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ON THE STRUCTURE OF COPPER(II) COORDINATION COMPOUNDS WITH L-HISTIDINE

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Quantum chemical calculations are performed for the spatial and electron structure of complex compounds of L-histidine and its ionized forms with copper(II) for a variety of compositions within the density functional theory (DFT) using the B3LYP functional and 6-311G(*d*) basis. The solvent (water) is considered within the PCM approximation. EPR spectroscopy is used to study the equilibrium in the copper(II)–L-histidine system in an aqueous solution at pH 2–11. A comparison between the theoretical calculations and the EPR spectra suggests the following geometry for the coordination environment of the copper(II) ion in the complex compounds: CuHLL – square-planar coordination; CuL_2, CuHLL′, and CuLL′ – distorted square pyramid; and CuL'_2 – octahedral environment.

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INTRODUCTION

Although the complexation of copper(II) ions with histidine is investigated in a large body of literature [1-5], the question about coordination modes of the amino acid remains debatable. The fact that the histidine molecule has several donor groups defines the various patterns of bonding with the metal ion, which depend on the conditions of the complexation reaction. In this respect, it is of interest to consider not only binary complexes [6] but also mixed ligand ones [7], including those involving peptides [8] and other polydentate ligands [9].

Despite much available data [10], this topic remains important and relevant [11]. For instance, there is interest in a quantum chemical calculation and theoretical explanation of the structure and composition of the resulting complex forms and in finding a correlation between the theory and the existing experimental data.

Previously, we showed [12] that the use of the EPR method allows not only the identification of parameters underlying the thermodynamic stability of the complexes but also the prediction of their structural characteristics. In our previous work [13], we looked for parameters of complex compounds by using computer simulations of EPR spectra of binary systems containing Cu(II) and the ligand at different pH and metal/ligand ratios. This approach allowed us to detect the presence of certain forms of complexes forming in solution and determine their thermodynamic and structural parameters.

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The aim of this study is to apply quantum chemical modelling methods to assess the structure and relative stability of isomeric forms of Cu(II) complexes with L-histidine and compare the calculated results with EPR spectroscopy data.

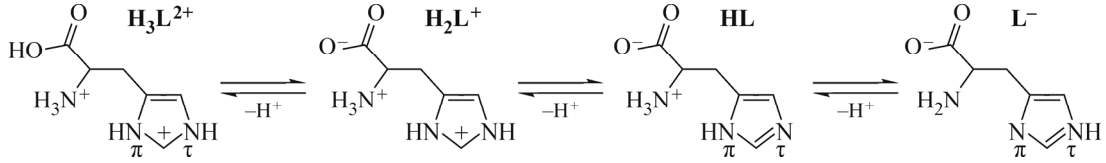
EXPERIMENTAL

We used $Cu(NO_3)_2$ obtained by dissolving a weighed portion of metallic copper in nitric acid and L-histidine hydrochloride. All the chemicals were analytical-grade reagents. 1M KNO_3 was used to maintain a constant ionic strength. pH was measured with an EV-74 ionomer. EPR spectra were recorded using a Radiopan SE-X 2543 EPR spectrometer. The EPR spectra were processed by the technique described in [14].

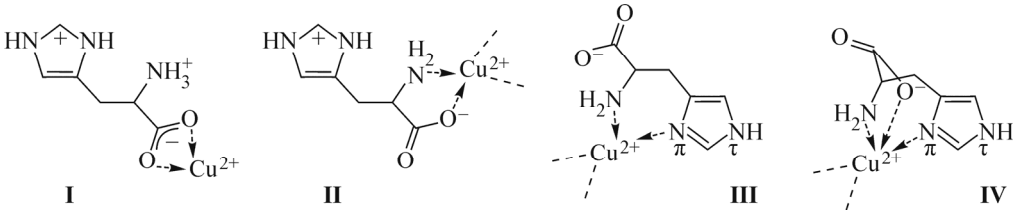
The quantum chemical calculations were made in Gaussian′09 within the density functional theory (DFT) using the B3LYP hybrid exchange–correlation potential in the 6-311G(*d*) basis. The geometry of the molecules was optimized with respect to all the coordinates without imposing any symmetry constraints. In calculating the ionized and neutral forms of L-histidine and complex compounds, we considered the effects of the solvent within the polarized continuum model (PCM). The solvent (water) was described using the standard parameters integrated into Gaussian′09. All the minima on the potential energy surface (PES) were characterized by calculating normal vibrations. The relative energies of the isomeric forms are corrected for the zero-point energy (ZPE).

RESULTS AND DISCUSSION

Based on the published data [2], equilibria in a free ligand (L-histidine) solution can be written as follows



Based on this scheme, L-histidine can form, as a potentially tridentate ligand, coordination bonds through three donor groups: the carboxyl group, the amino group, and the imidazole group. Thus, the main coordination modes of L-histidine to the copper(II) ion follow the carboxyl group coordination scheme (I), carboxyl–amino group scheme (glycine-like coordination (II)), and amino and imidazole groups (histamine-like coordination (III)). The ligand can also be coordinated through three donor centers (IV).



If we consider the data on deprotonation constants [2], then at low pH (of about 3-4) there can be complex compounds in which the metal ion is coordinated through the deprotonated carboxyl group, forming an unstable four-member ring with the complexing ion. At pH above 6, complexation can occur through the imidazole nitrogen atom of histidine. Joint coordination through the imidazole nitrogen atom and other donor groups, i.e., the carboxyl and amino groups, leads to the formation of, respectively, a thermodynamically unstable seven-member ring and a sufficiently stable six-member ring. It is also possible that there are complex compounds with coordination through the carboxyl group and amino group with the formation of a five-membered chelate ring, known for its stability. At pH above 9, the proton comes off the amino group of the ligand.

Nonetheless, this theory, however attractive it may seem, does not reflect the real situation because of the important role played by the thermodynamics of the processes, particularly, the formation of chelates, and due to some other factors,

such as the metal–ligand bonding force (which indirectly defines the stability constants of the complexes being formed), stoichiometry of the complex forms, entropy of the process, and ligand field stabilization energy.

Calculation of the geometry of the complexes. The presence of two mobile protons and five donor centers combined with the flexibility of the propionic aliphatic chain generates a great diversity of possible tautomeric and conformer forms of L-histidine and its protonated and deprotonated ions. A substantial contribution to the stability of the isomers, in addition to the basicity of the donor center, also comes from the arising intramolecular hydrogen bonds (IHBs). The DFT calculation with and without reference (in the PCM approximation) to the effects of the medium on the structure of isomers of molecular and singly charged forms of L-histidine gives the following results (Fig. 1 shows the structure of some of the most stable isomers among all those possible; Table 1 shows the total energies and relative stabilities of isomers of histidine (**HL**) and its protonated ($\mathbf{H_2L^+}$) and deprotonated forms ($\mathbf{L^-}$).

As is evident from the data, there is a considerable difference in the nature of the particles and their relative stability in solution and in vacuum. Thus, for the protonated and neutral forms of L-histidine in an aqueous medium, the most stable ones are the zwitterion isomers $\mathbf{H_2L^+}$ (**3**) and **HL** (**5**) with a deprotonated carboxyl group, which are stabilized by a pair of IHBs ($N_{amine}H\cdots O$ and $N_{imide}H\cdots O$) and ($N_{amm}H\cdots O$ and $N_{amm}H\cdots N_{imide}$), respectively. It should be noted, if the solvent is left out of consideration, the zwitterion structures are either heavily destabilized (see **HL** (**5**)) or not consistent with the PES minima. An attempt to optimize the geometry of the isomers $\mathbf{H_2L^+}$ (**3**) and **HL** (**3**) revealed a barrier-free transfer of the proton from the ammonium group to the carboxyl one with the formation of the isomers $\mathbf{H_2L^+}$ (**2**) or **HL** (**4**), respectively. The structure of $\mathbf{H_2L^+}$ (**2**) corresponds to a global minimum among the monocationic forms in the gaseous phase, being considerably more stable than $\mathbf{H_2L^+}$ (**1**), likely due to the better delocalization of the positive charge in the imidazole fragment. In an aqueous solution, the isomers $\mathbf{H_2L^+}$ (**2**) and $\mathbf{H_2L^+}$ (**3**) differ in stability by less than 1 kcal/mol in favour of the latter. In the gaseous phase, the three neutral isomers **HL** (**1**), **HL** (**2**), and **HL** (**4**) are very close in stability. The difference in relative stability becomes slightly larger in moving to an aqueous solution, and the stability sequence of the isomers changes completely. Thus, **HL** (**2**), the most stable one in vacuum, becomes one of the least stable isomers after considering the solvent.

As shown by the results of a search of the Cambridge Structural Database [15], zwitterion structures are typically preferred not only in solution but also in the crystal state both for the neutral [16, 17] and monoprotonated forms of L-histidine [18-20].

In the case of the monoanionic form, the much greater stability of the isomer $\mathbf{L^-}$ (**2**) is due to the different basicity of the N_π and N_τ nitrogen atoms in the imidazole ring and the presence of the $N_{imide}H\cdots N_{am}$ IHBs. In an aqueous solution, this isomer is 2.02 kcal/mol more stable than $\mathbf{L^-}$ (**1**).

TABLE 1. Total Energy With Zero-Point Energy (E, a.u.) and Relative Stability (ΔE, kcal/mol) of Isomeric Ligand Forms

Ligand form	Vacuum		Water	
	E+ZPE, a.u.	ΔE, kcal/mol	E_{PCM}+ZPE, a.u.	ΔE, kcal/mol
H_2L^+ (**1**)	–549.27885	8.33	–549.20016	2.38
H_2L^+ (**2**)	–549.29213	0	–549.20311	0.52
H_2L^+ (**3**)	–	–	–549.20394	0
HL (**1**)	–548.74148	0.37	–548.76302	0.19
HL (**2**)	–548.74207	0	–548.76037	1.85
HL (**3**)	–	–	–548.76015	1.99
HL (**4**)	–548.74181	0.16	–548.76120	1.34
HL (**5**)	–548.72672	9.63	–548.76333	0
L^- (**1**)	–548.33857	13.77	–548.31595	2.02
L^- (**2**)	–548.36051	0	–548.31918	0

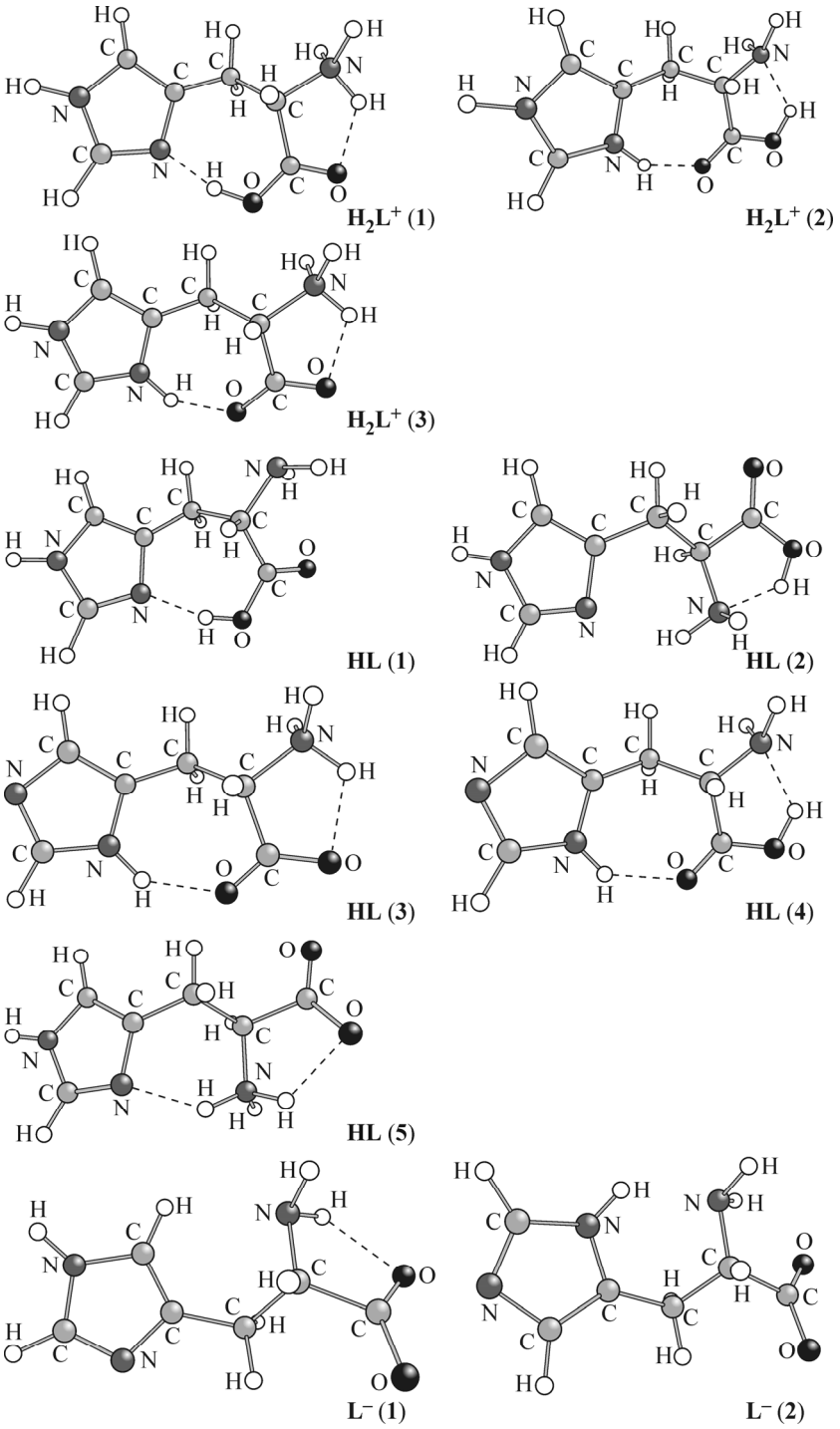


Fig. 1. Structure of isomeric forms of the neutral (**HL**), protonated ($\mathbf{H_2L^+}$), and deprotonated $\mathbf{L^-}$ forms of L-histidine.

Thus, the calculated results are consistent with the previously suggested sequence for the deprotonation of the L-histidine cation: the proton of the imidazoline fragment is the first to split off, followed by the proton of the ammonium group (see the scheme above); however, for a few cations and neutral isomers of histidine, the difference in stability is very low, suggesting the possibility of an equilibrium between them.

The results of experimental studies show that in solution there is a vast system of equilibria including, *inter alia*, several 1:1 complex compounds. Fig. 2 shows the optimization results for the geometry of M:L (1:1) copper complexes with

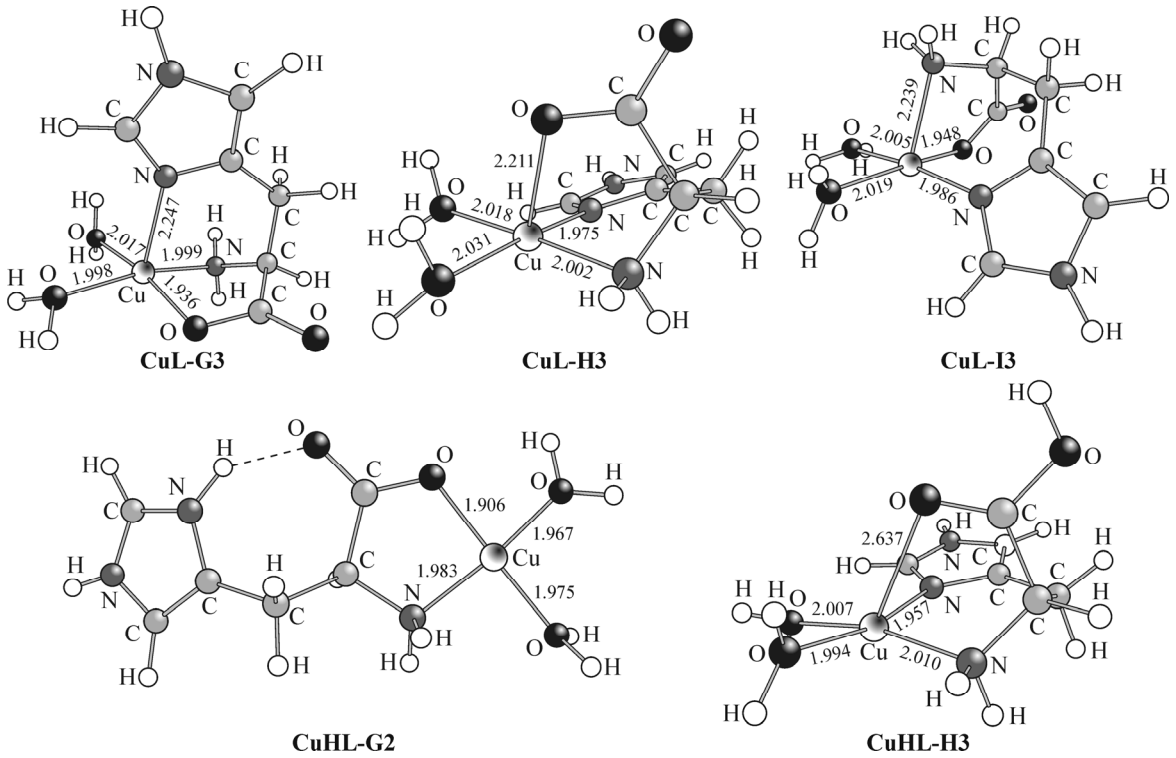


Fig. 2. Structure of isomeric forms of M:L (1:1) complexes with neutral and monoanionic ligand forms.

neutral and protonated forms of histidine. Free positions in the coordination sphere of the copper(II) ion were filled with water molecules.

The degree of histidine protonation affects the possible denticity of the ligand in complexes with copper(II) ions. Evidently, $\mathbf{H_2L^+}$ can have no more than a bidentate function, but **HL** and $\mathbf{L^-}$ can have both bi- and tridentate coordination. In the latter case, three donor centers are involved in the complexation: the oxygen atom of the carboxyl group and the nitrogen atoms of the amino and 2-imidazole fragment. Owing to a considerable static Jahn–Teller effect, which is typical of the copper ion with the d^9 electron configuration and the spatial arrangement of the donor atoms, in this case, two coordination bonds (lying in the equatorial plane of the coordination sphere) with the copper ion have a standard length and the third bond (in the axial position) is extended. This gives rise to three different structural isomers shown in Fig. 2, each of which corresponds to a minimum on the PES: **CuL-G3** (glycine-like coordination (G); the oxygen atoms of the carboxyl group and the nitrogen atoms of the amino group are in the equatorial position; the nitrogen atom of the imidazole fragment is in the axial position), **CuL-H3** (histamine-like coordination (H); the nitrogen atoms of the amino group and imidazole ring are in the equatorial position; the oxygen atom of the carboxyl group is in the axial position), and **CuL-I3** (the nitrogen atoms of the imidazole ring (I) are in an equatorial position; the amino group is in the axial position). The digit in the designations of the isomers shows the denticity of the ligand in the complex.

As is evident from Fig. 2, all the three isomers have a structure close to a square pyramid. The average changes in the length of the coordination bonds in the equatorial and axial positions are 0.24, 0.27, and 0.27 Å for N_{am}, N_{im}, and O_{carb}, respectively. The calculated results for the total energy of the isomeric forms of the M:L (1:1) complex with monodeprotonated L-histidine in an aqueous solution (Table 2) show that the most stable isomer is **CuL-G3**, followed by **CuL-I3** (the difference in stability is 1.69 kcal/mol), and the least stable one is **CuL-H3** (by 2.66 kcal/mol relative to **CuL-G3**). The isomers with a bidentate coordination of the L-histidine anion are destabilized relative to the complexes with a tridentate coordination.

The transition to the neutral HL ligand due to the protonation of the **CuL–G3**, **CuL-H3**, and **CuL-I3** complexes through the noncoordinated oxygen atom of the carboxyl group is accompanied by their transformation into a single stable

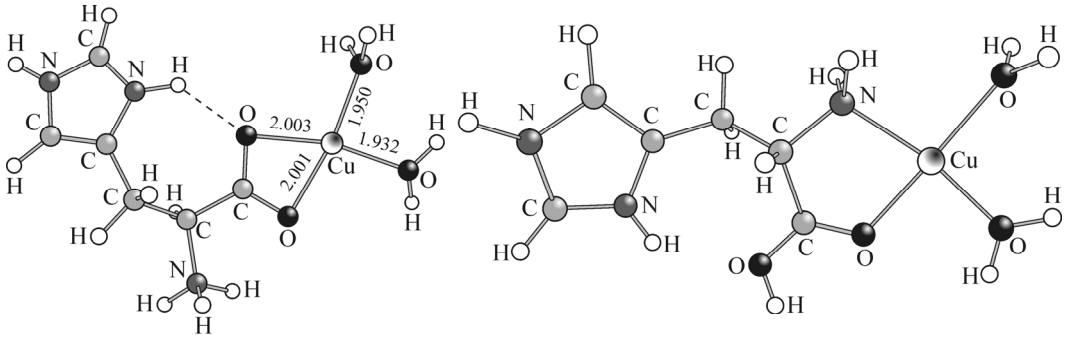
TABLE 2. Total Energy (E) and Relative Stability (ΔE) of Isomeric Forms of M:L (1:1) Complexes (with water as a solvent)

Ligand form	E_{PCM}+ZPE, a.u.	ΔE, kcal/mol	Ligand form	E_{PCM}+ZPE, a.u.	ΔE, kcal/mol
CuL-G3	–2341.41421	0	**CuHL-G2**	–2341.84604	0
CuL-H3	–2341.40996	2.66	**CuHL-H3**	–2341.84087	3.25
CuL-I3	–2341.41151	1.69	**CuHL-H2**	–2341.84147	2.87
CuL-G2	–2341.40619	5.26	**CuH_2L^+ (COO)**	–2342.23627	2.60
CuL-H2	–2341.40220	7.54	**CuH_2L^+-G2**	**–2342.24042**	**0**

isomer–**CuHL-H3** with a histamine-like tridentate ligand coordination. The reasons for the transformation are the increased basicity of the donor oxygen center of the carboxyl group and the displacement of this center into a position typical of this coordination mode. The Cu–O_{carb} increases from 2.211 (**CuL-H3**) to 2.637 Å (**CuHL-H3**). However, this isomer is 3.25 kcal/mol less stable, compared with **CuHL-G2**, which has a histamine-like bidentate ligand coordination. In the case of protonated histidine, the maximum possible denticity drops to two (Fig. 3).

As expected, priority is given to the **CuH_2L^+-G2** isomer with coordination through the carboxyl and amino group, and **CuH_2L^+** (**COO**) with coordination through the carboxyl group is destabilized by 2.6 kcal/mol.

The calculated results for the relative energy of the M:L (1:2) isomeric copper complexes are shown in Table 3 and Fig. 4. Evidently, there can be a great diversity of both homo- and heteroleptic complexes. Due to the enantiomeric purity of



CuH_2L^+ (COO) **CuH_2L^+-G2 CuH_2L^+ (ON)**

Fig. 3. Structure of isomeric forms of M:L (1:1) complexes with a protonated ligand form.

TABLE 3. Total energy (E) and relative stability (ΔE) of isomeric forms of M:L (1:2) complexes (with water as a solvent)

Isomer	E_{PCM}+ZPE, a.u.	ΔE, kcal/mol	Isomer	E_{PCM}+ZPE, a.u.	ΔE, kcal/mol
$Cu(H_2L^+)_2$ (COO)	–2738.58077	0	**CuL_2-G3G2**	–2736.91017	0
$Cu(H_2L^+)_2$-G2	–2738.58936	5.39	**CuL_2-I3H2**	–2736.90471	3.42
$Cu(HL)_2$-G2G2	–2737.79270	0	**CuL_2-G3H2**	–2736.90641	2.35
$Cu(HL)_2$-G2H2	–2737.78738	3.34	**CuL_2-H3H2**	–2736.90261	4.74
$Cu(HL)_2$-H3H3	–2737.77993	8.01	**CuL_2-H3G2-*cis***	–2736.90924	0.58
$Cu(HL)_2$-H2H2-*cis*	–2737.78061	7.58	**CuL_2-H3G2-*trans***	–2736.90826	1.19
CuL_2-G3G3	–2736.90968	0.30	**CuL_2-I3G2-*cis***	–2736.90672	2.16
CuL_2-H3H3	–2736.90334	4.28	**CuL_2-I3G2-*trans***	–2736.90821	1.23
CuL_2-I3I3	–2736.90380	3.99	**$CuHLL^-$-G2G3**	–2737.34107	0
CuL_2-G3H3	–2736.90652	2.29	**$CuHLL^-$-G2G2**	–2737.33489	3.88
CuL_2-G3I3	–2736.90629	2.43	**$CuHLH_2L^+$-G2-COO**	–2738.21930	2.70
CuL_2-H3I3	–2736.90784	1.46	**$CuHLH_2L^+$-G2G2**	–2738.22361	0

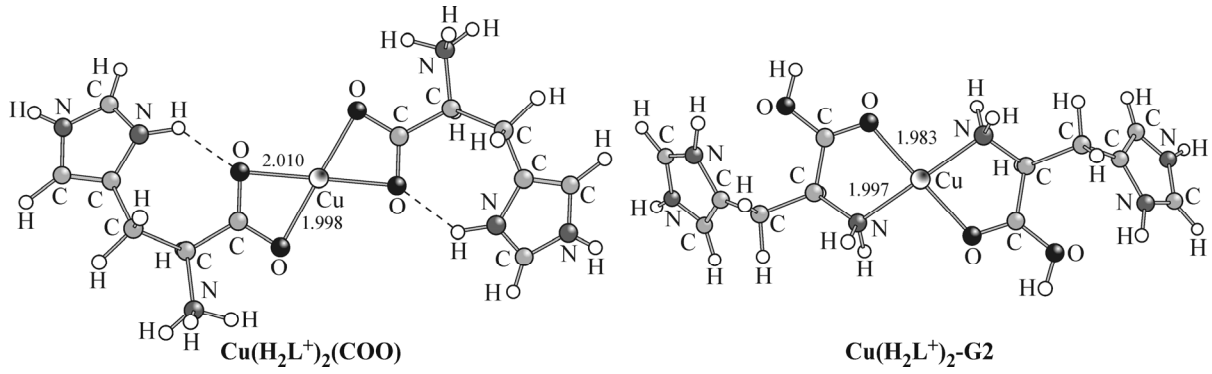


Fig. 4. Structure of isomeric forms of M:L (1:2) complexes with a protonated ligand form.

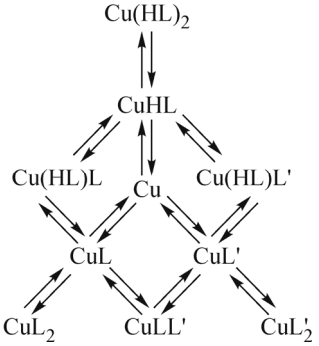
the ligand for homoleptic bis-complexes, the only possibility is a second-order rotational symmetry since a central symmetry is not possible.

Based on the total energy calculations, the **Cu(H_2L^+)$_2$** form with coordination through the carboxyl group is destabilized relative to the glycine-like **Cu(H_2L^+)$_2$-G2** form by 5.39 kcal/mol.

Among the neutral homoleptic complexes with tridentate ligand coordination and a coordination number (CN) of six for the copper ion (Fig. 5 and Table 3), the stability sequence of the isomers is similar to that for the M:L (1:1) complexes. The most stable isomer is **CuL_2-G3G3**, followed by the considerably less stable isomers **CuL_2-I3I3** and **CuL_2-H3H3**. Interestingly, the mixed ligand complexes of this type are much more stable than the latter, particularly, the **CuL_2-H3I3** isomer is only 1.16 kcal/mol less stable than **CuL_2-G3G3**. The most stable isomer among all the neutral ones is a complex with a six-cooridnated (rather than five-coordinated) copper(II) ion–**CuL_2-G3G2**, which has a structure of a distorted square pyramid. The reason is the mutual *trans*-influence of the ligands through the metal ion; this influence destabilizes pseudooctahedral structures. Thus, the absence of axial coordination of imidazole nitrogen in one of the ligands leads to a considerable strengthening of the Cu–N_{im} bond of the second ligand; the interatomic distance Cu–N_{im} decreases from 2.495 Å to 2.410 Å. Similarly small destabilization relative to the most stable isomer is typical of the pentacoordinated complexes with mixed coordination–**CuL_2-H3G2-*cis***, **CuL_2-H3G2-*trans***, and **CuL_2-I3G2-*trans*.**

Bicationic complexes with a neutral form of L-histidine typically prefer CN 4 (Fig. 6 and Table 4), the most stable being the **Cu(HL)$_2$-G2G2** complex with glycine-like coordination. The single possible complex with a CN of six is destabilized by more than 8 kcal/mol.

EPR spectroscopy. Previously, we investigated the system by the EPR method using a simplified scheme of chemical equilibria [12, 21, 22]. In this work, we calculated the equilibrium concentrations and molar fractions of the complex forms using the following scheme of equilibria (here and below, the ion charges are omitted):



where CuHL and $Cu(HL)_2$ are complex forms with monodentate ligand coordination; CuL and CuL_2 are complex forms with glycine-like bonding; CuL′ and CuL'_2 are complex forms with histamine-like bonding; and the other bis-complexes in the scheme combine different types of coordination. The molar fractions of the components were determined by solving a mass-balance equation system by Newton's method [23].

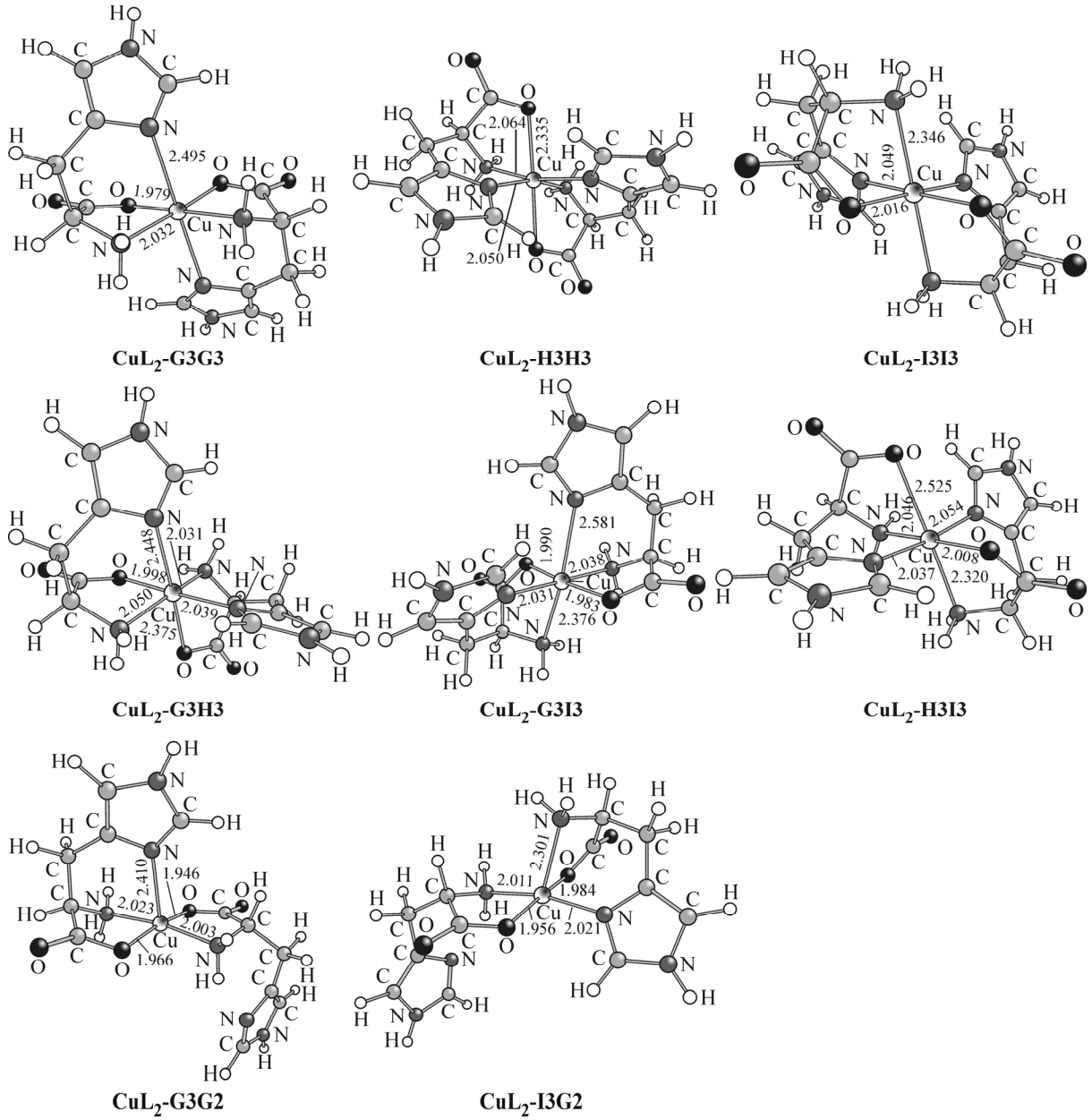


Fig. 5. Structure of isomeric forms of neutral M:L (1:2) complexes with an L-histidine anion.

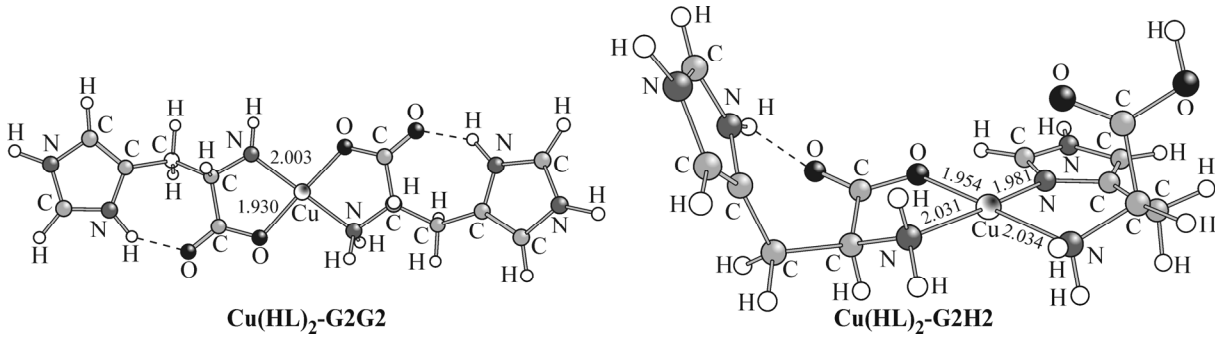


Fig. 6. Structure of isomeric forms of M:L (1:2) complexes with the neutral form of L-histidine.

A diagram of the metal ion distribution between the different forms of complex compounds is shown in Fig. 7.

TABLE 4. Stability Constant and Spin-Hamiltonian Parameter for Copper(II) Complexes with L-Histidine (t = 25 °C, μ = 1 mol/l KNO_3)

Complex	lgβ*	g	A, mT	Complex	lgβ*	g	A, mT
CuHL	15.1(1)	2.1594(4)	5.1(1)	CuL′	11.1(1)	2.1304(2)	6.3(1)
$Cu(HL)_2$	29.2(1)	2.1352(2)	5.6(1)	CuLL′	14.3(1)	2.1173(2)	7.6(1)
CuHLL′	26.5(1)	2.1268(2)	6.2(1)	CuL'_2	19.5(1)	2.1187(2)	8.2(1)

* $\beta = [Cu_pL_qH_r]/[Cu]^p[L]^q[H]^r]$.

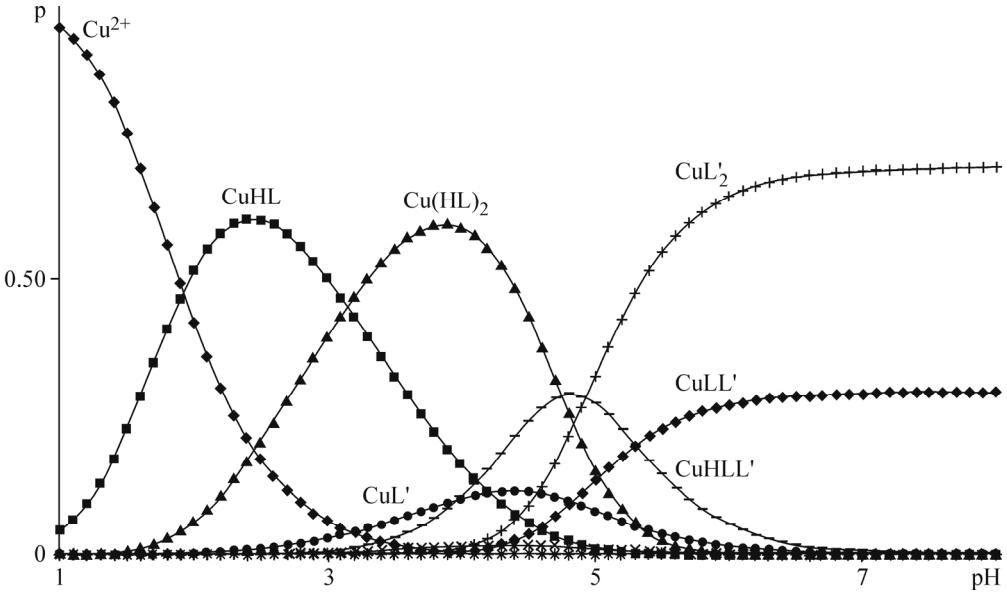


Fig. 7. Dependence of the molar fractions of the components on pH in the copper(II)–L-histidine system at C_M:C_L = 1:2.

We derived chemical information from the EPR spectra by varying the parameters that define the shape of the spectral line and by seeking a consistency between the experimental and theoretical spectra.

To improve the accuracy of the results obtained, we performed simultaneous calculations for four spectra of the system, which were recorded at different metal–ligand ratios and different pH. As an optimization criterion, we used a function of the standard deviation [24] calculated as a mean for the four spectra.

The theoretical spectrum was built using a superposition of Lorenz curves; the width of the hyperfine-structure components from copper nuclei were determined from the Wilson–Kivelson theory [25], which shows that the averaging of the anisotropic tensors of magnetic interaction in liquid solutions does not lead to a complete loss of information about their anisotropy and this anisotropy defines the values of the coefficients in the relation

$$\Delta H = \alpha + \beta m + \gamma m^2 + \delta m^3 + \ \dots\ , \qquad (1)$$

where m is a projection of the nuclear spin related to the anisotropic superfine interaction. The α, β, γ, δ, etc. coefficients form a decreasing sequence (most calculations are limited to three or four parameters); therefore, when there are many lines from hyperfine structures (HFSs) it is more convenient to use equation (1) to determine the width of the HFS component than to consider the values of ΔH for each line as variable parameters.

The coefficients of equation (1) ("relaxation coefficients") determine the contributions attributed to the modulation of the anisotropic parts of the Zeeman and hyperfine interactions by the rotational movement of the paramagnetic complex. These coefficients for the axial-symmetric complex depend on the anisotropy parameters $\Delta g = g_{\|} - g_{\perp}$ and $\Delta A = A_{\|} - A_{\perp}$ and

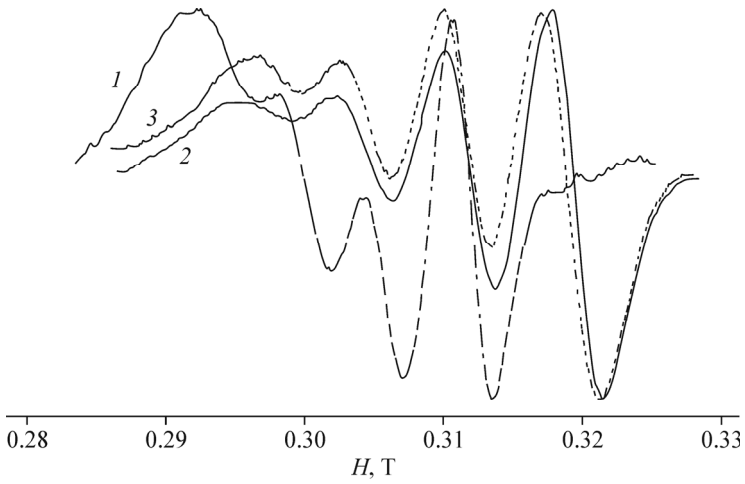


Fig. 8. EPR spectra of the L-histidine–copper(II) system at C_M:C_L = 1:2 and a pH of 1.98 (*1*); 5.02 (*2*); and 7.01 (*3*).

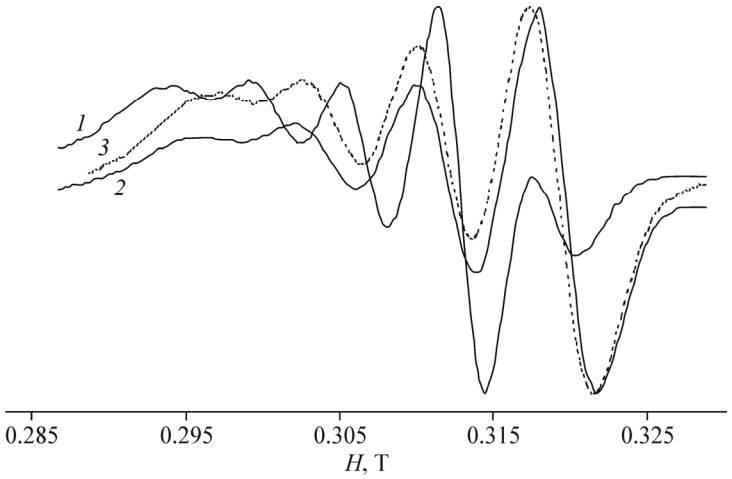


Fig. 9. EPR spectra of the copper(II)–L-histidine system at C_M:C_L = 1:4 and a pH 2.04 (*1*); 5.06 (*2*); and 6.97 (*3*).

the resonance field value H_0. The temperature and viscosity dependence of the width of EPR lines is defined by the characteristic correlation time τ_R of the Brownian rotation of the paramagnetic aquaion.

Examples of EPR spectra for the solutions at room temperature are shown in Figs. 8 and 9. An increase in pH and amino acid content leads to a shift of the signal to the strong field, suggesting a change in the environment of the metal ion and the nature of the metal–ligand bond. The results of the processing of the EPR spectra at room temperature are given in Table 4.

The values of the stability constants are comparable to those given in the literature [26]. The values of the parameters of the spin-Hamiltonian reflect a well-known dependence [27]: an increase in the number of nitrogen atoms in the inner coordination sphere of a complex leads to an increase in the covalence of the metal–ligand bond, leading to a decrease in the *g*-factor and an increase in the hyperfine interaction (HFI) constant.

CONCLUSIONS

We conducted a theoretical study to show the possibility of existence of mixed equilibria in solution, which involve homo- and heteroligand complexes with different CNs of the copper(II) ion. For complexes with an L-histidine anion, stable molecules have a CN of 5 and 6 with bi- and tridentate coordination of the ligand; complexes with a neutral ligand prefer CN 4.

The ratio between the CuL'_2 and CuLL′ complexes varies in the range pH 4-6 and is virtually stable with the further increase in pH. The invariability of the spectra when pH is above 10 suggests that there is no deprotonation of the water molecule in the system, i.e., the axial positions are occupied by the third donor group of the ligand. Thus, we can conclude that the complexes CuL'_2 and CuLL′ have the structures **CuL_2–H3H3** and **CuL_2–G3H3**, respectively.

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