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Effect of pH on Copper (II) Chelate with L-Histidine According to ESR Spectra Data

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Chelation of copper (II) with L-histidine at different metal/ligand ratio and pH is investigated by means of ESR-spectroscopy. Structural characteristics of 1:1 and 1:2 composition chelates are determined by means of the spin matrix method, also the pH effect on the chelate structure is deduced.

Copper chelates with amino acids are of great interest as models of metal compounds with proteins, playing a principal part in human vital activity. The interest is backed up by the present information on copper (II) compounds with α-aminoacids as biologically active substance stabilizing different organism functions.

The goal of the work is to investigate the structure of copper (II) with L-histidine compositions. A number of contradictory data exist in literature on the pH effect on the character of the metallic ion bonding with a ligand. IR-spectrometric data [1] show that at lower pH Cu (II) ion bonds with the carboxyl oxygen. At higher pH a heptary chelate ring is proven to form, where the second donor atom is the nitrogen of the imidazole ring. Analysis of the chelate crystal structure, which crystallizes at pH 3.7, has shown that histidine molecules coordinate via the amino nitrogen and carboxy oxygen, both atoms are in the imidazole group protonated and do not participate in chelation.

We have investigated the effect of pH upon structural characteristics of chelates, determined by ESR-spectroscopy.

Figures 1 and 2 show spectra of copper (II) – histidine systems with different ratios of concentrations of the aminoacid (C_L) and copper (II) (C_M) at different pH. It is seen from the analysis that chelation of the 1:1 chelates already takes place at pH 2, the evidence of which is the presence of four lines of superfine structure of ^{63,65}Cu nuclei with $I=3/2$. At pH $\geq$ 3 and with increase of the ligand concentration one more signal appears in the spectrum with $g \approx 2{,}11$-$2{,}12$, which belongs to the 1:2 composition chelate. Further increase of pH results in growth of the 1:2 chelate signal intensity and apparent appearance of other components of hyperfine coupling structure (see Fig. 2).

The spectra of the two chelates due to closeness of g-factors and enough big hyperfine coupling constants overlap, the lines of the $[\mathrm{CuL}]^+$ chelate spectrum with increase of C_L change the dislocation due to $[\mathrm{CuL_2}]$ chelate signal overlapping.

In order to determine spin-Hamiltionian parameters, stability constants (K_1, K_2) and average lifetimes (τ_{21}, τ_{10}) for the chelates more precisely, an iterative adjustment procedure

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was applied by a minimization criterion of rms error between the experimental and theoretical spectra, the latter built by means of the spin matrix density method [3, 4].

Presenting the below equilibrium

$$Cu^{2+} + 2L^- \Leftrightarrow [CuL]^+ + L^- \Leftrightarrow [CuL_2] \tag{1}$$

as

$$\rho_0 \Leftrightarrow \rho_1 \Leftrightarrow \rho_2 \tag{2}$$

(where ρ_0, ρ_1, ρ_2, are density spin matrices, corresponding to conditions Cu^{2+} , $[CuL]^+$, $[CuL_2]$ respectively), we obtain the system of modified Liouville equations for the case of slow passing through the resonance:

$$\begin{aligned} &\frac{i}{\hbar}\left[\hat{H}_0, \rho_0\right] - \frac{\rho_0}{T_2^0} + \frac{\rho_1 - \rho_0}{\tau_{01}} = 0 \\ &\frac{i}{\hbar}\left[\hat{H}_1, \rho_1\right] + \rho_1 R_1 + \frac{\rho_0 - \rho_1}{\tau_{10}} + \frac{\rho_2 - \rho_1}{\tau_{12}} = 0 \\ &\frac{i}{\hbar}\left[\hat{H}_2, \rho_2\right] + \rho_2 R_2 + \frac{\rho_1 - \rho_2}{\tau_{21}} = 0 \end{aligned} \tag{3}$$

where $\hat{H}_0$, $\hat{H}_1$, $\hat{H}_2$ are spin-Hamiltonians for Cu^{2+}, CuL^+ and CuL_2 conditions, R_1 and R_2 are relaxation matrices for CuL^+ and CuL_2 conditions, the elements of which depend upon the values of the nucleus spin and are determined by the Kivelson equation [5]:

$$R^{ii} = \alpha + \beta m_i + \gamma m_i^2 + \ldots \tag{4}$$

The form of the ESR spectrum line is determined by the below expression:

$$Y(H) = Im\,(p_0 Sp(\rho_0 S^+) + p_1 Sp(\rho_1 S^+) + p_2 Sp(\rho_2 S^+)) \tag{5}$$

In the course of the iterative adjustment procedure – in order to improve accuracy – several spectra were treated simultaneously, obtained at the same pH and different metal ion – ligand concentration ratios.

Table 1 shows the resulting data of the processing (*1* index marks $[CuL]^+$ chelate parameters, *2* corresponds to the $[CuL_2]$ ones).

Table .

Structural parameters of copper (II) – histidine chelate parameters.

pH	α_1. $10^8$1/c	α_2. $10^8$1/c	A_1. mT	A_2. mT	g_1	g_2
2.0	7.3±0.2	7.2±0.2	5.6±0.2	7.4±0.3	2.152±0.001	2.120±0.002
2.5	7.5±0.2	7.4±0.2	5.7±0.2	7.4±0.3	2.150±0.001	2.118±0.002
3.0	7.6±0.2	7.5±0.2	5.8±0.2	7.4±0.3	2.150±0.001	2.116±0.002
3.5	7.5±0.2	7.5±0.2	5.7±0.2	7.3±0.3	2.150±0.001	2.117±0.002
4.0	7.5±0.2	7.5±0.2	5.6±0.2	7.2±0.2	2.150±0.001	2.115±0.002
4.5	7.8±0.2	8.1±0.2	4.5±0.2	7.0±0.2	2.148±0.001	2.12±0.002
5.0	7.9±0.2	8.2±0.2	4.5±0.2	7.0±0.2	2.148±0.001	2.112±0.002
5.5	8.0±0.2	8.1±0.2	4.6±0.2	7.0±0.2	2.148±0.001	2.111±0.002

The change of parameters, depending on the structure of a chelate at pH increase, allows us to make a supposition about the change of the copper ion and histidine coordination character, i.e. the chelation takes place with additional coordination of the copper ion with the nitrogen of the imidazole ring at lower pH, and bonding with the amino nitrogen at pH > 4.

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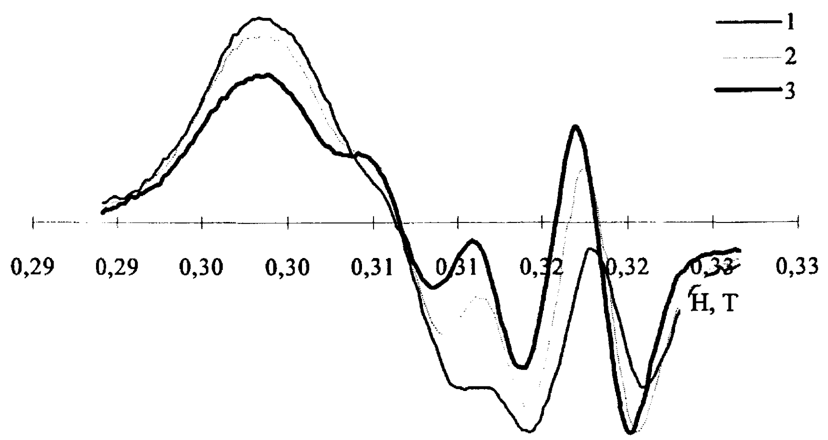

Figure 1. ESR spectra for the solutions under investigation at pH 2 and ratio C_L:C_M = 1 (1), 2 (2), 4 (3).

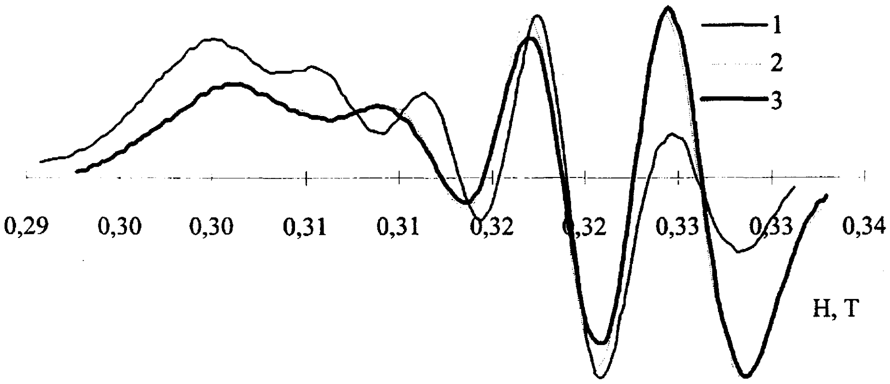

Figure 2. ESR spectra for the solutions under investigation at pH 4 and ratio C_L:C_M = 1 (1), 2 (2), 3 (3).