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Metal Complexes of Amino Acids. XIV.[1) Carbon-13 NMR of Cobalt(III) Complexes Containing *N*-Substituted Glycines

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Synopsis. The down-field shifts of α-carbons in *N*-alkylglycines, which were caused by the chelation to cobalt(III), were larger than those in *C*-alkylglycines. The down-field shifts of *N*-(carboxymethyl)glycine (ida) and *N*-(2-aminoethyl)glycine (enma) in fac complexes were also larger than those of ida and enma in mer complexes, respectively, and those of the *C*-alkylglycines.

In the previous paper,2) we reported that the chelation of α-amino acids to cobalt(III) ion brigns about down-field changes in ^{13}C NMR chemical shifts of their carboxyl-carbons (C_{oxy}) and α-carbons (C_α). However, references were not made concerning the difference in ^{13}C NMR behavior between α-amino acids containing $-NH_2$ group and those containing –NH–R group. In the present paper, we will describe the difference in the NMR behavior. In addition, we will discuss about the relationship between the coordination forms of the tridentate ligand and the ^{13}C NMR chemical shifts, in connection with the chelation shifts of the α-amino acids containing the –NH–R group.

Experimental

The complexes examined were prepared by the procedures similar to those described in previous papers.2–7)

^{13}C NMR spectra at 22.5 MHz were recorded on a JEOL FX-90Q spectrometer, 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 internal dioxane (δ=67.40).

Table 1. ^{13}C Chemical shifts (ppm) of substituted glycines and their cobalt(III) complexes

Ligand (Structure and abbreviation (Acidic form))		δ $(C_{oxy})^{a)}$	δ_{ch} $(C_{oxy})^{b)}$	Δ_{ch} $(C_{oxy})^{c)}$	δ $(C_\alpha)^{a)}$	δ_{ch} $(C_\alpha)^{b)}$	Δ_{ch} $(C_\alpha)^{c)}$
Glycine $NH_3^+CH_2COOH$, H_2gly)	$[Co(gly)(NH_3)_4]^{2+}$	170.14	186.15	+16.01	40.95	46.65	+5.07
L-Alanine ($NH_3^+CH(CH_3)COOH$, L-H_2ala)	$[Co(L\text{-}ala)(NH_3)_4]^{2+}$	173.02	186.97	+13.95	49.59	54.03	+4.44
α-Aminobutyric acid ($NH_3^+CH(C_2H_5)COOH$, α-H_2abu)	$[Co(\alpha\text{-}abu)(NH_3)_4]^{2+}$	172.38	186.44	+14.06	54.86	59.93	+5.07
Norvaline ($NH_3^+CH(C_3H_7)COOH$, H_2nva)	$[Co(nva)(NH_3)_4]^{2+}$	172.82	186.73	+13.91	53.44	58.13	+4.69
Sarcosine ($(CH_3)NH_2^+CH_2COOH$, H_2sar)	$[Co(sar)(NH_3)_4]^{2+}$	169.40	183.85	+14.45	49.59	57.88	+8.29
N-Ethylglycine ($(C_2H_5)NH_2^+CH_2COOH$, H_2etgly)	$[Co(etgly)(NH_3)_4]^{2+}$	169.60	184.43	+14.83	47.59	54.22	+6.63
N-Propylglycine ($(C_3H_7)NH_2^+CH_2COOH$, H_2prgly)	$[Co(prgly)(NH_3)_4]^{2+}$	169.31	184.39	+15.08	47.98	54.66	+6.68
L-Proline ($NH_2^+(CH_2)_3CHCOOH$, L-H_2pro)	$[Co(L\text{-}pro)(NH_3)_4]^{2+}$	172.24	186.97	+14.73	60.28	65.69	+5.42
L-Hydroxyproline ($NH_2^+CH_2CH(OH)CH_2CHCOOH$, L-$H_2hyp$)	$[Co(L\text{-}hyp)(NH_3)_4]^{2+}$	172.04	186.58	+14.54	58.96	64.47	+5.51
Iminodiacetic acid ($NH_2^+(CH_2COOH)_2$, H_3ida)	$[Co(ida)(NH_3)_3]^+$	169.16	184.68	+15.52	47.88	59.30	+11.42
	u-fac-$[Co(ida)_2]^-$		184.93 184.19	+15.77 +15.03		59.59 57.98	+11.71 +10.10
	s-fac-$[Co(ida)_2]^-$		185.66	+16.50		58.32	+10.44
	mer-$[Co(ida)_2]^-$		184.53 184.34	+15.37 +15.18		57.05 56.91	+9.17 +9.03
	$[Co(glygly)(ida)]^-$		184.19	+15.03		56.32	+8.44
Ethylenediamine-*N*-acetic acid ($NH_3^+(CH_2)_2NH_2^+CH_2COOH$, H_3enma)	$[Co(enma)(NH_3)_3]^{2+}$	169.11	185.17	+16.06	48.56	56.52	+7.96
	trans(O)-$[Co(enma)_2]^+$		185.32	+16.21		55.44	+6.88
	$[Co(glygly)(enma)]$		184.68	+15.57		53.83	+5.27

a) $\delta(C_\alpha)$ and $\alpha(C_{oxy})$: Chemical shifts of C_α and C_{oxy} in the free ligand (in acidic D_2O solution). b) $\delta_{ch}(C_\alpha)$ and $\delta_{ch}(C_{oxy})$: Chemical shifts of C_α and C_{oxy} in the chelated ligand. c) $\Delta_{ch}(C_\alpha)$ and $\Delta_{ch}(C_{oxy})$: $\Delta_{ch}(C_\alpha)=\delta_{ch}(C_\alpha)-\delta(C_\alpha)$ and $\Delta_{ch}(C_{oxy})=\delta_{ch}(C_{oxy})-\delta(C_{oxy})$.

Results and Discussion

The chemical shift changes arising from the chelation of amino acids are listed in Table 1, together with the structures and abbreviations of the ligands. The $\Delta_{ch}(C_\alpha)$ and $\Delta_{ch}(C_{oxy})$ values of *C*-alkylglycines ($NH_2CHRCOOH$) are smaller than those of glycine. This result is consistent with those described in the previous papers.[2,3] That is, the $\Delta_{ch}(C_\alpha)$ values of L-val, L-leu, L-ile, L-ser, L-thr, and L-phe were included in the range +3.8—+5.4 ppm, compared with +5.7 ppm of glycine.

On the other hand, the $\Delta_{ch}(C_\alpha)$ values of *N*-alkylglycines (R–$NHCH_2COOH$) are larger than that of glycine, though the $\Delta_{ch}(C_{oxy})$ values of the *N*-alkylglycines are smaller than that of glycine. The $\Delta_{ch}(C_\alpha)$ values of L-pro and L-hyp, which may belong to *N*-alkyl-*C*-alkylglycines, are intermediate between the $\Delta_{ch}(C_\alpha)$ value of the *N*-alkylglycine and that of the *C*-alkylglycine.

N-(Carboxymethyl)glycine (=iminodiacetic acid; ida) and *N*-(2-aminoethyl)glycine (=ethylenediamine-*N*-acetic acid; enma) containing –NH–R groups are able to coordinate to cobalt(III) in both of meridional (*mer*) and facial (*fac*) forms. It is known that the tridentate ida prefers the fac form to the mer form in both $[Co(ida)(NH_3)_3]^+$ and $[Co(ida)_2]^-$ complexes,[4–7] although recently the *mer*-$[Co(ida)_2]^-$ complex was isolated.[9,10] The $\Delta_{ch}(C_\alpha)$ values of the ida taking the fac form are larger than that of glycine. Similarly, the $\Delta_{ch}(C_\alpha)$ values of the enma, taking the fac form in $[Co(enma)(NH_3)_3]^{2+}$ and *trans(O)*-$[Co(enma)_2]^+$,[8] are larger than that of glycine. One of the important factors which are responsible for the large $\Delta_{ch}(C_\alpha)$ values will be the –NH–R groups of ida and enma, as is suggested by the present result that the $\Delta_{ch}(C_\alpha)$ values of *N*-alkylglycines are larger than that of glycine.

The chemical shifts of cobalt(III) complexes are affected by the anisotropic effect of cobalt(III) and by the trans influence of the coordinating atoms.[12–15] These effects in *mer*-$[Co(ida)_2]^-$ are equal to those in *s-fac*-$[Co(ida)_2]^-$. However, the $\Delta_{ch}(C_\alpha)$ value of *mer*-$[Co(ida)_2]^-$ is smaller than that of *s-fac*-$[Co(ida)_2]^-$. This difference may result from the difference of the geometrical structures of the ida. Similar result was obtained for the complexes containing diethylenetriamine (dien) by Ha *et al.*[16] They pointed out that the ^{13}C NMR spectral pattern of the *mer* forms of dien is distinguishable from the *fac* forms of dien. The carbons attaching to the central –NH– in the *mer* dien were resonated at lower field than those in the *fac* dien, that is, the Δ_{ch} values of the *mer* dien are smaller than those of the *fac* dien. The $\Delta_{ch}(C_\alpha)$ value of $[Co(glygly)(ida)]^-$, which includes a *mer* ida,[11] is also smaller than the $\Delta_{ch}(C_\alpha)$ values of the complexes including the *fac* ida. Similar result was obtained for the enma complexes. That is, the $\Delta_{ch}(C_\alpha)$ value of enma in *mer*-[Co(glygly)(enma)],[11] is smaller than those of the *fac* enma in the other enma complexes (Table 1).

The differences of the $\Delta_{ch}(C_{oxy})$ values among the ligands examined were not so distinct as those of the $\Delta_{ch}(C_\alpha)$ values.

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