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Preparation and Stereochemistry of Cobalt(III) Complexes with Ethylenediamine-*N*-acetate and 3-Azapentane-1,5-diamine or 3-Methyl-3-azapentane-1,5-diamine

Takaji YASUI,* Toshie SHIKIJI, Norio KOINE,† Tomoharu AMA, and Hiroshi KAWAGUCHI
Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780
†Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Bunkyo-cho, Matsuyama 790
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Four geometrical isomers possible in each of $[Co(edma)(dien)]^{2+}$ and $[Co(edma)(mdien)]^{2+}$, where edma, dien, and mdien denote ethylenediamine-*N*-acetate, 3-azapentane-1,5-diamine, and 3-methyl-3-azapentane-1,5-diamine respectively, and facial isomer of $[Co(edma)(NH_3)_3]^{2+}$ were prepared and resolved into optically active isomers by a column-chromatographic method. The structural assignments of these geometrical isomers were carried out on the basis of the absorption, ^1H NMR, and ^{13}C NMR spectral data. The absolute configurations of the optically active isomers containing facially coordinated edma were determined by ^1H NMR measurements of the glycinate-ring methylene (-CHD-) of edma stereospecifically deuterated in a weak basic D_2O. The relationship between the absolute configurations and the CD spectral behaviors of these isomers is also discussed.

The octahedral complexes of cobalt(III) with terdentate ligands, such as iminodiacetate (ida), *N*-methyliminodiacetate (mida), 3-azapentane-1,5-diamine (dien), 3-methyl-3-azapentane-1,5-diamine (mdien), and ethylenediamine-*N*-acetate (edma), provide varieties of geometrical and optical isomers. Therefore, the complexes with these ligands are useful for the investigations of spectroscopic properties, stereochemistry, and reactivity (isomerization and racemization reactions). Keene and coworkers first isolated three geometrical isomers (u-fac, s-fac, and mer) possible for $[Co(dien)_2]^{3+}$.[1] Thereafter, a complete series of geometrical isomers have been reported for the complexes of $[Co(ida)_2]^-$,[2] $[Co(mida)_2]^-$,[2] $[Co(ida)(mida)]^-$,[3] $[Co(ida)(dien)]^+$,[4] $[Co(mida)(dien)]^+$,[5] $[Co(ida)(mdien)]^+$,[5] $[Co(mida)(mdien)]^+$,[5] $[Co(dien)(mdien)]^{3+}$ [6,7] (three isomers), $[Co(edma)_2]^+$ (six isomers),[8-10] [Co(ida)(edma)],[9,10] and [Co(mida)(edma)][11] (four isomers). However, there is no report for the mixed-ligand complexes of $[Co(edma)(dien)]^{2+}$ and $[Co(edma)(mdien)]^{2+}$. Both the complexes provide four geometrical isomers with chiral structure, as shown in Fig. 1.

In the present paper, the preparation and optical resolution of $[Co(edma)(dien)]^{2+}$, $[Co(edma)(mdien)]^{2+}$ and $[Co(edma)(NH_3)_3]^{2+}$ will be described, and the stereochemistry will be discussed on the basis of their absorption, ^1H NMR, ^{13}C NMR, and CD spectral data.

Experimental

Preparation and Optical Resolution of the Complexes. Preparation of Four Geometrical Isomers of $[Co(edma)(mdien)]^{2+}$: An aqueous solution containing 2.27 g (0.01 mol) of ethylenediamine-*N*-acetic acid dihydrochloride dihydrate[12] (Hedma·2HCl·$2H_2O$) and 2.26 g (0.01 mol) of 3-methyl-3-azapentane-1,5-diamine trihydrochloride[13] (mdien·3HCl) in 60 cm^3 of water was passed through an anion-exchange resin (Dowex 1×8, ClO_4^- form) column to convert the chloride ions to the perchlorate ions, and then the solution was evaporated to a volume of 20 cm^3. Similarly, an aqueous solution containing 2.23 g (0.01 mol) of $CoCl_2·6H_2O$ in 30 cm^3 of water was passed through an anion-exchange resin column of ClO_4^- form. These two solutions were mixed and the solution was adjusted to pH 6.5—6.9 with 1 mol dm^{-3} NaOH solution. Lead dioxide (8.0 g) was stirred into the solution in small portions at 40 °C over a 1 h period, the pH of the solution being kept at 6.5—6.9. After insoluble materials had then been removed by filtration, the filtrate (red-purple) was charged on an SP-Sephadex C-25 column (ϕ 4.7 cm×90 cm, NH_4^+ form). The adsorbed band was developed with 0.2 mol dm^{-3} $(NH_4)_2SO_4$ solution. The band was separated into several bands by recyclic developement: red-orange (a mixture of four isomers of $[Co(edma)_2]^+$), red (a mixture of two isomers of $[Co(edma)_2]^+$), orange (desired isomer, el 1), red-orange (el 2), orange (el 3), violet (unidentified complex), orange (el 4), and orange ($[Co(mdien)_2]^{3+}$) bands (formation ratio of el 1, el 2, el 3, and el 4 was 39 : 48 : 2 : 11). The eluate from each band of el 1—el 4 was evaporated under reduced pressure, and methanol was added to the concentrated solution. Ammonium sulfate deposited was removed by filtration and the filtrate was again evaporated. A crude complex was obtained from the concentrated solution by addition of methanol. The isomers of el 1, el 3, and el 4 were isolated in a crystal by recrystallizing the crude complexes from water-methanol

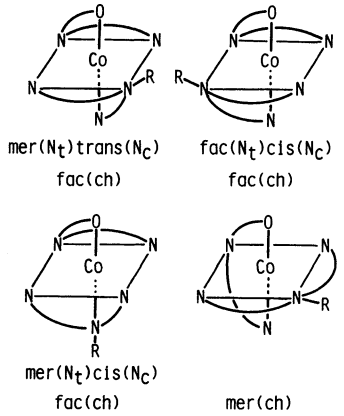

Fig. 1. Four geometrical isomers of $[Co(edma)(dien)]^{2+}$ (R=H) or $[Co(edma)(mdien)]^{2+}$ ($R=CH_3$). N_t and N_c denote terminal and central nitrogens, respectively, and fac(ch) and mer(ch) represent the isomers with facially and meridionally chelated ligands, respectively.

solvent. The isomer of el 2 was obtained as a crystal of bromide salt by converting the sulfate salt to the bromide salt using a short QAE-Sephadex (Br^- form) column. Found for el 1: C, 25.51; H, 6.45; N, 16.42%. Calcd for $[Co(edma)(mdien)]SO_4 \cdot 2H_2O = C_9H_{28}N_5O_8SCo$: C, 25.41; H, 6.64; N, 16.47%. Found for el 2: C, 23.60; H, 5.42; N, 14.97%. Calcd for $[Co(edma)(mdien)]Br_2 \cdot 0.5H_2O = C_9H_{25}N_5O_{2.5}Br_2Co$: C, 23.39; H, 5.45; N, 15.16%. Found for el 3: C, 24.96; H, 6.50; N, 16.15%. Calcd for $[Co(edma)(mdien)]SO_4 \cdot 2.5H_2O = C_9H_{29}N_5O_{8.5}SCo$: C, 24.89; H, 6.73; N, 16.12%. Found for el 4: C, 26.19; H, 6.76; N, 16.53%. Calcd for $[Co(edma)(mdien)]SO_4 \cdot 1.5H_2O = C_9H_{27}N_5O_{7.5}SCo$: C, 25.96; H, 6.54; N, 16.82%.

Resolution of $[Co(edma)(mdien)]^{2+}$: The racemates of el 1—el 4 were resolved into optically active isomers by a column-chromatographic method.

A solution containing ca. 1 g of each racemate of el 1—el 4 in a small amount of water was poured onto an SP-Sephadex column (ϕ 4.7 cm×50 cm, Na^+ form), and the adsorbed band was developed with a 0.2 mol dm^{-3} $Na_2Sb_2(d\text{-}tart)_2$ solution. On each chromatographic run of el 1, el 3, and el 4, the adsorbed band separated completely into two bands by repeating recyclic developement 5—6 times, and each band was eluted out from the column. Whereas on the run of el 2, the band separation was incomplete. The front and rear fractions of the broadening band, which showed enantiomeric CD curves with (+) and (−) signs at 528 nm respectively, were eluted out. Each eluate was evaporated, and a saturated KCl solution was added to the concentrated solution to make deposit $K_2Sb_2(d\text{-}tart)_2$ salt, which was removed by filtration. The filtrate was again evaporated, and methanol was added to the concentrated solution to eliminate KCl. The methanolic solution was evaporated, and the concentrated solution was charged on a short QAE-Sephadex (Br^- form) column to convert Cl^- ion to Br^- ion. The solution eluted with water was evaporated and methanol was added to the concentrated solution. A crude complex obtained was recrystallized from water by addition of methanol. Found for the early eluted $(-)^{CD}_{509}$ isomer of el 1: C, 23.22; H, 5.63; N, 14.95%. Found for the $(-)^{CD}_{528}$ isomer (from rear fraction) of el 2: C, 23.18; H, 5.65; N, 14.64%. Found for the early eluted $(-)^{CD}_{540}$ isomer of el 4: C, 22.92; H, 5.59; N, 15.03%. Calcd for $[Co(edma)(mdien)]Br_2 \cdot H_2O = C_9H_{26}N_5O_3Br_2Co$: C, 22.95; H, 5.56; N, 14.85%. Found for the early eluted $(+)^{CD}_{514}$ isomer of el 3: C, 23.65; H, 6.01; N, 14.30%. Calcd for $[Co(edma)(mdien)]Br_2 \cdot H_2O \cdot 0.5CH_3OH = C_{9.5}H_{28}N_5O_{3.5}Br_2Co$: C, 23.42; H, 5.79; N, 14.38%.

Preparation and Resolution of $[Co(edma)(dien)]^{2+}$: The crude isomers (el 1—el 4) of $[Co(edma)(dien)]SO_4$ were obtained by the same method as that used for the isomers of $[Co(edma)(mdien)]SO_4$. Formation ratio of el 1, el 2, el 3, and el 4 was 18 : 55 : 12 : 15. The sulfate salts were converted to the chloride salts using a QAE-Sephadex A-25 (Cl^- form) column. The crude complexes obtained were recrystallized from water by addition of methanol. The isomers of el 1 and el 3 were obtained in orange crystals and the isomers of el 2 and el 4 in red-orange crystals. Found for el 1: C, 27.03; H, 6.36; N, 19.34%. Calcd for $[Co(edma)(dien)]Cl_2 \cdot 0.5H_2O = C_8H_{23}N_5O_{2.5}Cl_2Co$: C, 26.75; H, 6.46; N, 19.50%. Found for el 2: C, 25.70; H, 6.67; N, 18.69%. Found for el 4: C, 25.44; H, 6.58; N, 18.54%. Calcd for $[Co(edma)(dien)]Cl_2 \cdot 1.5H_2O = C_8H_{25}N_5O_{3.5}Cl_2Co$: C, 25.48; H, 6.68; N, 18.57%. Found for el 3: C, 24.96; H, 6.78; N, 17.85%. Calcd for $[Co(edma)(dien)]Cl_2 \cdot 2H_2O = C_8H_{26}N_5O_4Cl_2Co$: C, 24.88; H, 6.79; N, 18.14%.

The optical resolutions of these isomers were carried out by the same method as that used for the four isomers of $[Co(edma)(mdien)]^{2+}$. Found for the late eluted $(+)^{CD}_{504}$ isomer of el 1: C, 25.70; H, 6.55; N, 18.27%. Calcd for $[Co(edma)(dien)]Cl_2 \cdot 1.5H_2O = C_8H_{25}N_5O_{3.5}Cl_2Co$: C, 25.48; H, 6.68; N, 18.57%. Found for the late eluted $(-)^{CD}_{514}$ isomer of el 2: C, 20.87; H, 5.33; N, 15.13%. Calcd for $[Co(edma)(dien)]Br_2 \cdot H_2O = C_8H_{24}N_5O_3Br_2Co$: C, 21.02; H, 5.29; N, 15.32%. Found for the early eluted $(-)^{CD}_{500}$ isomer of el 3: C, 22.61; H, 5.66; N, 15.08%. Calcd for $[Co(edma)(dien)]Br_2 \cdot CH_3OH = C_9H_{26}N_5O_3Br_2Co$: C, 22.95; H, 5.56; N, 14.86%. Found for the late eluted $(-)^{CD}_{527}$ isomer of el 4: C, 27.07; H, 6.41; N, 19.58%. Calcd for $[Co(edma)(dien)]Cl_2 \cdot 0.5H_2O = C_8H_{23}N_5O_{2.5}Cl_2Co$: C, 26.75; H, 6.46; N, 19.50%.

Preparation and Resolution of *fac*-$[Co(edma)(NH_3)_3]^{2+}$: Although the geometrical structure of this complex has been reported in the preceding paper,[14] the preparative method was not described. A solution containing 4.0 g of Hedma · 2HCl · $2H_2O$ in 40 cm^3 of water was poured onto a column containing anion-exchange resin (Dowex 1×8, NO_3^- form) and eluted out with water, in order to exchange Cl^- ion to NO_3^- ion. The eluate was evaporated to ca. 3 cm^3 and then added to a solution containing 6.0 g of $[Co(NH_3)_5(H_2O)](NO_3)_3$ in 250 cm^3 of 25% aqueous NH_3. The mixed solution was heated at 80 °C for 3 h and then cooled to room temperature. The resultant solution was evaporated to ca. 20 cm^3 to charge again on an SP-Sephadex column (ϕ 4.7 cm×50 cm, Na^+ form). The adsorbed band was developed with 0.5 mol dm^{-3} $NaNO_3$ solution. The second band of red-orange color was eluted out, and then the eluate was concentrated. Methanol was added to the concentrated eluate to make deposit $NaNO_3$ salt, which was removed by filtration. Red-orange complex was obtained from the filtrate by evaporation and by addition of methanol. This complex was used for the resolution without further purification.

The racemate obtained above was dissolved into 50 cm^3 of water to charge on an SP-Sephadex column (ϕ4.7 cm×50 cm, K^+ form). The adsorbed band was completely separated into two bands by developing it with a 0.1 mol dm^{-3} $K_2Sb_2(d\text{-}tart)_2$ solution. Each band was eluted out with a 0.2 mol dm^{-3} KCl solution. The first and second eluates which exhibited (+) and (−) CD signs at 512 nm, respectively, were evaporated to ca. 5 cm^3 and 100 cm^3 of methanol was added to the concentrated solutions. Potassium chloride deposited was removed by filtration. Ethanol was added to the filtrates to obtain crude complexes, which were recrystallized from water by addition of ethanol. Found for the $(-)^{CD}_{512}$ isomer: C, 15.40; H, 6.35; N, 22.34%. Calcd for $[Co(edma)(NH_3)_3]Cl_2 \cdot H_2O = C_4H_{20}N_5O_3Cl_2Co$: C, 15.20; H, 6.38; N, 22.16%.

Determination of Absolute Configurations of the Complexes by ^1H NMR Technique. Determination of the absolute configurations of the optically active *fac*-$[Co(edma)(dien)]^{2+}$ and *fac*-$[Co(edma)(NH_3)_3]^{2+}$ complexes was carried out by the method modified that used for the $[Co(edma)_2]^+$ complex in our previous study.[8]

About 0.2 g of $(+)^{CD}_{504}$ el 1 $[Co(edma)(dien)]Cl_2 \cdot 1.5H_2O$ was dissolved into a buffer solution (pH 10), and the solution was allowed to stand at 40 °C for ca. 1 h to deuterate one of the two methylene protons on the edma glycinate ring (G-ring) (Fig. 2). The deuteration reaction was stopped by acidifing the solution (pH 5—6) with 1 mol dm^{-3} HCl, and zinc powder (2 g) was added to the solution. After stirring the mixture for 5 min at ca. 25 °C, unreacted zinc was removed

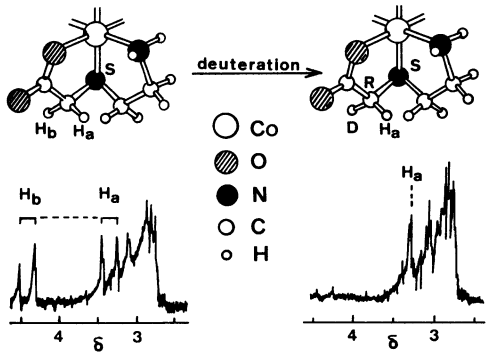

Fig. 2. Stereospecific deuteration on the G-ring $-CH_2-$ of coordinated edma in $(+)^{CD}_{504}$ el 1 of $[Co(edma)(dien)]^{2+}$

by filtration. To the filtrate, 52 mg of $CuSO_4 \cdot 5H_2O$ (to make produce a blue copper(II) complex of dien) and 95 mg of Hedma $\cdot$ 2HCl $\cdot$ $2H_2O$ were added, and the solution was adjusted to pH 7.0—7.5 with 1 mol dm^{-3} NaOH. Lead dioxide (1.5 g) was added to the solution and the mixture was stirred for 15 min at ca. 25 °C. The reactant solution was filtered, and the filtrate was poured onto an SP-Sephadex column (ϕ 3 cm×35 cm, Na^+ form). The adsorbed band was separated into red, orange-red, and blue bands by elution with a 0.2 mol dm^{-3} NaCl solution. The red band including C_2- and C_i-*trans(O)*-$[Co(edma)_2]^+$ isomers was transfered to another SP-Sephadex column and developed with a 0.1 mol dm^{-3} $Na_2Sb_2(d\text{-tart})_2$ solution. The band separated into three bands of $(-)^{CD}_{543}$ C_2-, C_i-, and $(+)^{CD}_{543}$ C_2-*trans(O)*-$[Co(edma)_2]^+$. Each band was eluted out and crystals of $(-)^{CD}_{543}$ and $(+)^{CD}_{543}$ isomers were obtained by the same procedure as that described in our previous paper,[9] and their ^{1}H NMR were measured.

Deuterations of the $(+)^{CD}_{514}$ el 2 and $(-)^{CD}_{527}$ el 4 isomers of $[Co(edma)(dien)]^{2+}$ and the $(-)^{CD}_{512}$ isomer of *fac*-$[Co(edma)(NH_3)_3]^{2+}$ were also carried out by the same method as that described for $(+)^{CD}_{504}$ el 1, except that $CuSO_4 \cdot 5H_2O$ was not used for the last isomer. The ^{1}H NMR spectra of the C_2-*trans(O)*-$[Co(edma)_2]^+$ (E-1) enantiomers obtained from the deuterated isomers are shown in Fig. 3.

Spectral Measurements. The absorption and CD spectra were measured by a Hitachi 557-type spectrometer and a JASCO J-22 spectropolarimeter, respectively. The ^{1}H NMR spectra were recorded on a JEOL MH-100 NMR spectrometer using DSS as an internal standard. The ^{13}C NMR spectra at 25 MHz were recorded on a JEOL JNM-FX 100 spectrometer. The peak positions were measured relative to internal dioxane (δ=67.40). The signals of the G-ring $-CH_2-$ carbons in coordinated edma were assigned by a ^{1}H selective decoupling method.

Results and Discussion

Assignments of Geometrical Isomers. As Fig. 1 shows, each of the mixed-ligand complexes, $[Co(edma)(mdien)]^{2+}$ and $[Co(edma)(dien)]^{2+}$, provides three facially chelated [fac(ch)] isomers of mer(N_t)-trans(N_c), fac(N_t)cis(N_c), and mer(N_t)cis(N_c) and one meridionally chelated [mer(ch)] isomer. All these isomers are chiral complexes which can be resolved into

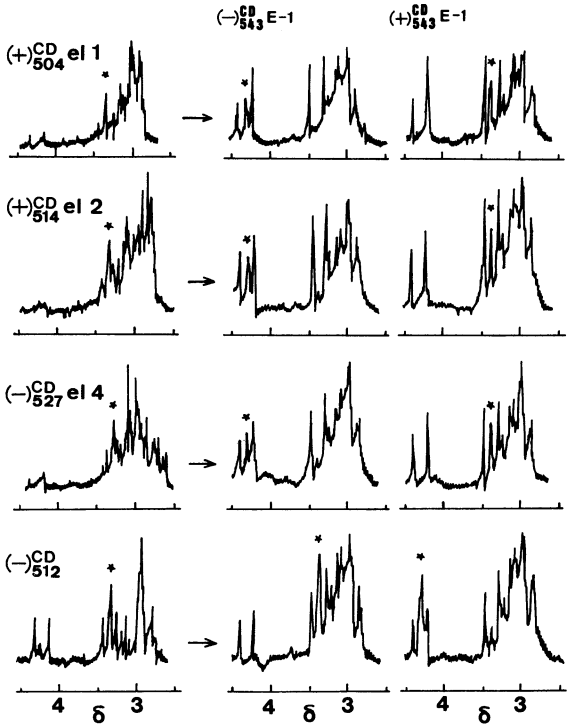

Fig. 3. ^{1}H NMR spectra of $(-)^{CD}_{543}$ [ΔΔΔ(N_R,N_R)] and $(+)^{CD}_{543}$ [ΔΔΛ(N_S,N_S)] C_2-*trans(O)*-$[Co(edma)_2]^+$ (E-1) obtained from the stereospecifically deuterated $(+)^{CD}_{504}$ el 1, $(+)^{CD}_{514}$ el 2, and $(-)^{CD}_{527}$ el 4 $[Co(edma)(dien)]^{2+}$ and $(-)^{CD}_{512}$ *fac*-$[Co(edma)(NH_3)_3]^{2+}$. (Aristerisked peaks: G-ring -CHD-.)

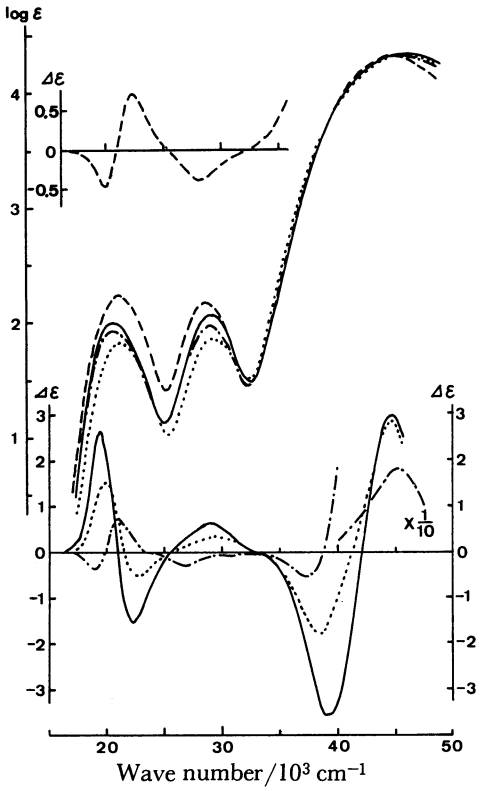

Fig. 4. Absorption and CD curves of [Co(edma)-(dien)]$^{2+}$: ····· $(+)^{CD}_{504}$ el 1, —— $(+)^{CD}_{514}$ el 2, ---- $(-)^{CD}_{500}$ el 3 (in 0.1 mol dm^{-3} HCl solution), and -·-·- $(-)^{CD}_{527}$ el 4.

Table 1. Absorption Spectral Data of the edma Complexes

Isomer	Structure	First band[a)]	Second band[a)]	CT band[a)]
$[Co(edma)(dien)]^{2+}$				
el 1	*mer*(N_t)*trans*(N_c)	21.05 (1.822)	28.99 (1.865)	45.66 (4.309)
el 2	*fac*(N_t)*cis*(N_c)	20.66 (1.990)	28.99 (2.056)	46.08 (4.325)
el 3	*mer*(ch)	21.05 (2.223)	28.65 (2.163)	44.64 (4.296)
el 4	*mer*(N_t)*cis*(N_c)	20.62 (1.922)	28.99 (1.946)	45.87 (4.305)
$[Co(edma)(mdien)]^{2+}$				
el 1	*mer*(N_t)*trans*(N_c)	20.81 (1.890)	29.07 (1.878)	44.84 (4.294)
el 2	*fac*(N_t)*cis*(N_c)	20.28 (2.092)	28.41 (2.078)	45.05 (4.310)
el 3	*mer*(ch)	20.45 (2.191)	28.25 (2.217)	43.29 (4.262)
el 4	*mer*(N_t)*cis*(N_c)	19.92 (1.892)	28.49 (1.926)	43.67 (4.266)
$[Co(edma)(NH_3)_3]^{2+}$				
	fac	20.41 (1.840)	28.82 (1.925)	47.90 (4.280)

a) Wave numbers and logε values (in parenthesis) are given in $10^3\,cm^{-1}$ and $mol^{-1}\,dm^3\,cm^{-1}$, respectively.

optically active isomers. The four geometrical isomers have the same chromophore of the [Co N_5O] type, but they show spectral behaviors slightly different from each other, especially in the d-d absorption region (Fig. 4 and Table 1). The structures of these isomers can be assigned on the basis of the absorption, ^1H and ^{13}C NMR spectral data.

It is known that the molar absorption coefficient of the first absorption band is larger in a mer(ch) isomer than in a fac(ch) isomer of the terdentate ligand complexes, such as $[Co(ida)_2]^-$,[2] $[Co(edma)_2]^+$,[8] and $[Co(dien)_2]^{3+}$.[1,15] In the present complexes the band intensities of el 3 are more enhanced than those of the other isomers, suggesting that the structure of the former isomer may be assigned to mer(ch) and those of the latter isomers to fac(ch). These assignments are consistent with those done on the basis of the ^1H and ^{13}C NMR data (vide infra).

The ^1H NMR spectra of the four isomers of $[Co(edma)(mdien)]^{2+}$ are illustrated in Fig. 5 and their chemical shifts are given in Table 2, together with those of $[Co(edma)(dien)]^{2+}$. The G-ring methylene protons of el 3 resonate as a singlet-like peak at 3.73 ppm, while those of el 1, el 2, and el 4 do as four peaks of a AB quartet. Such a difference in signal pattern has also been observed between the mer(ch) and fac(ch) isomers of $[Co(edma)_2]^+$.[9] A comparison in signal pattern between the $[Co(edma)(mdien)]^{2+}$ complex and the $[Co(edma)_2]^+$ complex leads to assign el 3 to mer(ch) and el 1, el 2, and el 4 to fac(ch). Similarly, the mer(ch) and fac(ch) structures for the four isomers of $[Co(edma)(dien)]^{2+}$ are assigned from the ^1H NMR data of the G-ring methylene protons.

The el 1, el 2, and el 4 isomers of $[Co(edma)(mdien)]^{2+}$ show the methyl proton signals in the range of 2.5—2.8 ppm (Fig. 5). Previously, in the study of the (*S*)-alaninato cobalt(III) complex Berends and Brushmiller suggested that the methyl signal shifts to the lower-field side when the methyl group lies at the position deshielded by an anisotropic effect arising from the C-O bond.[16] The molecular model examinations of the three fac(ch) isomers of $[Co(edma)(mdien)]^{2+}$ show that the methyl group attaching to the central nitrogen of mdien lies at the deshielded position only in the mer(N_t)trans(N_c) structure. The methyl signal of el 1 (δ= 2.81) locates at a lower magnetic field than those of el 2 (2.63) and el 4 (2.54), which leads to assign the structure of el 1 to mer(N_t) trans(N_c).

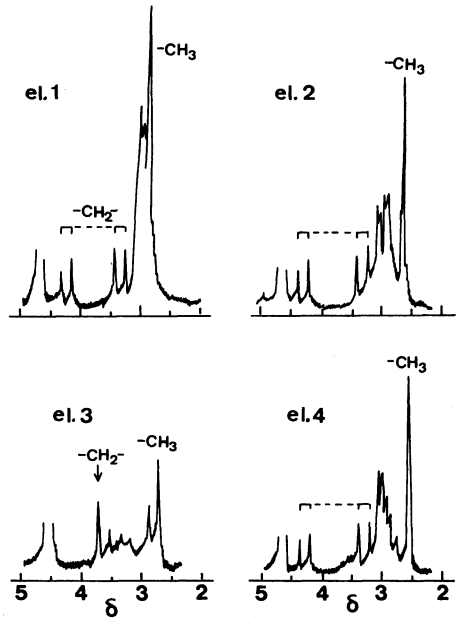

Fig. 5. ^1H NMR spectra of four geometrical isomers in $[Co(edma)(mdien)]^{2+}$.

The structural assignment of el 4 can be made on the basis of the ^{13}C NMR data. In our previous work[10] for the $[Co(edma)_2]^+$ and [Co(ida)(edma)] complexes, their geometrical structures were determined from the ^{13}C chemical shifts; the carbon neighboring to the central nitrogen (N_c) of a terdentate ligand resonates at a lower magnetic field when the trans position to N_c was occupied with oxygen atom than when the position was occupied with nitrogen atom. Figure 6(b) shows the ^{13}C NMR shift patterns of the four isomers of $[Co(edma)(mdien)]^{2+}$, and their shift data are summa-

Table 2. ^{1}H and ^{13}C NMR Data[a] of [Co(edma)(dien)]$^{2+}$ and [Co(edma)(mdien)]$^{2+}$

Isomer	Proton			J_{AB}	Carbon[b]				
	G-ring	$-CH_AH_B-$	$-CH_3$	Hz	a	*b, c	f, h	i	d, e, g
[Co(edma)(dien)]$^{2+}$									
el 1	4.63	2.89		18.5	184.93	57.21	53.94		44.20(d)
						*56.77	53.51		41.37
el 2	4.81	2.82		18.5	184.64	*57.11	54.63		45.08
						56.87	53.87		43.56
									41.32
el 3	3.92	3.64		16.5	183.56	*54.72	50.63		48.29
						53.07	50.39		47.46
									46.68
el 4	4.32	2.86		19.0	185.22	57.65	56.62		43.27
						*55.85	55.07		42.20
									41.42
[Co(edma)(mdien)]$^{2+}$									
el 1	4.23	3.33	2.81	18.0	184.44	57.31	63.93	51.26	42.59
						*57.16	62.96		42.44
									41.27
el 2	4.31	3.31	2.63	19.0	185.51	56.82	64.47	50.53	44.10
						*55.99	62.38		42.25
									40.98
el 3	3.73(s)		2.71	—	183.62	*54.43	61.50	45.80	46.20
						53.75	61.35		45.42
									45.27
el 4	4.26	3.28	2.54	19.0	184.88	*57.16	66.27	51.61	43.03
						57.06	66.08		41.71
									40.84

a) δ Values from DSS (^{1}H) and TMS (^{13}C). b) Labeling of carbons is given in Fig. 6. The marked (*) signal were determined by the selective decoupling method. (s): Singlet-like peak. (d): Doublet peak.

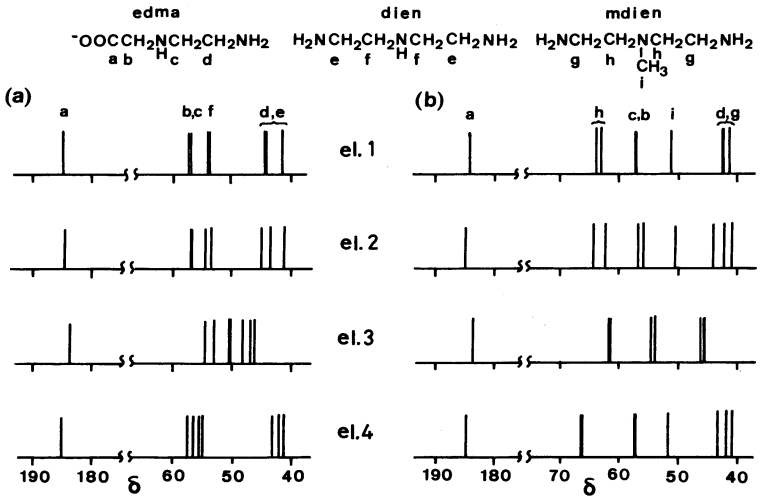

Fig. 6. ^{13}C NMR signal patterns of four geometrical isomers in (a) [Co(edma)(dien)]$^{2+}$ and in (b) [Co(edma)(mdien)]$^{2+}$.

rized in Table 2. Among three fac(ch) isomers, el 4 exhibited resonance peaks of h carbons at the lowest field: δ values for el 4, 66.08 and 66.27; for el 1, 62.96 and 63.93; for el 2, 62.38 and 64.47. Accordingly, the structure of el 4 is assigned to mer(N_t)cis(N_c), in which the trans position to N_c is occupied with oxygen atom.

The geometrical structure of el 2 was assigned on the basis of shift behavior of methyl carbon resonance. In our previous ^{13}C NMR study of [Co(ida)(mida)]$^{-}$, the higher-field shift of methyl carbon resonance observed for the u-fac isomer was ascribed to a steric interaction between the methyl group of the mida ligand and the G-ring methylene of the ida ligand.[3] Steric interaction is also expected to occur between the methyl group of mdien and the G-ring methylene of edma in [Co(edma)(mdien)]$^{2+}$ with fac(N_t)cis(N_c) structure. As given in Table 2, the methyl carbon of el 2 (δ=50.53) resonates at a higher-field relative to those of el 1

Table 3. CD Spectral Data and Absolute Configurations of the edma Complexes

Isomer	Absolute configuration[a]	First band region[b]	Second band region	CT band region[b]
[Co(edma)(dien)]$^{2+}$				
el 1 $(+)^{CD}_{504}$	Λ(GE)Δ(EE)(N_S)	19.84 (+1.532)	29.41 (+0.345)	38.31 (−1.82)
		22.57 (−0.518)		45.05 (+2.84)
el 2 $(+)^{CD}_{514}$	Λ(EE)Δ(GE)Λ(GE)(N_S)	19.46 (+2.611)	29.24 (+0.620)	39.06 (−3.594)
		22.27 (−1.547)		44.84 (+3.00)
el 3 $(-)^{CD}_{500}$[c]		20.00 (−0.437)	28.25 (−0.353)	
		22.22 (+0.705)		
el 4 $(-)^{CD}_{527}$	Δ(GE)Λ(EE)Δ(EE)(N_S)	18.98 (−0.373)	27.10 (−0.268)	37.45 (−0.508)
		21.05 (+0.697)		45.25 (+18.00)
[Co(edma)(mdien)]$^{2+}$				
el 1 $(+)^{CD}_{509}$	Λ(GE)Δ(EE)(N_S)	19.65 (+2.011)	29.85 (+0.135)	38.17 (−3.22)
		22.37 (−0.490)		45.66 (+9.87)
el 2 $(+)^{CD}_{528}$	Λ(EE)Δ(GE)Λ(GE)(N_S)	18.94 (+2.752)	28.57 (+0.735)	41.67 (−1.39)
		21.41 (−1.328)		45.05 (+5.46)
et 3 $(-)^{CD}_{514}$[c]		19.57 (−0.490)	28.41 (−0.165)	37.04 (+1.79)
		21.74 (+0.730)		
el 4 $(-)^{CD}_{540}$	Δ(GE)Λ(EE)Δ(EE)(N_S)	18.52 (−0.560)	26.32 (−0.392)	37.88 (−2.23)
		20.41 (+0.181)	30.21 (−0.042)	43.48 (+11.65)
		22.42 (−0.310)		
[Co(edma)(NH_3)$_3$]$^{2+}$				
fac $(+)^{CD}_{512}$	(N_S)	19.53 (+1.641)	29.41 (+0.306)	38.17 (−0.439)
		22.52 (−0.811)		

a) G and E denote glycinate-ring and ethylenediamine-ring, respectively. b) Wave numbers and $\Delta\varepsilon$ values (in parenthesis) are given in 10^{-3} cm^{-1} and mol^{-1} dm^3 cm^{-1}, respectively. c) Measured in 0.1 mol dm^{-3} HCl solution.

(51.26) and el 4 (51.61) with the same facially chelated form. From this result we can assign the structure of el 2 to fac(N_t)cis(N_c).

The geometrical structures of el 1, el 2, and el 4 of [Co(edma)(dien)]$^{2+}$ were assigned by comparing their absorption and CD spectra in the d-d absorption region with those of el 1, el 2, and el 4 of [Co(edma)-(mdien)]$^{2+}$.

Absolute Configurations of the fac(ch) Isomers. When unsymmetrical edma was facially coordinated to a cobalt(III) ion as a terdentate ligand, the secondary nitrogen becomes an asymmetric center. In the case that a geometrical structure is given for the edma complex, the configurational chirality around the cobalt-(III) is restricted by the chirality (N_R or N_S) of the asymmetric nitrogen (vice versa).

In the previous works,[9,11] it has been shown that one of the G-ring -CH_2- protons of facially chelated edma is stereospecifically deuterated in basic D_2O. For example, when the secondary nitrogen of chelated edma takes N_S chirality, the outside proton (H_b in Fig. 2) is deuterated before the inside proton (H_a) is deuterated, and the methylene carbon becomes an asymmetric center (-CHD-) with C_R chirality. In this case NMR signal of the undeuterated G-ring methylene-proton is observed as a single peak in a higher magnetic field.

Stereospecific deuteration method was also applied to the fac(ch) isomers of [Co(edma)(dien)]$^{2+}$ and [Co-(edma)(NH_3)$_3$]$^{2+}$ (detailed deuteration procedures are described in the Experimental section). Figure 3 shows the ^{1}H NMR spectra of $(-)^{CD}_{543}$ E-1 and $(+)^{CD}_{543}$ E-1 (of which the absolute configurations are $\Delta\Delta\Delta$(N_R, N_R) and $\Lambda\Delta\Lambda$(N_S, N_S),[9] respectively) obtained from the deuterated $(+)^{CD}_{504}$ el 1, $(+)^{CD}_{514}$ el 2, and $(-)^{CD}_{527}$ el 4 isomers of [Co(edma)(dien)]$^{2+}$ and the deuterated $(-)^{CD}_{517}$ isomer of *fac*-[Co(edma)(NH_3)$_3$]$^{2+}$

When the deuterated $(+)^{CD}_{504}$ el 1 isomer was used as a starting material, a single peak (marked with *) due to G-ring -CHD- was observed at δ ca. 4.3 (lower-field side) for $(-)^{CD}_{543}$ E-1 and at δ ca. 3.35 (higher-field side) for $(+)^{CD}_{543}$ E-1. As described above (Fig. 2), the single peak at lower-field is assigned to outside proton (H_b) and the single peak at higher-field to inside proton (H_a). This indicates that the chirality of the deuterated methylene carbon is C_R. As the starting isomer containing C_R exhibited a single peak in the higher-field side, the absolute configuration should be assigned to Λ(GE)Δ(EE)(N_S) (where G and E denote glycinate ring and ethylenediamine ring, respectively). Similar considerations for the ^{1}H NMR spectral data of the $(+)^{CD}_{512}$ el 2 and $(-)^{CD}_{527}$ el 4 isomers lead to conclude that their absolute configurations are Λ(EE)Δ(GE)Λ-(GE)(N_S) and Δ(GE)Λ(EE)Δ(EE)(N_S), respectively, as given in Table 3.

When the deuterated $(-)^{CD}_{512}$ isomer of *fac*-[Co(edma)-(NH_3)$_3$]$^{2+}$ was used as a starting material, a single peak appeared in the higher-field side for $(-)^{CD}_{543}$ E-1 and in the lower-field side for $(+)^{CD}_{543}$ E-1 (Fig. 3). Such signal patterns suggest that the chiralities of asymmetric nitrogens and carbons in $(-)^{CD}_{543}$ and $(+)^{CD}_{543}$ E-1 are N_RC_S and N_SC_S, respectively. Accordingly, the absolute con-

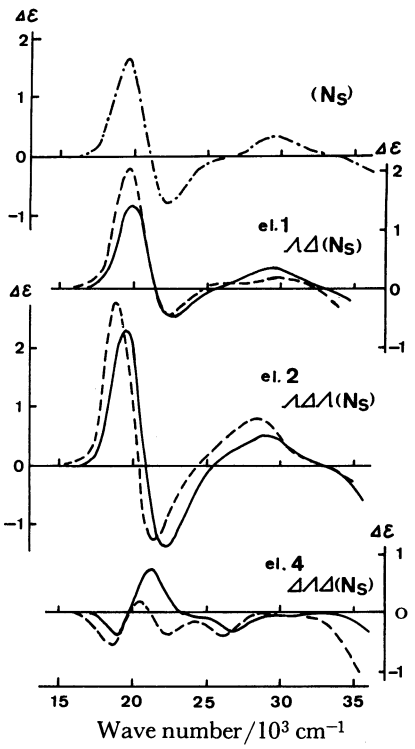

Fig. 7. The absolute configurations and CD spectra of the fac(ch) isomers in [Co(edma)-$(NH_3)_3]^{2+}$ (-·-·-), [Co(edma)(dien)]$^{2+}$ (——), and [Co(edma)(mdien)]$^{2+}$ (----).

figuration of the starting $(-)^{CD}_{512}$ isomer, which exhibited a single peak in the higher-field side, is assigned to N_R.

Absolute configurations for the optically active fac(ch) isomers of [Co(edma)(mdien)]$^{2+}$ were determined by comparing their CD spectral behaviors in the d-d absorption region with those of the corresponding fac(ch) isomers of [Co(edma)(dien)]$^{2+}$ (Table 3).

CD Spectra. The CD spectra and numerical data of the present edma complexes are shown in Figs. 4 and 7 and Table 3. The optical activities of the fac(ch) isomers of [Co(edma)(dien)]$^{2+}$ and [Co(edma)(mdien)]$^{2+}$ arise dominantly from two effects of configurational chirality due to skew pairs of the chelate rings and chirality due to the secondary nitrogen of coordinated edma. In the [Co(edma)(dien)]$^{2+}$ complex, the CD curve of $(+)^{CD}_{504}$ el 1 with Λ(GE)Δ(EE)(N_S) configuration is quite similar in pattern and intensity to that of $(+)^{CD}_{512}$ *fac*-[Co(edma)$(NH_3)_3]^{2+}$ with only N_S chirality (Fig. 7). This similarity suggests that the CD contributions from the configurational chiralities of Λ(GE) and Δ(EE) cancellate to each other. Similar considerations are also made on el 2 and el 4; the higher intense CD of $(+)^{CD}_{514}$ el 2 with ΛΔΛ(N_S) [net Λ(N_S)] is ascribed to the additive contribution from the Λ and N_S chiralities, while the lower intense CD of $(-)^{CD}_{527}$ el 4 with ΔΛΔ(N_S) [net Δ(N_S)] is ascribed to the differential contribution from the Δ and N_S chiralities.

The CD spectra of the mer(ch) isomers (el 3) of the dien and mdien complexes were measured in an acidic solution because their rapid racemization occurred in water.

The optical activity of the mer(ch) isomers arises from two effects due to chiral disposition of the nonplanar ligands and N chirality of coordinated edma. The relatively intense CD observed for two el 3, compared with the mer isomers of $[Co(dien)_2]^{3+}$,[17] [Co(mida)(dien)]$^{+}$,[18] and [Co(dien)(mdien)]$^{3+}$,[6] is ascribed to the summed effect of such two chiralities.

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