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Switching of the Exchange Interaction Character in the Binuclear Copper(II) Complexes Based on the Hetaryl Derivatives of 1,3-Diaminopropanol-2

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Abstract—The binuclear copper(II) complex with bis-azomethine, viz., the product of condensation of 1,3-diaminopropanol-2 with 4-hydroxy-3-formylcoumarin (H_3L), of the composition $[Cu_2L(\mu_2\text{-}CH_3COO)]$ (**I**) is synthesized and studied. Complex **I** is characterized by the exchange interaction of the antiferromagnetic type ($2J = -112$ cm^{-1}), which is switched to the ferromagnetic one ($2J = +106$ cm^{-1}) after the recrystallization of the complex from dimethyl sulfoxide (DMSO) to form solvate $[Cu_2L(\mu_2\text{-}CH_3COO)(\mu_2\text{-}DMSO)] \cdot 0.5DMSO$ (**II**). The structure of solvate **II** is studied by X-ray diffraction analysis (CIF file CCDC no. 982198). The difference in the exchange character is explained by the stabilization by the μ_2-coordinated DMSO molecule of a distorted (roof-shaped type) conformation of the polydentate ligand and the complex as a whole, unlike the symmetric conformation characteristic of the nonsolvated complex. The data obtained are compared with those on similar compounds synthesized earlier and with the quantum chemical modeling results for the exchange interaction in the framework of the DFT-BS approximation.

Keywords: coordination compounds, binuclear complexes, exchange interaction, quantum chemical calculation

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INTRODUCTION

Binuclear complexes of paramagnetic ions with compartmental ligands (polydentate organic ligands, whose structure assumes the chelate coordination of two or more ions of complexing metals) are widely used as convenient models for the investigation of the main factors determining the character and strength of exchange interactions between heterobridged paramagnetic centers [1–5]. Bis-azomethines based on 1,3-diaminopropanol-2 allow one a wide variation of the carbonyl components of the Schiff base and the nature of the exogenic bridging ligand, which provides an exchange channel additional to the alkoxide oxygen atom [6–10]. An interaction of nonequivalent exchange channels in combination with flexibility of the isopropanol linker provides a high variability of the structures and magnetic properties of the synthesized coordination compounds, in particular, due to a change in the conformation of the polydentate ligand. We have previously studied the binuclear copper(II) complexes with *N*,*N*'-bis(3-formyl-5-*tert*-butylsalicylidene) 1,3-diaminopropanol-2 of type **III** [11] and with bis-azomethine, which is the condensation product of 5-hydroxy-1-phenyl-3-methyl-4-formylpyrazol-5 and 1,3-diaminopropanol-2 of type **IV** [12] with the acetate exogenic bridging group. The complexes are characterized by the antiferromagnetic exchange between the Cu(II) ions in which the character of exchange is “switched” to the ferromagnetic one after recrystallization from a DMSO solution.

In this report, we present the results of X-ray diffraction analysis and physicochemical investigation of the binuclear copper(II) complex with bis-azomethine, viz., the condensation product of 1,3-diaminopropanol-2 with 4-hydroxy-3-formylcoumarin (H_3L), of type **I** and its DMSO solvate **II** demonstrating an antagonistic character of exchange. The results obtained are compared with the data on the earlier studied binuclear copper(II) complexes **III** and **IV** with similar properties.

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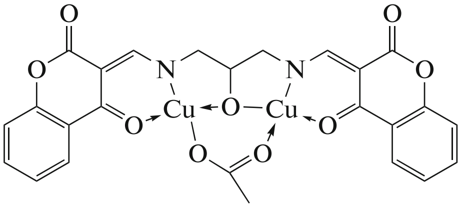
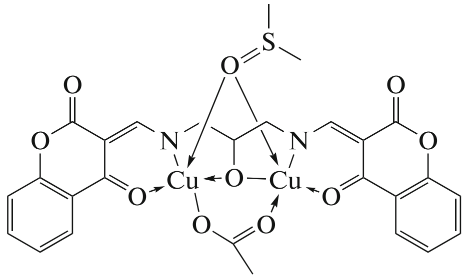


(I)



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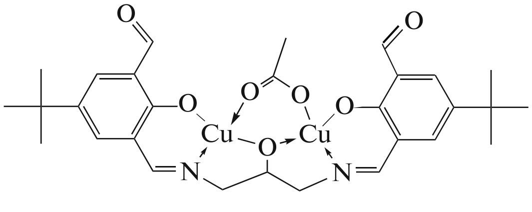

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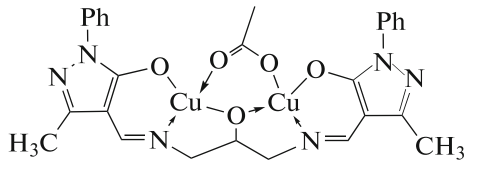

(IV)

EXPERIMENTAL

Commercially available reagents were used as the starting compounds. Solvents were purified and dried by standard procedures. IR spectra were recorded on a Varian Scimitar 1000 FT-IR instrument in a range of 400–4000 cm^{-1} for samples prepared as a suspension in Nujol. Elemental analysis was carried out on a PerkinElmer 240C instrument at the Laboratory of Microanalysis of the Southern Federal University (Rostov-on-Don, Russia).

Azomethine H_3L was synthesized according to a described procedure [13].

Synthesis of compound I. A hot solution of copper(II) acetate dihydrate (2 mmol) in methanol (10 mL) was added to a boiling suspension of ligand H_3L (1 mmol) in methanol (10 mL). The obtained mixture was refluxed for 4 h. The precipitate was filtered off, washed with hot methanol, and dried in vacuo. The yield of a dark blue finely crystalline powder of compound **I** was 57% (mp > 250°C).

For $C_{25}H_{18}Cu_2N_2O_9$

Anal. calcd., %: C, 48.63; H, 2.91; N, 4.53; Cu, 20.58.

Found, %: C, 48.90; H, 2.73; N, 4.714; Cu, 20.3.

IR (ν, cm^{-1}): 1703 ν(C=O), 1626, 1567 ν(C=N).

Complex **II** was obtained by the recrystallization of compound **I** from DMSO (blue-green crystals with mp > 250°C).

IR (ν, cm^{-1}): 1714 ν(C=O), 1645, 1607 ν(C=N), 1054 ν(S=O, DMSO uncoord.), 1008 ν(S=O, DMSO coord.).

Magnetic susceptibility of the complexes was determined on a Quantum Design SQUID magnetometer in the 2–300 K temperature range in a magnetic field of 1 kOe. The Heisenberg–Dirac–Van Vleck isotropic exchange Hamiltonian was used for data interpretation

$$\hat{H} = -2J\hat{S}_1\hat{S}_2. \tag{1}$$

The exchange parameter was calculated by multimeric fitting of the parameters of the modified Bleaney–Bowers equation [14] for the reproduction of the experimental temperature dependence of the magnetic susceptibility (the correction to temperature-independent diamagnetism was calculated using additive Pascal's scheme [15]). For binuclear complexes with paramagnetic centers with half-integer spin (Cu(II) complexes), the exchange parameter takes the form

$$\chi'_{\mathrm{M}} = \frac{2N_{\mathrm{A}}g^2\beta^2}{3kT} \times \left[(1-f)\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1} + fS(S+1)\right] + N_{\alpha}. \tag{2}$$

Here χ'_{M}, N_{A}, g, β, k, J, f, S, and N_α are the molar magnetic susceptibility corrected to diamagnetism of atoms, Avogadro's number, Landé g factor, Bohr's magneton, Boltzmann constant, exchange interaction parameter, molar fraction of paramagnetic impurity, total spin of paramagnetic impurity, and temperature-independent paramagnetism, respectively.

The intermolecular exchange interaction was taken into account in terms of the molecular field approxi-

Table 1. Crystallographic data and experimental and refinement characteristics for compound **II**

Parameter	Value
Empirical formula	$C_{28}H_{27}N_2O_{10.50}S_{1.50}Cu_2$
FW	734.69
Crystal size, mm	0.33 × 0.23 × 0.09
Temperature, K	150(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	7.7189(18)
b, Å	19.389(4)
c, Å	20.826(5)
β, deg	91.514(6)
V, Å^3	3115.8(12)
Z	4
ρ_{calcd}, g/cm^3	1.566
μ, mm^{-1}	1.53
F(000)	1500
Scan range over θ, deg	2.3–25.8
Number of measured reflections	9788
Number of independent reflections	5780
Number of reflections with $I > 2\sigma(I)$	2047
Ranges of reflection indices	$-5 \le h \le 9$, $-23 \le k \le 21$, $25 \le l \le 19$
Number of refined parameters	415
GOOF (all reflections)	1.015
R_1 ($I > 2\sigma(I)$)	0.0778
wR_2 (all reflections)	0.2246
$\Delta\rho_{max}/\Delta\rho_{min}$, eÅ^{-3}	1.27/–0.71

mation (zJ' is the product of the number of nearest binuclear molecules in the crystal lattice (z) by the intermolecular exchange constant J') [16]

$$\chi_M = \frac{\chi'_M}{1 - 7.6853 zJ'\chi'_M / g^2}. \qquad (3)$$

The goodness-of-fit of the multimeric fitting is characterized by the Y factor

$$Y = \left[\Sigma(\chi_M^{obs} - \chi_M^{calc})^2 / \Sigma(\chi_M^{obs})^2\right]. \qquad (4)$$

X-ray diffraction analysis of complex **II** was carried out on a Bruker APEXII CCD diffractometer (MoK_α, λ = 0.71073 Å, graphite monochromator, ω scan mode) at 150 K. The initial array of measured intensities was processed using the SAINT and SADABS programs included into the APEX2 program package [17, 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 ($U_{iso}(H) = nU_{iso}(C)$, where n = 1.5 for the carbon atoms of the methyl groups, and n = 1.2 for other C carbon atoms). The structures were decoded and refined using the SHELXTL program [19]. The PLATON program [20] was used for analysis of the molecular and crystal structures. The experimental characteristics and crystallographic data are presented in Table 1. Selected interatomic distances and bond angles are given in Table 2.

The coordinates of atoms and temperature factors were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 982198; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac. uk/data_request/cif).

X-ray absorption Cu *K*-edges of compound **I** were recorded at the Strukturnoe Materialovedenie station of the Kurchatov Synchrotron Radiation Source (Moscow) [21]. The X-ray absorption spectra were processed by standard procedures of background sub-

Table 2. Selected interatomic distances and bond angles in the coordination polyhedra of the copper atoms in a molecule of compound **II**

Bond	d, Å	Bond	d, Å
Cu(1)–N(1)	1.901(12)	Cu(2)–O(9)	1.908(10)
Cu(1)–O(3)	1.924(9)	Cu(2)–N(2)	1.908(13)
Cu(1)–O(4)	1.930(8)	Cu(2)–O(4)	1.934(8)
Cu(1)–O(8)	1.939(10)	Cu(2)–O(7)	1.938(8)
Cu(1)–O(1S)	2.494(9)	Cu(2)–O(1S)	2.526(9)
Cu(1)···Cu(2)	3.113(2)		
Angle	**ω, deg**	**Angle**	**ω, deg**
Cu(1)O(4)Cu(2)	107.4(4)	Cu(1)O(1S)Cu(2)	76.7(3)
N(1)Cu(1)O(3)	92.9(4)	N(2)Cu(2)O(7)	92.9(4)
N(1)Cu(1)O(4)	84.4(4)	N(2)Cu(2)O(4)	84.6(4)
O(3)Cu(1)O(4)	177.3(4)	O(4)Cu(2)O(7)	173.8(4)
O(3)Cu(1)O(8)	90.8(4)	O(9)Cu(2)O(7)	88.7(4)
O(4)Cu(1)O(8)	91.7(4)	O(9)Cu(2)O(4)	93.3(4)

traction, normalization to the value of K-edge jump, and isolation of atomic absorption μ_0 [22] after which the Fourier transform of the obtained extended X-ray absorption fine structure (EXAFS) χ spectrum was performed in the range of photoelectron wave functions k from 2.5 to 13 Å^{-1} with the weight function k^3. The obtained module Fourier transformant (MFT) of the EXAFS corresponded to the radial distribution function of the atoms around the absorbing metal ion with the phase shift accuracy. The exact values of parameters of the nearest environment of the metal ion in the studied compounds were determined by nonlinear fitting of the parameters of the corresponding coordination spheres comparing the calculated EXAFS spectrum and that subtracted from the overall spectrum by the Fourier filtration method. The nonlinear fitting was performed using the IFFEFIT program package [23]. The scattering phases and amplitudes of the photoelectron wave necessary for the construction of the model spectrum were calculated using the FEFF7 program [24] for the model complexes with similar structures found in the Cambridge Structural Database [25].

In the fitting process, the χ^2 function was minimized by the following equation:

$$\chi^2 = \frac{N_{\text{ind}}}{N_{\text{pts}}\varepsilon^2}\sum_{i=1}^{N_{\text{pts}}}\Big\{[\mathrm{Re}(\tilde{\chi}_{\text{data}}(R_i) - \tilde{\chi}_{\text{th}}(R_i))]^2 + [\mathrm{Im}(\tilde{\chi}_{\text{data}}(R_i) - \tilde{\chi}_{\text{th}}(R_i))]^2\Big\}, \quad (5)$$

where N_{pts} is the number of points in the fitted region. The absolute root-mean-square deviation between the model and experimental spectra was determined by the $\Re$ factor, which was calculated by the equation

$$\Re = \sum_{i=1}^{N_{\text{pts}}}\frac{[\mathrm{Re}(\chi_{\text{data}}(R_i) - \chi_{\text{th}}(R_i))]^2 + [\mathrm{Im}(\chi_{\text{data}}(R_i) - \chi_{\text{th}}(R_i))]^2}{[\mathrm{Re}(\chi_{\text{data}}(R_i))]^2 + [\mathrm{Im}(\chi_{\text{data}}(R_i))]^2}. \quad (6)$$

Quantum chemical calculations were performed using the Gaussian'03 program [26]. The exchange interaction parameters for the complexes and their possible isomers were calculated in terms of the broken symmetry approximation (DFT-BS) using the B3LYP hybrid exchange-correlation functional [27] in combination with the extended basis set of Gaussian functions 6-311G(d) of the Pople group. For the detailed description of the DFT-BS approximation [11, 28–31].

The compromised Eq. (7) derived by Yamaguchi et al. [32] was used for the calculation of the exchange parameter $2J$ from the energies of the low- (BS is the broken symmetry state) and high-spin (HS) states

$$2J = \frac{2(E_{BS} - E_{HS})}{\langle S_{HS}^2\rangle - \langle S_{BS}^2\rangle}, \quad (7)$$

where $\langle S_{HS}^2\rangle$, and $\langle S_{BS}^2\rangle$ are the expected values of the squared total spin for the HS and BS states, respectively. The complete geometry optimization without symmetry constraints was performed for all spin states of the complexes.

Table 3. Magnetic properties of complexes **I**–**IV**

Complex	$2J$, cm^{-1}	zJ', cm^{-1}	g	Y	Literature
I	–112	0	2.11	0.001	This work
II	+106	–6	2.20	0.001	
III	–95	0	2.20	0.001	[11]
III · DMSO	+121	–0.2	2.09	0.002	
IV	–169	0	2.11	0.003	[12]
IV · DMSO	+174	–13	2.18	0.002	

RESULTS AND DISCUSSION

Complex $[Cu_2L(CH_3COO)]$ of type **I** was synthesized by the reaction of copper(II) acetate with ligand H_3L in methanol. According to the data of magnetochemical measurements, the complex is characterized by the exchange of the antiferromagnetic type ($2J = -112$ cm^{-1}), which is typical of the acetate-bridged copper complexes with bis(azomethines) based on 1,3-diaminopropanol-2 [1, 33–35]. However, the product of its recrystallization from DMSO (complex of type **II**) of the composition $[Cu_2L(CH_3COO)DMSO] \cdot 0.5DMSO$ demonstrates the ferromagnetic exchange between the copper(II) ions: $2J = +106$ cm^{-1} (Table 3).

The magnetic properties of single-crystal complex **II** are shown in Table 3. The structure of solvate **II** was determined by X-ray diffraction analysis (Fig. 1).

The copper atoms in complex **II** are linked through three bridges: alkoxide O(4) atom, O(1S) atom of the coordinated DMSO molecule, and carboxylate group O(8)–C(25)–O(9). The coordination polyhedron of both copper atoms is a square pyramid in which the common apical position is occupied by the oxygen atom of the μ_2-coordinated DMSO molecule: O(1S) (Cu–O 2.494 and 2.526 Å). The binuclear molecule is substantially distorted because of the inflection along the line connecting the alkoxide bridges O(4) and C(25) of the carboxylate group. The angle between the mean planes of the donor atoms is 58.2°. Thus, the distorted (roof-shaped type) conformation of the azomethine ligand is observed, which is additionally favored by the bidentate bridging coordination of the DMSO molecule. The crystal structure of complex **II** includes one more solvate DMSO molecule, which is not coordinated to the copper ions. This DMSO molecule has an fractional population in crystal (~0.5).

The six-membered metallochelate cycle containing the Cu(1) atom is ideally planar: the deviation of the Cu(1) atom from the plane passing through other atoms of the cycles is only 0.001 Å. The six-membered metallochelate cycle of the Cu(2) atom is distorted: the Cu(2) atom shifts from the plane of other atoms by 0.304 Å. Two five-membered metallocycles with the common C(12)–O(4) bond have the envelope conformation, and the "valves" (C(11) and C(13) atoms) deviate from the planes of other atoms to opposite

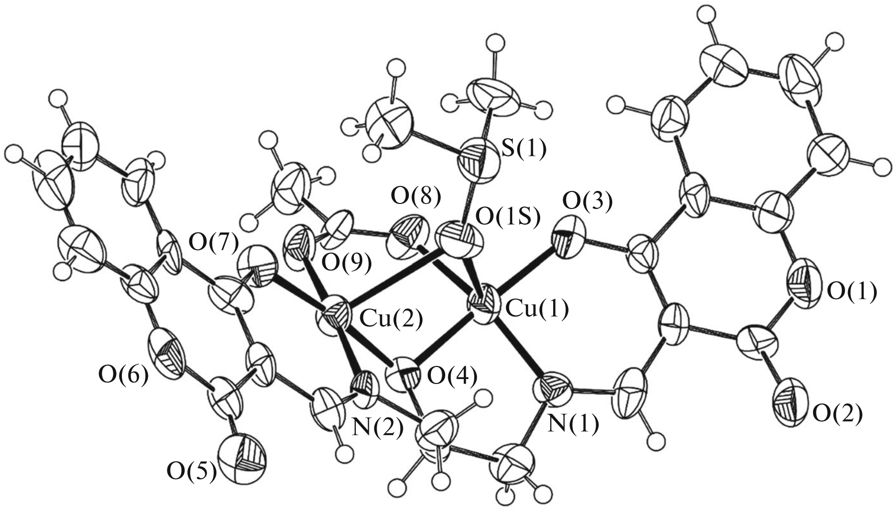

Fig. 1. Molecular structure of complex **II** in the representation of atoms by atomic shift ellipsoids with 50% probability and the numeration of atoms used in discussion.

Table 4. Selected structural parameters of complexes **II**, **III** · DMSO, and **IV** · DMSO according to the X-ray diffraction data (δ is the inflection angle of the molecule of the complex relative to the C–O_{alk} bond, and Σ(O_{alk}) is the sum of bond angles formed by the bonds around the bridging alkoxide oxygen atom)

Parameter	II	III · DMSO*	IV · DMSO*
Cu···Cu, Å	3.113(2)	3.168(3)	3.0780(9)
Cu–O_{DMSO}, Å	2.494(9) 2.526(9)	2.400(3) 2.717(3)	2.373(4) 2.433(4)
Cu–O_{alk}, Å	1.930(8) 1.933(8)	1.944(2) 1.940(2)	1.938(4) 1.947(4)
Cu–O_{ac}, Å	1.938(11) 1.909(10)	1.946(2) 1.958(2)	1.954(4) 1.976(4)
Σ (O_{alk}), deg	332.1	331.2	329.9
$CuO_{alk}Cu$, deg	107.4(4)	109.3(1)	104.75(18)
δ, deg	58.2	58.2	61.9

* Solvates of the compounds studied earlier in [11] and [12], respectively.

Table 5. Energies of the triplet state (HS) and broken symmetry state (BS) and the calculated and experimental values of 2*J* of complexes **I** and **II** for the optimized geometry (B3LYP/6-311G(d))

Compound	HS		BS		$2J$, cm^{-1}	$2J_{exp}$, cm^{-1}
	E(HS), au	$\langle S^2\rangle$	*E*(BS), au	$\langle S^2\rangle$		
I-*r*	–5031.597233	2.005	–5031.597069	0.999	71	–112
I-*s*	–5031.599511	2.005	–5031.599820	0.992	–134	
II	–5584.874513	2.004	–5584.874246	1.000	116	106

directions by 0.427 and 0.356 Å, respectively. The O(4) atom is strongly pyramidalized, and the sum of bond angles at this atom is 332.1°. The distance between the copper atoms in complex **II** is 3.113(2) Å.

The DMSO solvates of the earlier studied compounds have similar structures. The X-ray diffraction data on the structures of three complexes are compared in Table 4.

The highest degree of distortion (among the considered complexes) is observed for compound **IV** · DMSO, which is manifested in the minimum Cu···Cu distance, the smallest sum of bond angles formed by the bonds around the bridging atom, and the smallest CuOCu bond angle in this series of complexes. A significant variation of the geometric parameters of the binuclear exchange fragment indicates a substantial influence of the nature of the carbonyl fragment of the Schiff base on the structures of the complexes.

The model of the exchange interactions performed in terms of the broken symmetry method (DFT-BS, B3LYP/6-311G(d), Table 3) showed that a possible structure of nonsolvated product **I** is the "symmetric" conformer of the complex **I**-*s* (Fig. 2a).

For conformer **I**-***s***, the calculated exchange parameter corresponds by sign and very well coincides with the experimental value (Table 5), whereas an average exchange of the ferromagnetic type is predicted for conformer **I**-***r***. Thus, the change in the exchange character is related to a change in the conformation of the compartmental ligand only and is not a consequence of the electronic effect of the μ_2-coordinated solvent molecule. A very good quantitative coincidence of the calculated and experimental values also can be mentioned for solvated complex **II**, which additionally confirmed indirectly the correctness of the chosen calculation procedure.

It should be mentioned that the optimum structures of conformers **I**-***s*** and **I**-***r*** are characterized by noticeably different interatomic distances Cu···Cu (3.500 and 3.266 Å, respectively). Therefore, X-ray absorption spectroscopy can be an appropriate method for the experimental identification of the isomeric form (*r* or *s* type), since this method makes it possible to study rather reliably the local environment of transition metal ions in the compounds. The Cu *K*-edge XANES (X-ray absorption near edge structure) for complex **I** and the corresponding MFT of the EXAFS are presented in Fig. 3.

The structural data for metal complex **I** obtained from the multisphere fitting of the EXAFS data compared with the data for complexes **III** and **IV** are presented in Table 6. For compound **I**, the Cu···Cu inter-

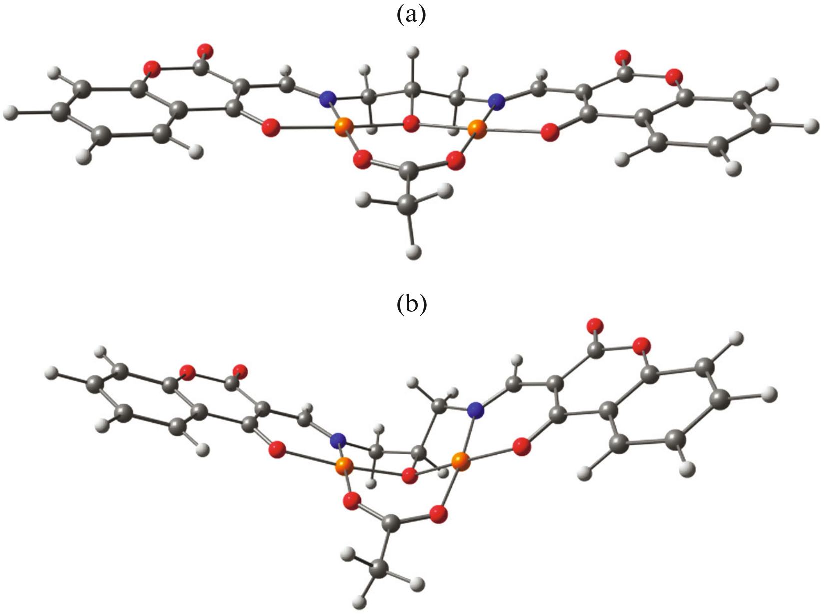

Fig. 2. Optimal structures of conformers of the complex of type **I**: (a) symmetric **I-*s*** and (b) roof-shaped **I-*r***.

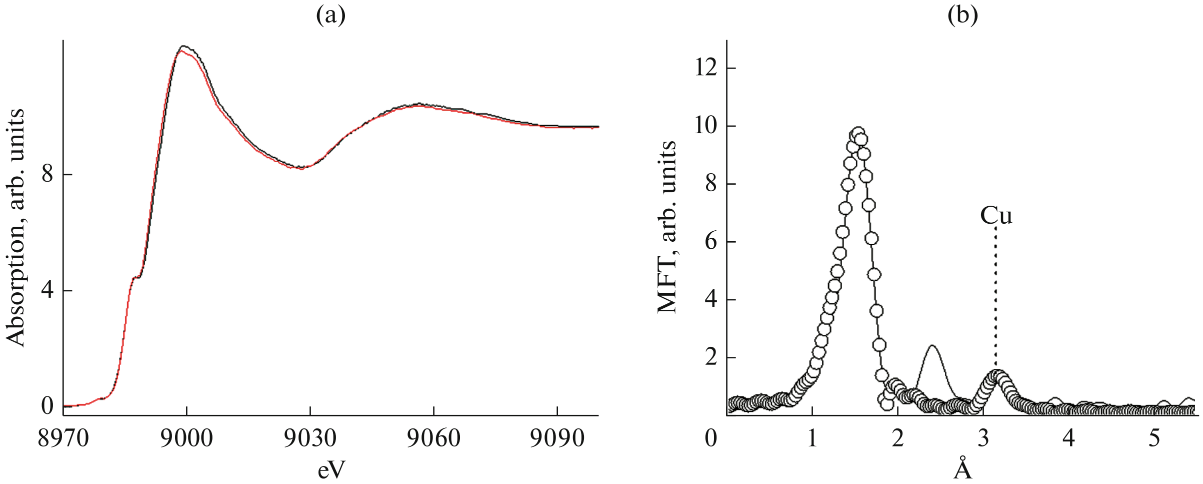

Fig. 3. X-ray absorption spectrum: (a) Cu *K*-edge XANES and (b) the corresponding MFT of the EXAFS for complex **I** (solid line is experiment, and theory is shown by empty circles).

atomic distance in the binuclear complex is 3.48 Å, which coincides very well with that in the optimum calculated geometry of conformer **I-*r*** (3.50 Å) and is close to the values of this distance in complexes **III** and **IV** (3.51 Å).

For all binuclear compounds, the calculated difference in energies between the isomeric *r* and *s* conformations is not high and ranges from 1 to 1.5 kcal/mol (Table 7). The symmetric *s* conformation for all compounds is preferable due to a lower steric stain and the best overlap of the orbitals of the metal and polydentate ligand. The *r* conformations of the roof-shaped type are considerably stabilized upon the coordination of the DMSO molecule. The solvation energies E_{solv} are presented in Table 7. For complex **I**, E_{solv} takes the form

$$E_{\mathrm{solv}} = E(\mathbf{II}) - E(\mathrm{DMSO}) - E(\mathbf{I}), \quad (8)$$

where $E(\mathbf{II})$, $E(\mathbf{I})$, and $E(\mathrm{DMSO})$ are the total energies calculated for the solvated and nonsolvated (in the *r* conformation) complexes and an isolated DMSO molecule, respectively. The energy effect from the interaction of the nonsolvated complex with the solvent molecule is significant, being ~20 kcal/mol with-

Table 6. Structural data for nonsolvated metal complexes **I**, **III**, and **IV** obtained by the multisphere fitting of the EXAFS data (R is interatomic distances, N is the coordination number, σ^2 is the Debye–Waller factor, and $\Re$ is the fitting goodness-of-fit)

Compound	N	R, Å	σ^2, Å^2	Atom	$\Re$, %	Literature
I	3	1.91	0.0036	N/O	1.3	This work
	2	2.01	0.0036	N/O		
	1	3.48	0.0055	Cu		
III	2	1.92	0.0037	N/O	4.5	[11]
	2	1.93	0.0037	N/O		
	1	3.51	0.0070	Cu		
IV	2	1.91	0.0035	N/O	1.0	[12]
	2	2.00	0.0035	N/O		
	1	3.51	0.0050	Cu		

Table 7. Calculated relative stability of the *r*- and *s*-isomers of the nonsolvated complexes ($\Delta E_{s-r} = E(s) - E(r)$) and the solvation energy E_{solv} (8) (B3LYP/6-311G(d))

Compound	ΔE_{s-r}, kcal/mol	E_{solv}, kcal/mol	E_{solv}*, kcal/mol
I, II	1.43	−19.4	−7.2
III	1.38	−21.0	−9.1
IV	1.18	−20.5	−8.4

* Taking into account a correction to the basis set superposition error.

out a correction to the basis set superposition error (BSSE) and ranging from −7.2 to −9.1 kcal/mol after the corresponding correction.

Thus, the new representative of binuclear copper complexes with the compartmental ligand of the bis-azomethine family based on 1,3-diaminopropanol-2 is studied. The complex is characterized by switching of the character of the exchange interaction between the metal ions from antiferro- to ferromagnetic upon the solvation of the complex. Similarly to the complexes studied earlier [11, 12], the phenomenon is caused by the stabilization of the distorted conformation of the complex stabilized by the bridging coordination of the DMSO molecule, unlike the symmetric conformation for the nonsolvated complex. The difference in the exchange character for the complex and solvate is due only to the conformation of the polydentate ligand and complex as a whole. An additional coordination of the DMSO molecule exerts no effect on the superexchange interaction mechanism.

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