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CARBON-13 NUCLEAR MAGNETIC RESONANCES OF COBALT(III) COMPLEXES CONTAINING AMINO-ACIDS

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The ^{13}C-NMR spectra of α-amino-acids and their trans(O)-[Co en_2-$(aaH)_2]^{3+}$ complex ions were measured. The changes in chemical shift on protonation of carboxyl anion group of amino-acids were 2.5~3.2 ppm and 1.1~2.1 ppm upfield for the carboxyl carbons and α-carbons, and on coordination of carboxyl group to the cobalt(III) ion 3.8~4.4 ppm downfield and almost zero for the former and latter carbons, respectively.

Recently the studies of carbon-13 nuclear magnetic resonance have been developed and their data give us many informations about the structures of organic compounds.[1,2] On the other hand, these studies concerning cobalt(III) complexes (d^6 low spin type, diamagnetic) are few.[3-6]

In this paper, we will discuss the comparison of Δ_{coord} values (difference in the chemical shift between the amino-acid in neutral aqueous solution and the amino-acid coordinating to cobalt(III) ion with its carboxyl group) with Δ_{proton} values (difference in the chemical shift between the amino-acid in neutral solution and the amino-acid in acidic solution).

The trans(O)-[Co $en_2(aaH)_2]Cl_3$ complexes used for the measurements were synthesized according to the method of Yasui et al.[7] ^{13}C-NMR spectra were recorded on a JEOL-MH 100 spectrometer in pulse Fourier transform/proton noise decoupled mode at 25.15 MHz and at room temperature. Peak positions were measured relative to external benzene, and D_2O is used as solvent of the samples. For the measurements of the protonated samples, the solutions were acidified with 50% D_2SO_4 solution. Chemical shifts are reported relative to TMS using the relation $\delta_{TMS} = \delta_{benzene} - 128.5$ ppm.

The chemical shifts for the carboxyl carbon (C-1) and the neibouring α-carbon (C-2) are shown in Table 1 and 2, respectively. The Δ_{proton} and Δ_{coord} values of the C-1 and C-2 carbons are also listed in Tables.

The C-1 resonances of various α-amino-acids in neutral solutions were found in the range 174.0 to 177.3 ppm. However, the resonances of the β- and γ-amino-acids were observed in the range 179.9 to 183.1 ppm. These resonances shifted upfield in acidic solutions, that is, the Δ_{proton} values of the C-1 carbons are -2.8 ± 0.4 ppm for the α-amino-acids and -4.1 ± 0.4 ppm for the β- and γ-amino-acids. In contrast, the resonances of the C-1 carbons in the unidentate amino-acids (in trans(O)-$[\text{Co en}_2(\text{aaH})_2]^{3+}$) shifted downfield, that is, their Δ_{coord} values are $+4.1 \pm 0.3$ ppm. In the case that the α-amino-acid forms five membered chelate ring, the downfield shift of the C-1 carbon resonance is considerably large. For example, the shifts of the C-1 carbons for the two diastereomers of $[\text{Co(L-ala)en}_2]^{2+}$ are 13.0 and 13.5 ppm downfield.[8] Therefore, the big difference of Δ_{coord} value for the C-1 carbon resonances between the unidentate and bidentate amino-acids will give us a usefull information to know the coordinating form of the amino-acid in cobalt(III) complexes.

Similar Δ_{proton} and Δ_{coord} values were found for the free γ-carboxyl carbon (C-1) of the bidentate L-glutamate anion in $\Lambda(+)_D$-$[\text{Co(L-glu)en}_2]^+$ ion. That is, the C-1 carbon resonances in $\Lambda(+)_D$-$[\text{Co(L-gluH)en}_2]^{2+}$ and $(+)_D$-trans(O)-$[\text{en}_2\text{Co}\{(\text{L-glu})\text{Co en}_2\}_2]^{5+}$ ions showed upfield shift of 4.8 ppm and downfield shift of 3.9 ppm, respectively. In $\Lambda(+)_D$-$[\text{Co(L-asp)en}_2]^+$ ion, however, the Δ_{proton} value of the free β-carboxyl carbon (C-1) is small (-2.5 ppm) and the Δ_{coord} value is large (+5.3 ppm). This may arise from that the free β-carboxyl of the $\Lambda(+)_D$-$[\text{Co(L-asp)en}_2]^+$ ion forms hydrogen-bond with intra-molecular NH_2 protons in aqueous solution [9] and that the hydrogen-bond is broken by protonation or by coordination of the β-carboxyl group.

The resonance for the C-2 carbon is also influenced by protonation of the carboxylate ion in an acidic solution. The Δ_{proton} values of the C-2 carbons for the α-amino-acids and for the β- and γ-amino-acids are -1.6 ± 0.5 and -3.3 ± 0.6 ppm, respectively. On the other hand, the resonance positions of these C-2 carbons are almost unchanged by coordination of the carboxyl groups to the cobalt(III) ion. In the case of the chelated α-amino-acid, the C-2 carbon resonance shifted to lower field side about 3 ppm (for example, the shifts of 3.3 and 2.6 ppm are observed for the two diastereomers of $[\text{Co(L-ala)en}_2]^{2+}$).[8]

The following conclusions were obtained from the results of the present ^{13}C-NMR data. The coordination of amino-acid through carboxyl group to the cobalt(III) ion,

Table 1. ^{13}C Chemical Shifts and Chemical Shift Changes of C-1 Carbons in Amino-acids and trans(O)-[Co en$_2$(aaH)$_2$]Cl$_3$

Compounds	—COO$^-$	—COOH		—COOCo	
	δ(C-1)	δ(C-1)	Δ_{proton}(C-1)	δ(C-1)	Δ_{coord}(C-1)
Glycine	174.1 ppm	171.6 ppm	- 2.5 ppm	177.9 ppm	+ 3.8 ppm
L-Alanine	177.3	174.1	- 3.2	181.3	+ 4.0
L-Serine	174.0	171.3	- 2.7	178.4	+ 4.4
L-Valine	175.8	172.8	- 3.0	180.2	+ 4.4
L-Proline	176.2	173.2	- 3.0	180.1	+ 3.9
L-Hpro[*1]	175.8	172.8	- 3.0	179.7	+ 3.9
β-Alanine	179.9	176.2	- 3.7	184.1	+ 4.2
γ-Amb acid[*2]	183.1	178.6	- 4.5	187.5	+ 4.4
Λ-[Co(L-asp)en$_2$]$^+$	179.1	176.6	- 2.5	184.4[*3]	+ 5.3
Λ-[Co(L-glu)en$_2$]$^+$	183.5	178.7	- 4.8	187.4[*4]	+ 3.9

[*1] L-Hpro = L-Hydroxyproline. [*2] γ-Amb acid = γ-Aminobutylic acid.

[*3] Value for trans(O)-[en$_2$Co{(L-asp)Co en$_2$}$_2$]Cl$_5$.

[*4] Value for trans(O)-[en$_2$Co{(L-glu)Co en$_2$}$_2$]Cl$_5$.

Table 2. ^{13}C Chemical Shifts and Chemical Shift Changes of C-2 Carbons in Amino-acids and trans(O)-[Co en$_2$(aaH)$_2$]Cl$_3$

Compounds	—COO$^-$	—COOH		—COOCo	
	δ(C-2)	δ(C-2)	Δ_{proton}(C-2)	δ(C-2)	Δ_{coord}(C-2)
Glycine	41.8 ppm	40.7 ppm	- 1.1 ppm	41.3 ppm	- 0.5 ppm
L-Alanine	50.7	49.2	- 1.5	50.1	- 0.6
L-Serine	56.7	55.2	- 1.5	56.1	- 0.6
L-Valine	60.8	58.7	- 2.1	60.1	- 0.7
L-Proline	61.7	59.8	- 1.9	61.0	- 0.7
L-Hpro	60.4	58.9	- 1.5	59.6	- 0.8
β-Alanine	33.7	31.0	- 2.7	34.1	+ 0.4
γ-Amb acid	34.6	30.7	- 3.9	34.5	- 0.1
Λ-[Co(L-asp)en$_2$]$^+$	38.7	36.5	- 2.2	39.0[*3]	+ 0.3
Λ-[Co(L-glu)en$_2$]$^+$	33.6	30.1	- 3.5	33.7[*4]	+ 0.1

forming the trans(O)-$[\mathrm{Co\ en_2(aaH)_2}]^{3+}$ complex ion, causes the downfield shift of the C-1 carbon resonance, and the Δ_{coord} value has opposite sign to the Δ_{proton} value of the C-1 carbon. The Δ_{coord} value of the C-2 carbon is almost zero, while the Δ_{proton} value of the C-2 carbon is a few ppm. The magnitude of the Δ_{coord} of the C-1 and C-2 carbons can be used to distinguish whether the α-amino-acid in cobalt(III) complex is unidentate or bidentate.

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