Metal Complexes of Peptides. VI. Di-μ-hydroxo–Dicobalt(III) Complexes Containing Peptides

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Two isomers of the dinuclear complex with β-alanyl-L-aspartate (β-ad), glycinate (gly), and ethylenediamine (en), $[Co(\beta\text{-ad})Co(gly)(en)(\mu\text{-OH})_2]^+$, were prepared by treating an aqueous solution containing $[Co(\beta\text{-ad})(OH_2)_2]$ and $[Co(gly)(en)(OH_2)_2]^{2+}$ under basic conditions. The geometrical structures and absolute configurations of these isomers were assigned on the basis of the NMR, UV, and CD spectral data; the assignments were confirmed on the basis of the spectral data of the mononuclear species that were obtained by the acid hydrolysis of the isomers. The faster eluted isomer (eluted with H_2O on an SP-Sephadex (K^+ form) column) consists of $[Co(\beta\text{-ad})(\mu\text{-OH})_2]$ (β-ad coordinates to cobalt(III) as a tetradentate) and Δ-*fac*(*O*)-$[Co(gly)(en)(\mu\text{-OH})_2]$ moieties, and the later consists of $[Co(\beta\text{-ad})(\mu\text{-OH})_2]$ and Λ-*fac*(*O*)-$[Co(gly)(en)(\mu\text{-OH})_2]$. Another di-$\mu$-hydroxo–dicobalt(III) complex containing β-alanyl-L-histidinate (car), $[Co_2(car)_2(\mu\text{-OH})_2]$, was also prepared by treating an aqueous solution containing $[Co(car)(OH_2)_2]^+$ under basic conditions. The dinuclear structures of these complexes are stable for several days in the neutral aqueous solutions.

In our previous paper,[1] it was suggested that the complicated dinuclear complex ion, $[Co(edda)Co(gly)(en)(\mu\text{-OH})_2]^+$ (ethylenediamine-*N,N'*-diacetate (edda), ethylenediamine (en), and glycinate (gly)) was easily prepared by condensing the parental mononuclear complexes, $[Co(edda)(OH_2)_2]^-$ and $[Co(gly)(en)(OH_2)_2]^{2+}$, in a basic aqueous solution. In addition, it was pointed out in the paper that two hydrogen bonds, which are formed between the amino groups on one of the two cobalt atoms and the carboxyl groups on the other cobalt atom in the dinuclear cobalt(III) complex ion, are important to stabilize the dinuclear structure. According to these suggestions, dinuclear complexes containing peptide (pep), such as $[Co_2(pep)_2(\mu\text{-OH})_2]^{n+}$ and $[Co(pep)Co(gly)(en)(\mu\text{-OH})_2]^{n+}$, can also be prepared in a manner similar to that for $[Co(edda)Co(gly)(en)(\mu\text{-OH})_2]^+$.

There are few reports on dicobalt(III) complexes containing peptides. However, the complexes seem to be important precursors of tri- or tetrapeptides, since a peptide and another peptide (or amino acid) are fixed very closely on one complex ion. In this paper, we will report on the preparation and characterization of the dicobalt(III) complexes containing pep (pep = β-ala–L-asp^{3-} (β-ad) or β-ala–L-his^{2-} (car)) and di-μ-hydroxo. It is expected that the preparation methods reported here are easily applicable to the preparation of the other new dicobalt(III) complexes containing peptides.

Experimental

Preparation of the Complexes. $K_2[Co(\beta\text{-ad})(CO_3)]$ (A): To a suspension containing 5.8 g of $KHCO_3$ in 6 cm^3 of H_2O which was stirred, a solution prepared from 2 g of $Co(NO_3)_2\cdot 6H_2O$, 2 cm^3 of H_2O, and 3.5 cm^3 of 30% H_2O_2 was added dropwise, keeping the temperature below 0 °C. The obtained green solution was stirred for 10 min in an ice bath, and then 1.5 g of $NaH_2\beta$-ad was added to it. The color of the solution turned to violet when the temperature was kept at 50 °C for 2 h. After removal of a brown precipitate, the filtrate was diluted to about 200 cm^3 and then put on a QAE-Sephadex column (HCO_3^- form; ϕ 4.5 cm×45 cm). The adsorbed band was developed with 0.2 M $KHCO_3$ (M = mol dm^{-3}). The eluate from the major band (the third violet band) was concentrated to a few milliliters by using a vacuum evaporator. A white precipitate ($KHCO_3$), which appeared in addition of 200 cm^3 of methanol to the concentrated solution, was removed by filtration. The filtrate was again concentrated to a few milliliters, and then about 100 cm^3 of ethanol was added to precipitate the crude powder of $K_2[Co(\beta\text{-ad})(CO_3)]$. The crude complex was recrystallized from water by adding ethanol. Found: C, 23.27; H, 2.53; N, 6.72%. Calcd for $K_2[Co(\beta\text{-ad})(CO_3)]\cdot H_2O = C_8H_{11}N_2O_9CoK_2$: C, 23.08; H, 2.66; N, 6.73%.

Isomers of $[Co(\beta\text{-ad})Co(gly)(en)(\mu\text{-OH})_2]$ (AD1 and AD2): Though the titled isomers could be prepared from $K_2[Co(\beta\text{-ad})(CO_3)]$ and *mer*(*O*)-$[Co(gly)(en)(CO_3)]$, they are conveniently prepared by the following method.

The pH of an solution containing $NaHCO_3$ (1.0 g) and β-alanyl-L-aspartic acid ($H_3\beta$-ad; 0.76 g) in 50 cm^3 of water was adjusted to 9.0 with 1 M NaOH solution. To this solution, $Na_3[Co(CO_3)_3]\cdot 3H_2O$[2] (1.7 g) was added with stirring. The suspension was kept in a water bath (50 °C) for 180 min with stirring. After this was cooled to room temperature, a dark-brown precipitate was filtered off. The filtrate (containing $[Co(\beta\text{-ad})(CO_3)]^{2-}$ ion), was concentrated to about 25 cm^3 under reduced pressure, and then *mer*(*O*)-$[Co(gly)(en)(CO_3)]\cdot H_2O$[3] (1.5 g) and 10 cm^3 of 60% perchloric acid were added to the solution. (This acidic solution contains $[Co(\beta\text{-ad})(OH_2)_2]$ and $[Co(gly)(en)(OH_2)_2]^{2+}$.) After this was stirred for 10 min, the pH of the solution was adjusted to 8.5 with 2 M NaOH solution. The solution was stirred for 1 h at room temperature and then the solution was concentrated to about 5 cm^3. About 300 cm^3 of acetone was added to the solution to obtain violet precipitates. The precipitates were dissolved into about 50 cm^3

of water. The solution was put on a QAE-Sephadex column (ϕ 6.5 cm×4 cm, Cl^- form) and eluted out with 500 cm^3 of water to remove anionic complexes. The eluate was collected and evaporated to about 50 cm^3 under reduced pressure. The concentrated solution was put on an SP-Sephadex column (ϕ 6.5 cm×4 cm, K^+ form) and then developed with water. A band that was elutable with water was transferred to another SP-Sephadex column (ϕ 4 cm×90 cm, K^+ form) and recyclically chromatographed on the column with water. The eluates from the major bands (the third violet (**AD1**) and fourth violet (**AD2**) bands) were concentrated to about 2 cm^3 by a rotary evaporator at 35—40 °C, respectively. About 100 cm^3 of acetone was added to the concentrated solution to precipitate a crude complex. The obtained crude complexes were recrystallized from water by adding ethanol. Found for **AD1**: C, 23.60; H, 5.59; N, 12.36%. Calcd for $[Co(\beta\text{-ad})Co(gly)(en)(\mu\text{-}OH)_2]\cdot 4H_2O = C_{11}H_{31}N_5O_{13}Co_2$: C, 23.62; H, 5.58; N, 12.52%. Found for **AD2**: C, 24.22; H, 5.77; N, 12.06%. Calcd for $[Co(\beta\text{-ad})Co(gly)(en)(\mu\text{-}OH)_2]\cdot 0.5EtOH\cdot 4.5H_2O = C_{12}H_{35}N_5O_{14}Co_2$: C, 24.38; H, 5.97; N, 11.84%. (It was confirmed by ^{1}H NMR that this crystal contains EtOH (ethanol) in this ratio).

$K[Co(car)(CO_3)]$ (C): This complex was prepared by the method described in the literature.[4)]

$[Co_2(car)_2(\mu\text{-}OH)_2]$ (CC): To a solution containing $K[Co(car)(CO_3)]\cdot 0.5EtOH\cdot 2H_2O$ (0.76 g) in 15 cm^3 of water, was added 60% perchloric acid (0.4 ml). (This acidic solution contains $[Co(car)(OH_2)_2]^+$.) After stirring for 10 min, we adjusted the pH of the solution to 8.35 with 2 M KOH solution. The solution was stirred for 1 h at room temperature and then filtered. About 500 cm^3 of acetone was added to the filtrate to obtain red-violet precipitates. The precipitates were dissolved in about 200 cm^3 of water. The solution was poured into an SP-Sephadex column (ϕ 6.5 cm×4 cm, K^+ form) and developed with water. The bands that were elutable with water were transferred to another SP-Sephadex column (ϕ 4 cm×90 cm) and developed with water. The bands separated into four bands. The second band was a major one with red-violet color. (The yields of the first, third, and fourth were very low, and we did not isolate pure complexes from these bands.) The eluted solution from the second band was concentrated to a few milliliters by a rotary evaporator at 35—40 °C. Crude complex obtained by adding ethanol to the concentrated solution were recrystallized from ethanol and water. Found: C, 29.69; H, 5.76; N, 14.79%. Calcd for $[Co_2(car)_2(\mu\text{-}OH)_2]\cdot 8H_2O\cdot 0.5EtOH = C_{19}H_{45}N_8O_{16.5}Co_2$: C, 29.73; H, 5.91; N, 14.60%.

Acid Hydrolyses of the Complexes. Acid hydrolyses of the complexes were done in the following manner. The complex (about 0.02 g) to be hydrolyzed was dissolved in 10 cm^3 of 0.4 M $HClO_4$; the solution was stirred for about 30 min at 40 °C. The reacted solution was adjusted to pH 6 with 2 M NaOH solution and then chromatographed on an SP-Sephadex column (Na^+ form; ϕ 1 cm×45 cm) using 0.1 M $NaClO_4$ as an eluent. The UV absorption and CD spectra of each eluate were measured. The results are summarized in Table 1.

Spectral Measurements. The UV absorption and CD spectra were measured by a JASCO V-550 spectrometer and JASCO J-720 spectropolarimeter, respectively. The ^{1}H and ^{13}C NMR 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 (^{1}H: 0 ppm) and dioxane (^{13}C: 67.4 ppm), respectively.

Results and Discussion

Structural Assignments of the Complexes Containing β-ad.

It is known that the ^{13}C NMR chemical shifts of a ligand on a cobalt(III) complex are affected dominantly by the coordination mode of the ligand but also affected subsidiarily by the other ligands on the cobalt(III) ion.[4—8)] For the β-ad ligand, we have reported many ^{13}C NMR shift data of mononuclear cobalt(III) complexes and shown that the coordination modes of the β-ad on the cobalt(III) complexes can be estimated on the basis of the ^{13}C NMR chemical shift patterns.[5)] Figure 1 shows the ^{13}C NMR shifts of the newly prepared complexes, together with those of the related compounds (the numbering of carbons in β-ad and their signal assignments adopted those described in the previous paper).[5)] In the cobalt(III) complexes containing tetradentate β-ad (C2-mode; Fig. 2 (C2)), it is known that the ^{13}C NMR signals of the L-asp moiety (C_4, C_5, C_6, and C_7) appear at about 61.2, 186.6, 41.5, and 180.0 ppm respectively, and those of the β-ala moiety (C_1, C_2, and C_3) do at about 35.7, 39.2, and 176.6 ppm respectively, as shown in $[Co(\beta\text{-ad})(en)]$ (Fig. 1).[5)] However, in the complexes of tridentate β-ad with an uncoordinated β-carboxyl group on the L-asp moiety (A2-mode; Fig. 2 (A2)) such as $[Co(\beta\text{-ad})(dien)]$ (Fig. 1), the C_5 carbon (α-COO^- carbon in L-asp moiety) resonates at about 188.5 ppm showing an obvious low-field shift (compared with the C_5 carbon in C2-mode β-ad).[5)] On the other hand, in the β-ad complexes with an uncoordinated amino group on the β-ala moiety (B2-mode; Fig. 2(B2)) such as $[Co(H\beta\text{-ad})(dien)]^+$ (Fig. 1), C_1 and C_2 carbons in the β-ala moiety resonate at about 30.7 and 37.3 ppm showing the high-field shifts.[5)] The ^{13}C shift patterns of the β-ad in **A** (chemical shifts (C_1—C_7): $\delta = 35.78$, 40.93, 176.80, 61.45, 186.71, 39.35, and 180.43), **AD1** ($\delta = 35.72$, 41.18, 177.01, 61.33, 187.07, 39.35, and 179.79), and **AD2** ($\delta = 35.39$, 40.45, 176.58, 61.36, 186.80, 39.11, and 179.54) are different from those in A2-mode (characteristically in C_5 carbon) and B2-mode (characteristically in C_1 and C_2 carbons), but similar to those in C2-mode. According to these results we propose that β-ad in **A**, **AD1**, and **AD2** coordinate to cobalt(III) in the C2-mode. The ^{13}C chemical shifts of en and gly carbons in **AD1** and **AD2** consistent with those in the cobalt(III) complexes containing en and gly as the chelating didentates.

AD1 and **AD2** containing β-ad (tetradentate), en (didentate), and gly (didentate) as mentioned above are not the mixture of $[Co(\beta\text{-ad})(OH_2)_2]$ and $[Co(gly)(en)(OH_2)_2]^{2+}$ (each chromatogram of **AD1** and **AD2** provided only one band on an SP-Sephadex column), but they can be assigned to dinuclear di-μ-hydroxo complexes as described below. Figure 3 shows the UV absorption and CD spectra of the β-ad complexes. **AD1** and **AD2** have the characteristic UV absorption bands arising from the $Co(\mu\text{-}OH)_2Co$ moieties at about 34000 cm^{-1} such as $[Co_2(NH_3)_8(\mu\text{-}OH)_2]^{4+}$ and $[Co_2(en)_4(\mu\text{-}OH)_2]^{4+}$ show,[9—11)] while the intense absorption bands were not observed at about 34000 cm^{-1} in the mononuclear cobalt(III) complexes such $[Co(\beta\text{-ad})(en)]^+$ and $[Co(\beta\text{-ad})(CO_3)]^{2-}$. The elemental analysis data of **AD1** and **AD2** also consistent with these dinuclear structures.

Although the coordination modes of en, gly, and β-ad

Table 1. Acid Hydrolysis Products of Di-μ-hydroxo–Dicobalt(III) Complexes and Carbonato–Cobalt(III) Complexes

Complexes	Mononuclear complexes obtained by the acid hydrolysis			
	$[Co(pep)(OH_2)_2]^{n+}$		$[Co(gly)(en)(OH_2)_2]^{2+}$	
	UV Peak	CD Sign	UV Peak (Structure)	CD Sign (Configuration)
$[Co(\beta\text{-ad})Co(gly)(en)(\mu\text{-OH})_2]$				
AD1	503 nm $([Co(\beta\text{-ad})(OH_2)_2])$	$(+)^{CD}_{585}$	514 nm (*fac*(*O*))	$(-)^{CD}_{504}$ (Δ)
AD2	503 nm $([Co(\beta\text{-ad})(OH_2)_2])$	$(+)^{CD}_{585}$	514 nm (*fac*(*O*))	$(+)^{CD}_{504}$ (Λ)
$[Co(\beta\text{-ad})(CO_3)]^{2-}$	503 nm $([Co(\beta\text{-ad})(OH_2)_2])$	$(+)^{CD}_{585}$	—	—
$[Co(gly)(en)Co(gly)(en)(\mu\text{-OH})_2]^{2+}$ $(-)^{CD}_{556}$-$\Delta\Delta$-*fac*(*O*)*fac*(*O*)	—	—	514 nm (*fac*(*O*))	$(-)^{CD}_{504}$ (Δ)
$[Co_2(car)_2(\mu\text{-OH})_2]$	530 nm $([Co(car)(OH_2)_2]^+)$	$(+)^{CD}_{522}$	—	—
$[Co(car)(CO_3)]^-$	530 nm $([Co(car)(H_2O)_2]^+)$	$(+)^{CD}_{522}$	—	—

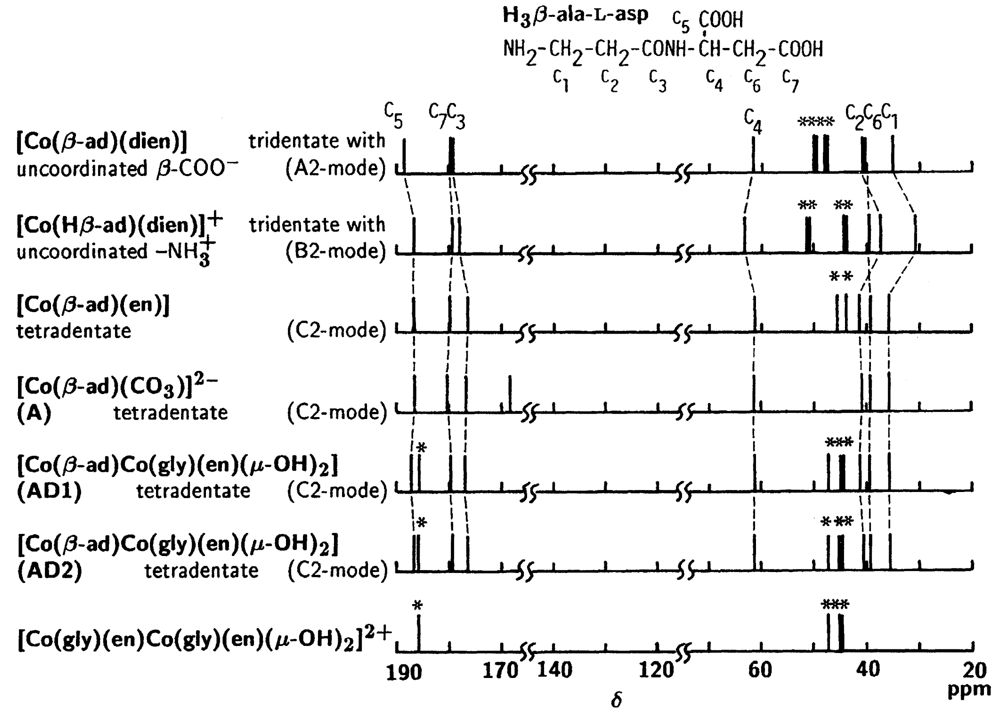


Fig. 1. ^{13}C NMR spectral patterns of the cobalt(III) complexes containing β-ad. (asterisked signals: arising from dien, en, or gly).

were identified, some geometrical structures are possible for the $[Co(gly)(en)(\mu\text{-OH})_2]$ moiety (on the other hand, only one geometry is possible for the $[Co(\beta\text{-ad})(\mu\text{-OH})_2]$ moiety because the tetradentate β-ad is very rigid (Fig. 2 (C2)). For the detailed geometrical and absolute configurational assignments, it is necessary to identify the mononuclear units in the dinuclear complexes. It is known that the hydrolysis of a di-μ-hydroxo-dicobalt(III) complex in the acidic aqueous solution gives the corresponding mononuclear species. Analyses of the cleavage reaction products serve to elucidate the composition of the structures of the polynuclear species.[1,9] In the solution obtained by the acid hydrolysis of **AD1**, $(-)^{CD}_{504}$-Δ-*fac*(*O*)-$[Co(gly)(en)(OH_2)_2]^{2+}$, (whose CD and UV spectra were identical with those obtained from the acid hydrolysis products of $(-)^{CD}_{556}$-$\Delta\Delta$-*fac*(*O*)*fac*(*O*)-$[Co(gly)(en)Co(gly)(en)(\mu\text{-OH})_2]^{2+}$) and $[Co(\beta\text{-ad})(OH_2)_2]$ (the CD and UV spectra of which were identical with those obtained from the acid hydrolysis products of $[Co(\beta\text{-ad})(CO_3)]^{2-}$) (Table 1). Accordingly, we can conclude that **AD1** has a Δ-*fac*(*O*)-$[Co(gly)(en)(\mu\text{-OH})_2]$ moiety; the possible structures of the **AD1** are restricted to (A) and (C) structures illustrated in Fig. 4. In the (A) structure, we can find two amino N on the coordination sites perpendicular to the $Co(\mu\text{-OH})_2Co$ plane. These amino N are close to the coordinating carboxyl

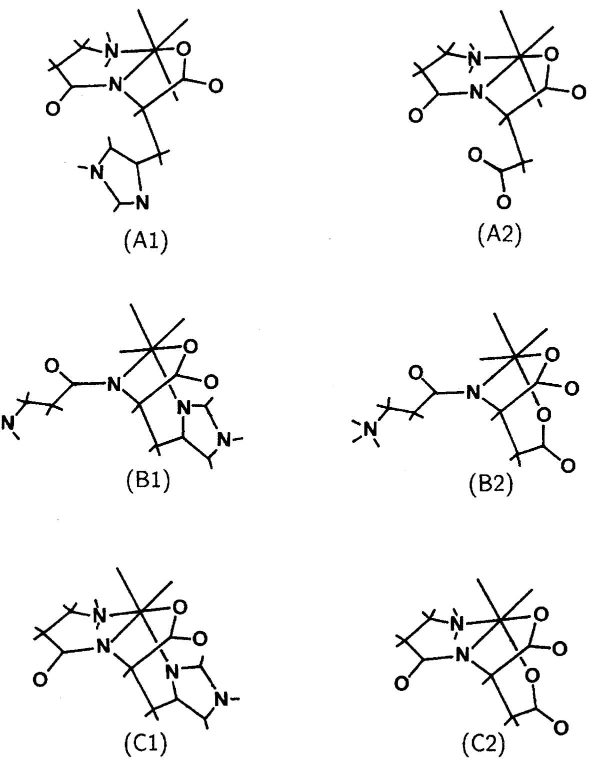


Fig. 2. Coordination modes of car (A1—C1) and β-ad (A2—C2). (A1) tridentate with uncoordinated imidazole group; (B1) tridentate with uncoordinated amino group; (C1) tetradentate; (A2) tridentate with uncoordinated β-carboxyl group; (B2) tridentate with uncoordinated amino group; and (C2) tetradentate.

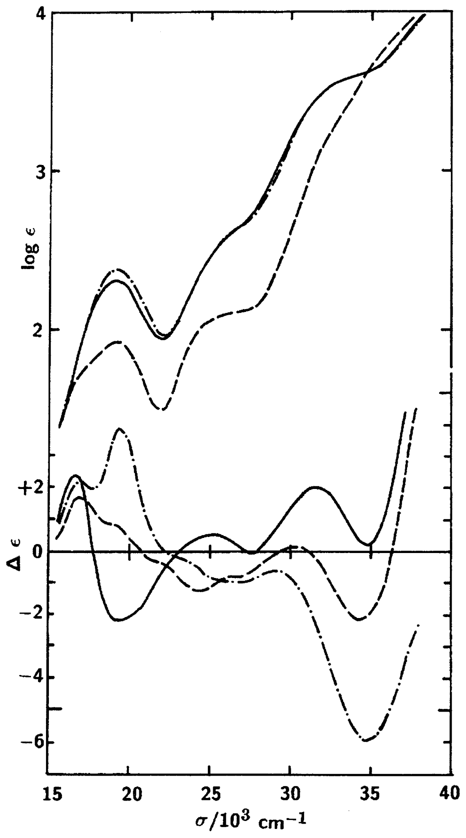


Fig. 3. UV absorption and CD spectra of the complexes containing β-ad: **AD1** (——), **AD2** (–•–), and **A** (– – –). The $\Delta\varepsilon$ and ε values are given in mol^{-1} dm^{-3} cm^{-1}.

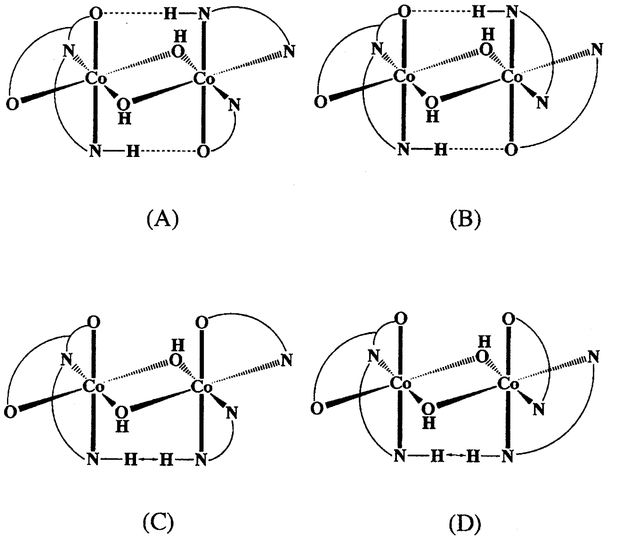


Fig. 4. Structures of the isomers of [Co(β-ad)Co(gly)(en)(μ-OH)$_2$]$^+$ containing [Co(β-ad)(μ-OH)$_2$] and *fac*(*O*)-[Co(gly)(en)(μ-OH)$_2$] moieties; (A) and (B): these structures are stabilized by two attractive N–H···O interactions; (C) and (D): these structures are unstabilized by the repulsive NH↔NH interaction.

O which are also perpendicular to the Co(μ-OH)$_2$Co plane; the separations between the N and O are predictable to be in the range 2.8—3.1 Å.[12,14,15] One of the amino H on the each N is forced to locate toward the carboxyl O, since the amino N has to bind to both of the Co(III) and the CH$_2$ in the chelate ring (β-ad or en); accordingly, the separation between the amino H and O is short enough to form a hydrogen bond (in the range 1.9—2.3 Å).[12,14] Therefore, attractive interactions (the two N–H···O hydrogen bonds) are expected in the (A) structure. However, the (C) structure would have short contact between the two amino H units across the Co(μ-OH)$_2$Co framework, because the separation between the amino N is very short (about 3.1—3.3 Å),[16,17] which results in the serious N–H↔H–N repulsive interaction. Accordingly, it is reasonable to consider that the (A) structure is more stable than the (C) structure and that the isolated **AD1** isomer has the (A) structure.

A similar discussion can be made for **AD2**. In the hydrolyzed solution of **AD2**, (+)$^{\mathrm{CD}}_{520}$-Λ-*fac*(*O*)-[Co(gly)(en)(OH$_2$)$_2$]$^{2+}$ and [Co(β-ad)(OH$_2$)$_2$]$^{2-}$ were detected (Table 1), which lead to the consideration that the possible structures of the **AD2** are restricted to (B) and (D) structures illustrated in Fig. 4. The N–H···O attractive interactions are expected in the (B) structure, while the N–H↔H–N repulsive interaction are expected in the (D) structure. Accordingly, the structure of the isolatable **AD2** isomer can be assigned to the more stable (B) structure.

Absorption spectral changes with time were measured in the neutral aqueous solutions of some of the di-μ-hydroxo complexes. Neutral aqueous solutions of **AD1** and **AD2** showed no spectral change for at least three days (that is, **AD1** and **AD2** were not hydrolyzed under these conditions), while those of $[Co_2(NH_3)_8(\mu\text{-}OH)_2]^{4+}$ and $[Co_2(en)_4(\mu\text{-}OH)_2]^{2+}$ showed obvious change after one day. This means that **AD1** and **AD2** are more stable than $[Co_2(NH_3)_8(\mu\text{-}OH)_2]^{4+}$ and $[Co_2(en)_4(\mu\text{-}OH)_2]^{2+}$, suggesting some attractive interaction between the two cobalt(III) units in **AD1** and **AD2**.

Structural Assignment of the Complex Containing car. As described in the experimental section, we prepared a non-electrolyte complex containing car (**CC**), which was not adsorbed on the SP-Sephadex (cation exchange Sephadex)) and QAE-Sephadex (anion exchange Sephadex) column, treating the $[Co(car)(OH_2)_2]^+$ under basic aqueous conditions.

The ^{13}C NMR stick diagram of the **CC**, together with the other car–cobalt(III) complexes, are shown in Fig. 5. In the cobalt(III) complexes containing tetradentate car such as **C** and $[Co(car)(en)]^{+}$[4] (C1-mode; Fig. 2 (C1)), it is known that the carbons in the L-his moiety (C_4—C_9) resonate at about $\delta = 60.4$, 186.8, 28.3, 135.1, 117.9, and 137.5 respectively, and those in the β-ala moiety (C_1—C_3) do at about $\delta = 35.5$, 41.5, and 176.0 respectively.[4] However, in the complexes of tridentate car with uncoordinated imidazole group such as $[Co(car)(dien)]^+$ (A1-mode; Fig. 2 (A1)), the C_7 and C_9 carbons (imidazole carbons in L-his moiety) resonates at about $\delta = 130.4$ and 134.2, showing the characteristic high-field shift (compared with the C_7 and C_9 carbons in C1-mode car). On the other hand, in the car complexes with the uncoordinated amino group such as $[Co(Hcar)(en)(OH_2)]^{2+}$ (B1-mode; Fig. 2 (B1)), C_1 and C_2 carbons in the β-ala moiety resonate at about $\delta = 31.0$ and 36.9, showing the characteristic high-field shifts.[4] The ^{13}C shift pattern of the car in **CC** (chemical shifts (C_1—C_9): $\delta = 35.60$, 41.03, 176.22, 60.66, 187.19, 28.10, 134.78, 117.31, and 136.28) is characteristically different from that of $[Co(car)(dien)]^+$ (A1-mode) in C_7 and C_9 carbon ($\delta = 130.36$ and C_9: $\delta = 134.20$), and that of $[Co(Hcar)(en)(OH_2)]^{2+}$ (B1-mode) in C_1 and C_2 carbons ($\delta = 31.00$ and 36.97), but similar to those in $[Co(car)(CO_3)]^-$ (C1-mode)][4] (Fig. 6). According to these results we propose that car in **CC** coordinate to cobalt(III) in the C1-mode.

Figure 6 shows the UV and CD spectra of **CC** and **C**. A characteristic UV absorption band arising from the $Co(\mu\text{-}OH)_2Co$ moiety was observed in **CC** at about 34000 cm^{-1}, while the band was not observed in **C**, which is a mononuclear complex.[4] The acid hydrolysis of **CC** gave only one complex and the UV and CD spectra of the hydrolysis product is the same as that of the acid hydrolysis product of $[Co(car)(CO_3)]^-$ (**C**) (Table 1). Considering these results together with those obtained from the ^{13}C NMR analyses, structure of this **CC** is assignable to $[Co_2(car)_2(\mu\text{-}OH)_2]$ structure.

There are two possible geometrical structures in the $[Co_2(car)_2(\mu\text{-}OH)_2]$, as shown in Fig. 7. The neutral aqueous solution of **CC** showed no spectral change for several days without the hydrolysis of the complex, suggesting that the dinuclear structure is stabilized by some factors. According to the similar discussion to those described for **AD1** and **AD2**, it is expected that the (A) structure is more stable than the (B) in Fig. 7; we are assigned the structure of **CC** to Fig. 7(A). The structure of $[Cr_2(car)_2(\mu\text{-}OMe)(\mu\text{-}OH)]$ has been identified by X-ray crystallographic method.[13] In this chromium(III) complex, the two N–H···O moieties were found, which suggests that the dinuclear structure bridged by the two N–H···O moieties is easily formed. This $[Co_2(car)_2(\mu\text{-}OH)_2]$ complex resembles that of $[Cr_2(car)_2(\mu\text{-}OMe)(\mu\text{-}OH)]$ (regarding two Co and one μ-OH to two Cr and one μ-OMe). Consequently, it is reasonable to consider that the isolated **CC** is similar to $[Cr_2(car)_2(\mu\text{-}OMe)(\mu\text{-}OH)]$ in the geometrical structure, suggesting the above mentioned assignment for **CC**.

Absorption and CD Spectra of the Dinuclear Complexes. The first absorption bands (the d–d transition bands observed at about 19000 cm^{-1}) of the dinuclear complexes, **AD1**, **AD2**, and **CC**, have clear peaks at 19200, 19200, and 18800 cm^{-1}, respectively (Figs. 3 and 6). On the other hand, the second absorption bands (the d–d transition bands

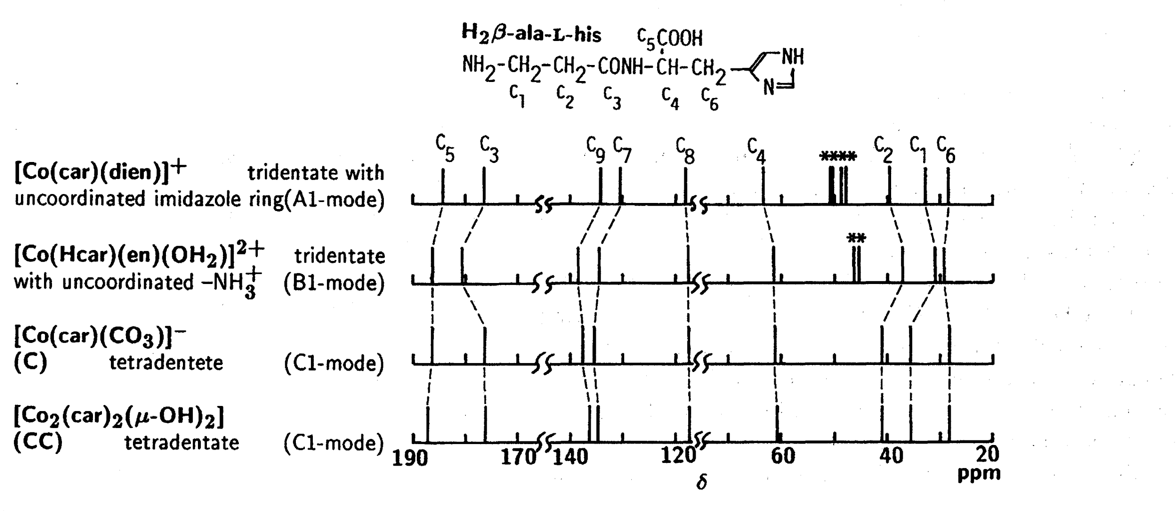


Fig. 5. ^{13}C NMR spectral patterns of the cobalt(III) complexes containing car. (asterisked signals: arising from dien or en).

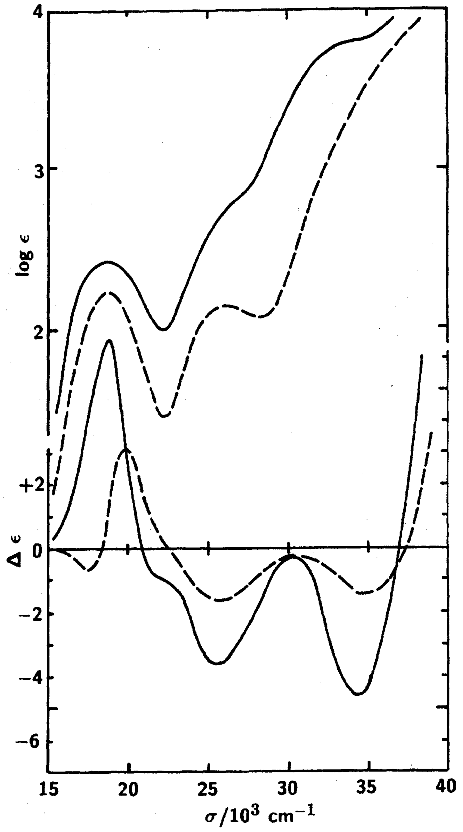
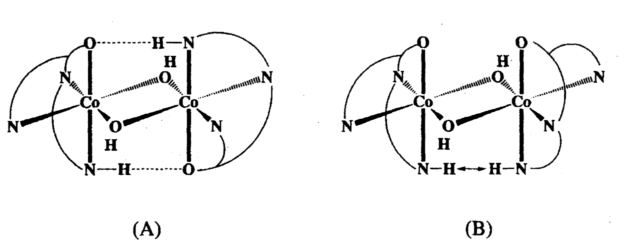


Fig. 6. Absorption and circular dichroism spectra of the complexes containing car: **CC** (—) and **C** (---). The $\Delta\varepsilon$ and ε values are given in mol^{-1} dm^3 cm^{-1}.



(A) (B)

Fig. 7. Structures of the isomers of $[Co_2(car)_2(\mu\text{-}OH)_2]$; (A): this structure is stabilized by the two attractive N–H···O interactions; and (B): this structure is unstabilized by the repulsive NH↔NH interaction.

observed at about 25000 cm^{-1}) of these complexes appear as shoulders beside the strong charge-transfer bands (at about 34000 cm^{-1}) arising from the bridging OH's. Similar shoulder second absorption bands beside the strong charge-transfer band have been reported for the di-μ-hydroxo dicobalt(III) complexes such as $[Co_2(en)_4(\mu\text{-}OH)_2]^{4+}$,[9—11] [Co(edda)Co-$(en)_2(\mu\text{-}OH)_2]^{2+}$,[15] and $[Co(edda)Co(gly)(en)(\mu\text{-}OH)_2]^{2+}$.[1]

The **AD1**, **AD2**, and **CC** are dinuclear complexes having two cobalt(III) chromophores. On the other hand, the carbonato complexes (**A** and **C**) are mononuclear ones having one chromophore. Reflecting the difference in the number of the chromophores, the intensities of the first absorption bands of **AD1**, **AD2**, and **CC** are about 2 times larger than those of $[Co(\beta\text{-}ad)(CO_3)]^{2-}$ and $[Co(car)(CO_3)]^{-}$.

The shape of the absorption spectrum of **AD1** is similar to that of **AD2**, since the isomer **AD2** consists of the $[Co(\beta\text{-}ad)(\mu\text{-}OH)_2]$ and *fac(O)*-$[Co(gly)(en)(\mu\text{-}OH)_2]$ chromophores in a similar manner as the isomer **AD1** does. However, the configuration around the $[Co(gly)(en)(\mu\text{-}OH)_2]$ chromophore in **AD1** is enantiomeric to that in **AD2**, though the configuration around the $[Co(\beta\text{-}ad)(\mu\text{-}OH)_2]$ chromophore in **AD1** is the same as in **AD2**. Accordingly, the CD spectrum of the **AD1** is much different and not symmetrical to that of **AD2**, while their UV absorption spectra are similar to each other. Assuming that the CD arising from the Δ-*fac(O)*-$[Co(gly)(en)(\mu\text{-}OH)_2]$ moiety in **AD1** is enantiomeric to that of Λ-*fac(O)*-$[Co(gly)(en)(\mu\text{-}OH)_2]$ moiety in **AD2** and that the CD of the $[Co(\beta\text{-}ad)(\mu\text{-}OH)_2]$ and *fac-(O)*-$[Co(gly)(en)(\mu\text{-}OH)_2]$ moieties are additive,[15] we can calculate the CD spectrum arising from the $[Co(\beta\text{-}ad)(\mu\text{-}OH)_2]$ moiety. The calculated CD spectrum of $[Co(\beta\text{-}ad)(\mu\text{-}OH)_2]$ moiety shows intense (−) CD (at 34500 cm^{-1} ($\Delta\varepsilon$: −2.8)) in the absorption band region of $Co(\mu\text{-}OH)_2Co$, as is observed for $[Co_2(car)_2(\mu\text{-}OH)_2]$. This calculated spectrum leads to the prediction that the $[Co_2(\beta\text{-}ad)_2(\mu\text{-}OH)_2]^{2-}$ ion has intense (−) CD ($\Delta\varepsilon$: about −6) in this region, though we have not succeeded in isolating the dinuclear complex ion yet.

References

1) T. Ama, T. Yonemura, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **67**, 410 (1994).

2) H. F. Bauer and W. C. Drinkard, *Inorg. Synth.*, **8**, 202 (1996).

3) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **39**, 1257 (1996).

4) T. Ama, H. Kawaguchi, M. Uchijima, N. Koine, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **62**, 3464 (1989).

5) T. Ama, R. Maki, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **64**, 459 (1991).

6) T. Ama, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **59**, 1471 (1986).

7) T. Ama and T. Yasui, *Bull. Chem. Soc. Jpn.*, **49**, 472 (1976).

8) T. Yasui, K. Okamoto, J. Hidaka, T. Ama, and H. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **60**, 2573 (1987).

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

10) H. Kuroya and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **15**, 427 (1940).

11) J. Springborg and C. E. Schäffer, *Inorg. Synth.*, **18**, 75 (1978).

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

13) C. M. Murdoch, M. K. Cooper, T. W. Hambley, W. N. Hunter, and H. C. Freeman, *J. Chem. Soc., Chem. Comuun.*, **1986**, 1329.

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

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

16) U. Thewalt and M. Zehnder, *Helv. Chim. Acta*, **60**, 2000 (1977).

17) C. K. Prout, *J. Chem. Soc.*, **1962**, 4429.