O$ and 5.54 g (0.02 mol) of ethylenediamine-*N*,*N*′-dipropionic acid dihydrochloride ($H_2eddp \cdot 2HCl$) in 60 cm^3 of water, 13.4 cm^3 of a 10% ethylenediamine aqueous solution was added; the mixed solution was then adjusted to pH 8 with 4 M NaOH ($M = mol\,dm^{-3}$). Lead dioxide (13 g) was added to the solution, and the mixture was stirred at 40 °C for 1 h. After the mixture was cooled to room temperature, the insoluble materials were removed by filtration. The filtrate was chromatographed on an SP-Sephadex C-25 column (4.7 cm × 90 cm, K^+ form) with 0.2 M KCl as an eluent. The elution gave purple (α) and red-purple (β) bands that were well separated from each other, besides blue-violet and red-brown bands which were eluted more rapidly and slowly, respectively, than those mentioned above. The red-purple (β) band was transferred to another column and repeatedly chromatographed on the same column. The elution gave two well-separated bands, denoted as β(e-1) and β(e-2) in order of elution. Each complex included in the three bands, α, β(e-1), and β(e-2), was obtained as a chloride salt by a method similar to that described previously,[4)] except that methanol–acetone mixture was used in place of methanol.

Optical Resolution. The α isomer was chromatographed on an SP-Sephadex column (4.7 cm × 90 cm, K^+ form) with

0.1 M $K_2[Sb_2(\mathrm{L}\text{-tart})_2]$ as an eluent, and a recycling chromatographic technique was employed. After two cycles, the $(-)^{\mathrm{CD}}_{552}$-α (earlier eluate) and $(+)^{\mathrm{CD}}_{552}$-α (later eluate) bands were sufficiently separated. Each eluate was concentrated under reduced pressure; methanol was then added into the concentrated solution in order to eliminate $K_2[Sb_2(\mathrm{L}\text{-tart})_2]$. Each isomer was converted to the chloride salt using a QAE-Sephadex A-25 (Cl^- form) column and then crystallized. Recrystallization was carried out from water by the addition of methanol and acetone. Found for $(-)^{\mathrm{CD}}_{552}$-α: C, 29.32; H, 7.00; N, 13.63%. Calcd for $[Co(eddp)(en)]Cl{\cdot}3H_2O = C_{10}H_{28}N_4O_7ClCo$: C, 29.24; H, 6.87; N, 13.64%.

The β(e-1) isomer was also optically resolved by the same recycling chromatographic method as that described above. After two cycles, the $(+)^{\mathrm{CD}}_{536}$-β(e-1) (earlier eluate) and $(-)^{\mathrm{CD}}_{536}$-β(e-1) bands were separated. In the case of β(e-2), however, the chromatographic method was ineffective; even a partial resolution could not be achieved after cycles for over 3 d. The use of $Na_2\mathrm{L}$-tart as an eluent did not give a good result. The resolution using optically active Ag[Co(edta)] as a resolving agent was also attempted, but was unsuccessful.

Optically active β(e-2) was obtained by an isomerization reaction of optially active β(e-1). In 75 cm^3 of a buffer solution (KH_2PO_4–Na_2HPO_4) adjusted to pH 8.16, 0.57 g of $(-)^{\mathrm{CD}}_{536}$-β(e-1)-$[Co(eddp)(en)]Cl{\cdot}3H_2O$ was dissolved at 40 °C. The solution was stirred for 45 min and then acidified to pH 6. The acidified solution was poured onto an SP-Sephadex C-25 column (4.7 cm × 90 cm, K^+ form) and repeatedly developed with 0.2 M KCl, by which means the $(-)^{\mathrm{CD}}_{536}$-β(e-1) and $(-)^{\mathrm{CD}}_{563}$-β(e-2) bands were separated. (In this reaction, a very small amount of $(+)^{\mathrm{CD}}_{552}$-α was also formed.) The $(-)^{\mathrm{CD}}_{563}$-β(e-2) isomer was isolated as a chloride salt by treating the eluate in the same manner as used for racemic β(e-2). The recrystallization was carried out from a small amount of water by the addition of methanol and ethanol. (Since the optical purity did not change by recrystallization, the recrystallized product was assumed to be optically pure and was used for an isomerization study.) Found for $(+)^{\mathrm{CD}}_{536}$-β(e-1): C, 29.29; H, 7.06; N, 13.50%. Calcd for $[Co(eddp)(en)]Cl{\cdot}3H_2O = C_{10}H_{28}N_4O_7ClCo$: C, 29.24; H, 6.87; N, 13.64%. Found for $(-)^{\mathrm{CD}}_{563}$-β(e-2): C, 33.62; H, 6.44; N, 15.05%. Calcd for $[Co(eddp)(en)]Cl{\cdot}0.5CH_3OH = C_{10.5}H_{24}N_4O_{4.5}ClCo$: C, 33.84; H, 6.49; N, 15.03%.

Isomerization. $(+)^{\mathrm{CD}}_{552}$-$\Lambda(R,R)$-α-$[Co(eddp)(en)]Cl{\cdot}3H_2O$: All of the chemicals used were of a reagent grade, and deionized water was degassed before use. The reaction was started by dissolving the complex (0.2706 g) in 120 cm^3 of a buffer solution [Na_2CO_3(0.1007 g)–$NaHCO_3$(0.3218 g)] in a reaction vessel kept in a thermostated bath. Throughout the kinetic run, the reaction solution was stirred and both the temperature and pH were checked with a thermistor thermometer (Takara D221) and a pH meter (Toa TSC-10A), respectively. The reaction conditions were as follows; complex concentration, 5.49×10^{-3} M; pH 9.27 ± 0.02; temperature, 40.0 ± 0.1 °C.

At prescribed time intervals, 20 cm^3 of the reaction solution was taken out and acidified to pH 6 with 1 M HCl in order to stop the reaction. The acidified solution was poured onto an SP-Sephadex C-25 column (3.0 cm × 80 cm, K^+ form) and developed with 0.2 M KCl. The adsorbed band was separated into three bands: α, β(e-1), and β(e-2). The eluates of the three bands were collected separately and concentrated under reduced pressure to a constant volume (20 cm^3). The amounts and optical purities of the isomers were calculated from the absorption and CD data of the concentrated eluates. These spectra were measured by a JASCO UVIDEC-670 spectrophotometer and a JASCO J-22 spectropolarimeter, respectively. The solution used for the spectral measurement contained a considerable amount of KCl, and the CD spectra of the isomers of $[Co(eddp)(en)]^+$ were affected by the amount of coexisting KCl. Therefore, calculations of the optical purity were carried out based on the CD data measured in a KCl aqueous solution. In weakly acidic and neutral solutions at room temperature, the absorption and CD spectral changes of all the isomers were slow. Therefore, the progress of the isomerization reaction during such procedures as chromatographic separation and concentration under reduced pressure was ignored.

$(-)^{\mathrm{CD}}_{536}$-$\Lambda(S,S^*)$-β(e-1)-$[Co(eddp)(en)]Cl{\cdot}3H_2O$ and Racemic β(e-2)-$[Co(eddp)(en)]Cl{\cdot}1.5H_2O{\cdot}CH_3OH$: The isomerization reactions of $(-)^{\mathrm{CD}}_{536}$-$\Lambda(S,S^*)$-β(e-1) and racemic β(e-2) were carried out by a method similar to that for the α isomer. The reaction conditions were as follows. For $(-)^{\mathrm{CD}}_{536}$-$\Lambda(S,S^*)$-β(e-1): complex concentration, 5.49×10^{-3} M; pH, 9.25 ± 0.02 or 8.13 ± 0.01 (KH_2PO_4–Na_2HPO_4 buffer); temperature, 40.0 ± 0.1 °C. For racemic β(e-2): complex concentration, 5.49×10^{-3} M; pH, 8.22 ± 0.01; temperature, 40.0 ± 0.1 °C.

Results and Discussion

Characterization of Three Isomers: Three kinds of complex chlorides, one purple colored and two red-purple colored complexes, were isolated and confirmed to be [Co(eddp)(en)]Cl from their elemental analyses, as described in the experimental section. The absorption spectra of these complexes are shown in Fig. 2 and their numerical data are listed in Table 1. On the basis of these spectral data, the geometry of the purple colored complex was assigned to the α form and those of two red-purple colored complexes to the β form (Fig. 1). (The two β isomers are denoted by β(e-1) and β(e-2) in the order of the elution in the column chromatography.) The assignment described above was also confirmed by the ^{13}C NMR spectral data; the purple colored complex,

Table 1. Absorption (AB) and CD Spectral Data of $[Co(eddp)(en)]^+$

Isomer	AB (log ε)/nm	CD ($\Delta\varepsilon$)/nm
$(+)^{\mathrm{CD}}_{552}$-$\Lambda(R,R)$-α	542 (1.97)	552 (+2.67)
(Purple)	455 (1.52)	452 (−1.99)
	362 (1.91)	357 (+0.08)
	242 (4.44)	
$(-)^{\mathrm{CD}}_{536}$-$\Lambda(S,S^*)$-β(e-1)	ca. 550 (sh)	536 (−0.54)
(Red-purple)	500 (2.31)	473 (+0.90)
	366 (2.08)	370 (−0.54)
	238 (4.26)	
$(-)^{\mathrm{CD}}_{563}$-$\Lambda(S,R^*)$-β(e-2)	ca. 550 (sh)	563 (−0.60)
(Red-purple)	508 (2.34)	474 (+0.42)
	367 (2.09)	366 (−0.55)
	236 (4.27)	

ε and $\Delta\varepsilon$ are given in mol^{-1} dm^3 cm^{-1}.

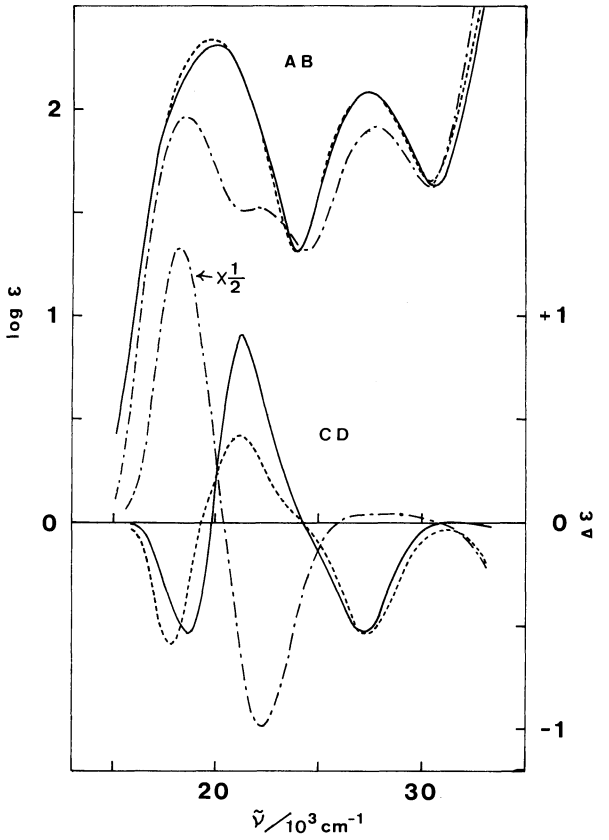


Fig. 2. Absorption (AB) and CD spectra of [Co(eddp)(en)]$^+$: $(+)^{\mathrm{CD}}_{552}$-purple (α) isomer (—·—·—·—), $(-)^{\mathrm{CD}}_{536}$-red-purple [β(e-1)] isomer (——), $(-)^{\mathrm{CD}}_{563}$-red-purple [β(e-2)] isomer (--------).

which was assigned to the α form with C_2 symmetry, showed five signal peaks due to ten carbons, and both of the two red-purple colored complexes, which were assigned to the β form with C_1 symmetry, showed ten signal peaks due to ten carbons, respectively.[6] The CD data of the three isomers are shown in Fig. 2 and Table 1. The $(+)^{\mathrm{CD}}_{552}$-α isomer is considered to take the Λ configuration, because (i) it has a dominant CD peak with a positive sign at the longer wave length and (ii) the CD spectral behavior in the visible region is similar to that of Λ-$(+)^{\mathrm{CD}}_{535}$-α-[Co(edda)(en)]$^+$.[4] The absolute configuration of $(-)^{\mathrm{CD}}_{536}$-β(e-1) was determined to be Λ by an X-ray analysis.[7] The $(-)^{\mathrm{CD}}_{563}$-β(e-2) isomer shows a CD spectral behavior similar to that of $(-)^{\mathrm{CD}}_{536}$-β(e-1) (Fig. 2). Accordingly, $(-)^{\mathrm{CD}}_{563}$-β(e-2) is thought to have the Λ configuration.

As shown in Fig. 1, the β-type isomer has two possible conformational diastereomers, which arise from a difference of the chirality around one of the asymmetric N atoms in the coordinated eddp ligand. Two β isomers, β(e-1) and β(e-2), which were isolated in this experiment are conformational diastereomers to each other, and were clarified to be a and b (Fig. 1), respectively, by X-ray analyses.[7] Table 2 shows the relationship between the CD signs and the absolute configurations for the isomers of [Co(eddp)(en)]$^+$. Even though the β-type complexes containing edda, pdda, and adao ligands[8] have been reported, only one of the two conformational diastereomers has been isolated.[1,9] In the case of β-[Co(adao)(L)] (L: mal^{2-}, ox^{2-}, and CO_3^{2-}), it is thought that only one of two conformational diastereomers is formed in an aqueous solution.[9] Although the β(e-1) isomer could be optically resolved on an SP-Sephadex column with the use of $K_2[Sb_2(\text{L-tart})_2]$ as an eluent, β(e-2) could not. This fact is of interest from the point of view of optical resolution mechanism.

Table 2. Possible Configurations and CD Signs of [Co(eddp)(en)]$^+$

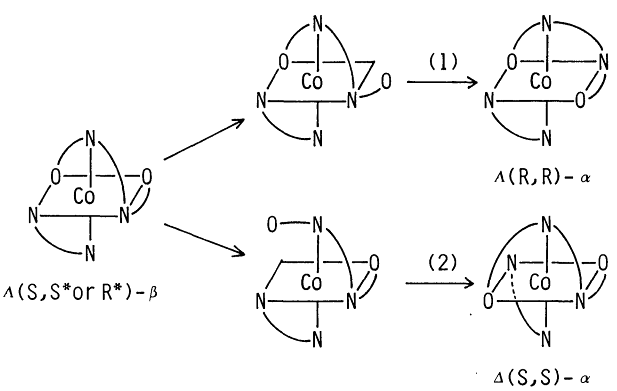
Isomer	Possible configuration and CD sign	
α	$(+)^{\mathrm{CD}}_{552}$-$\Lambda(R,R)$	$(-)^{\mathrm{CD}}_{552}$-$\Delta(S,S)$
β(e-1)	$(-)^{\mathrm{CD}}_{536}$-$\Lambda(S,S^*)$	$(+)^{\mathrm{CD}}_{536}$-$\Delta(R,R^*)$
β(e-2)	$(-)^{\mathrm{CD}}_{563}$-$\Lambda(S,R^*)$	$(+)^{\mathrm{CD}}_{563}$-$\Delta(R,S^*)$

Inversion Reaction at Coordinated Sec-N Atom: The isomerization reaction of $\Lambda(S,S^*)$-β(e-1) was followed under the conditions of pH 8.13 and 9.25 at 40.0 °C. Table 3 shows the change in the proportions of the starting material and products together with the enantiomeric excess percentage of each isomer.

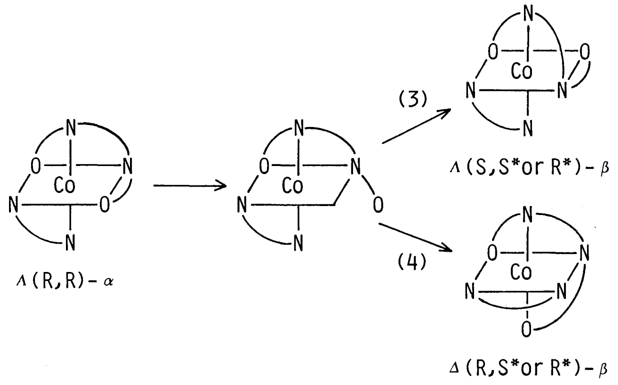
In the reaction at pH 8.13, $\Lambda(S,S^*)$-β(e-1) mainly isomerized to $\Lambda(S,R^*)$-β(e-2), of which the optical purity was considerably high (ca. 95%) at the initial stage of the reaction (Table 3). (The formation of α was not detected during the first ca. 30 min; after that time its amount increased slowly.) When $\Lambda(S,R^*)$-β(e-2) was allowed to react for 5 min under the conditions of pH 8.22 and 40.0 °C, $\Lambda(S,S^*)$-β(e-1) with an optical purity of 87% was obtained. (As the optically active β(e-2) isomer was isolated in only a small amount, the isomerization study of the isomer could not be carried out sufficiently. The reaction data concerning racemic β(e-2) are listed in Table 3.) Accordingly, it is thought that the interchange between β(e-1) and β(e-2) proceeds by an inversion at the asymmetric sec-N in the in-plane β-alaninate ring of the coordinated eddp. This inversion reaction might be explained by the mechanism proposed for the epimerization of $[Co(en)_2(sar)]^{2+}$[10] and $[Co(NH_3)_4(\text{Me-en})]^{3+}$[11] and for the racemization of *mer*-$[Co(dien)_2]^{3+}$[12] and *mer*-[Co(edma)(dien or mdien)]$^{2+}$.[13] However, the rate of inversion is much slower in the eddp complex than in the complexes described above. In the reaction of $\Lambda(S,S^*)$-β(e-1) at pH 9.25, the ratio of β(e-1) and β(e-2) was almost constant after 15 min from the start of the reaction; the equilibrium between β(e-1) and β(e-2) was established. The ratio is roughly β(e-1): β(e-2) = 5 : 6, indicating that β(e-2) is more stable than β(e-1). Two factors, the slow inversion rate at the sec-N atom of the in-plane β-alaninate ring of the coordinated eddp, and the small difference in the free energies of β(e-

Table 3. The Proportions and Optical Purities of the Starting Materials and Products in the Isomerization Reaction of [Co(eddp)(en)]$^+$ (40.0 °C)

t	(i) Λ(*R*,*R*)-α (pH 9.27) Isomer proportion (Optical purity/%)		
min	Λ(*R*,*R*)-α	Λ(*S*,*S**)-β(e-1)	Λ(*S*,*R**)-β(e-2)
15	0.81 (95)	0.08 (39)	0.11 (44)
30	0.66 (87)	0.15 (34)	0.19 (38)
60	0.50 (61)	0.22 (22)	0.28 (27)
120	0.44 (27)	0.25 (11)	0.31 (12)
180	0.45 (11)	0.25 (5)	0.30 (4)
t	(ii) Λ(*S*,*S**)-β(e-1) (pH 8.13) Isomer proportion (Optical purity/%)		
min	Λ(*S*,*S**)-β(e-1)	Λ(*S*,*R**)-β(e-2)	Λ(*R*,*R*)-α
10	0.77 (99)	0.23 (95)	
20	0.60 (95)	0.40 (95)	
30	0.51 (90)	0.49 (94)	
45	0.44 (89)	0.52 (93)	0.04 (29)
60	0.41 (84)	0.53 (90)	0.06 (25)
t	(iii) Λ(*S*,*S**)-β(e-1) (pH 9.25) Isomer proportion (Optical purity/%)		
min	Λ(*S*,*S**)-β(e-1)	Λ(*S*,*R**)-β(e-2)	Λ(*R*,*R*)-α
15	0.38 (71)	0.49 (72)	0.13 (29)
30	0.34 (47)	0.42 (49)	0.24 (23)
60	0.28 (18)	0.36 (22)	0.36 (19)
120	0.25 (2)	0.33 (3)	0.42 (9)
180	0.26 (0)	0.31 (0)	0.43 (4)
t	(iv) Racemic-β(e-2) (pH 8.22) Isomer proportion		
min	β(e-2)	β(e-1)	α
10	0.73	0.27	
30	0.60	0.40	
60	0.53	0.40	0.07
90	0.51	0.40	0.09
120	0.50	0.38	0.12



Scheme 1.



Scheme 2.

1) and β(e-2), enabled us to isolate all possible conformational diastereomers in β-[Co(eddp)(en)]$^+$.

Coordination-Site Exchange Reaction: The data concerning the isomerization of the [Co(eddp)(en)]$^+$ system are listed in Table 3. Isomerization from β(e-1) to α is considerably slower compared with the β(e-1)→β(e-2) change (inversion). Λ(*R*,*R*)-α formed from Λ(*S*,*S**)-β(e-1) (actually, from the mixture of Λ(S,S*)-β(e-1) and Λ(*S*,*R**)-β(e-2)) at pH 9.25 has an optical purity of ca. 30%. In the isomerization reaction of Λ(*R*,*R*)-α at pH 9.27, Λ(*S*,*S**)-β(e-1) (optical purity: 39%) and Λ(*S*,*R**)-β(e-2) (optical purity: 44%) were simultaneously formed. These results may be interpreted in terms of the Co–O bond-rupture mechanism (Scheme 1 and 2), which is proposed concerning the isomerization reactions of [Co(edda)(en)]$^+$ and [Co(edda)(gly)].[4)]

In β-type isomers, the two O atoms of the coordinated eddp ligand are in different situations; one is in the in-plane β-alaninate ring, and the other is in the out-of-plane β-alaninate ring. When a bond-rupture occurs between the Co(III) ion and the O atom of the out-of-plane β-alaninate ring, the vacant position in the intermediate is occupied by the neighboring sec-N of the eddp ligand, with an accompanying concurrent shift of the "bond-ruptured O" atom to the position vacated by the sec-N atom ((1) of Scheme 1). When a bond-rupture occurs between the Co(III) ion and the O atom of the in-plane β-alaninate ring, the sec-N atom of the eddp ligand can not occupy the vacant position in the intermediate. In this case, the vacant position may be occupied by the N atom of the en ligand along with a moving of the "bond-ruptured O" atom to the position originally occupied by the N(en) atom ((2) of Scheme 1). The experimental results for Λ(*S*,*S**)-β(e-1) may be explained by the simultaneous occurence of the two paths shown in Scheme 1, where the path of (1) is the major one.

When a Co–O bond-rupture occurs in the α isomer, the vacant position in the intermediate may be occupied by the sec-N(eddp) or N(en) atom, and the "bond-ruptured O" atom simultaneously shifts to the position originally occupied by the sec-N(eddp) or N(en) atom, respectively, as shown Scheme 2. The isomerization of Λ(*R*,*R*)-α may be interpreted as a simultaneous occurence of the two paths shown in Scheme 2, where the path of (3) is the major one. (The path of (3) is reverse one of the path (1) in Scheme 1.) The α ⟶ β change was observed in the $[Co(eddp)(en)]^+$ system, but was not in the $[Co(edda)(en)]^+$ system.[4] This means that the β form is stabilized relative to the α form in $[Co(eddp)(en)]^+$, which forms a 6-membered chelate ring. The equilibrium ratio of three isomers was $\alpha : \beta$(e-1) : β(e-2) = 45 : 25 : 30.

As is shown in Table 3, a gradual decrease in the optical purity of each isomer with the passage of time may be attributed to reversible isomerization between the α and two β isomers, where the stereoselectivity is not so high. In the reaction of $\Lambda(R,R)$-α, the optical purity of the formed $\Lambda(S,S^*)$-β(e-1) isomer decreased slightly faster than that of the formed $\Lambda(S,R^*)$-β(e-2) isomer. This phenomenon presumably indicates that $\Delta(R,R^*)$-β(e-1) is formed from $\Lambda(R,R)$-α more easily than is $\Delta(R,S^*)$-β(e-2); the $\Lambda(R,R)\text{-}\alpha \longrightarrow \Delta(R,R^*)$-$\beta$(e-1) change does not require an inversion at the sec-N center. The isomerization reaction of the $[Co(eddp)(en)]^+$ system could be explained by the mechanism proposed for the $[Co(edda)(en)]^+$ system: The isomerization path with an inversion at the sec-N center is the major one in the $[Co(eddp)(en)]^+$ complex, which has 6-membered chelate rings. The stereoselectivity in the isomerization reaction of the $[Co(eddp)(en)]^+$ system was comparable to that of the $[Co(edda)(en)]^+$ system.

This work was supported by a Grant-in-Aid for Scientific Research No. 02640481 from the Ministry of Education, Science and Culture.

References

1) D. J. Radanovic, *Coord. Chem. Rev.*, **54**, 159 (1984), and the references cited therein.

2) a) K. Kuroda and F. Mohri, *Chem. Lett.*, **1972**, 719. b) K. Kuroda, *Chem. Lett.*, **1974**, 17. c) Y. Kitamura, *Bull. Chem. Soc. Jpn.*, **49**, 1002 (1976).

3) The absolute configuration of the coordinated sec-N atom is described according to the method of Cahn et al. (*Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966)). Therefore, for example, the absolute configurations of the sec-N atoms in Λ-α forms of $[Co(edda)(en)]^+$ and $[Co(eddp)(en)]^+$ are represented by (*S,S*) and (*R,R*), respectively.

4) H. Kawaguchi, N. Uchiyama, T. Ama, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **63**, 3535 (1990).

5) N. Maruyama, T. Ama, H. Kawaguchi, and T. Yasui, presented at the 40th Symposium on Coordination Chemistry of Japan, Kanazawa, October 1990, Abstr., No. 3CP05.

6) The chemical shifts (ppm) of ^{13}C NMR peaks: α, 178.962, 54.350, 48.618, 45.172, 31.330; β(e-1), 180.852, 178.413, 52.886, 49.197, 48.164, 46.453, 45.050, 44.563, 35.507, 29.623; β(e-2), 180.029, 178.962, 53.740, 53.618, 48.953, 47.124, 45.904, 44.715, 35.446, 31.208.

7) T. Yasui, H. Kawaguchi, T. Ama, N. Sakagami, and S. Kaizaki, 61st National Meeting of the Chemical Society of Japan, Yokohama, March 1991, Abstr., No. 1P20.

8) Abbreviations used: pdda, 1,3-propanediamine-*N,N'*-diacetate; adao, 8-amino-3,6-diazaoctanate.

9) K. Watanabe, *Bull. Chem. Soc. Jpn.*, , **49**, 3068 (1976).

10) a) M. Fujita, Y. Yoshikawa, and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **50**, 3209 (1977). b) B. Halpern, A. M. Sargeson, and F. R. Turnbull, *J. Am. Chem. Soc.*, **88**, 4630 (1966).

11) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 825 (1967).

12) G. H. Searle and F. R. Keene, *Inorg. Chem.*, **11**, 1006 (1972).

13) H. Kawaguchi, H. Fukaki, T. Ama, T. Yasui, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **61**, 2359 (1988).