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Nickel(II), Copper(II) and Zinc(II) Complexes with *N*-Phenylglycine in Water—Methanol Solution

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The complex equilibria of the Ni(II), Cu(II), and Zn(II) complexes with *N*-phenylglycine have been studied by computer analysis of potentiometric data. The mode of coordination has been established by ^{1}H NMR and IR studies.

[Keywords: Complexes, Copper(II), Nickel(II), N-Phenylglycine, Zinc(II)]

Nickel(II), Kupfer(II) und Zink(II)-Komplexe mit N-Phenylglycin in Wasser—Methanol-Lösung

Anhand der Computer-Analyse von potentiometrischen Daten wurden die Bildungsgleichgewichte von Nickel(II), Kupfer(II) und Zinc(II)-Komplexen mit *N*-Phenylglycin untersucht. Zur Bestätigung des Koordinationstyps wurden ^{1}H-NMR- und IR-Messungen vorgenommen.

The presence of a substituent in an amino acid molecule modifies the complex-forming properties of the ligand. These changes result mainly from differences in the acid—base nature of the amino acid (basicity of both functional groups) as well as from changes in steric conditions. In the case of *N*-phenylglycine (*N-PHEN*), the substitution of an acceptor phenyl group at nitrogen leads to a clear decrease in the basicity of amino group. (A considerable reduction in pK_2 value as compared with glycine.) This results both from an inductive effect as well as from a resonance effect.

Dissociation constants of *N*-phenylglycine and—for comparison—of non-substituted glycine and *N*-methylglycine in a water—methanol are given in Table 1. Poor solubility of *N-PHEN* did not allow to carry out accurate measurements of the dissociation constants in water.

Moreover, a decrease is also observed in the pK_1 value (corresponding to the dissociation of a carboxyl group proton) in comparison with glycine and its *N*-alkyl derivatives[1] (Table 1).

It is worth to add that a similar effect of phenyl group interaction occurs also in phenylglycine[1], though the range of the change observed is considerably smaller. The fact that the benzene ring (known for its acceptor properties) is substituted at the α-carbon in the case of phenylglycine causes a reduction of the pK_2 value, equal only to about 0.4 pK units (as compared with glycine) and of the pK_2 value to about 0.8 pK units. However, also in the case of the latter value it does not reach the level of the change observed for *N*-phenylglycine. The pK_1 values listed in Table 1 show a linear dependence on the reciprocal of the dielectric constant of a solvent. The values of pK_2 also obey approximately the linear dependence.

Table 2 shows the stability constants of the *N-PHEN* complexes with Ni, Cu and Zn in water—methanol solution (50%/50% *v*/*v*).

Nickel forms complexes of types NiL and NiL_2 with N-phenylglycine. The successive stability constants K_1 and K_2 are by about two orders of magnitude smaller than in the case of *N*-methylglycine[1]. NiLOH has been also found in the system.

In the system *N-PHEN*/Cu the presence of CuL, CuL_2 and CuLOH has been established. The stability of the copper complexes is also markedly reduced as compared with compounds of glycine and its methyl derivatives. For instance, stability constants of compounds CuL and CuL_2 are smaller, as compared with *N*-methylglycine[1], by 3.8 and 2.9 pK units, respectively.

The analysis of steric models suggests that steric reasons play an insignificant role in the reaction of *N*-phenylglycine complex formation. Thus the decrease in stability of the compounds results mainly from changes in basicities of amino and carboxyl groups due to the presence of a phenyl group at the nitrogen atom.

Unexpected results have been obtained for the system *N-PHEN*/Zn. Computer analysis of potentiometric titration data revealed that—in addition to ZnLOH—only ZnL_2 is formed, whereas ZnL is absent (at least to small amount for detection). Therefore the reaction does not occur step by step; the Zn^{2+} cation reacts simultaneously (or nearly simultaneously) with two L^- anions.

A distinct type of interaction between zinc and *N*-phenylglycine is confirmed by ^{1}H-NMR data. In the spectrum of the pure ligand there are two signals: at 3.90 ppm a singlet corresponding to methylene protons and at 6.69–7.53 ppm the phenyl protons (type AB_2X_2). The presence of Zn^{2+} ions has no influence on the latter band but the $-CH_2-$ signal is shifted to 3.57 ppm. This indicates that only the carboxyl group of the

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

Mole fraction of methanol	*N*-Phenyl-glycine		Amino acids Glycine		*N*-Methyl-glycine	
	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
0.10	1.78	4.95	2.70	9.48	2.44	9.93
0.16	1.85	4.93	2.81	9.46	2.52	9.88
0.23	1.92	4.89	2.93	9.41	2.67	9.81
0.31	2.02	4.83	3.17	9.35	2.82	9.77
0.41	2.10	4.80	3.40	9.30	3.01	9.70

Table 2. *Overall stability constants of nickel(II), copper(II), and zinc(II) complexes with N-phenylglycine in water—methanol (50%/50% v/v), mole fraction = 0.31*

Metal	Chemical reaction	log β
Ni	$M + L \rightleftharpoons ML$	3.02 (6)
	$M + 2L \rightleftharpoons ML_2$	5.87 (6)
	$M + L + H_2O \rightleftharpoons MLOH + H^+$	− 4.08 (9)
Cu	$M + L \rightleftharpoons ML$	4.45 (5)
	$M + 2L \rightleftharpoons ML_2$	8.34 (7)
	$M + L + H_2O \rightleftharpoons MLOH + H^+$	− 0.72 (11)
Zn	$M + 2L \rightleftharpoons ML_2$	4.43 (9)
	$M + L + H_2O \rightleftharpoons MLOH + H^+$	− 6.02 (13)

ligand takes part in the coordination. As a result of the proton exchange in CD_3OD/D_2O (as well as of the effect of the quadrupole moment of the nitrogen nucleus) the $-\overset{+}{N}H_2-$ protons are not suited to supply any additional information on the coordination mode. NMR and IR studies of nickel and copper complexes suggest a participation of both amino and carboxyl groups of the ligand in coordinating these metals. In the case of IR studies of the system *N-PHEN*/Zn a considerable shift (compared with the broader band of the ligand itself) towards lower frequencies is observed for the band originated from asymmetric stretching vibrations of the —COO group. This indicates a symmetric structure of the carboxyl group (smaller differences in frequencies of symmetric and asymmetric vibrations)[2]; therefore contribution of both oxygen atoms to the complex formation. The occurrence of a shift towards shorter waves in the case of copper and nickel complexes—where amino and carboxyl group take part in the coordination—provides additional support.

Identification of complex species and determination of stability constants was done by means of a computer analysis of potentiometric titration data; the programs SCOGS[3] and MINIQUAD[4] were used. Calculations were performed on a computer RIAD-32. Potentiometric titrations were carried out by using the *pH*-meter Radiometer PHM-26 with an electrode GK 2401 C as well as an autoburette ABU-1 and a titrator TTT 11. Titration conditions were as follows: temperature 21 ± 1 °C, argon atmosphere, ionic strength 0.1 ($NaClO_4$). The absolute calibration factor U_H^0 has been used to determine the hydrogen ion activity from *pH* readings in the water—methanol solvent[5]. Concentrations of *N*-phenylglycine (Fluka, Switzerland) were 0.005 *M* or 0.01 *M*, whereas those of metals ranged between 0 and 0.005 *M*. IR spectra of compounds dissolved in D_2O/CD_3OD (50%/50% *v/v*) were recorded by using a Perkin-Elmer Model 180 spectrophotometer and CaF_2 cells. Measurements of ^1H NMR spectra in D_2O/CD_3OD (50%/50% *v/v*) were carried out on the spectrometers Varian EM-360 and BS-467 Tesla, using *DSS* as an internal standard.

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