Metal Complexes of Amino Acids. IX.[1)]Carbon-13 Nuclear Magnetic Resonances of Cobalt(III) Complexes

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The ^{13}C NMR spectra of cobalt(III) complexes containing various amino acids as unidentate or bidentate ligands were measured. The relation between the coordination types and the changes of the chemical shifts was clarified. The changes of chemical shift on coordination of α-amino acid to cobalt(III) (NH_3^+-R-COOH→NH_3^+-R-COOCo) were about 7 and 1 ppm for the carboxy-carbon and α-carbon, respectively. On the other hand, those on chelation (NH_3^+-R-COOH→chelated amino acid) were about 15 and 5 ppm for each carbon, respectively. However, the changes of chemical shift on chelation of β-alanine were different from those of α-amino acids.

There have been numerous reports containing the application of ^{13}C NMR to organic compounds, and the technique has proven to be a very powerful tool for the structural investigation of organic compounds.[2,3)] However, there have been few reports of application of the technique to transition metal complexes, except for organometallic compounds. As octahedrally coordinated Co(III) complexes (Werner type) are diamagnetic and there are no direct bonds between cobalt and carbon atoms in the complexes, many results in organic researches are applicable to these complexes with little modification.[4—10)]

Previously we reported the ^{13}C NMR of the *trans(O)*-[Co $en_2(aaH)_2]X_3$ complexes containing various amino acids,[1,11)] which were bound to cobalt(III) ion as unidentate ligands through their carboxylate groups, the $-NH_3^+$ groups being free. In the present paper, we wish to describe not only more detailed ^{13}C NMR study of the *trans(O)*-[Co $en_2(aaH)_2]X_3$ complexes, but also new ^{13}C NMR study of the $[Co(NH_3)_4(aa)]X_2$ complexes containing amino acids bound to cobalt(III) ions as bidentate ligands. The relation between the coordination types and the changes in the ^{13}C chemical shifts of amino acid-cobalt(III) complexes will be clarified from the results of ^{13}C NMR spectra.

Experimental

Preparation of Complexes. The *trans(O)*-[Co $en_2(aaH)_2](ClO_4)_3$ (aaH=glyH, L-alaH, L-valH, L-leuH, L-serH, L-thrH, L-proH, L-hyproH, β-alaH, and γ-ambH (γ-aminobutyric acid)) complexes were prepared by the procedure similar to those described in previous papers.[12,13)]

trans(O)-[Co $en_2(ac)_2$]Cl·0.5 NaCl·3.5 H_2O: This complex was obtained by the modification of Linhard's method.[14)] To an aqueous solution containing 5 g of [Co $en_2(OH_2)_2](ClO_4)_3$ in 10 ml of water, 5 ml of 1 M aqueous solution of NaOH and 10 ml of acetic acid (acH) were added. The mixture was evaporated almost to dryness on steam-bath. After cooling, the resultant was dissolved in 50 ml of water. The solution was poured into a SP-sephadex column (C-25, Na^+ form) and eluted with 5% aqueous solution of NaCl. The first eluted solution (reddish violet) was concentrated in vacuum evaporator till a large excess of NaCl was deposited out. The deposited NaCl was removed off by filtration. A dark red complex, *trans(O)*-[Co $en_2(ac)_2$]Cl, contaminated with some sodium chloride, was obtained by adding ethanol and ether to the filtrate. The crude product was recrystallized from water by adding ethanol and ether.

Found: C, 22.92; H, 6.83; N, 12.95%. Calcd for $C_8H_{29}N_4O_{7.5}Cl_{1.5}Na_{0.5}Co$: C, 22.61; H, 6.88; N, 13.19%.

trans(O)-[Co $en_2(pr)_2$]Cl·0.5 H_2O: This complex was prepared by a similar method to that for the acetato complex except for using propionic acid (prH).

Found: C, 32.64; H, 7.37; N, 15.26%. Calcd for $C_{10}H_{27}N_4O_{4.5}ClCo$: C, 32.48; H, 7.36; N, 15.15%.

trans(O)-[Co $en_2(bu)_2$]ClO_4·0.5 H_2O: The complex of butyric acid (buH) was prepared by a procedure similar to those described above. However, this complex was obtained directly from the reacted solution as crystals of perchlorate salt without using SP-sephadex column. The crude product was recrystallized from warm water.

Found: C, 31.34; H, 6.78; N, 11.75%. Calcd for $C_{12}H_{31}N_4O_{8.5}ClCo$: C, 31.20; H, 6.75; N, 12.13%.

$[Co(NH_3)_4gly]Cl_2$·0.5 H_2O: To an aqueous solution containing 6 g of $[Co(NH_3)_6]Cl_3$ and 1.5 g of glycine in 100 ml of water, about 2 g of activated carbon was added. The mixture was warmed at 60 °C for 30 min with stirring. After filtering off a large amount of insoluble materials, the filtrate was poured into a column containing SP-sephadex (C-25, Ca^{2+} form) and eluted with 3% aqueous solution of calcium chloride. The eluted solution from the orange band was evaporated to about 5 ml in vaccum evaporator. To the concentrated solution 200 ml of ethanol was added, and the desired complex deposited was filtered. The complex was recrystallized from water by adding ethanol.

Found: C, 8.38; H, 6.08; N, 24.54%. Calcd for $C_2H_{17}N_5O_{2.5}Cl_2Co$: C, 8.55; H, 6.10; N, 24.93%.

$[Co(NH_3)_4(aa)]SO_4$ (aa=L-ala, L-val, L-leu, L-ser, L-thr, L-pro, and L-hypro): These complexes were prepared by modification of the methods described in previous papers.[12,15)]

$[Co(NH_3)_4(β\text{-}ala)]Cl_2·H_2O$: To an aqueous solution containing 5 g of $[Co(NH_3)_5(β\text{-}alaH)](ClO_4)_3$[13)] in 50 ml of water, 2 g of activated carbon was added. The mixture was warmed at 60 °C for 5 min with stirring. After the solution was filtered, the filtrate was poured into SP-sephadex column. The adsorbed band was eluted with 3% calcium chloride solution, and the solution eluted from the orange band was concentrated by using a vacuum evaporator. The crude complex was deposited by adding ethanol to the concentrated solution. The complex was recrystallized from water by adding ethanol.

Found: C, 11.82; H, 6.59; N, 23.13%. Calcd for $C_3H_{20}N_5O_3Cl_2Co$: C, 11.85; H, 6.64; N, 23.03%.

Measurements. ^{13}C NMR spectra at 25.15 MHz were recorded on a JEOL MFT-100 spectrometer with JEC-6 spectrum computer, in pulsed Fourier transform/proton noise decoupled mode. The field frequency ratio was stabilized by locking to internal D_2O. Peak positions were measured relative to external benzene (capillary). Chemical shifts in

TABLE 1. ^{13}C CHEMICAL SHIFTS AND CHEMICAL SHIFTS-CHANGES OF C_0-CARBONS IN AMINO ACIDS AND FATTY ACIDS

	NH_3^+-R-COOH or R-COOH	NH_3^+-R-COO$^-$ or R-COO$^-$		NH_2-R-COO$^-$		NH_3^+-R-COOCo or R-COOCo		Chelated amino-acids	
	δ (C_0)	δ_{-H} (C_0)	Δ_{-H} (C_0)$^{a)}$	δ_{-H_2} (C_0)	Δ_{-H_2} (C_0)$^{b)}$	δ_{Co} (C_0)	Δ_{Co} (C_0)	δ_{ch} (C_0)	Δ_{ch} (C_0)
gly	171.1ppm	174.0ppm	+2.9ppm	183.5ppm	+12.4ppm	177.9ppm	+6.8ppm	187.1ppm	+16.0ppm
L-ala	174.0	177.3	+3.3	186.4	+12.4	181.3	+7.3	188.0	+14.0
L-val	172.9	175.8	+2.9	184.7	+11.8	180.2	+7.3	187.0	+14.1
L-leu	172.9			185.7	+12.8	180.0	+7.1	188.0	+15.1
L-ser	171.5	174.1	+2.6	182.6	+11.1	178.4	+6.9	186.6	+15.1
L-thr	171.8	174.2	+2.4	182.7	+10.9	178.7	+6.9	186.7	+14.9
L-pro	173.0	176.1	+3.1	184.4	+11.4	180.1	+7.1	188.0	+15.0
L-hypro	172.8	175.8	+3.0	183.7	+10.9	179.7	+6.9	187.5	+14.7
β-ala	175.9	180.1	+4.2	183.3	+7.4	184.1	+8.2	181.8	+5.9
γ-amb	178.4	183.1	+4.7	185.0	+6.6	187.5	+9.1		
ac	177.5	183.1	+5.6			187.2	+9.7		
pr	180.4	186.3	+5.9			190.7	+10.3		
bu	180.3	185.5	+5.2			189.9	+9.6		
asp$^{c)}$	176.6	179.1	+2.5			184.4$^{e)}$	+7.8$^{e)}$		
glu$^{d)}$	178.7	183.5	+4.8			187.4$^{e)}$	+8.7$^{e)}$		

a) $\Delta_{-H}(C_0)=\delta_{-H}(C_0)-\delta(C_0)$. b) $\Delta_{-H_2}(C_0)=\delta_{-H_2}(C_0)-\delta(C_0)$. c) "asp" indicates the chelated L-aspartate with uncoordinated γ-carboxyl group in $[Co\,en_2(L\text{-}asp)]^+$. d) "glu" indicates the chelated L-glutamate with uncoordinated δ-carboxyl group in $[Co\,en_2(L\text{-}glu)]^+$. e) These values are for the trinuclear complexes, *trans*(*O*)-$[en_2Co\{(L\text{-}asp)Co\,en_2\}_2]^{5+}$ and -$[en_2Co\{(L\text{-}glu)Co\,en_2\}_2]^{5+}$. (Ref. 1)

TABLE 2. ^{13}C CHEMICAL SHIFTS AND CHEMICAL SHIFT-CHANGES OF C_α-CARBONS IN AMINO ACIDS AND FATTY ACIDS

	NH_3^+-R-COOH or R-COOH	NH_3^+-R-COO$^-$ or R-COO$^-$		NH_2-R-COO$^-$		NH_3^+-R-COOCo or R-COOCo		Chelated amino acids	
	δ (C_α)	δ_{-H} (C_α)	Δ_{-H} (C_α)$^{a)}$	δ_{-H_2} (C_α)	Δ_{-H_2} (C_α)$^{b)}$	δ_{Co} (C_α)	Δ_{Co} (C_α)	δ_{ch} (C_α)	Δ_{ch} (C_α)
gly	40.0ppm	41.5ppm	+1.1ppm	45.4ppm	+5.0ppm	41.3ppm	+0.9ppm	46.1ppm	+5.7ppm
L-ala	49.2	50.7	+1.5	51.8	+2.6	50.1	+0.9	53.4	+4.2
L-val	58.9	60.8	+1.9	62.4	+3.5	60.1	+1.2	62.9	+4.0
L-leu	52.1			54.9	+2.8	52.8	+0.8	55.9	+3.8
L-ser	55.1	56.7	+1.6	58.3	+3.2	56.1	+1.0	58.9	+3.8
L-thr	58.9	60.7	+1.8	62.4	+3.5	59.6	+0.7	62.7	+3.8
L-pro	60.0	61.7	+1.7	62.3	+2.3	61.0	+1.0	65.4	+5.4
L-hypro	58.6	60.3	+1.7	60.9	+2.3	59.6	+1.0	63.8	+5.2
β-ala	31.2	33.6	+2.4	38.1	+6.9	34.1	+2.9	33.4	+2.2
γ-amb	30.8	34.5	+3.7	35.2	+4.4	34.5	+3.7		
ac	19.8	23.7	+3.9			24.3	+4.5		
pr	26.7	30.7	+4.0			31.1	+4.4		
bu	35.7	39.8	+4.1			39.9	+4.2		
asp$^{c)}$	36.6	38.7	+2.1			38.5$^{e)}$	+1.9$^{e)}$		
glu$^{d)}$	30.1	33.6	+3.5			33.7$^{e)}$	+3.6$^{e)}$		

a) $\Delta_{-H}(C_\alpha)=\delta_{-H}(C_\alpha)-\delta(C_\alpha)$. b) $\Delta_{-H_2}(C_\alpha)=\delta_{-H_2}(C_\alpha)-\delta(C_\alpha)$. c), d) and e); see Table 1.

Figures and Tables are reported relative to TMS using the relation $\delta_{TMS}=\delta_{benzene}-128.5$ ppm.

Amino acids, of which concentrations in D_2O, 10% NaOD-D_2O and 10% DCl-D_2O were 2 mmol/ml, were used for NMR measurements. However, L-alaH, L-thrH and L-valH were sparingly soluble in D_2O, so that these amino acids were measured with saturated solutions in D_2O. Acetic and propionic acids which were dissolved in equivolumes of D_2O containing small amount of DCl, and butyric acid which was saturated in D_2O containing small amount of DCl were used. For the measurements of fatty acidate anions, the saturated solutions of their sodium salts in D_2O containing small amount of 10% NaOD were used.

The perchlorate or sulfate salts of the complexes were converted to the more soluble chlorides by treating with anion-exchange resin (Cl^- form). The saturated solutions of the *trans*(*O*)-$[Co\,en_2(aaH)_2]Cl_3$ complexes which have free $-NH_3^+$ groups were acidified with a small amount of 20% DCl to obtain the complete protonation of free amino groups. The other complexes were examined in saturated solutions. Experimental errors were within ±0.1 ppm.

Results and Discussion

The ^{13}C chemical shifts of carboxy-carbons (C_0) and α-carbons (C_α) of amino acids and fatty acids are summerized in Tables 1 and 2. The symbols of

$\delta(C_0)$ and $\delta(C_\alpha)$ represent the chemical shifts of the carbons of C_0 and C_α of NH_3^+–R–COOH or R–COOH (in acidic solution), $\delta_{-H}(C_0)$ and $\delta_{-H}(C_\alpha)$ those of NH_3^+–R–COO^- or R–COO^-, and δ_{-H_2} (C_0) and δ_{-H_2} (C_α) those of NH_2–R–COO^-. The chemical shifts of C_0 and C_α of unidentate ligands in *trans(O)*-[Co en$_2$(acid)$_2$]$^+$ and -[Co en$_2$(aaH)$_2$]$^{3+}$ complex ions are given by the symbols of $\delta_{Co}(C_0)$ and $\delta_{Co}(C_\alpha)$, respectively. The chemical shifts of C_0 and C_α of the chelated amino acidates in [Co(NH$_3$)$_4$(amino acidato)]$^{2+}$ complex ions are denoted in the symbols of $\delta_{ch}(C_0)$ and $\delta_{ch}(C_\alpha)$, respectively.

The $\delta(C_0)$ values for α-amino acids were found in the range of 171—174 ppm. However, those for β- and γ-amino acids and fatty acids were observed at a furthermore lower magnetic field region (175.9—180.4 ppm).

The resonances for C_α were observed over a fairly wide region, 18.9—60.0 ppm, for the fatty acids and amino acids having various α-substituted groups.[16,17)]

trans*(O)-[Co en$_2$(OCO-R)$_2$] Type Complexes.* It is known that a large number of amino acids and fatty acids form inert complexes in which they coordinate to cobalt(III) with only carboxyl-groups. When the proton attaching to the carboxyl group was substituted with Co(III), down-field shift was observed in the resonance of carboxy-carbon ($\Delta_{Co}(C_0)$: $\delta_{Co}(C_0)$ minus $\delta(C_0)$). Similar down-field shifts were also observed when the corresponding carboxylate anions were formed. It is interesting that the chemical shifts of coordinated carboxy-carbon ($\delta_{Co}(C_0)$) are closer to those of the deprotonated carboxy-carbon ($\delta_{-H}(C_0)$) than to those of the protonated carboxy-carbon($\delta(C_0)$), (though the $\delta_{Co}(C_0)$ located at lower field region than the $\delta_{-H}(C_0)$) (Table 1).

The $\Delta_{Co}(C_0)$ values of α-amino acids were 7.0± 0.3 ppm. Those of the β- and γ-amino acids and fatty acids were rather diverse, showing 7.8—10.3 ppm. These $\Delta_{Co}(C_0)$ values increase with increasing $\delta_{-H}(C_0)$ values, and it appears that there are linear correlation between them (Fig. 1). For the practical purpose in predicting the $\Delta_{Co}(C_0)$ value, we propose the following relation (Eq. (1)).

$$\Delta_{Co}(C_0) = 0.268\,\delta_{-H}(C_0) - 40.00 \qquad (1)$$

We could also obtain linear correlation between Δ_{Co}-(C_0) and $\delta(C_0)$ values in a similar manner as above, though the deviation of the data from the calculated straight line was larger than those in Fig. 1.

The resonances of the C_α in α-amino acids appear over the wide region, compared with those of the carboxy-carbons. This is caused by the different character of the groups attaching to the α-carbon in α-amino acid. In spite of the fairly large difference of the chemical shifts ($\delta(C_\alpha)$), the $\Delta_{Co}(C_\alpha)$ values ($\delta_{Co}(C_\alpha)$ minus $\delta(C_\alpha)$) were approximately constant in α-amino acids, showing 1.0±0.2 ppm.

Similarly to the C_0, the chemical shifts of the C_α in the unidentate coordination form ($\delta_{Co}(C_\alpha)$) are closer to those in the deprotonated form ($\delta_{-H}(C_\alpha)$) than to those in the protonated form ($\delta(C_\alpha)$) (Table 2). In the α-amino acids, the chemical shifts, $\delta_{Co}(C_\alpha)$, appear in a field higher than $\delta_{-H}(C_\alpha)$. This behavior is different from that of carboxy-carbon, that is, $\delta_{Co}(C_0)$ appears in a field lower than $\delta_{-H}(C_0)$. On the other hand, in β- and γ-amino acids and fatty acids, the $\delta_{Co}(C_\alpha)$ values were observed in a field lower than $\delta_{-H}(C_\alpha)$.

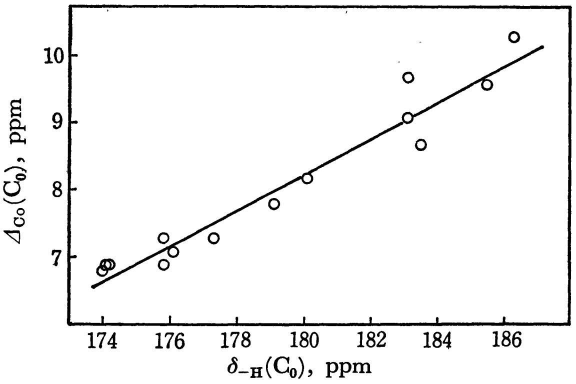

Fig. 1. Variation of $\Delta_{Co}(C_0)$ for the unidenate complexes with $\delta_{-H}(C_0)$ for the fatty acids and amino acids. The line is determined by Eq. (1).

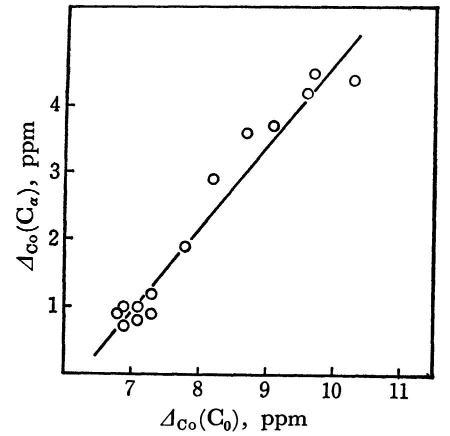

Fig. 2. Variation of $\Delta_{Co}(C_\alpha)$ with $\Delta_{Co}(C_0)$ for the unidentae complexes. The line is determined by Eq. (2).

Figure 2 shows the relationship between the $\Delta_{Co}(C_0)$ and $\Delta_{Co}(C_\alpha)$ values. It is evident from the figure that the acid showing a large $\Delta_{Co}(C_0)$ value possesses a large $\Delta_{Co}(C_\alpha)$ value. It is probable that the change in chemical shift of α-carbon, which is neighboring to the carboxy-carbon, becomes larger as the change in chemical shift of carboxy carbon becomes larger. It appears that there are a simple linear correlation between the $\Delta_{Co}(C_0)$ and $\Delta_{Co}(C_\alpha)$ values (Eq. (2)).

$$\Delta_{Co}(C_\alpha) = 1.228\,\Delta_{Co}(C_0) - 7.67 \qquad (2)$$

If the extrapolation of linear plot to the smaller value is correct, the following results will be obtained. In the case where the $\Delta_{Co}(C_0)$ value is equal to 0 ppm, that is, in the case where the chemical shift of the coordinated carboxy-carbon is equal to that of the protonated carboxy-carbon, the $\Delta_{Co}(C_\alpha)$ value will be about −8 ppm. Some portion of the −8 ppm may be caused by the direct interaction between the α-carbon and Co(III).

[Co(NH$_3$)$_4$(amino acidato)]$^{2+}$ Type Complexes. It is well known that the α-amino acid also forms an

inert complex chelated to Co(III) with both carboxyl and amino groups. The chemical shifts of the carboxy-carbon in the chelated α-amino acids were observed in a field lower than those of the carboxy-carbons in the protonated α-amino acids, that is, the $\Delta_{\mathrm{ch}}(\mathrm{C_0})$ values ($\delta_{\mathrm{ch}}(\mathrm{C_0})$ minus $\delta(\mathrm{C_0})$) are 15.0±1.0 ppm. The chemical shifts of the chelated carboxy-carbons of α-amino acids are closer to those of their carboxy-carbons in basic solution rather than in acidic and neutral solutions (Table 1).

Figure 3 shows the plots of $\Delta_{\mathrm{ch}}(\mathrm{C_0})$ against $\delta(\mathrm{C_0})$ for some α-amino acids. It appears that the $\Delta_{\mathrm{ch}}(\mathrm{C_0})$ values decrease with increasing $\delta(\mathrm{C_0})$ values. On the contrary, $\Delta_{\mathrm{Co}}(\mathrm{C_0})$ values increase with increasing $\delta(\mathrm{C_0})$ values, as previously described.

Chemical shifts of C_α in chelated α-amino acids, $\delta_{\mathrm{ch}}(\mathrm{C}_\alpha)$, are closer to $\delta_{-\mathrm{H_2}}(\mathrm{C}_\alpha)$ than $\delta(\mathrm{C}_\alpha)$, $\delta_{-\mathrm{H}}(\mathrm{C}_\alpha)$ and $\delta_{\mathrm{Co}}(\mathrm{C}_\alpha)$. The $\Delta_{\mathrm{ch}}(\mathrm{C}_\alpha)$ ($\delta_{\mathrm{ch}}(\mathrm{C}_\alpha)$ minus $\delta(\mathrm{C}_\alpha)$) values are 4.8±1.0 ppm and independent from $\delta_{\mathrm{ch}}(\mathrm{C_0})$, $\delta(\mathrm{C}_\alpha)$ and $\delta_{\mathrm{ch}}(\mathrm{C}_\alpha)$ values. Difference of the interaction between substituting group on the C_α of α-amino acids and the other ligands in the complex, and difference among the natures of amino-nitrogen will be responsible for the variance of the $\Delta_{\mathrm{ch}}(\mathrm{C}_\alpha)$ values. The α-amino acids with pyrrolidine ring, *i.e.*, L-proline and hydroxy-L-proline, show larger $\Delta_{\mathrm{ch}}(\mathrm{C}_\alpha)$ values than the other α-amino acids (except for glycine). This may be caused by the large steric interactions between the pyrrolidine ring and the other ligands in the complex, and/or by the coordination of the secondary amino-nitrogen to cobalt(III). However, the $\Delta_{\mathrm{Co}}(\mathrm{C}_\alpha)$ values of L-proline and hydroxy-L-proline in the complexes in which the amino acids are coordinated to Co(III) with their carboxyl groups as unidentate ligands are nearly equal to those of the other amino acids in the corresponding complexes. This means that there are no steric interactions in these unidentate complexes.

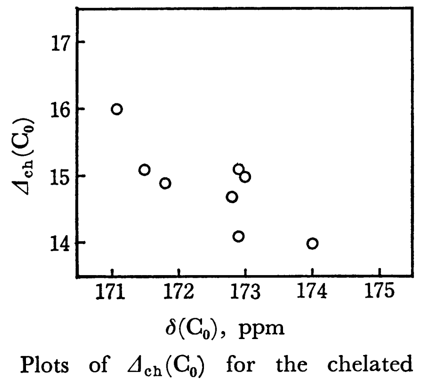

Fig. 3. Plots of $\Delta_{\mathrm{ch}}(\mathrm{C_0})$ for the chelated α-amino acids *vs.* $\delta(\mathrm{C_0})$ for the α-amino acids.

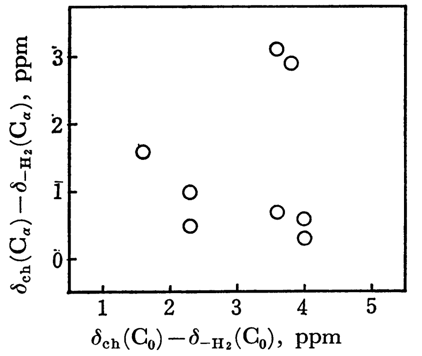

Fig. 4. Plots of $\delta_{\mathrm{ch}}(\mathrm{C_0})-\delta_{-\mathrm{H_2}}(\mathrm{C_0})$ *vs.* $\delta_{\mathrm{ch}}(\mathrm{C}_\alpha)-\delta_{-\mathrm{H_2}}(\mathrm{C}_\alpha)$ for the α-amino acids.

Table 3. Chemical shifts of $\mathrm{C_0}$-carbons in cobalt(III) complexes containing chelated glycine

Complex	δ_{ch} $(\mathrm{C_0})$	
$[\mathrm{Co(NH_3)_4(gly)]Cl_2}$	187.1 ppm	
[Co en$_2$ (gly)]Cl$_2$$^{\mathrm{a)}}$	186.7	
C$_1$-*cis*(*O*)-[Co en (gly)$_2$]Cl$^{\mathrm{a)}}$	186.0	187.4
trans(*O*)-[Co en (gly)$_2$]Cl$^{\mathrm{a)}}$	187.5	
C$_1$-*cis*(*N*)-Li[Co ox (gly)$_2$]$^{\mathrm{a)}}$	186.8	187.2
C$_2$-*cis*(*N*)-Li[Co ox (gly)$_2$]$^{\mathrm{a)}}$	187.0	
trans(*N*)-Li[Co ox (gly)$_2$]$^{\mathrm{a)}}$	188.6	

a) Preparation; Ref. 18.

Figure 4 illustrates plots of $\delta_{\mathrm{ch}}(\mathrm{C_0})$ minus $\delta_{-\mathrm{H_2}}(\mathrm{C_0})$ *versus* $\delta_{\mathrm{ch}}(\mathrm{C}_\alpha)$ minus $\delta_{-\mathrm{H_2}}(\mathrm{C}_\alpha)$. It is evident from the figure that L-proline and hydroxy-L-proline differ from the other α-amino acids. It appears that the values of $\delta_{\mathrm{ch}}(\mathrm{C}_\alpha)$ minus $\delta_{-\mathrm{H_2}}(\mathrm{C}_\alpha)$ decrease with increasing values of $\delta_{\mathrm{ch}}(\mathrm{C_0})$ minus $\delta_{-\mathrm{H_2}}(\mathrm{C_0})$, except for L-proline and hydroxy-L-proline.

Table 3 shows the chemical shifts of carboxy-carbons in chelated glycinato complexes. It is interesting that these values (187.3±1.3 ppm) were observed in a considerably narrow range, in spite of the difference of the net charge among the complex ions and the difference among the other ligands.

Chemical shift-changes of chelated β-alanine deviated largely from those of the α-amino acids. The $\delta_{\mathrm{ch}}(\mathrm{C_0})$ of β-alanine was observed in higher magnetic field region than $\delta_{-\mathrm{H_2}}(\mathrm{C_0})$ and $\delta_{\mathrm{Co}}(\mathrm{C_0})$, while the $\delta_{\mathrm{ch}}(\mathrm{C_0})$ of the α-amino acids were observed in a field lower than $\delta_{-\mathrm{H_2}}(\mathrm{C_0})$ and $\delta_{\mathrm{Co}}(\mathrm{C_0})$. Similar result was obtained for the $\delta_{\mathrm{ch}}(\mathrm{C}_\alpha)$. The factors affecting them could be as follows; size of the chelate ring of β-alanine being larger than that of the α-amino acid; carboxy-carbon and α-carbon of β-alanine being remote from the amino-group, compared with those of the α-amino acids; the absence of amino-group on α-carbon of β-alanine. Since there are insufficient data, it is not clear which factor is a most dominant one.

In summary, we obtained the following results for the Co(III) complexes. The $\Delta_{\mathrm{Co}}(\mathrm{C_0})$ and $\Delta_{\mathrm{Co}}(\mathrm{C}_\alpha)$ values for α-amino acids were about 7 ppm and 1 ppm, respectively. On the other hand, those values for β- and γ-amino acids and fatty acids were 8—10 ppm and 2—4 ppm, respectively. The changes in chemical shifts of carboxy- and α-carbons caused by the chelation of α-amino acids, $\Delta_{\mathrm{ch}}(\mathrm{C_0})$ and $\Delta_{\mathrm{ch}}(\mathrm{C}_\alpha)$, were 14—15 ppm and 4—6 ppm, respectively. The $\Delta_{\mathrm{ch}}(\mathrm{C_0})$ and $\Delta_{\mathrm{ch}}(\mathrm{C}_\alpha)$ values of β-alanine were different from those of the α-amino acids and were 5.8 ppm and 2.2 ppm, respectively.

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