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Metal Complexes of Amino Acids. VI.[1] μ-L-Aspartato and μ-L-Glutamato Complexes of Cobalt(III)

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Some binuclear and trinuclear complexes containing μ-L-aminocarboxylato ligands, $(+)_D$- and $(-)_D$-[en$_2$Co(OCOCH(NH$_2$)(CH$_2$)$_n$COO)Co(OH$_2$)en$_2$](ClO$_4$)$_4$, $(+)_D$-[en$_2$Co(OCOCH(NH$_2$)(CH$_2$)$_n$COO)Co(NH$_3$)$_5$](ClO$_4$)$_4$, and $(+)_D$- and $(-)_D$-[en$_2$Co{(OCOCH(NH$_2$)(CH$_2$)$_n$COO)Co en$_2$}$_2$](ClO$_4$)$_5$ ($n=1$ for L-aspartato and $n=2$ for L-glutamato), have been newly prepared. The structure and vicinal CD effect of these complexes were discussed on the basis of their absorption, ^{13}C NMR and CD spectra data. Their geometrical structures were assigned as *cis* to the μ-L-aminocarboxylato-OH$_2$ binuclear complexes (with respect to the β-COO or γ-COO end of μ-aminocarboxylato bridge and the aquo ligand), and as *trans* to the di-μ-L-aminocarboxylato trinuclear complexes (with respect to the β-COO or γ-COO ends of two μ-aminocarboxylato bridges).

In the previous paper[1] we reported the study on the formation and preparations of the binuclear and trinuclear complexes containing μ-aminocarboxylato ligand, [(NH$_3$)$_5$Co(OCORNH$_2$)Co NO$_2$(acac)$_2$]ClO$_4$ and [en$_2$Co{(OCORNH$_2$)Co NO$_2$(acac)$_2$}$_2$]ClO$_4$. In these complexes the μ-aminocarboxylato ligand is the bidentate which bridged two cobalt(III) ions with the COO and NH$_2$ ends.

In the present paper, the preparations of some new binuclear and trinuclear complexes containing L-aspartato or L-glutamato as the μ-aminocarboxylato ligand are reported. The complexes isolated are characterized on the basis of their elemental analyses, visible and ultraviolet absorption, CD, and ^{13}C NMR spectra.

Experimental

Preparation of Starting Materials—L-Aspartato and L-Glutamato-bis(ethylenediamine)cobalt(III) Complexes. $(+)_D$-[Co(L-asp)en$_4$]ClO$_4\cdot$2H$_2$O, $(-)_D$-[Co(L-asp)en$_2$]ClO$_4\cdot$H$_2$O, $(+)_D$- and $(-)_D$-[Co(L-glu)en$_2$]ClO$_4$ were prepared and separated by the same method as that of Legg and Steele.[2] Elemental analyses and $[\alpha]_D$ values of these complexes are listed in Table 1.

Preparation and Separation of μ-L-Aspartato Binuclear Complexes—$(+)_D$-[en$_2$Co(L-asp)Co(OH$_2$)en$_2$](ClO$_4$)$_4\cdot$H$_2$O (abbreviation: $(+)_D$-μ-L-asp-OH$_2$). An aqueous solution containing 1.78 g (0.004 mol) of $(+)_D$-[Co(L-asp)en$_2$]ClO$_4\cdot$2H$_2$O $[\alpha]_D=+445°$) and 3.10 g (0.006 mol) of [Co(OH$_2$)$_2$en$_2$](ClO$_4$)$_3$ in 40 ml of water was gradually evaporated almost to dryness at 50—55 °C on a water-bath. The residue was dissolved in 15—20 ml of water, and the solution was repeatedly evaporated to dryness. The final residue was dissolved in about 100 ml of water and then the solution was loaded on a SP-Sephadex cation-exchange column (C–25, Na-form, 3.6 cm × 70 cm). The red band adsorbed was developed with 0.1—0.3 N aqueous solution of NaClO$_4$. Each band which splitted from the red band was eluted in the order of orange-yellow ([Co(L-asp)en$_2$]$^+$), orange ([Co(L-aspH)en$_2$]$^{2+}$), pinkish-red ([Co(OH$_2$)$_2$en$_2$]$^{3+}$), and orange (μ-L-asp-OH$_2$ binuclear complex ion) bands. The latest orange eluate was concentrated by using a vacuum evaporator at 35—40 °C, and the deposited NaClO$_4$ was filtered off. After repeating the evaporation of the solution and the removal of NaClO$_4$, finally the solution was completely dried, and a large amount of absolute ethanol was added to the residue. The complex which remained as orange powder was collected by filtration and washed with absolute ethanol and then ether. Recrystallization of the complex was carried out by adding a small amount of NaClO$_4$ and ethanol to a concentrated solution and by allowing to stand the mixture in a refrigerator overnight. The complex deposited as reddish-orange crystals was filtered, washed with ethanol and then ether, and dried in a vacuum desiccator at room temperature. The yield was about 0.7 g. The complex obtained was readily soluble in water, and sparingly soluble in methanol and acetone, but insoluble in ethanol and ether.

$(-)_D$-[en$_2$Co(L-asp)Co(OH$_2$)en$_2$](ClO$_4$)$_4\cdot$H$_2$O. This complex was prepared by the same method as used for the $(+)_D$-isomer, except for using $(-)_D$-[Co(L-asp)en$_2$]ClO$_4\cdot$2H$_2$O ($[\alpha]_D=-315°$) instead of $(+)_D$-[Co(L-asp)en$_2$]ClO$_4\cdot$H$_2$O.

$(+)_D$-[en$_2$Co(L-asp)Co(NH$_3$)$_5$](ClO$_4$)$_4\cdot$H$_2$O (abbr.: $(+)_D$-μ-L-asp-NH$_3$). To an aqueous solution containing 2.25 g (0.005 mol) of $(+)_D$-[Co(L-asp)en$_2$]ClO$_4\cdot$2H$_2$O ($[\alpha]_D=+445°$) in 10 ml of water was added 2.4 g (0.005 mol) of [Co(NH$_3$)$_5$(OH$_2$)](ClO$_4$)$_3\cdot$H$_2$O, and the mixture was gradually evaporated almost to dryness at 50—55 °C on a water-bath. The residue was dissolved in 10 ml of water, and the solution was evaporated again. The final residue was dissolved in 10 ml of water, and the solution was loaded on a SP-Sephadex cation-exchange column (C-25, Na-form, 3.6 cm × 70 cm). The adsorbed band splitted into five bands in sweeping with 0.3 N aqueous solution of NaClO$_4$. The eluate from the third band was concentrated to about 5 ml by using a vacuum evaporator at 35—40 °C, and a large amount of ethanol was added to the concentrated solution. The μ-L-aspartato binuclear complex which deposited as a pinkish-orange powder was filtered, and washed with a mixture of water-methanol (1 : 3) mixture, methanol and then ether. Recrystallization was carried out by adding a small amount of methanol to the concentrated solution and by keeping in a refrigerator overnight. The pinkish-orange complex was obtained as needle crystals. The yield was 1.2 g.

Preparation and Separation of μ-L-Glutamato Binuclear Complexes—$(+)_D$-[en$_2$Co(L-glu)Co(OH$_2$)en$_2$](ClO$_4$)$_4\cdot$2H$_2$O (abbr.: $(+)_D$-μ-L-glu-OH$_2$). This complex was obtained by a procedure similar to that of the $(+)_D$-μ-L-aspartato binuclear complexes, except for using 2.3 g (0.0045 mol) of [Co(OH$_2$)$_2$en$_2$](ClO$_4$)$_3$ and 1.27 g (0.003 mol) of $(+)_D$-[Co(L-glu)en$_2$]ClO$_4$ ($[\alpha]_D=+348°$) instead of $(+)_D$-[Co(L-asp)en$_2$]ClO$_4\cdot$2H$_2$O. The yield was about 0.8 g. The reddish-orange complex was readily soluble in water, sparingly soluble in methanol and acetone, but insoluble in ethanol and ether.

$(-)_D$-[en$_2$Co(L-glu)Co(OH$_2$)en$_2$](ClO$_4$)$_4\cdot$2H$_2$O. This $(-)_D$-isomer was obtained by the same procedure as that for $(+)_D$-isomer, except for using $(-)_D$-[Co(L-glu)en$_2$]ClO$_4$ in-

stead of $(+)_D$-[Co(L-glu)en$_2$]ClO$_4$.

$(+)_D$-[en$_2$Co(L-glu)Co(NH$_3$)$_5$](ClO$_4$)$_4\cdot$H$_2$O (abbr.: $(+)_D$-μ-L-glu-NH$_3$). To an aqueous solution containing 2.4 g (0.005 mol) of [Co(NH$_3$)$_5$(OH$_2$)](ClO$_4$)$_3\cdot$H$_2$O in 20 ml of warm water was added 2.12 g (0.005 mol) of $(+)_D$-[Co(L-glu)en$_2$]ClO$_4$ ($[\alpha]_D=+348°$). The solution was gradually evaporated to dryness at 60—65 °C on a water-bath. The residue was dissolved in 5—10 ml of water, and the solution was evaporated again. This procedure was repeated six or seven more times. Finally the residue was dissolved in 100 ml of warm water, and the solution was loaded on a SP-Sephadex cation-exchange column (C-25, Na-form, 3.6 cm × 70 cm). The elution and the isolation of the complex were performed by the same way as the case of $(+)_D$-[en$_2$Co(L-asp)Co(NH$_3$)$_5$](ClO$_4$)$_4\cdot$H$_2$O. The crude complex obtained was recrystallized from a minimum amount of water by adding a small amount of ethanol to the concentrated solution and by keeping in a refrigerator overnight. The yield was 0.2 g.

Preparations and Separations of Di-μ-L-aspartato and -L-glutamato Trinuclear Complexes—$(+)_D$-[en$_2$Co{(L-asp)Co en$_2$}$_2$](ClO$_4$)$_5\cdot$5H$_2$O (abbr.: di-μ-L-asp). To an aqueous solution of 0.82 g (0.006 mol) of [Co(OH$_2$)$_2$en$_2$](ClO$_4$)$_3$ containing in 20—30 ml of water was added 1.31 g (0.003 mol) of $(+)_D$-[Co(L-asp)en$_2$]ClO$_4\cdot$2H$_2$O ($[\alpha]_D=+445°$). The solution was evaporated to dryness at over 80 °C on a steam-bath. The residue was dissolved in about 10 ml of water and evaporated again. This procedure was repeated two more times. Finally the residue was dissolved in 50 ml of water, and the solution was loaded on a SP-Sephadex cation-exchange column (C-25, Na-form, 3.6 cm × 50 cm), and the adsorbed band was developed with 0.1—0.3 N aqueous solution of NaClO$_4$. Each band splitted was eluted in the order of orange-yellow ([Co(L-asp)en$_2$]$^+$), orange ([Co(L-aspH)en$_2$]$^{2+}$), pinkish-red ([Co(OH$_2$)$_2$en$_2$]$^{3+}$), pinkish-red ([en$_2$Co(L-asp)Co(OH$_2$)en$_2$]$^{4+}$), and reddish-orange (di-μ-L-asp trinuclear complex ion) bands. The latest eluate was concentrated by using a vacuum evaporator and the deposited NaClO$_4$ was filtered off. After repeating the procedure of the evaporation of the solution and the removal of an excess of NaClO$_4$, finally the solution was completely evaporated to dryness, and a large amount of methanol was added to the residue until the deposited NaClO$_4$ disappeared. The reddish-orange complex deposited as needle crystals was filtered and washed with methanol and then acetone. Recrystallization was carried out from a minimum amount of warm water by adding a few drops of saturated solution of NaClO$_4$, and by keeping in a refrigerator for 2—3 hours. The yield was 1.1 g.

$(-)_D$-[en$_2$Co{(L-asp)Co en$_2$}$_2$](ClO$_4$)$_5\cdot$5H$_2$O. The $(-)_D$-isomer was prepared by the same method as used for the $(+)_D$-isomer.

$(+)_D$- and $(-)_D$-[en$_2$Co{(L-glu)Co en$_2$}$_2$](ClO$_4$)$_5\cdot n$H$_2$O (n= 4 and 5 for $(+)_D$- and $(-)_D$-isomers) (abbr.: $(+)_D$- and $(-)_D$- di-μ-L-glu). These complexes were prepared by a similar way to that used for the $(+)_D$-di-μ-L-asp trinuclear complex, except for using 1.03 g (0.002 mol) of [Co(OH$_2$)$_2$en$_2$](ClO$_4$)$_3$ and 1.70 g (0.004 mol) of $(+)_D$-[Co(L-glu)en$_2$]ClO$_4$ ($[\alpha]_D=+348°$)/and $(-)_D$-[Co(L-glu)en$_2$]ClO$_4$ ($[\alpha]_D=-409°$) instead of $(+)_D$-[Co(L-asp)en$_2$]ClO$_4\cdot$2H$_2$O. The reddish-orange complexes were obtained as needle crystals. The yields were about 0.7 g.

Measurements. The absorption spectra were obtained by using a Hitachi Model EDS-3T spectrophotometer. The CD measurements were made by a JASCO Model ORD/UV-5 spectrophotometer with CD attachment. The ^{13}C NMR spectra were recorded on a JEOL MH-100 spectrometer with pulsed Fourier transform/proton noise-decoupled mode. The samples used for the ^{13}C NMR measurements were converted perchlorate to the chloride to obtained higher solubility in D$_2$O. An external benzene was used as a standard signal.

The chemical shifts (ppm) in the figures are shown by adopting chemical shift of benzene down field of 128.50 ppm from that of TMS.[3]

Results and Discussion

Elemental analyses and CD data for the μ-L-aminocarboxylato binuclear and trinuclear complexes are listed in Table 1.

Absorption Spectra. The absorption curves of the L-asp mononuclear ([Co(L-asp)en$_2$]$^+$), μ-L-asp binuclear and di-μ-L-asp trinuclear complexes are shown in Fig. 1. In Figs. 2, 4 and 5, the residual absorption curves for the μ-L-asp-OH$_2$ and μ-L-asp-NH$_3$ binuclear complexes, and di-μ-L-asp trinuclear complex are shown. The absorption spectra of these complexes indicate almost analogous absorption curve each other, although their intensities are different (Fig. 1). However, the residual curve for the trinuclear complex (Fig. 5) shows quite different behavior from those for the binuclear complexes (Figs. 2 and 4), and consists of two splitted bands in the first band region. Such split for the trinuclear complex coincides with the absorption behavior which generally appears in the *trans(O)*-[Co O$_2$N$_4$] type complexes.[4,5] Therefore, it can be concluded that the di-μ-L-asp trinuclear complex obtained in the present study takes the *trans(O)* structure with respect

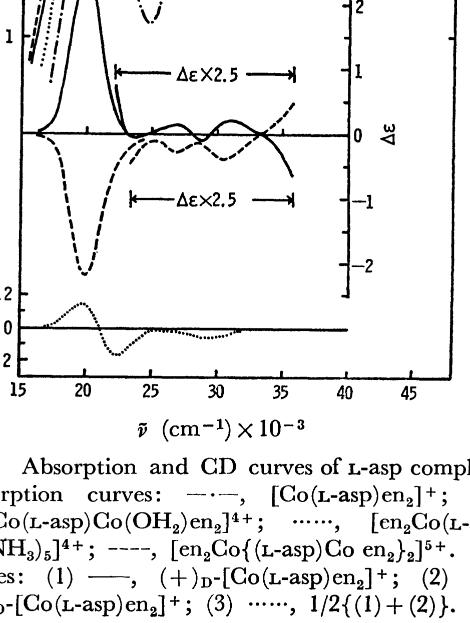

Fig. 1. Absorption and CD curves of L-asp complexes. Absorption curves: —·—, [Co(L-asp)en$_2$]$^+$; ——, [en$_2$Co(L-asp)Co(OH$_2$)en$_2$]$^{4+}$; ······, [en$_2$Co(L-asp)-Co(NH$_3$)$_5$]$^{4+}$; ----, [en$_2$Co{(L-asp)Co en$_2$}$_2$]$^{5+}$. CD curves: (1) ——, $(+)_D$-[Co(L-asp)en$_2$]$^+$; (2) ----, $(-)_D$-[Co(L-asp)en$_2$]$^+$; (3) ······, 1/2{(1)+(2)}.

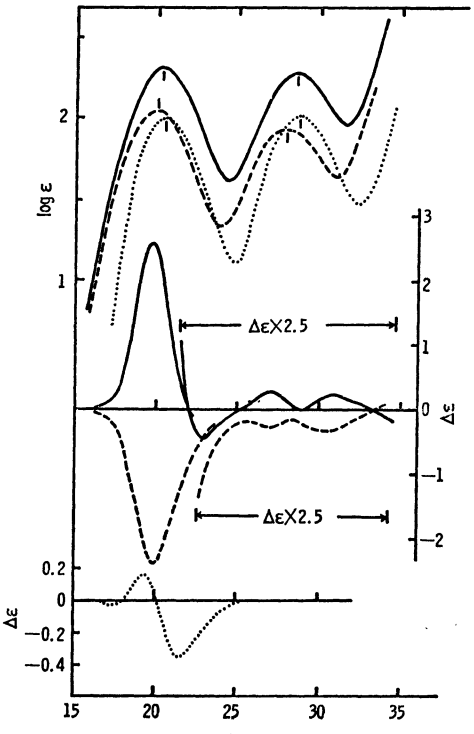

Fig. 2. Absorption, CD and their residual curves for μ-L-asp-OH_2 binuclear complex.
Absorption curves: (1) ——, $[\mathrm{en_2Co(L\text{-}asp)Co(OH_2)en_2}]^{4+}$; (2) ······, $[\mathrm{Co(L\text{-}asp)en_2}]^{+}$; (3) ----, (1)—(2). CD curves: (1) ——, $(+)_D$-$[\mathrm{en_2Co(L\text{-}asp)Co(OH_2)en_2}]^{4+}$; (2) ----, $(-)_D$-$[\mathrm{en_2Co(L\text{-}asp)Co(OH_2)en_2}]^{4+}$; (3) ······, (1)—$\{(+)_D$-$[\mathrm{Co(L\text{-}asp)en_2}]^{+}\}$.

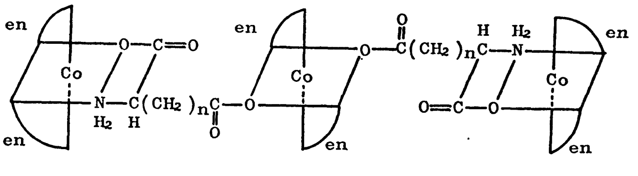

Fig. 3. The structure of di-μ-L-asp ($n=1$) or di-μ-L-glu ($n=2$) trinuclear complex.

to the two β-carboxyl groups of the μ-L-aspartato ligands, as shown in Fig. 3. On the other hand, the residual curve for the μ-L-asp-OH_2 binuclear complex does not indicate such splitted band as observed for the trinuclear complex. In addition the first and second band maxima (502 and 358 nm) in the residual curve appear at the positions corresponding to the *cis(O)*-[Co O_2N_4] type complexes.[5,6] Therefore, it is reasonable to conclude that this binuclear complex takes the *cis* structure with respect to the β-carboxyl group of the μ-L-aspartato and the coordinated OH_2 (Fig. 6). The same conclusions can also be obtained for the corresponding μ-L-glutamato complexes.

Circular Dichroism Spectra. Gillard *et al.* prepared the $(+)_D$- and $(-)_D$-$[\mathrm{Co(L\text{-}glu)en_2}]ClO_4$ by the reaction between $[\mathrm{Co\ CO_3en_2}]ClO_4$ and L-glutamic acid, and showed that the $(+)_D$-isomer produces more preferentially than the $(-)_D$-isomer.[7,8] They have also determined that the absolute configutation of the $(+)_D$-isomer is Λ-form by the X-ray analysis.[9]

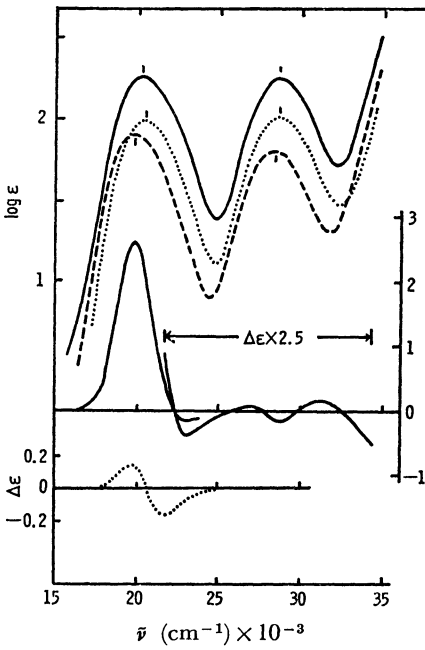

Fig. 4. Absorption, CD and their residual curves for μ-L-asp-NH_3 binuclear complex.
Absorption curves: (1) ——, $[\mathrm{en_2Co(L\text{-}asp)Co(NH_3)_5}]^{4+}$; (2) ······, $(+)_D$-$[\mathrm{Co(L\text{-}asp)en_2}]^{+}$; (3) ----, (1)—(2). CD curves: (1) ——, $(+)_D$-$[\mathrm{en_2Co(L\text{-}asp)Co(NH_3)_5}]^{4+}$; (2) ······, (1)—$\{(+)_D$-$[\mathrm{Co(L\text{-}asp)en_2}]^{+}\}$.

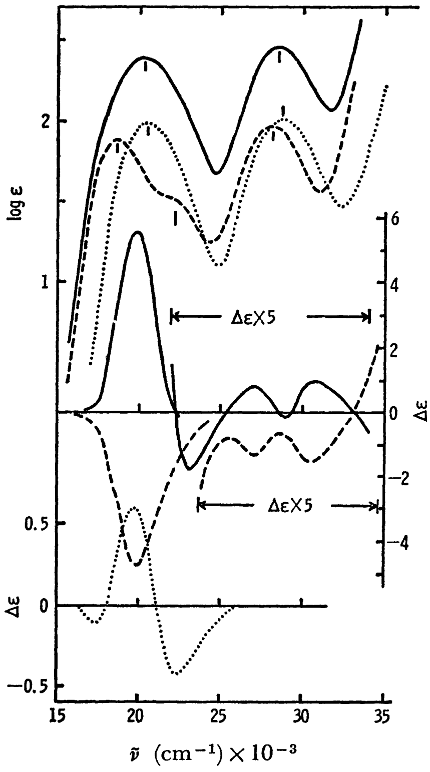

Fig. 5. Absorption, CD and their residual curves for di-μ-L-asp trinuclear complex.
Absorption curves: (1) ——, $(+)_D$-$[\mathrm{en_2Co\{(L\text{-}asp)Co\ en_2\}_2}]^{5+}$; (2) ······, $(+)_D$-$[\mathrm{Co(L\text{-}asp)en_2}]^{+}$; (3) ----, (1)—(2)×2. CD curves: (1) ——, $(+)_D$-$[\mathrm{en_2Co\{(L\text{-}asp)Co\ en_2\}_2}]^{5+}$; (2) ----, $(-)_D$-$[\mathrm{en_2Co\{(L\text{-}asp)Co\ en_2\}_2}]^{5+}$; (3) ······, (1)—2$\{(+)_D$-$[\mathrm{Co(L\text{-}asp)en_2}]^{+}\}$.

TABLE 1. ELEMENTAL ANALYSES AND CD DATA

Complexes	$[\alpha]_D$ (°)	C, % Found (Calcd)	H, % Found (Calcd)	N, % Found (Calcd)	$\tilde{\nu}_{ext}$, 10^3 cm^{-1} ($\Delta\varepsilon$) First Band	Second Band
$(+)_D$-[Co(L-asp)en$_2$]ClO$_4\cdot$2H$_2$O	+445	21.79 (21.55)	5.87 (5.66)	15.44 (15.71)	19.92(+2.476) 23.53(−0.014)	27.03(+0.055) 28.70(−0.042) 30.77(+0.072)
$(-)_D$-[Co(L-asp)en$_2$]ClO$_4\cdot$H$_2$O	−315	22.14 (22.46)	5.45 (5.43)	16.33 (16.38)	19.92(−2.190)	26.90(−0.106) 30.40(−0.160)
$(+)_D$-[Co(L-glu)en$_2$]ClO$_4$	+348	25.50 (25.50)	5.62 (5.48)	16.61 (16.53)	19.96(+2.470) 23.26(−0.087)	26.81(+0.036) 28.70(−0.060) 31.00(+0.060)
$(-)_D$-[Co(L-glu)en$_2$]ClO$_4$	−409	25.54 (25.50)	5.58 (5.48)	16.42 (16.53)	19.61(−2.207)	27.30(−0.231) 29.85(−0.261)
$(+)_D$-[en$_2$Co(L-asp)Co(OH$_2$)en$_2$]- (ClO$_4$)$_4\cdot$2H$_2$O	+220	15.19 (15.31)	4.81 (4.61)	13.48 (13.40)	19.80(+2.571) 22.99(−0.191)	26.88(+0.110) 30.77(+0.089)
$(-)_D$-[en$_2$Co(L-asp)Co(OH$_2$)en$_2$]- (ClO$_4$)$_4\cdot$H$_2$O	−166	15.74 (15.61)	4.72 (4.49)	13.43 (13.66)	20.00(−2.396)	27.03(−0.114) 30.50(−0.156)
$(+)_D$-[en$_2$Co(L-glu)Co(OH$_2$)en$_2$]- (ClO$_4$)$_4\cdot$2H$_2$O	+166	16.45 (16.34)	4.98 (4.76)	13.02 (13.20)	19.92(+3.000) 22.99(−0.204)	27.03(+0.444) 28.60(−0.070) 30.80(+0.080)
$(-)_D$-[en$_2$Co(L-glu)Co(OH$_2$)en$_2$]- (ClO$_4$)$_4\cdot$2H$_2$O	−222	16.44 (16.34)	4.96 (4.76)	13.24 (13.20)	19.80(−2.620)	27.20(−0.160) 30.40(−0.180)
$(+)_D$-[en$_2$Co(L-asp)Co(NH$_3$)$_5$]- (ClO$_4$)$_4\cdot$3H$_2$O	+211	10.77 (10.60)	4.65 (4.68)	15.36 (15.46)	19.80(+2.645) 23.00(−0.103)	26.81(+0.074) 28.41(−0.030) 31.00(+0.094)
$(+)_D$-[en$_2$Co(L-glu)Co(NH$_3$)$_5$]- (ClO$_4$)$_4\cdot$H$_2$O	+161	12.40 (12.22)	4.68 (4.56)	15.68 (15.84)	19.92(+2.584) 23.00(−0.159)	27.03(+0.029) 28.70(−0.061) 31.00(+0.061)
$(+)_D$-[en$_2$Co{(L-asp)Co en$_2$}$_2$]- (ClO$_4$)$_5\cdot$5H$_2$O	+265	17.06 (17.32)	5.17 (4.95)	14.06 (14.14)	19.88(+5.566) 22.99(−0.376)	27.03(+0.170) 28.82(−0.041) 30.77(+0.205)
$(-)_D$-[en$_2$Co{(L-asp)Co en$_2$}$_2$]- (ClO$_4$)$_5\cdot$5H$_2$O	−236	17.28 (17.32)	5.00 (4.95)	14.19 (14.14)	19.90(−4.716)	27.10(−0.270) 30.50(−0.320)
$(+)_D$-[en$_2$Co{(L-glu)Co en$_2$}$_2$]- (ClO$_4$)$_5\cdot$4H$_2$O	−217	18.99 (18.91)	5.12 (5.06)	14.12 (14.04)	19.88(+5.854) 22.99(−0.311)	26.67(+0.124) 28.57(−0.124) 31.00(+0.156)
$(-)_D$-[en$_2$Co{(L-glu)Co en$_2$}$_2$]- (ClO$_4$)$_5\cdot$5H$_2$O	−283	18.61 (18.67)	5.23 (5.14)	13.77 (13.86)	19.69(−4.911)	26.90(−0.364) 30.10(−0.347)

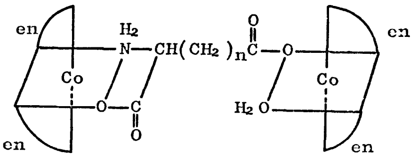

Fig. 6. The structure of μ-L-asp ($n=1$) or μ-L-glu ($n=2$) binuclear complex.

Recently, Buckingham *et al.* have demonstrated from the kinetical and thermodynamical studies that there is no substantial preference for the formation of one diastereomer relative to the other in the [Co(L-glu)en$_2$]$^+$ complex ion.[10] The complete separation of the $(+)_D$- and $(-)_D$-isomers of L-aspartato-bis(ethylenediamine)-cobalt(III) complexes was performed by Legg *et al.*,[2,11] and Kojima and Shibata.[12]

The CD curves of the mononuclear, binuclear and trinuclear L-aspartato complexes are shown in Figs. 1, 2, 4 and 5, and those of L-glutamato complexes are shown in Fig. 7. The absolute configurations of the mononuclear complexes for the $(+)_D$- and $(-)_D$-isomers are assigned respectively as Λ- and Δ-form from the sign of the main CD band in the first band region (in Fig. 1).[13] The μ-L-asp binuclear and di-μ-L-asp trinuclear complexes indicate the CD curves of similar type to those of the L-asp mononuclear complexes. This suggests that the CD bands of these binuclear and trinuclear complexes arise from the contributional CD effect of the mononuclear complex. The same discussion can also be made for the L-glutamato complexes.

The residual CD curves which were obtained by subtracting the CD curve of the mononuclear complex from that of each binuclear and trinuclear complex are shown in Figs. 2, 4, 5 and 7. These residual curves mean that the CD band of the mononuclear complex is intensified by the coordination of another cobalt(III) complex ion to the free β- or γ-carboxyl group of the

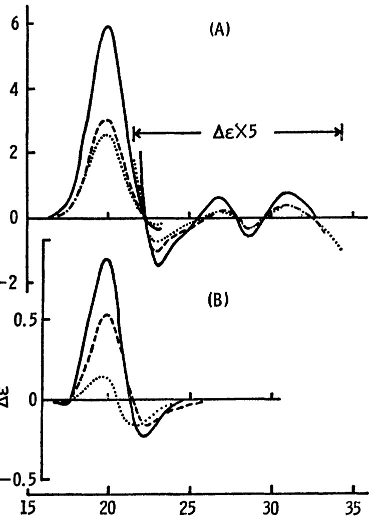

Fig. 7. CD and its residual curves for (+)$_D$-μ-L-glu complexes.
(A) (1) ……, [en$_2$Co(L-glu)Co(NH$_3$)$_5$]$^{4+}$; (2) ----, [en$_2$Co(L-glu)Co(OH$_2$)en$_2$]$^{4+}$; (3) ——, [en$_2$Co{(L-glu)Co en$_2$}$_2$]$^{5+}$. (B) ……, (1)—{(+)$_D$-[Co(L-glu)en$_2$]$^+$}; ----, (2)—{(+)$_D$-[Co(L-glu)en$_2$]$^+$}; ——, (3)—{(+)$_D$-[Co(L-glu)en$_2$]$^+$}.

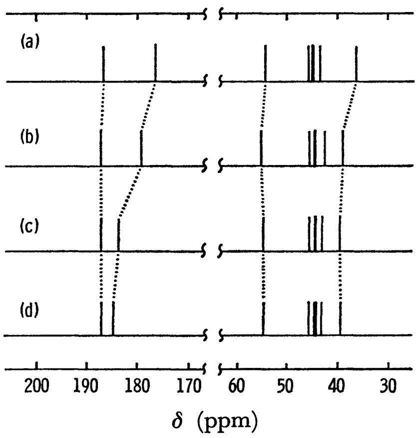

Fig. 8. ^{13}C NMR patterns of (+)$_D$-L-asp complexes in D$_2$O: (a) [Co(L-aspD)en$_2$]$^{2+}$ (acidified with D$_2$SO$_4$), (b) [Co(L-asp)en$_2$]$^+$, (c) [en$_2$Co(L-asp)Co(NH$_3$)$_5$]$^{4+}$, (d) [en$_2$Co{(L-asp)Co en$_2$}$_2$]$^{5+}$.

former complex, and that no configurational change of the original mononuclear complex occurs in the preparing process of the binuclear and trinuclear complexes. The almost symmetrical curves of the main CD bands for the (+)$_D$- and (−)$_D$-isomers of the binuclear and trinuclear complexes with μ-L-aspartato also support the complete retention of the configuration in the original mononuclear complex.

The intensities of these residual CD bands increase in the order of the μ-L-aa-NH$_3$, μ-L-aa-OH$_2$ binuclear and di-μ-L-aa trinuclear complexes. The residual CD band of the μ-L-aa-OH$_2$ binuclear complex indicates lower intensity of about half as compared with that of the trinuclear complex. This suggests that the former complex consists of the equivalent mixture of the two diastereomers (Λ(L)-Λ and Λ(L)-Δ).

^{13}C Nuclear Magnetic Resonance Spectra. The ^{13}C NMR patterns of some (+)$_D$-L-aspartato complexes are shown in Fig. 8. Two kinds of resonance signals which appear in the low magnetic field (176.55—186.98 ppm) correspond to the carbon atoms of the two carboxyl groups (α- and β-carboxyl groups) in the L-aspartato. Of these signals, the ones at the lower field side exhibit hardly change in chemical shift, but the ones at the higher field side do the considerable different chemical shift among the mononuclear and μ-L-asp complexes. The change of the chemical shift in the carboxyl group can be related to the change of its chemical environment. Quirt *et al.* have demonstrated from the pH titration study for the various amino acids that the carbon resonance of the carboxyl group indicates large shift with pH change.[11] The signal of 179.32 ppm in the (+)$_D$-[Co(L-asp)en$_2$]$^+$ ion shifts to higher field side (176.55 ppm) when its solution was acidified with D$_2$SO$_4$, and contrarily to lower field side (183.83 and 184.43 ppm) in the binuclear and trinuclear complexes. The former shift can be related to the protonation of the free β-carboxyl group and the latter ones to the coordination of the β-carboxyl group to the cobalt(III) ion. The signals at the lower field side exhibit nearly constant chemical shift (186.74—187.35 ppm) for all the L-aspartato complexes. This result suggests that these signals can be assigned to the carbon atoms of the α-carboxyl groups which take the same coordination form in these complexes.

The carbon signals of methin and methylene of L-aspartato, and of ethylenediamine appear at the positions of about 55, 36—40, and 43—46 ppm, respectively. The change of the chemical shift is also observed in the methylene carbon of the protonated mononuclear complex. More detailed discussion relating to the ^{13}C NMR of these complexes will be made in the successive study.

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