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Thermodynamics of the Formation of Copper(II) Complexes with *L*-Histidine in Aqueous Solution

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Abstract—The heat effects from the reaction between *L*-histidine solutions and $Cu(NO_3)_2$ solutions at 298.15 K in the 0.2 to 1.0 (KNO_3) range of ionic strength are measured by means of direct calorimetry. The experimental data is treated with allowance for the simultaneous proceeding of several processes. The heat effects of the formation of complexes $Cu(His)^+$, $Cu(His)_2$, $CuHHis^{2+}$, $CuH(His)_2^+$, and $CuH_2(His)_2^{2+}$ are calculated from calorimetric measurements. The standard enthalpies of formation for complexes of *L*-histidine with Cu^{2+} ions are obtained via extrapolation to zero ionic strength. The relationship between the thermodynamic characteristics of the formation of complexes of copper(II) with *L*-histidine and their structure is determined.

Keywords: complexes of Cu(II) with *L*-histidine, structure, thermodynamic parameters, calorimetry.

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INTRODUCTION

The reaction of Cu(II) ions with *L*-histidine (Y) was studied by means of potentiometric titration in [1]. The composition of the resulting complexes and their stability constants were determined: $\log\beta^\circ(CuY^+) = 10.80 \pm 0.02$; $\log\beta^\circ(CuHY^{2+}) = 14.57 \pm 0.05$; $\log\beta^\circ(CuY_2) = 18.94 \pm 0.02$; $\log\beta^\circ(CuH_2Y_2^{2+}) = 27.76 \pm 0.02$; $\log\beta^\circ(CuHY_2^+) = 24.81 \pm 0.03$. We recalculated the constants to values of ionic strength (I) using the equation proposed in [2].

Data on the enthalpies of complexation of Cu^{2+} ion with *L*-histidine are scarce [3–6]. The results from the thermochemical studies of various authors are contradictory, and there are no data on the dependence of the heat effects of the formation of complexes on the ionic strength of a solution.

The aim of this work was to determine the heat effects of the formation of copper(II) complexes with *L*-histidine at 298.15 K via direct calorimetry while studying the effect the concentration of background electrolyte has on the thermodynamic characteristics of complexation.

EXPERIMENTAL

The heat effects of mixing and dilution were measured in a calorimeter with an isothermal shell and automatic data acquisition [7]. A crystalline specimen of *L*-histidine of chemically pure grade, dried to a constant weight at 343 K, was used. The initial pH value of the *L*-histidine solutions was adjusted by adding calculated amounts of HNO_3 and KOH solutions of chemically pure grade. Carbonate-free alkali was prepared according to the familiar procedure in [8]. The concentration of $Cu(NO_3)_2$ solution was determined via complexometry and iodometry. Constant ionic strength was maintained using potassium nitrate recrystallized from distillate. The experiments were conducted at 298.15 K and ionic strengths of 0.2, 0.5, and 1.0. The pH values were controlled using a pH-meter. The shots of the solutions were weighed on VLR-200 scales with a precision of 1×10^{-5} g. The equilibrium composition of solutions under experimental conditions was calculated using the RRSU program [9]. The required data on the ionization constants of water against the background of KNO_3 were taken from [10]. Student's criterion at a probability of 0.95 was used to calculate the confidence interval of the mean ΔH value from three to four parallel experiments.

In order to determine the heat effect of the formation of CuY_2 complex, the heats of reaction of $Cu(NO_3)_2$ solutions (1.0438 mol/kg solution) with *L*-histidine solutions (0.051 mol/L) were measured in the pH range of 8.7–9.7. Each measured shot of copper nitrate solution (~0.39 g) was placed in an ampoule; *L*-histidine solution (39.86 mL) neutralized to a particular pH value with KOH solution was placed in the calorimetric cell. The metal : ligand ratio at the end of each calorimetric experiment was 1 : 5. The heats of dilution of $Cu(NO_3)_2$ solutions in background

Table 1. Heat effects (kJ/mol) of the reaction between $Cu(NO_3)_2$ (1.0438 mol/kg) and L-histidine solutions (0.05100 mol/L, pH 9.7–8.7)

m, g	$-\Delta_{mix}H_1$	m, g	$-\Delta_{dil}H$	$-\Delta_rH(CuY_2)$
		$I = 0.2$		
0.39010	83.68	0.38995	1.04	83.01
0.39025	83.41	0.39015	1.06	82.74
0.39020	83.43	0.39030	1.00	82.76
		$I = 0.5$		
0.38995	86.25	0.39045	2.48	84.18
0.39020	86.14	0.39010	2.55	84.07
0.39000	85.95	0.38995	2.45	83.88
		$I = 1.0$		
0.39000	88.50	0.39010	4.18	84.81
0.39000	88.74	0.39020	4.19	85.05
0.39000	88.45	0.38995	4.15	84.76

m is the shot of L-histidine solution and I is ionic strength (KNO_3).

electrolyte KNO_3 solution were also measured. The experimental data are given in Table 1.

The change in enthalpy upon the formation of complex $CuHY_2^+$ was determined from the data on the heats of the reaction between $Cu(NO_3)_2$ and L-histidine solutions at metal : ligand ratios of ~1 : 5 in the pH range of 5.6 to 6.8. The required pH value was achieved by adding HNO_3 solution to L-histidine solutions. The experimental data are given in Table 2.

The heat effects of the formation of CuY^+ and $CuHY^{2+}$ complexes were determined in the pH ranges of 5.9–10.9 and 3.0–5.5 at a metal : ligand ratio of ~1 : 1. To accomplish this, an ampoule with a measured shot of copper nitrate solution (~0.39 g) was broken into L-histidine solution, where the required amount of alkali KOH was preliminarily added for the formation of CuY^+ complex and acid HNO_3 for the formation of $CuHY^{2+}$ complex. The experimental data are given in Tables 2 and 3.

To determine the change in enthalpy upon the complex formation of $CuH_2Y_2^{2+}$ particles, the heat effects of the reaction between $Cu(NO_3)_2$ solutions (1.0438 mol/kg solution) and L-histidine solutions (0.051 mol/L) in the pH range of 3.5 to 5.9 were measured. The metal : ligand ratio was 1 : 5 in our calorimetric experiments. The experimental data are given in Table 3.

RESULTS AND DISCUSSION

The following reactions can occur in the Cu(II)–L-histidine system under study:

$$HY^{\pm} \leftrightarrow Y^- + H^+, \quad (1)$$

$$H_2Y^+ \leftrightarrow Y^- + 2H^+, \quad (2)$$

$$H_3Y^{2+} \leftrightarrow Y^- + 3H^+, \quad (3)$$

$$Cu^{2+} + Y^- \leftrightarrow CuY^+, \quad (4)$$

$$Cu^{2+} + 2Y^- \leftrightarrow CuY_2, \quad (5)$$

$$Cu^{2+} + H^+ + Y^- \leftrightarrow CuHY^{2+}, \quad (6)$$

$$Cu^{2+} + H^+ + 2Y^- \leftrightarrow CuHY_2^+, \quad (7)$$

$$Cu^{2+} + 2H^+ + 2Y^- \leftrightarrow CuH_2Y_2^{2+}, \quad (8)$$

$$Cu^{2+} + OH^- \leftrightarrow CuOH^+, \quad (9)$$

$$Cu^{2+} + Y^- + OH^- \leftrightarrow CuOHY, \quad (10)$$

$$Cu^{2+} + 2Y^- + OH^- \leftrightarrow CuOHY_2^-, \quad (11)$$

$$Cu^{2+} + 2Y^- + 2OH^- \leftrightarrow Cu(OH)_2Y_2^{2-}, \quad (12)$$

$$H^+ + OH^- \leftrightarrow H_2O. \quad (13)$$

The enthalpies of the formation of Cu^{2+} complexes with L-histidine can be calculated according to the equation

$$\begin{gathered}\Delta_{mix}H - \Delta_{dil}H = \Delta_rH(CuY^+)\alpha(CuY^+)\\ + \Delta_rH(CuY_2)\alpha(CuY_2) + \Delta_rH(CuHY^{2+})\\ \times \alpha(CuHY^{2+}) + \Delta_rH(CuHY_2^+)\alpha(CuHY_2^+)\\ + \Delta_rH(CuH_2Y_2^{2+})\alpha(CuH_2Y_2^{2+}) \quad (14)\\ \times \Delta_{dis}H(HY^{\pm})\alpha(HY^{\pm}) + \Delta_{dis}H(H_2Y^+)\alpha(H_2Y^+)\\ + \Delta_{dis}H(H_3Y^{2+})\alpha(H_3Y^{2+}) + \Delta_rH(CuOH^+)\alpha(CuOH^+)\\ + \Delta_rH(CuOHY)\alpha(CuOHY)\\ + \Delta_rH(CuOHY_2^-)\alpha(CuOHY_2^-) + \Delta_rH(Cu(OH)_2Y_2^{2-})\\ \times \alpha(Cu(OH)_2Y_2^{2-}) + \Delta_rH_w\alpha(OH^-),\end{gathered}$$

where $\Delta_{mix}H$ is the heat effect from mixing L-histidine and $Cu(NO_3)_2$ solutions; $\Delta_{dil}H$ is the heat effect from diluting $Cu(NO_3)_2$ solution in a background electro-

Table 2. Heat effects (kJ/mol) of the reaction between $Cu(NO_3)_2$ (1.0438 mol/kg) and L-histidine solutions

I	$c_Y^0 = 0.05100$ mol/L, pH 6.8–5.6		$c_Y^0 = 0.01021$ mol/L, pH 10.9–5.9	
	$-\Delta_{mix}H_2$	$-\Delta_rH(CuHY_2^+)$	$-\Delta_{mix}H_3$	$-\Delta_rH(CuY^+)$
0.2	52.35 ± 0.23	110.18 ± 0.34	48.03 ± 0.25	48.86 ± 0.29
0.5	54.54 ± 0.22	111.06 ± 0.32	49.52 ± 0.17	50.53 ± 0.19
1.0	56.47 ± 0.24	111.85 ± 0.34	50.70 ± 0.25	52.23 ± 0.29

Table 3. Heat effects (kJ/mol) of the reaction between $Cu(NO_3)_2$ (1.0438 mol/kg) and L-histidine solutions

I	$c_Y^0 = 0.01000$ mol/L, pH 5.5–3.0		$c_Y^0 = 0.05000$ mol/L, pH 5.9–3.5	
	$-\Delta_{\mathrm{mix}}H_4$	$-\Delta_r H(\mathrm{CuHY^{2+}})$	$-\Delta_{\mathrm{mix}}H_5$	$-\Delta_r H(\mathrm{CuH_2Y_2^{2+}})$
0.2	2.36 ± 0.10	61.68 ± 0.26	27.78 ± 0.10	109.92 ± 0.29
0.5	3.68 ± 0.10	61.91 ± 0.23	29.47 ± 0.10	112.52 ± 0.30
1.0	5.06 ± 0.10	61.83 ± 0.21	31.33 ± 0.10	115.10 ± 0.26

lyte solution; $\Delta_r H(\mathrm{CuY^+})$, $\Delta_r H(\mathrm{CuY_2})$, $\Delta_r H(\mathrm{CuHY^{2+}})$, and $\Delta_r H(\mathrm{CuHY_2^+})$, $\Delta_r H(\mathrm{CuH_2Y_2^{2+}})$ are the enthalpies of the formation of $\mathrm{CuY^+}$, $\mathrm{CuY_2}$, $\mathrm{CuHY^{2+}}$, $\mathrm{CuHY_2^+}$, and $\mathrm{CuH_2Y_2^{2+}}$ complexes, respectively; $\Delta_{\mathrm{dis}}H(\mathrm{H_3Y^{2+}})$, $\Delta_{\mathrm{dis}}H(\mathrm{H_2Y^+})$, and $\Delta_{\mathrm{dis}}H(\mathrm{HY^\pm})$ are the enthalpies of dissociation of L-histidine [11]; $\Delta_r H(\mathrm{CuOH^+})$, $\Delta_r\mathrm{HCuOHY}$, $\Delta_r H(\mathrm{CuOHY_2^-})$, and $\Delta_r H(\mathrm{Cu(OH)_2Y_2^{2-}})$ are the enthalpies of formation of hydroxocomplexes; $\Delta_r H_w$ is the enthalpy of formation of water in KNO_3 solution [12]; and $\alpha(\mathrm{CuY^+})$, $\alpha(\mathrm{CuY_2})$, $\alpha(\mathrm{CuHY^{2+}})$, $\alpha(\mathrm{CuHY_2^+})$, $\alpha(\mathrm{CuH_2Y_2^{2+}})$, $\alpha(\mathrm{H_3Y^{2+}})$, $\alpha(\mathrm{H_2Y^+})$, $\alpha(\mathrm{HY^\pm})$, $\alpha(\mathrm{CuOH^+})$, $\alpha(\mathrm{CuOHY})$, $\alpha(\mathrm{CuOHY_2^-})$, $\alpha(\mathrm{Cu(OH)_2Y_2^{2-}})$, and $\alpha(\mathrm{OH^-})$ are the degrees of conversion of the corresponding reactions.

As follows from the results of calculating the equilibrium composition of system using the RRSU program, under the chosen experimental conditions ($c_M^0 : c_Y^0 = 1:5$, $\Delta\mathrm{pH} = 8.7$–9.7), 99.9% of the copper ions bound to $\mathrm{CuY_2}$ complex. The contribution from other processes to the measured heat effect did not exceed 0.5 kJ/mol. The change in enthalpy upon the formation of $\mathrm{CuY_2}$ particles was calculated using the equation

$$\Delta_r H_{\mathrm{CuY_2}} = (\Delta_{\mathrm{mix}}H_1 - \Delta_{\mathrm{dil}}H - \alpha_{\mathrm{HY^\pm}}\Delta_{\mathrm{dis}}H_{\mathrm{HY^\pm}} - \alpha_{\mathrm{OH^-}}\Delta H_{\mathrm{w}})/\alpha_{\mathrm{CuY_2}}, \tag{15}$$

where $\Delta_{\mathrm{mix}}H_1$ is heat effect from mixing $Cu(NO_3)_2$ and L-histidine solutions, and $\Delta_{\mathrm{dil}}H$ is the heat effect from diluting $Cu(NO_3)_2$ solution in a background electrolyte solution (Table 1). The enthalpies of formation of $\mathrm{CuY_2}$ complex are given in Table 1.

$\mathrm{CuHY_2{}^+}$ complex was studied under conditions ($c_M^0 : c_Y^0 = 1:5$, $\Delta\mathrm{pH} = 5.6$–6.8) of concentrations at which the formation of $\mathrm{CuY^+}$, $\mathrm{CuHY^{2+}}$, and $\mathrm{CuH_2Y_2^{2+}}$ complexes was reduced to a minimum. The conversion of reaction (7) was ~69%; that of reaction (5), 30%. Reactions (1) and (13) also proceeded in a system with a contribution of ~50 kJ/mol. The equation for calculating the heat effect of the formation of $\mathrm{CuHY_2^+}$ particles has the form

$$\Delta_r H_{\mathrm{CuHY_2^+}} = (\Delta_{\mathrm{mix}}H_2 - \Delta_{\mathrm{dil}}H - \alpha_{\mathrm{CuY_2}}\Delta_r H_{\mathrm{CuY_2}} - \alpha_{\mathrm{HY^\pm}}\Delta_{\mathrm{dis}}H_{\mathrm{HY^\pm}} - \Delta H_{\mathrm{w}}\alpha_{\mathrm{OH^-}})/\alpha_{\mathrm{CuHY_2^+}}, \tag{16}$$

where $\Delta_{\mathrm{mix}}H_2$ is heat effect from mixing $Cu(NO_3)_2$ and L-histidine solutions (Table 2) and $\Delta_{\mathrm{dil}}H$ is heat effect from diluting $Cu(NO_3)_2$ solution in a background electrolyte solution (Table 1). The results from calculations are given in Table 2.

During the reaction between $Cu(NO_3)_2$ solution and L-histidine solution at a reagent ratio of $c_M^0 : c_Y^0 = 1:1$ in the pH range of 5.9–10.9, the formation of $\mathrm{CuY^+}$ is the dominant process; in the pH range of 3.0 to 5.5, the formation of $\mathrm{CuHY^{2+}}$ dominates. Calculations for the equilibrium composition of solutions before and after calorimetric experiments showed that the conversion of these processes was 85 and 39%, respectively. Corrections for the change in enthalpy at the formation of complexes $\mathrm{CuY_2}$ and $\mathrm{CuHY_2^+}$, dissociation of L-histidine and formation of water were also made. The contribution from the heat effects of other processes was negligible. The change in enthalpy upon the formation of $\mathrm{CuY^+}$ complex at $c_M^0 : c_Y^0 = 1:1$ ratio was calculated according to the equation

$$\Delta_r H_{\mathrm{CuY^+}} = (\Delta_{\mathrm{mix}}H_3 - \Delta_{\mathrm{dil}}H - \alpha_{\mathrm{CuY_2}}\Delta_r H_{\mathrm{CuY_2}} - \alpha_{\mathrm{CuHY_2^+}}\Delta H_{\mathrm{CuHY_2^+}} - \alpha_{\mathrm{HY^\pm}}\Delta_{\mathrm{dis}}H_{\mathrm{HY^\pm}} - \Delta H_w\alpha_{\mathrm{OH^-}})/\alpha_{\mathrm{CuY^+}}, \tag{17}$$

where $\Delta_{\mathrm{mix}}H_3$ is the heat effect from mixing $Cu(NO_3)_2$ and L-histidine solutions (Table 2), and $\Delta_{\mathrm{dil}}H$ is heat effect from diluting $Cu(NO_3)_2$ solution in background electrolyte solution (Table 1). The results from our calculations are given in Table 2.

Table 4. Standard thermodynamic characteristics of complex formation in the Cu^{2+}–L-histidine system

Process	$\log\beta°$	$-\Delta_rH°$, kJ/mol	$-\Delta_rG°$, kJ/mol	$\Delta_rS°$, J/(mol K)
(4)	10.80 ± 0.02	47.34 ± 0.30	61.65 ± 0.11	48.0 ± 0.5
(5)	18.94 ± 0.02	81.24 ± 0.30	108.11 ± 0.11	90.1 ± 0.5
(6)	14.57 ± 0.05	61.29 ± 0.30	83.16 ± 0.29	73.4 ± 0.6
(7)	24.81 ± 0.03	108.42 ± 0.35	141.62 ± 0.17	111.3 ± 0.5
(8)	27.76 ± 0.02	108.06 ± 0.48	158.45 ± 0.11	169.0 ± 1.2

The heat effect from the formation of $CuHY^{2+}$ complex was calculated with allowance for $\Delta_rH(CuY^+)$ according to the equation

$$\begin{aligned}\Delta_rH_{CuHY^{2+}} &= (\Delta_{mix}H_4 - \Delta_{dil}H - \alpha_{CuY^+}\Delta_rH_{CuY^+} \\ &- \alpha_{CuHY_2^+}\Delta H_{CuHY_2^+} - \alpha_{HY^\pm}\Delta_{dis}H_{HY^\pm} \\ &- \alpha_{H_2Y^+}\Delta_{dis}H_{H_2Y^+} - \alpha_{H_3Y^{2+}}\Delta_{dis}H_{H_3Y^{2+}} \\ &- \Delta H_w\alpha_{OH^-})/\alpha_{CuHY^{2+}},\end{aligned} \tag{18}$$

where $\Delta_{mix}H_4$ is heat effect from mixing $Cu(NO_3)_2$ and L-histidine solutions (Table 3), and $\Delta_{dil}H$ is heat effect from diluting $Cu(NO_3)_2$ solution in a background electrolyte solution (Table 1). The results from our calculations are given in Table 3.

The maximum yield of $CuH_2Y_2^{2+}$ complex under experimental conditions at $c_M^0 : c_Y^0 = 1 : 5$ and ΔpH 5.9–3.5 was ~25%. Corrections for side processes of acid–base interaction and complexation were also made. Conversion in reactions (4), (6), and (7) was 7, 32, and 35%, respectively. The equation for determining the heat effect from the formation of $CuH_2Y_2^{2+}$ particles is

$$\begin{aligned}\Delta_rH_{CuH_2Y_2{}^{2+}} &= (\Delta_{mix}H_5 - \Delta_{dil}H - \alpha_{CuY^+}\Delta_rH_{CuY^+} \\ &- \alpha_{CuHY^{2+}}\Delta_rH_{CuHY^{2+}} - \alpha_{CuHY_2^+}\Delta H_{CuHY_2^+} \\ &- \alpha_{HY^\pm}\Delta_{dis}H - \alpha_{H_2Y^+}\Delta_{dis}H_{H_2Y^+} \\ &- \alpha_{H_3Y^{2+}}\Delta_{dis}H_{H_3Y^{2+}} - \Delta H_w\alpha_{OH^-})/\alpha_{CuH_2Y_2^{2+}},\end{aligned} \tag{19}$$

where $\Delta_{mix}H_5$ is the heat effect from mixing $Cu(NO_3)_2$ and L-histidine solutions (Table 3), and $\Delta_{dil}H$ is heat effect from diluting $Cu(NO_3)_2$ solution in a background electrolyte solution (Table 1). The results from our calculations are given in Table 3.

The enthalpies of complexation in standard solution were determined by extrapolating the heat effects at specific values of ionic strength to zero using an equation with one individual parameter [13]:

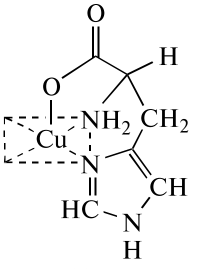
$$\Delta H - \Delta Z^2\Psi(I) = \Delta H° + bI, \tag{20}$$

where ΔH and $\Delta H°$ are the changes in enthalpy at finite ionic strength and $I = 0$, respectively; $\Psi(I)$ is a function of ionic strength calculated theoretically; ΔZ^2 is difference between the squares of the charges of the products of reaction and the initial components; and b is an empirical coefficient. The values calculated for the standard thermodynamic characteristics of complexation in the Cu^{2+}–L-histidine system are given in Table 4. The standard enthalpy of complexation of CuY_2 particles given in Table 4 is in good agreement with the data in [3]. in the differences between the heat effects from the formation of CuY^+, $CuHY^{2+}$, $CuHY_2^+$, and $CuH_2Y_2^{2+}$ in our data and the data from [3] are likely related to the use of other, less reliable constants for the formation of the above complexes in [3].

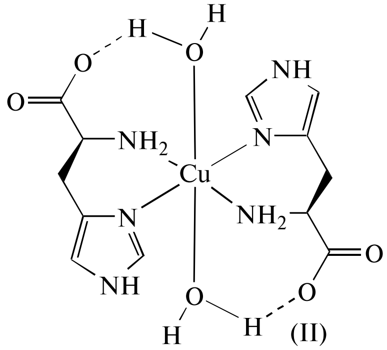
In comparing the enthalpies of complexation in glycine—Cu(II) ($\Delta_rH(CuGly^+) = -27.04 \pm 0.39$ kJ/mol, $\Delta_rH(Cu(Gly)_2) = -53.87 \pm 0.30$ kJ/mol [14])—and L-histidine–Cu(II) systems (Table 4), it is clear there are considerable differences between the ΔH of formation of their mono- and bis-complexes, due to differences in the coordination of these amino acids. Glycine-like coordination (through the nitrogen atoms of amino groups and oxygen atoms of carboxylic groups) is characteristic of amino acids that have no additional donor groups in side chain. In [14], no appreciable differences were found between the thermodynamics of complexation with glycine, L-asparagine, L-glutamine, or L-valine. L-histidine has additional donor groups in its side chain (pyridine and pyrrol nitrogen atoms of imidazole ring). Carboxyl, amino, and imidazole groups participate in the coordination of L-histidine with d-metal ions [15].

Structures of complexes of Cu(II) with L-histidine, obtained in X-ray, IR, CD, EPR, and other studies conducted by different authors, were described in [16].

The structures for CuY^+ and CuY_2 particles proposed in [16] were

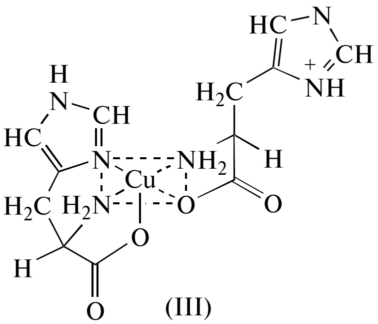


(I)



(II)

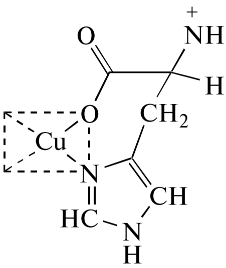
The standard heat effect given in Table 4 for the formation of protonated $CuHY_2^+$ complex is in agreement with the results from studying its structure using a variety of spectral means:



(III)

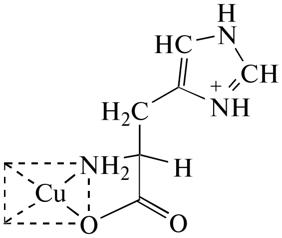
In structure III, it is proposed that one tridentate ligand of *L*-histidine be combined with the weakly coordinated carboxylic group in the axial position and one bidentate of *L*-histidine in solution. The imidazole group, the enthalpy of dissociation of which is $\Delta_{dis}H(H_2Y^+) = 29.92 \pm 0.21$ kJ/mol [11], is protonated. The dissociation of the amino group of *L*-histidine is more endothermic: $\Delta_{dis}H(HY^{\pm}) = 44.02 \pm 0.21$ kJ/mol [11].

Two types of coordination were proposed in [16] for $CuHY^{2+}$ complex. In the structure



(IV)

obtained on the basis of IR spectral data, the coordination of *L*-histidine with Cu^{2+} ion through the imidazole and carboxylic groups was proposed. In addition, the structure

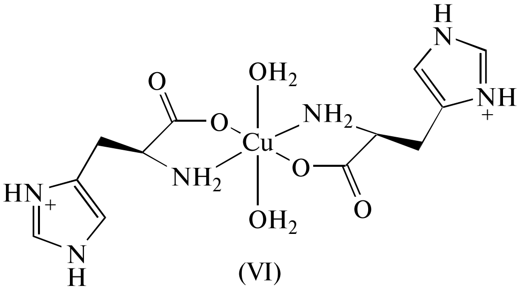


(V)

was proposed for $CuHY_2^+$ complex, since CD studies showed that the imidazole group of *L*-histidine is not involved in copper binding.

Our thermodynamic data (Table 4) indicate that the second variant (V) is more likely, since the standard heat effect from the formation of protonated $CuHY_2^+$ complex ($\Delta_rH(CuHY_2^+) = -108.42 \pm 0.35$ kJ/mol) corresponds to the total heat effects from the formation of CuY^+ and $CuHY^{2+}$ particles ($\Delta_rH(CuY^+) = -47.34 \pm 0.30$ kJ/mol; $\Delta_rH(CuHY^{2+}) = -61.29 \pm 0.30$ kJ/mol).

The X-ray structure [16] of protonated $CuH_2Y_2^{2+}$ complex showed that two nitrogen atoms of the amino group and two oxygen atoms of the carboxylic group participate in coordination with copper ions:



(VI)

Being protonated, nitrogen atoms of imidazole group are not bound to copper. Our thermodynamic data for $CuH_2Y_2^{2+}$ are in accordance with the X-ray data.

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