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# Physico-Chemical Study of the Complex Formation between 2-(Tosylamino)benzaldehyde Bishydrazones and Transition Metal Ions

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**Abstract**—New 2-(tosylamino)benzaldehyde bishydrazones and their complexes with copper(II) and zinc(II) have been synthesized. Structure and properties of the prepared compounds have been studied by means of IR and $^1$H NMR spectroscopy as well as magnetochemistry. Quantum-chemical simulation of the relative stability of tautomeric forms of the bishydrazones has been performed.

**Keywords:** bishydrazone, quantum-chemical simulation, coordination compound, magnetochemistry

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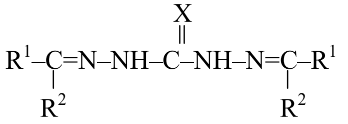
The products of carbonyl compounds condensation with carboxylic and thiocarboxylic acid hydrazines (bishydrazones **I**) are attractive due to their strong coordinating properties and pronounced biological activity [1–4]. Numerous coordination compounds based on bishydrazones **I** are known [5–18]; hydrazones of 2-(tosylamino)benzaldehyde and their metal complexes have been less studied [19–22].



$$R^1\text{–}\underset{\underset{R^2}{|}}{C}\text{=N–NH–}\overset{\overset{X}{\|}}{C}\text{–NH–N=}\underset{\underset{R^2}{|}}{C}\text{–}R^1$$

**I**

$R^1$ = Ar, Alk, Het; $R^2$ = H, $CH_3$; X = O, S.

We have earlier prepared and comprehensively studied a series of transition metal chelates based on 2-(tosylamino)benzaldehyde and 1,3-diaminopropan-2-ol [23]. Magnetic properties of binuclear copper(II) complexes have been investigated in detail, and the correlations between the nature of the bridging group of the exchange fragment and the value of the exchange interaction parameter 2*J* have been revealed. Exchange of the diaminopropanol component in the ligand system with the carbo(thiocarbo)hydrazide fragment allowed tracking the changes of the structure, physico-chemical, and magnetic properties of the metal chelates.

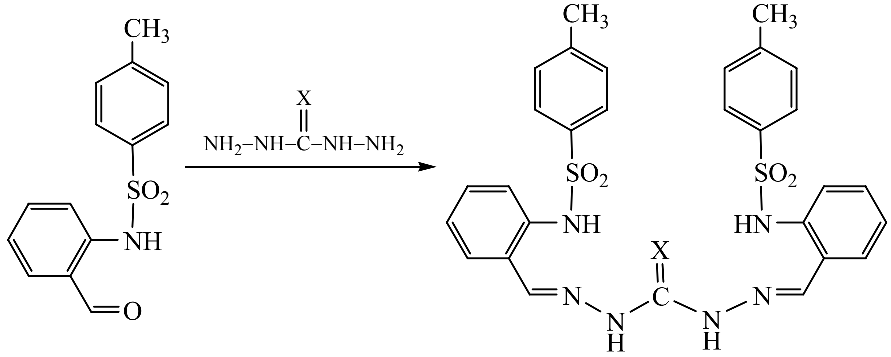
In this work we prepared bishydrazones based on 2-(tosylamino)benzaldehyde and their metal complexes and studied their structure and properties.

Ligands **II** and **III** were synthesized via condensation of 2-(tosylamino)benzaldehyde with carbo(thiocarbo)hydrazide.

Composition and structure of the prepared compounds were elucidated based on the data of elemental analysis and IR and $^1$H NMR spectroscopy.

The labile protons at the NH groups of ligands **II** and **III** allowed for existence of the bishydrazones in the oxo(thioxo)- and enol(enthiol) forms. The tautomers could be of either *cis*- or *trans*- structure. The most probable structures of tautomers and geometry isomers of compounds **II** and **III** are presented in Scheme 1.

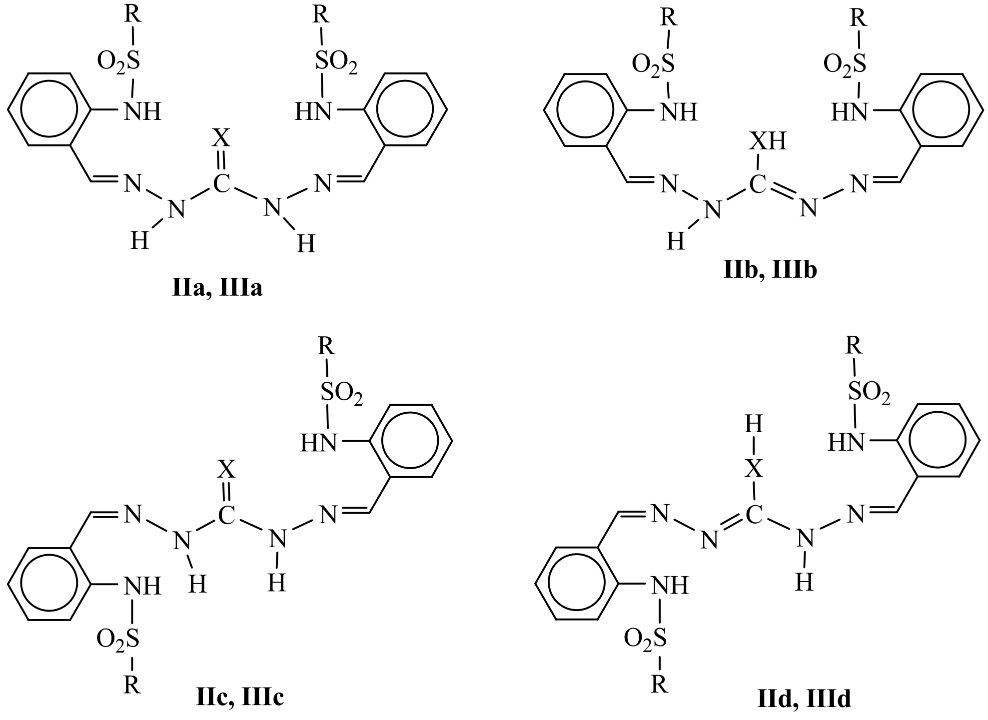
**Scheme 1.**



**II, III**

X = O (**II**), S (**III**).

**Scheme 2.**



**IIa, IIIa**

**IIb, IIIb**

**IIc, IIIc**

**IId, IIId**

X = O (**a, c**), S (**b, d**); R = 4-CH$_3$C$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, CH$_3$.

Since tautomeric equilibriums of hydrazones affect their complex formation ability [24, 25], we theoretically investigated the stability of tautomeric forms of hydrazones **IIa–IId** and **IIIa–IIId** (Scheme 2). On top of that, quantum-chemical simulation of the total energy as well as electronic and spatial structures of the tautomers was performed in the frame of the density functional theory (DFT) in vacuum and ethanol medium taking advantage of the B3LYP hybrid exchange-correlation functional [26–28]. Geometry of the discussed molecules was first optimized along all the natural variables without any symmetry restrictions. The extended split-valence 6-311G(d,p) basis set was used. The solvent effect was accounted for via the polarized continuous medium (PCM) approximation [29]. In order to elucidate the effect of the substituent R at the aromatic ring of the sulfonamide fragment on the molecules structure, the systems with substituents R = 4-CH$_3$C$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, and CH$_3$ were investigated. The total energies of the systems are given in Tables 1 and 2.

**Table 1.** Total energy and relative stability of tautomeric forms **IIa–IId**

| Tautomer | R | *E*, arb. units | $\Delta E$, kcal/mol |
|---|---|---|---|
| **IIa** | 4-$CH_3C_6H_4$ | –2623.33 | 0 |
| | 4-$NO_2C_6H_4$ | –2953.77 | 0 |
| | $CH_3$ | –2161.12 | 0 |
| | $CH_3$ (in MeOH) | –2161.16 | 3.56 |
| | 4-$CH_3C_6H_4$ | –2623.31 | 13.35 |
| **IIb** | 4-$NO_2C_6H_4$ | –2953.75 | 13.96 |
| | $CH_3$ | –2161.09 | 14.48 |
| | $CH_3$ (in MeOH) | –2161.14 | 15.65 |
| | 4-$CH_3C_6H_4$ | –2623.32 | 1.64 |
| | 4-$NO_2C_6H_4$ | –2953.77 | 1.16 |
| **IIc** | $CH_3$ | –2161.11 | 2.03 |
| | $CH_3$ (in MeOH) | –2161.16 | 0 |
| | 4-$CH_3C_6H_4$ | –2623.31 | 11.70 |
| | 4-$NO_2C_6H_4$ | –2953.16 | 11.25 |
| | $CH_3$ | –2161.10 | 11.17 |
| **IId** | $CH_3$ (in MeOH) | –2161.14 | 13.61 |

The oxo(thioxo) form was the most stable in the cases of compounds **II** and **III** in gas phase and in methanol solution. Stabilization of the tautomeric form was possible due to the formation of strong hydrogen bond between the X and one of the amine hydrogens atoms. The presence of $SO_2$ group distorted the planar geometry of the molecule. The *cis*-configuration of the hydrazone fragment with respect to the C=N–N bond was found to be stable for compound **II** in gas phase. The *trans*-configuration was destabilized by 1.64, 1.16, and 2.03 kcal/mol (for R being 4-$CH_3C_6H_4$, 4-$NO_2C_6H_4$, and $CH_3$, respectively) (Table 1). Quantum-chemical simulation of total energy and the molecule geometry optimization were carried out for compound **II** (R = $CH_3$) accounting for the solvent (methanol) effect. The presence of the solvent stabilized the *trans*-configuration of the hydrazone fragment owing to the solvation; the *cis*-configuration was destabilized by 3.56 kcal/mol.

The thioxo form was the most stable for compound **III** as well. However, unambiguous determination of the azomethine fragment location (*cis*- or *trans*-) was impossible: the difference in the forms energy was very small (0.04, 0.2, and 0.59 kcal/mol for R = 4-$CH_3C_6H_4$, 4-$NO_2C_6H_4$, and $CH_3$, respectively) (Table 2). Such difference in the energies evidenced about the possible coexistence of the *cis* and *trans* configurations in equilibrium.

**Table 2.** Total energy and relative stability of tautomeric forms **IIIa–IIId**

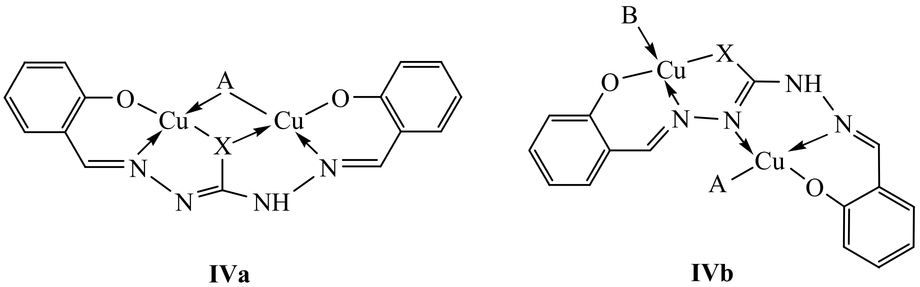
| Tautomer | R | *E*, arb. units | $\Delta E$, kcal/mol |
|---|---|---|---|
| **IIIa** | 4-$CH_3C_6H_4$ | –2946.28 | 0 |
| | 4-$NO_2C_6H_4$ | –3276.73 | 0.2 |
| | $CH_3$ | –2484.07 | 0 |
| **IIIb** | 4-$CH_3C_6H_4$ | –2946.26 | 11.88 |
| | 4-$NO_2C_6H_4$ | –3276.71 | 13.74 |
| | $CH_3$ | –2484.05 | 11.58 |
| **IIIc** | 4-$CH_3C_6H_4$ | –2946.28 | 0.04 |
| | 4-$NO_2C_6H_4$ | –3276.71 | 0 |
| | $CH_3$ | –2484.07 | 0.59 |
| **IIId** | 4-$CH_3C_6H_4$ | –2946.26 | 9.83 |
| | 4-$NO_2C_6H_4$ | –3276.73 | 9.43 |
| | $CH_3$ | –2484.06 | 9.62 |

Variation of the substituent did not significantly affect the geometry of bishydrazones and the tautomeric forms energy.

The results of quantum-chemical simulation were well agreed with the IR spectra of the ligands. In particular, IR spectra of compounds **II** and **III** contained the bands assigned to stretching of the N–H bonds of the tosylamine and hydrazone fragments, respectively, at 3083, 3210, 3363, and 3117, 3263, 3329 $cm^{-1}$. The absorption band of azomethine groups ν(C=N) was observed at 1615–1610 $cm^{-1}$. Symmetric and asymmetric vibrations of $SO_2$ group were detected at 1159–1160 and 1250–1276 $cm^{-1}$, respectively. The stretching band of the C=O group was registered in the IR spectrum of biscarbohydrazone at 1688 $cm^{-1}$, and the similar band assigned to the C=S bond stretching was observed at 1340 $cm^{-1}$ in the spectrum of bisthiocarbohydrazone; those features confirmed the existence of the ligands in the oxo(thioxo)form in the solid state.

$^1$H NMR spectra of the ligands also revealed the predominance of the oxo(thioxo) form. In detail, two singlets of the NH groups of hydrazone and tosylamine fragments at 10.6 and 10.8 ppm, respectively, were observed in the $^1$H NMR spectrum of biscarbohydrazone **II** recorded in DMSO-$d_6$, indicating the symmetric structure of molecule **IIa**; the singlet of azomethine protons resonance at 8.23 ppm, two doublets of tosyl fragment protons at 7.2 and 7.7 ppm ($^3J$ = 8 Hz), a multiplet of the protons of benzylidene rings at 6.8–7.1 ppm, and a singlet of the protons of $CH_3$ groups at 2.2 ppm were found as well. Addition of $D_2O$ led to the complete suppression of the signals of protons of NH groups.

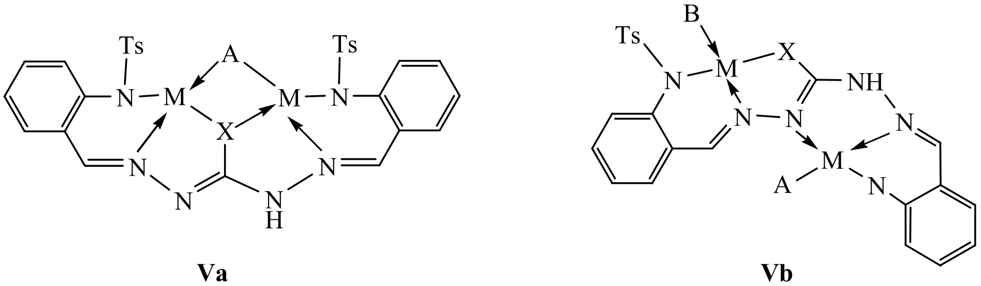
**Scheme 3.**



**IVa** **IVb**

X = O, A = $CH_3COO^-$ (**IVa**); X = O, S, A = $CH_3COO^-$, B = $CH_3OH$, DMF (**IVb**).

**Scheme 4.**



**Va** **Vb**

**Va**, X = O, M = Cu(II), A = $CH_3COO^-$; **Vb**, X = S, M = Cu(II), Zn(II), A = $CH_3COO^-$, pyrazole (Pz), B = $OCH_3$, DMF.

$^1$H NMR spectrum of bisthiocarbohydrazone **III** in DMSO-$d_6$ contained the singlets at 12.1, 11.7, 11.4, and 9.8 ppm, corresponding to the resonance of NH protons of the hydrazone and tosylamine fragments. The nonequivalence of the NH protons could be explained by existence of the bisthiocarbohydrazone in the *trans*-form **IIIc**, in accordance with the data of the quantum-chemical simulation. All the four signals disappeared upon addition of $D_2O$, indicating the acidic character of the NH-protons in the ligand. The protons of azomethine and methyl groups resonated as singlets at 8.4 (2H) and 2.3 (6H) ppm, respectively. The aromatic protons resonated as a multiplet at 7.2–8.1 ppm.

Owing to the presence of additional donating nitrogen atoms in the structure, bishydrazones of salicylic aldehyde derivatives can form both binuclear coordination compounds **IVa** (structurally similar to the complexes with the ligands based on 1,3-diaminopropan-2-ol [9, 23, 30–42]), and metal chelates **IVb** with two metal ions having nonequivalent coordination surroundings [4, 9, 43–45].

Analysis of the data available on magnetic properties of the complexes **IVa** [9, 23, 30–42] and quantum-chemical simulation of the exchange parameters [38–42] demonstrated that realization of the symmetric structure assumed strong antiferromagnetic exchange interaction between ions of the metal, significantly affected by the electronic properties of the substituents both in the chelate fragment and in the salicylic aldehyde part of the molecule. In the case of complexes **IVb**, antiferromagnetic exchange of intermediate strength ($2J = -160$ to $-290$ cm$^{-1}$) was observed; the value was not much affected by the substituents nature [43–45].

The reaction of ligands **II** and **III** with copper(II) and zinc(II) acetates yielded the binuclear complexes with the metal : ligand ratio of 2 : 1. Such composition was possible for the two binuclear structures **Va** and **Vb**, similarly to the case of the complexes based on biscarbo(thiocarbo)hydrazones of salicylic aldehyde derivatives.

The absorption bands assigned to stretching of the tosylamine N–H bond and the hydrazone C=O(S) disappeared in IR spectra of the complexes, whereas the ν(C=N) bands of the azomethine fragments were shifted towards lower frequency by 10–15 cm$^{-1}$. Those changes indicated the ligand coordination at the metal

**Table 3.** Magnetic properties of copper(II) binuclear chelates

| X | A | $T$, K | $\mu_{eff}$, M.B.[a] | $-2J$, $cm^{-1}$ |
|---|---|---|---|---|
| O | $CH_3COO$ | 77.4 | 0.84 | 221.6 |
| | | 293 | 1.62 | |
| S | $CH_3COO$ | 77.4 | 0.56 | 278.6 |
| | | 293 | 1.49 | |
| S | Pz | 77.4 | 0.9 | 241.4 |
| | | 293 | 1.6 | |

[a] Values of $\mu_{eff}$ are given per one copper atom in binuclear molecule.

ions via the nitrogen atoms in the thrice deprotonated enol (enthiol) form. The low-frequency shifting of the $SO_2$ group stretching evidenced about possible participation of the oxygen atoms of tosyl fragment in the coordination. Participation of the acetate group in the coordination was indicated by the appearance of the absorption band at 1640 $cm^{-1}$ in the spectrum. On top of that, a weak absorption band 3363–3370 $cm^{-1}$ corresponded to the ν(N–H) of hydrazone fragment.

The thrice deprotonated ligand form in the complexes was confirmed by the data of $^1H$ NMR spectroscopy of zinc(II) metal chelate based on bis-thiocarbohydrazone **III**. In detail, a broadened singlet of NH group of the hydrazone fragment (12 ppm), a singlet of the azomethine groups (8.5 ppm), a multiplet of the aromatic protons (7.1–7.8 ppm), and a singlet of the acetate group (1.9 ppm) were observed in the spectrum. The methyl protons of tosyl fragment of the metal chelate resonated as two singlets at 2.3 and 2.4 ppm, indicating their nonequivalence. That could be explained by formation of the intramolecular hydrogen bond between the methyl and acetate groups. The presence of DMF molecule in the complex was confirmed by the signals at 2.8, 2.9, and 8.1 ppm.

The results of magnetochemical investigation were crucial for elucidation of the most probable structure of the prepared complexes. In particular, the magnetic properties of copper(II) metal chelates over the temperature range of 77.4–293 K were characterized by the interaction of antiferromagnetic type of intermediate strength (Table 3).

The exchange interaction parameter $2J$ ranged from –222 to –279 $cm^{-1}$ and was independent of the nature of the exogenous bridge group A. The strength of antiferromagnetic exchange interaction between copper ions was lower in the case of the complex with pyrazole fragment that that in the case of the complex with acetate group, contrary to the earlier studied case of the complexes with bisazomethine derivatives of salicylic aldehyde and 2-tosylaminobenzaldehyde [23]. Therefore, the binuclear complexes of copper(II) and zinc(II) based on bishydrazones of 2-tosylaminobenzaldehyde 2 existed most likely in the form of structure **Vb**, the exchange binding between the metal ions being absent. The nature of atom X practically did not affect the strength of the exchange interaction in the complexes (Table 3), further confirming the *trans* conformation of the structure **Vb**.

## EXPERIMENTAL

IR spectra of the samples (suspension in paraffin oil) were recorded using a Varian Scimitar spectrophotometer at 400–4000 $cm^{-1}$. $^1H$ NMR spectra were registered with a UNITY-300 instrument with TMS as internal reference.

Specific magnetic susceptibility was determined using the relative Faraday method at 77.4–300 K; the sample temperature was measured with a copper–constantan thermocouple. Calibration of the device was performed using $Hg[Co(CNS)_4]$ as reference. The parameters of exchange interaction in the copper binuclear complexes were calculated within the frame of the Heisenberg–Dirac–van Fleck isotropic model taking advantage of the modified Bleaney–Bowers formula, accounting for the presence of paramagnetic admixture in the complex [46].

**Methodology of quantum-chemical simulation.** Electronic and spatial structure of the compounds was determined under non-empiric approximation within the frame of density functional theory (DFT); the exchange-correlation functional B3LYP [26] was applied with the Becke'88 exchange part in the form proposed in [47] and the Lee–Yang–Parr correlation part [28]. The geometry structure of the molecules was preliminarily optimized over all the natural variables without any symmetry restrictions. A 6-311G(d,p) split-valence basis set was used. All quantum-chemical simulations were performed in GAUSSIAN'03 software [48] using the equipment installed at the Cluster of Computing Centrum of South-Russian Regional Center of Informatization of the Southern Federal University.

**1,3-Bis{(*E*)-[2-*p*-tosylsulfonylamino)phenyl]-methyleneamino}urea (II).** A hot solution of *o*-tosylaminobenzaldehyde (0.006 mol) in 5 mL of ethanol was added to a hot solution of carbohydrazide

(0.003 mol) in 15 mL of ethanol. Four drops of glacial acetic acid were added to the obtained mixture, and it was refluxed during 3 h. The formed precipitate was filtered off, washed with ethanol, and recrystallized from a DMF–isopropanol mixture. Yield 65%, mp >250°C. IR spectrum, ν, cm$^{-1}$: 3083 (N–H), 3210 (N–H), 3363 (N–H), 1688 (C=O), 1615 (C=N), 1160 ($SO_2$), 1276 ($SO_2$). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.2 s (6H, 2$CH_3$), 6.8–7.1 m (8$H_{arom}$), 7.2 d (4$H_{arom}$, $^3J$ 8.0 Hz), 7.7 d (4$H_{arom}$, $^3J$ 8.0 Hz), 8.23 s (2H, 2CH=N), 10.6 s (2H, NH), 10.8 s (2H, NH). Found, %: C 57.15; H 4.21; N 14.37. $C_{29}H_{28}N_6O_5S_2$. Calculated, %: C 57.6; H 4.67; N 13.90.

**1,3-Bis{(*E*)-[2-*p*-tosylsulfonylamino)phenyl]methyleneamino}thiourea (III)** was prepared similarly from thiocarbohydrazide (0.003 mol). Yield 69%, mp 208°C. IR spectrum, ν, cm$^{-1}$: 3117 (N–H), 3263 (N–H), 3329 (N–H), 1610 (C=N), 1340 (C=S), 1160 ($SO_2$), 1276 ($SO_2$). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.3 s (6H, 2$CH_3$), 7.2–8.1 m (16$H_{arom}$), 8.4 s (2H, 2CH=N), 9.8 s (1H, NH), 11.4 s (1H, NH), 11.7 s (1H, NH), 12.1 s (1H, NH). Found, %: C 55.71; H 4.53; N 13.16; $C_{29}H_{28}N_6O_4S_3$. Calculated, %: C 55.11; H 4.55; N 13.54.

**Cu(II) complex with biscarbohydrazone II.** A hot solution of copper(II) acetate (0.0004 mol) in 10 mL of methanol was added to a hot suspension of compound **II** (0.0002 mol) in 15 mL of methanol; the mixture was refluxed during 4 h. The formed precipitate was filtered off, washed with hot methanol, and dried in vacuum. Yield 36%, mp >250°C. IR spectrum, ν, cm$^{-1}$: 3363 (N–H), 1640 (C=O), 1595 (C=N), 1135 ($SO_2$), 1250 ($SO_2$). Found, %: C 45.71; H 4.23; Cu 16.12; N 10.74; $C_{31}H_{32}Cu_2N_6O_8S_2$. Calculated, %: C 46.15; H 3.87; Cu 15.75; N 10.42.

**Cu(II) and Zn(II) complexes with bisthiocarbohydrazone III.** A hot solution of the metal acetate (0.0004 mol) in 10 mL of ethanol was added to a hot suspension of compound **III** (0.0002 mol) in a mixture of DMF (1 mL) and ethanol (10 mL); the reaction mixture was refluxed during 4 h. The formed precipitate was filtered off, washed with hot methanol, and dried in vacuum.

**[$Cu_2$(HL)($CH_3COO$)$OCH_3$].** Yield 40%, fine crystalline dark-brown powder, mp >250°C. IR spectrum, ν, cm$^{-1}$: 3365 (N–H), 1646 (C=O), 1596 (C=N), 1138 ($SO_2$), 1254 ($SO_2$). Found, %: C 45.93; H 4.16; Cu 15.78; N 10.85; $C_{31}H_{32}Cu_2N_6O_7S_3$. Calculated, %: C 45.25; H 3.8; Cu 15.44; N 10.21.

**[$Zn_2$(HL)($CH_3COO$)DMF].** Yield 48.9%, amorphous yellow powder, mp >250°C. IR spectrum, ν, cm$^{-1}$: 3359 (N–H), 1642 (C=O), 1598 (C=N), 1133 ($SO_2$), 1251 ($SO_2$). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 1.9 s (3H, $OCH_3$), 2.3 s (3H, $CH_3$), 2.4 s (3H, $CH_3$), 2.8 s (3H, $CH_3$), 2.9 s (3H, $CH_3$), 7.1–7.8 m (16$H_{arom}$), 8.1 s (1H, CH), 8.5 s (2H, CH=N), 12 br.s (1H, NH). Found, %: C 46.18; H 4.87; Zn 14.33; N 11.12; $C_{33}H_{36}Zn_2N_7O_7S_3$. Calculated, %: C 46.43; H 4.25; Zn 14.81; N 11.49.

**Cu(II) complex with bisthiocarbohydrazone III (A = Pz).** A solution of copper(II) acetate (0.0004 mol) in 10 mL of methanol was added to a hot suspension of the ligand (0.0002 mol) in 15 mL of methanol; 0.0004 mol of pyrazole was then added to the mixture, and it was refluxed during 8 h. The formed precipitate was filtered off, washed with hot methanol, and dried in vacuum. Yield 73%, mp 230°C. IR spectrum, ν, cm$^{-1}$: 3365 (N–H), 1603 (C=N), 1131 ($SO_2$), 1254 ($SO_2$). Found, %: C 46.71; H 4.13; Cu 14.15; N 14.27; $C_{33}H_{32}Cu_2N_9O_5S_3$. Calculated, %: C 46.25; H 3.65; Cu 14.83; N 14.71.

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