ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 9, pp. 704–709. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.M. Maharramov, R.A. Alieva, K.T. Mahmudov, A.V. Kurbanov, R.K. Askerov, 2009, published in Koordinatsionnaya Khimiya, 2009, Vol. 35, No. 9, pp. 715–720.

Copper(II) Complex with 3-(2-Hydroxy-3-Sulfo-5-Nitrophenylhydrazo)pentane-2,4-Dione: Synthesis and Structure

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Received October 20, 2008

Abstract—The copper(II) complex with 3-(2-hydroxy-3-sulfo-5-nitrophenylhydrazo)pentane-2,4-dione (H_3L) is studied, and its crystal structure is studied by X-ray diffraction analysis. The crystals of $[Cu(H_2O)_2]_2(\mu\text{-}L)_2[Cu(H_2O)_4]$ (**I**) are triclinic (space group $P\bar{1}$) at 100 K, a = 7.085(3), b = 10.373(5), c = 12.265(6) Å, α = 0.842(5)°, β = 104.996(6)°, γ = 99.156(6)°, Z = 1). The C=O and NH groups of hydrazone and the OH and SO_3H groups from the aromatic moiety of the molecule are involved in coordination with the copper(II) atom. In the centrosymmetric trinuclear molecule the central Cu(2) atom has the coordination number six, and the terminal Cu(1) atoms have the coordination number five. The thermal properties of complex **I** are studied. The complex formation of copper(II) with the H_3L ligand in an aqueous solution at temperatures 298 ± 0.5, 308 ± 0.5, and 318 ± 0.5 K is studied by potentiometric titration. The standard thermodynamic functions of the complex formation are determined.

DOI: 10.1134/S1070328409090139

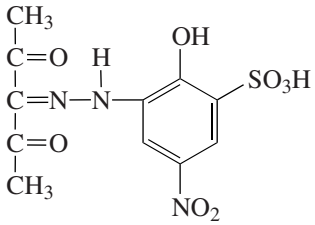
INTRODUCTION

It is known that selectivity of reactions depends on several factors: the method of analysis, scheme of analysis, pH of the medium, ionic strength of the solution, affinity of the metal ion to functional analytical groups, matrix (composition of the analyzed solutions), and others [1–4].

Reagents having tautomeric forms (for instances azo derivatives of β-diketones) are required for the development of direct photometric procedures of determination of elements without their preliminary separation (selectively). Tautomerism results in the selectivity of the reagents and affects the character of its interaction with elements, the thermodynamic stability [5–9], and conditions of formation of complexes. Depending on the affinity of the metal ion to functional analytical groups, the tautomeric equilibrium shifts to a change in the ratio between the amounts of various functional analytical groups, due to which the complex formation reaction becomes selective [10–14].

However, studies become difficult because of many tautomeric forms of organic reagents [15]. The X-ray diffraction data of the complexes formed are needed for the establishment of the tautomeric form participating in the complex formation.

In the present work, we used potentiometric titration to determine the standard thermodynamic functions of the complex formation of copper(II) with 3-(2-hydroxy-3-sulfo-5-nitrophenylhydrazo)pentane-2,4-dione (**H_3L**) in an aqueous solution.



The complex $[Cu(H_2O)_2]_2(\mu\text{-}L)_2[Cu(H_2O)_4]$ (**I**) was synthesized, and its crystal structure was studied by X-ray diffraction analysis. In addition, complex **I** was studied by thermogravimetry.

EXPERIMENTAL

Synthesis of H_3L. *Dinitration.* 2-Amino-4-nitro-6-sulfo-1-phenol (5.85 g, 0.025 mol) and crystalline KOH (1 g) were dissolved in water (50 ml) on weak heating. The resulting solution was cooled to 0°C, and $NaNO_2$ (1.725 g, 0.025 mol) in water (10 ml) was added. The solution was cooled in an ice bath to 0°C, and concentrated HCl (5 ml) was added gradually for 30 min (the temperature should not be higher than +5°C).

Azocoupling. Crystalline CH_3COONa (7.0 g) was added to a mixture of acetylacetone (2.45 ml, 0.025 mol) and ethanol (40 ml). The solution was cooled in an ice bath, and a suspension of 2-amino-4-nitro-6-sulfo-1-phenol diazonium was added by portions. It was monitored during azocoupling that the pH value would range from 8 to 10, and crystalline CH_3COONa was added if

necessary. On the next day an orange precipitate of the product was filtered off, washed with ethanol, and dried in air.

The individual character of the compound was proved by the data of IR and 1 ^{1}H and ^{13}C NMR spectroscopy [15]. ^{1}H NMR (DMSO, δ, ppm): 9.87 (OH), 14.52 (NH), 1.72 (CH_3), 2.08 (CH_3), 8.15–8.28 (Ar). ^{13}C NMR (DMSO, δ, ppm): 26.43 (CH_3), 31.26 (CH_3), 195.53 (C=O), 196.22 (C=O), 175.34 (C=N), 140.75 (NH–(C)Ar), 127.45 (OH–(C)Ar), 128.98 [HO_3S–(C)Ar], 124.71 [O_2N–(C)Ar], 134.45 (H–(C)Ar), 133.38 (H–(C)Ar).

IR (ν, cm^{-1}): 1580 (C=N), 1600 (C=O···H), 1640 (C=O), 1375, 1380 (CH_3), 3450 (NH), 3145 (OH).

The purity of the reactants was monitored by the absorption spectra of solutions and by paper chromatography.

Synthesis of complex I. A 2×10^{-1} M aqueous solution of $CuSO_4 \cdot 5H_2O$ (10 ml) was added to a 2.22×10^{-2} M aqueous solution of H_3L (90 ml). The reaction mixture was stirred for 10 min in a water bath. The resulting mixture was left to evaporate at room temperature. After several days, black crystals precipitated in the bottom of the vessel. The crystals were filtered off and recrystallized from ethanol. The yield was 85.73%.

Solutions of reactants and apparatus. The starting solution of copper(II) (2×10^{-1} M) was prepared by the dissolution of the $CuSO_4 \cdot 5H_2O$ salt in water. The volume of titrated solutions was 50 ml (($c_{H_3L} = 2 \times 10^{-3}$ mol/l, $c_{Cu} = 1 \times 10^{-3}$ mol/l). Titration was carried out at temperatures 298 (308, 318) ± 0.5 K in a thermostat. The ionic strength of the solutions was maintained constant ($I = 0.1$) by the introduction of the calculated amount of KCl. The titrant was a 2×10^{-2} M solution of caustic potash free of carbonic acid. The solutions were magnetically stirred.

The pH values of solutions were monitored on an I-130 pH meter equipped with glass (ESL-43-07) and silver-chloride (EVL-1M3.1) electrodes.

X-Ray diffraction patterns were obtained on an MKh-1321 instrument with the direct sample injection into the ionization area at an ionizing voltage of 70 eV and the temperature of the source 220°C. The crystals of complex **I** are triclinic, space group $P\bar{1}$ at 100 K; a = 7.085(3), b = 10.373(5), c = 12.265(6) Å, α = 90.842(5)°, β = 104.996(6)°, γ = 99.156(6)°, V = 858.1(7) Å^3, FW = 1019.28, Z =1, space group $P\bar{1}$, ρ_{calcd} = 1.972 g/cm^3, μ(MoK_α) = 2.071 mm^{-1}, F(000) = 517. The unit cell parameters and the intensities of 6626 reflections (3298 independent reflections, R_{int} = 0.0542) were measured on an Xcalibur 3 automated four-circle diffractometer (MoK_α radiation, graphite monochromator, CCD detector, ω scan mode, $2\theta_{max}$ = 25.99°). An absorption correction was applied semiempirically by the data on the intensities of equivalent reflections [16] (T_{min} = 0.55, T_{max} = 0.60).

The structure was solved by a direct method using the SHELXTL program package [17]. The positions of hydrogen atoms were objectively revealed from the dif-

Table 1. Bond lengths and bond angles in the structure of complex **I**

Bond	d, Å	Bond	d, Å
Cu(1)–N(1)	1.916(4)	O(8)–C(10)	1.241(6)
Cu(1)–O(7)	1.929(4)	N(1)–N(2)	1.273(6)
Cu(1)–O(1)	1.971(4)	N(1)–C(1)	1.410(6)
Cu(1)–O(10)	1.975(4)	N(2)–C(7)	1.352(6)
Cu(1)–O(9)	2.368(4)	N(3)–C(5)	1.456(6)
Cu(2)–O(2)	1.954(3)	C(1)–C(6)	1.369(7)
Cu(2)–O(11)	1.915(3)	C(1)–C(2)	1.433(7)
Cu(2)–O(12)	1.979(3)	C(2)–C(3)	1.430(7)
S(1)–O(4)	1.459(4)	C(3)–C(4)	1.381(7)
S(1)–O(2)	1.462(4)	C(4)–C(5)	1.395(7)
S(1)–O(3)	1.467(4)	C(5)–C(6)	1.400(7)
S(1)–C(3)	1.778(5)	C(7)–C(8)	1.446(7)
O(1)–C(2)	1.290(6)	C(7)–C(10)	1.466(7)
O(5)-N(3)	1.242(6)	C(8)–C(9)	1.498(7)
O(6)-N(3)	1.239(6)	C(10)–C(11)	1.512(7)
O(7)–C(8)	1.272(6)		
Angle	**φ, deg**	**Angle**	**φ, deg**
N(1)Cu(1)O(7)	89.14(17)	O(6)N(3)O(5)	122.9(4)
N(1)Cu(1)O(1)	84.30(16)	O(6)N(3)C(5)	118.4(4)
O(7)Cu(1)O(1)	173.35(15)	O(5)N(3)C(5)	118.7(4)
N(1)Cu(1)O(10)	157.46(16)	C(6)C(1)N(1)	125.0(5)
O(7)Cu(1)O(10)	92.21(15)	C(6)C(1)C(2)	122.9(5)
O(1)Cu(1)O(10)	93.43(15)	N(1)C(1)C(2)	112.1(4)
N(1)Cu(1)O(9)	112.41(15)	O(1)C(2)C(3)	123.9(5)
O(7)Cu(1)O(9)	91.39(14)	O(1)C(2)C(1)	119.6(5)
O(1)Cu(1)O(9)	92.13(14)	C(3)C(2)C(1)	116.5(4)
O(9)Cu(1)O(10)	90.06(14)	C(4)C(3)C(2)	121.1(5)
O(11)Cu(2)O(12)	92.30(15)	C(4)C(3)S(1)	119.8(4)
O(2)Cu(2)O(11)	90.54(16)	C(2)C(3)S(1)	119.0(4)
O(2)Cu(2)O(12)	91.04(15)	C(3)C(4)C(5)	119.2(5)
O(2)Cu(2)O(2Ä)	179.09(15)	C(4)C(5)C(6)	122.3(5)
O(4)S(1)O(2)	113.4(2)	C(4)C(5)N(3)	121.3(5)
O(4)S(1)O(3)	111.7(2)	C(6)C(5)N(3)	116.4(5)
O(2)S(1)O(3)	113.3(2)	C(1)C(6)C(5)	117.8(5)
O(4)S(1)C(3)	105.8(2)	N(2)C(7)C(8)	125.1(5)
O(2)S(1)C(3)	107.1(2)	N(2)C(7)C(10)	111.5(4)
O(3)S(1)C(3)	104.8(2)	C(8)C(7)C(10)	123.4(5)
C(2)O(1)Cu(1)	111.3(3)	O(7)C(8)C(7)	122.9(5)
C(8)O(7)Cu(1)	128.6(3)	O(7)C(8)C(9)	115.6(4)
N(2)N(1)C(1)	115.2(4)	C(7)C(8)C(9)	121.5(5)
N(2)N(1)Cu(1)	132.2(4)	O(8)C(10)C(7)	121.4(5)
C(1)N(1)Cu(1)	112.5(3)	O(8)C(10)C(11)	119.8(5)
N(1)N(2)C(7)	121.5(4)	C(7)C(10)C(11)	118.7(5)

ference electron density synthesis and refined by the riding model with $U_{iso} = nU_{eq}$ of the non-hydrogen atom bonded to the given hydrogen atom (n = 1.5 for the hydrogen atoms of the water molecules and n = 1.2 for the hydrogen atoms of the H_2L^- ligand). The structure was refined for F^2 by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms to $R_1 = 0.0543$, $wR_2 = 0.1299$ for 2484 reflections with $F > 4\sigma(F)$, $S = 97.8\%$. Selected bond lengths and bond angles are given in Table 1. The torsion angles are listed in Table 2. The coordinates of atoms and other parameters of complex **I** were deposited with the Cambridge Crystallographic Data Centre (no. 728 492; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Thermogravimetric studies were carried out on a Paulik–Paulik–Erdey *Q* derivatograph. Samples were heated in air from 20 to 1000°C with a rate of 10°C/min. A weighed sample was 70 mg, the holder of the sample was a platinum crucible without a cap, and the reference was calcined alumina.

RESULTS AND DISCUSSION

In the $[Cu(H_2O)_2]_2(\mu\text{-}L)_2[Cu(H_2O)_4]$ structure (**I**) (Fig. 1) the L^{3-} ligand acts as a tetradentate bis(chelating) bridge: the oxygen and nitrogen atoms of the C=O and NH groups of the hydrazone form of the reactant and the OH group of the aromatic ring (five- and six-membered metallocycles are formed as a result), water molecules, and SO_3H groups are involved in coordination with copper(II).

The Cu(1)–O(1) and Cu(1)–O(7) bonds are nonequivalent in length (1.971(4) and 1.929(4) Å, respectively) (Table 1). The C(8)–O(7) bond with the coordinated oxygen atom is longer than the terminal C(10)–O(8) bond (1.272(6) and 1.241(6) Å, respectively). In the five-membered metallocycle the N(1)Cu(1)O(1) bond angle (84.30(16)°) is smaller than N(1)Cu(1)O(7) (89.14(17)°) in the six-membered chelate cycle. The coordination polyhedron of the Cu(1) atom is a tetragonal pyramid (4 + 1) with the O(9) atom in the axial position. The coordination polyhedron of the Cu(2) atom is a centrosymmetric extended tetragonal bipyramid (4 + 1) with the O(2) atoms in the axial positions.

In $[Cu(H_2O)_2]_2(\mu\text{-}L)_2[Cu(H_2O)_4]$ the angles are synclinal of the gauche type having the same sign and lying in the range –174° ± 10°. The angles O(1)Cu(1)N(1)N(2), Cu(1)N(1)C(1)C(6), C(6)C(1)C(2)O(1), N(1)C(1)C(2)C(3), O(1)C(2)C(3)C(4), C(1)C(2)C(3)S(1), C(3)C(4)C(5)N(3), N(3)C(5)C(6)C(1), N(1)N(2)C(7)C(10), and C(10)C(7)C(8)O(7) lie in the range 178° ± 4° (Table 2). The crystal packing of structural units of compound **I** is shown in Fig. 2.

Using the Schwartzenbach equations [18], we determined the dissociation constants of H_3L at different temperatures and calculated the thermodynamic functions of H_3L dissociation according to the known equations [19, 20] (Table 3).

Based on the data obtained (Table 3), we can conclude the following. The pK value decreases with the temperature increase, i.e., the acidic properties of H_3L enhance [21, 22]. The positive ΔH value indicates that this process is endothermic [21–23]. The ΔG change of this process is positive and, hence, the dissociation of H_3L is not spontaneous [22, 23]. The ΔS change is negative during the dissociation of H_3L, which is related to the solvation process [21, 22].

The number of functional groups capable of dissociation with proton abstraction (sulfo group, –NH–N= of the hydrazone form, OH of enol, and OH group of the aromatic ring in the *ortho* position to the azo group) increases because of tautomeric equilibrium. The high acidity of the cationic form of the reactants does not allow one to determine the dissociation constants of the sulfo group. To determine the reactivity of the tautomeric forms of H_3L and specifics of deprotonation (pK) of the groups composing these forms, we performed the MO LCAO quantum-chemical calculations in the Hückel approximation [24–26] and constructed their molecular diagrams [27].

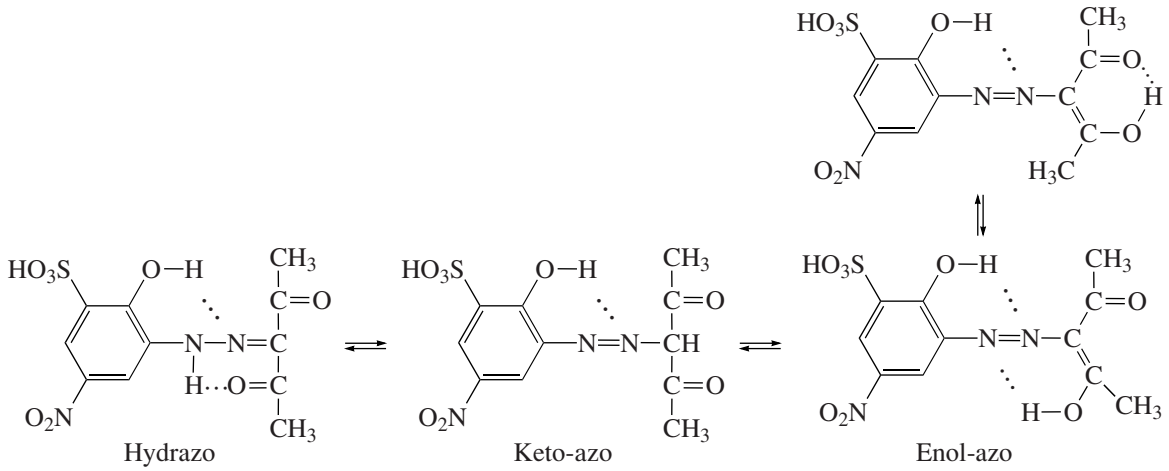


Table 2. Torsion angles in the structure of complex **I**

Angle	τ, deg	Angle	τ, deg
N(1)Cu(1)O(1)C(2)	–3.9(3)	O(7)Cu(1)N(1)C(1)	–175.2(3)
O(10)Cu(1)O(1)C(2)	153.6(3)	O(1)Cu(1)N(1)C(1)	3.6(3)
O(9)Cu(1)O(1)C(2)	–116.2(3)	O(10)Cu(1)N(1)C(1)	–81.6(5)
N(1)Cu(1)O(7)C(8)	–6.9(4)	O(9)Cu(1)N(1)C(1)	93.6(3)
O(10)Cu(1)O(7)C(8)	–164.3(4)	Cu(1)N(1)N(2)C(7)	4.5(7)
O(9)Cu(1)O(7)C(8)	105.5(4)	Cu(1)N(1)C(1)C(6)	176.8(4)
O(7)Cu(1)N(1)N(2)	0.5(5)	Cu(1)N(1)C(1)C(2)	–2.8(5)
O(1)Cu(1)N(1)N(2)	179.4(5)	Cu(1)O(1)C(2)C(3)	–176.3(4)
O(10)Cu(1)N(1)N(2)	94.2(6)	Cu(1)O(1)C(2)C(1)	3.5(6)
O(9)Cu(1)N(1)N(2)	–90.7(5)		

Table 3. Thermodynamic characteristics of the dissociation of H_3L in an aqueous solution

T, K	pK_1	pK_2	ΔG_1^0, kJ/mol	ΔG_2^0, kJ/mol	ΔH_1^0, kJ/mol	ΔH_2^0, kJ/mol	ΔS_1^0, J mol^{-1} K^{-1}	ΔS_2^0, J mol^{-1} K^{-1}
298 ± 0.5	5.71 ± 0.01	8.84 ± 0.01	32.58 ± 0.07	50.44 ± 0.09			–33.08 ± 1.30	–7.65 ± 2.57
308 ± 0.5	5.60 ± 0.02	8.57 ± 0.02			22.72 ± 1.20	48.16 ± 2.48		
318 ± 0.5	5.46 ± 0.02	8.31 ± 0.01						

It can be assumed on the basis of the quantum-chemical calculation results that pK_1 characterizes the deprotonation of the OH group in the *ortho* position of the aromatic moiety of H_3L, and pK_2 characterizes that of the hydrozone form (=N–NH–) (Table 3).

The Bjerrum method [28] was used for the calculation of the stability constants for the complexes. The free Gibbs energy, enthalpy, and entropy of the complex formation were calculated by the known equations [19, 20]. The obtained values of the stability constants of the complexes at different temperatures were used for the calculation of the Gibbs energy, enthalpy, and entropy of the complex formation by the equations: $\Delta G_1^0 = -RT\ln K_1$ и $\Delta G_2^0 = -RT\ln K_2$; $\Delta H_1^0 = -R\dfrac{\ln K_{1(T_3)} - \ln K_{1(T_1)}}{\dfrac{1}{T_3} - \dfrac{1}{T_1}}$ and $\Delta H_2^0 = -R \times \dfrac{\ln K_{2(T_3)} - \ln K_{2(T_1)}}{\dfrac{1}{T_3} - \dfrac{1}{T_1}}$; $\Delta S_1^0 = \dfrac{\Delta H_1^0 - \Delta G_1^0}{T_1}$ and $\Delta S_2^0 = \dfrac{\Delta H_2^0 - \Delta G_2^0}{T_1}$.

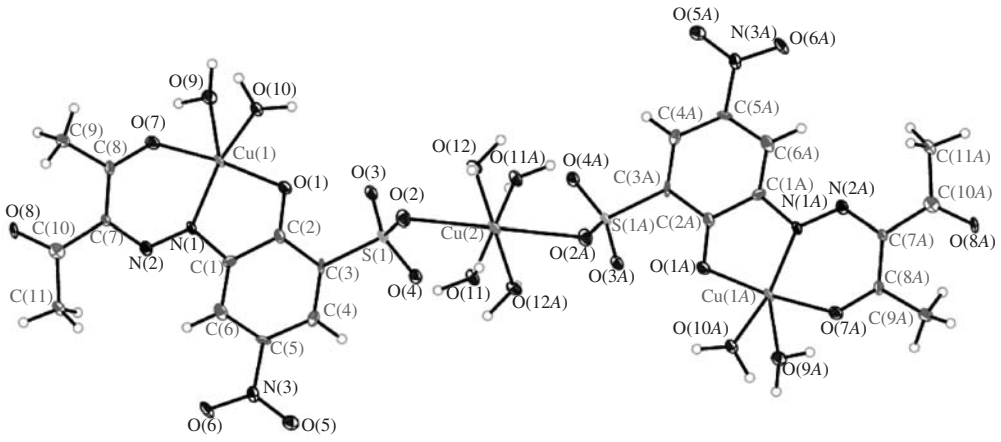


Fig. 1. Structure of the $[Cu(H_2O)_2]_2(\mu\text{-}L)_2[Cu(H_2O)_4]$ complex.

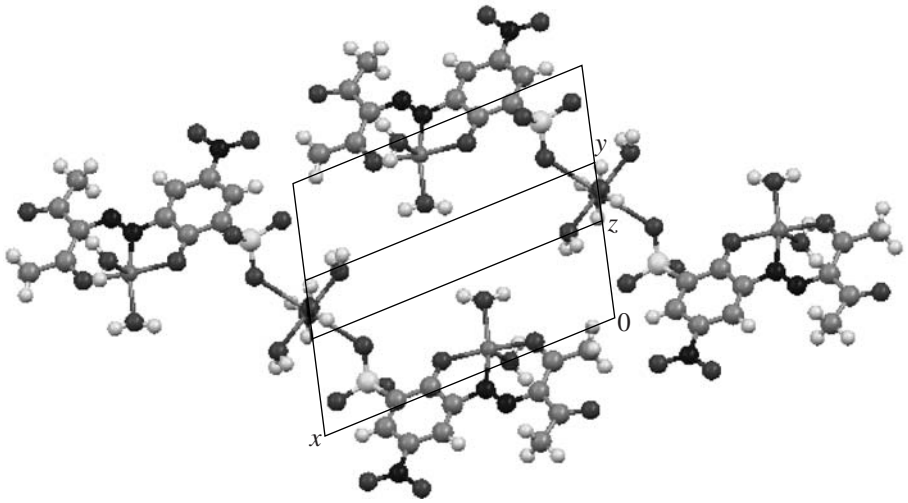


Fig. 2. Crystal packing of structural units in the $[Cu(H_2O)_2]_2(\mu\text{-}L)_2[Cu(H_2O)_4]$ complex.

The results of calculations are presented in Table 4.

The negative values of the enthalpy change of the complex formation are related to an increase in the degree of covalence of the Cu–N and Cu–O (hydrazo) bonds ("internal" part of the enthalpy change) and, correspondingly, to a decrease in the electrostatic contribution ("external" part of the enthalpy change) [27], and to the predominance of the functional groups (enthalpies of the tautomeric equilibrium shift) depending on the affinity of copper(II) ions.

The positive values of the entropy change are related to the liberation of water molecules during complex formation and to the formation of a complex with a smaller charge than that of the initial ions, due to which the complexes obtained are less solvated [18].

Thus, the data in Table 4 indicate that the stability of the complexes decreases with the temperature increase. The negative ΔG value indicates that the complex formation reactions are spontaneous [21–23] and exothermic ($\Delta H < 0$) and the enthalpy plays the decisive role in these reactions. The positive entropy change confirms that the complex formation occurs indeed in the solution.

The results of thermal studies show that the complex is thermally stable up to 110°C. The thermal decomposition of the complex that occurred in three stages was observed in the temperature interval from 110 to 670°C (Fig. 3).

The isolation of $Cu(H_2O)_4$ (110°C) occurs through the cleavage of the bridge between the $Cu(H_2O)_2(\mu\text{-}L)$ chelates (1), liberation of coordination water from the internal sphere of the copper atom (280–320°C) (2) (the process is exothermic, a minimum at 300°C is observed in the DTG curve), and decomposition of the $[Cu(\mu\text{-}L)]_2$ complex (3) in the temperature interval from 430 to 670°C (the decomposition occurs simultaneously with

Table 4. Thermodynamic characteristics of the complex formation of copper(II) with H_3L in an aqueous solution

T, K	$\log K_1$	$\log K_2$	ΔG_1^0, kJ/mol	ΔG_2^0, kJ/mol	ΔH_1^0, kJ/mol	ΔH_2^0, kJ/mol	ΔS_1^0, J mol^{-1} K^{-1}	ΔS_2^0, J mol^{-1} K^{-1}
298 ± 0.5	10.08 ± 0.03	8.95 ± 0.02	–57.51 ± 0.11	–51.07 ± 0.09			80.16 ± 1.82	64.66 ± 1.72
308 ± 0.5	9.89 ± 0.02	8.77 ± 0.04			–33.62 ± 1.71	–31.80 ± 1.63		
318 ± 0.5	9.71 ± 0.05	8.60 ± 0.03						

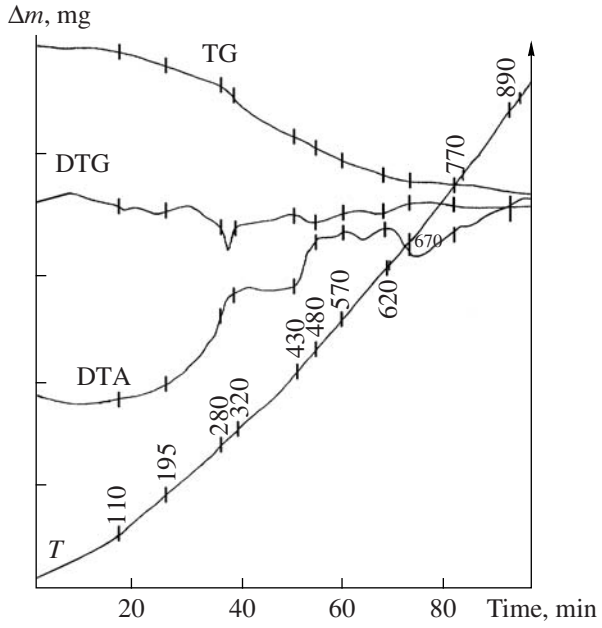


Fig. 3. Thermoderivatogram of the $[Cu(H_2O)_2]_2(\mu\text{-}L)_2[Cu(H_2O)_4]$ compound.

burning out of the organic ligand of the residue and formation of CuO). The process is characterized by the exotherm with three maxima at 480, 570, and 620°C.

$$[Cu(H_2O)_2]_2(\mu\text{-}L)_2[Cu(H_2O)_4] \xrightarrow{110^\circ C} [Cu(H_2O)_2]_2(\mu\text{-}L)_2 + Cu(H_2O)_4, \quad (1)$$

$$[Cu(H_2O)_2]_2(\mu\text{-}L)_2 \xrightarrow{280\text{–}320^\circ C} [Cu(\mu\text{-}L)]_2 + 4H_2O, \quad (2)$$

$$[Cu(\mu\text{-}L)]_2 \xrightarrow{430\text{–}670^\circ C} 2CuO. \quad (3)$$

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