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Crystal Structures of the (Ethylenediamine-*N*,*N'*-dipropionato)(ethylenediamine)cobalt(III) Isomers

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The crystal structures of the isomers (one α and two β) of $[\mathrm{Co(eddp)(en)}]^+$ were determined by X-ray diffraction methods. Crystal data for $(-)^{\mathrm{CD}}_{552}$-$\Delta(S,S)$-α-$[\mathrm{Co(eddp)(en)}]\mathrm{Br}\cdot 5\mathrm{H_2O}$ (**1**) are monoclinic with space group $P2_1$: $a=10.558(2)$, $b=8.523(2)$, $c=11.868(2)$ Å, $\beta=112.11(1)°$, and $Z=2$. Crystal data for $(+)^{\mathrm{CD}}_{536}$-$\Delta(R,R^*)$-β(e-1)-$[\mathrm{Co(eddp)(en)}]\mathrm{Br}\cdot\mathrm{H_2O}$ (**2-a**) are orthorhombic with $P2_12_12_1$: $a=11.809(2)$, $b=16.144(2)$, $c=8.340(2)$ Å, and Z=4. *rac*-β(e-1)-$[\mathrm{Co(eddp)(en)}]\mathrm{Cl}\cdot\mathrm{H_2O}$ (**2-b**) is characterized in the triclinic space group $P\bar{1}$: $a=9.084(2)$, $b=10.800(2)$, $c=8.337(1)$ Å, $\alpha=99.37(1)$, $\beta=93.14(2)$, $\gamma=105.72(2)°$, and $Z=2$. *rac*-β(e-2)-$[\mathrm{Co(eddp)(en)}](\mathrm{PF_6})\cdot 3\mathrm{H_2O}$ (**3**) crystallizes in the monoclinic ($C2/c$): $a=23.216(2)$, $b=11.980(2)$, $c=19.768(2)$ Å, $\beta=133.314(2)°$, and $Z=8$. Two β isomers (β(e-1) and β(e-2)) were found to be conformational diastereomers arising from a difference in the chirality around one of two asymmetric nitrogen atoms in the coordinated eddp ligand.

For the title complex, $[\mathrm{Co(eddp)(en)}]^+$ (eddp^{2-}=ethylenediamine-N,N'-dipropionate), there are two possible geometrical isomers (α and β). Furthermore, it is possible for the β isomer to form two types of conformational diastereomers due to the chiralities of the secondary nitrogen atom (R or S) of the in-plane β-alaninate ring (G-ring), as shown in Fig. 1. Such conformational diastereomers were obtained for some cobalt(III) complexes containing the triethylenetetramine (trien) ligand,[1,2] but not for the $[\mathrm{Co(edda)(en)}]^+$ (edda=ethylenediamine-N,N'-diacetate) complex.[3] We have recently isolated[4] one α and two β isomers in the complex with eddp, which has longer carboxylate arms than does edda. The two β isomers could not be discriminated by means of spectroscopic methods. Thus, an X-ray structure determination of these β isomers is required for a series of stereoisomerization reaction studies. This paper presents the X-ray structures of the two conformational diastereomers of β-$[\mathrm{Co(eddp)(en)}]^+$, together with that of the α isomer.

Experimental

Materials. The preparation and optical resolution of the diastereomers were described previously.[4]

$(-)^{\mathrm{CD}}_{552}$-$\Delta(S,S)$-α-$[\mathrm{Co(eddp)(en)}]\mathrm{Br}\cdot 5\mathrm{H_2O}$ (1): The chloride salt was converted to the bromide salt by using a QAE-Sephadex A-25 anion-exchanger in the bromide form. Anal. Calcd for $[\mathrm{Co(eddp)(en)}]\mathrm{Br}\cdot 5\mathrm{H_2O}$ = $\mathrm{C_{10}H_{32}N_4O_9BrCo}$: C, 24.45; H, 6.57; N, 11.41%. Found: C, 24.34; H, 6.60; N, 11.32%.

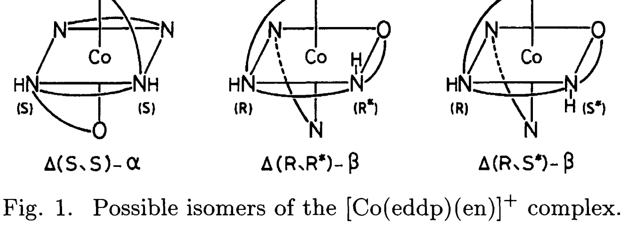

Fig. 1. Possible isomers of the $[\mathrm{Co(eddp)(en)}]^+$ complex.

$(+)^{\mathrm{CD}}_{536}$-$\Delta(R,R^*)$-β(e-1)-$[\mathrm{Co(eddp)(en)}]\mathrm{Br}\cdot\mathrm{H_2O}$ (2-a): The chloride salt was converted to the bomide salt by using a QAE-Sephadex A-25 anion-exchanger. Anal. Calcd for $[\mathrm{Co(eddp)(en)}]\mathrm{Br}\cdot\mathrm{H_2O}$=$\mathrm{C_{10}H_{24}N_4O_5BrCo}$: C, 28.65; H, 5.77; N, 13.37%. Found: C, 28.76; H, 5.51; N, 13.79%.

***rac*-β(e-1)-$[\mathrm{Co(eddp)(en)}]\mathrm{Cl}\cdot\mathrm{H_2O}$ (2-b):** Red crystals were obtained in a water–methanol–acetone mixed solution of *rac*-β(e-1) complex of the chloride salt. Anal. Calcd for $[\mathrm{Co(eddp)(en)}]\mathrm{Cl}\cdot\mathrm{H_2O}$=$\mathrm{C_{10}H_{24}N_4O_5ClCo}$: C, 32.05; H, 6.46; N, 14.95%. Found: C, 32.26; H, 6.43; N, 14.99%.

***rac*-β(e-2)-$[\mathrm{Co(eddp)(en)}](\mathrm{PF_6})\cdot 3\mathrm{H_2O}$ (3):** To a solution of *rac*-β(e-2)-$[\mathrm{Co(eddp)(en)}]\mathrm{Cl}\cdot 1.5\mathrm{H_2O}\cdot\mathrm{CH_3OH}$ (0.80 g) in 10 cm^3 of water was added a solution of $\mathrm{NH_4PF_6}$ (0.33 g) in 1 cm^3 of water. To this solution was added 30 cm^3 of a methanol–ethanol (1 : 2) mixed solution. The solution was allowed to stand in a refrigerator over night. Dark-red crystals were obtained. Recrystallization was carried out from water. Anal. Calcd for $[\mathrm{Co(eddp)(en)}](\mathrm{PF_6})\cdot 3\mathrm{H_2O}$= $\mathrm{C_{10}H_{28}N_4O_7CoPF_6}$: C, 23.09; H, 5.42; N, 10.77%. Found: C, 22.95; H, 5.52; N, 10.64%.

X-Ray Crystallography. Crystallographic data are given in Table 1. All of the measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo $K\alpha$ radiation; the calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation by a VAX computer at the X-ray diffraction service of the department of chemistry of Osaka University.

The single crystals selected for X-ray measurements were loaded into glass capillaries. The data were collected at 23±1 °C using the ω–2θ scan technique. Intensity data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods. The positions of the non-hydrogen atoms, except for the oxygen atoms of water in **3**, were refined together with their anisotropic thermal parameters. All hydrogen atoms were fixed at the calculated positions. The absolute configurations of **1** and **2-a** were determined by the anomalous dispersion method. The final R and R_w values of **1** were 0.038 and 0.049 for the Δ form, and 0.059 and 0.077 for the Λ form. The final R and R_w values of **2-a** were 0.038 and 0.038 for the Δ form and 0.047 and 0.050 for the Λ form.

Table 1. Crystallographic Data of $[Co(eddp)(en)]^+$ Complexes

	1	**2-a**	**2-b**	**3**
Formula	$C_{10}H_{22}N_4O_4CoBr\cdot5H_2O$	$C_{10}H_{22}N_4O_4CoBr\cdot H_2O$	$C_{10}H_{22}N_4O_4CoCl\cdot H_2O$	$C_{10}H_{22}N_4O_4CoPF_6\cdot3H_2O$
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1$	$P2_12_12_1$	$P\bar{1}$	$C2/c$
a/Å	10.558(2)	11.809(2)	9.084(2)	23.216(2)
b/Å	8.523(2)	16.144(2)	10.800(2)	11.980(2)
c/Å	11.868(2)	8.340(2)	8.337(1)	19.768(1)
α/deg	90.0	90.0	99.37(1)	90.0
β/deg	112.11(1)	90.0	93.14(2)	133.314(2)
γ/deg	90.0	90.0	105.73(2)	90.0
Z	2	4	2	8
$D_{\text{calcd}}/\text{g cm}^{-3}$	1.649	1.751	1.611	1.727
Crystal size/mm	0.20×0.20×0.10	0.10×0.10×0.20	0.10×0.08×1.00	0.20×0.25×0.90
$\mu(\text{Mo }K\alpha)/\text{cm}^{-1}$	29.10	35.81	12.98	10.26
No. of observations	2423	1595	3815	4850
No. of valiables	249	210	210	280
$R^{a)}$	0.038	0.038	0.029	0.076
$R_w{}^{b)}$	0.049	0.038	0.040	0.114

a) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. b) $R_w=[(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o{}^2)]^{1/2}$; $w=1/\sigma^2(F_o)$.

Table 2. Fractional Coordinates and Temperature Factors (Å^2) for Δ-α Isomer (**1**)

Atom	x	y	z	$B_{\text{eq}}{}^{a)}$
Co$^{b)}$	0.27552(6)	0	0.21051(5)	1.53(2)
Br	0.47606(7)	0.0105(1)	0.75739(7)	3.98(3)
O(1)	0.1151(4)	0.0368(4)	0.0713(3)	2.2(1)
O(2)	−0.0835(5)	0.1314(6)	−0.0467(4)	4.2(2)
O(3)	0.4449(4)	−0.0385(4)	0.3397(3)	2.1(1)
O(4)	0.5989(4)	−0.1433(6)	0.5012(3)	2.9(2)
N(1)	0.2373(4)	0.1630(5)	0.3083(4)	1.9(1)
N(2)	0.1713(4)	−0.1441(5)	0.2683(4)	1.9(1)
N(3)	0.3167(5)	−0.1622(6)	0.1130(4)	2.1(2)
N(4)	0.3762(5)	0.1410(6)	0.1451(4)	2.4(2)
C(1)	0.1607(6)	0.3002(7)	0.2373(5)	2.4(2)
C(2)	0.0208(6)	0.2601(7)	0.1418(5)	2.6(2)
C(3)	0.0179(6)	0.1357(6)	0.0499(5)	2.5(2)
C(4)	0.2506(6)	−0.2802(7)	0.3402(5)	2.4(2)
C(5)	0.3710(6)	−0.2330(7)	0.4510(5)	2.7(2)
C(6)	0.4780(5)	−0.1340(6)	0.4291(5)	2.0(2)
C(7)	0.1742(6)	0.0911(8)	0.3885(5)	2.7(2)
C(8)	0.0947(6)	−0.0541(7)	0.3295(5)	2.6(2)
C(9)	0.3612(7)	−0.0867(8)	0.0218(6)	3.2(3)
C(10)	0.4534(7)	0.0456(8)	0.0887(6)	3.5(3)
W(1)	0.2190(6)	0.2432(7)	0.7371(5)	5.0(3)
W(2)	0.0376(5)	−0.008(1)	0.6155(5)	6.3(3)
W(3)	0.7783(6)	0.2524(8)	0.2940(6)	6.1(3)
W(4)	0.7909(5)	−0.0217(6)	0.4225(4)	3.9(2)
W(5)	0.2039(9)	0.350(1)	0.9526(6)	7.8(4)

a) $B_{\text{eq}}=4/3\{\sum_i\sum_j B_{ij}\,a_i\,a_j\}$. b) The y coordinates of Co is fixed.

Table 3. Fractional Coordinates and Temperature Factors (Å^2) for Δ-β(e-1) Isomer (**2-a**)

Atom	x	y	z	$B_{\text{eq}}{}^{a)}$
Co	0.93178(6)	0.83822(5)	0.1283(1)	1.76(3)
Br	1.32687(6)	1.13252(5)	0.1400(1)	3.56(3)
O(1)	0.8300(4)	0.9297(3)	0.1653(5)	2.7(2)
O(2)	0.6820(4)	0.9967(4)	0.2510(6)	4.4(3)
O(3)	0.8168(3)	0.7871(3)	0.0014(5)	2.5(2)
O(4)	0.7455(4)	0.7219(3)	−0.2077(6)	3.4(2)
N(1)	0.8759(4)	0.7774(3)	0.3151(6)	2.1(2)
N(2)	1.0319(4)	0.7441(3)	0.0934(6)	2.0(2)
N(3)	1.0476(4)	0.8986(3)	0.2475(6)	2.2(2)
N(4)	0.9806(4)	0.9059(3)	−0.0539(6)	2.2(2)
C(1)	0.8362(6)	0.8268(4)	0.4519(8)	2.7(3)
C(2)	0.7379(6)	0.8809(4)	0.4058(8)	3.1(3)
C(3)	0.7506(6)	0.9393(4)	0.2684(8)	2.7(3)
C(4)	1.0433(5)	0.7145(4)	−0.0722(8)	2.5(3)
C(5)	0.9330(6)	0.6908(5)	−0.150(1)	4.3(4)
C(6)	0.8264(5)	0.7378(4)	−0.1178(8)	2.3(2)
C(7)	0.9634(5)	0.7148(4)	0.3607(9)	2.8(3)
C(8)	1.0016(6)	0.6756(4)	0.2056(8)	2.9(3)
C(9)	1.1181(6)	0.9475(4)	0.135(1)	3.8(3)
C(10)	1.0444(6)	0.9782(4)	0.005(1)	3.7(4)
W(1)	0.9860(5)	1.0054(3)	0.5190(6)	4.6(3)

The fractional coordinates and temperature factors are given in Tables 2, 3, 4, and 5. Selected bond distances, angles and torsion angles are listed in Tables 6 and 7. Tables of the anisotropic thermal parameters, coordinates of the hydrogen atoms, and the observed and calculated structure factors have been deposited as Document No. 67016 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Molecular Structures. The molecular structures of the $[Co(eddp)(en)]^+$ isomers are given in Figs. 2, 3, 4, and 5, and their selected bond lengths, angles and torsion angles are given in Tables 6 and 7. For all of the complexes, the cobalt is coordinated by a tetradentate eddp and a didentate en ligand, producing an octahedral CoN_4O_2 geometry. The bond lengths and angles are similar to those of EDTA-type Co(III) complexes.[5—9] The Co–N lengths are shorter (1.938—

Table 4. Fractional Coordinates and Temperature Factors (Å^2) for *rac*-β(e-1) Isomer (**2-b**)

Atom	x	y	z	$B_{eq}$$^{a)}$
Co	0.17354(2)	0.19385(2)	0.20184(3)	1.511(7)
Cl	0.25648(7)	0.60725(5)	0.29251(7)	3.26(2)
O(1)	0.2436(1)	0.0748(1)	0.0511(1)	2.04(4)
O(2)	0.3167(2)	−0.1000(1)	−0.0276(2)	2.92(5)
O(3)	0.0312(1)	0.0449(1)	0.2565(1)	1.90(4)
O(4)	−0.1643(2)	−0.0726(1)	0.3604(2)	2.66(4)
N(1)	0.3159(2)	0.1938(1)	0.3846(2)	1.90(4)
N(2)	0.1070(2)	0.3197(1)	0.3547(2)	1.89(4)
N(3)	0.3135(2)	0.3340(1)	0.1163(2)	2.08(4)
N(4)	0.0289(2)	0.1915(1)	0.0195(2)	2.01(4)
C(1)	0.4515(2)	0.1494(2)	0.3440(2)	2.59(6)
C(2)	0.4040(2)	0.0119(2)	0.2458(2)	2.61(6)
C(3)	0.3179(2)	−0.0052(2)	0.0794(2)	2.08(5)
C(4)	−0.0605(2)	0.2845(2)	0.3701(2)	2.42(6)
C(5)	−0.1224(2)	0.1555(2)	0.4267(3)	2.63(6)
C(6)	−0.0850(2)	0.0347(2)	0.3412(2)	1.95(5)
C(7)	0.3527(2)	0.3236(2)	0.4917(2)	2.47(6)
C(8)	0.2000(2)	0.3492(2)	0.5170(2)	2.49(6)
C(9)	0.2506(3)	0.3351(2)	−0.0518(2)	2.75(6)
C(10)	0.0806(3)	0.3108(2)	−0.0494(2)	2.81(6)
W(1)	0.6208(2)	0.3299(2)	0.0433(3)	4.83(8)

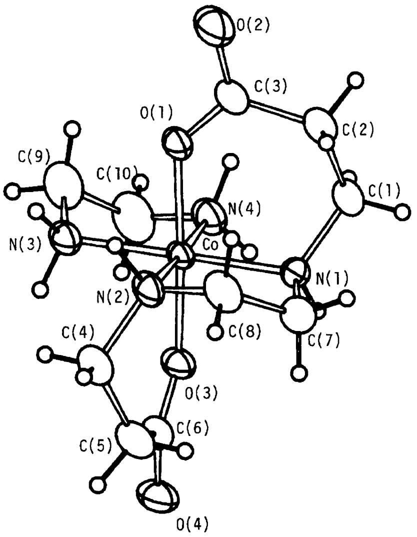

Fig. 2. Molecular structure of $(-)^{\mathrm{CD}}_{552}$-$\Delta(S,S)$-α-[Co(eddp)(en)]Br·5H_2O (**1**).

1.956 Å) than those of [Co(edtp)]$^-$ (1.956—1.973 Å),$^{5)}$ whereas the Co–O lengths of both are nearly the same. As given in Table 6, the O–Co–N angles at the G-ring and R-ring$^{10)}$ and the Co–O–C angles are larger than the ideal 90° and 109.5°, respectively, as found for the edtp complex.$^{5)}$

As in Fig. 2, complex **1** takes a *cis*-α configuration, where both of the two β-alaninate chelates coordinate at the *trans*-axial position for the N_4 plane. The absolute configuration about the metal ion is found to be Δ, as predicted on the basis of the sign of a dominant CD peak at the longer wavelength of the first absorption band.$^{4)}$ The absolute configurations of the two coordinated asymmetric nitrogens for the secondary amine are both S. The *gauche* conformations of the five-membered ethylenediamine chelates in the eddp and

Table 5. Fractional Coordinates and Temperature Factors (Å^2) for *rac*-β(e-2) Isomer (**3**)

Atom	x	y	z	$B_{eq}$$^{a)}$
Co$^{a)}$	0.26196(4)	0.10224(5)	0.17046(4)	1.63(2)
P	0.4646(1)	0.1615(2)	0.5544(1)	3.60(6)
F(1)	0.5526(2)	0.1221(4)	0.6113(3)	4.9(2)
F(2)	0.3790(3)	0.2051(5)	0.5027(4)	7.3(2)
F(3)	0.4828(3)	0.1565(4)	0.6481(3)	5.3(2)
F(4)	0.4489(3)	0.1674(5)	0.4628(3)	7.0(2)
F(5)	0.4911(3)	0.2856(4)	0.5725(3)	5.6(2)
F(6)	0.4371(3)	0.0346(4)	0.5386(4)	6.8(2)
O(1)	0.2828(2)	0.2350(3)	0.1343(2)	2.2(1)
O(2)	0.2632(3)	0.3795(3)	0.0533(3)	3.7(2)
O(3)	0.2468(2)	0.1993(3)	0.2351(2)	2.2(1)
O(4)	0.2066(3)	0.2578(3)	0.3012(3)	3.1(1)
N(1)	0.1491(3)	0.1037(4)	0.0582(3)	2.5(1)
N(2)	0.2429(3)	−0.0322(3)	0.2075(3)	2.4(1)
N(3)	0.2852(3)	0.0126(4)	0.1088(3)	2.2(1)
N(4)	0.3773(3)	0.1028(4)	0.2773(3)	2.6(1)
C(1)	0.1148(3)	0.2179(5)	0.0266(4)	3.0(2)
C(2)	0.1484(4)	0.2835(5)	−0.0047(4)	3.5(2)
C(3)	0.2362(3)	0.2991(4)	0.0649(4)	2.4(2)
C(4)	0.2655(4)	−0.0240(4)	0.2987(4)	3.0(2)
C(5)	0.2210(4)	0.0644(5)	0.3015(5)	3.2(2)
C(6)	0.2238(3)	0.1820(4)	0.2770(4)	2.2(2)
C(7)	0.1086(4)	0.0331(6)	0.0760(5)	3.8(2)
C(8)	0.1589(4)	−0.0686(5)	0.1292(5)	3.7(2)
C(9)	0.3694(3)	−0.0201(5)	0.1755(4)	3.0(2)
C(10)	0.4149(3)	0.0751(5)	0.2419(4)	3.1(2)
W(1)	0.5583(4)	0.3525(6)	0.2006(5)	7.1(2)
W(2)	0.4008(4)	0.4713(6)	0.1187(5)	7.6(2)
W(3)$^{b)}$	0.4018(7)	0.681(1)	0.1771(8)	8.9(3)
W(4)$^{c)}$	0.235(2)	0.205(2)	0.506(2)	7.6(7)

a) The y coordinates of Co is fixed. b) The multiplicity of the atom is 0.75. c) The multiplicity of the atom is 0.25.

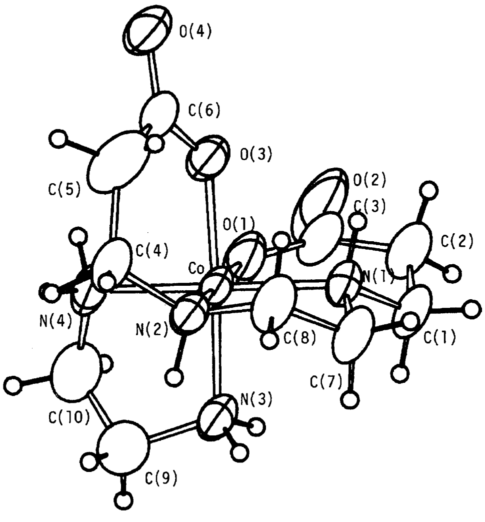

Fig. 3. Molecular structure of $(+)^{\mathrm{CD}}_{536}$-$\Delta(R,R^*)$-β(e-1)-[Co(eddp)(en)]Br·H_2O (**2-a**).

Table 6. Selected Bond Distances (Å) and Angles for [Co(eddp)(en)]$^+$ Complexes

	1	**2-a**	**2-b**	**3**
Co–O(1)	1.895(3)	1.929(4)	1.908(1)	1.936(5)
Co–O(3)	1.895(3)	1.910(4)	1.909(1)	1.930(5)
Co–N(1)	1.947(5)	1.956(5)	1.944(2)	1.953(4)
Co–N(2)	1.938(5)	1.947(5)	1.950(2)	1.941(6)
Co–N(3)	1.954(5)	1.952(5)	1.955(2)	1.957(7)
Co–N(4)	1.949(6)	1.958(5)	1.946(2)	1.968(4)
O(1)–Co–O(3)	174.6(2)	88.7(2)	87.68(6)	87.4(2)
O(1)–Co–N(1)	94.8(2)	92.7(2)	94.41(6)	93.1(2)
O(1)–Co–N(2)	88.5(2)	178.6(2)	178.31(6)	178.9(2)
O(1)–Co–N(3)	85.7(2)	88.4(2)	86.70(6)	88.6(2)
O(1)–Co–N(4)	89.6(2)	83.2(2)	85.48(6)	83.8(2)
O(3)–Co–N(1)	89.2(2)	89.1(2)	89.05(6)	92.0(2)
O(3)–Co–N(2)	95.3(2)	90.6(2)	94.19(6)	93.3(3)
O(3)–Co–N(3)	90.2(2)	175.3(2)	172.51(5)	174.8(2)
O(3)–Co–N(4)	86.5(2)	91.2(2)	90.08(6)	91.1(2)
N(1)–Co–N(2)	88.2(2)	86.1(2)	85.36(7)	87.8(2)
N(1)–Co–N(3)	179.1(2)	94.7(2)	96.10(6)	91.4(2)
N(1)–Co–N(4)	93.7(2)	175.8(2)	179.12(6)	175.5(3)
N(2)–Co–N(3)	92.5(2)	92.3(2)	91.66(7)	90.6(3)
N(2)–Co–N(4)	177.4(2)	98.1(2)	94.76(7)	95.3(2)
N(3)–Co–N(4)	85.6(2)	84.9(2)	84.77(7)	85.2(2)
Co–O(1)–C(3)	132.0(3)	131.0(4)	129.3(1)	130.8(4)
Co–O(3)–C(6)	131.5(4)	129.6(4)	131.5(1)	132.9(3)
Co–N(1)–C(1)	114.4(3)	117.0(4)	116.6(1)	113.6(3)
Co–N(1)–C(7)	109.4(4)	108.0(4)	107.4(1)	107.5(3)
Co–N(2)–C(4)	115.0(4)	116.8(4)	115.1(1)	114.7(3)
Co–N(2)–C(8)	109.3(4)	109.8(4)	110.2(1)	108.9(4)
Co–N(3)–C(9)	109.2(4)	109.8(4)	108.9(1)	110.6(4)
Co–N(4)–C(10)	108.5(4)	109.4(4)	110.5(1)	107.5(3)
C(1)–N(1)–C(7)	114.0(5)	112.9(5)	114.3(1)	112.4(6)
C(4)–N(2)–C(8)	114.3(5)	111.8(5)	112.0(1)	113.3(8)
N(1)–C(1)–C(2)	114.4(4)	111.3(5)	111.0(1)	111.9(7)
N(2)–C(4)–C(5)	113.5(5)	114.2(5)	114.1(2)	114.1(5)
C(1)–C(2)–C(3)	116.4(5)	119.1(6)	115.5(2)	116.8(5)
C(4)–C(5)–C(6)	116.2(5)	121.4(6)	119.4(2)	117.7(9)

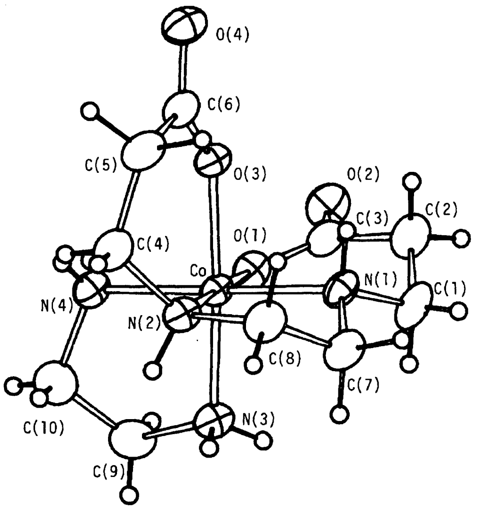

Fig. 4. Molecular atructure of *rac*-β(e-1)-[Co(eddp)(en)]Cl·H$_2$O (**2-b**) with the Δ form.

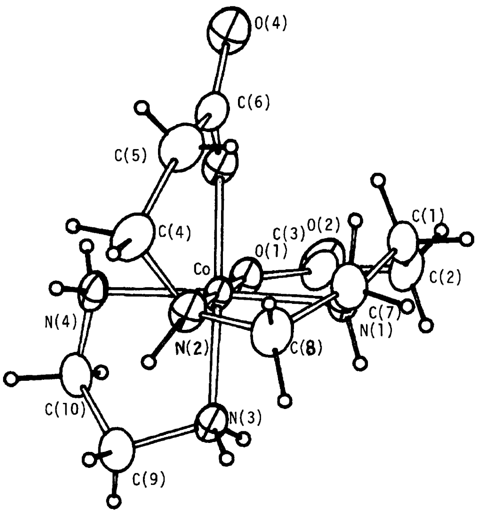

Fig. 5. Molecular structure of *rac*-β(e-2)-[Co(eddp)(en)](PF$_6$)·3H$_2$O (**3**) with the Δ form.

en are δ and λ, respectively (Fig. 2). The N–C–C–N torsion angle of the eddp is small (40.0(6)°) for this complex **1** compared to those for the β isomers and of the en for all of the eddp isomers, as shown in Table 7. The ethylenic *gauche* conformations of the two six-membered β-alaninates are λ. The combination of these conformation is also described as being the ob$_2$ form.[11] Only one (lel$_2$) isomer has been determined cyrstallographically for [M(edtp)]$^-$ [5] (edtp=ethylenediaminetetrapropionate, M=Co(III), Cr(III)), although the three diastereoisomers arising from a combination of the conformations of two out-of-plane (R-) rings,[12] ob$_2$, ob·lel and lel$_2$, are predicted spectroscopically.[6] Therefore, this is the first evidence of R-rings with the ob$_2$ form, which corresponds to the I isomer of [Cr(edtp)]$^-$.[6] The torsion angles around the two R-rings are almost identical, as shown in Table 7. Both the β-alaninate rings in complex **1** take an envelope-like conformation in which all of the atoms, except for one β-carbon, are coplanar with each other, as shown in Fig. 2. This is in contrast to the two R-rings with the lel$_2$ form of the edtp complex, which take a skew-boat conformation.[5] A similar envelope-like conformation has been found for the two β-alaninates attached to the tertiary amine and coordinated meridionally in the aqua(ethylenediaminetripropionato)chromium(III) (*trans-eq*-[Cr(edtrp)(H$_2$O)]) type complexes.[6] It is noted that there is no other diastereoisomers with ob·lel and lel$_2$ conformation. This indicates that the ob$_2$ conformation in the eddp complex is more stable than the lel$_2$ (or ob·lel) one. In other words, the absence of two in-plane (G-) rings of the edtp may enable the R-rings to form a stable ob$_2$ conformation.

Figures 3 and 4 show the molecular structures of the two β(e-1) complexes (**2-a** and **2-b**, respectively). Both geometrical structures are *cis*-β, where one β-alaninate of the eddp coordinates at the R-ring and the other one coordinates at the in-plane G-ring. The absolute config-

Table 7. Selected Torsion Angles (deg) for $[Co(eddp)(en)]^+$ Complexes

	1	**2-a**	**2-b**	3
G-ring				
Co–N(1)–C(1)–C(2)		61.2(6)	58.1(2)	−65.9(6)
N(1)–C(1)–C(2)–C(3)		−55.4(8)	−63.8(2)	58.0(8)
C(1)–C(2)–C(3)–O(1)		−18(1)	−24.5(2)	21(1)
C(2)–C(3)–O(1)–Co		−11.7(9)	−18.6(2)	3(1)
C(3)–O(1)–Co–N(1)		5.1(6)	19.8(1)	3.8(7)
O(1)–Co–N(1)–C(1)		−31.4(4)	−19.6(1)	36.7(6)
R-ring				
Co–N(1)–C(1)–C(2)	60.1(7)			
N(1)–C(1)–C(2)–C(3)	−55.2(8)			
C(1)–C(2)–C(3)–O(1)	−21.1(9)			
C(2)–C(3)–O(4)–Co	−4.0(9)			
C(3)–O(1)–Co–N(1)	−0.9(6)			
O(1)–Co–N(1)–C(1)	−31.4(4)			
Co–N(2)–C(4)–C(5)	58.4(7)	−56.7(6)	−59.4(2)	−61.1(7)
N(2)–C(4)–C(5)–C(6)	−59.8(8)	36.3(9)	50.2(2)	55.5(7)
C(4)–C(5)–C(6)–O(3)	−31.2(8)	16(1)	20.4(3)	16.0(6)
C(5)–C(6)–O(3)–Co	4.9(8)	−18.8(9)	−4.0(2)	14.4(6)
C(6)–O(3)–Co–N(2)	−3.6(5)	30.6(5)	11.2(2)	−7.2(4)
O(3)–Co–N(2)–C(4)	−28.9(4)	47.6(4)	37.2(1)	29.5(5)
Diamine (eddp)				
N(1)–Co–N(2)–C(4)	−117.9(4)	136.7(4)	125.9(1)	121.4(5)
N(2)–Co–N(1)–C(1)	−119.7(4)	149.3(4)	158.7(1)	−144.1(7)
N(1)–Co–N(2)–H(2)	125.7	−106.0	−119.4	−121.0(4)
N(2)–Co–N(1)–H(1)	123.7	−92.7	−86.4	96.7(4)
N(1)–Co–N(2)–C(8)	12.3(3)	8.1(4)	−1.9(1)	−6.7(6)
N(2)–Co–N(1)–C(7)	9.6(3)	20.6(4)	28.9(1)	−19.1(5)
Co–N(1)–C(7)–C(8)	−29.3(5)	−44.1(5)	−48.9(2)	40.5(7)
Co–N(2)–C(8)–C(7)	−31.4(5)	−34.7(6)	−25.1(2)	31(1)
N(1)–C(7)–C(8)–N(2)	40.0(6)	51.1(6)	47.9(2)	−47(1)
Diamine (en)				
Co–N(3)–C(9)–C(10)	41.4(5)	35.8(6)	−40.4(2)	35.0(8)
Co–N(4)–C(10)–C(9)	40.8(5)	41.6(6)	−41.2(2)	44.1(5)
N(3)–C(9)–C(10)–N(4)	−53.5(6)	−50.0(7)	52.5(2)	−51.5(7)

urations of **2-a** was found to be Δ, as predicted by the CD spectra.[4] The absolute configurations of the coordinated asymmetric *sec*-N atoms in the R- and G-rings of the eddp ligand are *R* and R^*,[13] respectively. The *gauche* conformations of the ethylenediamine chelates in the eddp and en are δ and λ, respectively. The *racemic* complex **2-b** has the same structure as does **2-a**, except for the *gauche* conformation of the en lignd; it takes the δ conformation when the absolute configuration about the metal center is Δ, as shown in Fig. 4. The ethylenic *gauche* conformations of the G- and R-ring are λ and δ, and are also described as the lel and ob form, respectively. The R-ring takes a *chair* conformations for **2-a** and an envelope-like conformation for **2-b**. For these β(e-1) isomers, quite large deviations of the torsion angles of the β-alaninate rings were realized, as given in Table 7. This reveals that the R-ring is flexible to some extent, though its *gauche* conformation is retained. The chelate conformations of the eddp and en may be influenced by the counter anion. The hydrogen bondings between the amine and the chloride anion (N(2)–H(2)···Cl and N(3)–H(3)···Cl) are observed for **2-b**. The corresponding hydrogen bonding is not found for the bromide salt **2-a**, while the bromide anion interacts with the amine or water molecule belonging to the neighboring cells.

Figure 5 shows the molecular structure of the β(e-2) complex (**3**) with a Δ configuration. Although this complex also takes a *cis*-β configuration, the absolute configuration of the asymmetric *sec*-N atom in the G-ring of the coordinated eddp is S^*. That is, this β(e-2) complex is a conformational isomer of the β(e-1) complex. The combination of the conformations of the ethylenediamine chelates in the eddp and en is $\lambda\lambda$. The ethylenic *gauche* conformations of the β-alaninate at the R-ring is δ(ob). This chelate also takes an envelope-like conformation, as found for **1** and **2-b**.

For the β isomers, the torsion angle, N(1)–Co–N(2)–C(8), is very different from that of N(2)–Co–N(1)–C(7). That is, N(1)–Co–N(2)–C(8) is small

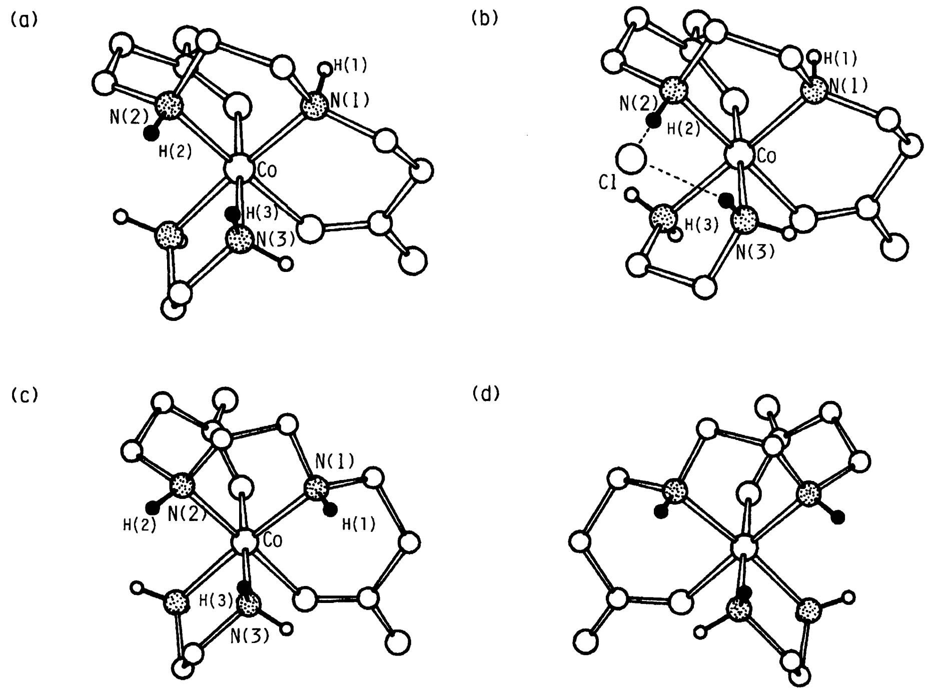

Fig. 6. View from the C_3 axis of the β isomers. (a) **2-a**; (b) **2-b** (Δ configuration); (c) **3** (Δ configuration); (d) **3** (Λ configuration).

(8.1(4)°, −1.9(1)° and −6.7(6)° for **2-a**, **2-b**, and **3**, respectively) compared with that of the related Co(III) edta-type complexes,[5—9] which take normal *gauche* conformations. This causes a distortion of the diamine chelate ring of the coordinated eddp to adopt an asymmetric envelope conformation, in which all but one carbon atom (C(7)) are located on a plane (Figs. 3, 4, and 5). Such an envelope conformation has been observed for $[Cr(edtrp)(H_2O)]$ type complexes[6] and $[Ru(pdtaH)(H_2O)]$[14] (pdtaH=1,2-propanediaminetetraacetate(-3)). As in Table 7, the torsion angles, N(1)–Co–N(2)–C(4) and N(1)–Co–N(2)–H(2), are no longer distinguishable for **2-b** and **3**, though the N(2)–C(4) bond is ordinarily oriented to the axial for the former and to the equatorial for the latter. A similar tendency has been obtained in the case of two out-of-plane β-alaninates (G′- and R-rings) attached to the tertiary amine of $[Cr(edtrp)(H_2O)]$ type complexes.[6] A modification of the torsion angles around the coordinated secondary nitrogen atom and the chelate conformations of the β-alaninate and diamine rings may be forced to take a less-strained conformation in these β-eddp complexes.

Optical Resolution Mechanism. During the preparation and optical resolution of $[Co(eddp)(en)]^+$ complexes for the isomerization study,[4] it was found that the β(e-2) isomer could not be optically resolved on an SP-Sephadex column by using $K_2[Sb_2(\text{L-tart})_2]$ as an eluent. According to a recent model proposed for the mechanism of the optical resolution by $[Sb_2(\text{L-tart})_2]^{2-}$,[15] however, there is no site difference for the chiral discrimination between the β(e-1) and the β(e-2). To explain the difference in the optical resolution between these β isomers, it is important to consider the orientation of the hydrogen atoms attached to the secondary and tertiary amines of the eddp and en. Figure 6 shows the view from the C_3 axis of complexes **2-a**, **2-b**, and **3**. The two N–H bonds (N(2)–H(2) and N(3)–H(3)) are oriented to the same side and one (N(1)–H(1)) is to the other side for **2-a** and **2-b**; all are oriented to the same side for **3**. The pair of N(2)–H(2) and N(3)–H(3) in the β(e-1) isomer can be a site for the interaction to $[Sb_2(\text{L-tart})_2]^{2-}$, as found for that to the chloride anion in **2-b** (Fig. 6(b)). It has been experimentally found that the Δ form is eluted first for the β(e-1) isomer.[4] This indicates that the L-Δ diastereomeric ion-pair is more favorable than the L-Λ one. The orientation of the N–H bonds pair may be effective in an interaction with $[Sb_2(\text{L-tart})_2]^{2-}$. Though there is a slight influence of the difference in the *gauche* conformation of en (δ or λ) on the orientation of N(3)–H(3), the same chirality for the interaction with $[Sb_2(\text{L-tart})_2]^{2-}$ is expected for **2-a** and **2-b**, as seen from the sign of the torsion angle. The sign of the torsion angle H(2)–N(2)–N(3)–H(3) is positive for the β(e-1) isomer with the Δ configuration (+44.5° for **2-a** and +37.6° for **2-b**, respectively). On the other hand, the β(e-2) isomer seems to have two pairs of interaction sites with $[Sb_2(\text{L-tart})_2]^{2-}$, N(1)–H(1) and N(3)–H(3), as well as N(2)–H(2) and N(3)–H(3). The former pair has the same chirality as that of the β(e-1) isomers; the torsion angle, H(2)–N(2)–N(3)–H(3), shows a positive sign (+56.8° for **3** with Δ configuration). In the case of the latter pair, the torsion angle, H(1)–N(1)–N(3)–H(3), has a similar value, but of the opposite sign to H(2)–N(2)–N(3)–H(3) (−49.1°). This indicates that the interaction sites with $[\mathrm{Sb_2(L\text{-}tart)_2}]^{2-}$ in complex **3** becomes achiral owing to the two pairs of N–H bonds with different chirality. As shown in Fig. 6(c) and its enantiomer Fig. 6(d), N(1)–H(1) and N(2)–H(2) are almost symmetrically directed to the opposite side with respect to N(3)–H(3), as if there exists a mirror plane containing the N(3)–H(3) bond and the bisecting axis between the N–Co–N angle in the eddp. Then, the two diastereomeric ion-pairs (L-Δ and L-Λ) are no longer distinguishable. Such a structural disadvantage on chiral discrimination may cause difficulty in the optical resolution of the β(e-2) isomer.

References

1) D. A. Buckingham, P. J. Cresswell, R. J. Dellaca, M. Dwyer, G. J. Gainsford, L. G. Marzilli, I. E. Maxwell, W. T. Robinson, A. M. Sargeson, and K. R. Turnbull, *J. Am. Chem. Soc.*, **96**, 1713 (1974).

2) D. A. Buckingham, M. Dwyer, G. J. Gainsford, V. J. Ho, L. G. Marzilli, W. T. Robinson, A. M. Sargeson, and K. R. Turnbull, *Inorg. Chem.*, **14**, 1739 (1975).

3) K. Kuroda, *Chem. Lett.*, **1972**, 197.

4) H. Kawaguchi, N. Maruyama, T. Ama, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **65**, 175 (1992).

5) M. Parvez, C. Maricondi, D. J. Radanović, M. I. Djuran, and B. E. Douglas, *Inorg. Chim. Acta*, **182**, 177 (1991).

6) a) N. Sakagami, M. Hayashi, and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, **1992**, 285; b) N. Sakagami and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, **1992**, 291.

7) K. Okamoto, T. Tsukihara, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **51**, 3534 (1978).

8) J. D. Bell and G. L. Blackmer, *Inorg. Chem.*, **12**, 836 (1973).

9) H. Okazaki, K. Tomioka, and H. Yoneda, *Inorg. Chem. Acta*, **74**, 169 (1983).

10) The G-ring and R-ring are the β-alaninates which coordinate at the in-plane and out-of-plane with respect to the plane containing en chelate in eddp.

11) The ob means that the ethylenic C–C bonds of the β-alaninate rings are oblique to the pseudo C_2 axis bisecting the N–Co–N angle. For the lel, the C–C bond is parallel to the C_2 axis.

12) It is found that the G-ring is rigid and that its conformation is fixed to the lel form.

13) S and R denote the chiralities of the *sec*-N atom in the R-ring and S^* and R^* denote those in the G-ring.

14) M. M. Taqui Khan, H. C. Bajaj, Z. Shirin, and K. Venkatasubramanian, *Polyhedron*, **11**, 1059 (1992).

15) H. Yoneda, *J. Chromatogr.*, **313**, 59 (1985).