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# Copper Complexes with N-Aminotriazolethione Azomethines: Structures and Magnetochemical Properties

**I. S. Vasil'chenko[a, *], A. S. Burlov[a, b], T. E. Shestakova[c], V. N. Ikorskii[d, †], T. A. Kuz'menko[a], V. G. Vlasenko[e], K. V. Bozhenko[f], L. N. Divaeva[a], A. S. Morkovnik[a], A. S. Bogomyakov[d], D. A. Garnovskii[a, b], A. I. Uraev[a, b], I. V. Pirog[e], G. S. Borodkin[a], A. N. Utenyshev[f], I. G. Borodkina[a], O. A. Karpov[a], A. A. Khrulev[f], I. E. Uflyand[c], A. D. Garnovskii[a, b], S. M. Aldoshin[f], and V. I. Minkin[a, b]**

[a] *Research Institute of Physical and Organic Chemistry, Southern Federal University, Rostov-on-Don, Russia*
[b] *Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, Russia*
[c] *Pedagogical Institute, Southern Federal University, Rostov-on-Don, Russia*
[d] *International Tomography Center, Siberian Division, Russian Academy of Sciences, Novosibirsk, Russia*
[e] *Research Institute of Physics, Southern Federal University, Rostov-on-Don, Russia*
[f] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia*
**E-mail: vas@ipoc.rsu.ru*

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**Abstract**—Azomethine derivatives of 4-amino-1,2,4-triazole-3-thiones ($H_2L$) and their metal complexes were obtained. The stabilities of the ligand conformers were calculated using quantum-chemical techniques. *Ab initio* (B3LYP/LANL2DZ) calculations of the complexes in the lower singlet and triplet states were performed with full geometry optimization. The structures and magnetochemical properties of the chelate complexes obtained were examined over a wide temperature range.

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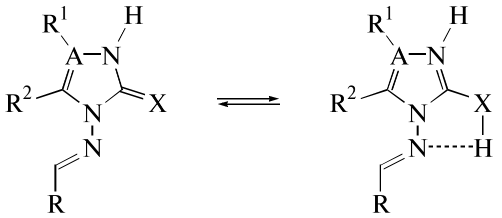
Stabilization of various tautomers of ligand systems coordinated to a metal atom is among fundamental problems of modern coordination chemistry [1–3]. Convenient models for the study of such processes are azomethine derivatives of N-amines of five-membered nitrogen heterocycles containing a functional group (NHR, OH, or SH) at the C atom adjacent to the amino group (e.g., compounds **I**). Tautomeric equilibrium in such systems can be represented by scheme (1). For X = O and S, the equilibrium is usually shifted toward keto (thione) form **Ia**, while for X = NR (R = H, Alk, or Ar), amino form **Ib** is dominant [4].



**(Ia)** **(Ib)** (1)

$X = NR^3$, O, S; R = Ar, *o*-HNTsPh, *o*-HOAr, *o*-HO(HS)Het;
A = C, $R^1$, $R^2 = C_6H_4$-*cyclo*; A = N, $R^1$ is absent, $R^2$ = H, Me, Et;
$R^3$ = H, Alk, Ac.

Current investigations of the coordination activity of such imino derivatives are restricted to the study of the structures and properties of aldimines of 1-aminobenzoimidazoline-2-thione [5] and, for some metals, 4-amino-1,2,4-triazoline-2-thione [6].

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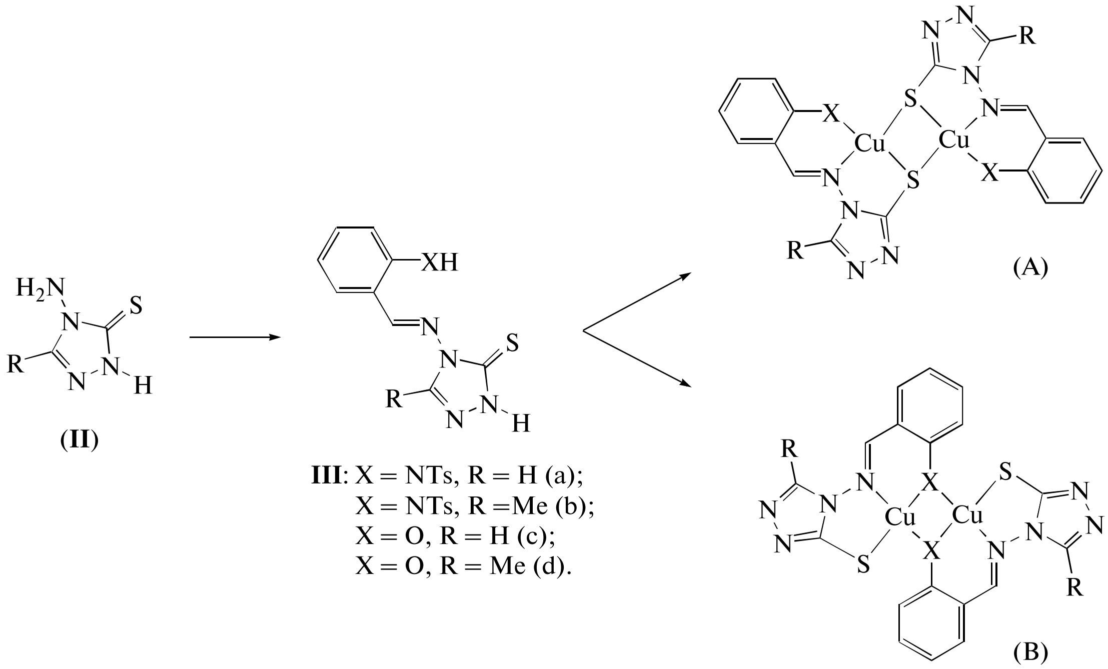

(II)

**III**: X = NTs, R = H (a);
X = NTs, R =Me (b);
X = O, R = H (c);
X = O, R = Me (d).

(2)

**IV**: X = NTs, R = H (a);
X = NTs, R =Me (b);
X = O, R = H (c);
X = O, R = Me (d).

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We obtained 4-amino-1,2,4-triazole-5(4H)-thiones (**II**), azomethines (**III**), and their metal complexes (**IV**), studied their structures and properties, and performed *ab initio* calculations of the total energies of the singlet- and triplet-excited chelate complexes in the B3LYP/6-31G** (for the ligands) and B3LYP/LANL2DZ approximations.

## EXPERIMENTAL

**Synthesis of 4-(2'-tosylaminobenzylidene)amino-1,2,4-triazoline-3-thione (IIIa).** A solution of 2-tosylaminobenzaldehyde (2.75 g) in glacial acetic acid (5 ml) was added to a solution of 4-amino-1,2,4-triazoline-3-thione (1.16 g, 0.01 mol) in glacial acetic acid (10 ml). The reaction mixture was refluxed for 4 h. On cooling, the white precipitate that formed was recrystallized from chloroform. The yield of compound **IIIa** was 2.8 g (75.5%), $T_m$ = 232°C.

IR (ν, cm$^{-1}$): 920 (ν(C=S)), 1602 (ν(C=N$_{azomet}$)), 3082 (δ(NH$_{triaz}$)), 3153 (δ(NHTs)).

$^1$H NMR (DMSO-d$_6$, δ, ppm): 2.38 (s, 3H, ArCH$_3$), 7.2–7.8 (m, 8H, H$_{ar}$), 8.80 (s, 1H, CH$_{triaz}$), 9.80 (s, 1H, HC=N), 10.15 (s, 1H, NH$_{triaz}$), 13.60 (s, 1H, ArSO$_2$NH).

For $C_{16}H_{15}N_5O_2S_2$

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 51.46; | H, 4.05; | N, 18.75. |
| Found, %: | C, 51.49; | H, 4.10; | N, 18.77. |

**Synthesis of 5-methyl-4-(2'-tosylaminobenzylidene)amino-1,2,4-triazoline-3-thione (IIIb).** A solution of 2-tosylaminobenzaldehyde (2.75 g, 0.01 mol) in ethanol and a catalytic amount of piperidine (one to two drops) were added to a solution of 4-amino-5-methyl-1,2,4-triazoline-3-thione (1.30 g, 0.01 mol) in ethanol. The reaction mixture was refluxed for an hour. On cooling, the white precipitate that formed was recrystallized from chloroform. The yield of compound **IIIb** was 2.9 g (74.3%), $T_m$ = 218–220°C.

IR (ν, cm$^{-1}$): 919 (ν(C=S)), 1608 (ν(C=N$_{azomet}$)), 3084 (δ(NH$_{triaz}$)), 3157 (δ(NHTs)).

$^1$H NMR (DMSO-d$_6$, δ, ppm): 2.38 (s, 3H, ArCH$_3$), 2.42 (s, 3H, TriazCH$_3$), 7.2–7.8 (m, 8H, H$_{ar}$), 10.15 (s, 1H, NH$_{triaz}$), 10.20 (s, 1H, HC=N), 13.63 (s, 1H, ArSO$_2$NH).

For $C_{17}H_{17}N_5O_2S_2$

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 52.70; | H, 4.42; | N, 18.07. |
| Found, %: | C, 52.67; | H, 4.45; | N, 18.01. |

**Synthesis of 4-(2'-hydroxybenzylidene)amino-1,2,4-triazoline-3-thione (IIIc).** Salicylaldehyde (1.2 g, 0.01 mol) was added to a solution of 4-amino-1,2,4-triazoline-3-thione (1.16 g, 0.01 mol) in glacial acetic acid (5 ml). The reaction mixture was refluxed for an hour. On cooling, the white precipitate that formed was recrystallized from butanol. The yield of compound **IIIc** was 1.66 g (75.6%), $T_m$ = 263–265°C.

IR (ν, cm$^{-1}$): 917 (ν(C=S)), 1612 (ν(C=N$_{azomet}$)), 3083 (δ(NH$_{triaz}$)), 3159 (δ(OH)).

$^1$H NMR (DMSO-d$_6$, δ, ppm): 6.8–7.7 (m, 4H, H$_{ar}$), 8.82 (s, 1H, H$_{triaz}$), 9.65 (s, 1H, HC=N), 10.50 (s, 1H, NH), 13.80 (s, 1H, OH).

| For $C_9H_8N_4OS$ | | | |
|---|---|---|---|
| anal. calcd., %: | C, 49.08; | H, 3.66; | N, 25.44. |
| Found, %: | C, 49.11; | H, 3.70; | N, 25.49. |

**Synthesis of 4-(2'-hydroxybenzylidene)amino-5-methyl-1,2,4-triazoline-3-thione (IIId).** Salicylaldehyde (1.22 g, 0.01 mol) was added to a solution of 4-amino-5-methyl-1,2,4-triazoline-3-thione (1.30 g, 0.01 mol) in glacial acetic acid (10 ml). The reaction mixture was refluxed for an hour. On cooling, the white precipitate that formed was recrystallized from anhydrous ethanol. The yield of compound **IIId** was 0.8 g (38%), $T_m = 210°C$.

IR (ν, cm$^{-1}$): 913 (ν(C=S)), 1598 (ν(C=N$_{azomet}$)), 3072 (δ(NH$_{triaz}$)), 3126 (δ(OH)).

$^1$H NMR (DMSO-d$_6$, δ, ppm): 2.40 (s, 3H, CH$_3$), 6.8–7.9 (m, 4H, H$_{ar}$), 10.15 (s, 1H, HC=N), 10.20 (s, 1H, NH), 13.50 (s, 1H, OH).

| For $C_{10}H_{10}N_4OS$ | | | |
|---|---|---|---|
| anal. calcd., %: | C, 51.27; | H, 4.30; | N, 23.91. |
| Found, %: | C, 51.19; | H, 4.26; | N, 23.86. |

Complexes **IVa**–**IVd** were synthesized according to the following standard procedure. A hot solution of copper acetate (2 mmol) in methanol (10 ml) was added to a boiling solution of an appropriate ligand (2 mmol) in methanol (20 ml). The reaction mixture was refluxed for 5 min. On cooling, the precipitate that formed was filtered off, washed with hot methanol, and dried in a vacuum desiccator. The yields were 40–65%, dark green solids, $T_m > 300°C$.

Elemental analysis of the ligand systems and the complexes for C, H, and N was performed on a Carlo Erba Instruments TCM 480 instrument at the Microanalysis Laboratory of the Research Institute of Physical and Organic Chemistry of the Southern Federal University.

IR spectra of the solid-state ligands and complexes were recorded on a Varian EXCALIBUR 3100 FT-IR spectrometer in the 400–4000 cm$^{-1}$ range.

$^1$H NMR spectra of the ligands were recorded on a UNITY-300 instrument (Varian) in DMSO-d$_6$.

Magnetochemical measurements were carried out on a MPMS-5S Quantum Design SQUID magnetometer (2–300 K, magnetic field strength 5 kOe). The temperature dependence of the effective magnetic moment was calculated by the formula $\mu_{eff}(T) = 8\chi T$, where $\chi$ is the molar paramagnetic susceptibility corrected for the diamagnetic contribution.

Cu*K*-edge X-ray absorption spectra of metal complexes were recorded in the absorption detection mode on an EXAFS spectrometer at the Siberian synchrotron center (Novosibirsk). The energy of an electron beam employed as a synchrotron X-ray source was 2 GeV at an average current of 80 mA. For X-ray monochromatization, a two-crystal Si(111) monochromator was used. The intensities of the incident and transmitted X-rays were measured in argon-filled ion chambers. Background subtraction, normalization for a *K*-edge jump, and removal of the atomic absorption $\mu_0$ were performed according to standard procedures. The EXAFS spectra were Fourier-transformed (EXAFS is an abbreviation for extended X-ray absorption fine structure) for each sample in a photoelectron wave vector range from 2.5 to 13 Å$^{-1}$ with the weight function $k^2$. The exact parameters of the local environment of the Cu atom were determined by approximating the calculated EXAFS spectra to the experimental one via variation of the parameters of the corresponding coordination spheres with the IFFEFIT program.

## RESULTS AND DISCUSSION

Structures **III** (R = H, Me, and Et; X = NMs) were determined using quantum-chemical calculations. These ligands contain a single asymmetric atom (tetrahedral N atom of the mesylamino group) and, according to the PM3-calculated structure for R = H, can exist as many (over 10) conformers. In the latter, both the rings are usually not coplanar, their planes making a large angle. However, in conformer **III'**, which is most stable and seems to correspond to the global minimum, both rings and the atoms of the aldimine fragment are virtually coplanar, while the mesyl group is out of plane (data from B3LYP/6-31G** calculations) (Fig. 1). The conformer has a relatively low dipole moment ($\mu_{calc}$ = 3.1 D) and contain a fairly strong endocyclic H bond between the NH group as a donor and the aldimine N atom as an acceptor (N–N, 2.71 Å; N···H, 1.87 Å; H···N bond order 0.12). This conformer has an unfavorable structure for tridentate coordination: the thione fragment is distant from the hydrogen ring because of the rotation of the triazole ring about the exocyclic N–N bond through an angle of ~180°, which corresponds to the *Z* configuration relative to this bond. A structurally similar lowest-energy *Z* conformer was discovered in the study of the conformations of ligands **III** (R = H; Y = NMs) by molecular mechanics (MM2).

At the same time, the conformational system corresponding to compound **III** (R = H; Y = NMs) also includes an *E* conformer relative to the N–N bond with the thione group oriented toward the chelated hydrogen. This conformer is responsible for potential tridentate coordination of the ligand and its total energy is higher by ~3 kcal/mol. Four constituent atoms in the potential tridentate coordination unit

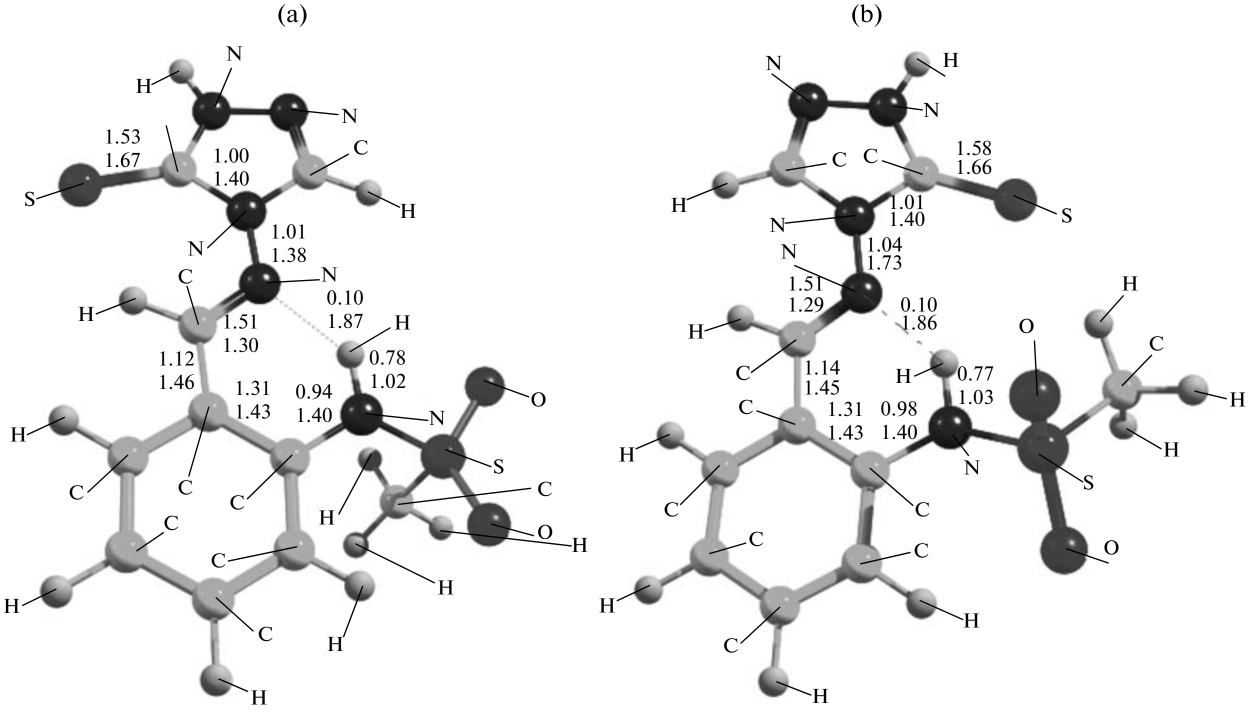

**Fig. 1.** B3LYP/6-31G**-calculated structure **III** (R = H; X = NMs) in (a) the lowest-energy *Z* conformation and (b) the *E* conformation relative to the N(4)-N(1') bond. For selected bonds, the bond order (upper number) and the length (**A**, lower number) are given.

(the NH group, the aldimine N atom, and the S atom) appreciably deviate in the *E* conformer from the mean-square plane (on average, by ~0.5 Å). However, to make the configuration completely planar requires only ~0.5 kcal/mol. Thus, the overall energy required to transform the dominant *Z* conformer into a planar configuration is only ~3.5 kcal/mol (in the absence of solvation). Obviously, a lower energy is required in polar solvents because the *E* conformer, according to the calculated dipole moments $\mu_{calc}$ (Table 1), is substantially polar than the *Z* conformer and should be stabilized by a high-polarity solvent.

Analogous pairs of conformers were found for methyl and ethyl derivatives of mesyl-containing ligands (**III**: R = Me and Et). In this case too, the *Z* conformer is thermodynamically more stable. In all six B3LYP/6-31G**-calculated structures, the order of the exocyclic N—N bond is nearly unity, which suggests the absence of noticeable conjugation between the triazole ring and the aldimine fragment and the influence of this factor on the barriers to rotation about this axis.

Replacement of the hydrogen atom in position 3 by a methyl or ethyl group results in additional considerable destabilization of the *E* conformers compared to the Z ones. In energy terms, this destabilization is virtually equal for both substituents ($\Delta E_{E-Z}^{\text{total}}$ ~ 6.3 kcal/mol). In both the conformers, the triazole ring makes a substantially larger angle with the rest of the π-system, the angle increase being equal for the methyl and ethyl derivatives. As the result, the torsion angle C(3)—N(4)—N(1')—C(2'), which is 4° and 19° in the *Z* and *E* conformers, respectively, of the 3-unsubstituted compound, increases to ~12° and ~44°. This structural effect is due to the electrostatic repulsion of the aldimine H atom from the similarly charged H(3) atom or from the methyl (methylene) H atoms and makes a major contribution to the barrier to rotation about the N—N bond.

Therefore, compounds **III** do not have substantial spatial or electronic factors precluding their tridentate coordination and hence they can form, e.g., binuclear metal complexes.

It follows from the IR and $^1$H NMR spectra, aldimines **III** in both solution and the solid state exist as an imine phenol (for the azomethine fragment) and triazoline thione tautomer (for the heterocyclic part). This is evident from the absorption bands at 900—1100 (C=S stretches) and 3200—3400 cm$^{-1}$ (N—H$_{\text{triaz}}$ stretches) in the IR spectra and from the signals for the XH and N—H$_{\text{triaz}}$ protons in the $^1$H NMR spectra.

An analysis of the IR spectra of the metal complexes revealed that the reactions of azomethines **III** with cupric acetate result in deprotonation of both parts of the ligand system (the XH group and the tria-

**Table 1.** B3LYP/6-31G**-calculated data for the conformers of complexes **III** (X = NMs; R = H, Me, and Et) and their enantiomers

| Conformer of complex **III** | R | Gibbs energy of the conformer, $G^{298}$, au | Gibbs energy of the conformer vs. that of the most stable conformer ($\Delta G^{298}$), kcal/mol | Torsion angles in the conformer | | | $\mu_{calcd}$, D |
|---|---|---|---|---|---|---|---|
| | | | | C(2)'–N–N–C(5), deg | Me–$SO_2$–NH–C(4)', deg | S–N–C(4)'–C(3)', deg | |
| **III'** | H | –1608.021275 | 0 | –6.3 | 62.0 | –156.0 | 3.1 |
| **III'** enantiomer | H | –1608.021275 | 0 | 5.8 | –62.7 | 157.4 | 3.2 |
| **III''** | | –1608.01618739 | 3.2 | –165.0 | 165.9 | 147.0 | 5.6 |
| **III''** enantiomer | H | –1608.016195 | 3.2 | 165.6 | –165.4 | –147.2 | 5.6 |
| **III'''** | H | –1608.0149888 | 3.9 | 0.3 | 68.4 | –123.9 | 5.9 |
| **III''''** | H | –1608.0139821 | 4.6 | –9.6 | 145.7 | –83.6 | 2.6 |
| **III''''** enantiomer | H | –1608.0139723 | 4.6 | 9.4 | –145.7 | 83.9 | 2.6 |
| **III'''''** | | –1608.01397234 | 4.6 | –44.5 | –168.9 | –106.8 | 2.1 |
| **III''''''** | H | –1608.00670204 | 9.0 | –41.4 | –142.3 | 87.7 | 1.0 |
| **III'''''''** | | –1608.00443033 | 10.6 | –9.5 | 16 | –92.5 | 4.4 |
| **III'** | Me | –1647.327098 | 0 | –17.3 | 59.1 | –151.4 | 2.2 |
| **III''** | Me | –1647.3167186 | 6.5 | –147.4 | 159.5 | 152.5 | 5.9 |
| **III'** | Et | –1686.6150072 | 0 | –17.0 | 59.8 | –152.8 | 2.0 |
| **III''** | Et | –1686.6073577 | 4.8 | –145.9 | 155.6 | 155.3 | 6.0 |
| **III''** enantiomer | Et | –1686.6073562 | 4.8 | 146.5 | –158.0 | –153.5 | 6.0 |

zole fragment). Based on these and elemental analysis data, we concluded that the complexes obtained can be formulated as $Cu_2L_2$ (where $H_2L$ are aldimines **III**).

However, it can be seen in (2) that binuclear molecules can form in two ways, the bridging atoms being the S atoms of the triazole substituent (structure **A**) or the X atoms of the aldehyde fragment (**B**).

In [7], we have demonstrated that the N atom of the tosylamino group cannot serve as a bridging atom; i.e., complexes **IV** (X = NTs) exist as structure **A**. Structures **IVb** and **IVd** were determined by EXAFS spectroscopy. The Fourier transform modules of the EXAFS functions of the Cu*K* edge for these complexes are shown in Fig. 2. The structural parameters of the nearest atomic environment of the copper ion in complexes **IVb** and **IVd** are given in Table 2.

In complex **IVd**, the first coordination sphere of the copper atoms is made up of three N/O atoms of the ligands at a distance of 1.93–1.97 Å and a S atom at a distance of 2.28–2.29 Å. Based on the EXAFS data, the coordination sphere of the central atom in complex **IVd** can be represented as $NO_2S$ and the complex exists as structure **B** with bridging O atoms of the phenol type. According to the EXAFS data for complex **IVb**, the coordination sphere of the copper atom consists of two S atoms and three light atoms (N/O) (Fig. 2, Table 2) and can be represented as $N_2OS_2$. Therefore, complex **IVb** exists as structure **A** with bridging S atoms, in which a tosyl O atom is also coordinated to copper. The third main MFT peak at $r$ = 2.87–3.07 Å was tested for the presence of coordina-

**Table 2.** Structural data obtained from the multisphere fit of EXAFS data*

| Complex | $N$ | $r$, Å | $\sigma^2$, $Å^2$ | Atom | $Q$, % |
|---|---|---|---|---|---|
| **IVb** | 1 | 1.92 | 0.0033 | N/O | 13.4 |
| | 2 | 1.94 | 0.0037 | N/O | |
| | 2 | 2.28 | 0.0064 | S | |
| | 1 | 3.07 | 0.065 | Cu | |
| **IVd** | 1 | 1.92 | 0.0045 | N/O | 6.3 |
| | 2 | 1.99 | 0.0041 | N/O | |
| | 1 | 2.28 | 0.0041 | S | |
| | 1 | 2.87 | 0.069 | Cu | |

* $r$ is the interatomic distance, $N$ is the coordination number, $\sigma^2$ is the Debye–Waller factor, and $Q$ is the mismatch function.

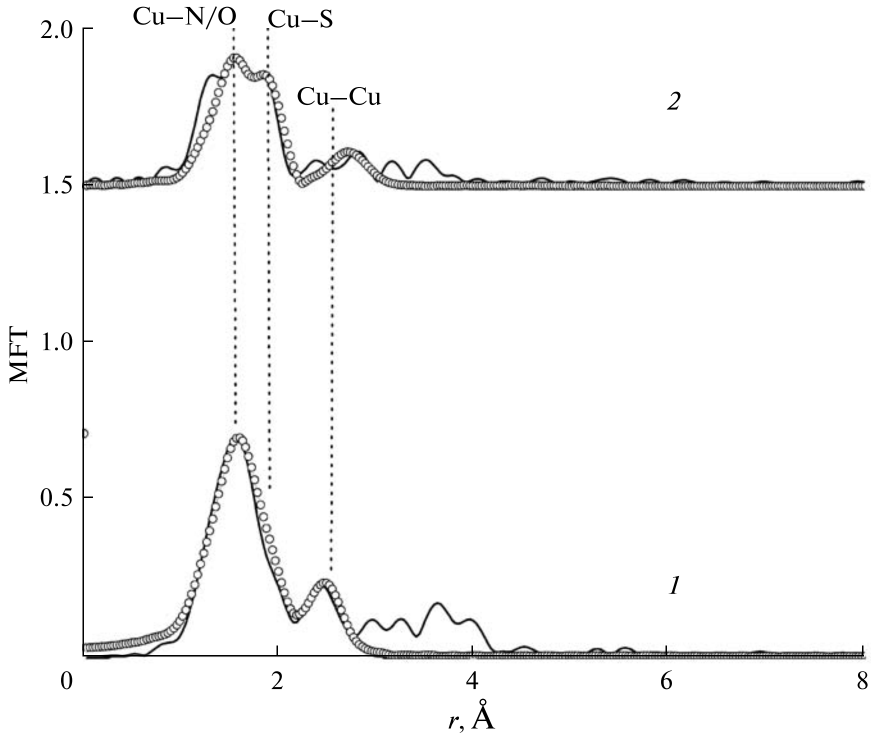

**Fig. 2.** Fourier transform modules of the EXAFS functions of the Cu*K* edge for (*1*) **IVb** and (*2*) **IVd**. Experimental MFTs are indicated with solid lines; calculated MFTs for the first coordination sphere are indicated with circles.

tion spheres with metal ions. Variation of the integration parameters in the Fourier transform of the $\chi$ function convincingly proved that this peak is due to the coordination sphere of copper ions. The quantitative characteristics of this coordination sphere are given in Table 2. The calculated copper–copper distance is typical of copper dimers (Cu–Cu, 2.90–3.1 Å [8]).

To study the dependence of ferromagnetic ordering in azomethine chelate complexes on structural factors, we performed quantum-chemical calculations of two series of isomers (**A** and **B**) with the GAUSSIAN-03 program[1] in the B3LYP/LANL2DZ approximation with full geometry optimization for the ground-state triplet and lower singlet molecules of each dimer. In addition, when calculating the "broken symmetry" energy in the approach [9] required to calculate exchange constants, we separately optimized the dimer geometry in the singlet state.[2] The calculated series have different central fragments: $(Cu–S)_2$ in series **A** and $(Cu–O)_2$ in series **B**.

In the complexes, their two "moieties" adjacent to the central fragments have different relative positions (Fig. 3). The total energies $E_{tot}$ of the calculated systems and the singlet-triplet splitting energies for their lower triplet and singlet states are also tabulated. Hereafter, we will understand under triplet and singlet states these lower states.

The presence of the S atom in the central fragment makes a planar triplet structure angular; this distinctive feature is fundamental for the influence of the sulfur atom on the structure of the complex.

To reveal the most significant geometrical parameters and study them in more detail, let us consider the spin density (SD) distributions in the complexes of series **A** and **B**. The spin densities for the ground-state triplet complexes under discussion are given in Table 4.

For all the calculated triplet states of the complexes, the SD is essentially distributed only over four atoms of the central fragment of each complex and over the nearest adjacent four atoms. The highest SD accumulates on copper atoms (~0.4–0.5 ē, Table 4). In complexes **IV**, types of R are different in the terminal rather than central fragments; that is why replacement of one type of R by another should have a weaker effect on SD of the copper atoms in the central fragment. Indeed, it can be seen in Table 4 that the variation in R produces virtually no effect on the SD distribution over the atoms in the central fragment. From ~1.93 to ~1.98 ē (out of the maximum possible 2.0 ē

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[1] License to Use Agreement: Gaussian, Inc., 340 Quinnipiac Street, Building 40, Wallingford, CT 06492.

[2] The option opt=loose was used.

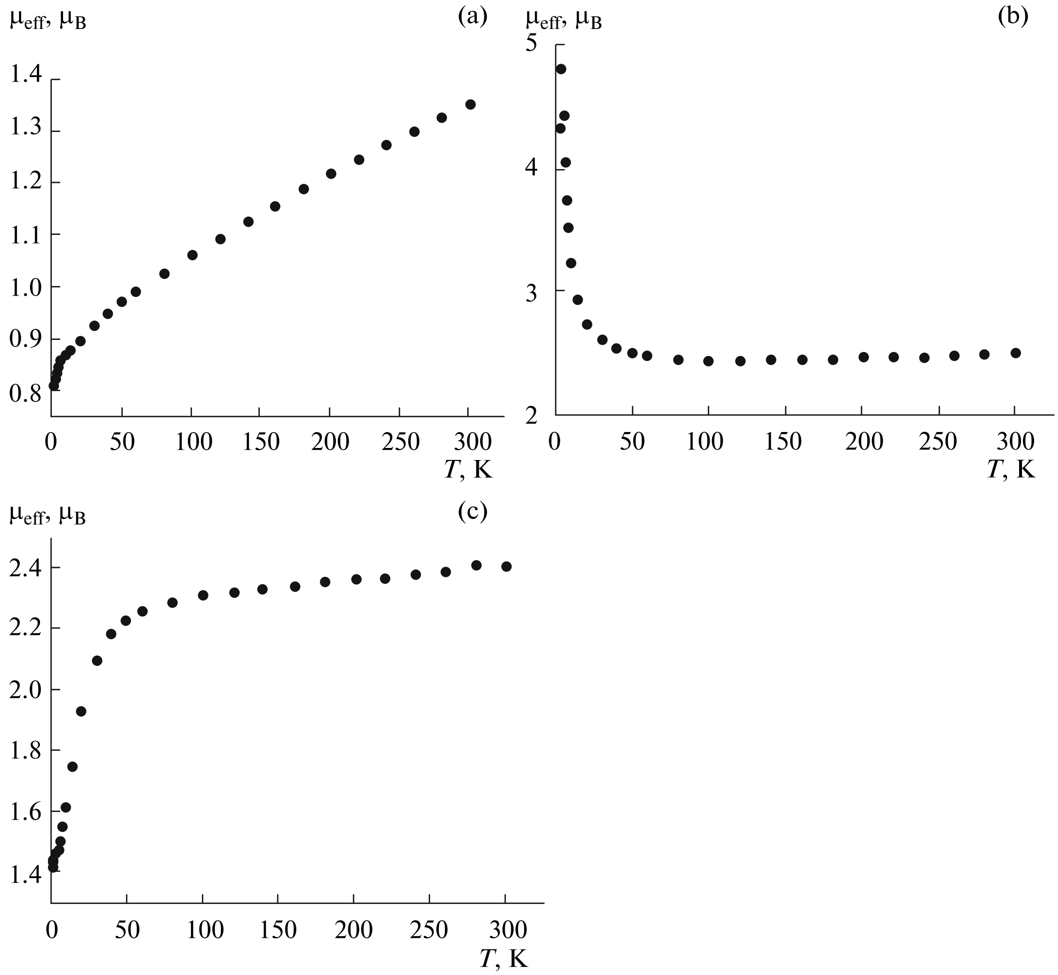

**Fig. 3.** Temperature dependence of the effective magnetic exchange for complexes (a) **IVb**, (b) **IVc**, and (c) **IVd**.

for the triplet state) accumulate on four atoms of the central fragments and the nearest adjacent four atoms. Note that each S atom in the complexes studied bears ~0.32–0.33 $\bar{e}$, i.e., with a decrease in SD on the copper atoms, it increases on the nearest other two atoms of the central fragment and vice versa. Thus, the four atoms of the central fragment have parallel spins, which is favorable for magnetic exchange because of relatively short distances between them.

For examination of the magnetic properties of these complexes, the singlet-triplet splitting energy is most interesting since this quantity numerically equals the exchange integral (i.e., it is a quantitative characteristic of electron exchange interactions). First of all, note that in all the calculated complexes, the triplet state is much lower than the singlet state and corresponds to their energy ground state, which suggests possible magnetic ordering in these systems.

Magnetochemical measurements over a wide temperature range showed that spin exchange occurs in all the complexes based on paramagnetic metal ions (Fig. 3).

Hence, complexes **IVb** and **IVd** exhibit antiferromagnetic spin-spin interactions, while dimer **IVc** is characterized by ferromagnetic exchange. These results can be explained by (1) the influence of additional coordination of the tosylamino O atom by the copper atom on the characteristics of magnetic exchange (it should be ferromagnetic in the case of exchange through sulfur bridges) in dimer **IVb** and (2) the formation of various types of the exchange chelate ring in salicylaldimine complexes: $Cu_2O_2$ for **IVd** (structure **B**) or $Cu_2S_2$ for **IVc** (structure **A**).

To sum up, quantum-chemical calculations and physicochemical studies showed that *o*-tosylamino(hydroxy)aldimines of 4-amino-1,2,4-triazole-5-thiones form dimeric copper complexes and that their magnetochemical properties depend on the bridging atoms.

**Table 3.** Selected geometrical features, total energies $E_{tot}$ of the ground triplet and lower singlet states, singlet-triplet splitting energy $\Delta E$, "broken symmetry" energy $E_{bs}$, eigenvalues of the operator $\hat{S}^2$, and exchange constants $J$ for series **A** and **B**

| R | Geometry | | $E_{tot}$, au | $\Delta E$, kcal/mol | $E_{HC}$, au | $J$, cm$^{-1}$ |
|---|---|---|---|---|---|---|
| | | | Series **A** | | | |
| H | S | Angular | −1693.849 | 13.18 | −1693.870 | |
| | T | Angular | −1693.870 | | $\hat{S}^2 = 0.980$ | −11.8 |
| $CH_3$ | S | Angular | −1772.480 | 13.81 | −1772.502 | |
| | T | Angular | −1772.502 | | $\hat{S}^2 = 0.977$ | 34.6 |
| $C_2H_5$ | S | Parallel to the plane | −1851.092 | 13.53 | −1851.114 | |
| | T | Angular | −1851.114 | | $\hat{S}^2 = 0.979$ | 7.5 |
| | | | Series **B** | | | |
| H | S | Angular | −1693.862 | 17.02 | −1693.891 | |
| | T | Angular | −1693.889 | | $\hat{S}^2 = 0.953$ | −433.9 |
| $CH_3$ | S | Angular | −1772.493 | 17.23 | −1772.523 | |
| | T | Angular | −1772.520 | | $\hat{S}^2 = 0.955$ | −409.8 |
| $C_2H_5$ | S | Angular | −1851.106 | | −1851.135 | |
| | T | Angular | −1851.133 | 17.27 | $\hat{S}^2 = 0.955$ | −399.0 |

**Table 4.** Spin densities of the complexes of series **A** and **B** in the triplet state

| Atom | R = H | R = $CH_3$ | R = $C_2H_5$ |
|---|---|---|---|
| | Series **A** | | |
| Cu | 0.408 | 0.407 | 0.407 |
| S | 0.325 | 0.339 | 0.338 |
| S | 0.326 | 0.339 | 0.338 |
| O | 0.152 | 0.140 | 0.141 |
| N | 0.079 | 0.080 | 0.079 |
| Cu | 0.408 | 0.407 | 0.407 |
| O | 0.152 | 0.140 | 0.142 |
| N | 0.107 | 0.080 | 0.080 |
| | Series **B** | | |
| Cu | 0.490 | 0.490 | 0.490 |
| O | 0.122 | 0.122 | 0.122 |
| O | 0.122 | 0.122 | 0.122 |
| S | 0.298 | 0.294 | 0.293 |
| Cu | 0.490 | 0.490 | 0.490 |
| S | 0.298 | 0.294 | 0.293 |
| N | 0.091 | 0.095 | 0.095 |
| N | 0.091 | 0.095 | 0.095 |

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