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Copper(II) and Nickel(II) Complexes with Bis(azomethine)—a Condensation Product of 1-Phenyl-3-Methyl-4-Formyl-5-Mercaptopyrazole with 1,3-Diaminopropan-2-ol

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Abstract—The copper(II) and nickel(II) complexes based on bis(azomethine), which is the condensation product of 1-phenyl-3-methyl-4-formyl-5-mercaptopyrazole with 1,3-diaminopropan-2-ol, are synthesized. Bis-azomethines can form both binuclear and mononuclear complexes in which the hydroxy group is not involved in coordination. The binuclear copper(II) complexes with the acetate and pyrazolate bridges exhibit an antiferromagnetic exchange, which strength is determined by the nature of the bridge ($2J = -154$ and -424 cm^{-1}, respectively). The structure parameters of the coordination spheres of the complexes are determined by X-ray absorption spectroscopy. The structure of the $CHCl_3$ solvate of the binuclear copper(II) complex with the pyrazolate bridge is solved by X-ray diffraction analysis (CIF file CCDC 964655).

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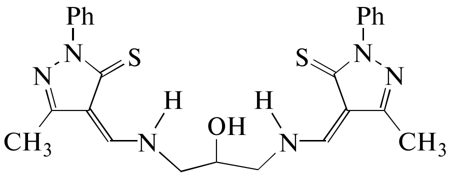
INTRODUCTION

Bis-azomethines, condensation products of polyfunctional aldehydes with 1,3-diaminopropan-2-ol, are classical binucleating ligand systems [1–5]. Binuclear complexes of transition metals with these ligands containing an unsymmetrical exchange fragment are being actively studied as models for revealing the main factors determining the character and strength of exchange interactions between the paramagnetic centers [5–8]. A large diversity of the isolated complexes is predetermined by the possibility of the variation of both the aldehyde component of bis-azomethines and the nature of the exogenic bridging ligand, usually being carboxylic acid residues or heterocyclic anions [9–14]. Bis-azomethines of the salicylaldehyde and β-diketone derivatives are well studied among the ligands of this type, but the complexation ability of bis-azomethines based on heterocyclic aldehydes was studied to a considerably less extent [15].

In this work, we present the results of the synthesis and physicochemical study of the copper(II) and nickel(II) complexes of type **I–IV** with the N_2OS_2-donor ligand, bis(azomethine) H_3L, obtained by the condensation of 1-phenyl-3-methyl-4-formyl-5-thiopyrazole with 1,3-diaminopropan-2-ol.



H_3L

EXPERIMENTAL

Commercially available reagents were used as the starting compounds. The solvents were purified and dried according to standard procedures. 1-Phenyl-3-methyl-4-formyl-5-mercaptopyrazole was synthesized using a described procedure [16].

Synthesis of bis(azomethine) H_3L. A solution of 1,3-diaminopropan-2-ol (1 mmol) in benzene (5 mL) was poured to a hot solution of 1-phenyl-3-methyl-4-formyl-5-mercaptopyrazole (2 mmol) in benzene (10 mL). The mixture was refluxed for 1 h. A precipitate formed after cooling was filtered off, washed with benzene, and dried in vacuo at room temperature. The product was recrystallized from a methanol–dimethylformamide (2 : 1) mixture. The yield was 0.32 g (65%), mp = 238°C.

For $C_{25}H_{26}N_6OS_2$

anal. calcd., %:	C, 61.20;	H, 5.34;	N, 17.13.
Found, %:	C, 61.35;	H, 5.18;	N, 17.47.

IR, (ν, cm^{-1}): 3309 ν(OH), 3190 ν(NH), 1651, 1585 ν(C=N), 1231 ν(C=S). UV-Vis, dichloromethane, λ, nm (ε, L cm^{-1} mol^{-1}): 281 (27050), 310 (28350), 382 (9400). ^{1}H NMR (DMSO-d_6; δ, ppm: 2.25 s (6H, CH_3); 3.58–3.65 m (2H, CH_2); 3.78–3.82 m (2H, CH_2); 4.02 br.s (1H, CH); 5.90 d (1H, J = 5.4 Hz, OH); 7.28–7.33 m (2H, CH_{arom}); 7.44 t (4H, J = 7.8 Hz, CH_{arom}); 7.90 d (4H, J = 7.8 Hz, CH_{arom}); 8.44 d (2 H, J = 14.1 Hz, CHN); 12.60 m (2 H, NH).

Synthesis of compound I. A hot solution of copper(II) acetate (1 mmol) in methanol (10 mL) was added to a hot solution of H_3L (0.5 mmol) in methanol (10 mL). The solution was refluxed for 1 h. A precipitate that formed was filtered off, washed with hot methanol, and dried in vacuo. The yield was 0.19 g (55%); mp > 250°C.

For $C_{27}H_{26}N_6O_3S_2Cu_2$

anal. calcd., %:	C, 48.13;	H, 3.89;	N, 12.47;	Cu, 18.86.
Found, %:	C, 48.40;	H, 4.00;	N, 12.33;	Cu, 18.61.

IR, (ν, cm^{-1}): 1614, 1597 ν(C=N).

Synthesis of compound II. Pyrazole (1 mmol) and a hot solution of copper(II) perchlorate (1 mmol) in methanol (5 mL) were added to a hot solution of H_3L (0.5 mmol) in methanol (10 mL). The solution was refluxed for 1 h. A precipitate that formed was filtered off, washed with hot methanol, and dried in vacuo. The yield was 0.17 g (50%); mp > 250°C.

For $C_{28}H_{26}N_8OS_2Cu_2$

anal. calcd., %:	C, 49.33;	H, 3.84;	N, 16.44;	Cu, 18.64.
Found, %:	C, 49.02;	H, 3.61;	N, 16.02;	Cu, 18.30.

IR, (ν, cm^{-1}): 1621, 1597 ν(C=N).

Complex **IIa** was obtained as a single crystal by the slow evaporation of a solution of complex **II** in chloroform.

Synthesis of compound III. A hot solution of copper(II) perchlorate (1 mmol) in methanol (5 mL) was added to a hot solution of H_3L (0.5 mmol) in methanol (10 mL). The solution was refluxed for 1 h. A precipitate that formed was filtered off, washed with hot methanol, and dried in vacuo. The yield was 0.19 g (70%); mp > 250°C.

For $C_{25}H_{24}N_6OS_2Cu$

anal. calcd., %:	C, 54.38;	H, 4.38;	N, 15.22;	Cu, 11.51.
Found, %:	C, 54.05;	H, 4.55;	N, 15.01;	Cu, 11.32.

IR, (ν, cm^{-1}): 3350 ν(OH), 1624, 1597 ν(C=N).

Synthesis of compound IV was carried out similarly to compound **III** using nickel(II) perchlorate instead of copper(II) perchlorate. The yield was 0.15 g (55%); mp > 250°C.

For $C_{25}H_{24}N_6OS_2Ni$

anal. calcd., %:	C, 54.86;	H, 4.42;	N, 15.35.
Found, %:	C, 54.94;	H, 4.19;	N, 15.70.

IR, (ν, cm^{-1}): 3317 ν(OH), 1596 ν(C=N). ^{1}H NMR (DMSO-d_6), δ, ppm: 2.27 s (6H, CH_3); 3.48–3.53 m(2H, CH_2); 3.93–4.03 m (3H, CH, CH_2); 5.32 d (1 H, J = 4.5 Hz, OH); 7.35 t (2H, J = 7.2 Hz, CH_{arom}); 7.47 t (4H, J = 7.6 Hz, CH_{arom}); 7.65 dd (4H, J_1 = 7.8 Hz, J_2 = 1.2 Hz, CH_{arom}); 7.86 s (2H, CH=N).

Elemental analyses were carried out on a Perkin-Elmer 240C instrument at the Laboratory of Microanalysis of the Southern Federal University (Rostov-on-Don). IR spectra were recorded on a Varian Scimitar 1000 FT-IR instrument in the range from 400 to 4000 cm^{-1} for samples as suspensions in Nujol. ^{1}H NMR spectra were detected in DMSO-d_6 on a Varian Unity 300 spectrometer (300 MHz). UV-Vis spectra were recorded on a Varian Cary 5000 spectrophotometer in the range from 200 to 800 nm. The specific magnetic susceptibility was determined by the relative Faraday method in the range 77.4–300 K. The thermal analyses of the complexes were carried out on a Diamond TG/DTA instrument (PerkinElmer). Samples were heated with a rate of 10 deg/min to 650°C.

The X-ray diffraction analysis of complex **IIa** was carried out on a Bruker SMART APEX2 CCD diffractometer (MoK_α, λ = 0.71073 Å, graphite monochromator). The initial array of the measured intensities was processed using the SAINT [17] and SADABS programs [18]. The structure was solved by a direct method and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms for F^2_{hkl}. Hydrogen atoms were placed in the geometrically calculated positions and refined by the riding model ($U_{iso}(H) = nU_{iso}(C)$; n = 1.5 for the carbon atoms of the methyl group, and n = 1.2 for other C atoms). All calculations were performed using the SHELXTL program package [19]. The experimental characteristics and crystallographic data are presented in Table 1. Selected interatomic distances and bond angles are given in Table 2. The atomic coordinates and other parameters for structure **IIa** were deposited with the Cambridge Crystallographic Data Centre (CCDC 964655; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

The EXAFS Cu and Ni X-ray absorption K-edge spectra of the complexes were obtained in the transmission mode on an EXAFS spectrometer at the Synchrotron Center of the Research Center Kurchatovskii Institut (Moscow). The energy of the electron beam, which was used as an X-ray synchrotron radiation source, was 2.5 GeV at a current of 80–100 mA. A double-crystal Si(111) monochromator was used for X-ray radiation monochromatization. The obtained spectra were processed using standard procedures of background removal, normalizing to the value of the K-edge step, and atomic absorption (μ_0) isolating [20], after which the obtained EXAFS χ spectra were subjected to the Fourier transform in the range of wave vectors of photoelectrons k from 3 to 13.0 Å^{-1} with the weight function k^3. The Fourier transformant moduli (MFT) are the pseudoradial distribution of atoms of the nearest coordination spheres around the absorbing copper or nickel atoms with the radii of the coordination spheres determined with the accuracy to phase corrections. The threshold ionization energy E_0 chosen by the value of the maximum of the K-edge first derivative was further varied in the fitting procedure. The structure parameters of the nearest environment of the metal atoms were determined by comparing the calculated EXAFS signal and those picked out from the full EXAFS spectrum by the Fourier filtration of the corresponding MFT. Fitting was performed using the IFFEFIT-1.2.11 program package [21]. The scattering phase and amplitudes of the photoelectron wave necessary for the construction of the model spectrum were calculated using the FEFF7 program [22] and atomic coordinates of model compounds. The latter were complexes with a similar local structure for which the X-ray diffraction data are known. The goodness-of-fit function Q, which was minimized when determining the structure parameters of the nearest environment, was calculated by the formula

$$Q = \frac{\sum\left[k\chi_{\text{exp}}(k) - k\chi_{\text{theor}}(k)\right]^2}{\sum\left[k\chi_{\text{exp}}(k)\right]^2} \times 100\%. \qquad (1)$$

The structure data for the local atomic environment of the metal atoms in complexes **I–IV** obtained from the EXAFS data are presented in Table 3.

RESULTS AND DISCUSSION

Bis-azomethine H_3L was obtained as a yellow amorphous powder by the condensation of 1-phenyl-3-methyl-4-formyl-5-mercaptopyrazole and 1,3-diaminopropan-2-ol in benzene. The ^{1}H NMR spectrum of H_3L (see Experimental) contains a multiplet signal from two NH protons and a doublet from the CHN protons. The spectrum is transformed into a singlet at 8.41 ppm upon the addition of D_2O, indicating that H_3L, similarly to other azomethines of 1-phenyl-3-methyl-4-formyl-5-mercaptopyrazole [23–25] and its oxygen analog [15], exists in the thiopyrazolone tautomeric form.

The reactions of bis(azomethine) H_3L with copper(II) acetate and copper(II) perchlorate in the pres-

Table 1. Crystallographic data and the experimental and refinement characteristics for complex **IIa**

Parameter	Value
Empirical formula	$C_{29}H_{27}N_8OS_2Cl_3Cu_2$
M	801.14
Crystal size, mm	0.24 × 0.18 × 0.03
Temperature, K	100(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	9.3783(6)
b, Å	9.7538(6)
c, Å	17.8658(10)
α, deg	75.4100(10)
β, deg	83.5420(10)
γ, deg	87.4070(10)
V, Å^3	1571.28(16)
Z	2
ρ_{calcd}, g/cm^3	1.693
μ, mm^{-1}	1.782
$F(000)$	812
$2\theta_{\max}$, deg	58
Number of measured reflections	17035
Number of independent reflections	8331
Number of reflections with $I > 2\sigma(I)$	5768
Ranges of reflection indices	$-12 < h < 12$, $-13 < k < 13$, $-21 < l < 24$
Number of clarified parameters	417
R_1 ($I > 2\sigma(I)$)	0.0401
wR_2 (all reflections)	0.0893
GOOF (all reflections)	0.993
$\Delta\rho_{\max}/\rho_{\min}$, e Å^{-3}	0.486/–0.463

Table 2. Selected interatomic distances and bond angles in the coordination polyhedra of the copper atoms in the structure of complex **IIa**

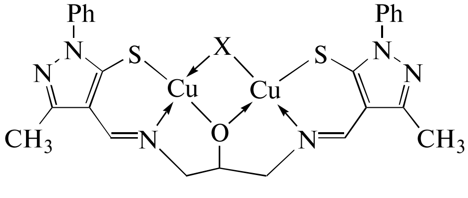
Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(1)	1.9110(19)	Cu(2)–O(1)	1.913(2)
Cu(1)–N(1)	1.954(2)	Cu(2)–N(4)	1.958(2)
Cu(1)–N(7)	1.968(2)	Cu(2)–O(8)	1.975(2)
Cu(1)–S(1)	2.2665(8)	Cu(2)–S(2)	2.2636(8)
Angle	ω, deg	Angle	ω, deg
O(1)Cu(1)N(1)	82.89(9)	O(1)Cu(2)N(4)	83.27(9)
O(1)Cu(1)N(7)	84.87(9)	O(1)Cu(2)N(8)	84.34(9)
N(1)Cu(1)N(7)	167.74(10)	N(4)Cu(2)N(8)	167.52(10)
O(1)Cu(1)S(1)	174.57(6)	O(1)Cu(2)S(2)	171.70(6)
N(1)Cu(1)S(1)	99.27(7)	N(4)Cu(2)S(2)	99.77(7)
N(7)Cu(1)S(1)	92.99(7)	N(8)Cu(2)S(2)	92.71(7)

Table 3. Structure data for the local atomic environment of the copper atom in complexes **I–IV** obtained from the multisphere fitting of the EXAFS data*

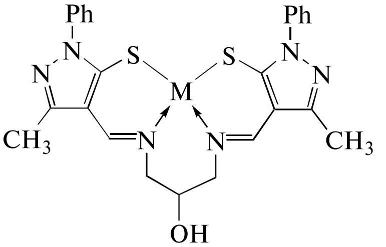
Complex	*N*	*R*, Å	σ^2, Å^2	Atom	*Q*, %
I	3	1.96	0.0032	O/N	2.3
	1	2.26	0.0035	S	
	1	3.44	0.0054	Cu	
II	3	1.94	0.0048	O/N	6.3
	1	2.28	0.0060	S	
	1	3.45	0.0054	Cu	
III	2	1.96	0.0045	N	3.5
	2	2.28	0.0035	S	
IV	2	1.91	0.0038	N	3.3
	2	2.19	0.0044	S	

* *R* are interatomic distances, *N* is the coordination number, σ^2 is the Debye–Waller factor, and *Q* is the goodness-of-fit function.

ence of triethylamine as a deprotonating agent and pyrazole afforded binuclear complexes [$Cu_2(L)(CH_3COO)$] (**I**) and [$Cu_2(L)(Pz)$] (**II**) (Pz is the pyrazolate anion). The reactions of bis-azomethine H_3L with copper(II) and nickel(II) perchlorates without deprotonating agents (this function is performed by the acetate ion in the synthesis of complex **I**) gave complexes **III** and **IV** of compositions [Cu(HL)] and [Ni(HL)], respectively. The data of IR spectroscopy indicate the coordination of bis-azomethine in complexes **I** and **II** in the triply deprotonated form, whereas this form is doubly protonated in complexes **III** and **IV**. The data of ^{1}H NMR spectroscopy for diamagnetic nickel complex **IV** confirm this assumption. The derivatograms of the complexes in the region lower than 290°C exhibit no mass loss and endotherms, indicating that they do not contain solvent molecules [26].



I, X = CH_3COO; **II**, X = Pz



III, M = Cu; **IV**, M = Ni

The measurement of the temperature dependences of the magnetic susceptibility of complexes **I** and **II** show the antiferromagnetic exchange interaction between the copper(II) ions, whose strength substantially depends on the nature of the exogenic bridging ligand (Table 4). The exchange parameters 2*J* calculated in the framework of the Heisenberg–Dirac–van Vleck isotropic model [27] by the Bleaney–Bowers equation [28] are –154 and –424 cm^{-1}, respectively, being within the range of usual values of the exchange parameters for the acetate and pyrazolate bridging copper(II) complexes with bis-azomethine based on 1,3-diaminopropan-2-ol [5]. The effective magnetic moment (μ_{eff}) of complex **III** is almost temperature-independent, which confirms its mononuclear structure. Nickel complex **IV** is diamagnetic indicating its square planar structure [27].

Complex **IIa** was obtained by the recrystallization of complex **II** from chloroform. Its structure was determined as [$Cu_2(L)(Pz)$] · $CHCl_3$ by X-ray diffraction analysis.

In crystals **IIa**, the formula unit is formed by the binuclear molecule of the complex (Fig. 1). The coordination polyhedra of both Cu atoms are distorted squares. The deviation of the copper atoms from the plane of the donor atoms N_2OS is 0.043 Å for the Cu(1) atom and 0.065 Å for the Cu(2) atom.

The molecule of the complex is nearly planar. The value of the dihedral angle between the Cu(1)O(1)C(1) and Cu(2)O(1)C(1) planes, which is usually used as a quantitative measure of binuclear fragment distortion in similar complexes [15], is 11.67°. The pyramidalization of the alkoxide bridging O(1) atom is very insignificant (the sum of the corresponding bond angles is 358.77°). The Cu(1)O(1)Cu(2) bond angle is 127.6(1)°, and the Cu···Cu interatomic distance is 3.4304(5) Å.

Both six-membered metallocycles are not strictly planar, and the S(1) and S(2) atoms shift from the plane of other atoms by 0.265 and 0.151 Å, respectively. The five-membered chelate cycles Cu(1)O(1)C(1)C(2)N(1) and Cu(2)O(1)C(1)C(14)N(4) adopt an envelope conformation, and the "valve" of the envelope (methine C(1) atom) deviates from the mean plane of other atoms by 0.417 and 0.392 Å, respectively.

A comparison of the structure of complex **IIa** with the structure of its pyrazolone analog [15] shows that the replacement of the nonbridging donor oxygen atom by the sulfur atom somewhat changes the structure of the complex but slightly affects the structure of the exchange fragment. In particular, the bond angles at the nonbridging donor atoms change substantially on going from the pyrazolone to thiopyrazolone ligand, resulting in a noticeably higher noncoplanarity of the pyrazole and benzene cycles. At the same time, the structure parameters of the complexes affecting the magnetic exchange between the copper(II) ions (bond angle at the alkoxide bridging atom and copper–copper interatomic distance) change insignificantly when oxygen is replaced by sulfur.

The magnetic properties of complex **IIa** are nearly similar to those for complex **II** (Table 4). The very close exchange parameters in these compounds indicate that the structure of the exchange fragment in complex **II** is very similar to that in complex **IIa**.

All complexes were studied by X-ray absorption near-edge structure (XANES) spectroscopy to establish the structure parameters of the coordination modes. The XANES Cu *K*-edge X-ray absorption spectra for complexes **I–III** and their first derivatives are presented in Fig. 2.

The XANES spectra of complexes **I–III** contain the pre-edge peak A at 8980.1–8980.6 eV assigned to the $1s \rightarrow 3d$ electron transition, indicating the low-symmetry environment of the copper ions in the oxidation state +2 [29]. This energy position of the pre-edge peak is characteristic of the oxidation state +2 of copper. The XANES fine structure of the complexes directly in the region of the edge and above the absorption edge is caused, first of all, by the $1s \rightarrow 4s$ and $1s \rightarrow 4p$ electron transitions along with the shake-down ligand–metal transitions. The shoulder (**B**) at 8988–8990 eV caused by the splitting of the 4*p* sublevel [30–32] indicates the square environment of the copper(II) ions in complexes **I–III**. The *K*-edges and their first derivatives are very similar for complexes **I** and **II**, indicating that the geometries of the coordination modes in these compounds are similar.

Table 4. Magnetic properties of complexes **I–III**

Complex	T, K	μ_{eff}, μB*	$2J$, cm^{-1}	g	f
I	295	1.76	−154	2.24	0.029
	77.4	0.97			
II	295	1.14	−424	2.12	0.037
	77.4	0.37			
IIa	295	1.14	−425	2.10	0.016
	77.4	0.24			
III	295	1.81			
	77.4	1.80			

* The values of μ_{eff} were calculated per copper ion.

The quantitative characteristics of the local atomic environment of the copper(II) ions in complexes **I–III** (Table 3) were obtained by the nonlinear multisphere fitting of the calculated EXAFS spectrum to the experimental one. The MFT EXAFS Cu *K*-edge X-ray absorption spectra for complexes **I** and **III** are shown in Fig. 3. In all cases, the main peak is caused by scattering on the first coordination sphere consisting of the oxygen or nitrogen atoms of the ligand. There peaks of smaller amplitudes at $r \approx 1.9$ Å, which correspond to the manifestation of the interaction with one (complexes **I** and **II**) or two (complex **III**) sulfur atoms, are observed from the side of longer distances from the main peak in the MFT. In the case of complexes **I** and **II**, there is also the peak at $r \approx 3.2$ Å caused by the scattering on the nearest copper atom, which unambiguously indicates their binuclear structure.

The copper–copper distance in complexes **I** and **II** is 3.44 and 3.45 Å, respectively, which is consistent with the X-ray diffraction data for complex **IIa** and corresponds to the copper–copper distance in all structurally characterized pyrazolate bridging copper(II) complexes with bis-azomethines based on 1,3-diaminopropan-2-ol in which the "symmetrical" conformation of the chelates is observed [5, 14].

The XANES and MFT EXAFS Ni *K*-edge X-ray absorption spectra of nickel complex **IV** are shown in Fig. 4. Note the absence of the pre-edge peak in the XANES and several maxima of the first derivative of the Ni *K*-edge for complex **IV**.

As said above, the origin of the pre-edge structure is related to the $1s \rightarrow 3d$ electron transitions, which are dipole-forbidden for the *K*-edges of 3*d* metals. The forbiddance is eliminated for the 4*p*–3*d* hybridization of atomic orbitals of the metal, which occurs in low-symmetry complexes only. In the case of centrosymmetrical coordination polyhedra, in particular, octahedron or square, the pre-edge peak intensity is predominantly due to the quadrupole transition $1s \rightarrow 3d$, whose composition is two orders of magnitude lower than that from the dipole one. In our case, for complex **IV**, the low intensity of the pre-edge peak

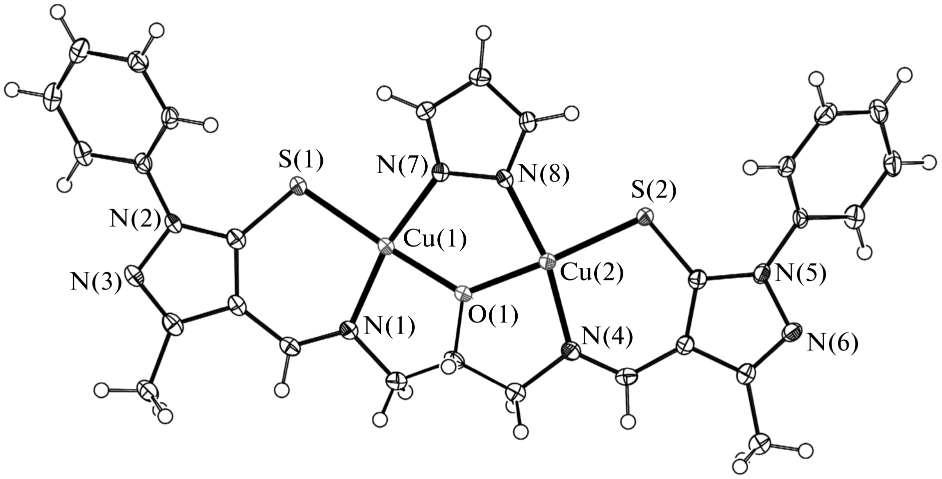


Fig. 1. Molecular structure of complex **IIa** in the representation of atoms by atomic displacement ellipsoids with the 50% probability (chloroform molecule is omitted).

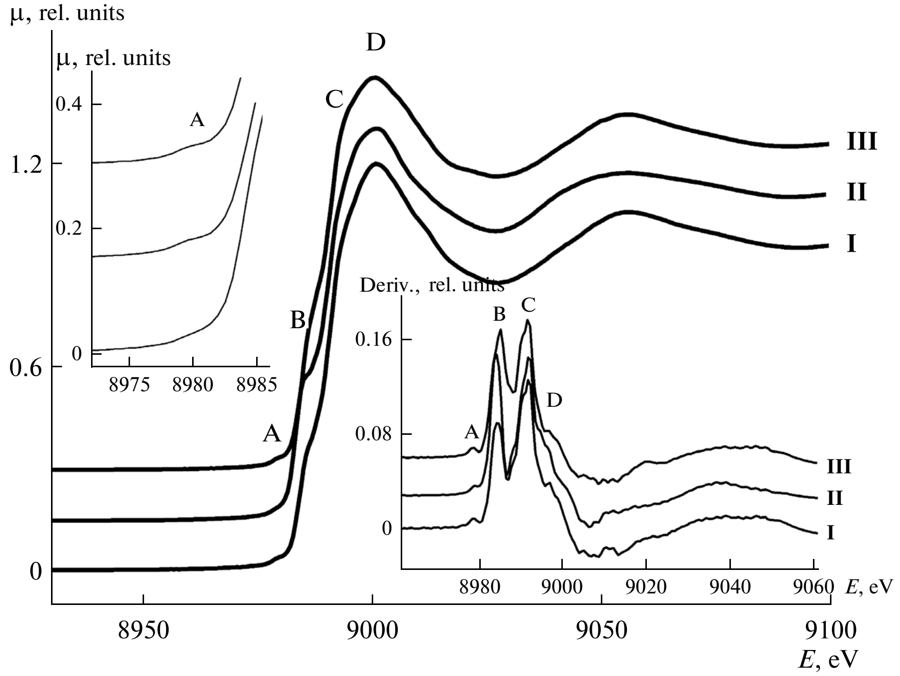


Fig. 2. XANES Cu *K*-edge X-ray absorption spectra for complexes **I–III**: (in inset at the left) the pre-edge structure of the spectrum and (in inset at the right) its first derivative.

indicates the symmetrical environment of nickel and the elimination of the degeneracy of the $4p_z$, $4p_x$, and $4p_y$ orbitals leading to the appearance of several maxima of the first derivative shows that the coordination sphere of nickel is not octahedral.

The conclusion about the square structure of complex **IV** is not confirmed by an analysis of the EXAFS giving quantitative characteristics of the coordination spheres of nickel ions. The MFT EXAFS Ni *K*-edge spectrum (Fig. 4b) exhibits a shoulder from the side of shorter distances at $r \approx 1.50$ Å and the main peak at $r \approx 1.74$ Å corresponding to the nearest environment consisting of the nitrogen and sulfur atoms. The best model of the nearest environment of the nickel(II) ion is the coordination sphere consisting of two nitrogen atoms and two sulfur atoms at fairly short distances corresponding to the planar square nickel complexes with other N_2S_2 donor ligands (Table 3). This conclusion is consistent with the data of magnetochemistry and ^{1}H NMR spectroscopy for complex **IV**.

Thus, depending on the synthesis conditions, bisazomethine H_3L forms with copper(II) ions either

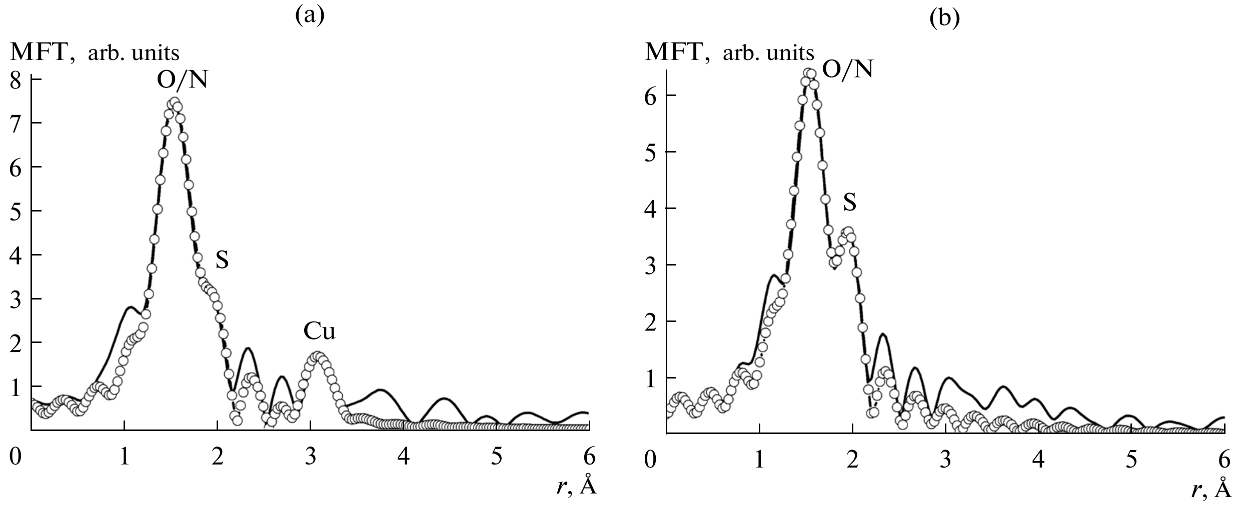


Fig. 3. MFT EXAFS Cu *K*-edge X-ray absorption spectra for complexes (a) **I** and (b) **III**; (–) experiment and (○) theoretical MFT calculated for the best model.

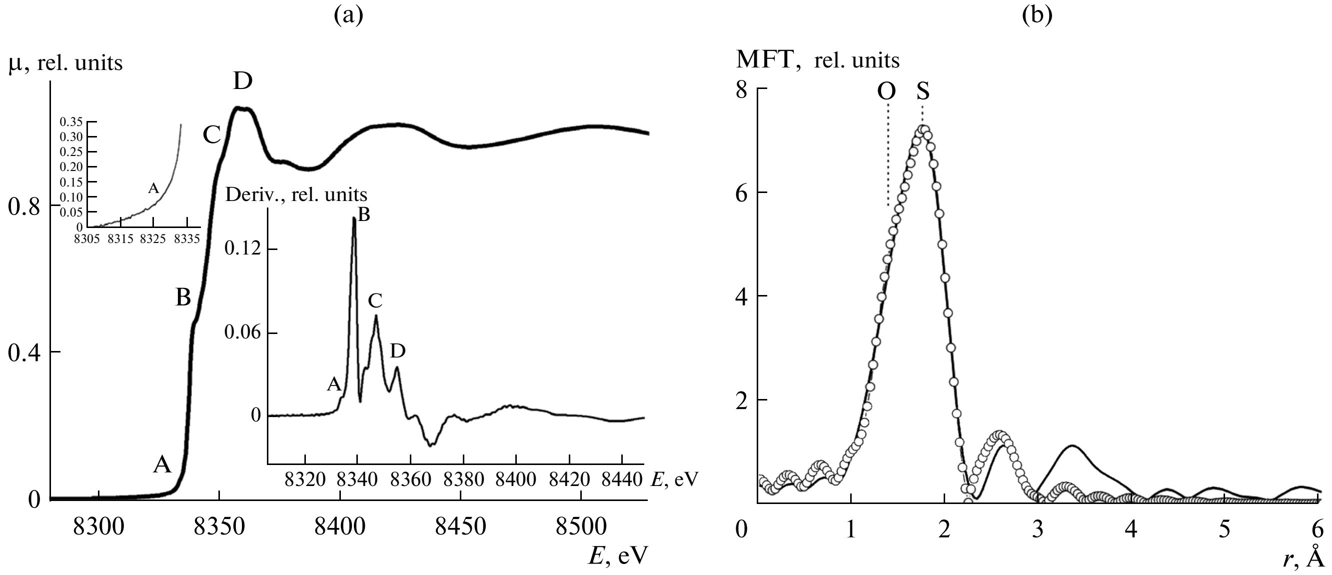


Fig. 4. XANES (left; the pre-edge region and first derivative of the Ni *K*-edge are shown in insets) and the MFT EXAFS (right) Ni *K*-edge X-ray absorption spectra for complex **IV**.

binuclear complexes **I** and **II** with the acetate or pyrazolate exogenic bridges, or mononuclear complex **III** in which the hydroxy group is not involved in the coordination with the metal [33]. Only square planar mononuclear complex **IV** with a similar structure was obtained with nickel(II) ions.

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