Preparation and Stereochemistry of the Mixed-Ligand Complex, Ammine(ethylenediamine)(ethylenediamine-*N*-acetato)cobalt(III)

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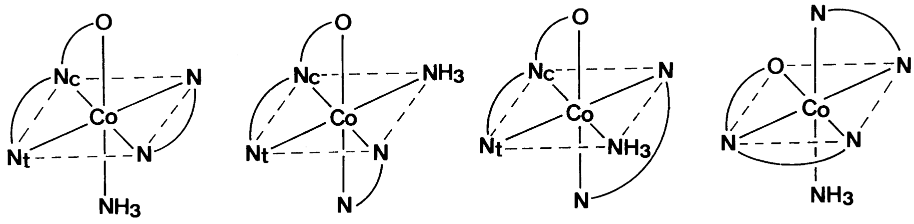
Four geometrical isomers for $[Co(edma)(NH_3)(en)]^{2+}$ (edma=ethylenediamine-*N*-acetate) were prepared for the first time; isomers with the facially chelated edma ligand were optically resolved. Geometrical structures were assigned on the basis of the absorption, ^1H NMR, ^{13}C NMR, and CD spectral data; the crystal structure of one of these isomers was determined by an X-ray diffraction method. The crystal is orthorhombic, space group $P2_12_12_1$, $a=8.345(1)$, $b=21.054(2)$, $c=7.914(1)$ Å, $V=1390.6(3)$ Å^3, $Z=4$, and $R=0.047$ for 1985 independent reflections $[F_o>3\sigma(F_o)]$. The cobalt atom is octahedrally surrounded by one ammine, the bidentate en, and the facially chelated edma ligands. The ammine ligand occupies the trans position of the secondary nitrogen atom in the edma, *trans*(N_c, NH_3) geometry. This cation, which shows a positive CD sign at 519 nm, takes a $\Lambda\Delta$ configuration around the cobalt atom and an *S* configuration around the secondary nitrogen atom. The absolute configurations of the other optically active isomers with the facially chelated edma ligand were assigned based on the stereospecific deuteration for the methylene protons of the glycinate ring in the edma ligand in a basic D_2O solution.

Bis-type cobalt(III) complexes with terdentate ligands, such as ethylenediamine-*N*-acetate (edma), iminodiacetate, 3-azapentane-1,5-diamine, and their derivatives, have been investigated regarding stereochemical and spectrochemical interests, as well as their reactivity. Especially, cobalt(III) complexes containing the edma ligand, which is an unsymmetrical terdentate ligand of the N–N–O type, have been widely studied in order to provide a variety of geometrical and optical isomers.[1-11] However, regarding the CD spectral analysis of the bis-type complexes, the additivity on CD curves between the configurational contribution and the chirality (*R* and *S*) due to the secondary nitrogen of the chelated edma ligand, were troublesome.[2,4,6] This kind of mixed-ligand complex with the edma, bidentate, and unidentate ligands has not been reported up to now.

In the present paper, the preparation and the optical resolution of a new type ammine(ethylenediamine)(ethylenediamine-*N*-acetato)cobalt(III) complex, $[Co(edma)(NH_3)(en)]^{2+}$, which is expected to take four geometrical isomers with one meridionally (*mer*) and three kinds of facially (*fac*) chelated edma ligand as shown in Fig. 1,[12] are described; their stereochemical and spectrochemical properties are discussed on the basis of the absorption, CD, ^1H NMR, and ^{13}C NMR spectra, as well as an X-ray structure analysis.

Experimental

Preparation of Four Geometrical Isomers of $[Co(edma)(NH_3)(en)]X_2$. To a solution containing 2.80 g (0.01 mol) of $[CoCl_2(NH_3)_2(en)]Cl$[13] and 2.28 g (0.01 mol) of ethylenediamine-*N*-acetic acid dihydrochloride dihydrate[14] (Hedma·2HCl·2H$_2$O) was added 28 cm^3 of 28% aqueous ammonia; the mixed solution was warmed at 80 °C for 2 h. The solution was cooled to room temperature and neutralized with a 0.1 M (M=mol dm^{-3}) HCl solution. This solution was poured onto an SP-Sephadex C-25 column (4.7 cm×50 cm, K$^+$ form). After sweeping the column with water, the adsorbed band was separated into red-violet, pink-violet, pink-orange containing the desired complex, and yellow bands by elution with a 0.5 M KCl solution. The same preparative reaction and chromatographic separation were carried out additional four times. Each pink-orange eluate obtained from the five preparative procedures was combined and concentrated to a small volume under reduced pressure. A large amount of methanol was added to the solution in order to eliminate KCl. After a methanolic solution was concentrated to a small volume again,



trans(O, NH3) (F-1) trans(Nt, NH3) (F-2) trans(Nc, NH3) (F-4) mer (F-3)

Fig. 1. Geometrical structures of $[Co(edma)(NH_3)(en)]^{2+}$.

it was chromatographed on an SP-Sephadex C-25 column (4.7 cm×90 cm, NH_4^+ form) using a 0.3 M $(NH_4)_2SO_4$ solution as an eluent. The band was separated into five bands (pink, orange (D-1), pink, orange (F-3), and orange (F-4)) by recyclic development for a week. The F-3 and F-4 bands were eluted out from the column, and the D-1 band was transferred to another SP-Sephadex C-25 column (4.7 cm×90 cm, Na^+ form) and developed with a 0.5 M $NaNO_3$ solution. The D-1 band was separated further into three bands (F-1, F-2, and $[Co(edma)(NH_3)_3]^{2+}$ [6)]) by recyclic development for 2 d.

The F-3 eluate was first concentrated to a small volume under reduced pressure, before adding a large amount of methanol. The deposited ammonium sulfate was removed by filtration. The filtrate was again concentrated to a few milliliters, and the residual $(NH_4)_2SO_4$ in the solution was removed completely by using a Sephadex G-10 column. The eluate was treated with a small QAE-Sephadex A-25 column (Cl^- form) to convert the SO_4^{2-} ion to Cl^-. Fine orange crystals were obtained upon the addition of methanol to the concentrated eluate. Recrystallization was carried out from water by adding methanol. Found for the F-3 isomer: C, 18.96; H, 6.65; N, 18.26%. Calcd for $[Co(edma)(NH_3)(en)]Cl_2\cdot 3H_2O=C_6H_{26}N_5O_5Cl_2Co$: C, 19.06; H, 6.93; N, 18.52%.

The F-4 eluate was treated in the same way as that described for the F-3 isomer in order to remove $(NH_4)_2SO_4$ from the solution. The eluate from a Sephadex G-10 column was concentrated to a small volume; methanol was then added until the orange needle-like crystals began to be deposited. Recrystallization was carried out from water by the addition of methanol. Found for the F-4 isomer: C, 18.16; H, 6.60; N, 17.67%. Calcd for $[Co(edma)(NH_3)(en)]SO_4\cdot 2.5H_2O=C_6H_{25}N_5O_{8.5}SCo$: C, 18.28; H, 6.39; N, 17.76%.

Each of the F-1 and F-2 eluates was concentrated to a small volume under reduced pressure before adding methanol. The deposited sodium nitrate was removed by filtration, and the filtrate was again concentrated. F-1 and F-2 isomers were obtained as orange needle-like crystals upon the addition of methanol to the concentrated solution. Recrystallization was carried out from water by the addition of methanol. Found for the F-1 isomer: C, 19.15; H, 5.46; N, 25.83%. Calcd for $[Co(edma)(NH_3)(en)](NO_3)_2=C_6H_{20}N_7O_8Co$: C, 19.11; H, 5.34; N, 25.99%. Found for the F-2 isomer: C, 18.25; H, 5.70; N, 24.61%. Calcd for $[Co(edma)(NH_3)(en)](NO_3)_2\cdot H_2O=C_6H_{22}N_7O_9Co$: C, 18.23; H, 5.61; N, 24.81%.

The yields of the F-1, F-2, F-3, and F-4 isomers were about 0.5, 0.3, 0.1 and 3.0 g, respectively.

Optical Resolution of the *fac* Isomers. A solution containing ca. 0.2 g of each racemate of the F-1, F-2, and F-4 isomers in a small amount of water was poured onto an SP-Sephadex C-25 column (4.7 cm×50 cm, Na^+ form). After sweeping the column with water, the adsorbed band was developed with a 0.2 M $Na_2Sb_2(d\text{-tart})_2$ solution. In each chromatographic run the adsorbed band was completely separated into two bands by repeating recyclic development (2 times for the F-1 and F-2 isomers, and 8 times for the F-4 one). The CD signs of the early and late eluted solutions were (+) and (−) at 513 nm for the F-1 isomer, (−) and (+) at 510 nm for the F-2 isomer, and (+) and (−) at 519 nm for the F-4 isomer, respectively. Each eluate was concentrated to a small volume; a saturated KCl solution was then added to it in order to make deposit $K_2Sb_2(d\text{-tart})_2$ salt, which was removed by filtration. The filtrate was concentrated to a small volume; methanol was added to it in order to eliminate KCl or NaCl. The methanolic solution was concentrated again before charging it on a short QAE-Sephadex A-25 column (Br^- form) in order to convert the Cl^- ion to Br^-. A crude complex, which was obtained by addition of methanol to the concentrated eluate, was recrystallized from water by the addition of methanol. Found for the $(-)^{CD}_{513}$ F-1 isomer: C, 16.25; H, 5.49; N, 15.56%. Calcd for $[Co(edma)(NH_3)(en)]Br_2\cdot 2H_2O=C_6H_{24}N_5O_4Br_2Co$: C, 16.05; H, 5.39; N, 15.60%. Found for the $(-)^{CD}_{510}$ F-2 isomer: C, 16.95; H, 5.17; N, 16.22%. Found for the $(-)^{CD}_{519}$ F-4 isomer: C, 16.89; H, 5.22; N, 16.12%. Calcd for $[Co(edma)(NH_3)(en)]Br_2\cdot H_2O=C_6H_{22}N_5O_3Br_2Co$: C, 16.72; H, 5.14; N, 16.25%.

Determination of Absolute Configuration of the *fac* Isomers by ^{1}H NMR Method. Each of the optically active *fac* isomers (about 0.2 g) of $[Co(edma)(NH_3)(en)]Br_2$ [$(-)^{CD}_{513}$ (F-1), $(+)^{CD}_{510}$ (F-2), and $(+)^{CD}_{519}$ (F-4)] was dissolved into a buffered D_2O solution (pH 10); the solution was then allowed to stand at 40 °C for 40 min (25 min for the F-4 isomer) in order to deuterate one of the two methylene protons on the glycinate ring (G-ring) in the edma ligand (Fig. 6). The deuteration reaction was stopped by acidifying the solution (pH ca. 5) with a 1 M HCl solution; zinc powder (2 g) was then added to the solution. After stirring the mixture for 5 min at ca. 25 °C, unreacted zinc was removed by filtration. Lead dioxide (2 g) and $Hedma\cdot 2HCl\cdot 2H_2O$ (0.105 g) were added to the filtrate, and the mixture was stirred for 15 min at ca. 25 °C. The solution was treated in the same way as that described in our previous paper[2)] to obtain the optically active *trans*(O)-$[Co(edma)_2]^+$. The absolute configurations of the *fac* isomers were determined on the basis of the ^{1}H NMR spectra of $(-)^{CD}_{543}$-C_2- and $(+)^{CD}_{543}$-C_2-*trans*(O)-$[Co(edma)_2]^+$, which were obtained from each of the deuterated *fac* isomers.[2)]

Crystallography. X-Ray Data Collection: Unit cell parameters and intensity data for the single crystal (ca. 0.13×0.16×0.35 mm³) were measured on an Enraf Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71069 Å, 50 kV and 26 mA).[15)] Unit-cell parameters were determined by least-squares refinement from 25 reflections with $22° < 2\theta < 28°$. Crystal data: $CoC_6H_{22}N_5O_3Br_2$, M=431.01, orthorhombic, space group $P2_12_12_1$, a=8.345(1), b=21.054(2), c=7.914(1) Å, V=1390.6(3) Å³, Z=4, D_c=2.06 g cm^{-3}, $F(000)$=856, μ=68.2 cm^{-1}, and room temperature.

Intensity data were collected using the $\omega-2\theta$ scan mode up to $2° < 2\theta < 60°$ $(+h, k, l)$ with a scan width of $(0.8+0.350 \tan\theta)°$; the scan rate varied from 1 to 5° min^{-1} (on ω). The intensities were corrected for Lorenatz and polarization effects, but not for absorption. A total of 1985 independent reflections with $F_o > 3\sigma(F_o)$ of the measured 2351 reflection were considered as having been "observed" and used for a structure determination.

Determination of Crystal Structure. The cobalt and two bromine atoms were located by direct methods of the crystallographic program package SDP/VAN.[15)] The remaining non-hydrogen atoms were found by using the conventional difference Fourier techniques to give a trial structure. The structure was then refined by full-matrix least-squares on F. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were fixed by a geometrical constraint (C–H=0.95 Å) and isotropic thermal parameters (U=0.05 Å²). The hydrogen atoms attached to the nitrogen atoms and water molecules were not included in the calculation. The final refinement gave R=0.047 and R_w=0.047 with the weighting scheme w=1.6326/

$\{\sigma^2(F_o)+0.000825F_o^2\}$. A refinement using the enantiomeric coordinates gave $R=0.064$ and $R_w=0.066$ with the weighting scheme $w=2.1871/\{\sigma^2(F_o)+0.000745F_o^2\}$. This enantiomeric structure could be rejected at the 0.005 significance level by a Hamilton test.[16] $\Delta_{max}=0.001\sigma$. The final difference Fourier synthesis indicated no significant peaks larger than 1.0 eÅ^{-3}. All calculations were performed with SHELX 76,[17] and molecular illustrations were drawn using ORTEP[18] on a FACOM M780/20 computer at the Computer Center of University of Tsukuba. Scattering factors were taken from the literature.[19] Atomic positional parameters are given in Table 1 and selected bond distances and angles within the cation are summarized in Table 2. Lists of the structure factors, anisotropic thermal parameters for non-hydrogen atoms, and positional parameters for hydrogen atoms have been deposited as Document No. 9010 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 1. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for the Non-H Atoms

Atom	x	y	z	B_{eq}
Co	0.5531(1)	0.60023(4)	0.7639(1)	1.20(3)
O(1)	0.6342(7)	0.5661(2)	0.5597(6)	1.78(19)
O(2)	0.6259(8)	0.5745(3)	0.2807(7)	2.86(25)
N(1)	0.6771(7)	0.5364(3)	0.8890(9)	1.87(24)
N(2)	0.4595(8)	0.6297(3)	0.9750(7)	1.76(22)
N(3)	0.3654(8)	0.5439(3)	0.7487(8)	1.78(22)
N(4)	0.7376(7)	0.6574(3)	0.7742(9)	2.22(25)
N(5)	0.4521(7)	0.6663(2)	0.6223(7)	1.38(19)
C(1)	0.3379(9)	0.5824(4)	1.0334(10)	2.08(28)
C(2)	0.2448(9)	0.5607(4)	0.8779(10)	2.02(27)
C(3)	0.7143(10)	0.7120(4)	0.6569(11)	2.57(33)
C(4)	0.5398(10)	0.7274(3)	0.6555(9)	2.28(30)
C(5)	0.4684(9)	0.6464(3)	0.4455(9)	1.83(27)
C(6)	0.5858(8)	0.5921(3)	0.4240(9)	1.59(25)
BR(1)	0.9406(1)	0.09610(4)	0.0190(1)	2.60(3)
BR(2)	0.6480(1)	0.76528(4)	1.1215(1)	2.94(3)
O(W)	−0.0740(8)	0.6152(4)	1.0740(8)	3.70(29)

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

Table 2. Bond Distances (Å) and Angles (°)

Co–O(1)	1.894(5)	N(2)–C(1)	1.496(9)
Co–N(1)	1.964(6)	N(3)–C(2)	1.478(9)
Co–N(2)	1.947(6)	N(4)–C(3)	1.491(10)
Co–N(3)	1.968(6)	N(5)–C(4)	1.503(9)
Co–N(4)	1.956(6)	N(5)–C(5)	1.467(9)
Co–N(5)	1.975(5)	C(1)–C(2)	1.525(11)
O(1)–C(6)	1.272(8)	C(3)–C(4)	1.492(12)
O(2)–C(6)	1.239(9)	C(5)–C(6)	1.515(10)
O(1)–Co–N(1)	89.0(2)	Co–O(1)–C(6)	116.3(4)
O(1)–Co–N(2)	175.7(2)	Co–N(2)–C(1)	109.0(4)
N(1)–Co–N(2)	89.8(3)	Co–N(3)–C(2)	110.8(4)
O(1)–Co–N(3)	90.2(3)	Co–N(4)–C(3)	110.3(5)
N(1)–Co–N(3)	92.2(3)	Co–N(5)–C(4)	107.2(4)
N(2)–Co–N(3)	85.7(3)	Co–N(5)–C(5)	107.5(4)
O(1)–Co–N(4)	89.3(3)	C(4)–N(5)–C(5)	111.5(6)
N(1)–Co–N(4)	89.1(3)	N(2)–C(1)–C(2)	107.2(6)
N(2)–Co–N(4)	94.8(3)	N(3)–C(2)–C(1)	106.5(6)
N(3)–Co–N(4)	178.6(3)	N(4)–C(3)–C(4)	107.4(6)
O(1)–Co–N(5)	86.3(2)	N(5)–C(4)–C(3)	106.9(6)
N(1)–Co–N(5)	173.1(3)	N(5)–C(5)–C(6)	112.5(6)
N(2)–Co–N(5)	95.2(2)	O(1)–C(6)–O(2)	123.9(6)
N(3)–Co–N(5)	92.9(2)	O(1)–C(6)–C(5)	115.9(6)
N(4)–Co–N(5)	85.8(2)	O(2)–C(6)–C(5)	120.2(6)

Spectral Measurements. The absorption and CD spectra were measured by JASCO UVIDEC-670 spectrophotometer and a JASCO J-22 spectropolarimeter, respectively. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Hitachi R-90H spectrometer relative to internal references of sodium 3-(trimethylsilyl)propionate-2,2,3,3-d_4 (TSP) and dioxane ($\delta=67.40$), respectively.

Results and Discussion

Assignment of Geometrical Isomers. As shown in Fig. 1, three *fac* isomers (*trans*(O, NH$_3$), *trans*(N$_t$, NH$_3$), and *trans*(N$_c$, NH$_3$)) and one *mer* isomer are possible for $[Co(edma)(NH_3)(en)]^{2+}$.[12] The absorption spectra of four geometrical isomers differ slightly from each other in the d–d absorption band region (Fig. 2), though all of the isomers have common $[Co(O)(N)_5]$-type chromophore (Fig. 1). It was previously reported that in a series of bis-type cobalt(III) complexes, the meridionally chelated isomers exhibit more intense d–d absorption bands than the facially chelated ones do.[2,4,6] Taking

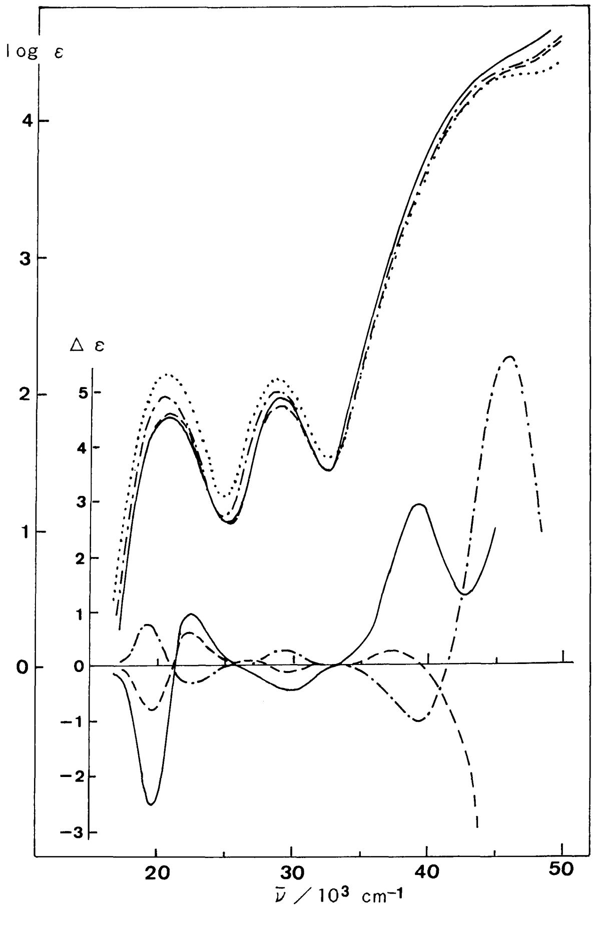


Fig. 2. Absorption and CD spectra of [Co(edma)-(NH$_3$)(en)]$^{2+}$; $(-)^{CD}_{513}$-*trans*(O, NH$_3$) (F-1) (—), $(-)^{CD}_{510}$-*trans*(N$_t$, NH$_3$) (F-2) (----), $(+)^{CD}_{519}$-*trans*(N$_c$, NH$_3$) (F-4) (-•-•-), and *mer* (F-3) (····) isomers.

this empirical rule into consideration, the F-3 isomer can be assigned to the *mer* isomer (Fig. 1). This assignment is in agreement with that based on the ^{1}H NMR chemical shift data; the *mer* isomer shows a singlet peak at δ=3.8 suggesting the equivalent methylene protons on the glycinate ring (G-ring), while the remaining three isomers exhibit AB quartet peaks due to the unequivalent methylene protons on the corresponding G-ring in the range of δ=3.2—4.3 (Fig. 3). Accordingly, the F-1, F-2, and F-4 isomers can be assigned to the *fac* isomers. The assignments of these *fac* isomers were made on the basis of their chemical shifts of the ^{13}C NMR spectra as follows.

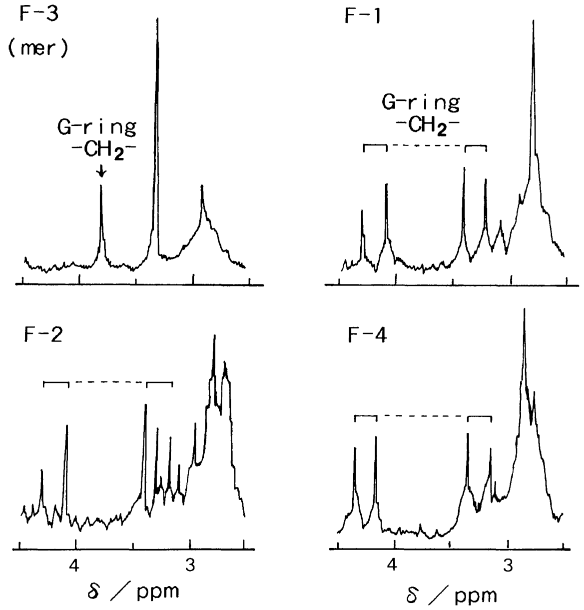


Fig. 3. ^{1}H NMR spectra of four geometrical isomers in [Co(edma)(NH$_3$)(en)]$^{2+}$.

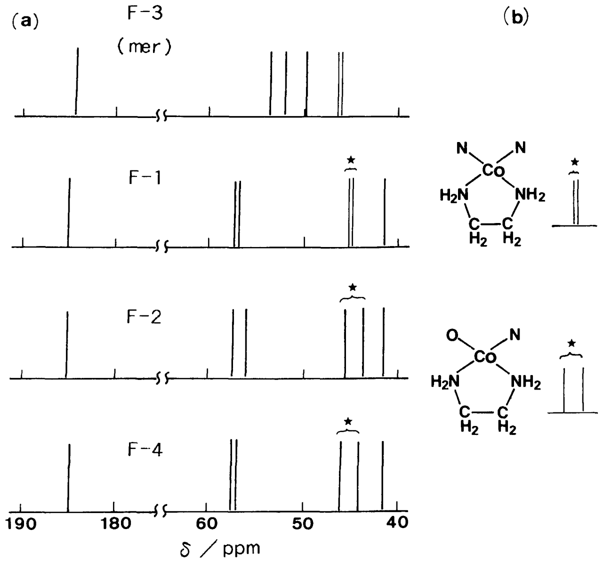


Fig. 4. ^{13}C NMR shift patterns of four geometrical isomers in [Co(edma)(NH$_3$)(en)]$^{2+}$.

As shown in Fig. 4(a), three *fac* isomers exhibit similar ^{13}C NMR chemical shift to each other; however, a slight difference in shift is observed between two signal peaks in the region of δ=43.8—46.1 due to the ethylenediamine carbons. The difference in shift is smaller in the F-1 isomer (0.18 ppm) than in the F-2 or F-4 isomer (1.80 ppm). The difference in shift between the F-1 isomer and the F-2 or F-4 isomer is related to the difference of ligating atoms at the trans position to each of the ethylenediamine carbons (Fig. 4(b)),[3] namely, a smaller difference in shift is expected for the configuration in which two trans ligating atoms are nitrogen (upper in Fig. 4(b)) than for a configuration in which two trans ligating atoms are nitrogen and oxygen (lower in Fig. 4(b)). Accordingly, the F-1 isomer is assignable to *trans*(O, NH$_3$). However, it is difficult to distinguish the F-2 and F-4 isomers because of their quite similar ^{13}C NMR spectral behavior. Hence, we attempted to determine the structure of the F-4 [(+)$^{CD}_{519}$] isomer by X-ray crystal analysis.

Crystal Structure of (+)$^{CD}_{519}$-[Co(edma)(NH$_3$)(en)]Br$_2$·H$_2$O (F-4). A perspective drawing of the complex cation of the F-4 isomer, which shows the positive CD sign at 519 nm, is shown in Fig. 5, together with its atomic numbering scheme. In the complex cation, the cobalt atom is octahedrally surrounded by the oxygen and five nitrogen atoms, and the edma ligand coordinates facially to the cobalt atom as a terdentate. The ammine ligand, N(1), occupies the trans position to the secondary nitrogen atom, N(5), of the edma ligand to take the *trans*(N$_c$, NH$_3$) configuration (Figs. 1 and 5). This suggests that the geometry of the F-2 isomer can be assigned to *trans*(N$_t$, NH$_3$) (Fig. 1). The result of the X-ray crystal structure analysis indicates that the absolute configuration of the (+)$^{CD}_{519}$ F-4 cation takes the Δ(EE) Δ(GE) (where G and E denote glycinate and ethylenediamine chelate rings, respectively) configuration, and the asymmetric nitrogen atom in the edma has an absolute configuration of

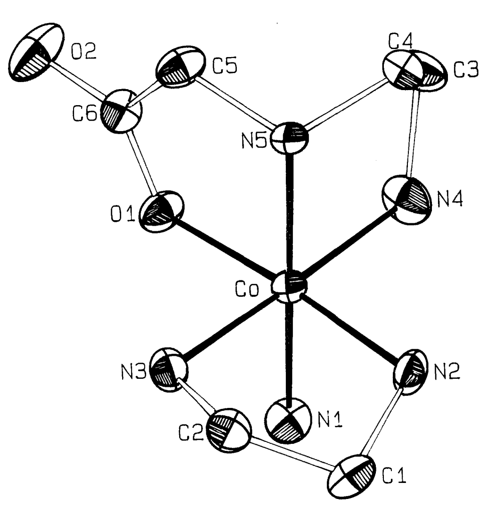


Fig. 5. Perspective view of (+)$^{CD}_{519}$-[Co(edma)(NH$_3$)(en)]$^{2+}$ (F-4) ion.

S[*S*(N)]. This result coincides with the suggestion made by the ^{1}H NMR method using stereospecific deuteration (vide infra). The ethylenediamine chelate ring takes a gauche form with a δ conformation. In the edma ligand, the G-ring is an envelope form and the E-ring is a gauche form with a λ conformation. The bond distances and angles of the complex cation fall assume reasonable values for the ethylenediamine and edma ligands.[2,5,8,11,20)]

Absolute Configuration of the *fac* Isomers. It has been shown that one of the methylene protons on the G-ring in the edma ligand chelated facially to the cobalt(III) ion is stereospecifically deuterated in basic D_2O.[2,4,6)] For example, when a secondary nitrogen atom (N_c) of the edma takes an *S*(N) chirality, the outside proton (H_b in Fig. 6) is deuterated faster than the inside one (H_a). As a result, the methylene carbon on G-ring becomes an asymmetric center (–CHD–) with an *R*(C) chirality. In this case, the ^{1}H NMR signal of the undeuterated methylene proton on G-ring is observed as a single peak in a higher magnetic field. This stereospecific deuteration method was applied to the *fac* isomers of $[Co(edma)(NH_3)(en)]^{2+}$.

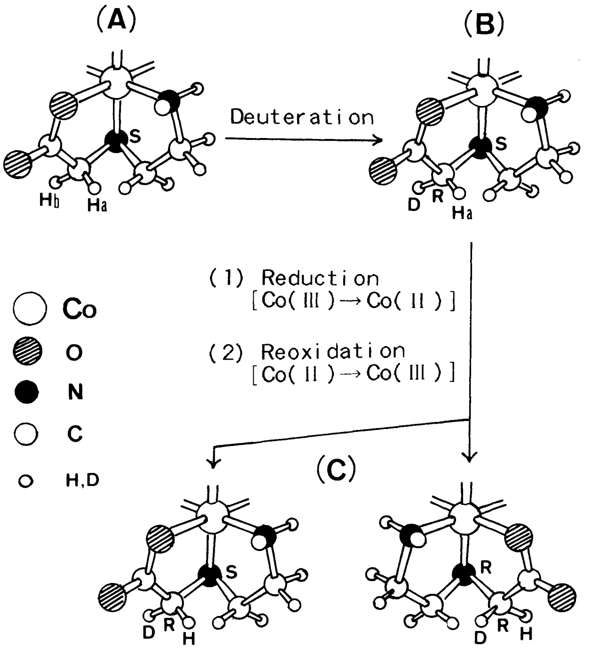


Fig. 6. Chemical environment of the facially coordinating edma ligand; (A): undeuterated, (B): deuterated, and (C): reprepared by oxidizing the reduction product of (B) (see Experimental).

Figure 7 shows the ^{1}H NMR spectra of $\Delta\Lambda\Delta$-*R*(N), *R*(N)-$(-)^{CD}_{543}$- and $\Lambda\Lambda\Lambda$-*S*(N), *S*(N)-$(+)^{CD}_{543}$-C_2-*trans*(O)-$[Co(edma)_2]^+$ (E-1), which are derived from each of the deuterated $(-)^{CD}_{513}$-*trans*(O,NH$_3$), $(+)^{CD}_{510}$-*trans*(N$_t$,NH$_3$), and $(+)^{CD}_{519}$-*trans*(N$_c$,NH$_3$) isomers of $[Co(edma)(NH_3)(en)]^{2+}$. When the deuterated $(-)^{CD}_{513}$-*trans*(O,NH$_3$) isomer was used as a starting material, a single peak (marked with * in Fig. 7) due to the methylene proton on G-ring was observed at δ=ca. 3.35 (higher field side) for $(-)^{CD}_{543}$-E-1 and at δ=ca. 4.3 (lower field side) for $(+)^{CD}_{543}$-E-1. As described above (Fig. 6), a single peak at higher field is assigned to the inside proton (H_a) and a single peak at lower field to the outside proton (H_b); when the asymmetric nitrogen atom in the edma takes an *S* chirality, and the undeuterated proton is in the outside, the asymmetric carbon has an *S* chirality. These behaviors indicate that the chirality of the deuterated methylene carbon on G-ring is an *S*(C) configuration. Accordingly, the absolute configuration of the $(-)^{CD}_{513}$-*trans*(O,NH$_3$) isomer is assigned to Δ(GE)-*R*(N), which contains an *S*(C) configuration. Similar consideraions for the ^{1}H NMR spectral data of the $(+)^{CD}_{510}$-*trans*(N$_t$, NH$_3$) and $(+)^{CD}_{519}$-*trans*(N$_c$,NH$_3$) isomers lead to conclude that their absolute configurations are Λ(EE)-*S*(N) and Λ(EE)Δ(GE)-*S*(N), respectively, as listed in Table 3. This configurational assignment for the $(+)^{CD}_{519}$-*trans*(N$_c$, NH$_3$) (F-4) isomer quite agrees with the result obtained from the X-ray study.

CD Spectra. The CD spectra of three *fac* isomers of $[Co(edma)(NH_3)(en)]^{2+}$ are shown in Fig. 2. Their optical activities arise mainly from the configurational chirality (Λ and Δ), due to skew pairs of the chelate rings between the edma and en ligands, as well as the chirality (*S* and *R*) due to the secondary nitrogen of the coordinated edma ligand, as the case of $[Co(edma)(dien)]^{2+}$, which has a similar chromophore to the present isomers.[6)] However, the CD spectral behaviors of the present isomers differ considerably from those of the isomers of $[Co(edma)(dien)]^{2+}$. For example, Λ(EE)-*S*(N)-*trans*(N$_t$,NH$_3$)-$[Co(edma)(NH_3)(en)]^{2+}$ shows the CD spectrum almost enantiomeric to $\Delta\Lambda\Delta$-*S*(N)-*mer*(N$_t$)*cis*(N$_c$)-$[Co(edma)(dien)]^{2+}$, although Λ(GE)-*S*(N)-*trans*(O,NH$_3$)-$[Co(edma)(NH_3)(en)]^{2+}$ shows a

Table 3. Absolute Configurations of *fac*-$[Co(edma)(NH_3)(en)]^{2+}$ Determined by ^{1}H NMR Method

Complex	Geometry	$(+)^{CD}_{\lambda}$-Isomer$^{b)}$	$(-)^{CD}_{\lambda}$-Isomer$^{b)}$
F-1	*trans*(O, NH$_3$)	$(+)^{CD}_{513}$-Λ(GE)-*S*(N)	$(-)^{CD}_{513}$-Δ(GE)-*R*(N)
F-2	*trans*(N$_t$, NH$_3$)	$(+)^{CD}_{510}$-Λ(EE)-*S*(N)	$(-)^{CD}_{510}$-Δ(EE)-*R*(N)
F-4	*trans*(N$_c$, NH$_3$)	$(+)^{CD}_{519}$-Λ(EE)Δ(GE)-*S*(N)	$(-)^{CD}_{519}$-Δ(EE)Λ(GE)-*R*(N)

a) N_t and N_c denote terminal and central (secondary) nitrogen atoms of the edma ligand, respectively.
b) G and E denote skew-paired glycinate and ethylenediamine rings, respectively, and *S* and *R* denote the chiralities of the central nitrogen atom.

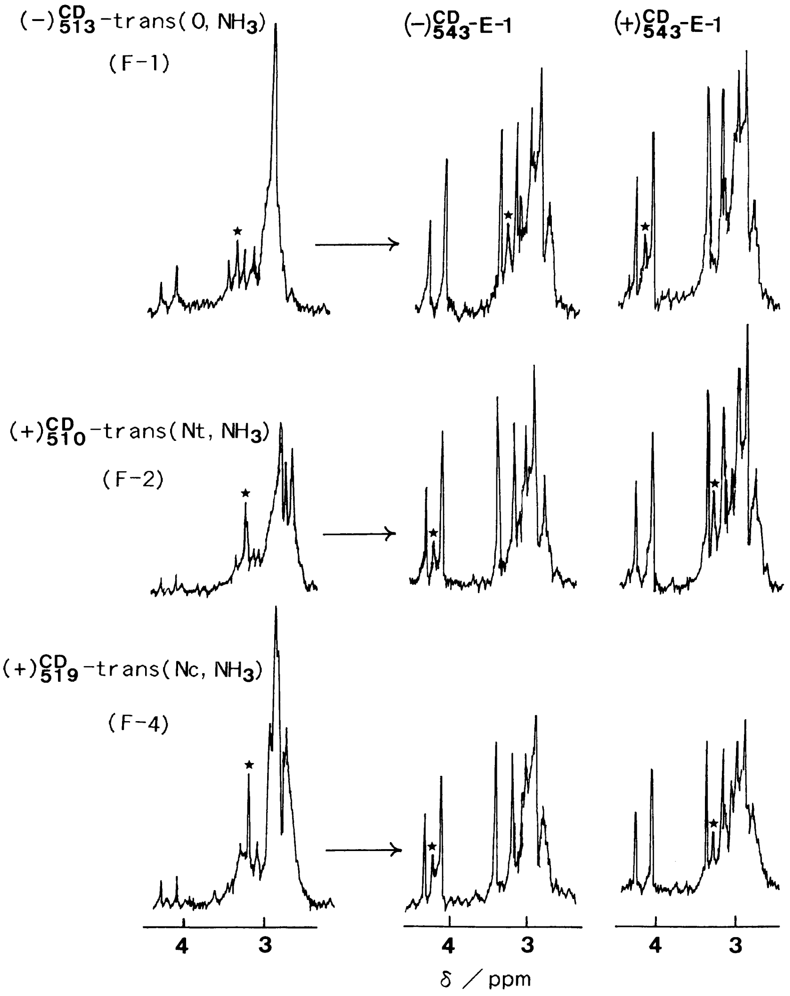


Fig. 7. ^{1}H NMR spectra of ΔΔΔ-*R*(N),*R*(N)-(−)$^{CD}_{543}$- and ΔΔΔ-*S*(N),*S*(N)-(+)$^{CD}_{543}$-C$_2$-*trans*(O)-[Co(edma)$_2$]$^+$ (E-1) obtained from the stereospecifically deuterated (−)$^{CD}_{513}$-*trans*(O, NH$_3$) (F-1), (+)$^{CD}_{510}$-*trans*(N$_t$, NH$_3$) (F-2), and (+)$^{CD}_{519}$-*trans*(N$_c$, NH$_3$) (F-4) isomers of [Co(edma)(NH$_3$)(en)]$^{2+}$. (Aristerisked peaks: G-ring -CHD-).

quite similar CD spectral behavior to ΔΔΔ-*S*(N)-*fac*(N$_t$)*cis*(N$_c$)-[Co(edma)(dien)]$^{2+}$ (Fig. 2).6) These facts indicate that care must be taken in relating the CD spectra to absolute configurations of complexes consisting of the terdentate, bidentate, and unidentate ligands.

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12) In this work, the *mer* and *fac* isomers denote the isomers with the meridionally and facially chelated edma ligands, respectively. In N$_t$ and N$_c$, the subscripts t and c denote the terminal NH$_2$ and secondary N in the edma ligand, respectively.

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