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Binuclear Complexes of Copper(II) with 1'-Phthalazinylhydrazones of Substituted Salicylic Aldehydes: Physico-Chemical Study and Quantum-Chemical Simulation

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Abstract—Binuclear complexes of copper(II) with 1'-phthalazinylhydrazones of substituted salicylic aldehydes have been prepared and studied. Antiferromagnetic exchange interaction between copper(II) ions has been revealed in all the complexes. Taking advantage of quantum-chemical simulation, we have investigated the influence of the complexes structural isomerism on the character of the exchange interaction between the paramagnetic centers. X-ray absorbance spectroscopy afforded the structural parameters of coordination spheres of copper(II) ions; it has been demonstrated that dimerization occurred via the nitrogen atoms of phthalazine fragments.

Keywords: phthalazinylhydrazones, copper(II), coordination isomerism, magnetochemistry, exchange interaction, density functional theory
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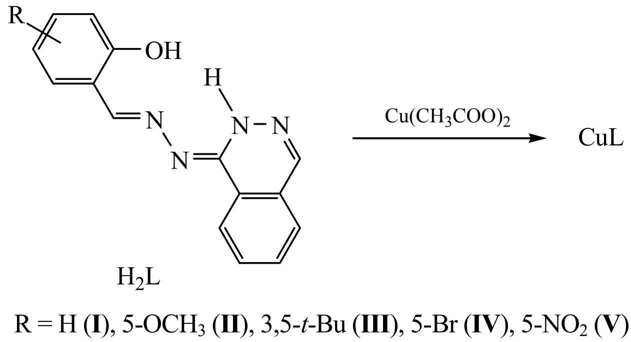
Complex forming ability of hydrazones of 1-hydrazinophthalazine (hydralazine) has been widely used due to biological activity of such compounds [1–4]. Even though hydrazones of salicylic aldehyde and its derivatives have been well known ligands in coordination chemistry studies, metal complexes with 1'-phthalazinylhydrazone of salicylic aldehydes have been discussed only in three papers so far [5–7]. Moreover, in two of the above-cited studies [5, 6] the complexes have not been isolated; instead, their solutions have been studied by means of spectroscopy. Three mononuclear complexes of the said ligand (hereafter denoted as H_2L) with Cu(II), Ni(II), Co(II) have been isolated and studied, their composition corresponding to [M(HL)Cl] [7]. Hydrazones of salicylic aldehyde and phthalazinylhydrazones are known to form binuclear metal chelates [3, 8–11] but such complexes based on 1'-phthalazinylhydrazone of salicylic aldehyde have not been described. Herein we report on preparation, study of physico-chemical properties, and quantum-chemical simulation of binuclear complexes of copper(II) with 1'-phthalazinylhydrazones of substituted salicylic aldehydes (Scheme 1).

1'-Phthalazinylhydrazones of salicylic aldehyde and its derivatives, similarly to other hetarylhydrazones of this class, can potentially act as dibasic tridentate ligands. We have described preparation and tautomerism of such compounds in [12]. According to

Scheme 1.



R = H (**I**), 5-OCH_3 (**II**), 3,5-*t*-Bu (**III**), 5-Br (**IV**), 5-NO_2 (**V**).

NMR spectroscopy data, quantum-chemical simulation, and X-ray diffraction studies, the hydrazones H_2L exist in the phthalazone tautomeric form.

Interaction of the hydrazones H_2L with copper(II) acetate yielded complexes **I**–**V**. The isolated compounds were studied by means of elemental analysis, IR spectroscopy, magnetochemistry, and X-ray absorption spectroscopy. Composition of the complexes **I**–**V** corresponded to the general formula CuL. IR spectroscopy data confirmed tridentate coordination of the ligands in their twice deprotonated form. In particular, absorption bands of phenol and NH groups were absent in the spectra, and the ν(C=N) absorption band was shifted towards longer wavelength by 6–13 cm^{-1} as compared to the spectra of the parent hydrazones [12].

Cooling the complexes **I**–**V** down to nitrogen boiling point led to significant decrease of their effective magnetic moment (Table 1). The result evidenced about strong antiferromagnetic exchange interaction between the copper(II) ions and thus confirmed the binuclear complexes formation.

Parameters of the exchange interaction were calculated in the frame of the Heisenberg–Dirac–van Vleck model using the modified Bleaney-Bowers equation (1) with χ'_M, molar magnetic susceptibility; N_A, the Avogadro’s number; g, the Landé factor; β, the Bohr magneton; k, the Boltzmann constant; $2J$, exchange parameter; f, molar fraction of the paramagnetic admixture; and N_α, temperature-independent paramagnetism [13].

Table 1. Magnetic properties of the **I**–**V** complexes

Comp. no.	T, K	μ_{eff}, μ_B[a]	g	f
I	292	1.09	2.24	0.036
	77.4	0.40		
II	291	1.24	2.24	0.066
	77.4	0.51		
III	297	1.17	2.10	0.045
	77.4	0.38		
IV	296	1.19	2.10	0.070
	77.4	0.47		
V	295	1.18	2.00	0.091
	77.4	0.52		

[a] Values of μ_{eff} were calculated with respect to one copper ion.

$$\chi'_M = \frac{2N_A g^2 \beta^2}{3kT}\left\{(1-f)\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1} + f S(S+1)\right\} + N_\alpha. \quad (1)$$

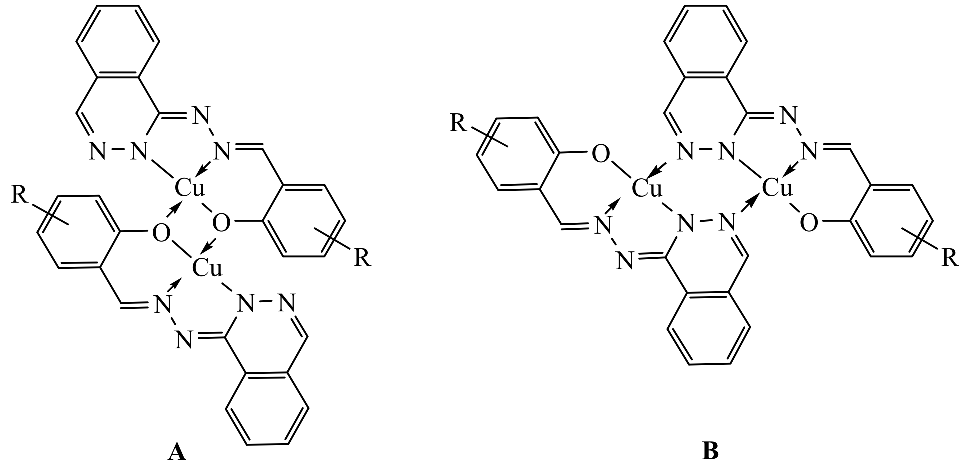
Parameters of the model allowing for the best correspondence between the theory and the experiment are collected in Table 1.

The presence of phthalazine fragment in the hydrazones H_2L extends the ability of such ligands to form binuclear complexes. Other previously described hetarylhydrazones could form the dimeric complexes exclusively when the phenoxide oxygen atom acted as the bridges [14–16]. Structure of the H_2L hydrazones allows for two types of dimerization: via the phenoxide atoms of the aldehyde fragment to form the four-membered chelate cycle Cu–O(O')–Cu or via the phthalazine fragment to form the six-membered chelate cycle Cu–N–N'(N''–N''')–Cu. In this regard the H_2L were somewhat similar to acyl- and aroylhydrazones of salicylic aldehyde capable of dimerization via the phenoxide or via the *o*-oxyazine oxygen atoms (via the aldehyde or the hydrazone fragment, respectively) [8]. Hence, two types of dimeric structures, **A** and **B**, were possible in the cases of complexes **I**–**V** (Scheme 2).

In the case of complex **III**, the presence of *tert*-butyl group *ortho*-positioned with respect to the phenol fragment excluded the possibility to form the dimeric structure A [17]. As the complex **III** was definitely binuclear (as evidenced by the strong antiferromagnetic exchange, $2J = -416$ cm^{-1}), it should have been of the B type (dimerization via the diazine bridges). In other cases the both dimerization types were theoretically possible.

Noteworthily, binuclear complexes of copper(II) with 1'-phthalazinylhydrazones of salicylic aldehyde derivatives significantly differed from those dimeric complexes of copper(II) with the acylhydrazones as far as the features of magnetic exchange interaction in the coordination isomers was concerned. In the cases of acylhydrazones of salicylic aldehydes, magnetic properties of the isomeric dimers were significantly

Scheme 2.



different [8, 18–23]. For both the isomers, the exchange was antiferromagnetic; however, in the case of dimerization via the phenoxide atoms the exchange interaction was much stronger (the exchange parameter –300 to –500 cm^{-1}) than that in the case of dimerization via the α-oxyazine oxygen atoms (–50 to –150 cm^{-1}) [8, 24]. Therefore, magnetochemical properties of the complex allowed elucidation of its structure. However, in the cases of binuclear complexes of copper(II) with 1'-phthalazinylhyd-razones of salicylic aldehydes such criterion [8] was not applicable, as strong antiferromagnetic exchange was observed in the complexes of various phthalazinylhydrazones via the diazine bridges [9, 10, 25–27].

In order to theoretically rationalize the effect of dimerization type of the binuclear complexes **I**–**V** on the exchange interaction, we performed quantum-chemical simulation of the exchange parameters taking advantage of the density functional theory. The $2J$ values were computed using the previously approved procedure [28, 29] based on the broken symmetry approach (BS) [30–33]. In particular, the Yamaguchi equation (2) was used with E, total energy; $<S^2>$, expected value of the squared total spin of the states; the HS subscript denoted the high-spin state, and the BS denoted the “broken symmetry” state [33].

$$2J = \frac{2(E_{\mathrm{BS}} - E_{\mathrm{HS}})}{\langle S^2\rangle_{\mathrm{HS}} - \langle S^2\rangle_{\mathrm{BS}}.} . \qquad (2)$$

Molecular structures of the dimers **A** and **B** (R = H) in vacuum according to the simulation are shown in Figs. 1 and 2, respectively.

In all the cases, geometry optimization gave the structures with non-planar exchange fragment. In the type A dimers, the four-membered cycle Cu–O(O')–Cu was slightly distorted due to bending along the line connecting the bridging oxygen atom; the dihedral angle between the mean-squared planes of copper coordination polyhedrons was of about 30° (Fig. 1). The Cu–Cu distance in the type **A** dimers was independent of the substituent R nature, being of 2.97–2.98 Å.

Noteworthily, the Cu–Cu distance in copper(II) complexes with hydrazones of salicylic aldehyde dimerized via the phenoxide oxygen atom was 3.01–3.05 Å according to the X-ray diffraction data [22, 23, 34–38], fairly close to the results of simulation of the type A dimers geometry. Somewhat underestimated distance was due to the above-described distortion of the exchange fragment. In the only case where such distortion was documented by X-ray diffraction studies [complex of copper(II) with S-methylisothiosemicarbazide of salicylic aldehyde] the Cu–Cu distance was of 2.946 Å [38].

In the type B dimers, the six-membered exchange fragment Cu–N–N'(N''–N''')–Cu was simulated to exist in the *boat* conformation with copper atoms located in the apical positions (Fig. 2). Similarly to the previously described case, the R substituent nature only slightly altered the degree of distortion of the exchange fragment, and the Cu–Cu distance was quite the same in all the complexes (3.70–3.73 Å). Noteworthily, X-ray diffraction study of binuclear copper(II) complex with 1'-phthalazinylhydrazone of 2(*N*-tosylamino)-benzaldehyde (dimerization via the diazine bridges) revealed noticeably shorter Cu–Cu distance, of 3.367 Å [10], due to the more deviation of copper ions from the phthalazine nitrogen atoms plane.

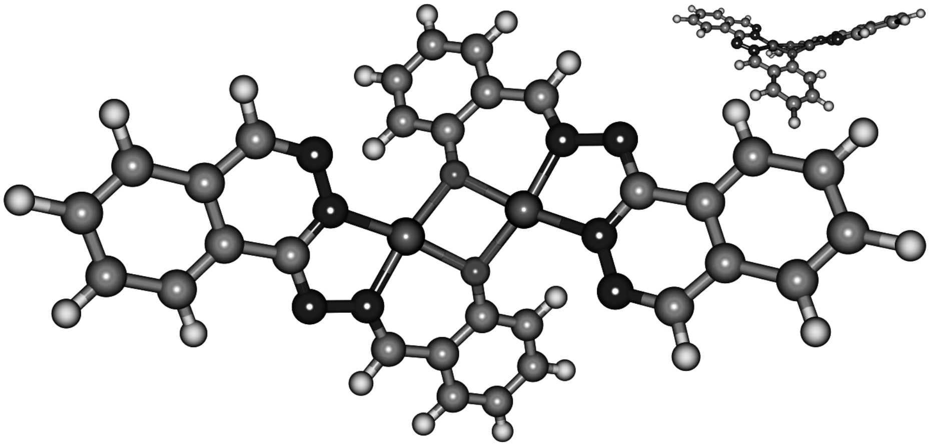


Fig. 1. Molecular structure of dimer **A** according to the simulation (right up, different viewpoint).

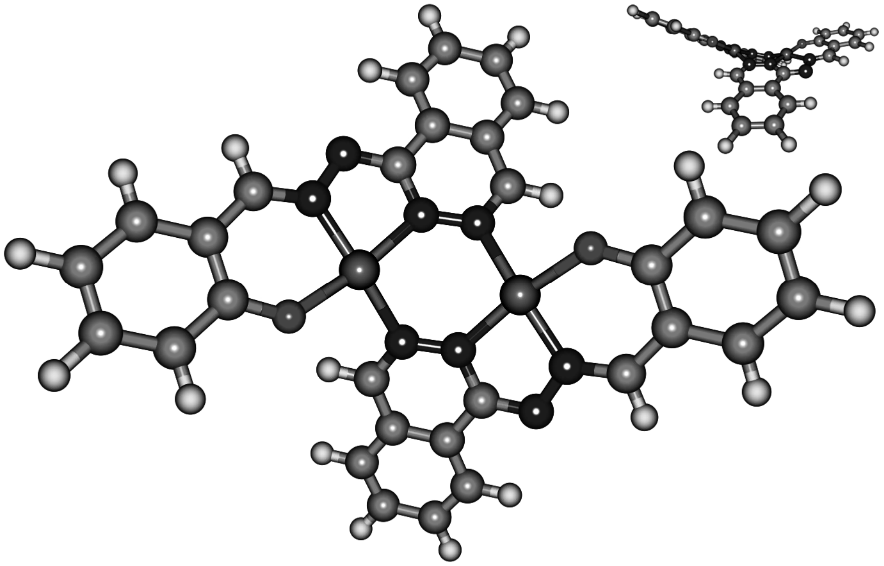


Fig. 2. Molecular structure of dimer **B** according to the simulation (right up, different viewpoint).

Comparison of total energy of triplet states of types **A** and **B** dimers demonstrated the more favorable dimerization via nitrogen atoms of the phthalazine fragments (the energy difference was of 8.8–12.9 kcal/mol lower in the case of the **B** type dimers). Hence, we concluded that dimerization of the complexes **I**–**V** occurred via the phthalazine bridges.

The computed exchange parameters of the **A** and **B** dimers of the studied complexes are given in Table 2. In the cases of all the substituents R, the absolute value of exchange parameter was noticeably higher for the type **A** dimer.

Independently of the dimerization type, the high-spin state of the dimers was fairly well corresponding to the triplet state (the expected squared total spin $<S^2>$ was close to 2). The low-spin state in all the cases was of significantly biradical nature; spin density at the both copper atoms was of the same absolute value but of the opposite signs, and the $<S^2>$ value was of 0.96–0.99.

Magnetic orbitals were in all the cases significantly delocalized along the donor atoms of the bridging groups and the interacting copper atoms. Independently of the bridge nature, the both spin orbitals (except for the $d_{x^2-y^2}$ atomic orbital level) of each of copper ions revealed noticeable contribution from the $d_{x^2-y^2}$ atomic orbital level of the other center (Fig. 3), thus allowing efficient overlap of the

Table 2. Calculated exchange parameters (cm^{-1}) of dimeric structures **A** and **B** along with experimental $2J$ values for the complexes **I**–**V**

Comp. no.	$2J_{calc}$		$2J_{exp}$
	dimer **A**	dimer **B**	
I	–712	–595	–485
II	–754	–593	–445
III	–	–609	–416
IV	–699	–606	–416
V	–642	–629	–402

magnetic spin orbitals causing the strongly antiferromagnetic nature of the exchange interaction.

Overall, the quantum-chemical simulation results did not allow unambiguous choice between the coordination isomers of type **A** and **B** of complexes **I**–**V**, even though the computed $2J$ values were closer to the experimental ones in the cases of dimers **B** (dimerization via the phthalazine fragments).

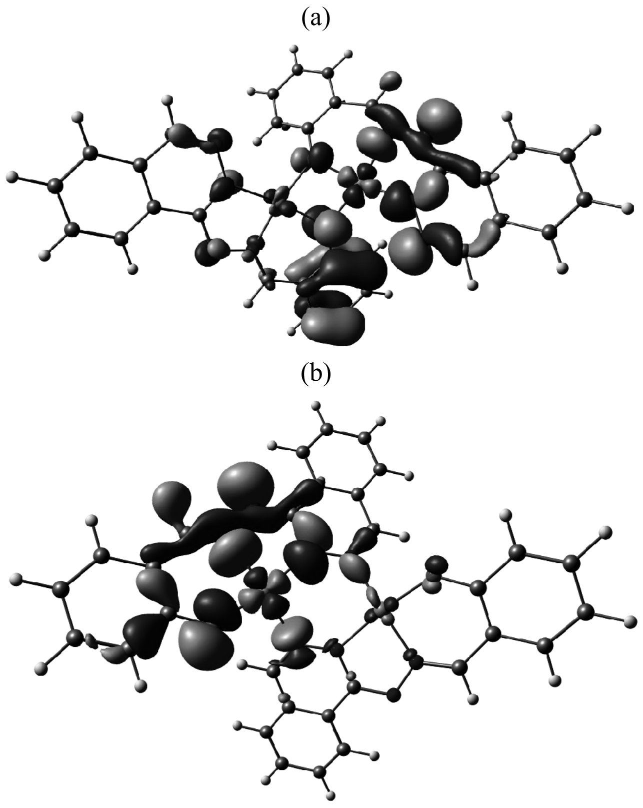


Fig. 3. Magnetic spin orbitals of electrons with α-oriented spin in the low-spin state of dimers (a) **A** and (b) **B**.

The killer argument to select the actual structure of complexes **I**–**V** between the **A** and **B** type dimers would be experimental elucidation of the structure. Unfortunately, we failed to prepare the complexes monocrystals suitable for the X-ray diffraction study. Therefore, we applied the other experimental method to determine the local structure of coordination sphere if the transition metal ions, X-ray absorption spectroscopy (XAS).

Figure 4 displays the normalized XANES Cu*K*-edges of the X-ray absorption spectra and their first derivatives recorded for the complexes **I**–**V**. The shape and the parameters of XANES were close for all the studied compounds, reflecting the similarity of the nearest surrounding of copper ions in the ctudied complexes. The low intensity of sub-edge peaks A and the presence of several maxima B, C, and D in the first derivatives curves pointed at the square coordination of copper ions in the studied compounds [39].

Quantitative parameters of the local atomic structure of complexes **I**–**V** were elucidated from analysis of EXAFS Cu*K*-edges of the X-ray absorption spectra. Figure 5 shows the modules of Fourier transformants of EXAFS Cu*K*-edges of the spectra, the parameters were fairly close. All the MFTs contained the base peak at r = 1.46 Å, unambiguously assigned to scattering at the nearest coordination spheres consisting of oxygen and nitrogen atoms of the ligands; the other two peaks were found at r = 2.30 and 2.95–2.98 Å.

The structural parameters elucidated from the above-described analysis of the complexes **I**–**V** were close (Table 3). Two nitrogen and two oxygen atoms of the ligand were located around copper ions at the distance of 1.91–1.95 Å. The coordination node was a planar square. The second peak of the MTFs was assigned to scattering at carbon/nitrogen atoms located at r = 2.91 Å. The third peak corresponded to the coordination sphere consisting of a single copper atom at r = 3.3–3.4 Å, confirming the dimeric structure of the complexes.

The close structural parameters of coordination nodes in complexes **I**–**V** confirmed the same dimerization type in all the studied compounds. The determined Cu–Cu distances led to the unambiguous elucidation of the complexes structure: as was mentioned above, the Cu–Cu distance could not exceed 3.1 Å in the case of dimerization via the phenoxide oxygen atom of the salicylic aldehyde fragment. As the EXAFS method allows determination of the metal–metal distance with

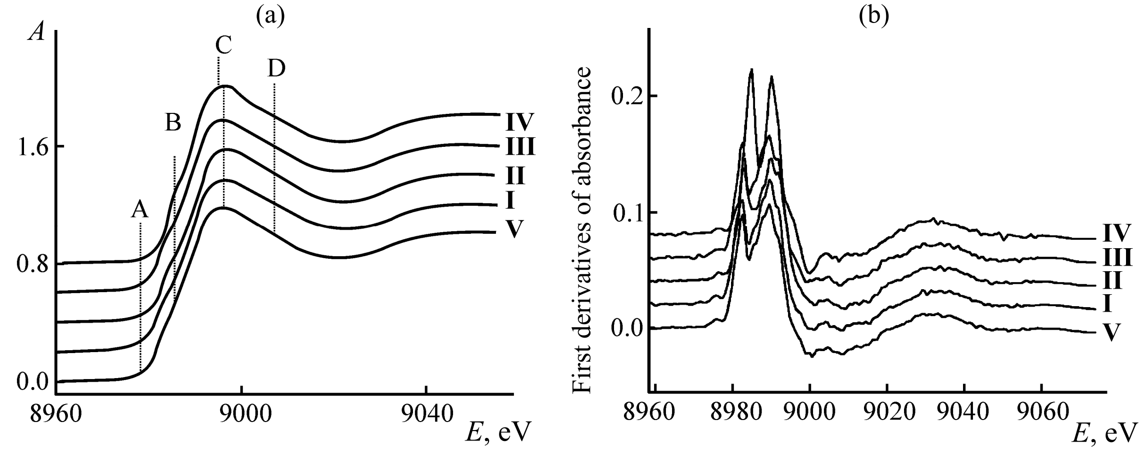


Fig. 4. XANES of Cu*K*-edges of X-ray absorption spectra of the type **B** complexes (a) along with their first derivatives (b).

the inaccuracy as low as 0.02–0.05 Å [39, 40], the obtained data excluded the type **A** dimerization of the studied complexes. The Cu–Cu distance shorter than the simulated one could be accounted for distortion of the binuclear molecules due to the intermolecular interactions in the crystal.

To conclude, the set of data obtained by means of magnetochemistry, quantum-chemical simulation, and X-ray absorption spectroscopy led to the conclusion that copper(II) complexes with 1'-phthalazinylhydrazones of salicylic aldehyde derivatives were dimerized via the nitrogen atoms of the phthalazine fragments.

EXPERIMENTAL

Elemental analysis was performed using the Perkin Elmer 240C instrument (Laboratory of Microanalysis, Southern Federal University). IR spectra of suspensions in Vaseline oil (400–4000 cm^{-1}) were recorded using the Varian Scimitar 1000 FT-IR spectrometer. Specific magnetic susceptibility was determined via the relative Faraday method at 77.4–300 K, $Hg[Co(CNS)_4]$ being used as reference.

X-ray absorption spectra of copper *K*-edge were recorded in the transmission mode using the EXAFS spectrometer the K1.3b station (Kurchatov Synchrotron Center). Energy of the X-ray source beam was of 2.5 GeV at current of 80–100 mA. The two-crystal Si(111) monochromator was used. The spectra were processed using the standard procedures of baseline subtraction, normalization with respect to the *K*-edge step, and deconvolution of atomic absorption μ_0 [40]; further, the obtained EXAFS (χ)-spectra were subject to Fourier transformation at the wave vector range of k 2.5 to 13.0 Å^{-1} with the k^3 weighing function. Threshold ionization energy E_0 was chosen according to the maximum of the *K*-edge first derivative, it was then varied during the fitting. Parameters of the nearest surrounding of copper atoms were determined via nonlinear fitting of the corresponding coordination spheres parameters so that

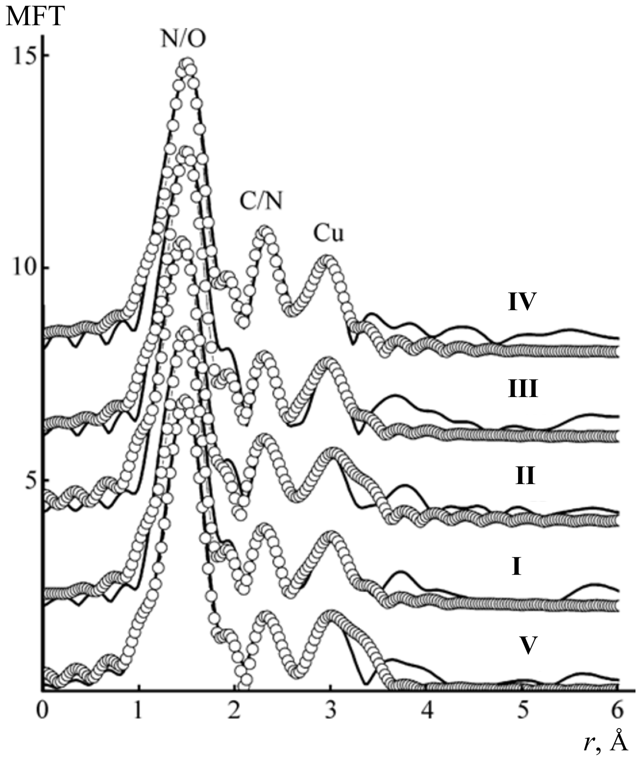


Fig. 5. Absolute values of EXAFS Fourier transforms of Cu*K*-edges of X-ray absorption spectra of the type **B** complexes (solid line, experiment and circles, calculation).

Table 3. Structural parameters of complexes **I–V** as determined via the multisphere fitting of the EXAFS data (r, interatomic distance; N, coordination number; σ^2, the Debye–Waller factor; and Q, goodness of fit)

Comp. no.	N	r, Å	σ^2, Å^2	Atom	Q, %
I	2	1.91	0.0046	N/O	1.7
	2	1.94	0.0046	N/O	
	1	3.32	0.0048	Cu	
II	2	1.90	0.0046	N/O	2.9
	2	1.92	0.0046	N/O	
	1	3.37	0.0055	Cu	
III	2	1.89	0.0040	N/O	4.6
	2	1.91	0.0040	N/O	
	1	3.27	0.0040	Cu	
IV	2	1.92	0.0045	N/O	4.6
	2	1.95	0.0045	N/O	
	1	3.27	0.0040	Cu	
V	2	1.91	0.0046	N/O	1.0
	2	1.94	0.0046	N/O	
	1	3.40	0.0047	Cu	

the simulated EXAFS signal coincided with the Fourier-filtered one. The fitting was performed taking advantage of IFFEFIT-1.2.11 software package [41]. The phases and amplitudes of photoelectron wave scattering (required for the spectrum simulation) were computed with aid of FEFF7 software [42] using atomic coordinates of model copper(II) compounds (complexes with the similar local structures characterized by X-ray diffraction analysis). The fitting quality was expressed using the Q function [Eq. (3)], being minimized in the course of fitting.

$$Q = \frac{\Sigma[k\chi_{\mathrm{exp}}(k) - k\chi_{\mathrm{th}}(k)]^2}{\Sigma[k\chi_{\mathrm{exp}}(k)]^2} \times 100\%. \quad (3)$$

Quantum-chemical simulation was performed in the frame of density functional theory using the hybrid exchange-correlation potential B3LYP [43, 44]. Geometry optimization was performed along all the parameters, with no symmetry constrains. The split-valence basis set 6-311G(d) was used. The simulation was performed at the WSD cluster (Computing Center, Southern-Russian Regional Center for Informatization) using GAUSSIAN03 software [45]. The data input and output were performed using Chemcraft software [46].

1'-Phthalazinylhydrazones of 5-R-salicylic aldehydes were prepared as described elsewhere [12].

Complexes I–V. A hot solution of 0.001 mol of copper(II) acetate in 10 mL of methanol was added to a hot solution or suspension of 0.001 mol of the corresponding hydrazone in 20 mL of methanol. The reaction mixture was refluxed during 3 h. The precipitate was filtered off, washed with methanol, and dried in vacuum at room temperature. Yield 60–80%.

Complex I. mp >250°C. IR spectrum, ν, cm^{-1}: 1606 (C=N). Found, %: C 55.3; H 3.09; N 17.2; Cu 19.5. $C_{15}H_{10}N_4OCu$. Calculated, %: C 55.8; H 3.20; N 17.5; Cu 19.3.

Complex II. mp >250°C. IR spectrum, ν, cm^{-1}: 1600 (C=N). Found, %: C 53.8; H 3.24; N 15.4; Cu 17.4. $C_{16}H_{12}N_4O_2Cu$. Calculated, %: C 54.0; H 3.40; N 15.7; Cu 17.9.

Complex III. mp >250°C. IR spectrum, ν, cm^{-1}: 1603 (C=N). Found, %: C 63.3; H 6.05; N 12.9; Cu 14.7. $C_{23}H_{26}N_4OCu$. Calculated, %: C 63.1; H 5.98; N 12.8; Cu 14.5.

Complex IV. mp >250°C. IR spectrum, ν, cm^{-1}: 1606 (C=N). Found, %: C 44.9; H 2.17; N 13.4; Cu 16.0. $C_{15}H_9BrN_4OCu$. Calculated, %: C 44.5; H 2.24; N13.8; Cu 15.7.

Complex V. mp >250°C. IR spectrum, ν, cm^{-1}: 1603 (C=N). Found, %: C 48.9; H 2.33; N 18.6; Cu 17.2. $C_{15}H_9N_5O_3Cu$. calculated, %: C 48.6; H 2.45; N 18.9; Cu 17.1.

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