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Preparation and Characterization of Dinuclear Cobalt(III) Complexes Containing Four Different Kinds of Ligands; Glycinato, Ethylenediamine, Ethylenediamine-*N*,*N*′-diacetato, and μ-Hydroxo

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Four geometrical isomers of $[Co(gly)(en)Co(edda)(\mu\text{-}OH)_2]^+$ were prepared by treating a solution containing $[Co(edda)(OH_2)_2]^+$ and $[Co(gly)(en)(OH_2)_2]^{2+}$ under basic condition and optically resolved by the chromatographic method. The geometrical structures and absolute configurations of the optically active isomers were assigned on the basis of the NMR, UV, and CD spectral data; the assignments were confirmed based on the spectral data of the mononuclear species which were obtained by the acid hydrolysis of each isomer. Two of the four geometrical isomers are constructed with the α-$[Co(edda)(\mu\text{-}OH)_2]$ and *mer*(*O*)-$[Co(gly)(en)(\mu\text{-}OH)_2]$ moieties, and the other two with the β-$[Co(edda)(\mu\text{-}OH)_2]$ and *fac*(*O*)-$[Co(gly)(en)(\mu\text{-}OH)_2]$ moieties, the dinuclear structures being stabilized by the two N–H···O hydrogen bonds between the amino H on one metal ion and the carboxyl O on the other metal ion in the dinuclear complex ion.

Although many reports concerning the preparation and characterization of dicobalt(III) complexes containing μ-hydroxo ligands have been published, there have been few concerning complexes containing two different cobalt(III) chromophores bridged by two μ-hydroxo groups.[1—7] However, complexes of this type are fundamentally poly-nuclear and are suitable for studying the interaction between the two cobalt atoms. In previous papers,[3] preparations of the complexes of the type $[Co(L_1^{(4)})Co(L_2^{(2)})_2(\mu\text{-}OH)_2]^{n+}$ ($L_1^{(4)}=(gly)_2$ or edda; $L_2^{(2)}=(NH_3)_2$ or en) were reported and the following suggestion was given: Dicobalt(III) complexes with two μ-hydroxo, in which two hydrogen bonds are formed between the amino groups on one of the two cobalt atoms and the carboxyl groups on the other cobalt atom, are preferentially produced. According to this suggestion, the complicated dinuclear-complexes of the type $[Co(L_1^{(4)})Co(L_2^{(2)})(L_3^{(2)})(\mu\text{-}OH)_2]^{n+}$ can also be prepared in a manner similar to that for $[Co(L_1^{(4)})Co(L_2^{(2)})_2(\mu\text{-}OH)_2]^{n+}$. In addition, a synthetic study of $[Co(L_1^{(4)})Co(L_2^{(2)})(L_3^{(2)})(\mu\text{-}OH)_2]^{n+}$ may clarify that the coordination mode of edda ($L_1^{(4)}$) is regulated by an interaction between the $[Co(L_1^{(4)})(\mu\text{-}OH)_2]$ moiety and the neighboring $[Co(L_2^{(2)})(L_3^{(2)})(\mu\text{-}OH)_2]$ moiety through the hydrogen bonds.

In the present paper we report on the preparation and chracterization of the $[Co(gly)(en)Co(edda)(\mu\text{-}OH)_2]^+$ isomers and discuss some attempts to clarify the geometries and absolute configurations of the isomers.

Experimental

Preparation of the Complexes. $[Co(gly)(en)Co(edda)(\mu\text{-}OH)_2]Cl$: To a solution containing $CoSO_4 \cdot 7H_2O$ (2.8 g) in 50 cm^3 of water, ethylenediamine-*N*,*N*′-diacetic acid (H_2edda; 1.8 g) was added. After the pH of the solution was adjusted to 9 with a 2 M (M= mol dm^{-3}) KOH solution, PbO_2 (5 g) was added. After the mixture had been stirred for 30 min at room temperature, the insoluble materials were filtered off. To the filtrate, $[Co(gly)(en)(CO_3)] \cdot H_2O$[8] (2.5 g) was added. The solution was adjusted to pH 1 with 60% $HClO_4$, stirred for 5 min at room temperature, adjusted to pH 8.3 with 2 M KOH, and then stirred for 30 min at 65 °C. The reacted solution was cooled to room temperature, neutralized using 2 M $HClO_4$, and then filtered. The filtrate was poured onto an SP-Sephadex column (4.7 cm×90 cm, K^+ form) and swept with 1 dm^3 of water. Being developed with 0.1 M KCl, the band separated into two bands: a brownish-violet band (**F** band: the first eluted band) and a violet band (**S** band: the second eluted band); a remaining dark-brown band was on the top of the column. Each of the **F** and **S** bands was transferred separately to another SP-Sephadex column (4.7 cm×90 cm, K^+ form) and chromatographed recyclically with 0.1 M $K_2[Sb_2(d\text{-}tart)_2]$. After the **F** band was completely separated into three bands (**F1**, **FM**, and **F4**; in the order of elution) by recyclic development for one day, the **F1** and **F4** bands were eluted out from the column separately. The **FM** band was separated into two bands (**F2** and **F3**) by recyclic development for 10 d; the **F2** and **F3** bands were eluted out. The **S** band was separated into four bands (**S1**, **S2**, **S3**, and **S4** in the order of the elution) by recyclic development for 2 d, which were eluted out with 0.1 M $K_2[Sb_2(d\text{-}tart)_2]$. Each of the **F1**—**F4** and **S1**—**S4** eluates was concentrated to a few milliliters by a rotary evaporator at 35—40 °C before adding about 200 cm^3 of methanol. After the deposited $K_2[Sb_2(d\text{-}tart)_2]$ was removed by filtration, the filtrate was again concentrated to a few milliliters. The solution was treated with a small QAE-Sephadex column to convert the $[Sb_2(d\text{-}tart)_2]^{2-}$ ion to the Cl^- ion. A crude complex obtained by adding ethanol to the concentrated solution was recrystallized from water upon the addition of ethanol. It was apparent from the CD spectra that each of the four pairs (**F1**—**F4**, **F2**—**F3**, **S1**—**S2**, and **S3**—**S4**) was an enantiomeric pair. Found for **F1**: C, 23.41; H, 4.98; N, 13.28%. Calcd for $[Co(gly)(en)Co(edda)(\mu-OH)_2]Cl \cdot H_2O = C_{10}H_{26}N_5O_9Co_2Cl$: C, 23.38; H, 5.10; N, 13.63%. Found for **F2**: C, 21.87; H, 5.31; N, 12.51%. Calcd for $[Co(gly)(en)Co(edda)(\mu-OH)_2]Cl \cdot 3H_2O = C_{10}H_{30}N_5O_{11}Co_2Cl$: C, 21.85; H, 5.50; N, 12.74%. Found for **S1**: C, 22.08; H, 5.49; N, 12.55%. Calcd for $[Co(gly)(en)Co(edda)(\mu-OH)_2]Cl \cdot 3H_2O = C_{10}H_{30}N_5O_{11}Co_2Cl$: C, 21.85; H, 5.50; N, 12.74%. Found for **S3**: C, 20.92; H, 5.67; N, 12.06%. Calcd for $[Co(gly)(en)Co(edda)(\mu-OH)_2]Cl\cdot4.5H_2O=C_{10}H_{33}N_5O_{12.5}Co_2Cl$: C, 20.83; H, 5.77; N, 12.14%.

Acid Hydrolyses of the Complexes. Acid hydrolyses of the complexes were carried out in the following manner. The complex (ca. 0.02 g) was dissolved in 10 ml of 0.4 M $HClO_4$; the solution was stirred for about 30 min at 40 °C. The reacted solution was diluted with 100 cm^3 of water and then chromatographed on an SP-Sephadex column (Na^+ form, 1 cm×45 cm) using 0.1 M $NaClO_4$ as an eluent. The absorption and CD spectra of each eluate were measured. The results are summarized in Table 1.

Spectral Measurements. The absorption and CD spectra were measured by a JASCO V-550 spectrophotometer and a JASCO J-720 spectropolarimeter, respectively. The ^1H and ^{13}C NMR spectra were recorded on a Hitachi R-90H spectrometer in a D_2O solution relative to internal references of sodium 3-(trimethylsilyl)propionate-2,2,3,3-d_4 (0 ppm) and dioxane (67.4 ppm), respectively.

Results and Discussion

Structural Assignments and Absorption Spectra. The ^{13}C chemical shift patterns of the present complexes are shown in Fig. 1 together with those of the related cobalt(III) complexes. The numbering of the carbons in edda is also given in Fig. 1.

Each **F** isomer shows ten $^{13}C\{^1H\}$ NMR signal peaks arising from the edda, en, and gly carbons. It is obvious from the ^{13}C shift patterns of en and gly in the isomer that these ligands coordinate to cobalt(III) as chelating bidentates, but not as unidentates or bridging bidentates.[9,10] The edda ligand in each **F** isomer coordinates as a quadridentate with the α mode (Fig. 2), since the chemical shift differences between C(3) and C(3′) are small and the shift pattern is quite similar to that of α-$[Co(edda)(en)]^+$. The α mode of the **F** isomers is also suggested based on their ^1H NMR spectra (Fig. 3); these isomers show two such AB quartets arising from the glycinate-rings in edda, as does α-[Co(edda)(gly)].[11,12]

A characteristic absorption band arising from the $Co(\mu\text{-}OH)_2Co$ moiety, such as $[Co_2(NH_3)_8(\mu\text{-}OH)_2]^{4+}$ and $[Co_2(en)_4(\mu\text{-}OH)_2]^{4+}$ show,[13] was also observed for each **F** isomer at ca. 34000 cm^{-1} (Fig. 4). The band intensities of these complexes are nearly equal to those of the complexes containing two bridging OH's. According to these results, the **F** isomers are assignable to $[Co(gly)(en)Co(edda)(\mu\text{-}OH)_2]^+$ in which the edda coordinates to cobalt(III) in the α mode. Although the coordination mode of the edda, en, and gly were clarified (as mentioned above), some geometries are possible for the **F** isomers. For the detailed geometrical and absolute configurational assignment, it is necessary to clarify the geometries of the mononuclear units in the dinuclear complexes (vide post).

Each **S** isomer also shows ten $^{13}C\{^1H\}$ NMR signal peaks arising from the edda, en, and gly carbons. The en and gly in the isomer coordinate to cobalt(III) as the chelating bidentates. However, the coordination mode of the edda in the **S** isomers is different from that in the **F** isomers. Namely, the edda in each **S** isomer functions as a quadridentate of β mode (β-edda mode), as expected from the following two results: (1) The ^{13}C chemical shift difference between C(3) and C(3′) is extremely large and the pattern is similar to that of β-$[Co(edda)(en)]^+$. (2) The ^1H NMR signal of each **S** isomer shows one AB quartet and one singlet-like peaks (or very close AB quartet)[14] arising from the glycinate rings in the edda (Fig. 3). Thus, the ^1H NMR signal pattern of the edda suggests that although one of the two glycinate rings in the edda is in a facial form to the back-bone ethylenediamine ring in the edda, the other glycinate ring is in a meridional form, that is, the edda takes the β-mode. A characteristic absorption band arising from the $Co(\mu\text{-}OH)_2Co$ was also observed in each of the **S** isomers at ca. 34000 cm^{-1} and the band intensities were nearly equal to those of the complexes with two bridging μ-OH's. Accordingly, the **S** isomers were assignable to $[Co(gly)(en)Co(edda)(\mu\text{-}OH)_2]^+$ in which the edda coordinate to cobalt(III) in the β mode.

The first absorption bands of the present complexes appeared at ca. 19000 cm^{-1} as clear peaks. However, the second absorption bands of the complexes appeared as shoulder bands at ca. 25000 cm^{-1} besides the strong charge-transfer bands (at ca. 34000 cm^{-1}) arising from the bridging OH's.

CD Spectra of the Complexes. The CD spectra of the optically active complexes are illustrated in Fig. 4. As the **F1** ($(-)^{\rm CD}_{567}$) shows a (−) CD band in the lower energy side of the first absorption band region expected for the *cis*-$[Co(N)_2(O)_4]$-type chromophore,[15] the configuration around this chromophore (that is, around the $[Co(edda)(\mu\text{-}OH)_2]$ moiety) is assignable to Δ (Δ_{edda}).[14,16] This isomer also shows a (+) CD band at 20400 cm^{-1} arising from the $[Co(gly)(en)(\mu\text{-}OH)_2]$ moiety, the first absorption band of which is expected to be observed at the higher energy side compared to that of the $[Co(edda)(\mu\text{-}OH)_2]$ moiety. Therefore, the configuration around the $[Co(gly)(en)(\mu\text{-}OH)_2]$ moiety is assignable to Λ ($\Lambda_{en,gly}$). The **F2** ($(-)^{\rm CD}_{572}$) shows two (−) CD bands in the first absorption band region. Such a CD pattern suggests that both of the configurations around the $[Co(edda)(\mu\text{-}OH)_2]$ and $[Co(gly)(en)(\mu\text{-}OH)_2]$ moieties are assignable to Δ_{edda} and $\Delta_{en,gly}$, respectively.

In a previous paper it was suggested that an isomer which has the Δ–Δ configuration shows a larger CD intensity at ca. 34000 cm^{-1} than that which has the Δ–Λ configuration in di(μ-hydroxo)dicobalt(III) complexes.[3] The CD intensity of **F2** at ca. 34000 cm^{-1} is much larger than of **F1**; accordingly, the configurations of **F2** and **F1** are assigned to Δ–Δ and Δ–Λ, respectively. These assignments are in line with those based upon the CD behaviors in the first absorption

Table 1. Acid Hydrolysis Products of Di-μ-hydroxo-dicobalt(III) Complexes and Carbonato-cobalt(III) Complexes

Complexes	Mononuclear complexes obtained by the acid hydrolyses			
(Assigned structure)	$[Co(edda)(OH_2)_2]^+$		$[Co(gly)(en)(OH_2)_2]^{2+}$	
	UP Peak (Structure)	CD Sign (Configuration)	UV Peak (Structure)	CD Sign (Configuration)
$[Co(gly)(en)Co(edda)(\mu\text{-}OH)_2]^+$				
F1 $(\Delta_{\alpha-edda}\Lambda_{mer-en,gly})$	540 nm (α)	$(-)^{CD}_{545}$ (Δ)	498 nm ($mer(O)$)	$(-)^{CD}_{535}$ (Λ)
F2 $(\Delta_{\alpha-edda}\Delta_{mer-en,gly})$	540 nm (α)	$(-)^{CD}_{545}$ (Δ)	498 nm ($mer(O)$)	$(+)^{CD}_{535}$ (Δ)
S1 $(\Delta_{\beta-edda}\Delta_{fac-en,gly})$	518 nm (β)	$(+)^{CD}_{564}$ (Δ)	514 nm ($fac(O)$)	$(-)^{CD}_{540}$ (Δ)
S3 $(\Delta_{\beta-edda}\Lambda_{fac-en,gly})$	518 nm (β)	$(+)^{CD}_{564}$ (Δ)	514 nm ($fac(O)$)	$(+)^{CD}_{540}$ (Λ)
$(-)^{CD}_{572}$-Δ-α-$[Co(edda)(CO_3)]^-$	540 nm (α)	$(-)^{CD}_{545}$ (Δ)	—	—
$(-)^{CD}_{580}$-$\Delta\Delta$-α-$[Co(en)_2Co(edda)(\mu\text{-}OH)_2]^{2+}$	540 nm (α)	$(-)^{CD}_{545}$ (Δ)	—	—
$(-)^{CD}_{538}$-Δ-β-$[Co(edda)(CO_3)]^-$	518 nm (β)	$(+)^{CD}_{564}$ (Δ)	—	—
$(-)^{CD}_{562}$-Δ-$mer(O)$-$[Co(gly)(en)(CO_3)]$	—	—	498 nm ($mer(O)$)	$(+)^{CD}_{535}$ (Δ)
$(-)^{CD}_{556}$-$\Delta\Delta$-$fac(O)fac(O)$-$[Co(gly)(en)Co(gly)(en)(\mu\text{-}OH)_2]^{2+}$	—	—	514 nm ($fac(O)$)	$(-)^{CD}_{540}$ (Δ)

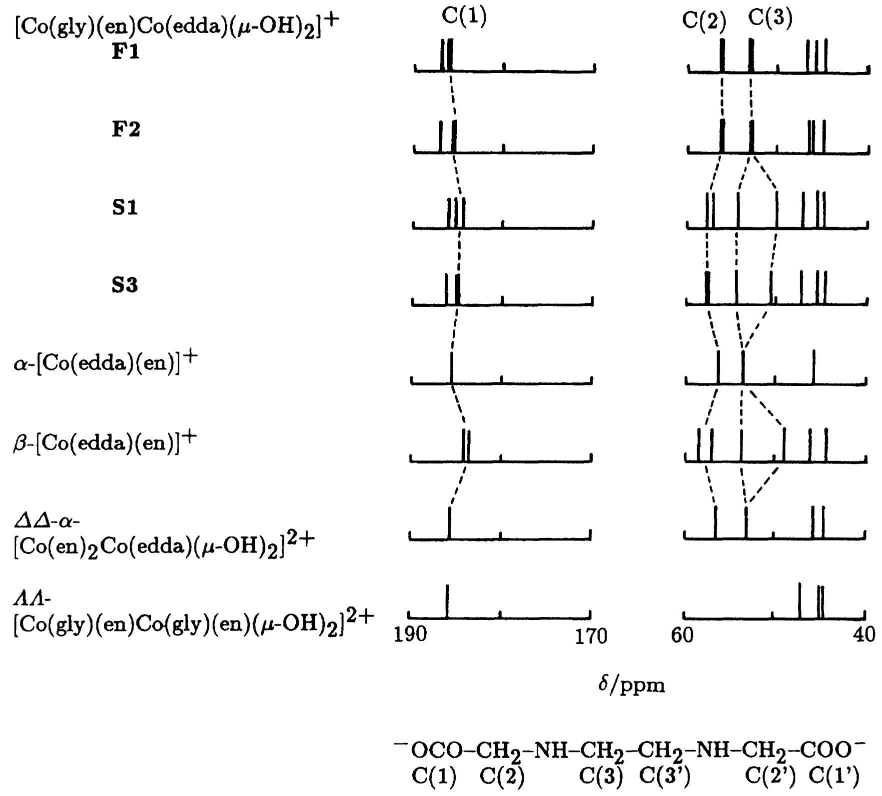
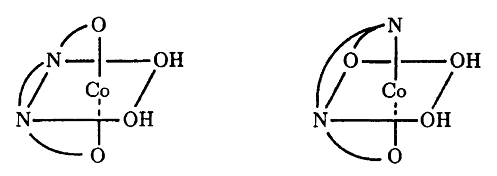


Fig. 1. ^{13}C chemical shift patterns of the complexes and numbering of the carbons in *edda*.

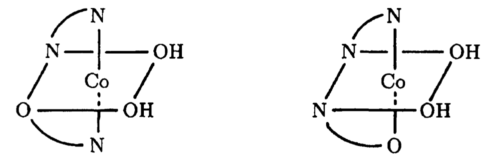
band region.

A similar discussion can be made for **S1** and **S3**. The **S1** ($(-)^{CD}_{588}$) exhibits two (−) CD peaks in the first absorption band region (Fig. 4); therefore, the configurations around the $[Co(edda)(\mu\text{-}OH)_2]$ and $[Co(gly)(en)(\mu\text{-}OH)_2]$ moieties are assignable to Δ_{edda} and $\Delta_{en,gly}$, respectively. Since the **S3** ($(-)^{CD}_{580}$) exhibits (−) (lower energy side) and (+) (higher energy side) CD peaks in the first absorption band region, the configurations around the $[Co(edda)(\mu\text{-}OH)_2]$ and $[Co(gly)(en)\text{-}$



α-$[Co(edda)(\mu\text{-}OH)_2]$ moiety

β-$[Co(edda)(\mu\text{-}OH)_2]$ moiety



mer(O)-$[Co(gly)(en)(\mu\text{-}OH)_2]$ moiety

fac(O)-$[Co(gly)(en)(\mu\text{-}OH)_2]$ moiety

Fig. 2. Structures of the α- and β-$[Co(edda)(\mu\text{-}OH)_2]$ moieties and the *mer(O)*- and *fac(O)*-$[Co(gly)(en)(\mu\text{-}OH)_2]$ moieties.

$(\mu\text{-}OH)_2]$ moieties are assignable to Δ_{edda} and $\Lambda_{en,gly}$, respectively. The CD intensity of **S3** at ca. 34000 cm^{-1} is much smaller than that of **S1**.

Although the structural assignments for the present dinuclear complexes were made on the basis of their CD spectral data, the assignments remain obscure because the first absorption bands of the $[Co(edda)(\mu\text{-}OH)_2]$ and $[Co(gly)(en)(\mu\text{-}OH)_2]$ chromophores in the dinuclear complexes are located in very close range. In order to confirm the assignments we measured the UV and CD spectra of the mononuclear complexes obtained by acid hydrolyses of the dinuclear complexes (as described below).

Acid Hydrolyses of the Di-μ-hydroxo-dicobalt(III) Complexes. It is known that the hydrolyses of di-μ-hydroxodicobalt(III) complexes in an acidic aqueous solution give the corresponding mononuclear species. An analysis of the products of the cleavage reactions serves to elucidate the composition and structures of the polynuclear species.[13]

In the present study the obtained dinuclear complexes were hydrolyzed in 0.4 M $HClO_4$ at 40 °C; then, the reacted solutions were chromatographed on an SP-Sephadex column (Na^+ form, eluent: 0.1 M $NaClO_4$). When the hydrolyzed solution of **F1** was chromatographed, mononuclear complexes (which do not show characteristic charge transfer bands arising from $Co(\mu\text{-}OH)_2Co$) were separated as two bands on a column. The UV and CD behaviors of the faster eluted mononuclear complex agreed with those of $(-)^{CD}_{545}$-Δ-α-$[Co(edda)(OH_2)_2]^+$ which was obtained from the $(-)^{CD}_{580}$-$\Delta\Delta$-$[Co(en)_2Co(edda)(\mu\text{-}OH)_2]^{2+}$[3] or $(-)^{CD}_{572}$-Δ-α-$[Co(CO_3)(edda)]^+$.[14] The UV and CD spectral behaviors of the later eluted mononuclear complex agreed with those of $(-)^{CD}_{535}$-Λ-*mer(O)*-$[Co(gly)(en)(OH_2)_2]^+$ which was obtained from $(+)^{CD}_{562}$-Λ-*mer(O)*-$[Co(gly)(en)(CO_3)]$.[17] Accordingly, the configurations of the **F1** dinuclear isomer is assigned to the $\Delta_{\alpha-edda}$ (Δ configuration on the α-$[Co(edda)(\mu\text{-}OH)_2]$ moiety) and $\Lambda_{mer-en,gly}$ (Λ configuration on the *mer(O)*-$[Co(gly)(en)(\mu\text{-}OH)_2]$ moiety) configurations. In the hydrolyzed solution of **F2**, only two mononuclear complexes ($(-)^{CD}_{545}$-Δ-α-$[Co(edda)(OH_2)_2]^+$ and $(+)^{CD}_{535}$-Δ-*mer(O)*-$[Co(gly)(en)(OH_2)_2]^+$) were detected. Consequently, the configuration of **F2** is assigned to $\Delta_{\alpha-edda}$ $\Delta_{mer-en,gly}$. The configurations of the **F3** (the enantiomer of **F2**) and **F4** (the enantiomer of **F1**) isomers are assigned to $\Lambda_{\alpha-edda}\Lambda_{mer-en,gly}$ and $\Lambda_{\alpha-edda}\Delta_{mer-en,gly}$, respectively.

The α-$[Co(edda)(OH_2)_2]^+$ and *mer(O)*-$[Co(gly)(en)(OH_2)_2]^{2+}$ were detected in hydrolyzed solutions of **F1**—**F4**, while the β-$[Co(edda)(OH_2)_2]^+$ and *fac(O)*-$[Co(gly)(en)(OH_2)_2]^{2+}$ were detected in hydrolyzed solutions of **S1**—**S4**. When a hydrolyzed solution of **S1** was chromatographed on an SP-Sephadex column, two mononuclear complexes were eluted. The UV and CD behaviors of the faster eluted mononuclear complex agreed with those of $(+)^{CD}_{564}$-Δ-β-$[Co(edda)(OH_2)_2]^+$, which was obtained from $(-)^{CD}_{538}$-Δ-β-$[Co(edda)(CO_3)]^+$.[14] The UV and CD spectral patterns of the later eluted mononuclear complex agreed with those of $(-)^{CD}_{540}$-Δ-*fac(O)*-$[Co(gly)(en)(OH_2)_2]^+$, which was obtained from $(-)^{CD}_{556}$-$\Delta\Delta$-*fac(O)fac(O)*-$[Co(gly)(en)Co(gly)(en)(\mu\text{-}OH)_2]^{2+}$.[3,7] Accordingly, the configuration of **S1** is assigned to $\Delta_{\beta-edda}\Delta_{fac-en,gly}$ and that of **S2** (the enantiomer of **S1**) to $\Lambda_{\beta-edda}\Lambda_{fac-en,gly}$. In the hydrolyzed solution of **S3**, two mononuclear complexes ($(+)^{CD}_{564}\Delta$-β-$[Co(edda)(OH_2)_2]^+$ and $(+)^{CD}_{540}$-Λ-*fac(O)*-$[Co(gly)(en)(OH_2)_2]^{2+}$) were obtained. Consequently, the configuration of **S3** is assigned to $\Delta_{\beta-edda}\Lambda_{fac-en,gly}$. The configuration of **S4** (the enantiomer of **S3**) is assigned to $\Lambda_{\beta-edda}\Delta_{fac-en,gly}$.

Based on X-ray study of $[Cr_2(\text{L-pro})_4(\mu\text{-}OH)_2]\cdot 4H_2O$ and $[Co(gly)(en)Co(gly)(en)(\mu\text{-}OH)_2](ClO_4)_2\cdot 2H_2O$ it was clarified that the two intramolecular N–H···O hydrogen bonds (bridging two chromophores) stabilize the di-μ-hydroxo structure.[2,18] Moreover, it was clarified that although the preparation of isomers having two hydrogen bonds is easy, the preparation of isomers having one or no hydrogen bond is difficult by the condensation of parental mononuclear diaqua complexes in a basic aqueous solution.[3] Accordingly, it is reasonable to propose that the present dinuclear complexes, which were prepared under basic aqueous condition, contain two hydrogen bonds. In the ^1H NMR spectrum of a freshly prepared D_2O solution of **F1**, we found the amino protons at ca. 5.6 ppm (en) and 6.0 ppm (gly), while the other amino protons were disappeared. This result shows that the found amino protons are bonded more tightly to the dinucler complex ion than are the disappeared ones, which suggests the possibility that the found ones form hydrogen-bonds. The found amino protons of **F2**, **S1**, and **S3** appeared at {ca. 5.7 ppm (en) and 6.0 ppm (gly)}, {ca. 4.8 ppm (en) and 6.5 ppm

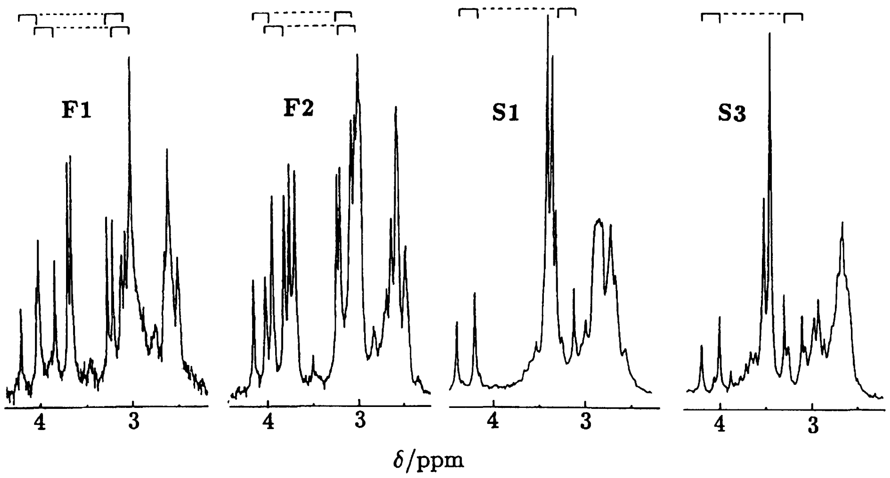


Fig. 3. ^{1}H NMR spectra of the isomers of $[Co(gly)(en)Co(edda)(\mu\text{-}OH)_2]^{2+}$ in D_2O (after deuteration of amine-protons).

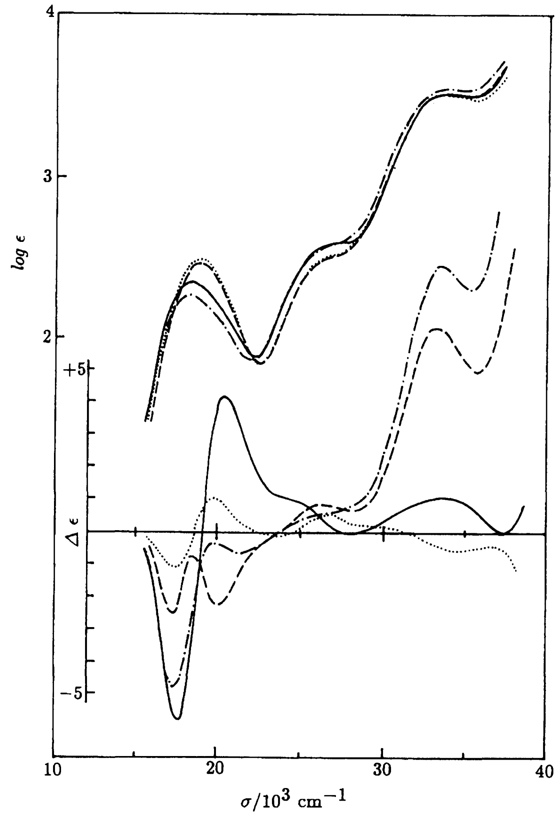
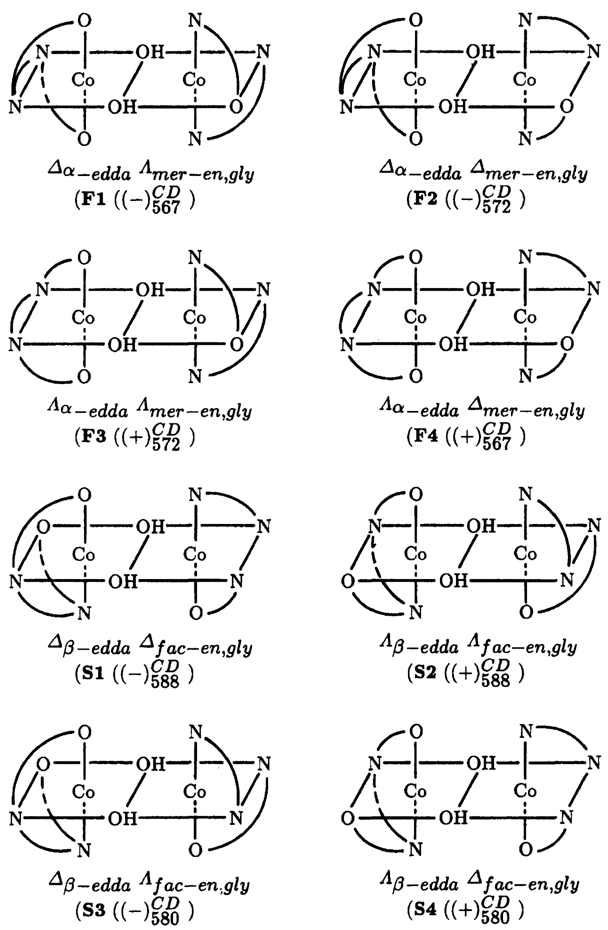


Fig. 4. Absorption and circular dichroism spectra of the isomers of $[Co(gly)(en)Co(edda)(\mu\text{-}OH)_2]^{2+}$: **F1** (——), **F2** (–·–), **S1** (- - -), and **S3** (····).



$\Delta_{\alpha\text{-edda}}\ \Lambda_{mer\text{-en,gly}}$ (**F1** $((-)^{CD}_{567}$)

$\Delta_{\alpha\text{-edda}}\ \Delta_{mer\text{-en,gly}}$ (**F2** $((-)^{CD}_{572}$)

$\Lambda_{\alpha\text{-edda}}\ \Lambda_{mer\text{-en,gly}}$ (**F3** $((+)^{CD}_{572}$)

$\Lambda_{\alpha\text{-edda}}\ \Delta_{mer\text{-en,gly}}$ (**F4** $((+)^{CD}_{567}$)

$\Delta_{\beta\text{-edda}}\ \Delta_{fac\text{-en,gly}}$ (**S1** $((-)^{CD}_{588}$)

$\Lambda_{\beta\text{-edda}}\ \Lambda_{fac\text{-en,gly}}$ (**S2** $((+)^{CD}_{588}$)

$\Delta_{\beta\text{-edda}}\ \Lambda_{fac\text{-en;gly}}$ (**S3** $((-)^{CD}_{580}$)

$\Lambda_{\beta\text{-edda}}\ \Delta_{fac\text{-en,gly}}$ (**S4** $((+)^{CD}_{580}$)

Fig. 5. Structures of the isomers of $[Co(gly)(en)Co(edda)(\mu\text{-}OH)_2]^{2+}$.

(edda)}, and {ca. 4.9 ppm (en) and 6.6 ppm (edda)} respectively. These protons can be regarded as forming hydrogen-bonds. By taking into account the above-mentioned results, we can obtain the structural assignments summarized in Table 1; the structures are illustrated in Fig. 5.

Stability of the Dinuclear Complexes. The absorption spectral changes with time were measured in the aqueous solutions of some di-μ-hydroxo complexes at room temperature. The neutral aqueous solutions of the present complexes showed no spectral change for one week, while that of $[Co_2(NH_3)_8(\mu\text{-}OH)_2]Br_4$ showed an obvious change after one day. This means that the present complexes are more stable than $[Co_2(NH_3)_8(\mu\text{-}OH)_2]^{4+}$, suggesting that the intramolecular N–H···O hydrogen bonds are important for the stability of the dinuclear structure. Furthermore, the present results suggest that the chelation mode of edda is regulated by the geometrical structure of the $[\mathrm{Co(gly)(en)}(\mu\text{-OH})_2]$ moiety through the two N–H···O hydrogen bonds. That is, the *mer*(*O*)-$[\mathrm{Co(gly)(en)}(\mu\text{-OH})_2]$ moiety forces the $[\mathrm{Co(edda)}(\mu\text{-OH})_2]$ one to take the α chelation mode to form two hydrogen bonds (N_{gly}–H···O_{edda} and N_{en}–H···O_{edda}); the *fac*(*O*)-$[\mathrm{Co(gly)(en)}(\mu\text{-OH})_2]$ moiety forces the $[\mathrm{Co(edda)}(\mu\text{-OH})_2]$ one to take the β chelation mode to form two hydrogen bonds (N_{edda}–H···O_{gly} and N_{en}–H···O_{edda}).

In the case of $[\mathrm{Co(en)_2Co(edda)}(\mu\text{-OH})_2]^{2+}$, the $[\mathrm{Co(en)_2}(\mu\text{-OH})_2]$ moiety can form two hydrogen bonds (N_{en}–H···O_{edda}) with the α-$[\mathrm{Co(edda)}(\mu\text{-OH})_2]$ one, but can form only one hydrogen bond (N_{en}–H···O_{edda}) with the β-$[\mathrm{Co(edda)}(\mu\text{-OH})_2]$ one. Accordingly, the isomers of $[\mathrm{Co(en)_2Co(edda)}(\mu\text{-OH})_2]^{2+}$ with α-mode edda should be more stable than those with β-mode edda. It was reported in a previous paper that although the former isomers were isolated, the latter were not.[3] The above-mentioned results for $[\mathrm{Co(en)_2Co(edda)}(\mu\text{-OH})_2]^{2+}$, together with the results reported in this paper for $[\mathrm{Co(gly)(en)Co(edda)}(\mu\text{-OH})_2]^+$, suggest that dinuclear complexes which have two N–H···O hydrogen bonds are selectively formed by the condensation of parental mononuclear complexes in the basic aqueous solutions.

In conclusion: (1) we prepared four geometrical isomers of the complicated dinuclear complex ion, $[\mathrm{Co(gly)(en)Co(edda)}(\mu\text{-OH})_2]^+$, by condensation of the parental mononuclear complexes, $[\mathrm{Co(edda)(OH_2)_2}]^+$ and $[\mathrm{Co(gly)(en)(OH_2)_2}]^{2+}$, in a basic aqueous solution and their structures were clarified; (2) the acid hydrolysis method used to characterize the mononuclear complexes derived from di-μ-hydroxodicobalt(III) complex was employed to reveal the structure of the complicated dinuclear complex, such as $[\mathrm{Co(gly)(en)Co(edda)}(\mu\text{-OH})_2]^+$; and (3) the number of the N–H···O hydrogen bonds is important for the stability of the dinuclear structure and the coordination mode of a ligand on one metal ion of the dinuclear complex is regulated through the N–H···O hydrogen bonds formed with the ligand on the other metal ion.

References

1) K. Okamoto, J. Hidaka, T. Ama, and T. Yasui, *Acta Crystallogr., Sect. C*, **C47**, 2099 (1991).

2) K. Hamada, E. Ohta, T. Fujiwara, and T. Ama, *Bull. Chem. Soc. Jpn.*, **62**, 1328 (1989).

3) T. Ama, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **61**, 1141 (1988).

4) T. Ama, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **60**, 1183 (1987).

5) K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc.*, **80**, 4817 (1958).

6) W. Hackbusch, H. H. Rupp, and K. Wieghardt, *J. Chem. Soc., Dalton Trans.*, **1975**, 1015.

7) T. Ama, A. Mukai, K. Miyauchi, H. Kawaguchi, and T. Yasui, *Mem. Fac. Sci. Kochi Univ., Ser. C*, **7**, 1 (1986).

8) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **39**, 1257 (1966).

9) T. Ama and T. Yasui, *Bull. Chem. Soc. Jpn.*, **52**, 79 (1979).

10) T. Ama, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **54**, 448 (1981).

11) H. Kawaguchi, N. Uchiyama, T. Ama, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **63**, 3535 (1990).

12) T. Ama, K. Kuwamura, H. Kawaguchi, and T. Yasui, *Mem. Fac. Sci. Kochi Univ., Ser. C*, **12**, 1 (1991).

13) J. Springborg, *Adv. Inorg. Chem.*, **32**, 55 (1988).

14) P. J. Garnett and D. W. Watts, *Inorg. Chim. Acta*, **8**, 293 (1974).

15) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).

16) Y. Shimura, *Kagaku Sosetsu*, No. 13, 83 (1976).

17) Partially resolved $(+)^{\mathrm{CD}}_{562}$-*mer*(*O*)-$[\mathrm{Co(gly)(en)(CO_3)}]$ was obtained by recyclic chromatography on a QAE-Sephadex column ($\mathrm{HCO_3^-}$ form; eluent water) or reaction of $(-)^{\mathrm{CD}}_{567}$-$[\mathrm{Co(gly)(en)_2Co(edda)}(\mu\text{-OH})_2]\mathrm{Cl_2}$ with $\mathrm{Na_2CO_3}$ in aqueous solution.

18) H. Oki and H. Yoneda, *Inorg. Chem.*, **20**, 3875 (1981).