The Stereochemistry of the Six Geometrical Isomers of the Bis(ethylenediamine-*N*-acetato)cobalt(III) Ion, $[Co(edma)_2]^{+}$1)

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All of the six geometrical isomers possible in $[Co(edma)_2]^+$ (edma: ethylenediamine-*N*-acetate) were isolated, and the five chiral isomers were resolved into optically active isomers by a column-chromatographic method. Their structures were determined on the basis of the X-ray analysis and the visible absorption, ^1H NMR, and CD spectral data. One of the methylene protons in the glycinate-ring of the facially coordinating edma is stereospecifically exchanged by a deuteron in the basic D_2O solution, and its deuteration rate is influenced by the ligating atoms in the *trans* position. A ^1H NMR method to determine the absolute configurations of the optically active isomers, which contain the stereospecifically deuterated edma, is reported and applied to the $[Co(edma)_2]^+$ systems. The relationship between the absolute configurations and the CD spectral behaviors of these complexes is also discussed.

The ethylenediamine-*N*-acetate anion ($NH_2CH_2CH_2NHCH_2COO^-$: edma) is a terdentate ligand of the N-N-O type. The $[Co(N\text{-}N\text{-}O)_2]$-type complex provides six geometrical isomers (Fig. 1). Although there have been several reports on this type of complex,2—7) there have been only a few reports which have dealt with all of the six isomers.1) In a previous letter1) we reported the preparation and tentative assignments of the six geometrical isomers for the $[Co(edma)_2]X$ complex. In order to confirm these assignments, we have now determined the structure (and the absolute configuration) of one of the isomers by means of X-ray analysis.

It was found that one of the methylene protons in the glycinate-ring of the facially coordinating edma was stereospecifically deuterated in a basic D_2O solution. Optically active edma ($NH_2CH_2CH_2NHC^*HDCOO^-$) was obtained from a stereospecifically deuterated, optically active $[Co(\text{e̊dma})_2]^+$. Further, the isomers of $[Co(edma)_2]^+$, which contain this deuterated edma, were used to determine the absolute configurations on the basis of the ^1H NMR data. In the present paper, this ^1H NMR method to determine the absolute configuration of the complex will be discussed in detail. In addition, the relationship between the absolute configuration and the CD spectral behavior will be discussed.

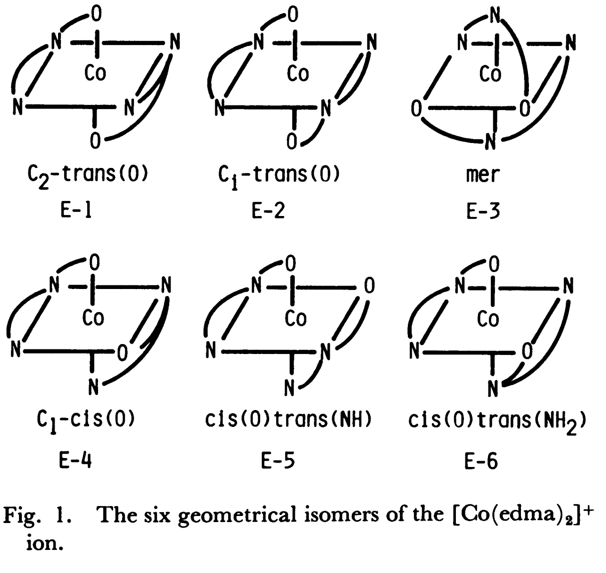

Fig. 1. The six geometrical isomers of the $[Co(edma)_2]^+$ ion.

Experimental

Preparation and Separation of the Isomers of the $[Co(edma)_2]^+$ Ion. The previously reported method1) was modified for the preparation of the complexes. A solution containing 10 g of ethylenediamine-*N*-acetic acid dihydrochloride dihydrate ($Hedma\cdot 2HCl\cdot 2H_2O$) in 50 ml of water and solution containing 4.75 g of $CoCl_2\cdot 6H_2O$ in 30 ml of water were separately passed through an anion-exchange resin (Dowex 1X8, ClO_4^- form) column to convert the chloride ions to perchlorate ions, and then the two solutions were combined. The pH of the combined solution was adjusted to 6—7 with 1 mol dm^{-3} NaOH solution. Lead dioxide (9.0 g) was stirred into the solution in small portions at 50 °C over a 1-h period, the pH of the solution being held at about 6.5. After the insoluble material had then been removed by filtration, the filtrate was charged on an SP-Sephadex column (K^+ form). The adsorbed band was developed by the method described in the previous paper1) (eluent: 0.1 mol dm^{-3} KCl solution).

The method of preparing the $[Co(edma)_2]Cl$ described above (PbO_2-oxidation in a weakly acidic solution) gave better overall yields, especially for E-5 and -6, than the method using $Na_3[Co(CO_3)_3]\cdot 3H_2O$8) as the starting material (carbonato method1)). (Under basic conditions, the PbO_2-oxidation method gave low yields for E-3, -5, and -6.)

All of the isomers except for E-2 (the achiral isomer) were optically resolved by the chromatographic method described in the previous paper1) (eluent: 0.05 mol dm^{-3} $K_2Sb_2(d\text{-tart})_2$ aqueous solution). The formulas of the optically active complexes (faster eluted isomers) finally obtained are as follows: $(-)^{\mathrm{CD}}_{543}$E-1: [Co(edma)$_2$]ClO$_4$; $(-)^{\mathrm{CD}}_{504}$E-3: [Co(edma)$_2$]Br; $(+)^{\mathrm{CD}}_{534}$E-4: [Co(edma)$_2$]Cl·2H$_2$O; $(-)^{\mathrm{CD}}_{521}$E-5: [Co(edma)$_2$]Br; $(+)^{\mathrm{CD}}_{509}$E-6: [Co(edma)$_2$]Cl·1.5H$_2$O.

The $(-)^{\mathrm{CD}}_{521}$E-5 (bromide salt) isomer was converted to a perchlorate salt using QAE-Sephadex ($\mathrm{ClO_4^-}$ form) to obtain single crystals suitable for X-ray analysis.

X-Ray Analysis of $(-)^{\mathrm{CD}}_{521}$*-[Co(edma)$_2$]ClO$_4$·2H$_2$O (E-5).* *Crystal Data*: Monoclinic, space group P2$_1$, a=11.530(2), b=11.157(2), c=6.489(1) Å, β=96.83(1)°, D_m=1.70 g cm^{-3}, Z=2, D_c=1.72 g cm^{-3}, μ(Mo $K\alpha$)=13.0 cm^{-1}. The unit-cell dimensions were determined from a least-squares analysis of 24 θ values of higher angle reflections (θ=8—14°), as measured on an automated diffractometer by the use of graphite-monochromated Mo $K\alpha$ radiation.

The intensity data ($2\theta<50°$) were collected on the diffractometer by means of the ω-scan method with Mo $K\alpha$ radiation (scan speed, 0.033° s^{-1}; scan width, (1.0+0.4 tan θ)°; background measurement, 10 s at each end of the scan; crystal size, 0.15×0.17×0.15 mm). Of the 1552 independent reflections measured, 1371 with $I>3\sigma(I)$ were used for the structure analysis. No correction was made for absorption.

The crystal structure was solved by the heavy-atom technique. The positional and thermal parameters were refined by the block-diagonal-matrix least-squares method. The minimized function was $\sum w(|F_\mathrm{o}|-|F_\mathrm{c}|)^2$, where $w=\sigma(F_\mathrm{o})^{-2}$. The large temperature factors found for the O atoms of the $\mathrm{ClO_4^-}$ ion were indicative of a disorder of the ion; therefore, the 4 O atoms were treated, in the subsequent least-squares calculation, as a rigid group in which the O atoms lie at the apices of the regular tetrahedron, with a Cl····O distance of 1.426 Å.[9] The parameters of the Cl atom were allowed to vary independently from those of the 4 O atoms.

The atomic scattering factors, with correction for the anomalous dispersion effect for Co and Cl atoms, were taken from Ref. 10. The convergence was attained with R 0.071 and R' $(=[\sum w\Delta F^2/\sum wF_\mathrm{o}^2]^{1/2})$ 0.100, whereas R and R' at convergence were 0.070 and 0.098 respectively for the inverted structure. All the parameter shifts in the final cycle of the refinement for either structure were $<0.2\sigma$. The absolute crystal structure was determined by means of the Bijvoet method. Table 1 shows several Bijvoet pairs, which showed a remarkable intensity difference on the Weissenberg photographs taken with Cu $K\alpha$ radiation. The inequality relationship between the intensities of the Bijvoet pair agrees well with that between $|F_\mathrm{c}(hkl)|^2$ and $|F_\mathrm{c}(h\bar{k}l)|^2$ calculated on the basis of the atomic coordinates (the inverted structure) listed in Table 2. The observed and calculated structure factors, thermal parameters, bond lengths and angles (Table 3), and the projection of the crystal structure along the b axis are preserved by the Chemical Society of Japan (Document No. 8532). The computation was carried out on an ACOS 900 computer at the Crystallographic Research Center, Institute of Protein Research, Osaka University, and a FACOM M180 computer at Osaka City University. The computer programs used were as follows: UNICS,[11] ORTEP,[12] and ORFLS.[13]

TABLE 1. OBSERVED INEQUALITY RELATIONSHIP BETWEEN THE INTENSITIES OF THE BIJVOET PAIR AND THE $|F_\mathrm{c}|^2$ VALUES CALCULATED ON THE BASIS OF THE ATOMIC COORDINATES LISTED IN TABLE 2

h k l	$\lvert F_\mathrm{c}(hkl)\rvert^2$	Observed inequality relationship	$\lvert F_\mathrm{c}(h\bar{k}l)\rvert^2$
3 1 1	375.2	<	954.8
9 1 1	216.1	<	420.3
$\bar{3}$ 2 1	376.4	>	269.0
$\bar{4}$ 2 1	225.0	<	372.5
4 2 1	139.2	<	338.6
4 1 2	488.4	<	718.2
5 2 1	635.0	>	327.6
$\bar{5}$ 1 2	102.0	<	400.0
$\bar{6}$ 1 2	39.7	<	246.5
$\bar{2}$ 2 2	59.3	<	174.2
$\bar{3}$ 2 2	246.5	<	388.1

Spectral Measurements. The ^{1}H NMR spectra were recorded on a JEOL MH-100 spectrometer, with DSS as the internal standard in D$_2$O. The visible and UV absorption spectra were recorded on a HITACHI 557 spectrophotometer, while the circular dichroism (CD) spectra were recorded on a JASCO J-22 spectropolarimeter in an aqueous solution.

Measurements of the Deuteration Rate of the G-ring. In order to measure the H-D exchange rate (deuteration rate) of the glycinate-ring (G-ring) -CH$_2$- in the coordinating

TABLE 2. FRACTIONAL COORDINATES AND TEMPERATURE FACTORS FOR $(-)^{\mathrm{CD}}_{521}$[Co(edma)$_2$](ClO$_4$)·2H$_2$O (E-5). STANDARD DEVIATIONS OF THE LEAST SIGNIFICANT FIGURES ARE GIVEN IN PARENTHESES

Atom	x	y	z	B(eq) or B
Co	−0.3363(1)	−0.69711(0)	−0.1726(2)	1.68(4)
Cl	−0.1958(4)	−0.1520(4)	−0.2863(8)	4.2(1)
N(1)	−0.478(1)	−0.784(1)	−0.138(2)	1.9(3)
N(2)	−0.3636(9)	−0.740(1)	−0.463(2)	2.7(3)
N(3)	−0.197(1)	−0.601(1)	−0.193(2)	2.8(3)
N(4)	−0.231(1)	−0.832(1)	−0.103(2)	2.6(3)
C(1)	−0.531(1)	−0.568(1)	−0.156(2)	1.9(3)
C(2)	−0.567(1)	−0.690(2)	−0.096(2)	2.5(3)
C(3)	−0.513(1)	−0.858(1)	−0.332(2)	2.8(4)
C(4)	−0.487(1)	−0.782(2)	−0.511(2)	3.0(4)
C(5)	−0.242(1)	−0.574(1)	0.165(2)	2.8(4)
C(6)	−0.177(1)	−0.525(1)	−0.013(2)	2.7(4)
C(7)	−0.098(1)	−0.681(2)	−0.230(2)	3.4(4)
C(8)	−0.109(1)	−0.792(2)	−0.081(3)	3.8(5)
O(1)	−0.5941(9)	−0.4813(9)	−0.137(2)	3.0(3)
O(2)	−0.4316(8)	−0.5592(9)	−0.227(2)	2.4(2)
O(3)	−0.2231(7)	−0.5323(8)	0.343(1)	3.4(2)
O(4)	−0.3189(9)	−0.657(1)	0.114(2)	2.2(3)
O(W1)	−0.1924(9)	−0.895(1)	−0.634(2)	3.9(3)
O(W2)	−0.039(1)	−0.399(1)	−0.481(3)	8.4(6)
O(1Cl)	−0.236(2)	−0.269(1)	−0.237(3)	8.9(5)
O(2Cl)	−0.135(2)	−0.154(2)	−0.457(3)	16. (1)
O(3Cl)	−0.293(2)	−0.080(1)	−0.334(2)	5.5(3)
O(4Cl)	−0.132(1)	−0.100(2)	−0.110(3)	15.2(9)

Table 3. Bond length and angles

Bond Lengths (l/Å):			
Co-N(1)	1.94(1)	Co-N(3)	1.95(1)
Co-N(2)	1.94(1)	Co-N(4)	1.95(1)
Co-O(2)	1.90(1)	Co-O(4)	1.90(1)
N(1)-C(3)	1.52(2)	N(3)-C(7)	1.49(2)
N(2)-C(4)	1.49(2)	N(4)-C(8)	1.46(2)
C(3)-C(4)	1.50(2)	C(7)-C(8)	1.58(3)
N(1)-C(2)	1.52(2)	N(3)-C(6)	1.44(2)
C(1)-C(2)	1.48(2)	C(5)-C(6)	1.55(2)
C(1)-O(2)	1.29(2)	C(5)-O(4)	1.29(2)
C(1)-O(1)	1.23(2)	C(5)-O(3)	1.24(2)
Bond Angles (ϕ/°):			
N(1)-Co-N(2)	86.9(5)	N(3)-Co-N(4)	86.8(5)
N(1)-Co-O(2)	87.0(5)	N(3)-Co-O(4)	86.8(5)
Co-N(1)-C(3)	108.7(9)	Co-N(3)-C(7)	109.6(11)
Co-N(2)-C(4)	108.6(9)	Co-N(4)-C(8)	110.7(11)
N(1)-C(3)-C(4)	106(1)	N(3)-C(7)-C(8)	105(1)
N(2)-C(4)-C(3)	107(1)	N(4)-C(8)-C(7)	109(1)
Co-N(1)-C(2)	106.0(9)	Co-N(3)-C(6)	108.8(10)
Co-O(2)-C(1)	113.0(8)	Co-O(4)-C(5)	114.1(10)
N(1)-C(2)-C(1)	112(1)	N(3)-C(6)-C(5)	111(1)
O(2)-C(1)-C(2)	117(1)	O(4)-C(5)-C(6)	116(1)
C(2)-C(1)-O(1)	121(1)	C(6)-C(5)-O(3)	121(1)
O(2)-C(1)-O(1)	122(1)	O(4)-C(5)-O(3)	123(1)
C(2)-N(1)-C(3)	114(1)	C(6)-N(3)-C(7)	116(1)

Bond lengths and angles in the ClO_4^-:

Cl-O = 1.38 − 1.43(2) Å

O-Cl-O = 106 − 112(2)°

edma, an equivolume mixture of 0.1 mol dm^{-3} Na_2CO_3–D_2O and 0.1 mol dm^{-3} $NaDCO_3$–D_2O was used as the solvent; the $-CH_2-$ signals were recorded at prescribed intervals on a ^{1}H NMR spectrometer at 40 °C.

Determination of the Absolute Configuration of the Complexes by ^{1}H NMR. A buffer solution (pH 10) was prepared by adding proper amount of 2 mol dm^{-3} DCl–D_2O to a solution containing 106 mg Na_2CO_3 in 10 cm^3 of D_2O. About 100 mg of $(+)^{\mathrm{CD}}_{521}$E-5 was dissolved into the buffer solution, and the temperature of the solution was kept at 40 °C. The deuteration of the G-ring $-CH_2-$ was checked by means of ^{1}H NMR measurements. When the singlet peak arising from the G-ring $-C\underline{H}D-$ increased in intensity in comparison with the AB quartet arising from the G-ring $-CH_2-$ (about 4 h), the solution was acidified to pH 6 with 1 mol dm^{-3} HCl to stop the deuteration reaction. The volume of the solution was adjusted to 20 cm^3 with water, and zinc powder (2 g) was added to the solution. After stirring for 5 min at room temperature, the excess of zinc was filtered off. To the filtrate, 1.5 g of PbO_2 was added, and then the mixture was stirred for 15 min at room temperature. After the solution had been filtered, the filtrate was poured into an SP-Sephadex column (Na^+ form, 2.7 cm×50 cm); then the adsorbed complexes were eluted with a 0.2 mol dm^{-3} NaCl solution. The earlier-eluted band (E-1 and -2) was transferred to another SP-Sephadex column (Na^+ form, 2.7 cm×60 cm) and developed with a 0.1 mol dm^{-3} Na_2Sb_2(d-tart)$_2$ solution by the recycle chromatographic method. The band separated into three bands: red ($(-)^{\mathrm{CD}}_{543}$E-1), orange (E-2), and red ($(+)^{\mathrm{CD}}_{543}$E-1). Each band of the E-1 enantiomers was once more transferred to another SP-Sephadex column, washed with 1 dm^3 of water, and then eluted out with a 0.2 mol dm^{-3} $NaClO_4$ solution. The eluate was evaporated almost to dryness under reduced pressure, and then 50 cm^3 of ethanol was added to the concentrate to obtain red-orange crystals. The ^{1}H NMR spectra of the E-1 enantiomers are illustrated in Fig. 2.

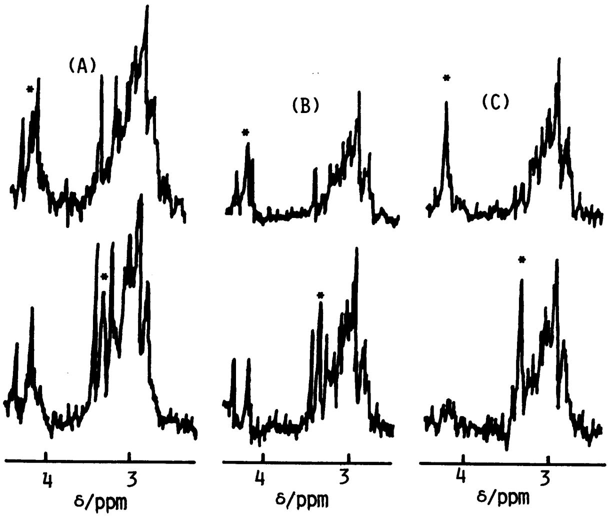

Fig. 2. ^{1}H NMR spectra of $(-)^{\mathrm{CD}}_{543}$ and $(+)^{\mathrm{CD}}_{543}$E-1 obtained from the deuterated $(+)^{\mathrm{CD}}_{534}$E-4, $(+)^{\mathrm{CD}}_{521}$E-5, and $(+)^{\mathrm{CD}}_{509}$E-6 isomers. Upper: $(-)^{\mathrm{CD}}_{543}$E-1. Lower: $(+)^{\mathrm{CD}}_{543}$ E-1. (A) from $(+)^{\mathrm{CD}}_{534}$E-4, (B) from $(+)^{\mathrm{CD}}_{521}$E-5, and (C) from $(+)^{\mathrm{CD}}_{509}$E-6. (Asterisked peaks: G-ring $-C\underline{H}D-$).

Similarly, the deuterated E-1 enantiomers were obtained from the optically active deuterated E-4 and E-6 isomers. Their ^{1}H NMR spectra are also shown in Fig. 2.

Results and Discussion

Assignments of the Geometrical Isomers. The structural assignments for the six isomers, given in our previous report,[1] are shown in Fig. 1. Although the structures of E-1, -2, -3, and -4 were assigned on the basis of unambiguous evidence, some uncertainty remained as to the tentative assignments for E-5 and -6; E-5 is either *cis*(O)*trans*(NH_2) or *cis*(O)*trans*(NH). The X-ray study which will be shown below revealed that E-5 is *cis*(O)*trans*(NH). (Consequently, E-6 is assigned to *cis*(O)*trans*(NH_2)).

Crystal Structure of $(-)^{\mathrm{CD}}_{521}$-[Co(edma)$_2$]$ClO_4\cdot 2H_2O$ (E-5). Figure 3 shows the absolute configuration of the $(-)^{\mathrm{CD}}_{521}$-isomer of E-5. This complex has a distorted octahedral coordination, with two O atoms in the *cis* positions and two secondary N atoms in the *trans* positions: *cis*(O)*trans*(NH). The complex cation has an approximate two-fold axis running through the Co atom and the mid point of the O···O edge. Each coordinating edma contains an asymmet-

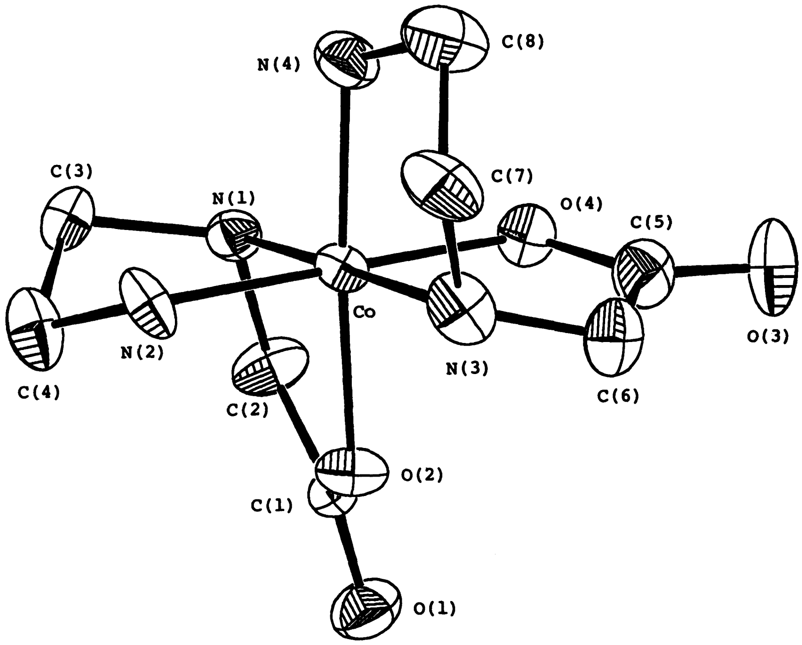

Fig. 3. The structure and absolute configuration of $(-)^{CD}_{521}$E-5 $[Co(edma)_2]^+$ ion in its perchlorate dihydrate crystal.

ric nitrogen whose chirality is *R*. The conformation of the ethylenediamine ring is δ. By modifying the conventional nomenclature,[14] the absolute configuration of this isomer is represented as Δ(GG)Δ(EE) in this paper, where G and E represent the glycinate-ring and the ethylenediamine-ring respectively.

The average Co–N (primary N) and Co–N (secondary N) bond lengths are nearly equal to those found in *u-fac* and *s-fac* $[Co(dien)_2]^{3+}$,[15,16] while the average Co–O bond length is nearly equal to that in $[Co(ida)_2]^-$.[17]

^{1}H NMR. Table 4 shows the ^{1}H NMR data of the glycinate methylene protons in the six isomers of the $[Co(edma)_2]^+$ ion. The methylene protons of the G-rings in E-1, -2, -4, -5, and -6, which contain the facially coordinating edma's, appeared as the AB quartet signals. On the other hand, those in E-3 with the meridionally coordinating edma's appeared as a singlet-like signal (slightly splitting) because of a slight difference in chemical shift between the two methylene protons. Such a singlet-like signal has also been observed for the meridionally chelated ring (in-plane G-ring methylenes) of edda in the β-$[Co(edda)(ch)]^{\pm}$ (where ch is ox, mal, or en) ions.[18] The coupling constant of the glycinate geminal protons in the meridionally coordinating edma is 16 Hz, and those in the facially coordinating edma are 18 Hz (Table 4); these findings are consistent with the results of the previous papers.[19–22]

The ^{1}H-NMR spectra of the facial isomers (E-1, -2, -4, -5, and -6) were measured in 0.5 mol dm^{-3} DCl-D$_2$O solutions. The ^{1}H NMR signal of each G-ring in these isomers splits into eight peaks as a result of the $J_{Ha,Hb}$, $J_{N-H,Ha}$, and $J_{N-H,Hb}$ couplings (Fig. 4(A)). The $J_{N-H,Hb}$ and $J_{N-H,Ha}$ values are *ca.* 8 Hz's (lower fields) and 1 Hz's (higher fields) respectively. On the basis of the Karplus equation,[23] the following assignments are possible: the dihedral angles of the protons resonating at higher fields ($\underline{H}$-C-N-H) are about 90°, and the protons can be assigned to H_a (inside; Fig. 4 (A)). The angles of the protons (which are assigned to H_b (outside)) resonating at lower fields are about 30°. Similar assignments for the G-ring methylene protons have been made by Legg and Cooke[27] and Schoenberg *et al.*[28] for the edda-Co(III) complexes.

It is known that the methylene protons of the

TABLE 4. ^{1}H NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS OF THE G-RINGS IN THE $[Co(edma)_2]^+$ COMPLEX IONS

Complex		G-ring -C$\underline{H}_2$-		
		H_a (δ/ppm)	H_b (δ/ppm)	J_{H_a,H_b} (J/Hz)
C_2-*trans*(O)	(E-1)	3.32	4.25	18
C_1-*trans*(O)	(E-2)	3.34	4.05	18
mer	(E-3)	3.85	3.79	16
C_1-*cis*(O)	(E-4)	3.14	4.18	18
		3.36	4.06	18
cis(O)*trans*(NH)	(E-5)	3.41	4.19	18
cis(O)*trans*(NH$_2$)	(E-6)	3.10	4.06	18

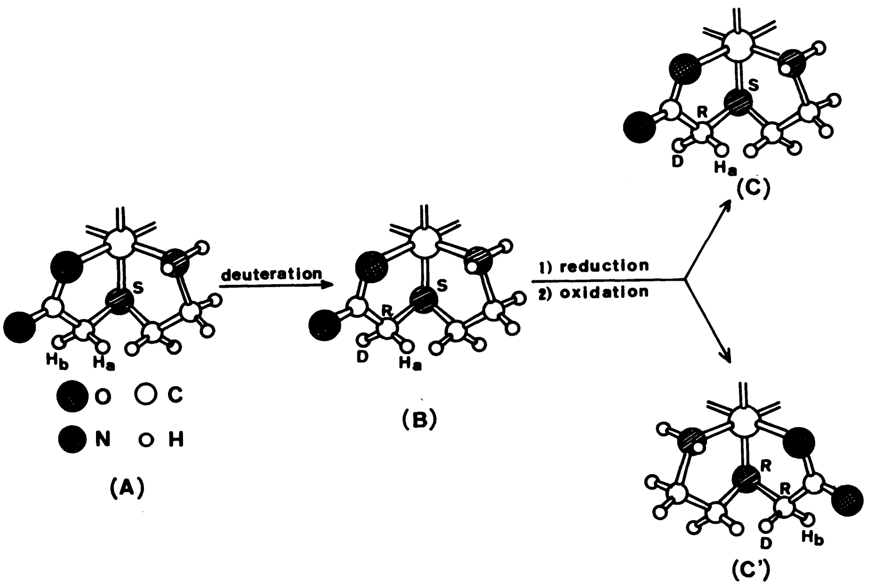

Fig. 4. Chemical environment of the G-ring of the facially coordinating edma.
(A): undeuterated, (B): deuterated, and (C) and (C′): reprepared by oxidizing the reduction product of (B) (See Experimental).

chelating glycinate are deuterated in a basic D_2O solution.[18,21–26] The G-ring methylene protons in the facially coordinated edma are also deuterated; this fact is confirmed from the intensity loss of the AB quartet peaks (Fig. 5). The deuteration occurs stereospecifically in all of the facial isomers; a new singlet appeared between the two higher-field peaks of the AB quartet, with an intensity loss of the AB quartet. In other words, the deuteration rates are different between the two protons; the deuteration of the higher-field proton is much slower than that of the lower-field one. (The new singlet signal disappeared after a long period). Sudmeier and Occupati[26] pointed out that the rate of the deuteration of the inside proton of the facial G-ring is slower than that of the outside proton for the edda-Co(III) complexes. The application of this result to the *fac*-$[Co(edma)_2]^+$ system leads to the conclusion that the two lower-field peaks of the AB quartet arise from the outside proton, which is easily deuterated, while the two higher-field peaks arise from the inside proton (Fig. 4 (B)). These assignments are consistent with those made by the Karplus equation mentioned above.

In a previous paper,[29] we reported that the deuteration rate of the G-ring methylene protons out of the O–Co–O plane which is present in C_1– or C_2-*cis*(*O*)-$[Co(gly)_2(en)]^+$ is smaller than that of the G-ring methylene protons in the O-Co-O plane which is present in C_1-*cis*(*O*)-$[Co(gly)_2(en)]^+$ and that of the G-ring methylene in *trans*(*O*)-$[Co(gly)_2(en)]^+$.

The deuteration rates of the six isomers were measured under the same conditions (40 °C; dissolved in an equivolume mixture of 0.1 mol dm^{-3} Na_2CO_3–D_2O and 0.1 mol dm^{-3} $NaDCO_3$–D_2O). The

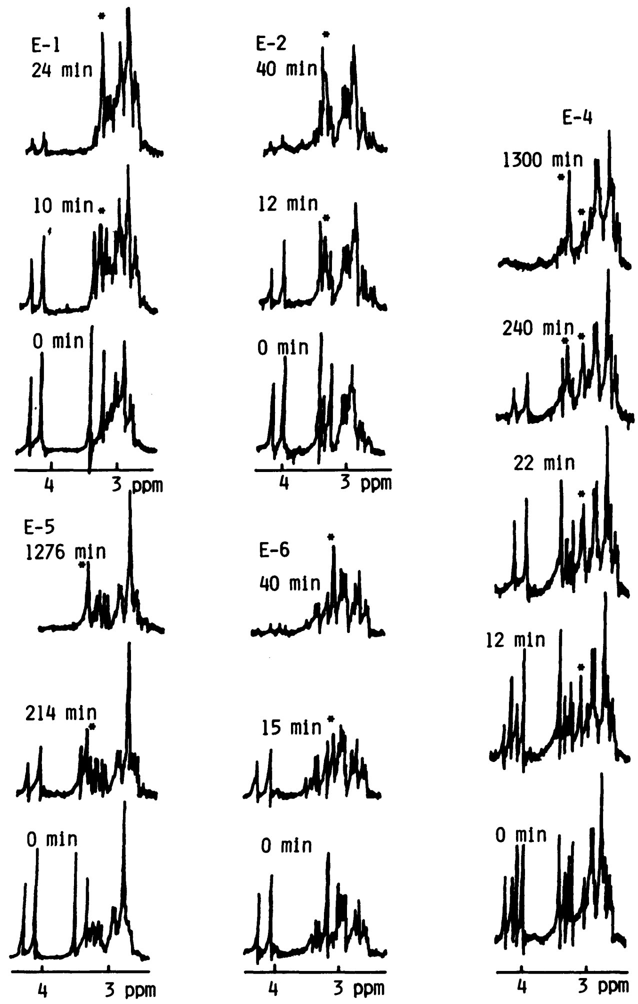

Fig. 5. Changes in ^1H NMR spectra of $[Co(edma)_2]^+$ in basic D_2O solutions. (Asterisked peaks: G-ring $-C\underline{H}D-$).

order of the deuteration rates are as follows: C_2-*trans*(O) (E-1)(half-life: *ca.* 15 min)≃*cis*(O)*trans*(NH_2) (E-6)≃C_1-*cis*(O) (E-4; in-plane)≃C_1-*trans*(O) (E-2)≫*cis*-(O)*trans*(NH) (E-5)(*ca.* 190 min)>C_1-*cis*(O) (E-4; out-of-plane) (*ca.* 230 min). This result corresponds well with that obtained for the $[Co(gly)_2(en)]^+$ ion.

The G-ring methylene protons of E-3 (*mer*) are deuterated very slowly; this slow deuteration may arise from the following two effects: (1) from the meridional form (Coleman *et al.*[18] pointed out, for the $[Co(edta)]^-$ ion, that the more strained glycinate-ring meridional to the back-bone ethylenediamine-ring does not prefer to remove one of the methylene protons) and (2) the methylene protons are not situated on the O–Co–O plane.

Determination of Absolute Configurations by ^{1}H NMR. When the edma ligand coordinates to a cobalt(III) ion in the facial form, the secondary nitrogen (C–$\underline{N}$H–C) becomes asymmetric (*R* or *S*) (Fig 4 (A)). Although each isomer of $[Co(edma)_2]^+$ may be expected to provide four diastereomers (*R,R, R,S, S,R,* and *S,S*), some of them do not exist because of the structural restrictions. For example, the nitrogen atoms in the E-1 isomer can take only the *S,S*($\Lambda\Delta\Lambda$) or *R,R*($\Delta\Lambda\Delta$) chiral configuration. The possible configurations for each geometrical isomer are listed in Table 5.

TABLE 5. POSSIBLE CONFIGURATIONS AND CD SIGNS OF THE $[Co(edma)_2]^+$ ION

Geometrical isomers	Possible configuration and CD signs	
E-1 C_2-*trans*(O)	$\Delta\Lambda\Delta(R,R)(-)^{\mathrm{CD}}_{543}$	$\Lambda\Delta\Lambda(S,S)(+)^{\mathrm{CD}}_{543}$
E-2 C_1-*trans*(O)	(*R,S*) (achiral isomer)	
E-4 C_1-*cis*(O)	$\Lambda\Delta\Lambda(S^*,R)(+)^{\mathrm{CD}}_{534}$	$\Delta\Lambda\Delta(R^*,S)(-)^{\mathrm{CD}}_{534}$
E-5 *cis*(O)*trans*(NH)	$\Delta(GG)\Lambda(EE)$-$(R,R)(-)^{\mathrm{CD}}_{521}$	$\Lambda(GG)\Delta(EE)$-$(S,S)(+)^{\mathrm{CD}}_{521}$
E-6 *cis*(O)*trans*(NH_2)	$\Lambda\Delta\Lambda(R,R)(-)^{\mathrm{CD}}_{509}$	$\Delta\Lambda\Delta(S,S)(+)^{\mathrm{CD}}_{509}$

R or *S*: Chirality around the asymmetric nitrogen. *R** or *S**: The asymmetric nitrogen being present on the in-plane (O–Co–O plane) G-ring.

The $(-)^{\mathrm{CD}}_{521}$E-5 isomer, whose structure was determined by the X-ray analysis in this work, has the configuration of $\Delta(GG)\Lambda(EE)(R,R)$. As has been mentioned, one of the G-ring $-CH_2-$ protons in $(+)^{\mathrm{CD}}_{521}$E-5 ($\Lambda(GG)\Delta(EE)(S,S)$) is stereospecifically deuterated in basic D_2O. When the outside proton (H_b in Fig. 4(A)) of $(+)^{\mathrm{CD}}_{521}$E-5 is deuterated, the G-ring –CHD– carbon in the facial edma becomes an asymmetric center with the *R* chirality (Fig 4 (B)). It is noteworthy that, when the nitrogen atom of the facially coordinated edma which contains *R* carbon takes the *S* chirality, the undeuterated proton (–C$\underline{H}$D–) occupies the inside position (Fig 4 (C)). Using this deuterated edma (containing *R* carbon), the E-1 isomer was prepared and optically resolved (See Experimental section). In the ^{1}H NMR spectrum of the deuterated $(-)^{\mathrm{CD}}_{543}$E-1, a singlet peak due to the G-ring –C$\underline{H}$D– appeared between the two lower-field peaks of the AB quartet due to the G-ring $-CH_2-$ (Fig. 2). On the contrary, in the spectrum of the $(+)^{\mathrm{CD}}_{543}$E-1, a singlet peak appeared between the two higher-field peaks of the AB quartet. As the chiralities of the asymmetric carbon and nitrogen atoms in the starting material ($(+)^{\mathrm{CD}}_{521}$E-5) are *R* and *S* respectively, it is concluded that the asymmetric nitrogens of the coordinating edma's in $(-)^{\mathrm{CD}}_{543}$E-1 and $(+)^{\mathrm{CD}}_{543}$E-1 should have *R* and *S* chiralities respectively (Fig 4.); the absolute configurations of the $(-)^{\mathrm{CD}}_{543}$E-1 and $(+)^{\mathrm{CD}}_{543}$E-1 isomers are $\Delta\Lambda\Delta(R,R)$ and $\Lambda\Delta\Lambda(S,S)$ respectively.

By using the stereospecifically deuterated $(+)^{\mathrm{CD}}_{509}$E-6 as a starting material, the $(+)^{\mathrm{CD}}_{543}$ and $(-)^{\mathrm{CD}}_{543}$E-1 isomers were also obtained, as has been shown in the Experimental section. The ^{1}H NMR spectra of the $(-)^{\mathrm{CD}}_{543}$E-1 and $(+)^{\mathrm{CD}}_{543}$E-1 isomers showed a singlet signal due to –C$\underline{H}$D– in the lower and higher fields respectively. These signal patterns suggest that the edma ligand contains the *R* asymmetric carbon. Accordingly, the configuration of $(+)^{\mathrm{CD}}_{509}$E-6 can be assigned to $\Delta\Lambda\Delta(S,S)$ (($(-)^{\mathrm{CD}}_{509}$E-6: $\Lambda\Delta\Lambda(R,R)$)).

Although the $\Lambda\Delta\Lambda(S^*,R)$E-4 isomer contains both the *R* and *S* asymmetric nitrogens, the in-plane G-ring which contains *S* nitrogen (*S**) is more rapidly deuterated than the out-of-plane G-ring which contains *R* nitrogen, as has been mentioned above. The deuteration was quenched at the time the G-ring containing *S** nitrogen was stereospecifically deuterated. By employing the same method as has been described for the determination of the absolute configuration of E-6, the configurations of the $(+)^{\mathrm{CD}}_{534}$E-4 and $(-)^{\mathrm{CD}}_{534}$E-4 isomers can be identified as $\Lambda\Delta\Lambda(S^*,R)$ and $\Delta\Lambda\Delta(R^*,S)$ respectively. The absolute configurations of the facial complexes are summarized in Table 5.

CD Spectra. The CD data of the isomers are summarized in Table 6.

The $E_g(D_{4h})$ component in the first absorption band of E-1 (*trans*-$[Co(N)_4(O)_2]$-type complex) is on a lower-energy side than the $A_{2g}(D_{4h})$.[30] According to the method of ring-pairing proposed by Legg *et al.*[32], the (+) CD component which is related to the E_g transition is assigned to the net Λ configuration. Based on the above recognition, Igi and Douglas[3] assigned $(+)^{\mathrm{CD}}_{543}$E-1 to the $\Lambda\Delta\Lambda$(net Λ) configuration, which is consistent with the result described in our ^{1}H NMR section. However, the $(+)^{\mathrm{CD}}_{534}$E-4 (*cis*-$[Co(N)_4(O)_2]$-type complex) shows (−) CD band in the region related to the E_g(D_{4h}: holohedrized symmetry) component (which is at a higher-energy side than the $A_{2g}(D_{4h})$ in the *cis*-$[Co(N)_4(O)_2]$-type), while $(+)^{\mathrm{CD}}_{521}$ $\Lambda(GG)\Delta(EE)$ E-5 shows a CD pattern similar to that of $(+)^{\mathrm{CD}}_{534}$E-4.

Table 6. CD data of optically active [Co(edma)$_2$]X

Complex[a]	First Band Region[b]	Second Band Region[b]	Charge-transfer Band Region[b]
$(-)^{\mathrm{CD}}_{543}$E-1	18.42(−3.197) 22.27(+2.135)	28.33(−1.198)	38.46(+4.156) 43.48(−8.621)
$(-)^{\mathrm{CD}}_{504}$E-3	17.99(+0.139) 19.84(−1.079) 21.93(+2.464)	28.09(−1.307)	39.37(+4.984) 42.92(−5.162)
$(+)^{\mathrm{CD}}_{534}$E-4	18.73(+1.302) 21.14(−0.930)	26.18(+0.429)	39.50(−1.19)[sh] 45.05(−5.458)
$(-)^{\mathrm{CD}}_{521}$E-5	19.19(−2.078) 21.88(+1.454)	28.74(−0.787)	38.02(+2.894) 45.05(−8.599)
$(-)^{\mathrm{CD}}_{509}$E-6	15.83(+0.008) 19.65(−0.335) 22.14(+0.091)	25.58(+0.110) 28.33(−0.397)	38.02(+1.481) 45.25(−17.28)

a) All these isomers are the faster eluted ones (eluent: 0.05 mol dm^{-3} K_2Sb_2(d-tart)$_2$). b) The wave numbers and $\Delta\varepsilon$ values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1} respectively. sh) Shoulder bands.

Table 7. Absorption spectral data of the six isomers of [Co(edma)$_2$]X

Complex	First Band Region[a]	Second Band Region[a]	Charge-transfer Band Region[a]
E-1	18.87(1.963) 22.14(1.60)[sh]	27.86(2.125)	45.46(4.35)
E-2	19.80(1.585) 21.93(1.56)[sh]	28.90(1.769)	45.66(4.40)
E-3	21.01(2.279)	28.24(2.240)	45.05(4.31)
E-4	19.96(2.002)	28.01(2.047)	45.46(4.36)
E-5	20.92(1.794)	28.56(1.932)	46.30(4.36)
E-6	20.00(2.061)	28.25(1.855)	45.46(4.33)

a) Wave numbers and log ε values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1} respectively. sh) Shoulder bands.

Although the CD intensity of E-6 in the d-d absorption-band region is very small, the CD band in *ca.* 45000 cm^{-1} is stronger than in the other isomers examined. The low CD intensity in the d-d region probably arises from the counteraction of the vicinal effects due to asymmetric nitrogens against the configurational effect.

The relationship between the CD pattern and the absolute configuration is difficult to account for by the method of ring-pairing for the E-4, -5, and -6 isomers. This is true for the following reasons: (1) The difference in the numbers of the Δ and Λ ring pairs is very small in the present systems (the same as in E-5). (2) The effect of the vicinal CD of asymmetric nitrogen is not negligible compared with that of the configurational CD, though it is difficult to separate the vicinal CD curves from the observed CD. This difficulty results from the geometrical structures of the complexes containing unsymmetrical terdentates.

Absorption Spectra. The absorption spectral data of the six geometrical isomers are listed in Table 7. The first absorption bands of E-1 and -2 show a marked split,[1] which is characteristic of the *trans*(*O*)-[Co(N)$_4$(O)$_2$]-type,[30,31] and the molar-absorption coefficient of the lower-energy component is larger in E-1 than in E-2. E-1 lacks the center of symmetry, which would give a more intense spectrum than E-2.[32]

The *cis*(*O*)-[Co(N)$_4$(O)$_2$]-type isomers, E-3, -4, -5, and -6, do not show such a marked split in the first-absorption-band region as the *trans*(O)-type isomers do. The molar-absorption coefficient of the first absorption band is larger in E-3 than in the other five isomers. By stereochemistry, the *mer* isomer is more distorted from a regular octahedron than are the other five isomers, which contains the facially coordinating edma's. The strained structure will give the more intense spectrum.[32,33] An analogous situation is observed for the geometrical isomers of [Co(ida)$_2$]$^-$[34] and [Co(ida)(dien)]$^+$.[32]

Of the *cis*(O)-type isomers, E-3 exhibits the first absorption maximum in the highest energy region, though the E-3 is the more distorted isomer. This fact may arise from the fact that the molar-absorption coefficient of the $E_g(D_{4h})$ component (on the higher-energy side) is much larger than the $A_{2g}(D_{4h})$ component (on the lower-energy side). In the other *cis*(O) isomers, the $E_g(D_{4h})$ component is not so intense that the absorption maximum may be pulled down to the lower-energy side by the A_{2g} component.

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