Circular Dichroism Spectra of the Dicobalt(III) Complexes Containing Two Bridging μ-Hydroxo Ligands

Tomoharu Ama,* Hiroshi Kawaguchi, and Takaji Yasui
Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780

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Five cobalt(III) complexes, $[(gly)_2Co(\mu\text{-}OH)_2Co(en)_2]^{2+}$ (two geometrical isomers), $[(edda)Co(\mu\text{-}OH)_2Co(en)_2]^{2+}$ (two geometrical isomers), and $[(nta)Co(\mu\text{-}OH)_2Co(en)_2]Cl$, were newly prepared and optically resolved. Their structures were assigned on the basis of visible and UV absorption, ^1H NMR, and circular dichroism (CD) spectral data. It was found that the CD contributions of the two different cobalt(III) chromophores are additive in the present complex systems. The vicinal CD which is induced on one of the two cobalt chromophores by the other chiral cobalt chromophore was strong ($|\Delta\varepsilon|$: ca. 2). These complexes are stable for several days in aqueous solution.

Although many reports on the preparation and characterization of dicobalt(III) complexes containing two bridging hydroxo ligands have been published, only a few reports have dealt with the complexes containing two different cobalt(III) chromophores bridged with the two hydroxo groups.[2–5] However, the complexes of this type are the fundamental polynuclear ones and are suitable for the investigation of the interaction between the two cobalt atoms. Accordingly, a reliable method to prepare many complexes of this type is required. In the pevious paper,[2] the preparation of ammine complexes such as $[(L)Co(\mu\text{-}OH)_2Co(NH_3)_4]^{2+}$ (L=$(gly)_2$, edda, or nta)[1] was reported and the following suggestion was given: the 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. In order to confirm the suggestion, we tried to prepare the complexes with two ethylenediamine ligands instead of four ammine ligands (Fig. 1). In the present paper, the interaction between the cobalt(III) chromophores and the additivity rule in the CD spectra of the polynuclear complexes will be described in detail on the basis of the CD spectral data of these optically active isomers of ethylenediamine complexes. The preparation and stability of the complexes will also be described.

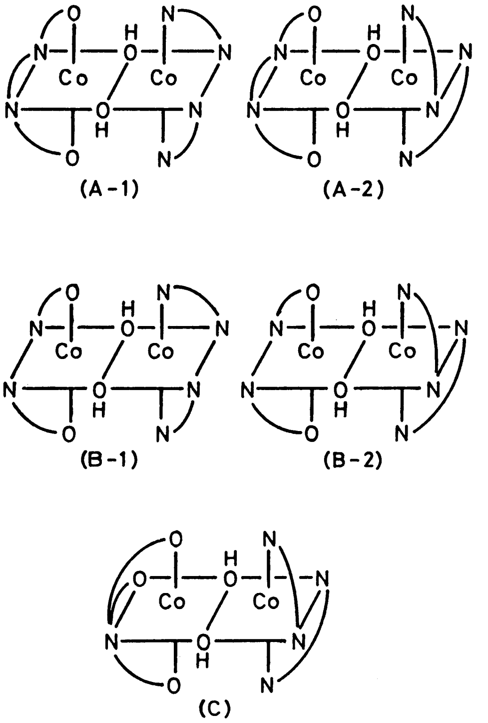

Fig. 1. Structures of the prepared complexes:
(A-1) (Λ, Δ)-$[(edda)Co(\mu\text{-}OH)_2Co(en)_2]^{2+}$ ($(+)^{\mathrm{CD}}_{565}$**E-1**);
(A-2) (Λ, Λ)-$[(edda)Co(\mu\text{-}OH)_2Co(en)_2]^{2+}$ ($(+)^{\mathrm{CD}}_{580}$**E-2**);
(B-1) (Λ, Δ)-$[(gly)_2Co(\mu\text{-}OH)_2Co(en)_2]^{2+}$ ($(+)^{\mathrm{CD}}_{560}$**G-1**);
(B-2) (Λ, Λ)-$[(gly)_2Co(\mu\text{-}OH)_2Co(en)_2]^{2+}$ ($(+)^{\mathrm{CD}}_{580}$**G-2**);
and (c) (Λ)-$[(nta)Co(\mu\text{-}OH)_2Co(en)_2]^{+}$ ($(-)^{\mathrm{CD}}_{625}$**N-1**).

Experimental

Preparation of the Complexes. $[(edda)Co(\mu\text{-}OH)_2Co(en)_2]Cl_2$: In 5 cm^3 of water, $K[Co(edda)(CO_3)]\cdot H_2O$ (2.0 g)[6] was suspended and then acidified with 60% $HClO_4$ (2 cm^3). Separately, $[Co(en)_2(CO_3)]ClO_4$ (2.0 g) was suspended in 5 cm^3 of water and acidified with 60% $HClO_4$ (2 cm^3). The two solutions were mixed. The pH of the mixed solution was adjusted to 8.5 with 2 mol dm^{-3} KOH and then stirred for 60 min in a water bath at 50 °C. The reacted solution was cooled to room temperature, neutralized using 2 mol dm^{-3} $HClO_4$ and filtered. The filtrate was loaded on a column (4.7 cm×50 cm) of SP-Sephadex (K^+ form), and the adsorbed band was developed with 0.4 mol dm^{-3} KCl. The eluate from the third band (dark-violet) was transferred to another SP-Sephadex column (K^+ form) and repeatedly developed on the column using a micropump until the adsorbed band completely separated into two bands [**E-1** (earlier band) and **E-2** (later band)]. The eluate from **E-1** was evaporated to about 10 cm^3 and the KCl which deposited was filtered off. Methanol was added to the filtrate and the KCl which deposited was again filtered off. After the filtrate was evaporated almost to dryness, the residue was dissolved in 50 cm^3 of water. The solution was poured onto a column (4.7 cm×50 cm) of SP-Sephadex (K^+ form) once more. The adsorbed band was developed with 0.1 mol dm^{-3} K_2Sb_2 (d-tart)$_2$. This development was repeated on the column using a micropump until the adsorbed band completely separated into two dark-violet bands. The earlier- and later-eluted bands exhibited (−) and (+) CD signs at 565 nm, respectively. Each band was eluted with 0.1 mol dm^{-3} of K_2Sb_2 (*d*-tart)$_2$, and the eluted solution was concentrated to small volume under reduced pressure. To the concentrated solution, methanol was added to deposit K_2Sb_2(*d*-tart)$_2$. After the deposited K_2Sb_2(*d*-tart)$_2$ was filtered off, the filtrate was evaporated almost to dryness to exclude methanol and was diluted with a little water. The solution was reloaded on a short column (3 cm×5 cm) of QAE-Sephadex (Cl^- form) and eluted with water. The eluted solution was concentrated to small volume. Crude complex of the optically active isomer was obtained by adding methanol and acetone to the concentrated solution, which was recrystallized from water by adding methanol and acetone.

The eluate from **E-2** was optically resolved by a method similar to that employed for **E-1**. The earlier and later eluates on the development with K_2Sb_2 (*d*-tart)$_2$ were $(+)^{\mathrm{CD}}_{580}$ and $(-)^{\mathrm{CD}}_{580}$ forms, respectively. Found for the $(+)^{\mathrm{CD}}_{565}$ **E-1** isomer: C, 22.14; H, 5.68; N, 15.52%. Calcd for [(edda)Co(μ-OH)$_2$Co(en)$_2$]Cl$_2\cdot$ 1.5H$_2$O=$C_{10}H_{31}N_6O_{7.5}Cl_2Co_2$: C, 22.07; H, 5.74; N, 15.44%. Found for the $(+)^{\mathrm{CD}}_{580}$ **E-2** isomer: 21.08; H, 6.06; N, 14.82%. Calcd for [(edda)Co(μ-OH)$_2$Co(en)$_2$]Cl$_2\cdot$3H$_2$O=$C_{10}H_{34}N_6O_9Cl_2Co_2$: C, 21.03; H, 6.00; N, 14.71%.

[(gly)$_2$Co(μ-OH)$_2$Co(en)$_2$]Br$_2$: By a method similar to that described above, this complex was prepared from K[Co(gly)$_2$(CO$_3$)] (2.0 g)[6] and [Co(en)$_2$(CO$_3$)]ClO$_4$ (2.0 g) (reaction conditions: pH 8.0, 50 °C, 45 min). The reacted solution was cooled to room temperature, neutralized using 2 mol dm^{-3} HClO$_4$ and filtered. The filtrate was loaded on a column (4.7 cm×50 cm) of SP-Sephadex C-25 (NH_4^+ form), and the adsorbed band was developed with 0.2 mol dm^{-3} (NH$_4$)$_2$SO$_4$. The eluate from the third band (dark-violet) was transferred to another SP-Sephadex column (NH_4^+ form) and repeatedly developed on the column using a micropump until the adsorbed band separated completely into two bands [**G-1** (earlier band) and **G-2** (later band)]. An eluate from **G-1** was evaporated to about 10 cm^3 and methanol was added to the concentrated solution. After the (NH$_4$)$_2$SO$_4$ which deposited was filtered off, the filtrate was evaporated almost to dryness. The crude complex was dissolved in 50 cm^3 of water and optically resolved on the column by the same method as that described for **E-1**. The earlier- and later-eluted bands on the development with K_2Sb_2(*d*-tart)$_2$ showed (−) and (+) CD signs at 560 nm, respectively. Finally, each of the resolved **G-1** was converted to the Br^- salt using a QAE-Sephadex column (Br^- form).

The eluate from **G-2** was optically resolved by the same method as that employed for **G-1**. The earlier and later eluates on the development with K_2Sb_2(*d*-tart)$_2$ were $(+)^{\mathrm{CD}}_{580}$ and $(-)^{\mathrm{CD}}_{580}$ isomers, respectively. Found for the $(+)^{\mathrm{CD}}_{560}$ **G-1** isomer: C, 15.78; H, 4.88; N, 13.82%. Calcd for [(gly)$_2$Co(μ-OH)$_2$Co(en)$_2$]Br$_2\cdot$1.5H$_2$O=$C_8H_{29}N_6O_{7.5}Br_2Co_2$: C, 15.83; H, 4.82; N, 13.84%. Found for the $(+)^{\mathrm{CD}}_{580}$ **G-2** isomer: C, 15.95; H, 4.67; N, 14.05%. Calcd for [(gly)$_2$Co(μ-OH)$_2$Co(en)$_2$]Br$_2\cdot$H$_2$O=$C_8H_{28}N_6O_7Br_2Co_2$: C, 16.07; H, 4.72; N, 14.05%.

[(nta)Co(μ-OH)$_2$Co(en)$_2$]Cl: By a method similar to that described for [(edda)Co(μ-OH)$_2$Co(en)$_2$]Cl$_2$, [(nta)Co(μ-OH)$_2$Co(en)$_2$]$^+$ (**N-1**) was prepared from K$_2$[Co(nta)(CO$_3$)] and [Co(en)$_2$(CO$_3$)]ClO$_4$ (reaction conditions: pH 8.5, 50 °C, 40 min). The reacted solution was cooled to room temperature, neutralized using 2 mol dm^{-3} HClO$_4$ and filtered. The filtrate was loaded on a column (4.7 cm×50 cm) of SP-Sephadex (K^+ form), and the adsorbed band developed with 0.2 mol dm^{-3} KCl. The eluate from the second band (dark-violet) was evaporated to about 10 cm^3 and methanol was then added to the concentrated solution. The KCl which deposited was filtered off and the filtrate was evaporated almost to dryness. The crude complex was dissolved in 50 cm^3 of water and optically resolved by the same method as that employed for **E-1**. The earlier and later eluates on the development with K_2Sb_2(*d*-tart)$_2$ were $(-)^{\mathrm{CD}}_{625}$ and $(+)^{\mathrm{CD}}_{625}$ isomers, respectively. Calcd for the $(+)^{\mathrm{CD}}_{625}$ isomer: C, 22.47; H, 5.33; N, 13.06%. Calcd for [(nta)Co(μ-OH)$_2$Co(en)$_2$]Cl$\cdot$2H$_2$O=$C_{10}H_{28}N_5O_{10}ClCo_2$: C, 22.59; H, 5.30; N, 13.17%.

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

Results and Discussion

Structural Assignments and Absorption Spectra. The Complexes Containing edda: The first absorption band of the edda complex **E-1** (or **E-2**) is very broad (Fig. 2), suggesting that **E-1** (or **E-2**) contains two chromophores of different types in the complex

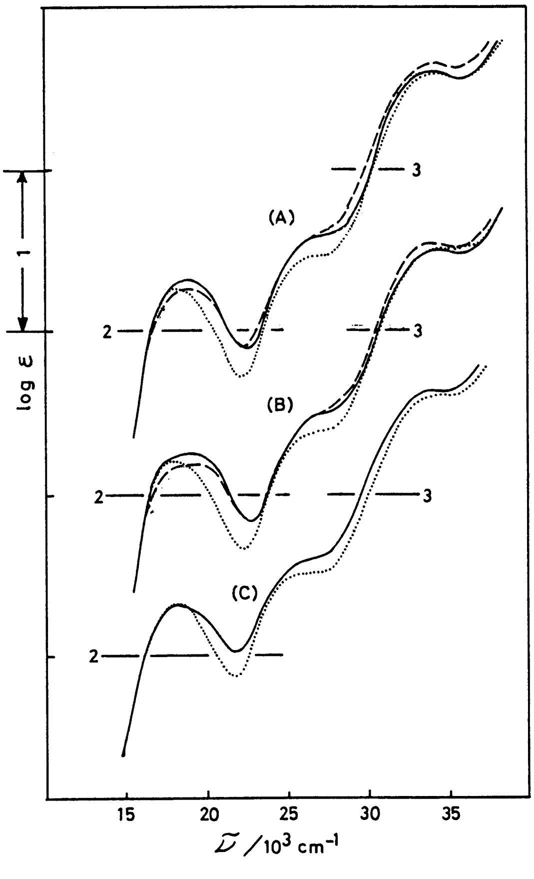

Fig. 2. Absorption spectra of the complexes: (A) **E-1** (——), **E-2** (----), and [(edda)Co(μ-OH)$_2$Co(NH$_3$)$_4$]$^{2+}$ (······); (B) **G-1** (——), **G-2** (----), and [(gly)$_2$Co(μ-OH)$_2$Co(NH$_3$)$_4$]$^{2+}$ (······); and (C) **N-1** (——) and [(nta)Co(μ-OH)$_2$(NH$_3$)$_4$]$^+$ (······). The ε values are given in mol^{-1}dm^{3}cm^{-1}.

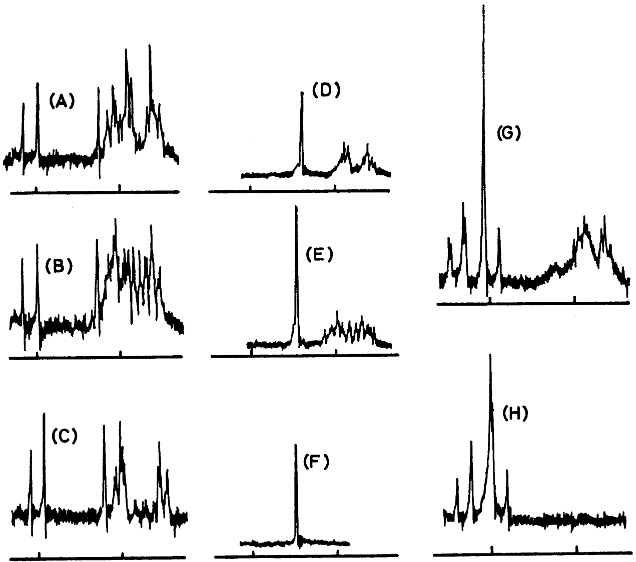

Fig. 3. ^{1}H NMR spectra of the complexes: (A) **E-1**, (B) **E-2**, (C) $[(\text{edda})\text{Co}(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4]^{2+}$, (D) **G-1**, (E) **G-2**, (F) $[(\text{gly})_2\text{Co}(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4]^{2+}$, (G) **N-1**, and (H) $[(\text{nta})\text{Co}(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4]^{+}$.

ion. However, the chromatographic development on an SP-Sephadex column gave only a single band, showing that the complex is cationic and not a mixture of cationic and anionic complexes. Accordingly, it is reasonable to propose that the two chromophores are bridged in the cationic complex ion.

The ^{1}H NMR spectral pattern of the glycinate protons of the coordinated edda in **E-1** (or **E-2**) resembles that in $[(\text{edda})\text{Co}(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4]^{2+}$ [2] (Fig. 3). That is, the glycinate methylene protons of edda in **E-1** (or **E-2**) appeared as an AB quartet signal (δ: ca 3.1 and ca. 4.0), suggesting that the two glycinate methylenes in edda are equivalent in their chemical environment; the edda takes α-cis chelation form.[9] In addition, the ethylenediamine backbones of edda appeared as multiplet signals (δ: ca. 2.7) in both the ammine and the ethylenediamine complexes. These similarities show that the present edda complexes have the same di-μ-hydroxo structure as that of $[(\text{edda})\text{Co}(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4]^{2+}$. The signals arising from ethylenediamine also appeared at ca. 2.7 ppm in **E-1** (or **E-2**) as a multiplet, overlapping with those arising from the backbone of edda. The intensity ratio of (quartet (δ: ca. 3.1 and 4.0))/(multiplets (δ: ca. 2.7)) was 4/12, indicating that the ratio of edda/en is 1/2. Moreover, the elemental analysis data suggest that the edda/en ratio in each complex is 1/2. Accordingly, both **E-1** and **E-2** contain (edda) and $(\text{en})_2$ moieties.

A characteristic UV absorption band arising from the $\text{Co}(\mu\text{-OH})_2\text{Co}$ moiety,[14] such as $[\text{Co}_2(\text{NH}_3)_8(\mu\text{-OH})_2]^{4+}$ and $[\text{Co}_2(\text{en})_4(\mu\text{-OH})_2]^{4+}$,[10-12] was also observed in the present edda complexes at ca. 34000 cm^{-1} (Fig. 3). The band intensities of **E-1** and **E-2** are nearly equal to those of the complexes containing two bridging OH's. These results also suggest that **E-1** and **E-2** have the $\text{Co}(\mu\text{-OH})_2\text{Co}$ moiety (Fig. 1).

Although the UV and visible spectral pattern of either **E-1** or **E-2** was similar to that of $[(\text{edda})\text{Co}(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4]^{2+}$, some minor differences were observed. The first absorption band (the d-d absorption band which appears at ca. 18000 cm^{-1}) of each ethylenediamine complex was broader than that of the ammine complex and the band maximum of the former was observed at higher energy than the latter. These observations can be explained as follows. The first absorption band maximum of the $\text{Co}(\text{en})_2(\mu\text{-OH})_2$ moiety can be assigned to the higher energy side with higher intensity than that of $\text{Co}(\text{NH}_3)_4(\mu\text{-OH})_2$ moiety, since the first absorption band of $[\text{Co}(\text{en})_2(\text{O-O})]^+$ (O-O: $\text{C}_2\text{O}_4{}^{2-}$ or $\text{CO}_3{}^{2-}$) shifts to the higher energy side with higher intensity than that of $[\text{Co}(\text{NH}_3)_4(\text{O-O})]^+$.[10,13] On the other hand, the first absorption band maximum of the $\text{Co}(\text{edda})(\mu\text{-OH})_2$ moiety can be assigned to the lower energy side with higher intensity than that of the $\text{Co}(\text{en})_2(\mu\text{-OH})_2$ or $\text{Co}(\text{NH}_3)_4(\mu\text{-OH})_2$ moiety. Accordingly, the overlapping band due to the $\text{Co}(\text{en})_2(\mu\text{-OH})_2$ and $\text{Co}(\text{edda})(\mu\text{-OH})_2$ moieties gives a broader first absorption band in $[(\text{edda})\text{Co}(\mu\text{-OH})_2\text{-Co}(\text{en})_2]^{2+}$ than the overlapping band due to the $\text{Co}(\text{NH}_3)_4(\mu\text{-OH})_2$ and $\text{Co}(\text{edda})(\mu\text{-OH})_2$ moieties in $[(\text{edda})\text{Co}(\mu\text{-OH})_2(\text{Co}(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4]^{2+}$.[2] The second absorption band (the d-d transition observed at ca. 25000 cm^{-1}) of these complexes appeared as a shoulder beside the strong charge-transfer band (at ca. 34000 cm^{-1}) arising from the bridging OH's.[14] The intensity of the second band of **E-1** (or **E-2**) is slightly stronger than that of $[(\text{edda})\text{Co}(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4]^{2+}$.

The Complexes Containing gly: The structural assignments of the glycinato complexes **G-1** and **G-2** also are made on the basis of the absorption and ^{1}H NMR spectral data. The possiblity that the $\text{Co}(\text{gly})_2(\mu\text{-OH})_2$ moiety in each complex has trans(N) structure can be ruled out. The shape of the absorption band of **G-1** (or **G-2**) is similar to those of **E-1** and **E-2** having C_2-*cis*(N)-$[\text{Co}(\text{N})_2(\text{O})_4]$ structure. Furthermore, the complexes do not exhibit such a shoulder band at ca. 16000 cm^{-1} as is characteristic to the *trans*-(N)-$[\text{Co}(\text{N})_2(\text{O})_4]$ type chromophore.[15,16] The possibility that the $\text{Co}(\text{gly})_2(\mu\text{-OH})_2$ moiety of each complex has the C_1-*cis*(N)-$[\text{Co}(\text{N})_2(\text{O})_4]$ structure is also ruled out, because the two glycinate methylene protons in the moiety appeared as a singlet signal in ^{1}H NMR (Fig. 3); this suggests that the moiety has a C_2 axis which makes the two methylenes equivalent. The two possible geometrical isomers based on the above discussion are shown in Fig. 1. The ^{1}H NMR and visible absorption spectra of **G-1** and **G-2** are similar to those of $[(\text{gly})_2\text{Co}(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4]^{2+}$ as those of **E-1** and **E-2** are to those of $[(\text{edda})\text{Co}(\mu\text{-OH})_2\text{Co}(\text{NH}_3)_4]^{2+}$.

The Complexes Containing nta: This complex **N-1** also showed the characteristic band arising from the

Co(μ-OH)$_2$Co moiety[14] at 34000 cm^{-1} with nearly the same intensity as that of **E-1** or **E-2**. The elemental analysis data showed that the nta/en ratio in the complex is 1/2. Accordingly, the structure [(nta)Co(μ-OH)$_2$Co(en)$_2$]$^+$ is assigned. Only one geometrical isomer (chiral) is possible for this complex ion.

The ^{1}H NMR spectra of **E-1**, **E-2**, **G-1**, and **G-2** (these are ethylenediamine Complexes) resemble those of the corresponding ammine complexes respectively, while the ^{1}H NMR spectrum of **N-1** is slightly different from the corresponding ammine complex, [(nta)Co(μ-OH)$_2$Co(NH$_3$)$_4$]$^+$. That is, the glycinate protons in nta appeared as two AB quartets and one singlet in **N-1**, while they appeared as one AB quartet (for four protons) and one singlet (for two protons) in the corresponding ammine complex (Fig. 3). This result is interpreted as follows. In the ammine complex, the two glyinate rings in nta are equivalent in chemical environment because the OH–Co–OH plane is a mirror plane. On the other hand, in **N-1**, the mirror plane is broken by the two coordinated ethylenediamines on the neighboring cobalt atom.

CD Spectra. The CD spectra of the optically active complexes are illustrated in Fig. 4. The $(+)^{\rm CD}_{565}$ **E-1** and $(+)^{\rm CD}_{560}$ **G-1** isomers (Fig. 4 shows the CD curve for $(-)^{\rm CD}_{560}$ **G-1** isomer) show two intense CD bands with opposite signs in the first absorption band region. As their main CD bands in the lower energy side corresponding to the *cis*-[Co(N)$_2$(O)$_4$] type chromophore are (+) sign, the configuration around the *cis*-[Co(N)$_2$(O)$_4$] type chromophore is assigned to Λ.[17] On the other hand, these complexes show (−) CD in the first absorption band region of the *cis*-[Co(N)$_4$(O)$_2$] type chromophore, suggesting that these complexes have Δ configurations[17] around the Co(en)$_2$(μ-OH)$_2$ moieties which belong to the *cis*-[Co(N)$_4$(O)$_2$] type chromophore. The deduced structures are illustrated in Fig. 1 (A-1 and B-1).

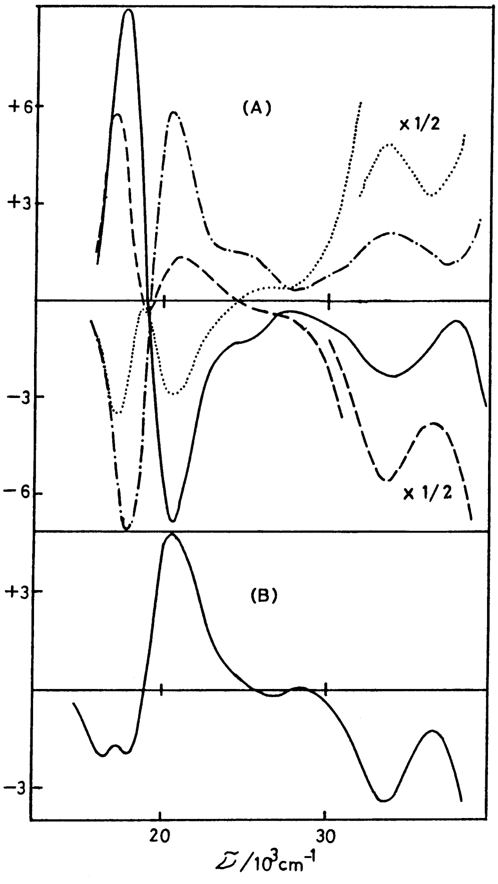

Fig. 4. CD spectra of the complexes: (A) $(+)^{\rm CD}_{565}$**E-1** (——), $(+)^{\rm CD}_{580}$**E-2** (----), $(-)^{\rm CD}_{560}$**G-1** (–·–·–), and $(-)^{\rm CD}_{580}$**G-2** (······); and (B) $(-)^{\rm CD}_{625}$**N-1** (——).

In contrast to these complexes, $(+)^{\rm CD}_{580}$ **E-2** and $(+)^{\rm CD}_{580}$ **G-2** showed two (+) CD components in the first absorption band region. Therefore, either **E-2** or **G-2** has Λ configurations in both *cis*-[Co(N)$_2$(O)$_4$] and *cis*-[Co(N)$_4$(O)$_2$] moieties (Fig. 1 (A-2 and B-2)).

The CD pattern of **G-1** resembles that of **E-1** in the region of 15000—38000 cm^{-1}. This result suggests that the geometrical structure of the Co(gly)$_2$(μ-OH)$_2$ moiety in **G-1** is similar to that of Co(edda)(μ-OH)$_2$ in **E-1** (*cis*(*N*)-[Co(N)$_2$(O)$_4$] type), as described above. The CD spectrum of **G-2** resembles that of **E-2**.

The $(-)^{\rm CD}_{625}$ **N-1** isomer shows three CD components in the first absorption band region (Fig. 4(B)). The small (−) CD (at 18000 cm^{-1}) and large (+) CD (at 20600 cm^{-1}) components are presumed to arise from the Λ-Co(en)$_2$(μ-OH)$_2$ moiety, because the CD components of this moiety is expected to appear in a higher energy region than that of the Co(nta)(μ-OH)$_2$ moiety. Since the Co(nta)(μ-OH)$_2$ moiety is achiral, it is supposed that no CD is observed in the first absorption band region corresponding to the Co(nta)(μ-OH)$_2$ moiety (near 16000 cm^{-1}). In spite of this supposition, CD was observed at 16200 cm^{-1}. This CD is the vicinal CD induced by the neighboring Co(en)$_2$(μ-OH)$_2$ moiety which is chiral. It is noteworthy that the sign of this CD component is opposite from that of the main CD in the first absorption band region of Co(en)$_2$(μ-OH)$_2$ moiety.

CD Additivity of the Two Neighboring Co(III) Chromophores: It has been clarified that the configurational CD of the Co(III) chromophore and the vicinal CD of the asymmetric carbon or nitrogen are additive in the d–d transition band region.[17] However, for the polynuclear complexes, there are few reports about the CD additivity of the Co(III) chromophores neighboring to one another.[18] In this work, assuming that the CD of one of the Co(III) chromophores in each di-μ-hydroxo complex is separable from that of the other Co(III) chromophore, the CD of the prepared complex is assigned to the CD contributions of the two Co(III) chromophores. The additivity is then confirmed by comparison of the analyzed data with other CD data, as described below.

The CD spectra arising from the Co(edda)(μ-OH)$_2$ and Co(en)$_2$(μ-OH)$_2$ moieties in **E-1** and **E-2** were separated by the following equations, where $\Delta_{\rm en}$ and

Λ_{en} mean the CD contributions arising from the Δ- and Λ-Co(en)$_2$(μ-OH)$_2$ moieties, and Δ_{edda} and Λ_{edda} mean those from the Δ- and Λ-Co(edda)(μ-OH)$_2$ moieties, respectively.

$$\Lambda_{\text{en}} = \frac{1}{2}\{(\Lambda_{\text{edda}}, \Lambda_{\text{en}}) - (\Lambda_{\text{edda}}, \Delta_{\text{en}})\}$$

$$= \frac{1}{2}\{((+)^{\text{CD}}_{580}\,\textbf{E-2}) - (+)^{\text{CD}}_{565}\,\textbf{E-1})\} \tag{1}$$

$$\Delta_{\text{en}} = -\Lambda_{\text{en}} \tag{2}$$

$$\Lambda_{\text{edda}} = \frac{1}{2}\{(\Lambda_{\text{edda}}, \Lambda_{\text{en}}) + (\Lambda_{\text{edda}}, \Delta_{\text{en}})\}$$

$$= \frac{1}{2}\{((+)^{\text{CD}}_{580}\,\textbf{E-2}) + ((+)^{\text{CD}}_{565}\,\textbf{E-1})\} \tag{3}$$

$$\Delta_{\text{edda}} = -\Lambda_{\text{edda}} \tag{4}$$

The CD curves for the calculated Λ_{edda} coincide well with the observed CD curve of Λ-[(edda)Co(μ-OH)$_2$-Co(NH$_3$)$_4$]$^{2+}$. This result suggests that the CD contributions arising from the Co(edda)(μ-OH)$_2$ moieties are similar to each other in the complexes having the same type chromophore ([Co(N)$_4$(O)$_2$] type) in the vicinity of Co(edda)(μ-OH)$_2$ moiety, showing the CD additivity of the two Co(III) chromophores. Similar additivity of the CD contributions of the cobalt chromophores were reported for *cis*-[Co(CN)$_2${(μ-OH)$_2$Co(en)$_2$}$_2$]$^{3+}$.[18,19]

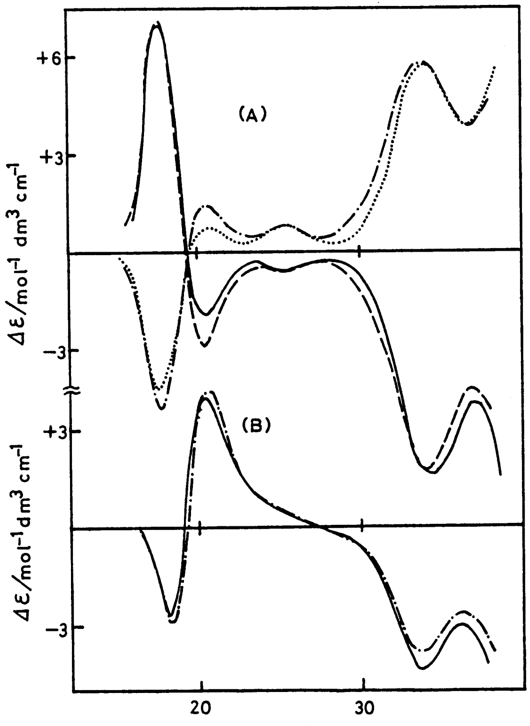

Fig. 5. Calculated and observed CD curves of the complexes: (A) Λ_{edda} in Eq. 3 (——), Λ-[(edda)Co(μ-OH)$_2$Co(NH$_3$)$_4$]$^{2+}$ (----), Δ_{gly} in Eq. 8 (-·-·-), and Δ-[(gly)$_2$Co(μ-OH)$_2$Co(NH$_3$)$_4$]$^{2+}$ (······); and (B) Λ_{en} in Eq. 1 (——) and Λ_{en} in Eq. 5 (-·-·-).

The same discussion as described above can be applied to the glycinato complexes, **G-1** and **G-2**, based on the following equations.

$$\Lambda_{\text{en}} = \frac{1}{2}\{(\Delta_{\text{gly}}, \Lambda_{\text{en}}) - (\Delta_{\text{gly}}, \Delta_{\text{en}})\}$$

$$= \frac{1}{2}\{((+)^{\text{CD}}_{580}\,\textbf{G-2}) - (+)^{\text{CD}}_{560}\,\textbf{G-1})\} \tag{5}$$

$$\Delta_{\text{en}} = -\Lambda_{\text{en}} \tag{6}$$

$$\Lambda_{\text{gly}} = -\Delta_{\text{gly}} \tag{7}$$

$$\Delta_{\text{gly}} = -\frac{1}{2}\{(\Lambda_{\text{gly}}, \Lambda_{\text{en}}) + (\Lambda_{\text{gly}}, \Delta_{\text{en}})\}$$

$$= -\frac{1}{2}\{((+)^{\text{CD}}_{580}\,\textbf{G-2}) + (+)^{\text{CD}}_{560}\,\textbf{G-1})\} \tag{8}$$

In these equations, Δ_{gly} and Λ_{gly} mean the CD contributions from the Δ- and Λ-Co(gly)$_2$(μ-OH)$_2$ moieties and the Δ_{en} and Λ_{en} mean the CD contributions of Δ- and Λ-Co(en)$_2$(μ-OH)$_2$ moieties in **G-1** and **G-2**. The calculated Δ_{gly} CD curve coincides with the observed curve of Δ-[(gly)$_2$Co(μ-OH)$_2$Co(NH$_3$)$_4$]$^{2+}$ as for the edda complexes.

The CD curve for the Λ_{en} obtained from **E-1** and **E-2** is similar to that obtained from **G-1** and **G-2** in the range 15000—38000 cm^{-1} (Fig. 5). This can be interpreted in a similar manner to that described above. The cobalt(III) chromophores existing in the vicinity of the Co(en)$_2$(μ-OH)$_2$ moieties are equally *cis*-[Co(N)$_2$(O)$_4$] type in each of **E-1** and **E-2** pair or **G-1** and **G-2** pair, the CD spectra arising from the Co(en)$_2$(μ-OH)$_2$ are similar to each other. However, the CD pattern of Λ_{en} is different from that of Λ-**N-1**. This result suggests that the CD pattern of Co(en)$_2$(μ-OH)$_2$ is affected by the neighboring chromophores, that is, the chromophore exisiting in the vicinity of Co(en)$_2$(μ-OH)$_2$ belongs to the [Co(N)(O)$_5$] type in **N-1** and differs from the *cis*-[Co(N)$_2$(O)$_4$] type which is found in **E-1**, **E-2**, **G-1**, and **G-2**.

The Λ_{en} CD curve has a relatively strong (−) CD component at ca. 18500 cm^{-1} compared to the vicinal CD of the mononuclear tris(bidentate) complexes (Fig. 5).[17] It is expected that this CD component may contain the vicinal (−) CD on the [Co(N)$_2$(O)$_4$] type chromophore induced by the Λ-Co(en)$_2$(μ-OH)$_2$ moiety, since the Λ-[(nta)Co(μ-OH)$_2$Co(en)$_2$]$^+$ shows a (−) vicinal CD on the first absorption band region of the Co(nta)(μ-OH)$_2$ moiety ($\Delta\varepsilon$: ca. −2) which is induced by the chiral Co(en)$_2$(μ-OH)$_2$ moiety. In addition, it is expected that the Λ-Co(en)$_2$(μ-OH)$_2$ moiety has another (−) CD component at ca. 18000 cm^{-1} similarly to Λ-**N-1** (at 18000 cm^{-1}). Accordingly, the overlapping of the induced (−) CD and this CD may give a relatively strong CD at 18500 cm^{-1}.

In the charge transfer band region of μ-OH (ca. 34000 cm^{-1}),14) strong CD bands are observed for the calculated CD curves. The averaged CD intensities calculated for the chiral Co(L)(μ-OH)$_2$ moieties are as follows: Λ-Co(en)$_2$(μ-OH)$_2$ (ca. −4), Λ-Co(gly)$_2$(μ-OH)$_2$ (ca. −6), Λ-Co(edda)(μ-OH)$_2$ (ca. −7), and Λ-*fac*(*O*)-Co(en)(gly)(μ-OH)$_2$ (ca. −5).5) These values are significantly different from each other, showing that the CD intensity is affected by the ligands except for μ-OH. However, the follwing rough prediction is possible for the chiral di(μ-hydroxo)dicobalt(III) complexes: the complexes which have (Δ-Δ) or (Λ-Λ) pairs show larger CD intensities (absolute values) than those which have (Δ-Λ) or (Λ-Δ) pairs.

Stability of the Complexes. Absorption spectral changes with time were measured in the aqueous solutions of some of the di-μ-hydroxo complexes at 20 °C. Solutions of these complexes showed no spectal change for several days, while that of [Co$_2$(μ-OH)$_2$(NH$_3$)$_8$]Br$_4$ showed an obvious change after one day. This means that these complexes are more stable than [Co$_2$(μ-OH)$_2$(NH$_3$)$_8$]$^{4+}$, suggesting that some stabilizing factors exist in the present complexes. On the X-ray study of [Cr$_2$(L-pro)$_4$(μ-OH)$_2$], Oki and Yoneda20) pointed out that the two intramolecular N-H···O hydrogen bonds (bridging two chromophores) stabilize the di-μ-hydroxo structure. Moreover, in the X-ray study of [(en)(gly)Co(μ-OH)$_2$Co(en)(gly)]$^{2+}$, it was confirmed that the two hydrogen bonds which bind amino and carboxylate groups stabilize the dinuclear structure.21) Accordingly, it is reasonable to propose two hydrogen bonds as the stabilizing factor of the present complexes. It was not easy to prepare the isomers having one or no hydrogen bonds, but it was easy to prepare those having two hydrogen bonds. This result agrees with that obtained for the isomers of [(en)(gly)Co(μ-OH)$_2$Co(en)(gly)]$^{2+}$ 5) and [(L)Co(μ-OH)$_2$Co(NH$_3$)$_4$]$^{n+}$ (L=(gly)$_2$, (edda), and (nta)),2) suggesting that the hydrogen bond is important as a stabilizing factor.

References

1) The following abbreviations will be used in the present paper: H$_2$edda=ethylenediamine-*N,N'*-diacetic acid; Hgly=glycine; H$_3$nta=nitrilotriacetic acid; en=ethylenediamine; *d*-H$_4$tart=*d*-tartaric acid.

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