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Study of Copper Chloride Coordination with L-α-Histidine

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Abstract—Thermochemical and kinetic equations for nonequilibrium reactions that occur at constant pressure and temperature were proposed. Thermodynamic and kinetic characteristics of copper(II) reaction with histidine (His) were obtained. The enthalpy of formation of copper(II) complex with histidine at temperatures from 298.15 to 323.15 K was determined by microcalorimetry. The standard enthalpy of formation of $\mathrm{Cu(His)_2^{2+}(aq)}$ was calculated. The enthalpy, entropy, and Gibbs energy of activation, rate constants, activation energies, preexponential factor, and reaction order were obtained on the basis of experimental and calculated data. The resulting data suggest that the title reaction readily proceeds at the indicated temperatures. The $\mathrm{Cu(His)_2Cl_2 \cdot H_2O}$ complex was isolated in the solid state and characterized by IR spectroscopy and thermal analysis.

Copper is one of essential trace elements for human organism, which have been known since 1928. L-α-Amino acids are structural units of proteins. Therefore, copper complexes with L-α-amino acids are of considerable practical and fundamental importance. The complex of copper(II) with L-α-histidine was studied by molecular modeling, electron diffraction, electron spin resonance, magnetochemistry, etc. [1–11], but its thermochemical properties and kinetics of its formation have not been reported in the literature. In this paper we determined by means of microcalorimetry the enthalpy of formation of $\mathrm{Cu^{2+}}$ complex with His at 298.15–323.15 K by the reaction between $\mathrm{CuCl_2}$ and His in aqueous solution. The reaction rate constant (k), activation enthalpy ($\Delta H^0_{\neq}$), activation entropy ($\Delta S^0_{\neq}$), activation Gibbs energy ($\Delta G^0_{\neq}$), and reaction enthalpy ($\Delta_r H^0_{\neq}$) were found. The $\mathrm{Cu(His)_2Cl_2 \cdot H_2O}$ complex was isolated in the solid state and characterized by IR spectroscopy and thermal analysis (TG and DTG).

Deduction of thermokinetic equation for irreversible reactions. To deduce a thermokinetic equation for an irreversible reaction, let as write down it in a general form.

$$\mathrm{A(aq)} + \mathrm{B(aq)} \leftrightarrow [\mathrm{AB}]^{\neq} \longrightarrow \mathrm{AB} + \text{heat}, \qquad (1)$$

$$\left.\begin{array}{llll} t = 0, & c_0 = 1\ c^{\neq} & a_i = 0 & H_0 = 0 \\ t = t, & c_i & a_i & H_i \\ t = \infty, & c_\infty & a_i = 1 & H_\infty \end{array}\right\} \qquad (2)$$

The relationship between the enthalpy of the reaction and its progress follows from boundary conditions (2).

$$\frac{c_0 - c_i}{c_0 - c_\infty} = \frac{0 - a_i}{0 - a_\infty} = \frac{0 - H_i}{0 - H_\infty}.$$

Hence, we have Eq. (3).

$$a_i = H_i/H_\infty \quad \frac{da_i}{dt} = \frac{1}{H_\infty}\frac{dH_i}{dt}. \qquad (3)$$

On the other hand, if reaction (1) is of the *n*th order, we can write down Eq. (4).

$$da_i/dt = k(1 - a_i)^n. \qquad (4)$$

Substituting (4) into (3), we obtain Eqs. (5) and (6).

$$\frac{1}{H_\infty}\frac{dH_i}{dt} = k\left(1 - \frac{H_i}{H_\infty}\right)^n, \qquad (5)$$

$$\ln\left(\frac{1}{H_\infty}\frac{dH_i}{dt}\right) = \ln k + n\ln\left(1 - \frac{H_i}{H_\infty}\right). \qquad (6)$$

Thus, the reaction rate constant k and the reaction order n can be obtained from thermokinetic experimental data by least-squares fitting.

According to Arrhenius equation (7):

$$\ln k = \ln A - (E/RT), \qquad (7)$$

the activation energy E and the preexponential factor A can be calculated from the temperature dependence of the rate constant k.

Equation (8) follows from the absolute rate theory.

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$$-\frac{d[\mathrm{AB}]}{dt} = \frac{c^{\neq}}{\tau}\nu = \nu[\mathrm{AB}]^{\neq} = \frac{\varepsilon}{h}[\mathrm{AB}]$$
$$= \frac{k_{\mathrm{B}}T}{h}[\mathrm{AB}]^{\neq} = \frac{RT}{N_{\mathrm{A}}h}[\mathrm{AB}]^{\neq}. \qquad (8)$$

Here ν is the frequency of vibrations along the reaction coordinate (it is assumed that transition complex $\mathrm{AB}^{\neq}$ dissociates after the first vibration), ε is the energy of the vibrational degree of freedom, *h* is the Planck constant, *kB* is the Boltzmann constant, and N_A the Avogadro number.

The rate of a bimolecular reaction and the component concentrations are known to be related to each other by Eq. (9).

$$-\frac{d[\mathrm{AB}]}{dt} = k[\mathrm{A}][\mathrm{B}]. \qquad (9)$$

When the reaction comes to equilibrium, we have Eq. (10).

$$[\mathrm{AB}]^{\neq} = K^{\neq}[\mathrm{A}][\mathrm{B}]. \qquad (10)$$

Combining Eqs. (8)–(10) gives Eq. (11).

$$k = \frac{RT}{N_{\mathrm{A}}h}K^{\neq}. \qquad (11)$$

In the case of the reaction system under discussion thermodynamic equations (12) and (13) assert.

$$\Delta G^0_{\neq} = -RT\ln K^{\neq}, \qquad (12)$$

$$\Delta G^0_{\neq} = \Delta H^0_{\neq} - T\Delta S^0_{\neq}. \qquad (13)$$

Combining Eqs. (11) and (12) gives Eq. (14).

$$\Delta G^0_{\neq} = RT\ln(RT/N_{\mathrm{A}}hk). \qquad (14)$$

Combining Eqs. (11), (12), and (13) gives Eq. (15).

$$k = \frac{RT}{N_{\mathrm{A}}h}e^{-\Delta G^0_{\neq}/RT} = \frac{RT}{N_{\mathrm{A}}h}e^{(T\Delta S^0_{\neq} - \Delta H^0_{\neq})/RT}$$
$$= \frac{RT}{N_{\mathrm{A}}h}e^{\Delta S^0_{\neq}/R}e^{-\Delta H^0_{\neq}/RT}. \qquad (15)$$

Finally, we obtain Eq. (16).

$$\ln\left(\frac{k}{T}\right) = \left(\ln\frac{k_{\mathrm{B}}}{h} + \frac{\Delta S^0_{\neq}}{R}\right) - \left(\frac{\Delta H^0_{\neq}}{RT}\right). \qquad (16)$$

In principle, this equation allows us to find $\Delta H^0_{\neq}$ and $\Delta S^0_{\neq}$ by the linear leastsquares regression techniques if the reaction is first-order in B. Thus, the thermodynamic and kinetic parameters of the irreversible reaction that occur at constant pressure and temperature can be obtained by Eqs. (6), (7), (14), and (16).

Determination of $\Delta_\mathrm{r}H^0_\mathrm{m}$ and calculation of $\Delta_{\mathrm{f,Cu(His)}_2^{2+}\mathrm{(aq)}}H^0_\mathrm{m}$. The formation of the copper–histidine complex can be represented by reaction (17).

$$\mathrm{Cu^{2+}(aq)} + \mathrm{2His(aq)} \longrightarrow \mathrm{Cu(His)_2^{2+}(aq)}. \qquad (17)$$

Within the temperature range under study, the reaction is exothermic. Its enthalpy $\Delta_\mathrm{r}H^0_\mathrm{m}$ at 298.15 K was measured six times to give the following values (kJ mol^{-1}): –34.150, –33.981, –33.896, –33.821, –33.828, and –33.693 (average –33.895 ± 0.157). The standard enthalpy of $\mathrm{Cu(His)_2^{2+}(aq)}$ formation was calculated by Eq. (17) in the terms of the Hess law.

$$\Delta_{\mathrm{f,Cu(His)_2^{2+}(aq)}}H^0_\mathrm{m} = \Delta_\mathrm{r}H^0_\mathrm{m} + (\Delta_{\mathrm{f,Cu^{2+}(aq)}}H^0_\mathrm{m}$$
$$+ 2\Delta_{\mathrm{f,L\text{-}\alpha\text{-}His(aq)}}H^0_\mathrm{m}) = [(-33{,}895 \pm 0.157) + (-65.77)$$
$$+ 2(-429.91 \pm 1.54)] = (-819.72 \pm 3.09)\ \mathrm{kJ\ mol^{-1}}.$$

The $\Delta_{\mathrm{f,Cu^{2+}(aq)}}H^0_\mathrm{m}$ and $\Delta_{\mathrm{f,L\text{-}\alpha\text{-}His(aq)}}H^0_\mathrm{m}$ were taken from [14] and [15], respectively.

Calculation of thermokinetic values for the complex-formation reaction. A typical thermokinetic curve for the reaction under study is presented in Fig. 1. The data obtained from the thermokinetic curves are summarized in Table 1. Table 2 lists the reaction rate constant (*k*), activation energy (*E*), pre-exponential factor (*A*), reaction order (*n*), activation enthalpy ($\Delta H^0_{\neq}$), activation entropy ($\Delta S^0_{\neq}$), activation Gobbs energy ($\Delta G^0_{\neq}$), and reaction enthalpy ($\Delta_\mathrm{r}H^0_{\neq}$) calculated by Eqs. (6), (7), (14), and (16).

The data in Table 2 clearly indicate that the reaction rate increases with temperature and that the reaction is first-order. The *E* and $\Delta H^0_{\neq}$ values are rather low, whereas the $\Delta S^0_{\neq}$ value is high. These facts show that the reaction readily proceeds within the temperature range 298.15–323.15 K.

Materials. Analytical grade $\mathrm{CuCl_2 \cdot 2H_2O}$ (A) and L-α-histidine (B) (purity >99.5%) were used. They were dissolved in distilled water. The concentration of the A and B solutions was 0.1000 M. The A : B molar ratio was 1 : 2. The conductivity of deionized water was 5.48×10^{-8} S cm^{-11}.

Experimental equipment and technique. Thermokinetic measurements were preformed in an RD496-III microcalorimeter (China, Southwest Institute of Electronic Engineering) which was equipped with two 15-ml vessels (Fig. 2). After equilibration, the glass rods in the sample and reference vessels were pushed down simultaneously, and the solutions were mixed. The microcalorimeter was calibrated by the Joule effect. Its sensitivity was 63.994 ± 0.042, 64.308 ± 0.027, 64.499 ± 0.064, 64.638 ± 0.078, 63.733 ± 0.077,

Table 1. Thermographic data for the reaction of copper(II) chloride with L-α-histidine[a]

t, s	298.15 K		303.15 K		308.15 K		313.15 K		318.15 K		323.15 K	
	H_i/H_0	$(dH_i/dt)\times10^4$, J s^{-1}	H_i/H_0	$(dH_i/dt)\times10^4$, J s^{-1}	H_i/H_0	$(dH_i/dt)\times10^4$, J s^{-1}	H_i/H_0	$(dH_i/dt)\times10^4$, J s^{-1}	H_i/H_0	$(dH_i/dt)\times10^4$, J s^{-1}	H_i/H_0	$(dH_i/dt)\times10^4$, J s^{-1}
200	0.3857	117.7	0.4291	143.7	0.4077	183.1	0.4170	243.0	0.4025	309.4	0.4266	376.3
250	0.4756	104.3	0.5197	124.3	0.4970	159.9	0.5064	208.8	0.4904	269.4	0.5094	323.1
300	0.5553	90.96	0.5978	105.7	0.5750	137.7	0.5844	178.1	0.5672	231.0	0.5808	276.4
350	0.6247	78.13	0.6642	89.07	0.6424	117.5	0.6492	150.8	0.6336	196.3	0.6424	235.5
400	0.6844	66.40	0.7204	74.76	0.7001	99.40	0.7051	127.2	0.6905	166.1	0.6952	200.7
450	0.7354	56.02	0.7678	62.45	0.7492	83.62	0.7524	107.0	0.7391	140.1	0.7404	171.2
500	0.7786	46.90	0.8075	52.09	0.7906	70.00	0.7925	90.05	0.7806	118.1	0.7791	145.9
550	0.8151	39.16	0.8408	43.41	0.8256	58.45	0.8263	75.87	0.8160	99.28	0.8123	124.4
600	0.8457	32.68	0.8687	36.24	0.8551	48.72	0.8550	63.84	0.8460	83.23	0.8406	106.2
650	0.8715	27.20	0.8920	30.26	0.8799	40.55	0.8792	53.72	0.8716	69.82	0.8648	90.69

[a] H_0 8.836 (298.15 K), 9.414 (303.15 K), 9.489 (308.15 K), 10.169 (313.15 K), 10.386 (318.15 K), 10.497 (323.15 K) kJ mol^{-1}.

and 64.639±0.059 μV mW^{-1} at 298.15±0.005, 303.15±0.005, 308.15±0.005, 313.15±0.005, 318.15±0.005, and 323.15±0.005 K, respectively. The experimental accuracy was checked by measuring the enthalpy of solution of crystalline KCl (special purity grade) in deionized water at 298.15 K. The resulting $\Delta_{sol}H^0_m$ value of 17.238±0.048 kJ mol^{-1} (t distribution, 99% confidence level) fits well the reference $\Delta_{sol}H^0_m$ value of 17.241±0.018 kJ mol^{-1} [13]. Thus, the measurement accuracy was 0.5%.

The IR spectra of the copper(II) complex with histidine were taken on an EQ UINOX-550 FT-IR Fourier spectrophotometer (Bruker, USA) in KBr pellets. The content of Cu^{2+} ions was determined by iodometry and of Cl^- ions, by the Fajans method. Analyses for carbon, hydrogen, and nitrogen were carried out on a PE-2400 analyzer. The TG and DTG data were obtained simultaneously on a Perkin Elmer analyzer. The TG and DTG curves were obtained under dry oxygen (60 ml min^{-1}) at a heating rate of 10 deg min^{-1}. The sample weight was about 1 mg.

Preparation and composition of the complex. Final solutions after each experiment were combined and mixed with a solution with a stoichiometric component ratio. The resulting mixture was concentrated on a water bath at 343.15–353.15 K until a crystalline film formed on the surface. The products were dried in a desiccator over P_4O_{10}. According to the elemental analysis, the solid phases in both cases had the same composition $Cu(His)_2Cl_2\cdot H_2O$. Found, %: Cu^{2+} 13.69; Cl^- 15.37; C 31.17; H 4.39; N 18.12. Calculated, %: Cu^{2+} 13.73; Cl^- 15.32; C 31.14; H 4.36; N 18.16.

Table 2. Values of n, k, A, $\Delta G^0_{\neq}$, $\Delta H^0_{\neq}$, and $\Delta S^0_{\neq}$ for the reaction of copper chloride with L-α-histidine (r is the correlation coefficient)[a]

T, K	Eq. (1)			Eq. (3), $\Delta G^0_{\neq}$, kJ mol^{-1}
	$k\times10^3$, s^{-1}	n	r	
298.15	2.192	0.946	0.999	92.11
303.15	2.635	0.946	1.000	91.16
308.15	3.255	0.952	1.000	90.23
313.15	4.058	0.966	1.000	89.26
318.15	5.002	0.977	1.000	88.20
323.15	6.203	0.988	1.000	93.02

[a] Eq. (2): E 33.61 kJ mol^{-1}, ln A 7.408, r 0.999. Eq. (4): $\Delta H^0_{\neq}$ 31.03 kJ mol^{-1}, $\Delta S^0_{\neq}$ –192.0 J mol^{-1} K^{-1}, r 0.999.

The principal IR absorption bands of the complex and the ligand are given in Table 3. The characteristic absorption bands of the amino and carboxy groups in the IR spectrum of the complex are essentially shifted with respect to those of the free ligand, implying that

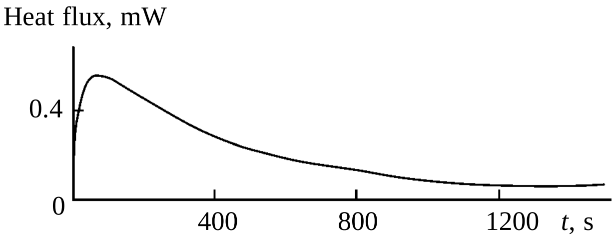

Fig. 1. Thermokinetic curve for the reaction of copper(II) chloride with L-α-histidine (298.15 K).

Table 3. Principal IR absorption bands of the solid complex and the ligand (cm^{-1})

Compound	$\nu_{as}(NH_3^+)$ [$\nu_{as}(NH_2)$]	$\nu_s(NH_3^+)$ [$\nu_s(NH_2)$]	$\delta_{as}(NH_3^+)$ [$\delta_{as}(NH_2)$]	$\delta_s(NH_3^+)$ [$\delta_s(NH_2)$]	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\nu(OH)$	$\nu_{as}(CCN)$	$\nu_s(CCN)$
L-α-His	3025	2860	1590	1456	1635	1415	–	1315	744
$Cu(His)_2Cl_2 \cdot H_2O$	[3275]	[3134]	[1613]	[1395]	1428	1344	3423, 826	1144	971

the nitrogen and oxygen atoms in the complex are coordinated to Cu^{2+} in a bidentate fashion. Moreover, the characteristic imidazole absorption band, too, is strongly shifted in the complex, which shows that the imidazole nitrogen is also coordinated to Cu^{2+}. The bands at 3423 and 826 cm^{-1} in the IR spectrum of the complex were assigned to water hydroxyl absorption, assuming that the complex contains a water molecule.

Thermal stability of the solid complex. The TG and DTG curves for a solid $Cu(His)_2Cl_2 \cdot H_2O$ complex are shown in Fig. 3. The compositions and relative amounts of the decomposition products, as well as the decomposition temperatures are given in Table 4. These data allow the following conclusions. The weight losses in the course of thermal decomposition are close to calculation. Thermal decomposition occurs in three stages: In the first stage the complex loses water of crystallization, in the second it decomposes partly to $CuCl_2$ and thus a mixture of $CuCl_2 \cdot H_2O$ and $Cu(His)_2Cl_2 \cdot H_2O$ is formed, and in the last stage the remaining complex decomposes completely to $CuCl_2$.

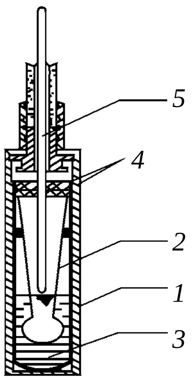

Fig. 2. Device for stidying the complex-formation reaction: (*1*) calorimetric cell, (*2*) test tube with copper(II) chloride solution, (*3*) test tube with histidine solution, (*4*) silicon seal, and (*5*) glass rod (its pushing down breaks the bottom of the test tube *2*, and the two solutions are mixed).

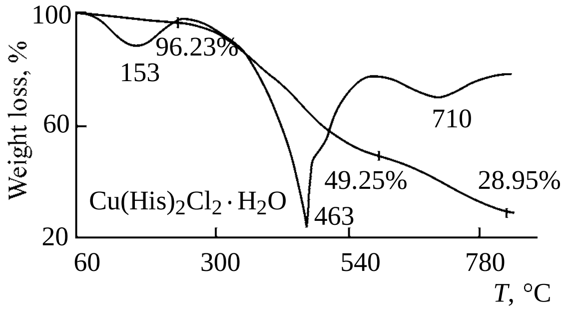

Fig. 3. (*1*) TG and (*2*) DTG curves for solid $Cu(His)_2Cl_2 \cdot H_2O$.

Table 4. Thermal decomposition of $Cu(His)_2Cl_2 \cdot H_2O$

Compound	Decomposition temperature, °C	Residue, %[a]
$Cu(His)_2Cl_2 \cdot H_2O$	51 – 153 – 237	96.23 (96.11)
$4Cu(His)_2Cl_2 \cdot 9CuCl_2$	237 – 463 – 598	49.25 (49.68)
$CuCl_2$	598 – 710 – 830	28.95 (29.05)

[a] Calculated data are given in parentheses.

To check the above-mentioned decomposition scheme, we identified the final products of thermal decomposition by IR spectroscopy. The resulting IR spectra of these compounds contain characteristic absorption bands of $Cu(His)_2Cl_2$, $Cu(His)_2Cl_2$ + $CuCl_2$, and $CuCl_2$, thus providing evidence for the proposed decomposition scheme.

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