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A Study of Complex Equilibria of Phenylglycine with Nickel(II), Copper(II) and Zinc(II) in Water and in Water—Methanol Solution

Lechosław Łomozik

Faculty of Chemistry, Adam Mickiewicz University, PL-60-780 Poznań, Poland

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The complex equilibria of the systems phenylglycine—nickel(II), copper(II) and zinc(II) in water and in water—methanol solution have been studied by computer analysis of potentiometric data. The mode of coordination has been established by ^{13}C-NMR and IR studies.

[Keywords: Complexes; Copper(II); Nickel(II); Phenylglycine; Zinc(II)]

Gleichgewichtsuntersuchungen der Komplexbildung von Phenylglycin mit Nickel(II), Kupfer(II) und Zink(II) in Wasser und Wasser—Methanol-Lösung

Anhand einer Computer-Analyse von potentiometrischen Daten wurden die Bildungsgleichgewichte in den Systemen Phenylglycin—Nickel(II), Kupfer(II) und Zink(II) untersucht. Der Koordinationstyp wurde mittels ^{13}C-NMR und IR festgestellt. Die Lösungsmittel waren Wasser und Wasser—Methanol.

It was found earlier[1—3] that the substitution of methyl or phenyl groups in the glycine molecule changes considerably the acid-base nature of both functional groups, i.e. the amino and carboxyl group. Consequently (also considering the modified spatial conditions) the complex-forming properties of its derivatives are altered when compared with the glycine molecule. This is particularly manifested in the lower stability of N-phenylglycine complexes[2]. A similar effect of the phenyl group is observed in phenylglycine (the benzene ring substituted at the α-carbon); however, the resulting changes are much less conspicuous. Table 1 presents the dissociation constants of phenylglycine (*PHEN*) and, for comparison, those of glycine and N-

Table 1. *Dissociation constants of phenylglycine and, for comparison, of glycine*[1] *and N-methylglycine*[1] *in water and in water—methanol solution*

Mole Fraction of Methanol	Phenylglycine pK_1	Phenylglycine pK_2	Amino Acids Glycine pK_1	Amino Acids Glycine pK_2	N-Methylglycine pK_1	N-Methylglycine pK_2
0	1.61	9.14	2.40	9.61	2.22	10.05
0.10	1.81	9.10	2.70	9.48	2.44	9.93
0.16	1.99	9.07	2.81	9.46	2.52	9.88
0.23	2.18	9.06	2.99	9.41	2.67	9.81
0.31	2.44	9.05	3.17	9.35	2.82	9.77
0.41	2.72	9.01	3.40	9.30	3.01	9.70

methylglycine in water and water—methanol solution. As in the case of N-phenylglycine (N-*PHEN*), the pK_1 values increase along with the increase of the mole fraction of methanol, whereas the pK_2 values decrease. A change in the dielectric constant of the solvent has a less pronounced effect on N—H bonds of a covalent character than on O—H bonds, where the contribution of electrostatic interaction is higher. The presented results indicate that a change in the pK_1 value is linearly correlated with the reciprocal of the dielectric constant of a solvent. This dependence is also approximately true for pK_2 values; an exact analysis, however, is hindered by the relatively small differences in pK_2 (Table 1). Considering the similar chemical nature of water and methanol molecules the above dependence suggests that the dielectric constant of the solvent, determining its "ionizing power", is a major factor influencing pK values.

A comparison of molecular models indicates that the presence of the phenyl group at the α-carbon has a smaller effect on the conditions for complex bond formation than the presence of two methyl groups in N,N-dimethylglycine (*DMG*). On the other hand, however, the basicity of both functional groups is lower (e.g. in water $pK_1 = 1.61$, $pK_2 = 9.14$ for *PHEN* and $pK_1 = 1.90$, $pK_2 = 9.77$ for *DMG*). It was found that the stabilities of phenylglycine complexes are similar to those of *DMG* complexes, lower than those of N-methylglycine compounds but distinctly higher than those of N-*PHEN* compounds[1].

The complexes formed in the analyzed systems as well as their stability constants are presented in Table 2. Nickel, both in water and water—methanol solvent (50%/50% *v*/*v*), forms only the complexes NiL and NiL_2. In systems with copper, apart from CuL and CuL_2, the occurrence of CuL_2OH in water and CuLOH and CuL_2OH in mixed solvent has been detected. Zinc, apart from ZnL and ZnL_2 compounds, forms in water non-stable ZnHL. In the investigated concentration

Table 2. *Overall stability constants of nickel(II), copper(II), and zinc(II) complexes with phenylglycine in water and in water—methanol solution (50%/50%, v/v)*

Solvent	Metal	Chemical Reaction	log β
H_2O	Ni	$M + L \rightleftharpoons ML$	4.68 (4)
		$M + 2L \rightleftharpoons ML_2$	8.51 (5)
	Cu	$M + L \rightleftharpoons ML$	7.75 (3)
		$M + 2L \rightleftharpoons ML_2$	13.04 (4)
		$M + 2L + H_2O \rightleftharpoons ML_2OH + H^+$	5.70 (9)
	Zn	$M + L \rightleftharpoons ML$	3.07 (4)
		$M + 2L \rightleftharpoons ML_2$	5.86 (6)
		$M + L + H^+ \rightleftharpoons MHL$	9.99 (5)
H_2O/CH_3OH	Ni	$M + L \rightleftharpoons ML$	4.92 (7)
		$M + 2L \rightleftharpoons ML_2$	8.84 (9)
	Cu	$M + L \rightleftharpoons ML$	7.89 (5)
		$M + 2L \rightleftharpoons ML_2$	13.74 (6)
		$M + L + H_2O \rightleftharpoons MLOH + H^+$	0.50 (10)
		$M + 2L + H_2O \rightleftharpoons ML_2OH + H^+$	2.20 (16)
	Zn	$M + L \rightleftharpoons ML$	4.22 (7)
		$M + 2L \rightleftharpoons ML_2$	7.11 (8)

Table 3. ^{13}C-*NMR chemical shifts of phenyglycine and its systems with* Ni^{2+} *and* Zn^{2+} *[ppm]*

	D_2O				CD_3OD/D_2O; 50%/50%, *v/v*			
System	*pD*	CH	COO	Ring	*pD*	CH	COO	Ring
FEN 0.025 *M*	6.4	59.24	173.99	134.83	6.4	59.37	173.21	135.29
				130.33				129.93
				130.20				129.92
				128.69				128.56
FEN 0.025 *M* + Ni^{2+} (5 : 1)	6.4	59.99	175.13		6.4	59.89	174.34	
FEN 0.025 *M* + Zn^{2+} (4 : 1)	7.4	59.24	174.98		7.7	59.83	175.95	

range the protonated complex combines with only approximately 4% of the metal. This has been determined by computing the metal distribution among the individual forms of complex compounds by means of the HALTAFALL program[4]. Based on an analysis of this distribution it has been determined that the formation of both types of copper hydroxo complexes proceeds similarly as in N-methylglycine systems, i.e.

$$\mathrm{Cu}L_2 + \mathrm{OH}^- \rightleftharpoons \mathrm{Cu}L\mathrm{OH} + L \text{ and } \mathrm{Cu}L_2 + \mathrm{OH}^- \rightleftharpoons \mathrm{Cu}L_2\mathrm{OH}.$$

However, in the discussed system CuLOH is partially formed also according to the scheme CuL + $\mathrm{OH}^- \rightleftharpoons$ CuLOH. The precipitation of copper hydroxide at high *pH* values proves that an OH^- ion may compete with the ligand. It can be expected that the intermediate forms between complexes of the ML_x type and the metal hydroxide are hydroxo complexes of the type ML_x(OH). It is also worth noting here that there are differences in complexing ability depending on the solvent. As a result of a change in the acid—base nature of functional groups as well as of differences in the solvation effect of a solvent, the OH^- ion may be added to CuL_2 or it can substitute one of the ligands of this form.

The distribution of protons in a phenylglycine molecule makes it impossible to draw conclusions about the coordination mode from an analysis of ^{1}H-NMR signal changes. Consequently the ^{13}C-NMR technique has been employed. The changes in chemical shifts resulting from the complexing of Zn^{2+} and Ni^{2+} ions are presented in Table 3. In nickel compounds, two functional amino acid groups participate in the complexing process. The chemical shifts observed in ^{13}C-NMR spectra are an averaged value reflecting the ligand exchanges between the coordination site and the solution[5]. Consequently there were only minor signal changes from the methin carbon at the amino group. This suggests a similar situation as in the case of alkyl derivatives of glycine[1], i.e. the carboxyl group of the ligand played a decisive role in the formation of bonds. In the *PHEN*/Zn system in $\mathrm{D_2O}$ only the band connected with carboxyl carbon undergoes a shift (which indicates that only the carboxyl group takes part in the coordination). In the mixed solvent a bidental coordination has been detected. The above conclusions are supported by the occurrence of the ZnHL complex (however, only in the water system), which is in agreement with the situation where the ligand reacts unidentally with the participation of oxygen from the carboxyl group only. In a similar situation where only the $-\mathrm{COO}^-$ group participates in the complexing in the system N-*PHEN*/Zn^2, the presence of MHL has not been detected. In the case of N-phenylglycine, however, the presence of the phenyl group at nitrogen results in a distinct lowering of the pK_2 value ($pK_2 = 4.83$ for N-*PHEN*, and $pK_2 = 9.05$ for *PHEN* in $\mathrm{CH_3/OH/H_2O}$, 50%/50%, *v*/*v*), in other words a proton from the amino group becomes much more labile and the proton—nitrogen interaction is additionally weakened by the presence of metal ion in the complex molecule[1]. Thus only a form with de-protonated nitrogen

R—NH—CH_2COO—Zn is formed in the N-*PHEN*/Zn system. In the case of phenylglycine (the pK_2 value of which is much higher, $pK_2 = 9.14$ in H_2O), the compound $\overset{+}{N}H_3CH(R)$—COO—Zn may be formed. With rising *pH* it converts into NH_2—CH(R)—COO—Zn. The different coordination type in zinc systems is confirmed by IR spectra. An analysis of positional changes of the asymmetric stretching vibrations band of the carboxyl group has confirmed that in all systems the $-COO^-$ group takes part in the coordination. However, in the *PHEN*/Zn system in water a much clearer change is observed (from 1 627 cm^{-2} for *PHEN* alone to 1 606 cm^{-1} for the system *PHEN*/Zn; metal ligand ratio 1 : 1, ligand concentration 0.02 *M*, $pD = 7.8$). This suggests an analogous coordination mode as in the N-*PHEN*/Zn system[2], i.e. with the participation of both carboxyl group oxygen atoms. Thus the lowering of the stability constants of the phenylglycine complexes with zinc (in H_2O) is less significant than should be expected in the case of the participation of only one oxygen atom from $-COO^-$ in the coordination, when compared with the *PHEN*/Ni system. This confirms conclusions about the structure of the *PHEN*/Zn compound presented above.

It is characteristic that the tendencies toward bond formation with the carboxyl group are only exhibited by zinc. According to the HSAB theory[6,7], Zn^{2+} is the hardest acid among the examined cations and its relative tendency toward bond formation with the carboxyl group (which is a harder base than $-NH_2$) is the strongest.

Determining the exact values of ^{13}C-NMR chemical shifts for the *PHEN*/Cu system has proved impossible due to a strong paramagnetic activity of the Cu^{2+} cations. However, a comparison of stability constants of complexes in such systems as sarcosine/Cu, Ni and N,N-dimethylglycine/Cu, Ni[1–3] and phenylglycine/Cu, Ni clearly indicates a similar coordination type for both metal ions. It can thus be assumed that both functional groups of phenylglycine participate in the complexing within these systems.

To determine all forms in the analyzed systems as well as their stability constants a computer analysis of potentiometric titration results was carried out by using the programs SCOGS[8] and MINIQUAD[9]. In order to determine hydrogen ion activity based on *pH* readings in mixed solvent, the *Van Uitert* method was used[10]. The conditions of the experiments have been presented earlier[1–3]. ^{13}C-NMR spectra were recorded on the JEOL Fx 90Q FT NMR spectrometer with dioxan as the internal standard. Positions of signals with respect to *TMS* are given in Table 3. In the *pD* range close to the neutral medium in which the study was carried out, positions of ^{13}C-NMR phenylglycine signals were not influenced by the hydrogen ion concentration. The values of *pH* readings in D_2O and CD_3OD/D_2O solutions were corrected according to the formula $pD = pH + 0.40$[11].

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