

# 1-[5-(Hydrazidomethylsulfinyl)pentyl]-3,5-dimethylisocyanurate: protolytic properties and complexation reactions

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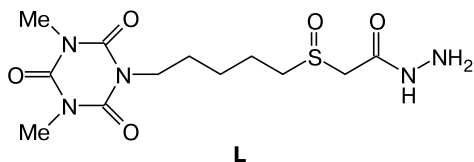
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The compound with antituberculosis activity, 1-[5-(hydrazidomethylsulfinyl)pentyl]-3,5-dimethylisocyanurate, was studied in aqueous dimethyl sulfoxide by potentiometric titration, spectrophotometry, and mathematical simulation of equilibria in solution (the CPESP program). The protolytic properties of the compound were examined. The compositions and stability constants of its complexes with copper(II) were determined. The geometries of the isocyanurate and its complexes were optimized by molecular mechanics computations.

**Key words:** 1-[5-(hydrazidomethylsulfinyl)pentyl]-3,5-dimethylisocyanurate, copper(II), acid–base properties, complexation, mathematical modeling of equilibria.

A number of compounds with antituberculosis activity have been obtained at the A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Research Center of the Russian Academy of Sciences. They are superior in activity to isonicotinohydrazide (accepted as a standard) and exhibit high species specificity and low toxicity. Some of them are patented drugs, *e.g.*, tubophen (a salt of bis(hydroxymethyl)phosphinic acid with isonicotinohydrazide<sup>1</sup>) and substituted triazines<sup>2</sup> and isocyanurates.<sup>3,4</sup>

Earlier,<sup>5–7</sup> we have studied the protolytic and complexing properties of tubophen and two triazine derivatives, *viz.*, 2,4-diamino-6-(amidomethylsulfinylmethyl)-1,3,5-triazine and 6-(acetohydrazidomethylsulfinylmethyl)-2,4-diamino-1,3,5-triazine. Such information is unavailable for isocyanurates, specifically for 1-[5-(hydrazidomethylsulfinyl)pentyl]-3,5-dimethylisocyanurate, although the knowledge of the above properties is required to predict the behavior of these compounds in various media.



1-[5-(Hydrazidomethylsulfinyl)pentyl]-3,5-dimethylisocyanurate (**L**) contains three fragments suitable as ligands for complexation reactions: 3,5-dimethylisocyanurate, sulfoxide, and hydrazide. The properties of com-

pounds featuring some or other of these functional groups have been documented. The protolytic and complexing properties of various acid hydrazides are most comprehensive for aqueous and aqueous organic media. Metal complexes of substituted isocyanurates have been mostly obtained preparatively. Data on reactions of isocyanuric and cyanuric acids with typical complexing agents in solutions are virtually lacking. The donating properties of the sulfoxide group depend on the central metal atom. For instance, dimethyl sulfoxide is coordinated through the O atom to "hard" (according to Pearson's HSAB concept) cations and through the S atom to "soft" ones.

The goal of the present work was to study the state and acid–base properties of the novel compound with antituberculosis activity, *viz.*, 1-[5-(hydrazidomethylsulfinyl)pentyl]-3,5-dimethylisocyanurate, in solution and its complexation with Cu<sup>II</sup>. In addition, using molecular mechanics (MM2) calculations, we intended to obtain primary data (estimates) on the structures of different forms of this compound and its donating properties (ways of coordination) in copper(II) complexes.

## Experimental

1-[5-(Hydrazidomethylsulfinyl)pentyl]-3,5-dimethylisocyanurate (**L**) was prepared and identified according to a known procedure.<sup>3</sup> Compound **L** is virtually insoluble in water but is soluble in aqueous DMSO (60 vol.% DMSO; the solubility of **L** is  $4 \cdot 10^{-3}$  mol L<sup>-1</sup>). Dimethyl sulfoxide was purified by distillation.<sup>8</sup> Solutions of compound **L** were prepared from its precisely

weighed samples. Cupric nitrate and hydrochloric acid (reagent grade) were used. The concentrations of working solutions were determined by volumetric analysis.

The acid–base properties of compound **L** and its complexation with copper(II) in aqueous DMSO were studied by potentiometric titration and spectrophotometry at  $T = 25 \pm 0.05$  °C as described earlier.<sup>6,7</sup> Measurements were carried out on a pH-673 M instrument. An ELS-43-07 glass electrode was precalibrated in aqueous DMSO solutions.<sup>9</sup> The ionic strength of the solutions was produced by their own components because addition of a supporting electrolyte makes test compounds less soluble and can affect association processes in solution. Electronic absorption spectra were recorded on a SHIMADZU UV mini-1240 spectrophotometer in quartz cells with the solvent as a reference (cell path length 1 cm). In the study of the acid–base properties, solutions of test compounds in aqueous DMSO were titrated with solutions of HCl in aqueous DMSO. The concentration of the organic solvent was the same in both titrants and solutions to be titrated. The latter were stirred on a magnetic stirrer. The reproducible values of the glass electrode potentials in aqueous DMSO solutions to be titrated were achieved in 30–40 min. During titration, this time lag became reduced to 3–7 min.

The composition and stability of the complexes formed in the copper(II)–**L** system were determined by analyzing the dependences of absorbance  $A$  on the variable ligand concentration ( $C_L = 1.0 \cdot 10^{-4}$ – $1.5 \cdot 10^{-3}$  and  $3.2 \cdot 10^{-4}$ – $3.9 \cdot 10^{-3}$  mol L<sup>-1</sup>) in two series of solutions with a fixed concentration of the complexing metal ( $C_{Cu^{2+}} = 2.0 \cdot 10^{-4}$  and  $5.0 \cdot 10^{-4}$  mol L<sup>-1</sup>). The optical densities and pH values of aqueous DMSO solutions containing copper(II) and compound **L** remained virtually unchanged with time (over a 30-min interval).

The quantitative characteristics of acid–base and complexation reactions at equilibrium in solutions were obtained by processing the experimental potentiometric and spectrophotometric data with the CPESP program.<sup>10</sup> For mathematical modeling of protolytic equilibria or complexation reactions from potentiometric data, the CPESP program employs the Bjerrum formation function<sup>11</sup>  $\bar{n}$  at different pH values of solutions as a modeled response. In the spectrophotometric method, the molar absorption coefficient serves as such a response. The validity of the solution was verified using the Fisher test<sup>12</sup> and the  $R$  factor as its analog.<sup>13</sup> The average fraction of experimental data deviating from the calculated ones ( $R$  factor) was less than 0.05 (5%).

The geometries of all the structures studied were optimized by the MM2 molecular mechanics method (the ChemOffice 12.0 program package<sup>14</sup>) successfully applied to structural problems of coordination chemistry.<sup>15</sup> The potential energy function to be minimized included the energy terms associated with stretching and bending vibrations (with bend–stretch corrections), internal rotation, and non-1,4-van der Waals, 1,4-van der Waals, and electrostatic interactions. The calculations were performed for individual species *in vacuo*.

## Results and Discussion

The optimized structures for the amide ( $E = 7.1$  kcal mol<sup>-1</sup>) and imidol forms ( $E = 15.0$  kcal mol<sup>-1</sup>) of compound **L** correspond to the local minima of the total potential energy. According to our calculations, the lowest-energy form adopts a compact, "folded" amide configuration (Fig. 1, *a*). This structure shows two rings formed by hydrogen bonding. A six-membered ring is closed through a bond between the sulfoxide O atom and the H atom of the secondary amino group of the hydrazide fragment; a five-membered ring is formed by the hydrazide fragment itself. Both the rings lie above the isocyanurate fragment. Such a folded configuration is stabilized by an intramolecular hydrogen bond between an O atom of the isocyanurate ring and an H atom of the primary amino group of the hydrazide fragment.

Potentiometric data for compound **L** are represented in Fig. 2, *a* as the Bjerrum formation function<sup>11</sup>  $\bar{n}$  plotted versus pH.

The protolytic equilibria revealed in solutions of compound **L** by modeling the experimental data are listed in Table 1. Species distributions in fractions  $\alpha$  as functions of pH are shown in Fig. 2, *b*.

Under experimental acidic conditions, compound **L** forms three protonated species:  $[\text{HL}]^+$  (monoprotonated),  $[\text{H}_3\text{L}]^{3+}$  (triprotonated), and  $[\text{HL}_2]^+$  (monoprotonated dimer). The fraction of the last is relatively low ( $\alpha_{\text{max}} = 0.12$ ) compared to the other two species. No diprotonated form was detected, as with 2,4-diamino-6-(amidomethylsulfanyl)methyl)-1,3,5-triazine.<sup>5</sup>

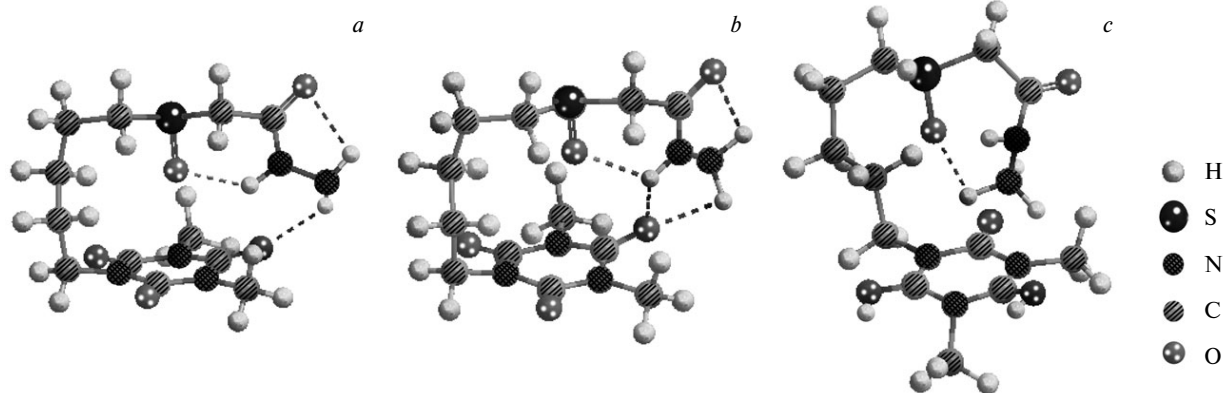
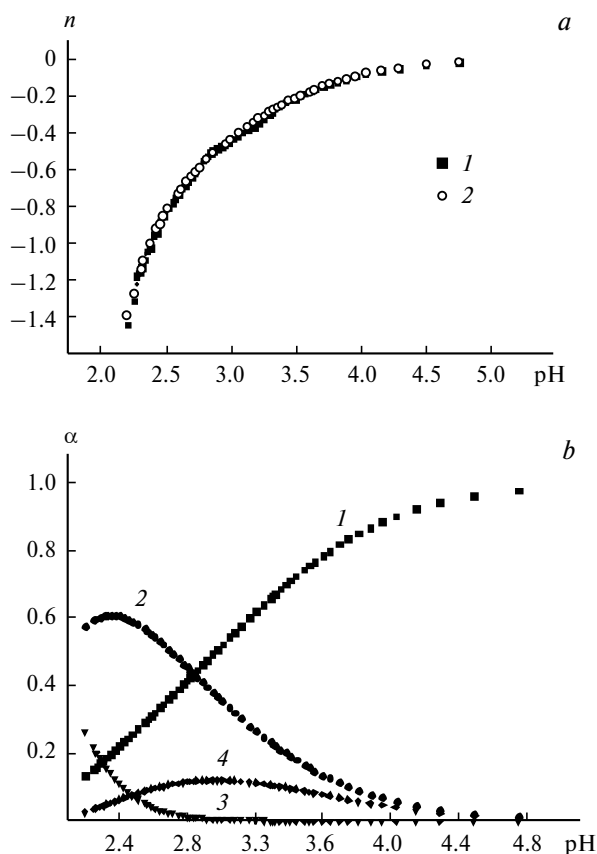


Fig. 1. Hypothetical 3D structures of compound **L** (*a*) and its monoprotonated  $[\text{HL}]^+$  (*b*) and triprotonated forms  $[\text{H}_3\text{L}]^{3+}$  (*c*).



**Fig. 2.** *a.* Experimental (1) and theoretical plots (2) of the formation function  $\tilde{n}$  vs. pH;  $C_L = 4.0 \cdot 10^{-3} \text{ mol L}^{-1}$  and  $C_{\text{HCl}} = 1.60 \cdot 10^{-2} \text{ mol L}^{-1}$ . *b.* Species distributions in fractions  $\alpha$  as functions of pH for the neutral and protonated forms: **L** (1), **[HL]<sup>+</sup>** (2), **[H<sub>3</sub>L]<sup>3+</sup>** (3), and **[HL<sub>2</sub>]<sup>+</sup>** (4).

The primary N atom of the hydrazide fragment seems to be protonated first, which is indirectly confirmed by close values of the logarithms of the protonation constants of compound **L** ( $\log K_1 = 2.84$ ) and benzoic acid ( $\text{p}K = 2.94 \pm 0.05$  (see Ref. 16)) in the same solvent. The species **[HL]<sup>+</sup>** (see Fig. 1, *b*) (with the plausible protonation center) is additionally stabilized ( $E = -7.2 \text{ kcal mol}^{-1}$  with respect to the neutral form) by another hydrogen bond between the H atom of the secondary amino group of the hydrazide fragment and the O atom of the isocyanurate ring.

**Table 1.** Protolytic equilibria of compound **L** ( $C_L = 4.01 \cdot 10^{-3} \text{ mol L}^{-1}$ ) in aqueous dimethyl sulfoxide (60 vol.% DMSO);  $R = 2.74\%$

Equilibrium		$\log K$	$\alpha_{\text{max}}^*$	$\text{pH}_{\text{max}}$
<b>L</b> + <b>H<sup>+</sup></b> $\leftrightarrow$ <b>[HL]<sup>+</sup></b>	(1)	$2.84 \pm 0.01$	0.61	2.35
<b>L</b> + 3 <b>H<sup>+</sup></b> $\leftrightarrow$ <b>[H<sub>3</sub>L]<sup>3+</sup></b>	(2)	$6.91 \pm 0.03$	0.27	2.20
2 <b>L</b> + <b>H<sup>+</sup></b> $\leftrightarrow$ <b>[HL<sub>2</sub>]<sup>+</sup></b>	(3)	$4.82 \pm 0.07$	0.12	2.98

\* The maximum fraction of the corresponding product at  $\text{pH}_{\text{max}}$ .

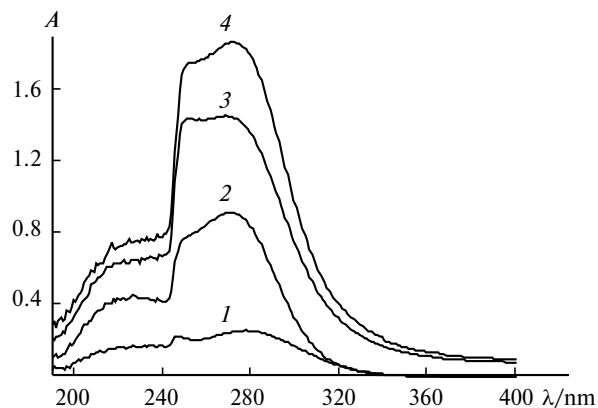
Monoprotonation at the N atoms in positions 1, 3, and 5 of the isocyanurate ring produces structures with  $E = -3.2$ , 14.4, and  $0.8 \text{ kcal mol}^{-1}$ , respectively; *i.e.*, they are less favorable than the structure shown in Fig. 1, *b*.

For triprotonated species (see Fig. 1, *c*), the lowest-energy structure ( $E = -23.5 \text{ kcal mol}^{-1}$ ) contains protons at the carbonyl O atoms of the isocyanurate ring in positions 2 and 4, apart from an extra proton on the primary N atom of the hydrazide fragment. Such a less compact but still folded structure shows no hydrogen bond between the isocyanurate and hydrazide fragments. The literature data on protonated isocyanurate forms are lacking.

Protonation of the carbonyl O atoms of the isocyanurate ring at positions 2 and 6 gives a higher-energy structure ( $E = 58.2 \text{ kcal mol}^{-1}$ ). Structures containing two protonated N atoms in positions 3 and 5 are even less favorable ( $E = 70.2 \text{ kcal mol}^{-1}$ ). For configurations with protons at the N atoms in positions 1 and 5 ( $E = -9.6 \text{ kcal mol}^{-1}$ ) or in positions 1 and 3 ( $E = 6.7 \text{ kcal mol}^{-1}$ ), the potential energies are also higher than that of the structure shown in Fig. 1, *c*. When the N atoms act as proton acceptors, the isocyanurate ring becomes nonplanar and the potential energy of the system increases.

The electronic absorption spectrum of compound **L** contains a rather wide band with a diffuse maximum at  $\lambda = 271 \text{ nm}$  ( $\epsilon_{271} = 4.40 \cdot 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and a shoulder at  $\lambda = 255 \text{ nm}$  ( $\epsilon_{255} = 3.82 \cdot 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) (Fig. 3, curve 2).

When copper(II) is added to a solution of compound **L** in aqueous DMSO, the solution turns yellowish brown; the spectrum shows a broadened absorption band with higher optical density over a range from 250 to 350 nm (see Fig. 3, curves 3, 4). The absorption intensity depends on the **Cu<sup>II</sup>** concentration. Such a band can be regarded as a charge-transfer (intraligand) band.<sup>17,18</sup> A second, wide and low-intensity absorption band due to the *d*–*d* transi-



**Fig. 3.** Electronic absorption spectra of **Cu(NO<sub>3</sub>)<sub>2</sub>** (1) and compound **L** in the absence (2) and in the presence of **Cu<sup>II</sup>** (3, 4) in aqueous dimethyl sulfoxide (60 vol.% DMSO) for  $C_{\text{Cu}^{2+}} = 2.0 \cdot 10^{-4} \text{ mol L}^{-1}$  (1, 3, 4) and  $C_L = 2.1 \cdot 10^{-4}$  (2, 3) and  $4.0 \cdot 10^{-4} \text{ mol L}^{-1}$  (4).

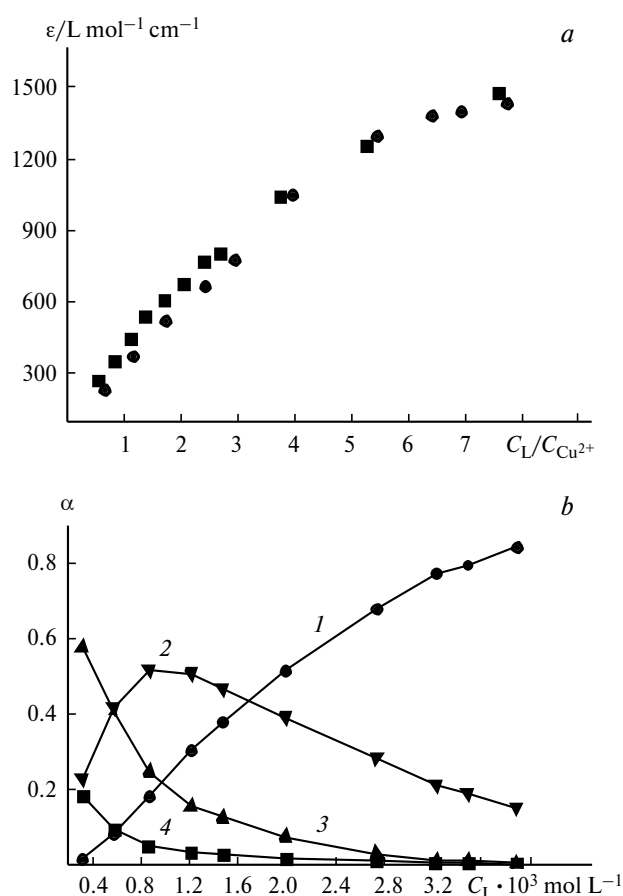
tions in copper(II) complexes (with DMSO as well<sup>19</sup>) is usually not detected under experimental conditions because of a low copper concentration and a path length of 1 cm.

The changed spectral pattern observed for the solution of compound **L** in the presence of copper(II) and the accompanying changes in pH suggest a reaction between these compounds. As with 6-(acetohydrazidomethylsulfanyl)-2,4-diamino-1,3,5-triazine,<sup>7</sup> the complexation makes the solution more acidic. For instance, the decrease in pH by 1.12 (for  $C_{\text{Cu}^{2+}} = 2 \cdot 10^{-4} \text{ mol L}^{-1}$  and  $C_{\text{L}} = 2.1 \cdot 10^{-4} \text{ mol L}^{-1}$ ) and 1.47 (for  $C_{\text{Cu}^{2+}} = 5 \cdot 10^{-4} \text{ mol L}^{-1}$  and  $C_{\text{L}} = 5.8 \cdot 10^{-4} \text{ mol L}^{-1}$ ) suggests coordination of compound **L** in the imidol form.

Construction of a mathematical model for a system in equilibrium



from the experimental data (Fig. 4, *a*) involves sequential searching for an adequate model in terms of the mass



**Fig. 4.** *a.* Plots of the molar absorption coefficient vs. the concentration proportion between compound **L** and copper(II) at pH 3.34–4.03 for  $C_{\text{Cu}^{2+}} = 1.98 \cdot 10^{-4} \text{ mol L}^{-1}$  (1) and  $5.04 \cdot 10^{-4} \text{ mol L}^{-1}$  (2). *b.* Species distributions in fractions  $\alpha$  for the copper(II)–**L** system:  $[\text{Cu}(\text{LH}_{-1})(\text{L})]^+$  (1),  $[\text{Cu}_2(\text{LH}_{-1})_2]^{2+}$  (2),  $[\text{Cu}_2(\text{LH}_{-1})]^{3+}$  (3), and  $\text{Cu}^{2+}$  (4) ( $C_{\text{Cu}^{2+}} = 5.04 \cdot 10^{-4} \text{ mol L}^{-1}$ ).

**Table 2.** Overdetermined equilibrium matrix for the copper(II)–**L** system

Equilibrium	Stoichiometric coefficients of the basic species*			$\alpha_{\text{max}}$
	$\text{Cu}^{2+}$ ( <i>p</i> )	<b>L</b> ( <i>q</i> )	$\text{H}^+$ ( <i>r</i> )	
1	1	1	1	$10^{-3}$
2	1	2	2	0.02
3	2	2	1	0.03
4	1	2	1	0.84
5	2	2	2	0.58
6	2	1	1	0.58

\* The stoichiometric coefficients *p*, *q*, and *r* for the formal equilibrium  $p\text{Cu}^{2+} + q\text{L} \leftrightarrow [\text{Cu}_p\text{L}_q(\text{H}_{-1})_r]^{(2-r)+} + r\text{H}^+$ .

action law and reduces to finding the coefficients *p*, *q*, and *r*. As a first approximation, we used as many hypothetical complexes as possible to form a so-called overdetermined matrix (Table 2). The approximation of the whole concentration sample allowed us to reveal and then exclude insignificant species from the matrix. By eliminating the contribution of insignificant complexes (with  $\alpha < 5\%$ ) to the mean-square deviation of the calculated values of the formation functions from the experimental ones and averaging this deviation, we obtained a final model with equilibrium constants specified in Table 3.

Thus, the solutions contain three cationic complexes. One complex is mononuclear (equilibrium (4)) and the other two are dinuclear (equilibria (5) and (6)) (see Table 3). The distribution of the complex species in fractions  $\alpha$  is shown in Fig. 4, *b*.

The stability constants  $\beta_4$ ,  $\beta_5$ , and  $\beta_6$  of  $[\text{Cu}(\text{LH}_{-1})(\text{L})]^+$ ,  $[\text{Cu}_2(\text{LH}_{-1})_2]^{2+}$ , and  $[\text{Cu}_2(\text{LH}_{-1})]^{3+}$  can be calculated by the formulas (7)–(9):

$$\log\beta_4 = \log K_4 - \log K_b, \quad (7)$$

$$\log\beta_5 = \log K_5 - 2\log K_b, \quad (8)$$

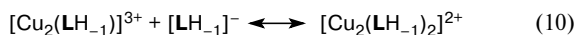
$$\log\beta_6 = \log K_6 - \log K_b, \quad (9)$$

where  $K_b$  is the dissociation constant of **L** in the form of carbohydrazonic acid. Its value is unknown and could not be determined experimentally because of transformation of isocyanurates into cyanurates in basic media.<sup>20</sup> Nevertheless,  $\log K_b$  can be taken to be about  $-8$  since the corresponding hydrazonic acid for 6-(acetohydrazidomethylsulfanyl)-2,4-diamino-1,3,5-triazine dissociates in aqueous dimethyl sulfoxide (40 vol.% DMSO) with  $\log K_b = -8.93$ .<sup>7</sup> Under this assumption, the stability constants of the detected complexes can be estimated at  $\log\beta_4 = 12.2$ ,  $\log\beta_5 = 21.5$ , and  $\log\beta_6 = 13.1$ . Addition of a second ligand to the dinuclear 2 : 1 complex (equilibri-

**Table 3.** Reaction equilibria for the complexation in the copper(II)–L system ( $R = 2.85\%$ )

Equilibrium		$\log K$	$\alpha_{\max}$	$\text{pH}_{\max}$	$\epsilon_{360}$
$\text{Cu}^{2+} + 2 \text{L} \leftrightarrow [\text{Cu}(\text{LH}_{-1})(\text{L})]^+ + \text{H}^+$	(4)	$4.20 \pm 0.08$	0.84	2.41	1433
$2 \text{Cu}^{2+} + 2 \text{L} \leftrightarrow [\text{Cu}_2(\text{LH}_{-1})_2]^{2+} + 2 \text{H}^+$	(5)	$5.49 \pm 0.02$	0.58	3.39	6
$2 \text{Cu}^{2+} + \text{L} \leftrightarrow [\text{Cu}_2(\text{LH}_{-1})]^{3+} + \text{H}^+$	(6)	$5.07 \pm 0.22$	0.58	3.50	104

um (10)) is thermodynamically favorable, which is evident from the value of the stepwise stability constant  $\log K_{10}$ .

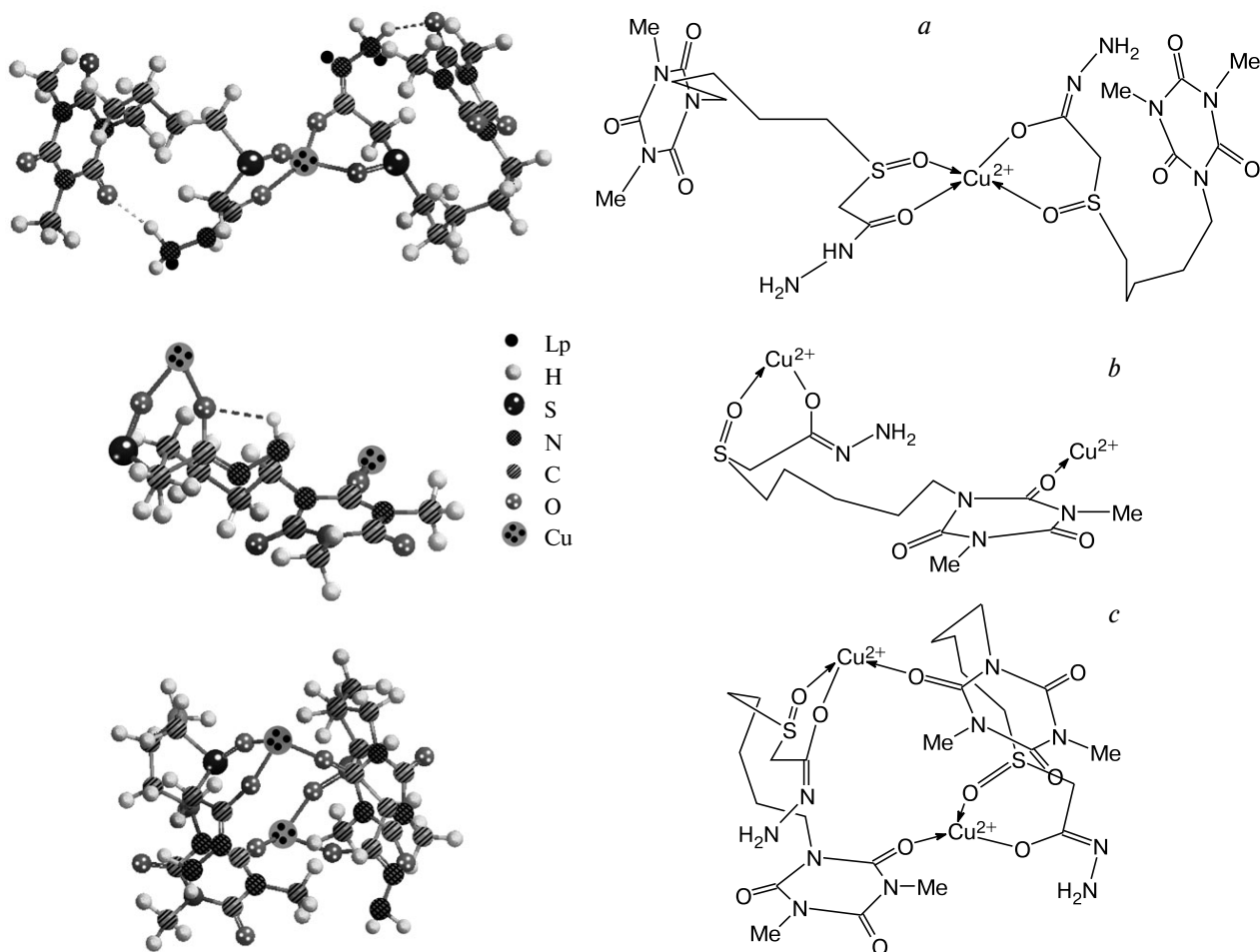


$$\log K_{10} = \log \beta_5 - \log \beta_6;$$

$$\log K_{10} = 0.42 - \log K_b \approx 8.4$$

The mononuclear complex  $[\text{Cu}(\text{LH}_{-1})(\text{L})]^+$  contains the neutral ligand and its deprotonated form. We assumed that the ligand  $\text{LH}_{-1}$  in this complex, as in the case of

6-(acetohydrazidomethylsulfinylmethyl)-2,4-diamino-1,3,5-triazine,<sup>7</sup> is coordinated through the sulfoxide and hydrazonate O atoms. The coordination of the neutral ligand **L** also involves the sulfoxide O atom and the carbonyl O atom of the hydrazide fragment (Fig. 5, *a*). The hydrazide and isocyanurate rings in the ligands **L** and  $\text{LH}_{-1}$  are linked by hydrogen bonds. An alternative way in which the ligands in  $[\text{Cu}(\text{LH}_{-1})(\text{L})]^+$  could be coordinated is less favorable: when the ligand  $\text{LH}_{-1}$  is coordinated through the sulfoxide and carbohydrazonate O atoms and the ligand **L**, through the N atom of the primary amino group of the hydrazide fragment and the carbonyl O atom, the total energy of the system is higher ( $E = 262.1 \text{ kcal mol}^{-1}$ ).

**Fig. 5.** Optimized hypothetical 3D structures of  $[\text{Cu}(\text{LH}_{-1})(\text{L})]^+$  (*a*),  $[\text{Cu}_2(\text{LH}_{-1})_3]^{3+}$  (*b*), and  $[\text{Cu}_2(\text{LH}_{-1})_2]^{2+}$  (*c*).

In the dinuclear 2 : 1 complex  $[\text{Cu}_2(\text{LH}_{-1})]^{3+}$  (see Fig. 5, *b*), the lowest-energy structure is formed by coordination of the second copper ion with the O atom of the cyanurate ring in position 2 or 6. It is known that the *symm*-triazine ring can be coordinated through the C=O group. For example, this type of coordination (also involving the phenolate group of the substituent) has been reported<sup>21</sup> for chelate complexes of 1,3-diallyl-5-(2-hydroxy-3-phenoxypropyl)isocyanurate (data from IR spectroscopy). In the dinuclear 2 : 2 complex  $[\text{Cu}_2(\text{LH}_{-1})_2]^{2+}$  (see Fig. 5, *c*), the coordination environment of copper(II) is made up of three O atoms of two ligands. In both dinuclear complexes,  $\text{LH}_{-1}$  acts as a bridging ligand. The remaining vacancies in the coordination sphere of the central metal ion in solution are occupied by solvent molecules.

In conclusion, it should be noted that no dinuclear structures have been detected under similar experimental conditions for related copper(II) complexes with ligands containing the *symm*-triazine ring (2,4-diamino-6-(amidomethylsulfinylmethyl)-1,3,5-triazine and 6-(acetohydrazidomethylsulfinylmethyl)-2,4-diamino-1,3,5-triazine<sup>6,7</sup>). Unlike the isocyanurate ring, the triazine ring of neither compound is involved in coordination.

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