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THE COBALT(III) COMPLEXES CONTAINING GLYCYLGLYCINATE AND IMINODIACETATE, N-METHYLIMINODIACETATE, OR ETHYLENEDIAMINEMONOACETATE AS THE MIXED LIGANDS

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The mixed ligand complexes, [Co(glygly)(L)] (L: ida, mida, and enma), have been prepared and their structures were discussed on the basis of the ^1H- and ^{13}C-NMR data. It has been shown that each terdentate ligand L in these complexes coordinates selectively to cobalt(III) in meridional form. Absorption spectra of these complexes are also reported.

Most of previous studies of cobalt(III) complexes with dipeptides have been concerned with the anionic bis-dipeptides series.$^{1)}$ The only report by Browning et al.$^{2)}$ dealt with the cationic mono-dipeptide complexes of the type $[Co(dipeptidate)(L)]^+$ (L: $(NH_3)_3$ and dien). In these complexes with dipeptide as terdentate ligand, the three donor atoms (amino-N, amido-N, and carboxylate-O) of a dipeptide ligand are located in meridional disposition. Diethylenediamine (dien) ligand can adopt both facial (fac) and meridional (mer) dispositions$^{3)}$ in coordinating to metals, but iminodiacetate (ida) ligand adopts preferably fac disposition. It is interesting to investigate the mixed ligand complexes containing dipeptide which adopts preferably mer disposition and another terdentate ligand such as ida. The present communication deals with the characterization of the mixed ligand cobalt(III) complexes containing glygly and ida, mida (N-methyliminodiacetate), or enma (ethylenediaminemonoacetate) as the ligands.

The complexes were prepared by the following methods:

$$(1)\quad [Co(NH_3)_5(H_2O)](ClO_4)_3 + idaH_2 + \text{glycylglycine } (glyglyH_2) \xrightarrow[\text{60°C, 2 h}]{\text{activated charcoal}} [Co(glygly)(ida)]^-$$

$$(2)\quad glyglyH_2 + midaH_2\cdot HCl \xrightarrow[\substack{\text{1) dropwise addition of } CoCl_2 \text{ aq. soln.} \\ \text{2) } PbO_2\text{, 40°C, 1 h}}]{pH \div 9.0} [Co(glygly)(mida)]^-$$

$$(3)\quad glyglyH_2 + enmaH\cdot 2HCl \xrightarrow[\substack{\text{1) dropwise addition of } Co(NO_3)_2 \text{ aq. soln.} \\ \text{2) } PbO_2\text{, 40°C, 1 h}}]{pH \div 9.0} [Co(glygly)(enma)]$$

After filtration of the reaction solution (1), the filtrate was chromatographed on a column containing QAE-Sephadex A-25 anion exchanger (Cl-form). The positive charged and neutral complexes were swept out with water. The adsorbed band was separated into five bands by elution with 0.05 M KCl solution. The eluate of the fourth band (dark gray) was concentrated under reduced pressure. The desired product, K[Co(glygly)(ida)]$^-$, was obtained by adding a mixture of methanol and ethanol to the concentrated solution. The complex was recrystallized from water-ethanol solution. The crystals obtained were dried over $\mathrm{CaCl_2}$ in a desiccator. (Anal. Calcd for $\mathrm{K[Co(glygly)(ida)]\cdot 2.5H_2O}$: C, 23.77; H, 3.99; N, 10.39%. Found: C, 23.62; H, 4.00; N, 10.44%.) The K[Co(glygly)(mida)] complex was obtained from the reaction solution (2) by the same chromatographical separation as that of the ida complex. Since this potassium salt deposited as gelatinous precipitate, it was converted to barium salt to give crystalline product. (Anal. Calcd for $\mathrm{Ba[Co(glygly)(mida)]_2\cdot 9H_2O}$: C, 22.34; H, 4.58; N, 8.68%. Found: C, 22.73; H, 4.73; N, 8.24%.) The neutral complex, [Co(glygly)(enma)], was obtained from the reaction solution (3) by use of both cation- and anion-exchange columns. (Anal. Calcd for $\mathrm{[Co(glygly)(enma)]\cdot 2H_2O}$: C, 28.08; H, 5.60; N, 16.37%. Found: C, 27.92; H, 5.97; N, 16.33%.)

Figure 1 shows the ^{1}H-NMR spectra of the new complexes, which were measured in a weak alkaline $\mathrm{D_2O}$ solution containing DSS as an internal reference. The [Co(glygly)(ida)]$^-$ ion shows two singlet peaks at 4.36 and 3.45 ppm which are assigned to the C- and N-terminal $\mathrm{CH_2}$ resonances of glygly, respectively, by comparison with the ^{1}H-NMR data of the $\mathrm{[Co(glygly)_2]^-}$, $\mathrm{[Co(glygly)(dien)]^+}$, and $\mathrm{[Co(glygly)(NH_3)_3]^+}$ complexes.[1,2] A sharp AB pattern ($\delta_A = 4.20$, $\delta_B = 4.05$ ppm, $J_{gem} = 15.5$ Hz) can be assigned to the $\mathrm{CH_2}$ groups of ida, indicating the equivalence of the two $\mathrm{CH_2}$ groups. The NMR spectrum suggests that the both terdentate ligands in the [Co(glygly)(ida)]$^-$ complex adopt the mer disposition. The ^{1}H-NMR spectrum of the [Co(glygly)(mida)]$^-$ complex (Fig. 1-b) shows a similar pattern to that of the ida complex, except for the appearance of the methyl signal at 3.07 ppm and the overlapping of two kinds of resonance peaks at 4.35 ppm. Here we can assign the overlapped singlet peak at 4.35 ppm and the singlet peak at 3.47 ppm to the C- and N-terminal $\mathrm{CH_2}$ resonances of glygly, respectively, by comparison with the ^{1}H-NMR of the ida complex. An AB pattern ($\delta_A = 4.42$, $\delta_B = 4.02$ ppm, $J_{gem} = 16.5$ Hz) can be assigned to the two $\mathrm{CH_2}$ groups of the mida. Therefore it is suggested that the structure of the mida complex is mer form, too. It is well-known that both ida and mida ligands have a marked tendency to coordinate to metals in fac form. The mer-$\mathrm{K[Co(ida)_2]}$ complex isolated recently by Koine et al.[4] was unstable in an

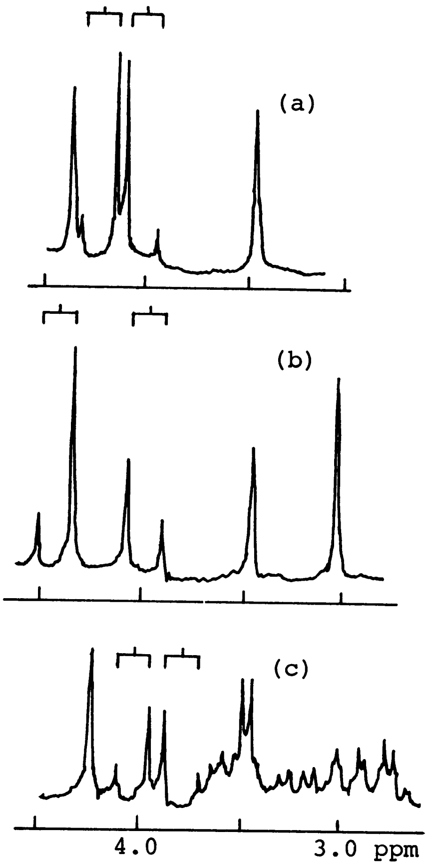

Fig. 1. ^{1}H-NMR spectra of K[Co(glygly)(ida)] (a), $\mathrm{Ba[Co(glygly)(mida)]_2}$ (b), and [Co(glygly)(enma)] (c) in alkaline $\mathrm{D_2O}$

aqueous solution, but the K[Co(glygly)(ida)] and Ba[Co(glygly)(mida)]$_2$ complexes are fairly stable.

In the ^{1}H-NMR spectrum of the [Co(glygly)(enma)] complex (Fig. 1-c), a singlet peak at 4.23 ppm may be assigned to the C-terminal CH$_2$ resonance of glygly, and two peaks at 3.46 and 3.43 ppm which are inner components of an AB pattern may be assigned to the N-terminal CH$_2$ resonance, by comparison with the ida and mida complexes. The resonance pattern of glygly in the [Co(glygly)(enma)] complex is quite similar to that in the [Co(glygly)$_2$]$^-$ complex. In the [Co(glygly)$_2$]$^-$ complex, the resonance of the C-terminal CH$_2$ appears as a sharp singlet, giving no hint of the expected inequivalence, whereas the resonance of the N-terminal CH$_2$ shows an AB pattern.$^{1)}$ An AB pattern ($\delta_A = 3.97$, $\delta_B = 3.79$ ppm, $J_{gem} = 15.5$ Hz) observed for the enma complex may be assigned to the acetate CH$_2$ group of the enma. However, it is difficult to determine the structure of the [Co(glygly)(enma)] complex on the basis of the present ^{1}H-NMR data.

Table 1. ^{13}C-NMR data of glygly complexes

	glygly				ida, mida		
	$-COO^-$	$-\underset{O}{\overset{}{\underset{\|}{C}}}-N$	$-CH_2-$		$-COO^-$	$-CH_2-$	$-CH_3$
[Co(glygly)$_2$]$^-$	188.3	181.0	48.8	48.3			
[Co(glygly)(ida)]$^-$	188.7	181.6	49.2	48.7	185.0	55.6	
[Co(glygly)(mida)]$^-$	188.6	183.1*	48.7	47.8	183.1*	66.1	46.6

* Overlapped signal

The ^{13}C-NMR data of the glygly complexes are listed in Table 1. The spectra were measured relative to external benzene, and the chemical shift values are reported relative to TMS using the relation $\delta_{TMS} = \delta_{benzene} - 128.5$ ppm. In the [Co(glygly)(ida)]$^-$ complex, the resonance peaks at 55.6 and 185.0 ppm which are assigned, respectively, to the methylene and carboxylate carbons of the ida were twice in intensity, compared with the peaks of the methylene and carboxylate carbons of the glygly. This result shows that two acetate groups in the ida are equivalent and that this complex consists of a single isomer with the mer configuration. A similar discussion can be made for the [Co(glygly)(mida)]$^-$ complex. The signal assignments of this complex are shown in Table 1. The ^{13}C-NMR spectrum of the enma complex was not obtained because of its poor solubility in D$_2$O.

In addition to the configurational isomerism, these complexes provide the problem of the conformation-geometrical isomerism arising from the choice of the conformation of ida, mida, and enma ligands. However, our present data are not sufficient to decide the conformation of the coordinated ida, mida, and enma ligands. The possibility of the rapid interconversion between the two conformational isomers may be ignored, because such interconversion requires the rupture of the coordination bond in the case of the mida complex.

Absorption spectra of the glygly complexes are shown in Fig. 2. The Co(III) complexes containing glygly exhibit the intense first d-d bands (log $\varepsilon \geqq 2.2$) relative to those of the amino-acidato Co(III) complexes containing the donor atoms of amino-N and carboxylate-O. It is very interesting that the ida complex exhibits two intense first bands (λ_{max}(log ε): 570 nm (2.28), 466 nm (2.31)). The spectrum of the [Co(glygly)(mida)]$^-$ complex is quite similar to that of the ida complex (λ_{max}(log ε): 578 nm (2.18), 475 nm (2.27)). The first band of the [Co(glygly)(enma)] complex is broad and shows a tendency of splitting. The Yamatera's theory[5)] explains well the first d-d band splitting of the Co(III) complexes containing the N and O donor atoms, but it is difficult to apply this theory to the present glygly complexes. In order to clarify the origin of the abnormal spectra of these glygly complexes, further studies on the peptide complexes are required.

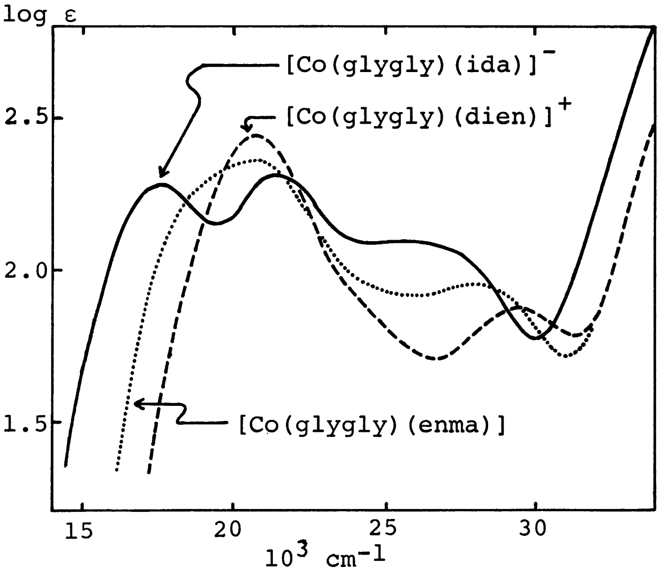

Fig. 2. Absorption spectra of the glygly complexes in water

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