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2,4-Diamino-6-(acetohydrazidomethylsulfinylmethyl)-1,3,5-triazine. State in Solution, Acid-Base and Complexing Properties

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Abstract — Solutions of a new drug, 2,4-diamino-6-(acetylhydrazidomethylsulfonylmethyl)-1,3,5-triazine, exhibiting tuberculocidal activity were studied using the methods of pH-metry, spectrophotometry, mathematical simulation of equilibria (CPESSP software), and molecular mechanics. Protolytic properties of the compound in the medium of aqueous dimethylsulfoxide (40 vol % of DMSO) were characterized. The composition of the copper(II) complex of this compound was determined and its stability constants were calculated. Based on the absorption spectra in the UV and visible regions the complexing ability of 2,4-diamino-6-(acetylhydrazidomethylsulfonylmethyl)-1,3,5-triazine toward nickel(II) and cobalt(II) were characterized in comparison with copper(II) under the same conditions.

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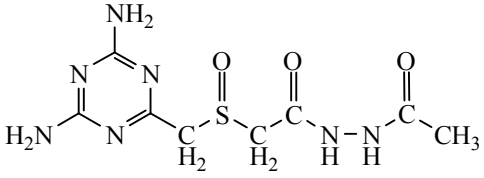
There is much evidence in the literature of the interesting biological properties of some *sym*-triazine derivatives [1]. The 2,4-diamino-6-(acetylhydrazidomethylsulfinylmethyl)-1,3,5-triazine (compound **I**) [2] is one among new antituberculosis drugs including the triazine moiety in its composition. In contrast to 2,4-diamino-6-(carbamoylmethylsulfinylmethyl)-1,3,5-triazine [2] considered by us earlier [3], the drug **I** contains acylated hydrazide group instead of the amide, which is known to results in some cases in a stronger effect and continuous action.

In this paper we investigated the state in solution and the acid–base properties of compound **I** and evaluated the possible interaction of compound **I** with typical complexing agents, copper(II), cobalt(II), and nickel(II).



I

The solvent used was aqueous dimethylsulfoxide containing 40 vol% of DMSO. Compound **I** is practically insoluble in water and ethanol.

Figure 1 shows the curves of pH-metric titration, Fig. 2 shows the dependence of the Bjerrum formation function $\tilde{n}$ [4] on the pH of solution of compound **I**. The characteristics of the protolytic equilibria of **I** in solutions identified by simulation of the obtained experimental data are given below.

Equilibrium	log *K*	α_{max}	pH_{max}
$T + H^+ \rightleftarrows [HT]^+$ (1)	2.35±0.02	0.38	2.56
$HT \rightleftarrows [T]^- + H^+$ (2)	–8.93±0.03	0.53	8.98

Here α_{max} is the maximum share of the form accumulated at the pH equal to pH_{max}.

Adequate description of the pH-metric experimental data over the entire range of pH (1.5–10.5) is achieved assuming that compound **I** in acidic area (pH < 3.5) is protonated [Eq. (1)], while in an alkaline medium (pH > 7.5) behaves as a proton donor

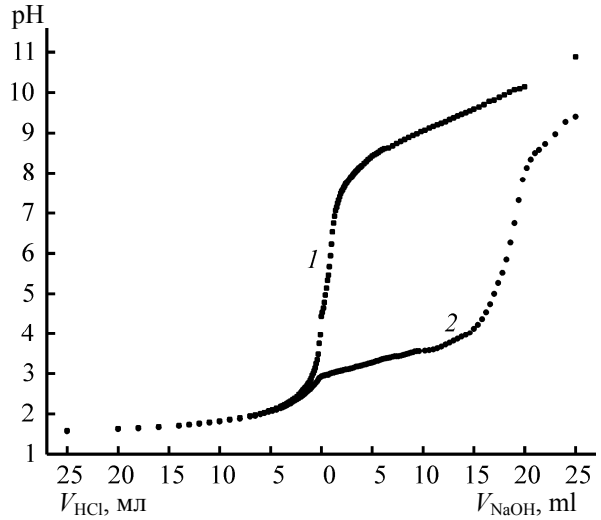


Fig. 1. Curves of pH-metric titration in the absence (*1*) and in the presence (*2*) of copper(II). The reactant concentrations, M: $c_{\mathbf{I}} = 5.01\times10^{-3}$, $c_{NaOH} = 5.30\times10^{-3}$, $c_{HCl} = 5.00\times10^{-2}$, $c_{Cu^{2+}} = 2.52\times10^{-3}$.

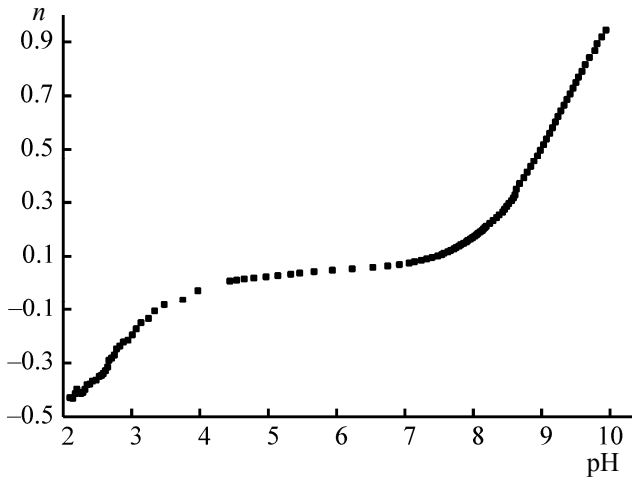
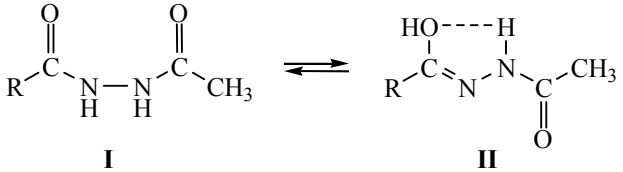


Fig. 2. The dependence of the Bjerrum's formation function ñ on the pH of the solution of compound **I**. Concentrations of reactants, M: $c_{\mathbf{I}} = 5.01\times10^{-3}$, $c_{NaOH} = 5.30\times10^{-3}$, $c_{HCl} = 5.00\times10^{-2}$.

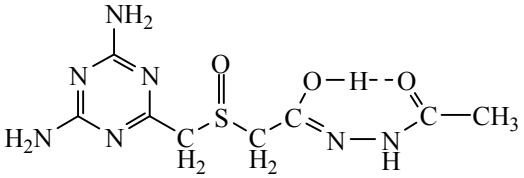
[Eq. (2)]. The neutral form of compound **I** dominates in the pH range from 2.5 to 8.0.

The deprotonation of compound **I** is possible if the hydrazide fragment containing acetyl group takes the imidol structure (**II**). According to literature data, appreciable amounts of imidol (enol) form of acid hydrazides usually appear in an alkaline medium, while in a weakly acidic medium (pH 3–5) the acid hydrazides are present in solution in a molecular amide form [5]. One of the factors that affect the ability of acid hydrazides to take certain structure is the nature of the organic substituent attached to the hydrazide fragment [6]. The organic substituents R with a negative inductive effect may cause in our case the appearance of the imidol form **II** in the tautomeric equilibrium:



I **II**

It is useful to consider another imidol configuretion, **III**, which also, in principle, may be further stabilized by an intramolecular hydrogen bond, provided that the OH groups and C=O are in the *cis* position. Finally a seven-membered ring with a unique aromatic character may be formed.



III

Geometry optimization of all proposed structures by molecular mechanics [7] showed that the calculated values of their potential energy differ markedly from each other.

Initially, we assumed that the compound **I**, as well as 2,4-diamino-6-(carbamoylmethylsulfinylmethyl)-1,3,5-triazine, has a *folded* configuration [3] due to the bent side chain location above the heterocycle plane (Fig. 3a). However, the *unfolded* amide structure of compound **I** (Fig. 3, *b*) with a value of E = –0.76 kcal mol^{-1} (compared to E = 1.66 kcal mol^{-1} for the *folded* structure) was found to be the preferred form.

The seven-membered ring configuration of imidol form **III** (E = 37.26 kcal mol^{-1}) was found to be less favorable than configuration **II** (E = 5.42 kcal mol^{-1}, ΔE = 31.8 kcal mol^{-1}). On the other hand, configuretion **II** of the imidol forms, in turn, is disadvantageous compared to the less compact amide form of the compound (Fig. 3b).

Experimental data support this conclusion. In the IR spectrum of the compound recorded in KBr pellet a

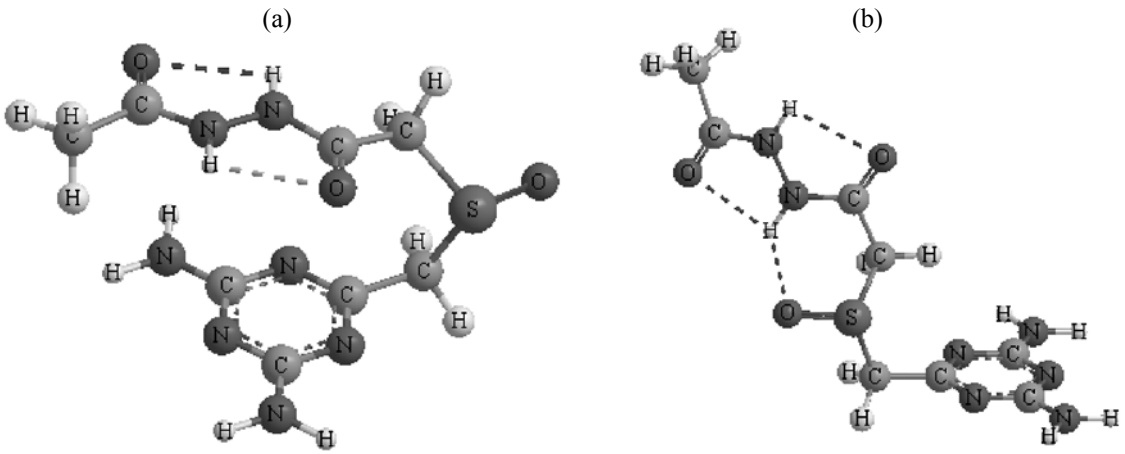
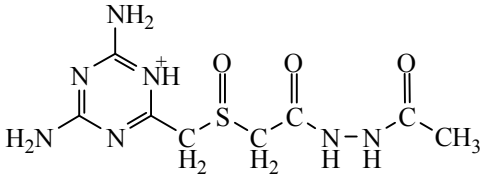


Fig. 3. The optimized geometry of the amide form of 2,4-diamino-6-(acetylhydrazidomethylsulfinylmethyl)-1,3,5-triazine: (a) *folded* configuration and (b) *unfolded* configuration.

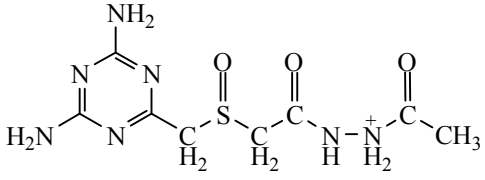
strong absorption band is present of stretching vibrations of carbonyl group at 1664 cm^{-1}. The presence in the ^1H NMR spectrum of the compound dimethylsulfoxide solution of two signals of equal intensity, at 9.98 and 10.16 ppm, belonging to the two NH groups, indicates that the compound exists in solution in the amide form.

Noteworthy are the results of a study of acid–base properties of compound **I**. The obtained value of the formation constant of monoprotonated form of compound **I** (log K = 2.35) is close to that for 2,4-diamino-6-(carbamoylmethylsulfinylmethyl)-1,3,5-triazine (log K = 2.55, solvent water–DMSO, 20 vol. % of DMSO) [3]. This means that the center of protonation [Eq. (1)] may be a nitrogen heteroatom in position *5* (structure **IV**).



IV

On the other hand, we cannot exclude the possibility of protonation of the amino hydrazide fragment (structure **V**), as is usually the case for the acid hydrazides [5].



V

Judging from the values of potential energy of compound **I** (–48.63 and –16.13 kcal mol^{-1} for the structures **IV** and **V**, respectively) calculated by the same method of molecular mechanics, the protonation of the nitrogen atom in position 5 of the heterocycle is preferred {as in 2,4-diamino-6-(carbamoylmethylsulfinylmethyl)-1,3,5-triazine [3]}. The intramolecular hydrogen bonds involving oxygen atoms of the sulfoxide and acetyl groups and the hydrogen atom of the amino group in 4 position and the proton itself apparently essentially contribute to the stabilization of this protonated form.

The value of log K in the Eq. (2) is –8.93 logarithmic units, which is smaller in absolute value compared with the values of dissociation constants, for example, of imidol forms of *p*-nitrobenzoic hydrazides (–9.86 ± 0.07, I = 0.3, KCl) [8] and isonicotinic acid in the tubofen (–10.34) in aqueous solution [9].

As concerns the complexing properties of the compound **I,** the following should be noted. The data in Fig. 1 show that the curves of pH-metric titration of **I** in the absence and the presence of copper(II) merge below the value of pH ≈ 2.0. At pH ≈ 3.4 turbidity of the solution containing copper(II) becomes visible. Upon further adding alkali until the pH ≈ 10.0 amorphous bluish-green precipitate separates becoming abundant at the end of the titration.

In the UV spectrum of compound **I** there is an intense absorption band in the wavelength range 260–262 nm (ε_{max} 2.40×10^3 l mol^{-1} cm^{-1}), as in the spectrum of 2,4-diamino-6-(carbamoylmethylsulfinylmethyl)-1,3,5-triazine (λ_{max} =267 nm, A_{267} = 0.500, ε_{max} $=2.50\times10^3$ l mol^{-1} cm^{-1}) [3]. An absorption band

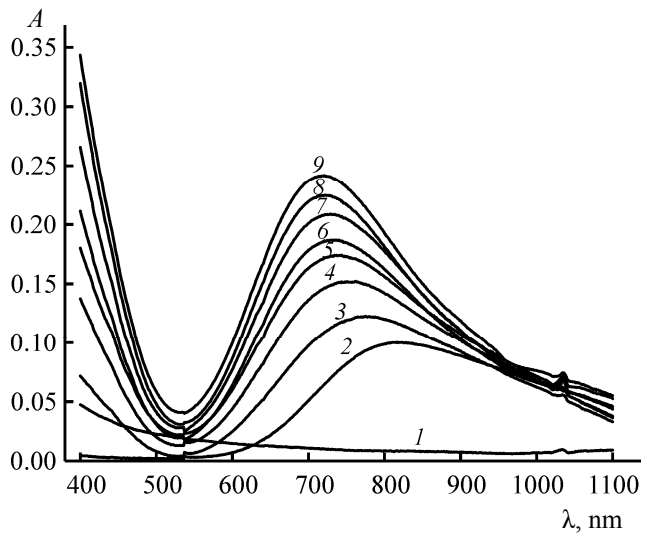


Fig. 4. The electron absorption spectra of solutions of compounds **I** (*1*), Cu(II) (*2*) and Cu(II) in the presence of **I** (*3–9*). Concentration, M, $c_{\mathbf{I}}$ =: (*1*) 7.31×10^{-3}, (*3*) 8.0×10^{-4}, (*4*) 1.84×10^{-3}, (*5*) 2.51×10^{-3}, (*6*) 3.79×10^{-3}, (*7*) 4.87×10^{-3}, (*8*) 5.88×10^{-3}, (*9*) 6.61×10^{-3}. $c_{Cu2+} = 4.85\times10^{-3}$ (*2–9*). λ_{max}, nm: (*2*) 817, (*3*) 775, (*4*) 751, (*5*) 744, (*6*) 735, (*7*) 729, (*8*) 722, (*9*) 721. ε, l mol^{-1} cm^{-1}: (*2*) $\varepsilon_{817} = 20.6$, (*3*) $\varepsilon_{775} = 25.3$, (*4*) $\varepsilon_{751} = 31.3$, (*5*) $\varepsilon_{744} = 35.9$, (*6*) $\varepsilon_{735} = 38.6$, (*7*) $\varepsilon_{729} = 43.1$, (*8*) $\varepsilon_{722} = 46.4$, (*9*) $\varepsilon_{721} = 49.9$. pH: (*1*) 1.4, (*2*) 4.58, (*3*) 3.03, (*4*) 2.86, (*5*) 2.81, (*6*) 2.76, (*7*) 2.74, (*8*) 2.74, (*9*) 2.75.

at 210 nm is poorly informative, and will not be discussed.

At adding copper(II) the water–dimethylsulfoxide solution of compound **I** takes blue-greenish color. The recorded spectrum has two absorption bands of copper(II). The absorption band of the compound at 260 nm undergoes a change: it is shifted to smaller wavelength (λ_{max} 250 nm), and its intensity increases almost twice (*1*, A_{260} = 0.508; *3*, A_{250} = 1.166). Such absorption band of the ligand (compound **I**) modified by the complexation with copper(II) can be, according to [10], described as intraligand one.

In the presence of compound **I,** the absorption band of copper(II) in the visible spectrum is also shifted to shorter wavelengths. The optical density of the solution increases (Fig. 4). This weak and more broadened band is probably due to *d–d* transitions in the complex. In this wavelength region the prorer dimethylsulfoxide copper(II) complexes absorb. Thus, in the 40% dimethylsulfoxide–water solution the maximum accumulationed fraction of the complex $[Cu(DMSO)_2]^{2+}$ is equal to 0.30 (log β = 1.21, λ_{max} = 830 nm, ε = 40 l mol^{-1} cm^{-1}, β is the complex stability constant) [11].

To determine the composition and stability of the complexes formed in the system of copper(II)–compound **I** we used the method of equilibrium shift. The optical density in the two series of solutions with constant concentrations of complexing agent (4.85×10^{-3} and 9.69×10^{-4} M, respectively) were measured at a varied concentration of the ligand. The maximum possible concentration of a substance in solution is determined by its solubility. The solutions containing copper(II) are quite stable: their optical density and pH virtually do not change over time (2 h). The experimental data for one series are shown in Fig. 4. As can be seen, the increase in the ligand concentration is accompanied by a blue shift of the absorption band maximum (from 775 to 720 nm) and remains almost constant for the ligand concentration 6.6×10^{-3} M.

Next we considered the dependences of the light absorption by the solutions containing copper(II) and compound **I** on the concentration of the substance at the wavelengths of 344 and 720 nm. Note that the complexation process is accompanied by acidification of the solution. Thus, the solution obtained by pouring together the solutions of copper(II) and compound **I** with similar initial pH (4.58 and 4.01, respectively), has pH = 2.75. This means that in the complexation the imidol form of the compound is involved and the coordination sphere of the complex includes the anion $\mathbf{I}^-$. The studied compound **I** forms with copper(II) complexes of 1:1 and 1:2 composition [Eqs. (3) and (4)].

Equilibrium	log *K*	α_{max}	ε_{344}	log β	pH_{max}
$Cu^{2+} + HT \rightleftarrows [Cu(T)]^+ + H^+$ (3)	–0.56±0.48	0.55	418	8.37	3.10
$Cu^{2+} + 2HT \rightleftarrows [Cu(T)_2] + 2H^+$ (4)	–1.75±0.62	0.35	913	16.11	2.23

The listed stability constants log β of the complexes were calculated with Eqs. (5) and (6).

$$\log \beta_1 = \log K_3 - \log K_2, \quad (5)$$

$$\log \beta_2 = \log K_4 - 2 \log K_2. \quad (6)$$

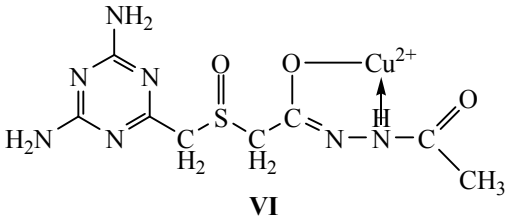
As seen, compound **I** forms with copper (II) strong complexes. By the stability, these complexes are comparable to imidol complexes of nitrobenzoic [12] and bromobenzoic [13] hydrazides in aqueous solution [for

example, for *p*-nitrobenzoic hydrazide, log β_1 = 8.57, log β_2 = 15.82 (I = 0.1, $HClO_4/KClO_4$)].

Thus, although for the test compound **I**, as follows from the above material, the amide tautomeric form is preferred, the complexes of copper(II) with this form of **I** were not detected. At the same time imidol form **II** forms complexes even in acidic solutions (pH ≈ 2.1–4.0). It should be noted that the examples of the complexes with the deprotonated imidol form of acid hydrazides are known in the literature. Thus, *o*-chlorobenzohydrazide forms a complex of this type with copper(II) at pH ≈ 5.4, and for this, as noted in [5], the accumulation in the solution of appreciable amounts of enol (imidol) form of the ligand is not necessarily. Imidol form of the complex is formed by the cleavage of a proton from the amide form of the hydrazide molecule in the coordination sphere [5]. The displacement of equilibrium amide ↔ imide form of the ligand under the influence of complexing agent has attracted attention formerly [6, 12, 13]

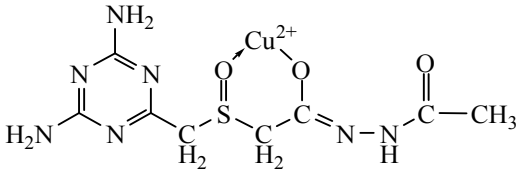
The difference in the behavior of compound **I** is the fact that the formation of its imidol complexes takes place even in a more acidic environment (pH ≈ 2.2), than in the formation of copper(II) complexes with bromobenzoic (pH > 6) [13] and nitrobenzoic (pH 4–6) hydrazides [12] in aqueous solution. The thermodynamically more favorable deprotonation process of the imidol form of compound **I** (log K = –8.93) compared with bromobenzhydrazides [13] (log K = –10.22 to –12.16) and nitrobenzhydrazides [12] (log K = –10.22 to –12.16) may contribute to this occasion.

It has been suggested that in the coordination imidol hydrazide fragment may be involved with the formation of a five-membered metallocycle (structure **VI**):



VI

Such mode of coordination of the hydrazides in the imidol complexes is generally accepted (provided that no other groups are involved in the donor–acceptor interaction with the complexing agent) [5, 6]. As an alternative, we also considered the mode **VII** of coordination with the oxygen atom of sulfoxide group:



VII

Close to this mode of coordination (with the oxygen atom of S=O group) is the coordination of previously studied ligand 2,4-diamino-6-(carbamoylmethylsulfinylmethyl)-1,3,5-triazine [3].

The geometry of the 1:1 complex of structures **VI** and **VII** optimized by the previously used method [7], is shown in Fig. 5. A comparison of the potential energy values of structures **VI** and **VII** (38.96 and –1.55 kcal mol^{-1}, respectively) and of structures with two ligands (93.11 and 76.28 kcal mol^{-1}), suggests a choice in favor of structure **VII**: bidentate coordination of **I** through the oxygen atoms of sulfoxide group and deprotonated imidol hydrazide fragment.

The complex of 1:2 composition [Cu•$\mathbf{I}_2$] is neutral. It was apparently this complex that precipitated (greenish-brown, marshy color) in the water–dimethylsulfoxide solution [c_{Cu2+} = 3.49×10^{-3}, $c_{\mathbf{I}}$ = 7.01×10^{-3} M, pH 2.96] in about a day after its preparation. The solution above the precipitate becomes colorless. A long-term (over one month) exposure of the precipitate in the mother liquor for further isolation and investigation, is apparently accompanied by its partial hydrolysis and decomposition.

The copper(II) complex with the composition, according to elemental analysis, corresponding to the formula $C_{16}H_{24}CuN_{14}O_6S_2$, or [Cu·$I_2$] we isolated from the ethanol solution in the form of greenish-gray powder. In the IR spectrum of this compound (KBr) there are significant changes compared with the spectrum of the parent compound. The intensity of the absorption band of carbonyl group is significantly reduced, the band itself appears as a shoulder on the intense band 1639 cm^{-1} related to ν(C=N). In the region of 1384 cm^{-1} there is a strong band ν(C–O). These changes indicate that the imidol hydrazide fragment is involved in the coordination [5, 6]. Also a broadening of the band of stretching vibrations ν(S=O) at 1029 cm^{-1} is observed, which can be interpreted [14] in favor of participation in the coordination of sulfoxide group.

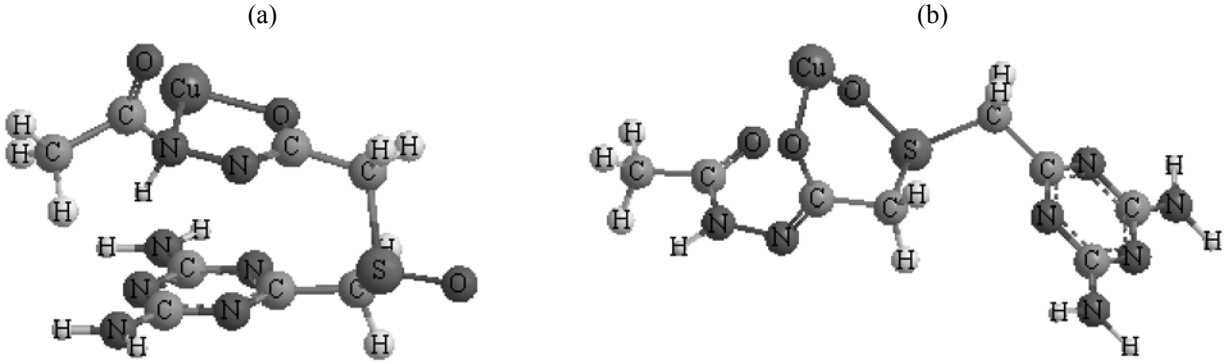


Fig. 5. Steric structure of the copper(II) complex with 2,4-diamino-6-(acetylhydrazidomethylsulfinylmethyl)-1,3,5-triazine of 1:1 composition, (a) **IV** and (b) **V**.

We also obtained a qualitative evidence of complexing ability of compound **I** with nickel(II) and cobalt(II). Thus, the intensity of the absorption band of the compound at 260 nm increases in the presence of nickel(II): the increase in the optical density was $\Delta A_{Ni^{2+}} = 288$ ($c_{Ni^{2+}} = 1.0\times10^{-4}$ M , $c_{\mathbf{I}} = 2.1\times10^{-4}$ M), and in the presence of cobalt(II), $\Delta A_{Co^{2+}} = 0.331$ ($c_{Co^{2+}} = 1.0\times10^{-4}$ M , $c_{\mathbf{I}} = 2.1\times10^{-4}$ M).

We revealed the changes in the visible region of the absorption spectra of solutions of both cobalt(II) and nickel(II) containing two-fold excess of the ligand (but they are less pronounced than the changes in the UV region). Thus, in the case of cobalt(II) somewhat increases the intensity of the absorption band at 515 nm of the complexing agent, $\Delta A_{Co^{2+}} = 0.0042$ [the band of octahedral (pink) form of the complex]. The band of nickel(II) at 397 nm takes the form of a shoulder, $\Delta A_{Ni^{2+}} = 0.0174$.

EXPERIMENTAL

The pH values of solutions were measured on a pH meter pH-673 M, glass electrode ELS–43-07) was used as the indicator, the reference was a saturated silver chloride electrode. The electron absorption spectra (EAS) of solutions taken relatively the solvent were recorded on a SHIMADZU UV mini-1240 spectrophotometer in quartz cells (l cm). The ^{1}H NMR spectra were recorded on a Bruker MSL-400 spectrometer, internal reference tetramethylsilane. IR spectra were recorded on a Vector 22 Fourier spectrometer (Bruker) from KBr pellets.

The ^{1}H NMR spectrum of 2,4-diamino-6-(acetyl-hydrazidomethylsulfinylmethyl)-1,3,5-triazine, δ, ppm (DMSO-d_6): 1.87 s (3H, CH_3), 3.75, 3.77, 3.78, 3.80 (AB system, 2H, CH_2), 3.92, 3.95, 4.07, 4.10 (AB system, 2H, CH_2), 6.78 ush.s (4H, NH_2); 9.98 s (1H, NH); 10.16 s (1H, NH).

Solutions of compound **I** were prepared by precise weighing. The compound was synthesized and identified according to the method [2]. Studies were carried out with aqueous dimethylsulfoxide solutions containing 40 vol % DMSO. Dimethyl sulfoxide was purified by distillation [15]. Glass electrode was calibrated for the water–organic solvent [16]. Ionic strength of solutions was created by the components, since the introduction of the supporting electrolyte decreases the solubility of compounds and can influence the processes of association in solution. Working solutions of the carbonate-free sodium hydroxide, hydrochloric acid, copper(II) nitrate, cobalt (II) and nickel(II) sulfates were prepared from reagent grade chemicals. The concentration of working solutions was determined by volumetric analysis.

In the course of the experiment a solution of compound **I** was titrated pH-metrically by the solutions of hydrochloric acid and alkali. The titration was carried out with the continuous introduction of a titrant in a thermostated glass cell (298 K) under permanent magnetic stirring. In the study of complexation reactions the titrated solutions contained additional copper(II).

The glass electrode potentials reached reproducible values in 2–3 min. However, in the region close to the equivalence point this time considerably increased, and the pH was measured in 10 min after the addition of a next portion of the titrant.

The experimental data, as in [3], were treated using CPESSP software [17]. The reliability of selected models was described by the factors F and R [18, 19].

The average relative deviations of experimental data from the calculated (*R*-factor [19]) were less than 0.05 (5%).

Geometry optimization of all the investigated structures was carried out using the molecular mechanics MM2 method (software package ChemOffice 12.0) [7].

Synthesis of complex [Cu I_2]. To white suspension consisting of 3.48×10^{-4} mol (0.1001 g) of 2,4-diamino-6-(acetylhydrazidomethylsulfinylmethyl)-1,3,5-triazine in 25 ml of ethanol heated on a water bath was added with vigorous stirring a half of the amount of copper(II) nitrate (1.73×10^{-4} mol) (in the form of an aqueous solution). The suspension took a blue-greenish color. A week later, the precipitate was separated from the colorless solution by filtration, washed with alcohol, dried, and weighed. Yield 0.1103 g (95.5%). Found, %: Cu 10.05, N 29.33; S 9.09. $C_{16}H_{24}CuN_{14}O_6S_2$. Calculated, %: Cu 9.99, N 30.83; S 10.08. *M* 636.1. IR spectrum, cm^{-1}, KBr: 3367, 3233, 3121 [br, ν(NH)]; 2925, 2854 [ν(CH)]; 1639 [ν(C=N)]; 1545 [δ(NH)]; 1465, 1384 [ν(CO)] , 1277 [δ(NH)]; 1105, 1029 [ν(S=O)]; 824 (triazine ring).

The copper content in the sample (*m*, g) was determined spectrophotometrically after dissolving it in ten-fold excess of complexone III solution in the presence of ammonium chloride buffer (pH 9.60) using a calibration curve built on reference solutions. Conditions of preparation of reference solutions are the same as at the sample analysis. The calibration function for λ 725 nm is given by: $A - (3.43\pm2.22)\times10^{-3} = (73.86\pm1.89)\,m$, $r = 0.99935$.

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