Photochemistry of Cobalt(III) Complexes. I. Optically Active Cobalt(III) Complexes Containing Co–C Bond Prepared by Photodecarboxylation of Amino Carboxylato Complexes

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Some cobalt(III) complexes with Co–C σ-bond have been prepared by photodecarboxylation reactions of the complexes containing ethylenediamine-N,N'-dipropionate (eddp) or its analogs. The crystal structure of α-[Co(Me$_2$eedmp-C,N,N′,O)(en)]$^+$ (Me$_2$eedmp: $^-$CH$_2$CH$_2$N(CH$_3$)(CH$_2$)$_2$N(CH$_3$)(CH$_2$)$_2$COO$^-$), which is the photolysis product of α-[Co(Me$_2$eddp)(en)]$^+$ (Me$_2$eddp: {CH$_2$N(CH$_3$)(CH$_2$)$_2$COO$^-$}$_2$), was determined by the X-ray diffraction method. The crystal is monoclinic, space group $P2_1/n$, $a=9.013(2)$, $b=13.420(1)$, $c=14.754(4)$ Å, $\beta=92.75(1)°$, $V=1782.5(6)$ Å^3, $Z=4$, and $R=0.038$. The coordination of C atom to Co center results in elongation of the Co–O bond located in the trans position of the C atom, compared with usual Co–O bonds. The photolysis products of optically active isomers (Λ-α, Λ-β(1), and Λ-β(2)) of [Co(eddp)(en)]$^+$ were studied on the basis of the absorption, CD, and ^{13}C NMR spectral data. The photolysis of Λ-β(1) provided Δ-α-[Co(eedmp-C,N,N′,O)(en)]$^+$ (eedmp; $^-$CH$_2$CH$_2$NH(CH$_2$)$_2$NH(CH$_2$)$_2$COO$^-$), while the photolysis of Λ-β(2), which is a conformational diastereomer of Λ-β(1), provided $(-)^{\mathrm{CD}}_{543}$-β-[Co(eedmp-C,N,N′,O)(en)]$^+$ (major product) and Λ-α-[Co(eedmp-C,N,N′,O)(en)]$^+$. Optically active $(+)^{\mathrm{CD}}_{553}$-β-[Co(etnmp-C,N,N′,O)(en)]$^+$ (etnmp: $^-$CH$_2$CH$_2$NH(CH$_2$)$_3$NH(CH$_2$)$_2$COO$^-$) was obtained by the photolysis of Δ-$(-)^{\mathrm{CD}}_{505}$-β-[Co(tndp)(en)]$^+$ (tndp: CH$_2${CH$_2$NH(CH$_2$)$_2$COO$^-$}$_2$).

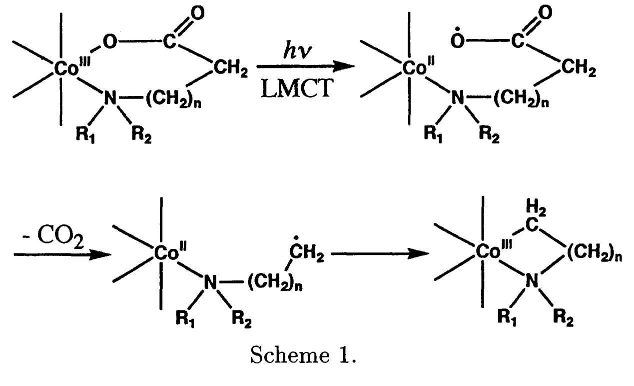
In recent years, a great deal of attention has been focused on the photochemical syntheses of the cobalt(III) complexes containing Co–C bond and their properties. The cobalt(III) complexes containing a Co–C bond had been thought to be unstable and labile. Since the discovery that the stable coenzyme Vitamin B$_{12}$ is a cobalt(III) complex containing a σ-bonded alkyl ligand,[1] many analogous complexes were prepared;[2] some of them exhibited interesting photochemical properties.[3—6]

Most of the known cobalt(III) complexes with stable Co–C bond have highly unsaturated ligands; however, the organo-cobalt(III) complexes containing only saturated ligands have also been prepared and characterized.[7—10] Poznyak et al. obtained the complexes with Co–C bond by photodecarboxylation of the corresponding amino carboxylato complexes.[11—13] In the case of photolysis reactions of the mixed-ligand cobalt(III) complexes containing amino carboxylates and amines such as bipy and phen, the stable products were isolated in crystalline form, and their structures were revealed by X-ray analyses.[14—17] The authors proposed the photolysis mechanism of amino carboxylato Co(III) complex shown in Scheme 1.[11]

Recently, we presented preliminary results concerning the photolysis of the racemic and optically active [Co(L)(en)]$^+$ complexes, where L was eddp, tndp, or Me$_2$eddp.[18,19] In this paper, we describe a detailed study of the photolysis products of these Co(III) complexes.

Experimental

Ligands and Complexes. **Trimethylenediamine-**



Scheme 1.

***N*,*N*′-dipropionic Acid ($\mathbf{H_2}$tndp):** Diethyl trimethylenediamine-*N*,*N*′-dipropionate, which was a precursor of H_2tndp, was prepared by the following procedure. A solution containing ethyl acrylate (36.8 cm^3, 0.34 mol) and 1,3-propanediamine (14.2 cm^3, 0.17 mol) in 50 cm^3 of dioxane was refluxed for 6 h. After cooling, the pH of the solution was adjusted to 1 with concd HCl and then the solution was concentrated until white crystals (diethyl trimethylenediamine-*N*,*N*′-dipropionate hydrochloride) deposited. The crystals were recrystallized from hot ethanol.

To a solution containing diethyl trimethylenediamine-*N*,*N*′-dipropionate hydrochloride (90 g, 0.26 mol) in water (200 cm^3), sodium hydoxide (42 g, 1.04 mol) was added. The mixed solution was stirred at 50 °C for 2 h. The reaction solution was acidified to pH 1—2 with concd HCl and concentrated till NaCl deposited. After removal of the deposit, the filtrate was added dropwise to a large amount of acetone with vigorous stirring. The crystalline powder which deposited was filtered, washed with acetone, and air-dried. The purification of the crude product was carried out by adding acetone to its aqueous solution. Found: C, 36.92; H, 6.81; N, 9.53%. Calcd for H_2tndp·2HCl=$C_9H_{20}Cl_2N_2O_4$: C, 37.13; H, 6.92; N, 9.62%.

***N*,*N*′-Dimethylethylenediamine-*N*,*N*′-dipropionic Acid ($\mathbf{H_2Me_2}$eddp):** An aqueous solution (10 cm^3) of 3-chloropropionic acid (10.85 g) was neutralized with a solution of NaOH (4 g). A solution (ca. 15 cm^3) containing 4.41 g of *N*,*N*′-dimethylethylenediamine and 4 g of NaOH was slowly added to the above-mentioned solution; the mixed solution was stirred at 60—70 °C for 6 h. The pH of the reaction solution was adjusted to 1 with concd HCl and then concentrated under reduced pressure until NaCl deposited. *N*,*N*′-Dimethylethylenediamine-*N*,*N*′-dipropionic acid hydrochloride was obtained from the desalted solution by adding ethanol–acetone (1 : 2) mixture. The crude product was recrystallized from water upon addition of acetone. The constitution of the product was confirmed by its ^{1}H- and ^{13}C NMR data.[20)]

The other ligands and chemicals were obtained commercially.

***α*-, *β*(1)-, and *β*(2)-[Co(eddp)(en)]$^+$ Complexes:** Three isomers of [Co(eddp)(en)]$^+$ (eddp: ethylenediamine-*N*,*N*′-dipropionate) were prepared and optically resolved according to the method described in our previous paper:[21)] $(+)^{\rm CD}_{552}$-*Λ*(*R*,*R*)-*α*-[Co(eddp)(en)]Cl·3H$_2$O; $(-)^{\rm CD}_{536}$-*Λ*(*S*,*S**)-*β*(1)-[Co(eddp)(en)]Cl·3H$_2$O; $(-)^{\rm CD}_{563}$-*Λ*(*S*,*R**)-*β*(2)-[Co(eddp)(en)]Cl·0.5CH$_3$OH.

***β*-[Co(tndp)(en)]$^+$ Complex:** This red-purple complex was prepared by the same method as that for the eddp complex, except for the use of tndp·2HCl instead of eddp·2HCl. Only *β*-isomer was obtained. Found: C, 32.37; H, 7.18; N, 13.39%. Calcd for [Co(tndp)(en)]Cl·2H$_2$O=$C_{11}H_{28}ClCoN_4O_6$: C, 32.48; H, 6.93; N, 13.77%.

The racemate of *β*-[Co(tndp)(en)]$^+$ was resolved into optically active isomers by a chromatographic method like that used for *α*- and *β*(1)-[Co(eddp)(en)]$^+$.[21)]

***α*-[Co($\mathbf{Me_2}$eddp)(en)]$^+$ Complex:** This complex was prepared in a similar manner to that described in *β*-[Co(tndp)(en)]$^+$, except for the use of Me$_2$eddp·2HCl instead of tndp·2HCl. *β*-Isomer was not obtained by the method used here. Found: C, 31.87; H, 7.35; N, 12.22%. Calcd for [Co(Me$_2$eddp)(en)]Cl·4H$_2$O=$C_{12}H_{34}ClCoN_4O_8$: C, 31.55; H, 7.50; N, 12.26%.

The optical resolution of this complex was carried out as follows: A solution containing 9.14 g (0.02 mol) of *α*-[Co(Me$_2$eddp)(en)]Cl·4H$_2$O in 50 ml of warm water (60 °C) was added to a solution containing 8.72 g (0.02 mol) of silver *α*-bromo-(*d*)-camphor-*π*-sulfonate (AgBCS) with stirring. The resulted AgCl precipitates were filtered with suction and washed with a small amount of water. The filtrate and washings were combined and evaporated under reduced pressure until the solution became syrupy. After the syrupy solution was allowed to stand for ca. 2 h at room temperature, the crystals which deposited were filtered. The obtained diastereomer showed (+) CD sign at 595 nm. The diastereomer was recrystallized from water.

The $(+)^{\rm CD}_{595}$diastereomer (3.0 g) was dissolved in ca. 50 ml of water, and the solution was treated on a small Dowex 1X8 column (Cl$^-$ form, 6.0 cm×3.5 cm) by elution with water in order to convert BCS$^-$ ion to Cl$^-$ ion. The eluted solution was evaporated to a small volume. A mixture of ethanol–acetone was added to the concentrated solution until crystals began to deposit. After the solution was allowed to stand for ca. 2 h at room temperature, the light-violet needle crystals were filtered, washed with a mixture of ethanol–acetone, and dried in air. The recrystallization was carried out from water upon addition of ethanol–acetone mixture. The yield was 0.8 g. $\Delta\varepsilon_{590}=+0.26$.

Photolysis and Isolation of Products. 1) *α*-[Co($\mathbf{Me_2}$eddp)(en)]$^+$: The photolysis experiments reported in this paper were performed using an internal irradiating type of apparatus (Shigemi Standard Trading Co.). An aqueous solution containing 0.3 g of *α*-[Co(Me$_2$eddp)(en)]Cl·4H$_2$O in 250 cm^3 of water was irradiated with a 400 W high-pressure mercury lamp at ca. 5 °C for 15 min while bubbling N$_2$ gas through the solution. The resulting solution was chromatographed on an SP-Sephadex C-25 column (2.7 cm×60 cm, K$^+$ form) using 0.2 M KBr (M=mol dm^{-3}) as an eluent. The band adsorbed on the column was separated into three bands by recyclic development: purple (starting material), orange (*α*-[Co(Me$_2$eedmp)(en)]$^+$ [22)]), and pink bands in the order of elution. The eluate from the orange band was desalted by adding methanol and by passing through a Sephadex G-10 column. The desalted solution was concentrated again; to this NH$_4$PF$_6$ was added. The fine crystals which deposited were recrystallized from water. Found for the orange complex: C, 24.55; H, 5.34; N, 11.65%. Calcd for [Co(Me$_2$eedmp)(en)]PF$_6$·0.5H$_2$O·0.5NH$_4$PF$_6$ = $C_{11}H_{29}CoF_9N_{4.5}O_{2.5}P_{1.5}$: C, 24.43; H, 5.41; N, 11.66%.

Crystals suitable for X-ray diffraction measurements were obtained from the concentrated aqueous solution of the bromide salt, after the solution was kept in a refrigerator for at least one month.

Photolysis of optically active $(+)^{\rm CD}_{590}$-*α*-[Co(Me$_2$eddp)(en)]Cl was also performed in a similar manner to that described above: $(+)^{\rm CD}_{490}$-*α*-[Co(Me$_2$eddmp)(en)]$^+$ was obtained.

2) *β*-[Co(tndp)(en)]$^+$: An aqueous solution containing 0.28 g of *β*-[Co(tndp)(en)]Cl·2H$_2$O in 250 cm^3 of water was irradiated with a 400 W high-pressure mercury lamp at ca. 5 °C. The resulting solution was chromatographed on an SP-Sephadex C-25 column (3.3 cm×65 cm, Na$^+$ form) using 0.2 M NaClO$_4$ as an eluent. The band adsorbed on the column was separated into three bands by recyclic development: Brownish-violet (β-[Co(etnmp)(en)]$^{+}$ [22]), red-purple (starting material), and pink bands in the order of elution. The eluate from the brownish-violet band was evaporated to 10 cm^3, and then passed through a Sephadex G-10 column using water as an eluent in order to eliminate $NaClO_4$. The eluate was again concentrated nearly to dryness to give brownish-violet crystalline powder. The crude product was recrystallized from water–dioxane. Found for the brownish-violet complex: C, 17.62; H, 4.15; N, 8.18%. Calcd for [Co(etnmp)(en)]$ClO_4 \cdot 2NaClO_4 \cdot 2H_2O$= $C_{10}H_{28}Cl_3CoN_4Na_2O_{16}$: C, 17.88; H, 4.20; N, 8.34%.

Photolysis of optically active β-[Co(tndp)(en)]$^{+}$ was also performed in the same manner as described above.

3) [Co(eddp)(en)]$^{+}$: The photolysis of [Co(eddp)(en)]$^{+}$ (racemic and optically active α-, β(1)-, and β(2)-isomers) and the isolation of the photolysis products were carried out in a similar manner to that described above. When the photoreaction solution of Λ-α-isomer was chromatographed on an SP-Sephadex C-25 column using 0.2 M $NaClO_4$ as an eluent, the violet (starting material) and orange bands were eluted out in the order of elution. $(+)^{\mathrm{CD}}_{483}$-α-[Co(eedmp)(en)]$^{+}$ [22] was isolated as perchlorate from the eluate of the orange band. Found: C, 28.82; H, 5.98; N, 14.68%. Calcd for [Co(eedmp)(en)]ClO_4=$C_9H_{22}ClCoN_4O_6$: C, 28.69; H, 5.88; N, 14.87%.

In the chromatography of the photoreaction solution of Λ-β(1)-isomer, three bands were eluted out: orange, red-purple, and red-violet (starting material) in the order of elution. The complex obtained from the eluate of the orange band was $(-)^{\mathrm{CD}}_{483}$-α-[Co(eedmp)(en)]$^{+}$. As the eluate of the red-purple was very slight in amount, the complex could not be isolated from the eluate.

In the development of the photoreaction solution of racemic β(2)-isomer on an SP-Sephadex C-25 column, three bands were separated out: orange (minor, α-[Co(eedmp)(en)]$^{+}$), red-purple (major), and red-violet (starting material). β-[Co(eedmp)(en)]$^{+}$ was isolated as ClO_4 salt from the eluate of the red-purple band. Found: C, 28.76; H, 5.90; N, 14.78%. Calcd for [Co(eedmp)(en)]ClO_4=$C_9H_{22}ClCoN_4O_6$: C, 28.69; H, 5.88; N, 14.87%.

In the photolysis of Λ-β(2)-isomer, $(+)^{\mathrm{CD}}_{483}$-α-[Co(eedmp)(en)]$^{+}$ and $(-)^{\mathrm{CD}}_{543}$-β-[Co(eedmp)(en)]$^{+}$ were obtained.

Measurements. The absorption and CD spectra were measured by a JASCO UVIDEC-670 spectrophotometer and a JASCO J-720 spectropolarimeter, respectively. The ^{13}C NMR spectra were recorded on a Hitachi R-90H spectrometer in a D_2O solution relative to internal reference of dioxane (67.4 ppm).

Crystallography. X-Ray Data Collection. A single crystal (ca. 0.38×0.50×0.50 mm^3) of [Co(Me_2eedmp)(en)]$Br \cdot 1.5H_2O$ was used for data collection on Enraf Nonius CAD4 diffractometer with a graphite-monochromatized Mo $K\alpha$ (0.71073 Å) radiation. Unit cell parameters were determined by least-squares refinements based on 25 reflections with $16^\circ < 2\theta < 20^\circ$.

Crystal Data: $C_{11}H_{26}BrCoN_4O_2 \cdot 1.5H_2O$, F.W.= 412.21, Monoclinic, space group $P2_1/n$ (No. 14), a= 9.013(2), b=13.420(1), c=14.754(4) Å, β=92.75(1)°, V= 1782.5(6) Å^3, Z=4, D_{calcd}=1.54 g cm^{-3}, $F(000)$=852, μ(Mo $K\alpha$)=32.0 cm^{-1}, and room temperature.

The intensity data were collected by the ω–2θ scan technique up to 2θ=50° with scan width (0.80+0.4 tan θ)° and the scan rate varied from 1 to 5° min^{-1} (on ω). The intensities were corrected for Lorentz and polarization. An empirical absorption corrections based on a series of Ψ scans were applied (max and min transmission factors 1.00 and 0.94). A total of 2715 independent reflections with $F_o > 3\sigma\ (F_o)$ of the measured 3438 reflections were considered as 'observed' and were used for structure determination.

Determination of Crystal Structure. The positions of cobalt and some donor atoms were determined by the direct method. The remaining non-hydrogen and hydrogen atoms were found by successive difference Fourier maps to give a trial structure. The structure was refined by a full-matrix least-squares on F using the anisotropic thermal parameters for non-hydrogen atoms and the isotropic thermal parameters for hydrogen atoms. The oxygen atoms of the water molecules exhibited positional disorder [occupancy factors: O (1W), 0.5; O (2W) to O (5W), 0.25]. All calculations were performed on VAX computer using the crystallographic package MOLEN.[23] The final refinement gave R=0.038, R_{w}=0.045, ($w=4F_o^2/\sigma^2(F_o)^2$). The largest parameter shift was 0.03 times e.s.d. and $|\Delta\rho|_{\max}$ in the final difference Fourier map was 0.90 eÅ^{-3}. The final atomic coordinates for non-hydrogen atoms are given in Table 1.[24]

Results and Discussion

Characterization of [Co(Me_2eddp)(en)]$^{+}$ and [Co(tndp)(en)]$^{+}$. The complex ions in the heading provide two possible geometrical isomers of α and β. The α isomer has a *trans*(O)-[Co(N)$_4$(O)$_2$]-type struc-

Table 1. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (B_{eq}/Å^2)$^{\mathrm{a)}}$ for Non-H Atoms of [Co(Me_2eedmp)(en)]$Br \cdot 1.5H_2O$

Atom	x	y	z	$B_{\mathrm{eq}}$$^{\mathrm{a)}}$
Co	0.70500(7)	0.64914(5)	0.33582(4)	2.59(1)
O(1)	0.7701(4)	0.7944(3)	0.3461(3)	3.96(8)
O(2)	0.9589(5)	0.8849(3)	0.3995(3)	5.5(1)
N(1)	0.8372(5)	0.6241(3)	0.2316(3)	3.28(9)
N(2)	0.5410(5)	0.6676(4)	0.2442(3)	3.8(1)
N(3)	0.5832(5)	0.6836(4)	0.4380(3)	3.68(9)
N(4)	0.8500(4)	0.6036(3)	0.4308(3)	2.95(8)
C(1)	0.9049(6)	0.8197(4)	0.3488(4)	3.8(1)
C(2)	1.0047(6)	0.7671(4)	0.2844(4)	3.8(1)
C(3)	0.9225(6)	0.7154(4)	0.2072(4)	3.9(1)
C(4)	0.7327(7)	0.6002(5)	0.1526(4)	4.5(1)
C(5)	0.6032(7)	0.6673(5)	0.1528(4)	5.0(1)
C(6)	0.4772(6)	0.5679(5)	0.2668(4)	4.1(1)
C(7)	0.6005(6)	0.5219(4)	0.3235(4)	3.5(1)
C(8)	0.9439(7)	0.5414(5)	0.2448(4)	4.5(1)
C(9)	0.4352(7)	0.7497(6)	0.2517(5)	5.7(2)
C(10)	0.6502(6)	0.6417(5)	0.5246(4)	4.2(1)
C(11)	0.8150(6)	0.6478(5)	0.5190(3)	3.8(1)
Br	0.22256(6)	0.63292(5)	0.47956(4)	3.96(1)
O(1W)	0.734(1)	0.0919(8)	0.5927(6)	6.7(2)
O(2W)	0.667(1)	−0.092(1)	0.527(1)	5.8(3)
O(3W)	0.559(2)	−0.089(1)	0.507(1)	6.4(5)
O(4W)	0.832(2)	−0.028(1)	0.5377(9)	3.8(3)
O(5W)	0.718(1)	−0.1136(9)	0.528(1)	4.0(3)

a) $B_{\mathrm{eq}}=(8\pi^2/3)\sum_i \sum_j U_{ij}\, a_i^*\, a_j^*\, \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

ture with C_2 symmetry and the β isomer has a *cis*(O)-$[Co(N)_4(O)_2]$-type one with C_1 symmetry. The absorption spectra of $[Co(Me_2eddp)(en)]^+$ and $[Co(tndp)(en)]^+$ are shown in Figs. 1 and 2, and their numerical data are listed in Table 2. On the basis of these spectral patterns, the geometry of $[Co(Me_2eddp)(en)]^+$ was assigned to the α form and that of $[Co(tndp)(en)]^+$ to the β form. These assignments were also confirmed by the ^{13}C NMR spectral data; $[Co(Me_2eddp)(en)]^+$, which was assigned to the α form, showed 6 signal peaks due to 12 carbons, and $[Co(tndp)(en)]^+$, which was assigned to the β form, showed 11 signal peaks due to 11 carbons.[25]

The CD data of those complexes are also shown in Figs. 1 and 2 and Table 2. The $(+)^{CD}_{590}$-α-$[Co(Me_2eddp)(en)]^+$ isomer is considered to take the Λ configuration, because the CD spectral behavior in the visible region is similar to that of Λ-α-$[Co(eddp)(en)]^+$.[21] The $(-)^{CD}_{505}$-β-$[Co(tndp)(en)]^+$ isomer shows a CD spectral pattern similar to that of Δ-β(1)-$[Co(eddp)(en)]^+$.[21] Accordingly, $(-)^{CD}_{505}$-β-$[Co(tndp)(en)]^+$ is thought to have the Δ configuration.

Photolysis Product of α-$[Co(Me_2eddp)(en)]^+$ (α-$[Co(Me_2eedmp)(en)]^+$). The structure of the orange complex, which was obtained by the photolysis of α-$[Co(Me_2eddp)(en)]^+$, was revealed by the X-ray analysis. A perspective drawing of the complex cation is shown in Fig. 3, together with its atomic numbering scheme. The main bond distances and angles within the complex cation are summarized in Table 3. The cobalt atom is octahedrally surrounded by two N atoms of the en ligand and a C atom, two N atoms, and an O atom

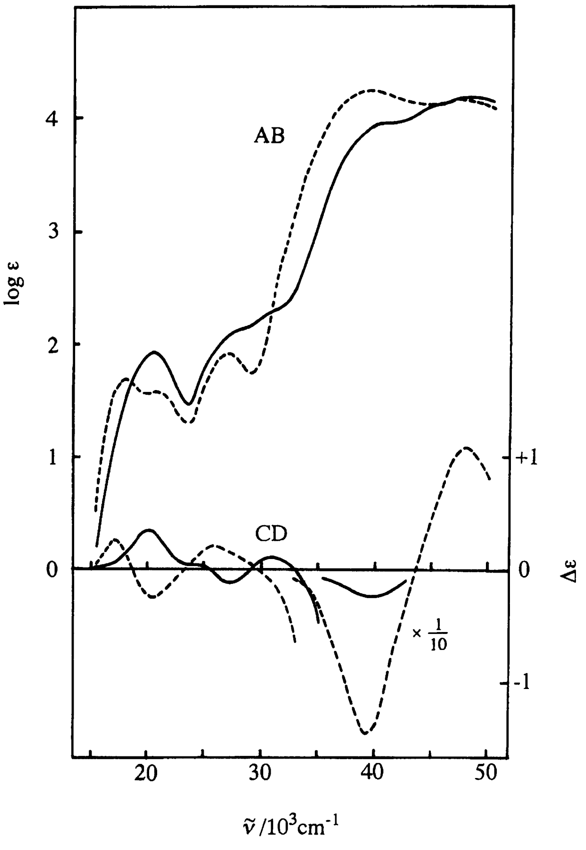


Fig. 1. Absorption and CD spectra of the $(+)^{CD}_{590}$-α-$[Co(Me_2eddp)(en)]^+$ (---) and $(+)^{CD}_{490}$-α-$[Co(Me_2eedmp)(en)]^+$ (orange) (—) complexes.

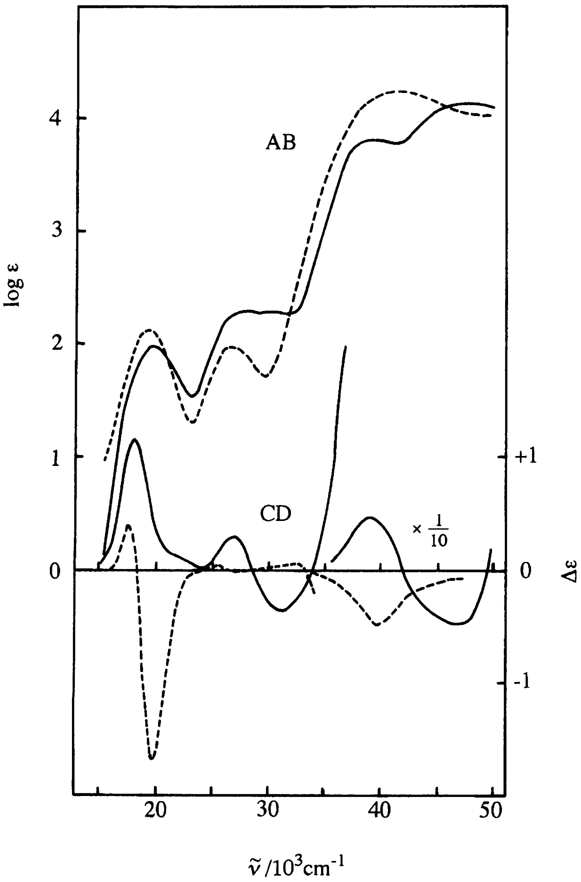


Fig. 2. Absorption and CD spectra of the $(-)^{CD}_{505}$-β-$[Co(tndp)(en)]^+$ (---) and $(+)^{CD}_{553}$-β-$[Co(etnmp)(en)]^+$ (brownish-violet) (—) complexes.

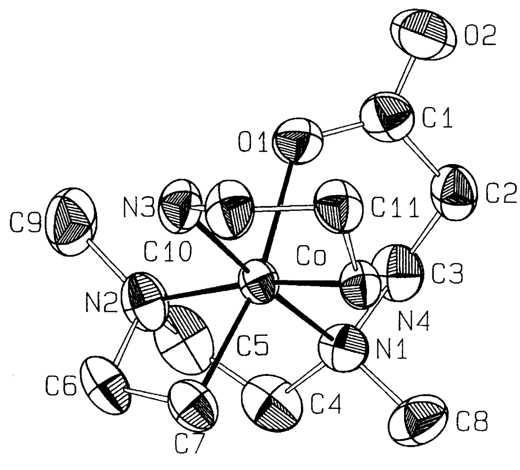


Fig. 3. A perspective drawing of the α-$[Co(Me_2eedmp)(en)]^+$ complex with the atom-numbering scheme.

Table 2. Absorption and CD Spectral Data of the Complexes

Complex	Absorption band[a)] $\nu/10^3$ cm^{-1} (log ε)	CD band[a)] $\nu/10^3$ cm^{-1} ($\Delta\varepsilon$)
Λ-α-$(+)^{CD}_{590}$-[Co(Me$_2$eddp)(en)]$^+$	17.89 (1.69)	16.95 (+0.26)
	20.70 (1.56)	20.37 (−0.25)
	26.74 (1.91)	25.77 (+0.21)
	38.91 (4.29)	39.53 (−14.77)
	46.95 (4.08)	48.31 (+11.12)
Λ-α-$(+)^{CD}_{490}$-[Co(Me$_2$eedmp)(en)]$^+$	20.24 (1.94)	20.41 (+0.34)
	27.0 (2.1sh)[b)]	24.10 (+0.046)
	31.3 (2.3sh)	27.32 (−0.12)
	40.0 (3.9sh)	30.49 (+0.092)
	48.08 (4.47)	39.68 (−2.30)
Δ-β-$(-)^{CD}_{505}$-[Co(tndp)(en)]$^+$	19.42 (2.14)	17.61 (+0.41)
	26.81 (1.99)	19.80 (−1.66)
	41.32 (4.29)	39.84 (−4.92)
β-$(+)^{CD}_{553}$-[Co(etnmp)(en)]$^+$	19.61 (1.98)	18.08 (+1.08)
	27.70 (2.31)	22.0 (+0.1sh)
	29.9 (2.3sh)	27.03 (+0.32)
	39.22 (3.85)	31.06 (−0.35)
	46.73 (4.17)	39.37 (+4.81)
		47.17 (−4.43)
Λ-α-$(+)^{CD}_{483}$-[Co(eedmp)(en)]$^+$	21.01 (2.00)	20.70 (+1.32)
	28.0 (2.1sh)	40.32 (−22.58)
	32.6 (2.3sh)	
	40.49 (3.92)	
β-$(-)^{CD}_{543}$-[Co(eedmp)(en)]$^+$	19.23 (1.99)	18.42 (−1.60)
	27.47 (2.26)	21.55 (+1.76)
	39.06 (3.87)	27.03 (−0.74)
		30.7 (−0.3sh)
		38.5 (+5.1sh)

a) ε and $\Delta\varepsilon$ values are given in units of mol^{-1} dm^3 cm^{-1}. b) sh denotes a shoulder.

Table 3. Selected Bond Distances (Å) and Angles (°) for [Co(Me$_2$eedmp)(en)]$^+$

Co–O(1)	2.040(4)	N(1)–C(4)	1.497(7)
Co–N(1)	2.018(4)	N(1)–C(8)	1.475(7)
Co–N(2)	1.970(4)	N(2)–C(5)	1.485(7)
Co–N(3)	1.962(4)	N(2)–C(6)	1.500(8)
Co–N(4)	1.967(4)	N(2)–C(9)	1.465(8)
Co–C(7)	1.954(6)	N(3)–C(10)	1.496(7)
O(1)–C(1)	1.261(7)	N(4)–C(11)	1.477(7)
N(1)–C(3)	1.499(7)		
O(1)–Co–N(1)	92.2(2)	Co–N(1)–C(4)	104.9(3)
O(1)–Co–C(7)	167.9(2)	Co–N(1)–C(8)	115.4(3)
N(1)–Co–N(2)	87.1(2)	Co–N(2)–C(5)	108.6(3)
N(1)–Co–N(3)	175.7(2)	Co–N(2)–C(6)	91.1(3)
N(2)–Co–N(4)	168.2(2)	Co–N(2)–C(9)	120.9(4)
N(2)–Co–C(7)	72.8(2)	Co–N(3)–C(10)	110.5(3)
N(3)–Co–N(4)	84.4(2)	Co–N(4)–C(11)	109.9(3)
Co–O(1)–C(1)	122.2(3)	Co–C(7)–C(6)	91.9(4)
Co–N(1)–C(3)	112.1(3)		

of the tetradentate Me$_2$eedmp ligand.[22)] The discovery of such a complex cation in the composition of the photolysis product indicates that the reaction of Scheme 1 occurred on one of the two carboxyl groups of the coordinated Me$_2$eddp. The coordination of the Me$_2$eedmp ligand to Co results in the formation of three types of chelate rings: a six-membered β-alaninate ring, a five-membered ethylenediamine ring, and a four-membered Co–C–C–N ring. The relative positions of these rings correspond to the α-isomer: Both the β-alaninate and the four-membered rings are perpendicular to the ethylenediamine ring.

The formation of the Co–C–C–N four-membered ring introduces significant distortions into the octahedral coordination around the Co atom. The ∠N(2)–Co–C(7) angle (72.8°) is reduced from the octahedral angle. In addition, the ∠O(1)–Co–C(7) (167.9°) and ∠N(2)–Co–N(4) (168.2°) angles differ significantly from 180°. The coordination of C atom to Co center results in elongation of the Co–O(1) bond (2.040 Å) located in the trans position of the C atom, compared with ordinary Co–O bonds (for example, 1.895—1.936 Å in α, β(1), and β(2) isomers of [Co(eddp)(en)]$^+$ [26)]). A similar trans influence has been noted for a number of Co(III) complexes containing Co–C σ-bond.[14,15)] The length of the Co–C(7) bond (1.954 Å) in the present complex is usual for a Co–C σ-bond length.[14,15,17)] The four-membered ring is practically planar and the sum of the endocyclic angles is equal to 357.9°.

The absorption maximum of $[\mathrm{Co(Me_2eedmp)(en)}]^+$ in the first absorption band region shifts to the high energy side compared to that (the mean of the splitting components) of α-$[\mathrm{Co(Me_2eddp)(en)}]^+$ (Fig. 1 and Table 2). This shift in the first absorption band region results from the ligand-field of the ligating C atom being stronger than that of the ligating O atom in the carboxyl group.

In the ^{13}C NMR spectrum of α-$[\mathrm{Co(Me_2eedmp)(en)}]^+$,27) a slightly broad signal was observed at very high magnetic field (−2.88 ppm), where no signal was observed in the spectrum of α-$[\mathrm{Co(Me_2eddp)(en)}]^+$. This signal at −2.88 ppm is attributable to the carbon σ-bonded to the Co(III). A ^{13}C NMR signal due to only one carboxyl carbon was found at 184.12 ppm.

Photolysis Product of β-[Co(tndp)(en)]$^+$ (β-[Co(etnmp)(en)]$^+$). The brownish-violet complex obtained by the photolysis of β-$[\mathrm{Co(tndp)(en)}]^+$ shows 10 signal peaks in the ^{13}C NMR spectrum.28) A signal at very high magnetic field (−6.75 ppm), where no signal was observed in β-$[\mathrm{Co(tndp)(en)}]^+$, was assigned to the carbon σ-bonded to Co(III). A ^{13}C NMR signal due to only one carboxyl carbon was found at 182.29 ppm. These results indicate that the brownish-violet complex is $[\mathrm{Co(etnmp)(en)}]^+$: The photodecarboxylation occurred on one of two carboxyl groups in β-$[\mathrm{Co(tndp)(en)}]^+$.

In order to confirm the geometrical structure of the brownish-violet complex, the X-ray analysis was performed.29) A perspective drawing of the complex cation is shown in Fig. 4. The octahedral coordination of the Co atom on the complex cation involves two N atoms of the en molecule and a C atom, two N atoms, and an O atom of the tetradentate etnmp ligand.22) The complex cation has a β-structure, where the $\overline{\mathrm{Co{-}C{-}C{-}N}}$ four membered chelate ring is perpendicular to the tn ring of the tetradentate ligand.

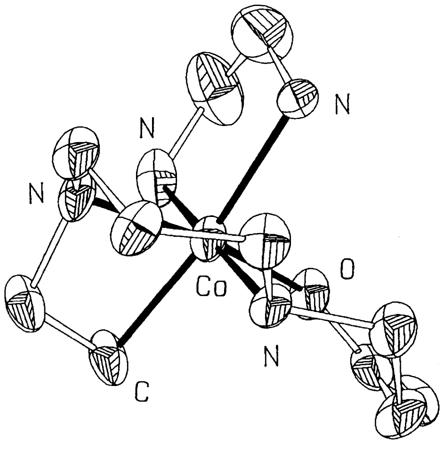


Fig. 4. A perspective drawing of the β-$[\mathrm{Co(etnmp)(en)}]^+$ complex.

The spectral data of β-$[\mathrm{Co(etnmp)(en)}]^+$ are shown in Fig. 2 and Table 2.

Photolysis Products of [Co(eddp)(en)]$^+$ (α- and β-[Co(eedmp)(en)]$^+$). Aqueous solutions of all three isomers, α, β(1), and β(2), of $[\mathrm{Co(eddp)(en)}]^+$ were irradiated with ultraviolet light. (The two β isomers are conformational diastereomers arising from a difference of the chirality around one of the asymmetric N atoms in the coordinated eddp ligand.26)) Photolysis of α-isomer provided the orange complex, which showed nine signal peaks due to nine carbons in the ^{13}C NMR spectrum.30) The ^{13}C signal at −5.01 ppm provides evidence for the formation of Co–C bond. A signal due to only one carboxyl carbon was found at 182.38 ppm. These spectral results and the elemental analysis indicate that the orange complex is $[\mathrm{Co(eedmp)(en)}]^+$.

Photolysis of β(1)-$[\mathrm{Co(eddp)(en)}]^+$ provided two decarboxylation products: The orange complex, which was identical with the photolysis product of α-$[\mathrm{Co(eddp)(en)}]^+$, and the red-violet complex, of which the amount was very small. On the other hand, in the photolysis of β(2)-$[\mathrm{Co(eddp)(en)}]^+$, the red-violet complex was a major product and the orange complex was a minor one. The ^{13}C NMR spectrum of the red-violet complex shows nine signal peaks due to nine carbons.31) The resonances at −4.44 and 180.97 ppm indicate that the red-violet complex is also $[\mathrm{Co(eedmp)(en)}]^+$. The elemental analysis supports this assignment.

Poznyak et al. have isolated orange and red-violet isomers of $[\mathrm{Co(eedmp)(phen)}]^+$ and assigned the former to α-isomer and the latter to β one.15) We also prepared these two isomers. The first d–d band peaks of α- and β-$[\mathrm{Co(eedmp)(phen)}]^+$ were observed at 20920 and 19250 cm^{-1}, respectively. These peak positions coincided very closely with those of the orange (21010 cm^{-1}) and red-violet (19230 cm^{-1}) isomers in the $[\mathrm{Co(eedmp)(en)}]^+$ system. In addition, the spectral patterns of the orange and red-violet isomers of $[\mathrm{Co(eedmp)(en)}]^+$ are similar to those of the α-$[\mathrm{Co(Me_2eedmp)(en)}]^+$ and β-$[\mathrm{Co(etnmp)(en)}]^+$ complexes, respectively (Figs. 1, 2, and 5). Therefore, we assigned the orange isomer of $[\mathrm{Co(eedmp)(en)}]^+$ to α one and the red-violet isomer to β one.

Photolysis of Optically Active [Co(Me$_2$eddp)(en)]$^+$. As is shown in Table 4, optically active $(+)^{\mathrm{CD}}_{490}$-α-$[\mathrm{Co(Me_2eedmp)(en)}]^+$ was obtained in the photolysis of $(+)^{\mathrm{CD}}_{590}$-$\Lambda(R,R)$-α-$[\mathrm{Co(Me_2eddp)(en)}]^+$.32) The possible configurations for α-$[\mathrm{Co(Me_2eedmp)(en)}]^+$ are $\Lambda(R,S')$ and $\Delta(S,R')$.32) The change from $\Lambda(R,R)$-α-$[\mathrm{Co(Me_2eddp)(en)}]^+$ to $\Delta(S,R')$-α-$[\mathrm{Co(Me_2eedmp)(en)}]^+$ must be very difficult.33) This change requires the inversion at two coordinated tertiary N atoms, but, it is impossible to invert at the tertiary N atoms without the fission of the Co–N bonds. Accordingly, the configuration of $(+)^{\mathrm{CD}}_{490}$-α-$[\mathrm{Co(Me_2eedmp)(en)}]^+$ was assigned to $\Lambda(R,S')$.33) The empirical rule, in which the Λ iso-

Table 4. The Photolysis Products Obtained from the Optically Active [Co(Me$_2$eddp)(en)]$^+$ and [Co(eddp)(en)]$^+$ Complexes

Starting material	Product	Absolute configuration
$(+)^{\mathrm{CD}}_{590}$-$\Lambda(R,R)$-α-[Co(Me$_2$eddp)(en)]$^+$	$(+)^{\mathrm{CD}}_{490}$-α-[Co(Me$_2$eedmp)(en)]$^+$	$\Lambda(R,S')$
$(+)^{\mathrm{CD}}_{552}$-$\Lambda(R,R)$-α-[Co(eddp)(en)]$^+$	$(+)^{\mathrm{CD}}_{483}$-α-[Co(eedmp)(en)]$^+$	$\Lambda(R,S')$
$(-)^{\mathrm{CD}}_{536}$-$\Lambda(S,S^*)$-$\beta(1)$-[Co(eddp)(en)]$^+$	$(-)^{\mathrm{CD}}_{483}$-α-[Co(eedmp)(en)]$^+$	$\Delta(S,R')$
$(-)^{\mathrm{CD}}_{563}$-$\Lambda(S,R^*)$-$\beta(2)$-[Co(eddp)(en)]$^+$	$(-)^{\mathrm{CD}}_{543}$-β-[Co(eedmp)(en)]$^+$	$\Lambda(R$ or $S,R')$
	$(+)^{\mathrm{CD}}_{483}$-α-[Co(eedmp)(en)]$^+$	$\Lambda(R,S')$

The abbreviations used for expressing the absolute configuration are shown in Ref. 32.

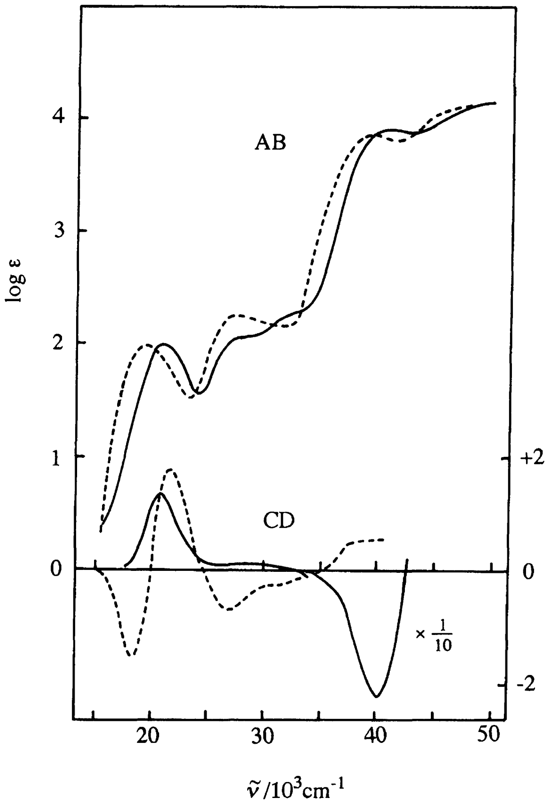


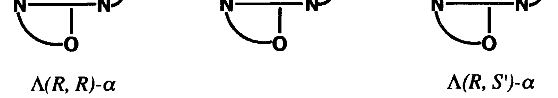
Fig. 5. Absorption and CD spectra of [Co(eedmp)(en)]$^+$: $(+)^{\mathrm{CD}}_{483}$-α (orange) isomer (——), $(-)^{\mathrm{CD}}_{543}$-β (red-violet) isomer (- - -).

mer has a dominant CD peak with a positive sign at the longer wavelength, seems to be maintained even in this complex with the ligating C atom (Fig. 1 and Table 2).[34]

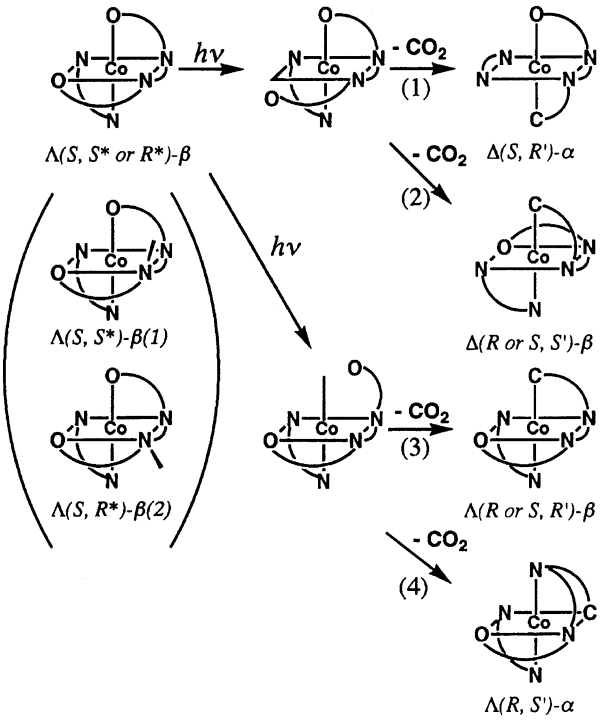
Photolysis of Optically Active [Co(eddp)(en)]$^+$. The photolysis data concerning the optically active [Co(eddp)(en)]$^+$ system are summarized in Table 4. The photolysis of $(+)^{\mathrm{CD}}_{552}$-$\Lambda(R,R)$-α-[Co(eddp)(en)]$^+$ provided $(+)^{\mathrm{CD}}_{483}$-α-[Co(eedmp)(en)]$^+$, but did not β-type products. In the photolysis of $(-)^{\mathrm{CD}}_{536}$-$\Lambda(S,S^*)$-$\beta(1)$-[Co(eddp)(en)]$^+$,[32] $(-)^{\mathrm{CD}}_{483}$-α-[Co(eedmp)(en)]$^+$ was obtained as a major decarboxylation product, and showed optical purity comparable with that of $(+)^{\mathrm{CD}}_{483}$-α-[Co(eedmp)(en)]$^+$ formed from the optically active α-[Co(eddp)(en)]$^+$. (The β-type decarboxylation product was obtained as a minor product, but its amount was too small to clarify whether the product was optically active or not.) The photolysis of $(-)^{\mathrm{CD}}_{563}$-$\Lambda(S,R^*)$-$\beta(2)$-[Co(eddp)(en)]$^+$ resulted in the formations of $(-)^{\mathrm{CD}}_{543}$-β-[Co(eedmp)(en)]$^+$ (major product) and $(+)^{\mathrm{CD}}_{483}$-α-[Co(eedmp)(en)]$^+$ (minor product). The optical purity of $(+)^{\mathrm{CD}}_{483}$-α-[Co(eedmp)(en)]$^+$ formed from $\Lambda(S,R^*)$-$\beta(2)$-[Co(eddp)(en)]$^+$ was low; its value was about 17% of that of α-[Co(eedmp)(en)]$^+$ obtained from $\Lambda(R,R)$-α-[Co(eddp)(en)]$^+$.

In order to explain the stereochemistry in the photodecarboxylation reaction of the [Co(eddp)(en)]$^+$ system, we propose the reaction paths shown in Schemes 2 and 3. When the three-steps-reaction of Scheme 1 occurs in α-[Co(eddp)(en)]$^+$, it is quite likely that the path of Scheme 2 prevails: The vacant position of the intermediate is occupied by the CH$_2$ radical of the decarboxylated ligand. Accordingly, $\Lambda(R,R)$-α-[Co(eddp)(en)]$^+$ changes to $\Lambda(R,S')$-α-[Co(eedmp)(en)]$^+$: the configuration of $(+)^{\mathrm{CD}}_{483}$-α-[Co(eedmp)(en)]$^+$ is assigned to $\Lambda(R,S')$. This assignment is also supported by the fact that the CD spectral behavior is similar to that of $\Lambda(R,S')$-α-[Co(Me$_2$eedmp)(en)]$^+$.

In the β-type isomers of [Co(eddp)(en)]$^+$, the two β-alaninate rings of the coordinated eddp ligand are in different situations: One lies in the same plane with the en ring of the eddp (in-plane β-ala) and the other is perpendicular to the en ring (our-of-plane β-ala). When the three-steps-reactions of Scheme 1 occurs in the in-plane β-ala, it is thought that the vacant position of the intermediate can not be occupied by the CH$_2$ radical of the decarboxylated ligand because of the high strain of the adjacent two chelate rings (4 and 5 membered rings) in the same plane. Therefore, the decarboxylation reactions through the paths of (1) and (2) in Scheme 3 are expected to occur. However, the path (2), in which three coordination sites are exchanged, can be presumed to be the minor one from the results of the coordination-site exchange reactions of the amino car-



Scheme 2.



Scheme 3.

boxylato cobalt(III) complexes.[35] When the reaction of Scheme 1 occurs in the out-of-plane β-ala, paths (3) and (4) are thought to prevail. The same idea as the path (4) has been proposed in the coordination-site exchange reaction of the amino carboxylato cobalt(III) complexes.[21,35] Thus the vacant position in the intermediate is occupied by the neighboring imino N atom of the decarboxylated ligand, with an accompanying concurrent shift of the CH_2 radical to the position vacated by the imino N atom.

The results in the photolyses of $\Lambda(S,S^*)$-$\beta(1)$- and $\Lambda(S,R^*)$-$\beta(2)$-[Co(eddp)(en)]$^+$ may be explained by assuming as follows. (i) The decarboxylation reaction occurs easily in the in-plane β-ala ring rather than in the out-of-plane β-ala ring. (ii) The path without the inversion at imino N center is predominant. Consequently, in the photolysis of $\beta(1)$-isomer, the reaction through the path (1) preferentially occurs, because the inversion at the imino N atom of the in-plane β-ala is not required. In the case of the photolysis of $\beta(2)$-isomer, however, no path in Scheme 3 can advantageously satisfy both these assumptions: The reactions through the paths of (1), (3), and (4) in Scheme 3 are expected to occur. (As mentioned above, the path (2), in which three coordination sites are exchanged, is thought to be minor.) Judging from the mechanistic consideration described above, we take the absolute configuration of $(-)^{\rm CD}_{543}$-β-[Co(eedmp)(en)]$^+$ to be Λ. The occurrence of both (1) and (4) paths is supported by the fact that the optical purity of Λ-α-[Co(eedmp)(en)]$^+$ formed from $\Lambda(S,R^*)$-$\beta(2)$-[Co(eddp)(en)]$^+$ is low.

Photolysis of Optically Active β-[Co(tndp)(en)]$^+$. Photolysis of $(-)^{\rm CD}_{505}$-β-[Co(tndp)(en)]$^+$, which was assigned to Δ on the basis of the CD spectral behavior, resulted in the formation of optically active decarboxylation product, $(+)^{\rm CD}_{553}$-β-[Co(etnmp)(en)]$^+$ (Fig. 2 and Table 2). In this photolysis, however, it is not clear which carboxyl group of the coordinated tndp ligand was eliminated out. This obscurity makes it difficult to estimate the configuration of the $(+)^{\rm CD}_{553}$-β-[Co(etnmp)(en)]$^+$.

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20) The chemical shifts (ppm) of ^{13}C NMR peaks: 29.56, 41.70, 50.97, 53.41, 174.30.

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22) Abbreviations used: Me$_2$eedmp, $^-$CH$_2$CH$_2$N(CH$_3$)CH$_2$CH$_2$N(CH$_3$)CH$_2$CH$_2$COO$^-$; etnmp, $^-$CH$_2$CH$_2$NHCH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$COO$^-$; eedmp, $^-$CH$_2$CH$_2$NHCH$_2$CH$_2$NHCH$_2$CH$_2$COO$^-$.

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24) Lists of structure factors, hydrogen atom coordinates, bond distances and angles, and anisotropic thermal parameters for non-hydrogen atoms are deposited as Document No. 68010 at the Office of the Editor of Bull. Chem. Soc. Jpn.

25) The chemical shifts (ppm) of ^{13}C NMR peaks: α-[Co(Me$_2$eddp)(en)]$^+$, δ=31.48, 45.02, 50.69, 58.71, 61.06, 179.36; β-[Co(tndp)(en)]$^+$, δ=21.94, 34.12, 34.35, 43.34, 46.00, 47.34, 47.95, 51.00, 51.21, 181.61, 184.76.

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27) The chemical shifts (ppm) of ^{13}C NMR peaks: δ=−2.88, 32.92, 43.43, 43.86, 47.61, 47.92, 57.31, 60.69, 60.87, 70.08, 184.12.

28) The chemical shifts (ppm) of ^{13}C NMR peaks: δ=−6.75, 22.76, 34.56, 42.40, 44.44, 45.57, 50.78, 51.94, 55.36, 182.29.

29) The crystal data are as follows: $C_{12}H_{28.5}N_4O_{8.75}CoCl$, F.W.=463.27, monoclinic, space group $C2/m$, a=25.681(9), b=24.655(4), c=7.350(3) Å, β=94.92(2)°, Z=8, D_{calcd}=1.33 g cm^{-3}, $D_{\mathrm{meas.}}$=1.47 g cm^{-3}, λ(Mo $K\alpha$)=0.71069 Å, μ=9.30 cm^{-1}, R=0.088, R_{w}=0.089 for 1472 reflections. The result is not so satisfactory, however, the arrangement of the chelate rings around the cobalt center can be reliable.

30) The chemical shifts (ppm) of ^{13}C NMR peaks: δ=−5.01, 32.43, 44.04, 44.44, 49.01, 49.26, 52.89, 57.77, 182.38.

31) The chemical shifts (ppm) of ^{13}C NMR peaks: δ=−4.44, 35.54, 43.16, 46.27, 48.89, 52.19, 58.83, 59.02, 180.97.

32) R and S denote the chiralities of the secondary (or tertiary) N atoms in the out-of-plane β-alaninate rings and R^* and S^* denote those in the in-plane β-alaninate rings. S' and R' denote the chiralities around the coordinated secondary (or tertiary) N atoms of the $\overline{\mathrm{Co{-}C{-}C{-}N}}$ four membered rings.

33) The change from R to R' means the inversion at the tertiary N atom of the four membered ring, but is due to "nomenclature". The change from R to S' does not mean the inversion.

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