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Peculiarities of Magnetic Exchange in Bi- and Tetranuclear Copper(II) Complexes with Organic Ligands Based on 1,3-Diaminopropan-2-ol

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Abstract—The main types of mechanisms of exchange interactions are considered in the review in the framework of experimental and theoretical analyses. The electronic and geometric factors that exert a determining effect on the magnetic properties of the bi- and tetranuclear complexes of transition metals based on hydrazones and azomethines of 1,3-diaminopropan-2-ol are revealed.

Keywords: magnetochemistry, exchange-bound complexes, quantum-chemical calculations, exchange parameters, magnetostructural relationships, hydrazones, azomethines, molecular magnetics

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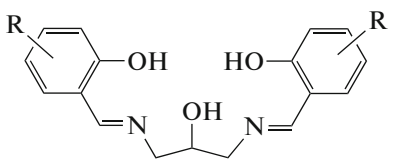
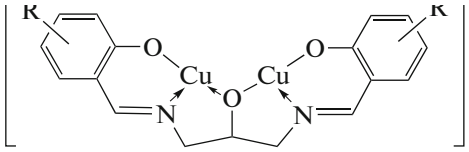
We have previously mentioned [1] that the study of the electronic structures and properties of the polynuclear complexes in which two or more paramagnetic centers are bound by the magnetic exchange interaction is one of the main trends in modern coordination chemistry. The elucidation of a relationship between the exchange interaction parameters and peculiarities of the structures of the polynuclear complexes plays the key role for the understanding of the magnetic properties of similar systems and provides a theoretical basis for the synthesis of clusters with specified magnetic characteristics and, finally, for the purposeful modification of magnetically active materials. One of the main approaches to the solution of the denoted problem in the experimental and theoretical investigation of the factors affecting the exchange interactions is the purposeful choice of the ligand system causing the possibility of the preparation of systematic series of exchange-bound complexes with predicted structures in which the nature (composition) and geometry of the exchange fragments are widely variable. Bis(azomethines) based on 1,3-diaminopropan-2-ol and substituted salicylaldehydes of type L or their analogs possess these properties.



(L)

These ligands can coordinate two transition metal ions to form a monocation of type **I** with the bridging oxygen atom of the isopropanol fragment and also have a possibility to coordinate the second (exogenic) bridge.



(**I**)

The nature of the latter can widely be varied among mono- and bidentate molecules (anions) with different distances between the donor atoms due to the mutual arrangement of the metal ions specified by the ligand and flexibility of the isopropanol fragment. Owing to this, there is a possibility to simulate the effect of the nature of the bridging group in the nonsymmetric exchange fragment and to evaluate the mutual influence of two channels of the exchange interaction binding the paramagnetic centers [2].

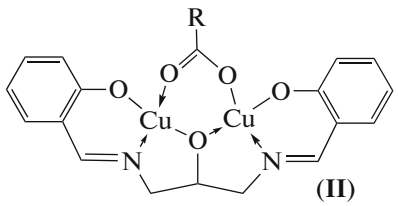
For the simulation of the effect of the bridging group nature in the nonsymmetric exchange fragment and for the evaluation of the mutual influence of two channels of the exchange interaction, we synthesized and studied the binuclear complexes of the bis(azomethine) derivatives of 1,3-diaminopropan-2-ol of types **II** and **III** with a number of bidentate halogen-substituted acetate and diazo heterocyclic exchange bridges: pyrazolate anion (Pyr), azaindolate anion (Az), 1,10-phenanthroline (Phen), and 2,2'-bipyridine (Bipy)

Table 1. Magnetic properties of complexes **II** and **III**

Type of complex	R, 	*T*, K	μ_{eff}, μ_B*	$2J$, cm^{-1}
II	CH_3	82 284	0.75 1.59	−173
II	CH_2Cl	82 288	0.97 1.61	−134
II	CCl_3	82 293	1.17 1.74	−116
II	CF_3	82 287	0.77 1.56	−188
III	Pyr	78 296	0.25 0.99	−332
III	Az**			+33.4
III	Phen	296 78	1.66 1.53	−42
III	Bipy			0

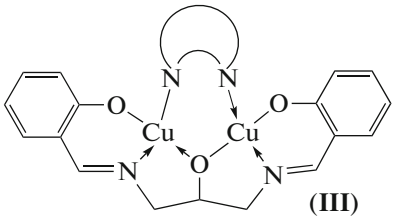
* The effective magnetic moment was calculated per 1 metal ion.
** The exchange parameter was determined earlier [4].

[3]. The exchange interaction between two copper(II) ions was studied in terms of the density functional theory (DFT) using the BP86 exchange–correlation functional in the 6-311G(d) basis set.

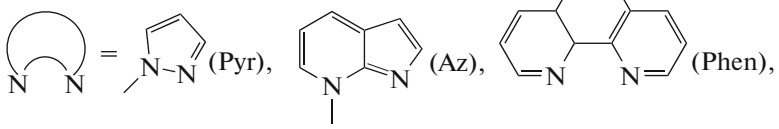


(II)

$R = CH_3, CH_2Cl, CCl_3, CF_3$



(III)



(Pyr), (Az), (Phen),

2,2'-bipyridine (Bipy)

The magnetic properties of complexes **II** are presented in Table 1. As can be seen, all the complexes are characterized by the antiferromagnetic exchange. The replacement of one or three hydrogen atoms of the acetate groups by chlorine atoms weakens the exchange. However, the replacement of chlorine by fluorine results in an increase in the exchange parameter instead of the further decrease, as is could be expected taking into account the electromeric effect of fluorine.

As shown by our calculations [5], the replacement of the hydrogen atoms by halogens in the acetate bridge should increase the exchange interaction of the antiferromagnetic type, which is a consequence of an antagonistic effect upon the interaction of two exchange channels in the nonsymmetric exchange fragment: through the alkoxide oxygen atom O_{alk} and carboxylate bridge. Nishida and coauthors pioneered in experimental discovering this character of the interaction of exchange channels in the nonsymmetric exchange fragment [6]. The model of anticomplementary orbitals of bridging fragments was proposed for the explanation of the effect [7–9].

Let us consider the shape of the molecular spin orbitals (MSOs) occupied by unpaired electrons in the high-spin state (Fig. 1). The magnetic MSO with a higher energy corresponds to the antiphase combination of atomic orbitals (d_{xy} AOs), and the lower-energy magnetic MSO corresponds to their synphase combination. The both orbitals are antibonding with respect

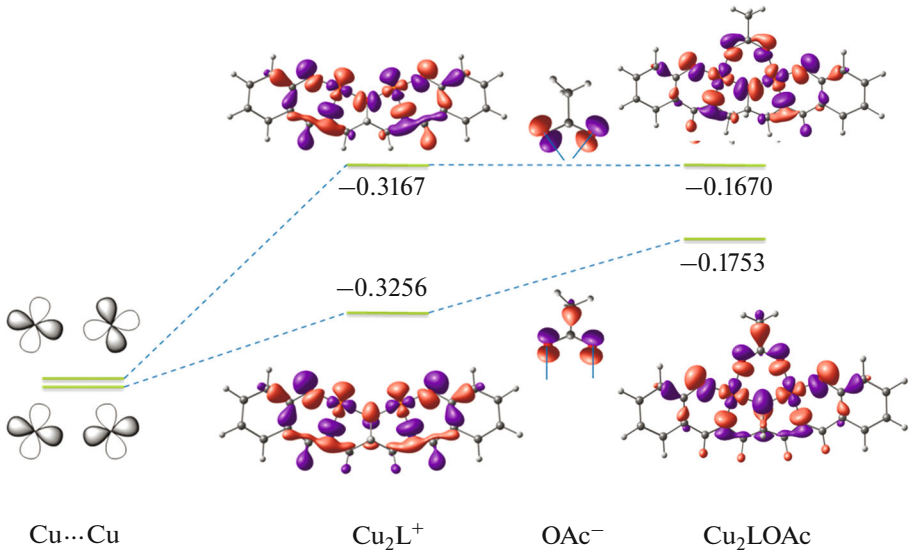


Fig. 1. Scheme of the molecular orbital interaction.

to the metal–ligand bonds and metal–exogenic bridge and, therefore, an increase in the metal–ligand overlapping would result in the destabilization of these MSOs (energy increase), whereas a decrease will lead to the stabilization (energy decrease).

The consecutive substitution of the hydrogen atoms of the acetate group by electron-acceptor halogen atoms results in electron density drawing off from the oxygen atoms of the carboxyl group and, as a consequence, in the weakening of the interaction of the exogenic bridge with the copper cations. This is confirmed by a change in the optimum geometric parameters of the complexes: the O_{ac}–Cu distances are 1.9342, 1.9413, 1.9550, and 1.9543 Å for R = CH_3, CH_2Cl, CCl_3, and CF_3, respectively.

The energies of the highest MSOs of α electrons in the high-spin state and the values of Δ^2 (square difference between them) are presented in Table 2. The calculated values of $2J$ in the considered series of compounds correlate with Δ^2. The higher the difference in energies of the spin orbitals in the high-spin state, the more negative the value of $2J$, which corresponds to a stronger antiferromagnetic interaction.

The exchange parameter calculated for R = CH_3 (−199 cm^{-1}) coincides with the experimental value (−173 cm^{-1}). A significant deviation from the experimentally observed tendency for a change in the exchange (Table 1) and its absolute value was observed for complexes **II** with R = CH_2Cl and CCl_3 and, to a lower extent, with R = CF_3 ($2J_{theor}$ = −222, −311, and −235 cm^{-1}, respectively). A probable reason for this phenomenon can be an additional coordination of the solvent molecule(s) to the metal ion(s).

To check this assumption, we calculated the optimum geometry and exchange interaction in model compounds **IV** in which the methanol molecule was additionally coordinated to one of the copper ions. The spatial structure of similar systems for R = CH_3 as an example is shown in Fig. 2.

The axially coordinated methanol molecule was established to decrease the calculated value of $2J$ by 50–70 cm^{-1} for all complexes without changing the order of changing the exchange parameter in the series of bridging fragments. This is due to a noticeable pyramidalization of the coordination mode of the copper(II) ion (Fig. 2) shifting from the plane of the donor atoms to the solvent molecule.

In the case of compounds with monochloro- and trifluoroacetate bridges and taking into account the

Table 2. Energies (au) of molecular spin orbitals of electrons with the α orientation of spin in the high-spin state of the complexes of types **II** and **III** and the squared difference between them (Δ^2, au)

Type	R, 	HOMO	HOMO-1	Δ^2
II*		−0.3167	−0.3256	0.000079
II	CH_3	−0.1670	−0.1753	0.000069
II	CH_2Cl	−0.1734	−0.1820	0.000074
II	CCl_3	−0.1789	−0.1887	0.000096
II	CF_3	−0.1780	−0.1868	0.000077
III	Pyr	−0.1610	−0.1745	0.000182
III	Az	−0.1676	−0.1746	0.000049

* The coordinates of atoms are the same as in complex **II** (R = CH_3).

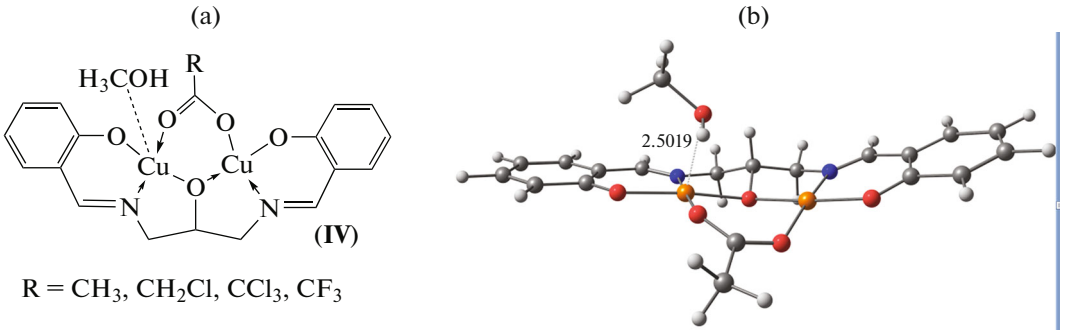


Fig. 2. Structures of (a) complex **IV** and (b) model compounds **IV** with R = CH_3 as an example.

methanol molecule, the coincidence between the values calculated in the framework of the DFT-BS (broken symmetry) method and experimental values of the exchange parameters becomes nearly quantitative ($2J$ = −132 vs. −134 and −181 vs. −188 cm^{-1} for R = CH_2Cl and CF_3, respectively).

Thus, we showed for three compounds of a series of the complexes with haloacetate bridges that the observed sequence of changing $2J$ can be explained in terms of the broken symmetry method and the exchange parameters can be calculated with a high accuracy if no additional coordination of the solvent is observed in the case of the acetate bridge or if one methanol molecule is coordinated in the cases of the monochloro- and trifluoroacetate bridges.

Indeed, the presence of the coordinated solvent molecule in crystals of the compounds was proved by the X-ray diffraction data for the corresponding single-crystal samples. The structure of complex **II** (R = CH_2Cl) was studied [3]. The structures of this complex and the complex with R = CF_3 are shown in Fig. 3.

It was also unambiguously proved by the X-ray diffraction method [10] that no additional coordination of the solvent molecule to the copper ion was observed in crystals of compound **II** (R = CH_3).

The distorted conformation of the complex can be a reason for the low experimental value of the exchange in the case of the trichloroacetate bridge. Two five-membered chelates involving the alkoxide oxygen atom of the diaminopropanol linker can exist in two different conformations of the envelope type (the vertex of the envelope in one cycle coincides with the carbon atom of the C–O group, whereas in another cycle it coincides with the carbon atom of the methylene group) (Fig. 4).

Table 3. Difference in the total energies of the symmetric (E_{sym}) and distorted (E_{dis}) conformers of the complexes of type **II**

R	$\Delta E = E_{sym} - E_{dis}$, kcal/mol
CH_3	0.23
CH_2Cl	0.30
CCl_3	0.37
CF_3	0.41

For all complexes **II**, the distorted conformation is a local minimum on the potential energy surface. The stability calculated relative to the symmetric conformer is very low (Table 3, lower than 0.5 kcal/mol) and, hence, can easily be overlapped by interactions in the crystal packing.

The value of $2J_{opt}$ in complex **II** (R = CCl_3) calculated for the distorted conformer is much lower (−28 cm^{-1}) than that for the symmetric one (−311 cm^{-1}) primarily due to a higher inflection of the exchange fragment along the C–O_{alk} line. This is indicated by the value of the exchange parameter calculated for cationic complex **I** with the geometry corresponding to the distorted conformation of the complex ($-2J$ = +21 cm^{-1}) caused by a difference in the changes in the MSO energy for the inflection along the C–O_{alk} bond (Fig. 5).

Therefore, a decrease in the inflection due to the influence of the crystal packing can be a reason for an increase in the exchange parameter (compared to that calculated for the isolated molecule) to the experimentally observed value equal to −116 cm^{-1} (Table 1).

The antiferromagnetic exchange interaction increases substantially on going from the carboxylate bridge to the pyrazolate anion (Table 1).

The calculated value of $2J$ in complex **III** (Pyr) is higher than that in the cation with the remote bridge, indicating an additive (complementary) interaction of the exchange channels in the nonsymmetric exchange fragment (−201 and −394 cm^{-1} for **I** and **III**, respectively). The "loops" of the pyrazolate anion appropriate in symmetry to the syn- and antiphase MSOs of cation **I** are directed differently (Fig. 6). A more optimum overlapping is provided for the antiphase MSO leading to its higher destabilization compared to the synphase MSO (Table 2), which increases the difference in energies of the magnetic MSOs in the complex

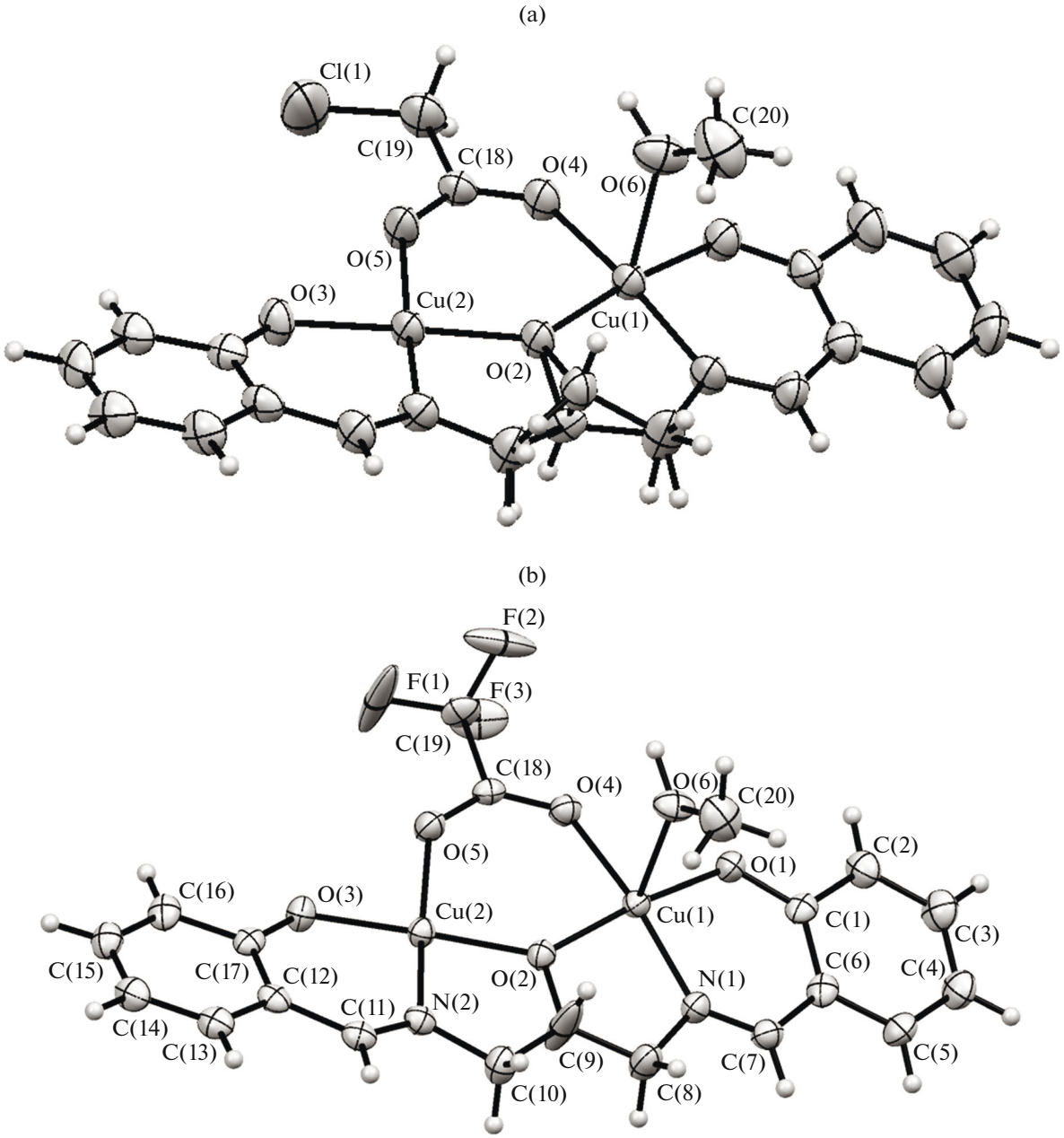


Fig. 3. Spatial structures of molecules of complexes **II** for (a) R = CH_2Cl and (b) R = CF_3 according to the X-ray diffraction data (thermal vibration ellipsoids are given with 50% probability).

and results in an increase in the interaction of the antiferromagnetic type.

In spite of a shorter distance between the donor centers compared to that in the acetate anion, a significant angle between the directions of the maxima of the $MOPyr^-$ anion results in the flattening of the molecule of the binuclear complex compared to the acetate-bound complex (Fig. 7), thus additionally contributing to an increase in the antiferromagnetic interaction.

The character of the exchange interaction changed to the ferromagnetic one when the pyrazolate bridge is replaced by the azaindolate anion (Table 1). The MO of the bridge appropriate by symmetry to the synphase MSO of cation **I** turns out to be higher in energy, resulting in a considerable destabilization of the synphase MSO in complex **III** at the optimum (for good overlapping) direction of the MO "loops" of the bridge.

The MO of the azaindolate anion interacting with the antiphase MSO of the cation lies significantly

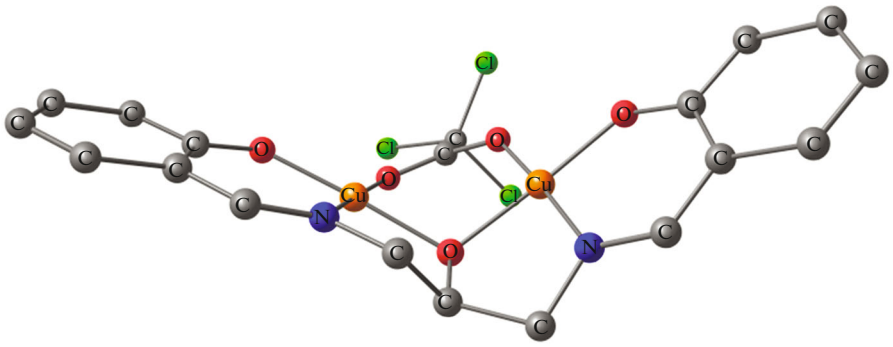


Fig. 4. Distorted conformation of complex **II** (R = CCl_3) (hydrogen atoms are omitted).

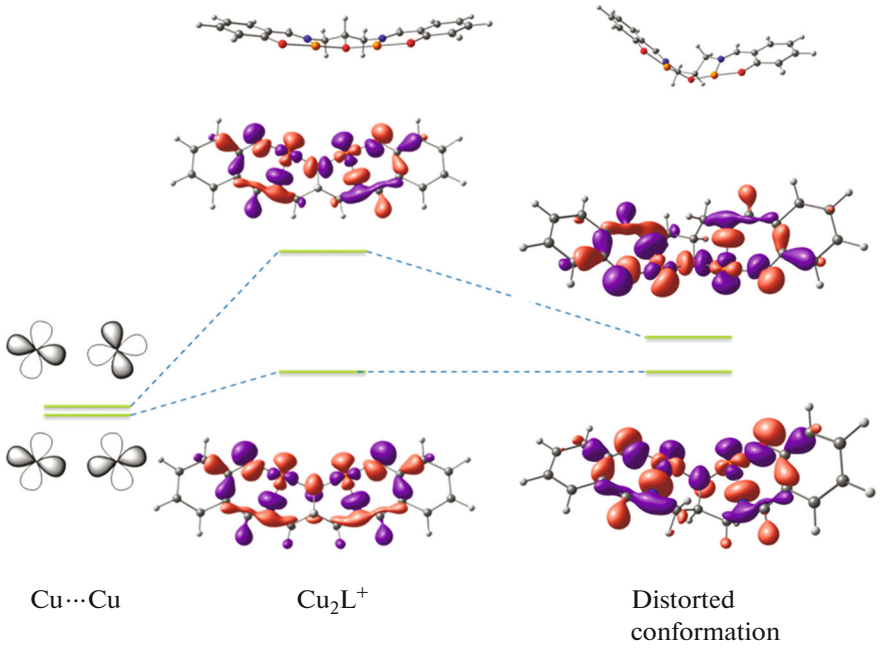


Fig. 5. Molecular orbital diagram for the distortion of cationic complex **I**.

lower by energy and its interaction with the MSO slightly affects the energy of the antiphase MSO in the complex. As a result, the difference in MSO energies in the complex is the lowest one of the compounds considered (Table 2).

In addition to the orbital factor, the geometric factor exerts a substantial effect. The distance between the donor nitrogen atoms in the azaindolate anion (2.441 Å) is substantially shorter than that between the copper ions in symmetric cation **I** (3.525 Å) but is equal to the distance between the oxygen atoms in the carboxylate bridges, and the maxima of the frontier orbitals of the anion diverge insignificantly (Fig. 8). Therefore, the optimum interaction of the MOs of cation **I** with the bridge is attained for the distorted conformation of the complex considered earlier for the acetate bridge (Fig. 7). The dihedral angle between the planes of the phenyl rings is 126.1°, and the $CuO_{alk}Cu$ angle is 113.9°. The calculated and theoretical values of the exchange parameter for the complex with the azaindolate bridge are +43 and +33.4 cm^{-1}, respectively.

The conclusion drawn is consistent with the results [11] of the experimental and theoretical study of binuclear copper(II) complex **IV** with the nonsymmetric exchange fragment containing the μ-6-methoxypurine bridge. The composition of the complex corresponds to the formula $[Cu_2(L)(\mu\text{-}6\text{-}Mp)(DMF)]$, where μ-6-Mp is μ-6-methoxypurinate, H_3L is 1,3-bis(3,5-*tert*-butylsalicylideneamino)-2-propanol, and DMF is *N*,*N*-dimethylformamide. The structure of complex **IV** is shown in Fig. 9.

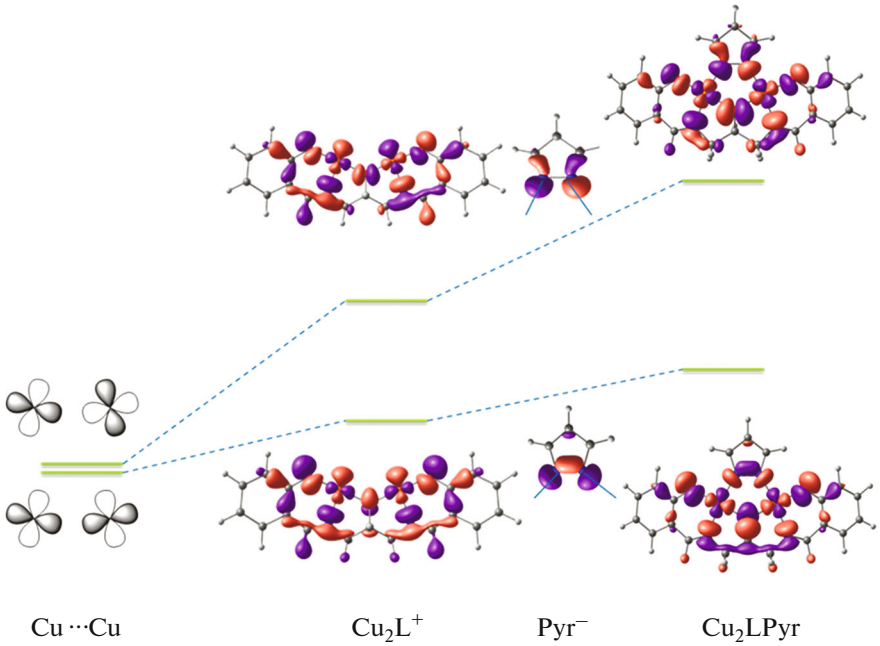


Fig. 6. Molecular orbital diagram for the formation of complex **III** (Pyr).

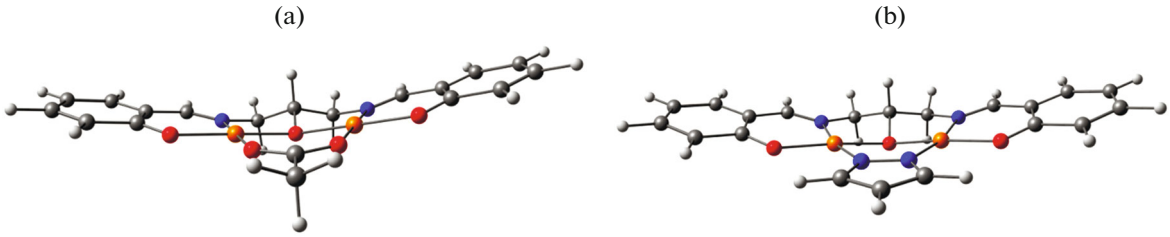


Fig. 7. View of molecules of complexes (a) **II** for R = CH_3 and (b) **III** for R = Pyr.

In the general case, the most part of similar binuclear complexes exhibit the antiferromagnetic character of the exchange for the arrangement of two planes of the coordination modes close to planar, which corresponds to the $CuO_{alkoxy}Cu$ bond angle lying in a range of 130.8°–135.0° [11]. At the same time, the sign of the interaction changes to the opposite one upon a substantial dihedral distortion of the binuclear molecule and, as a consequence, upon a decrease in the bond angle mentioned above. This confirms the ferromagnetic character of the exchange in the complex of type **IV** shown in Fig. 9 ($2J = +56.2$ cm^{-1}). The dihedral angle between the planes of the coordination modes is 58.2(3)°, and the $CuO_{alkoxy}Cu$ bond angle is 110.30(11)°. The DFT calculations indicate a substantial anticomplementary character of the influence of the 6-methoxypurinate bridge, resulting in the energy degeneration of the symmetric and antisymmetric MSOs.

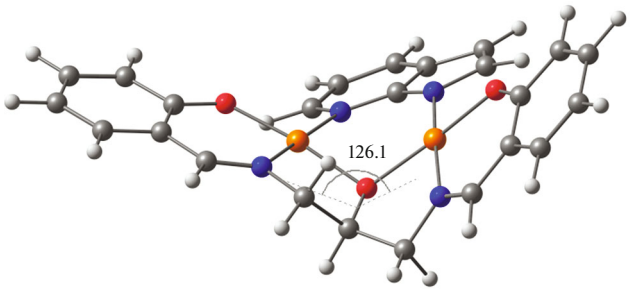


Fig. 8. Spatial structure of complex **III** (Az).

It should be noted, however, that the variation of details of the structures of the carbonyl components of ligand system L makes it possible to change both the strength and character of the exchange between the copper(II) ions even in the case of the same exogenic

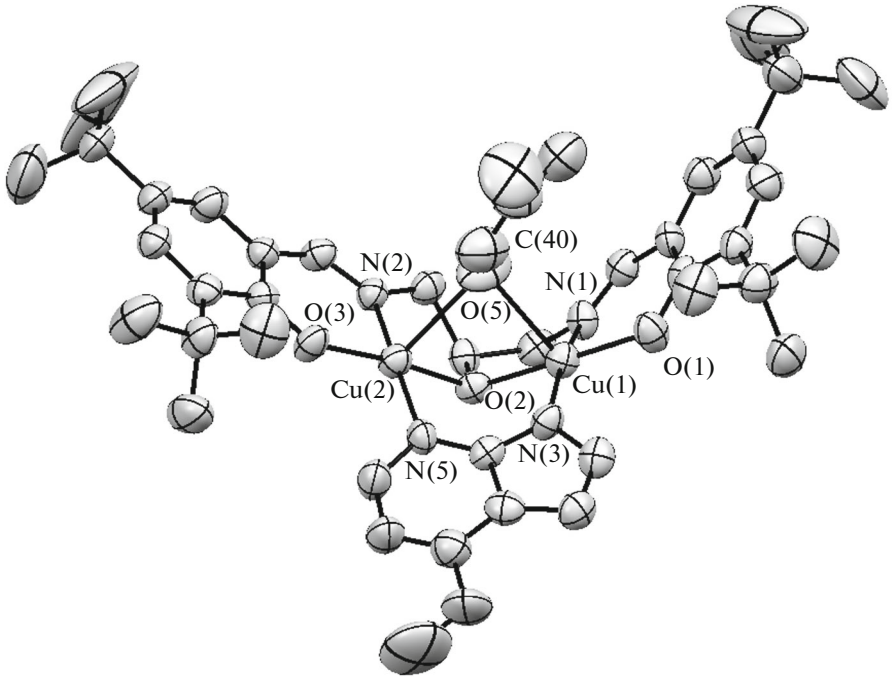
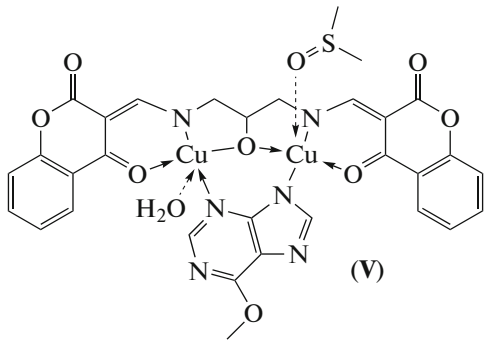


Fig. 9. Structure of the binuclear complex $[Cu_2(L)(\mu\text{-}6\text{-}Mp)(DMF)]$ (**IV**) [11].

bridge. For example, the following binuclear complex of type **V** was described [12]:



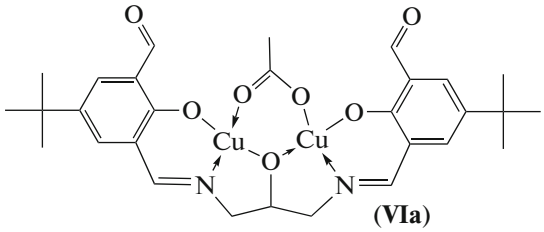
(**V**)

Complex **V** of the composition $[Cu_2(L)(Mp)(H_2O)(DMSO)]$ (Fig. 10) was synthesized by the reaction of bis(azomethine) and copper(II) perchlorate in the presence of 6-methoxypurine followed by recrystallization from aqueous dimethyl sulfoxide (DMSO). The structure of the binuclear complex is close to planar. The bridging alkoxide oxygen atom is not almost pyramidalized: the sum of bond angles of the bonds at the O(4) atom is 359.2(3)°, the Cu(1)O(4)Cu(2) bond angle at the alkoxide bridging atom is 136.29(14)°, and the Cu–Cu distance is 3.6044(6) Å.

The study of the temperature dependence of the magnetic susceptibility of complex **V** showed a fairly strong antiferromagnetic exchange interaction between the copper(II) ions, which agrees with its planar structure ($2J = -348$ cm^{-1}). A possible explanation can be a specific feature of the structure of the carbonyl fragment of the bis(azomethine) ligand: the short coordinated exocyclic C=O bond (1.270 Å) compared to those of the salicylaldehyde and pyrazolone derivatives (1.300–1.310 Å) in similar complexes. This decrease favors the opening of the angle at the alkoxide bridge and the flattening of the molecule of the complex.

The relationships considered were further confirmed in both our last works and publications of foreign researchers, and the subsequent part of the present review is devoted to the theoretical experimental analyses performed by the latter.

For example, two binuclear copper(II) metallochelates of types **VIa** and **VIb** were theoretically and experimentally studied in detail [13]. Their main distinction is the presence of the axially coordinated DMSO molecule in one of the metallochelates. However, as shown below, this distinction is principal and determines drastically different characters of the exchange.



(**VIa**)

Binuclear complex **VIa** containing no coordinated DMSO molecule is characterized by a rather pronounced antiferromagnetic character of the exchange

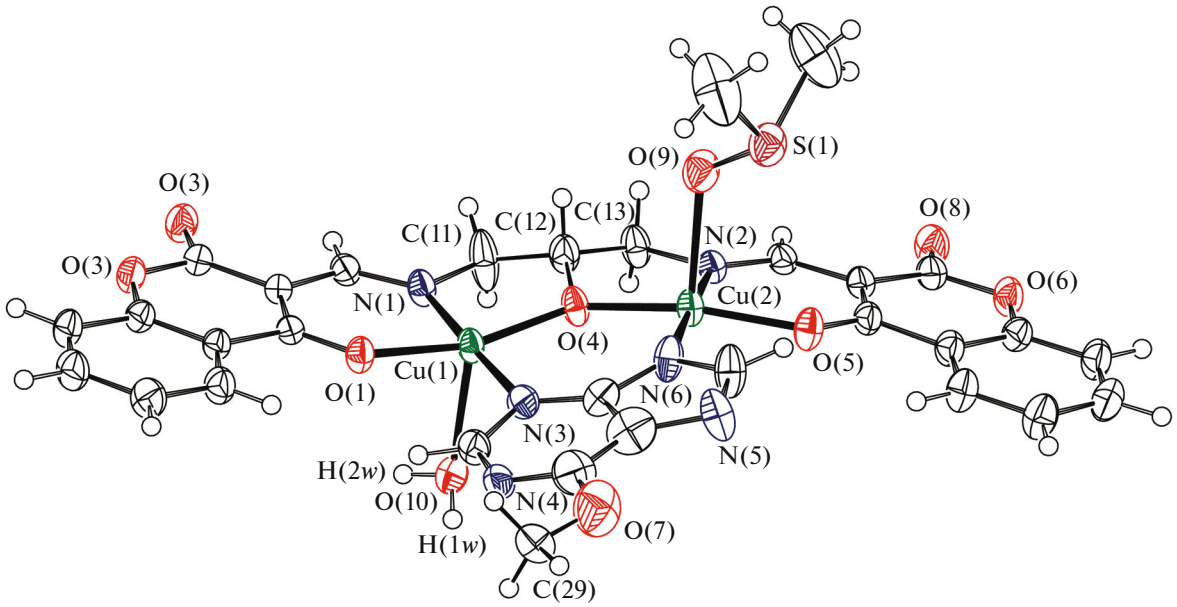


Fig. 10. Structure of complex **V** in the representation of atoms by atomic shift ellipsoids with 50% probability.

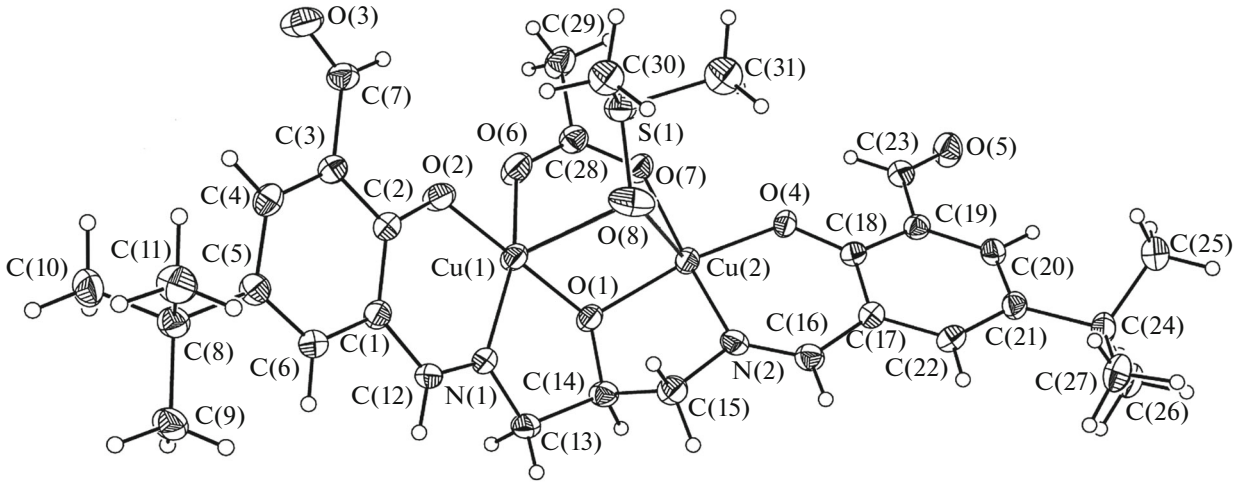


Fig. 11. Structure of the binuclear copper(II) complex of type **VIb**.

between the copper(II) ions ($2J$ = –94.8 cm^{-1}), whereas the product of recrystallization, which allowed one to obtain a single crystal with the coordination of the DMSO molecule, from a mixture of solvents (**VIb**) corresponds to a substantial ferromagnetic exchange ($2J$ = +121 cm^{-1}). The structure of compound **VIb** is presented in Fig. 11.

The μ^2-bridging DMSO molecule coordinates the copper ions through the O(8) atom to form a potential additional exchange channel and to favor the distortion of the binuclear molecule (similarly to that presented above in Figs. 3 and 5). The dihedral angle between the planes of atoms Cu(1)–O(1)–C(14) and Cu(2)–O(1)–C(14) (δ), being a quantitative measure of a similar distortion, is 58.2°. The DFT calculations of the singlet–triplet splitting were performed in the broken symmetry approximation to elucidate the role of the DMSO molecule in magnetic exchange "controlling." The results showed that the exchange remained ferromagnetic and the influence of the exchange channel involving the DMSO molecule was negligible for the distorted conformation, regardless of the fact whether the coordinated DMSO molecule is present ($2J$ = +150 cm^{-1}) or not ($2J$ = +152 cm^{-1}). The role of the coordinated molecule is thus reduced

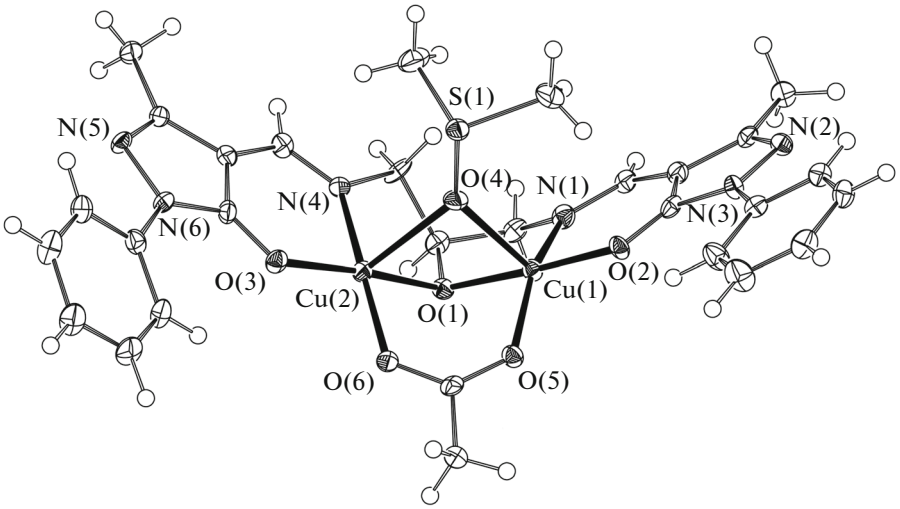
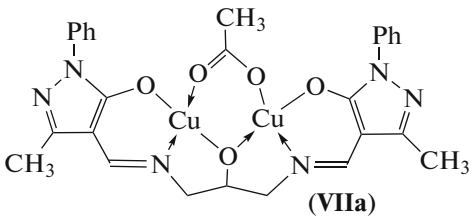


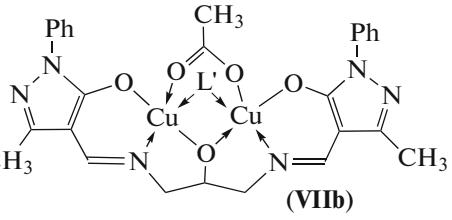
Fig. 12. Structure of complex **VIIa** in the representation of atoms by atomic shift ellipsoids with 50% probability.

to the stabilization of the distorted conformation of binuclear complex **VIb**, and the removal of this molecule, as follows from the calculation results, leads to some decrease in the distortion (the corresponding dihedral angle decreases to 48.4°), but the exchange remains ferromagnetic ($2J_{theor}$ = +79 cm^{-1}). This divergence was completely eliminated by the calculation of the theoretical value $2J = -82$ cm^{-1}, which is close to the experimental value (−94.8 cm^{-1}) assuming the planar structure of complex **VIa** similar to the model structures presented above (Figs. 2, 3).

The presented results are completely consistent with the published data [14–20], the theoretical interpretation of which can be accomplished in terms of the approach developed. For example, the role of the DMSO molecule as a "switcher" of the exchange interaction character that stabilizes the distorted conformation of the metallocycles was unambiguously proved [14] by the detailed physicochemical study of the exchange-bound complexes of types **VIIa** and **VIIb**, and the structure of complex **VIIa** was determined by X-ray diffraction analysis.



(VIIa)



(VIIb)

L = DMSO

The structure of the binuclear molecule is substantially distorted in complex **VIIb** (Fig. 12): the exogenic acetate bridge fixes the bent conformation of the azomethine ligand. This distortion is additionally favored by the bidentate bridging coordination of the DMSO molecule. The crystal structure of complex **VIIa** includes one more DMSO molecule that is not coordinated to the copper ions.

Both six-membered metallocycles in complex **VIIa** are nearly planar: all atoms lie on the plane of the pyrazole cycle. The deviation of the copper atoms from the plane passing from nine atoms of the chelate and pyrazole cycles is 0.024(4) and 0.038(4) Å, for Cu(1) and Cu(2), respectively. The dihedral angle between the above indicated planes is 60.22(14)°. The Cu(1)O(1)Cu(2) bond angle is 104.7(2)°. The alkoxide bridging O(1) atom is strongly pyramidalized: the sum of bond angles at this atom is 329.9°. As a whole, the molecule of complex **VIIa** is generally "roof-shaped." The dihedral angle φ between the Cu(1)O(1)C(13) and Cu(2)O(1)C(13) planes is 61.92°.

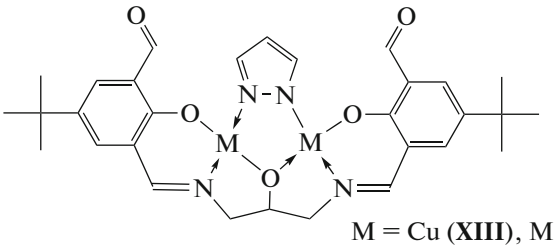
The study of the magnetic properties of complexes **VIIa** and **VIIb** shows that the former is characterized by the antiferromagnetic exchange ($2J = -169$ cm^{-1}), while the exchange in the second complex is ferromag-

netic ($2J = 174$ cm^{-1}). The quantum-chemical calculation of the $2J$ parameter was performed in terms of the broken symmetry method for the theoretical investigation of the exchange interactions in synthesized complexes **VIIa** and **VIIb**. The exchange parameters were calculated for both the fixed (from the X-ray diffraction data) and preoptimized geometry of the complexes. The quantum-chemical calculation of the exchange interaction parameter in complex **VIIb** using the fixed geometry ($2J = 174$ cm^{-1}) gives an excellent agreement with the experiment. The removal of the DMSO molecule even with geometry retention (complex **VIIb**) exerts almost no effect on the difference in energies between the triplet and broken-symmetry states ($2J = 180$ cm^{-1}). This indicates that the DMSO molecule is not involved in magnetic field translation because of the formally orthogonal character of the magnetic orbitals of the paramagnetic centers and the axially coordinated solvent molecule [18].

The geometry optimization of complexes **VIIb** in the distorted conformation decreases the exchange parameter ($2J = 120$ cm^{-1}) but does not change its character, which contradicts the experimental data on the antiferromagnetic exchange in complex **VIIa**. The total energy of the symmetric conformation of complex **VIIa** in the triplet state is lower by 1.39 kcal/mol than that of the distorted conformation. The value calculated for the exchange parameter ($2J = -146$ cm^{-1}) of this conformation has a correct sign and also corresponds to the experimental value ($2J = -169$ cm^{-1}). The Cu–Cu distance for this conformation (3.514 Å) is consistent with that obtained by the EXAFS data (3.51 Å). These results assert surely that the symmetric conformation of the molecule of the complex takes place in the absence of the coordinated DMSO molecule.

The peculiarities of the magnetic exchange in the binuclear copper(II) complexes can be interpreted more reliably from the positions considered above [15]. The following compounds were synthesized [15]: $[Cu_2(L)(OAc)] \cdot 3DMF$ (**VIII**), $[Cu_2(L)(OAc)]_2 \cdot 3DMF$ (**IX**), $[Cu_2(L)(BNPP)] \cdot 3CH_3CN$ (**X**), $[Cu_2(L)(Fa)] \cdot 2DMF$ (**XI**), and $[Cu_2(L)(Pa)] \cdot DMF$ (**XII**), where H_3L is *N*,*N*'-bis(3,5-*tert*-butylsalicylidene-2-hydroxy)-1,3-propanediamine, OAc is acetate anion, BNPP is bis(4-nitrophenyl)phosphate, Fa is tetrahydrofurancarboxylic acid ion, and Pa is benzoate ion. The structures of all synthesized compounds were established by X-ray diffraction analysis. The structures of complexes **VIII** and **X** [15] are presented in Fig. 13. The copper(II) ions in these complexes are bound by the exchange interactions different in both character and strength: $2J = 56.24$ (**VIII**), 50.48 (**XI**), −169.23 (**X**), and −71.38 cm^{-1} (**XII**). The authors [15] chose the value of the Cu(1)O(2)Cu(2) bond angle, being 107.06°, 105.48°, 137.75°, and 128.25°, respectively, for these compounds, as the single reason explaining the presented peculiarities of the magnetic properties of the complexes. At the same time, it is doubtless that the character of changes in the MSO energies of these complexes determining the sign and value of the exchange parameters is mainly governed by a change in the degree of distortion of the binuclear molecule. The dihedral angles agree excellently with the following values of $2J$: 62.6° (**VIII**), 63.7° (**XI**), 10.5° (**X**), and 25.4° (**XII**).

As mentioned above, the antiferromagnetic exchange interaction increases substantially in going from the carboxylate bridge to the pyrazolate anion, indicating the additive (complementary) interaction of the exchange channels in the nonsymmetric exchange fragment. The experimental data presented below are consistent with the considered theoretical positions. The synthesis of the binuclear copper(II) and nickel(II) complexes of types **XIII** and **XIV** based on the ligand system used in the preparation of metallochelates of type **VI** was described [21].



M = Cu (**XIII**), M = Ni (**XIV**)

The structures of complexes **XIII** and **XIV** were established by X-ray diffraction analysis [21].

In complex **XIII** (Fig. 14a), the coordination polyhedra of both Cu atoms are distorted squares. The deviation of the copper atoms from the plane of the N_2O_2 donor atoms is 0.020 Å for Cu(1) and 0.045 Å for Cu(2). The molecule of the complex is nearly planar (the dihedral angle between the CuO_2N_2 coordination planes is 173.18°) with the minimum pyramidalization of the alkoxide O(1) atom (the sum of the bond angles

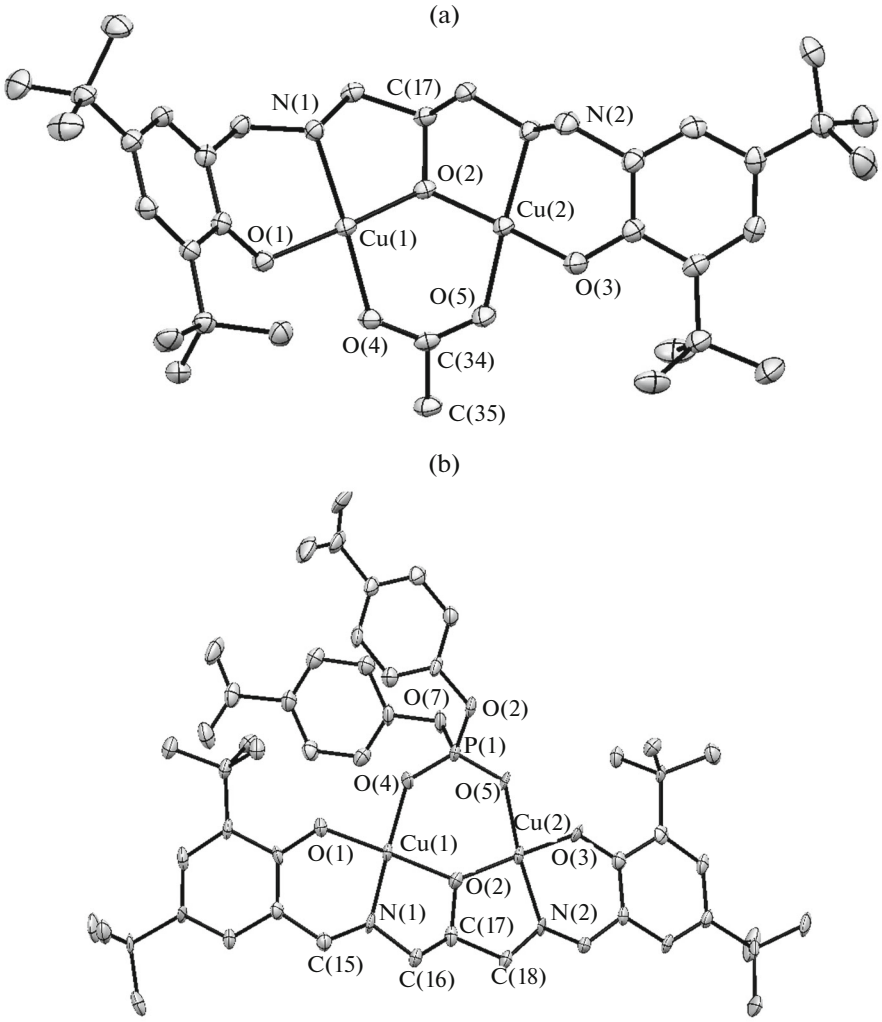


Fig. 13. Structures of complexes (a) **VIII** and (b) **X** [15].

is 348.30°). The Cu(1)O(1)Cu(2) bond angle is 124.21°. On the whole, the structure of complex **XIII** is very similar to the structures of the binuclear copper complexes based on the products of 1,3-diaminopropan-2-ol condensation with the salicylaldehyde derivatives bearing pyrazolate bridges [22–26]. The crystal structure of nickel compound **XIV** (Fig. 14b) resembles the structure of copper compound **XIII** and is characterized by similar crystallographic parameters. The alkoxide O(1) atom in complex **XIV** is not almost pyramidalized (the sum of the bond angles is 356.82°). Complex **XIII** is characterized by a sufficiently strong antiferromagnetic exchange ($2J = -340$ cm^{-1}). The ranges of the exchange parameter are characteristic of those for the earlier described copper(II) complexes with the pyrazolate bridge based on *N*,*N*'-bis(salicylidene)-1,3-diaminopropan-2-ol and its derivatives ($-2J = 300$–600 cm^{-1}) [23, 24, 27]. As should be expected, complex **XIV** is diamagnetic. The quantum-chemical calculation of the $2J$ parameter was performed in terms of the broken symmetry method for the theoretical investigation of the exchange interactions in binuclear copper(II) complex **XIII**. The calculated exchange parameter for the optimized geometry of complex **XIII** resulted in the agreement with the experimental data ($2J_{theor} = -336$ cm^{-1}) in full accord with the considered above theoretical statements and results [28].

The binuclear copper complexes of types **XV** and **XVI** based on the derivatives of 1-phenyl-3-methyl-4-formylpyrazol-5-one and its thio analog [29, 30] are also nearly planar (proved by X-ray diffraction analysis), which provides a pronounced antiferromagnetism of the complexes ($2J = -449$ and -425 cm^{-1} for **XV** and **XVI**, respectively).

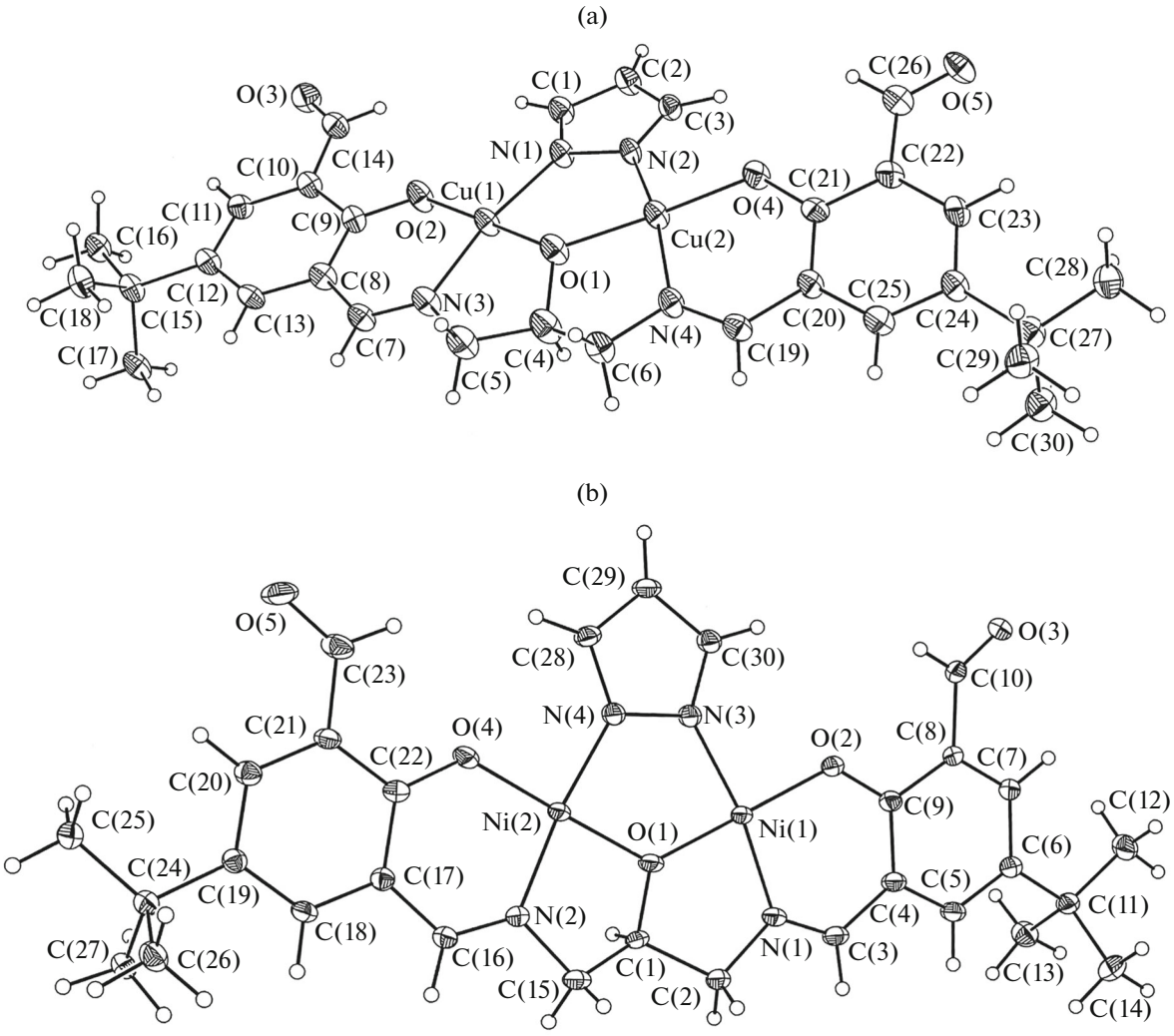
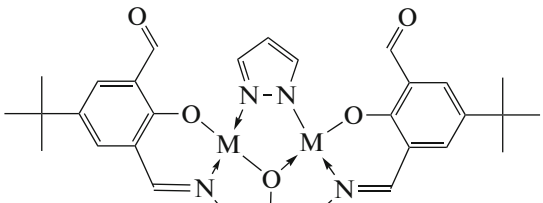


Fig. 14. Structures of complexes (a) **XIII** and (b) **XIV** [21].



M = Cu (**XV**), M = Ni (**XVI**)

A considerable transformation of the magnetic properties occurs when the pyrazolate ion in derivative **XV** is replaced by the azaindolate ion (compound **XVII**) similarly to the changes mentioned above in Table 1 (compound **III**, R = Az). This occurs due to a substantial distortion of the structure of the complex shown in Fig. 15.

In the molecule of complex **XVII**, two copper atoms are also linked through three bridges: the alkoxide O(2) atom, N(7)–C(18)–N(8) atoms of the azaindolate anion, and weakly coordinated O(1) atom of the DMSO molecule. The nonsymmetric 7-azaindolate anion predetermines the difference in coordination spheres of the copper atoms in complex **XVII**. The Cu(2)–N(7) distance is noticeably shorter than Cu(1)–N(8) (1.966(4) and 1.999(4) Å, respectively). The coordination polyhedron of the Cu(1) atom bound to the nitrogen atom of the six-membered ring

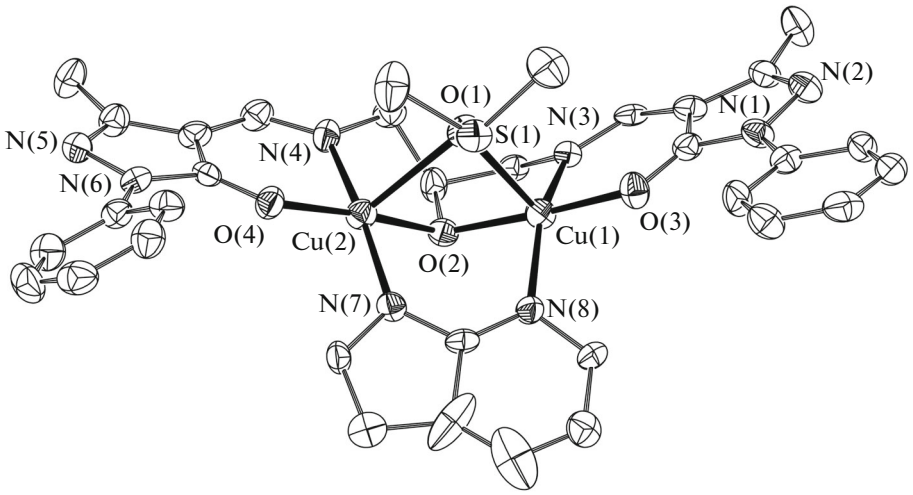


Fig. 15. Structure of complex **XVII** in the representation of atoms by atomic shift ellipsoids with 50% probability (hydrogen atoms are omitted).

of the azaindolate ion is intermediate between a trigonal bipyramid and a square pyramid (closer to the latter). The coordination polyhedron of the Cu(2) atom is a square pyramid (4 + 1). The copper atom shifts from the plane of the basal donor atoms O(2)O(4)N(4)N(7) to the O(1) atom of the DMSO molecule by 0.1504(6) Å. The six-membered chelate of the Cu(1) atom is almost planar, whereas this cycle of the Cu(2) atom has an envelope conformation, and its "valve" (copper atom) deviates from the mean plane of other five atoms by 0.477 Å. The bridging O(2) atom is substantially pyramidalized: the sum of the bond angles at this atom is 332.2°. The inflection of the molecule of complex **XVII** results in a small value of the angle at the alkoxide bridging oxygen atom Cu(1)O(2)Cu(2), which is equal to 105.33(15)°. This geometric factor and the above considered orbital factors predetermine the ferromagnetic character of the exchange in compound **XVII** ($2J = 106$ cm^{-1}).

Binuclear metallochelates **I** and **II** can join into more complicated supramolecular structures (tetra-, hexa-, and octanuclear derivatives) via the purely "additive" mechanism or can lead to a wide variety of peculiarities of the magnetic exchange between the paramagnetic centers. The final part of the present work is devoted to an analysis of the magnetic properties of some representatives of the tetranuclear exchange-bound complexes with the ligand systems denoted above.

For example, the cross-linking of the binuclear fragments of type **I** due to dicarboxylic acid ions allowed the authors [31] to synthesize tetranuclear complex **XVIII**, the structure of which is shown in Fig. 16.

It is convenient to describe tetranuclear complex **XVIII** as consisting of two binuclear fragments linked by the malonate dianion (Fig. 16). The binuclear fragment containing the Cu(3) and Cu(4) atoms is almost planar. The deviations of the atoms from the mean plane of the bimetallic chelate Cu(3)–O(9)–C(34)–O(10)–Cu(4)–O(8) is 0.067 Å, on the average, and the dihedral angle between the coordination planes of the Cu(3) and Cu(4) atoms is 13.0(2)°. The second binuclear fragment is somewhat distorted because of the inflection along the line connecting the alkoxyl bridging oxygen atom and the carbon atom of the malonate dianion. The dihedral angle between the coordination planes of the Cu(1) and Cu(2) atoms is 40.62(14)°.

The difference in geometries of the indicated fragments appears in the distance between the copper atoms: Cu(1)···Cu(2) (3.3115(8) Å) is noticeably shorter than Cu(3)···Cu(4) (3.5047(7) Å). The complex is antiferromagnetic, and the parameters of the intra- and interdimer exchange are $2J = -59$ and $zJ' = 7.5$ cm^{-1}, respectively. The antiferromagnetic exchange interaction in complex **XVIII** is somewhat weaker than that in the above considered binuclear copper(II) complexes based on *N*,*N*'-bis(salicylidene)-1,3-diaminopropan-2-ol. In this case, the antiferromagnetic exchange interaction can weaken because of the distortion of the exchange fragment due to steric hindrances created by the closely arranged tosyl groups and due to an additional coordination of the copper atoms by the oxygen atoms of the tosyl fragments. A similar additional coordination of the oxygen atoms of the tosyl fragments is observed in almost all earlier described transition metal complexes with azomethines based on 2-*N*-tosylaminobenzaldehyde [26, 32, 33].

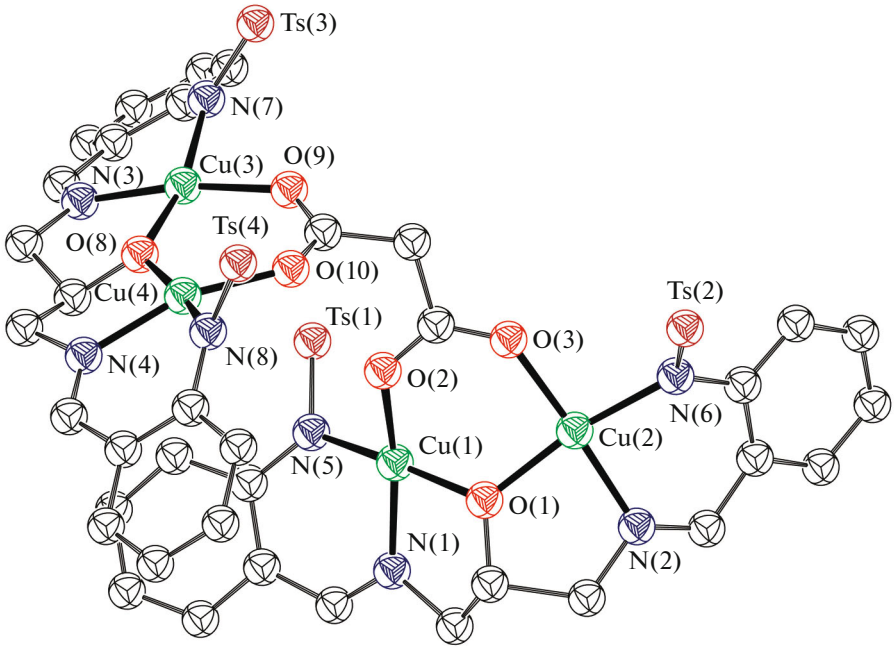


Fig. 16. Structure of complex **XVIII** in the representation of atoms by atomic shift ellipsoids with 50% probability (hydrogen atoms are omitted, tosyl groups $SO_2C_7H_7$ are designated as Ts(1), Ts(2), etc. (the numeration of Ts coincides with that of S atoms)).

Using the ligand system of type L, the authors [34] synthesized tetranuclear complex **XIX**, the structure of which is shown in Fig. 17.

Similarly to complex **XVIII** considered above, the tetranuclear structure of complex **XIX** is formed due to the binding of two binuclear fragments by the terephthalate anion. In the fragments themselves, two copper ions contain the μ_2-axially coordinated DMF molecule. The complex is characterized by the ferromagnetic exchange ($2J = 18.70$ cm^{-1}), which is due to the translation of exchange effects via the Cu(1)–O(6)–Cu(2) channel (bond angle 77.44°) involving the oxygen atom of the DMF molecule [34]. This value of the bond angle (substantially lower than 90°) determines the sign of the exchange interaction. The latter fact can hardly be considered as convincing one. It seems doubtless for complex **XIX** that the exchange interactions are translated via the "traditional" channels considered above and the ferromagnetism of this complex is caused by a substantial distortion of the binuclear molecule: the dihedral angle in the above representation is 115.2° due to which the Cu(1)O(2)Cu(2) bond angle decreases to 104.3°.

The authors [35] described the results of the X-ray diffraction analysis and magnetochemical study of the tetranuclear copper(II) complex with the azomethine ligand, which is the condensation product of 1-phenyl-3-methyl-4-formylpyrazol-5-one and 1,3-diaminopropan-2-ol (H_3L), i.e., the ligand system from which the above described complexes **VII** were synthesized. Complex **XX** of the composition $[Cu_{12}L_6(N_3)_6] \cdot 9C_2H_3N \cdot H_2O$, the structure of which is shown in Fig. 18, was synthesized by the reaction of bis(azomethine) H_3L with copper(II) perchlorate in the presence of triethylamine and sodium azide followed by recrystallization from acetonitrile.

The symmetrically independent part of the unit cell of compound **XX** contains 1.5 molecules of the complex (A and B; B exists in the partial position on the 2-fold symmetry axis), 4.5 acetonitrile molecules, and 0.5 water molecule. The ratio of molecules of complexes A and B in the unit cell is 2 : 1. The structures of both complexes A and B can formally be described as two binuclear fragments linked by the azide bridging groups. This produces a distorted central cubic fragment $Cu_4N_2O_2$ in which the copper atoms occupy the vertices of the tetrahedron inscribed into this cube. The coordination modes of the copper atoms in complex **XX** are different, and the structures of these symmetrically independent molecules also differ. In both molecules, the copper atoms are most strongly bound to four N and O atoms to form a square geometry. The Cu–O and Cu–N bond lengths lie in ranges of 1.91–1.99 and 1.93–2.07 Å, respectively. The most substantial difference in complexes A and B appear in the structures of their central cubic fragments $Cu_4N_2O_2$. All copper atoms have an additional axial contact together with square coordination. In complex A, the shortest additional coordination is observed for the Cu(3) atom (Cu(3)–O(1)

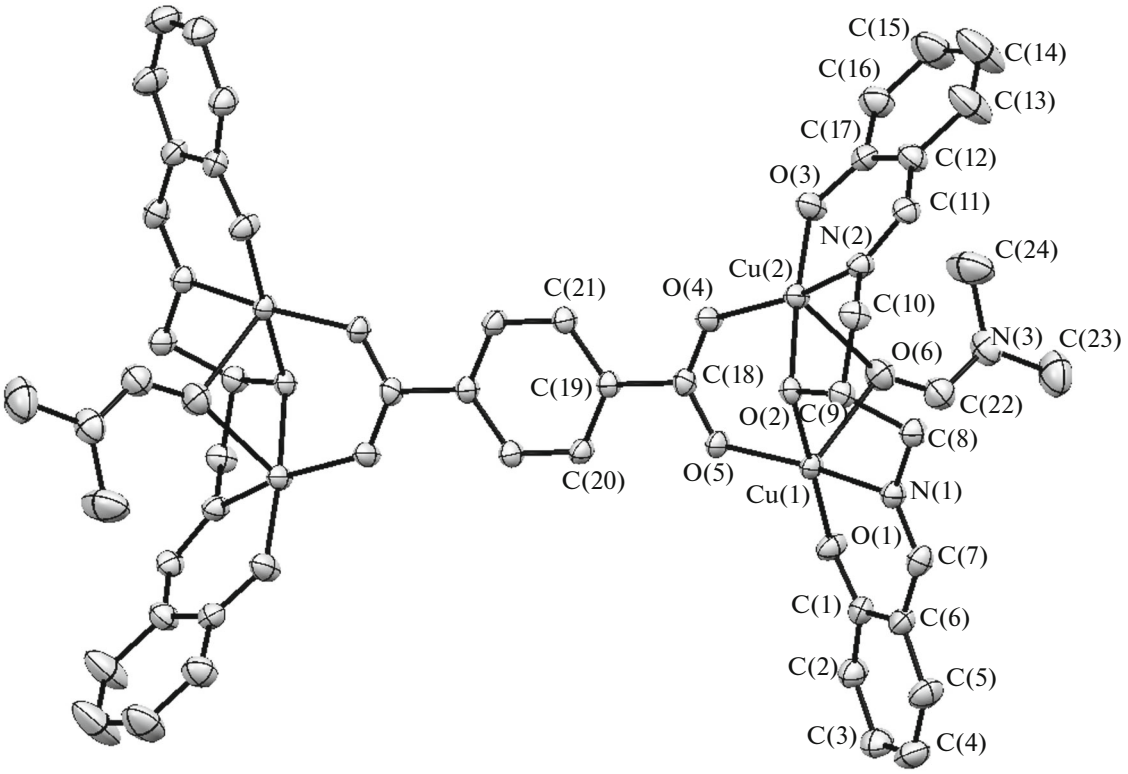


Fig. 17. Structure of complex **XIX**.

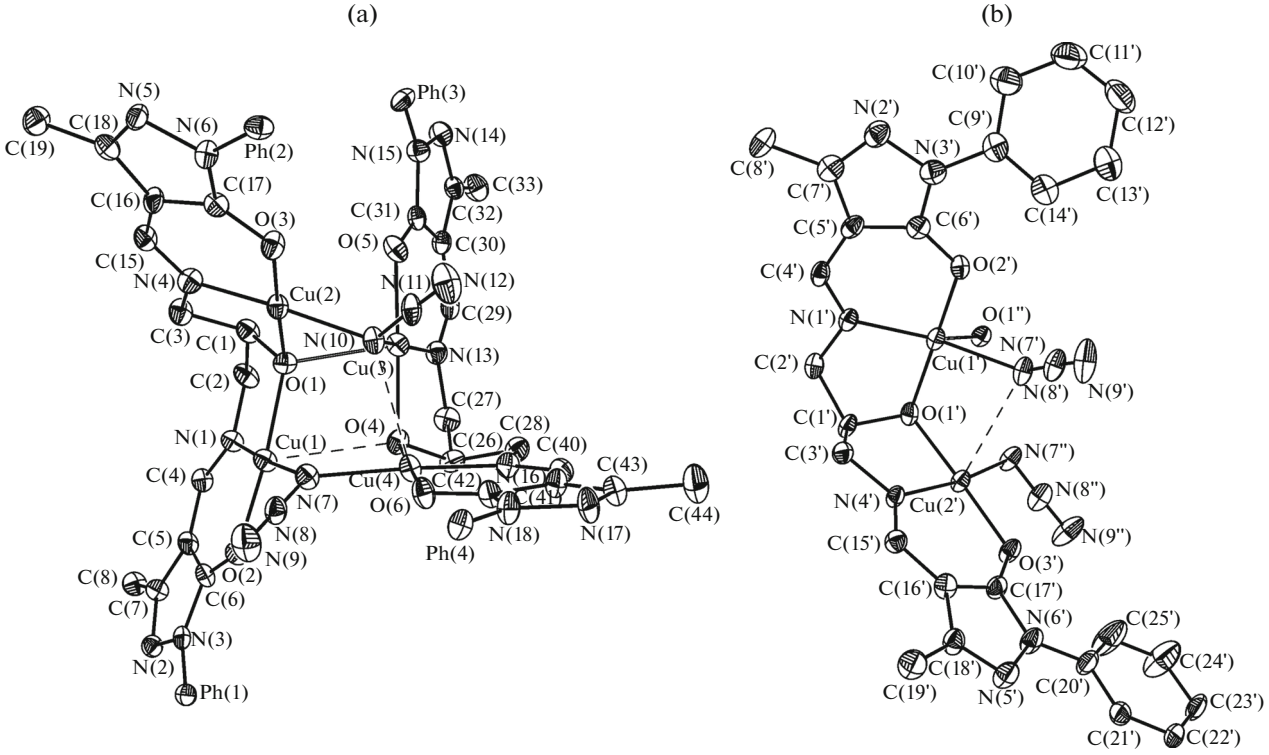


Fig. 18. General view of molecules A and B of complex **XX** in the representation of atoms by atomic shift ellipsoids with 50% probability (hydrogen atoms are omitted; the phenyl groups of molecule A are replaced by Ph; for molecule B, only the symmetrically independent part is shown, except for the coordination modes of the Cu atoms shown completely; the atoms marked by two strokes are generated by the symmetry procedures $1 - x, y, -z$; the Cu–N(O) bonds (2.1–2.5 Å) are shown by open lines, and the Cu–N(O) bonds (2.5–3.0 Å) are shown by dash).

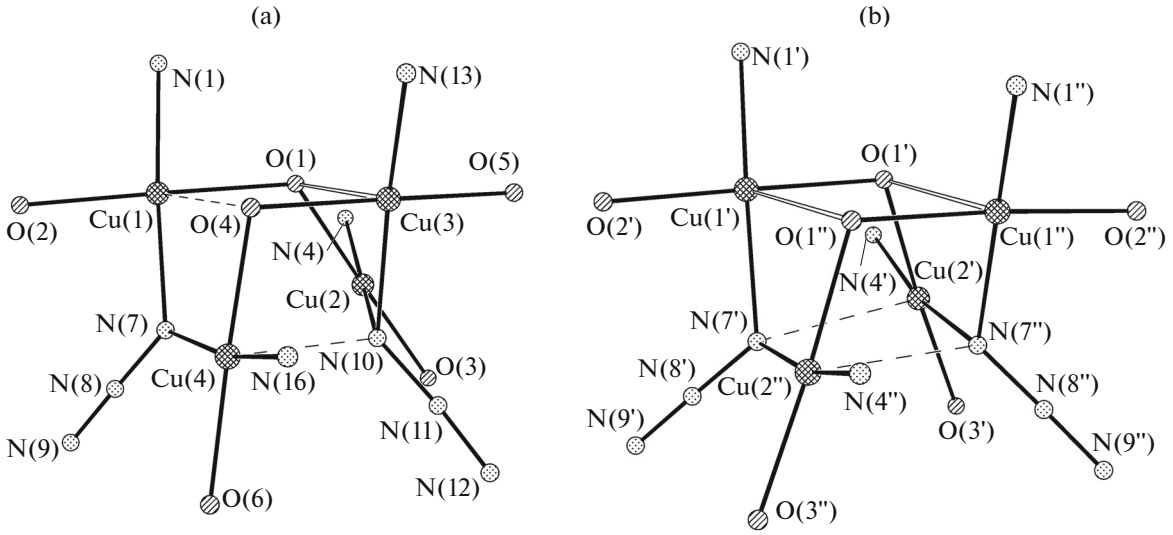


Fig. 19. Structures of the exchange fragments in molecules A and B of complex **XX** (only the donor atoms of the ligands and the bridging N_3 groups are shown).

2.289(3) Å), due to which the interpretation of the coordination polyhedron of the Cu(3) atom as 4 + 1 (tetragonal pyramid) seems doubtless. The distances to the O and N atoms that supplement the coordination mode of other copper atoms are substantially longer (Cu(1)–O(4) 2.688(3), Cu(2)–N(7) 3.331(4), Cu(4)–N(10) 2.563(4) Å). According to these data, it seems most reasonable to describe the coordination mode of the Cu(2) atom as a square one and that of other copper atoms as 4 + 1. Molecule B has the C_2 symmetry, and the cubic fragment is distorted to a considerably lower extent. The coordination mode of both symmetrically independent copper atoms is 4 + 1. The Cu(1)'–O(1)" and Cu(2)'–N(7)' distances are 2.437(3) and 2.829(4) Å, respectively; i.e., they are somewhat longer than the shortest analogous distance in A and are somewhat shorter than the longest distance. The distortions of the cubic fragment are also manifested in the Cu···Cu contacts. In complex A, the Cu(2)···Cu(3) and Cu(3)···Cu(4) distances are rather short (2.9743(8) and 3.0187(9) Å, respectively), and the range of distances is 2.97–4.03 Å. In the cubic fragment of molecule B, the range of Cu···Cu distances is somewhat smaller (3.17–3.92 Å). The single any close analog of complex **XX** is the tetranuclear complex based on *N*,*N*'-(2-hydroxylpropane-1,3-diyl)bis(salicylideneimine) described earlier [36].

According to the aforesaid, the structures of the exchange fragments in molecules A and B shown in Fig. 19 predetermine a very complicated character of the exchange interaction. In both cases, the spin-Hamiltonian should include many parameters.

In the exchange fragment of molecule A, the magnetic exchange between the paramagnetic centers Cu(1) and Cu(2), Cu(1) and Cu(3), Cu(3) and Cu(4) mainly occurs through the alkoxide bridging O(1) and O(4) atoms, and a fairly strong antiferromagnetic interaction can be expected in the first two cases [37]. The exchange between the Cu(2) and Cu(3), Cu(1) and Cu(4) ions can be translated mainly through the nitrogen atoms of the azide bridges (N(10) and N(7), respectively). The exchange channel involving the alkoxide O(1) atom can contribute noticeably to the interaction between the Cu(2) and Cu(3) ions. According to the known magnetostructural relationships [38–42], the exchange between the Cu(2) and Cu(3) ions should be ferromagnetic. A substantial exchange interaction between the Cu(2) and Cu(4) atoms is poorly probable because of a long distance between them and a weak Cu(4)–N(10) bond (2.563 Å). In order to decrease the number of varied parameters in the interpretation of the temperature dependence of the magnetic susceptibility in complex **XX**, it was assumed [36] that in nonsymmetric cluster A the pair parameters for the exchange between the Cu(1)–Cu(2) and Cu(1)–Cu(3) ions and between the Cu(1)–Cu(4) and Cu(3)–Cu(4) ions are close. In this case, the spin-Hamiltonian for cluster A takes the following form: $\hat{H}_A = -J_1(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3) - J_2(\hat{S}_2\hat{S}_3) - J_3(\hat{S}_1\hat{S}_4 + \hat{S}_3\hat{S}_4)$ [43, 44].

In the "symmetric" exchange fragment of molecule B, the magnetic exchange between the Cu(1)' and Cu(2)', Cu(1)" and Cu(2)" paramagnetic centers can occur through the alkoxide bridges, whereas that between Cu(1)'–Cu(2)" and Cu(1)"–Cu(2)' can occur through the azide bridges with the exchange parameters J_1 and J_3, respectively. Taking into account the values of the bond angles at the bridging atoms, one can expect that the character of the exchange interaction would be different, and the J_1 parameter would be negative, whereas J_3 would be positive. The

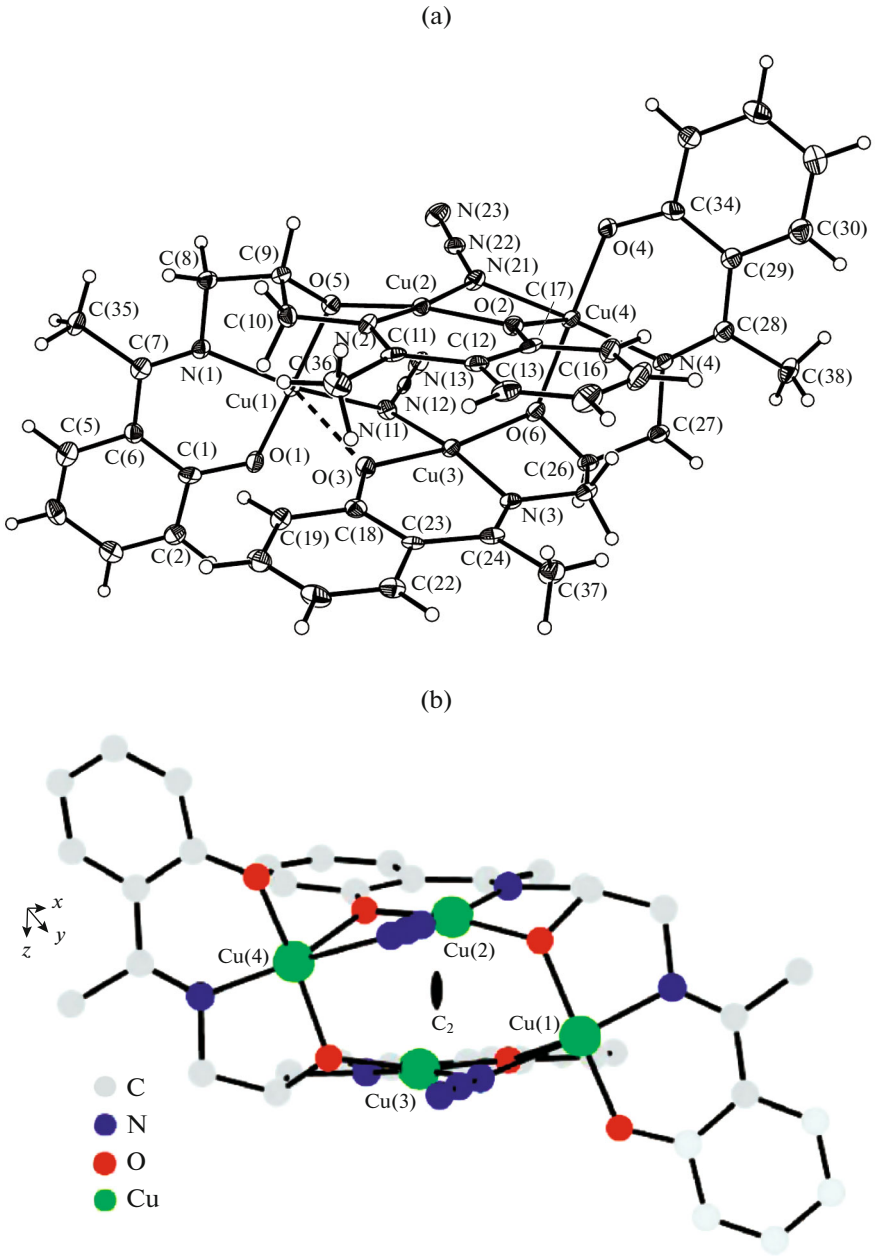


Fig. 20. Structures of (a) complex **XXII** and (b) its simplified variant.

antiferromagnetic exchange with the J_2 parameter is possible between the Cu(1)' and Cu(1)" ions. Any substantial exchange between the Cu(2)' and Cu(2)" ions in the symmetric cluster is poorly probable and, therefore, the spin-Hamiltonian for cluster B includes three exchange parameters: $\hat{H}_B = -J_1(\hat{S}_{1'}\hat{S}_{2'} + \hat{S}_{1''}\hat{S}_{2''}) - J_2(\hat{S}_{1'}\hat{S}_{1''}) - J_3(\hat{S}_{1'}\hat{S}_{2''} + \hat{S}_{1''}\hat{S}_{2'})$.

The theoretical values of the exchange parameters obtained by the indicated spin-Hamiltonians are as follows: $J_{1A} = -178$, $J_{2A} = 80$, $J_{3A} = 18$, $J_{1B} = -26$, $J_{2B} = -74$, and $J_{3B} = 46$ cm^{-1}. The complication of the model using four or five pair parameters for "nonsymmetric" cluster A deteriorates the agreement of the theory with experiment [35].

It should be mentioned that the combination of the ferro- and antiferromagnetic exchange channels in the tetranuclear transition metal complexes (first of all, in the copper(II) complexes with ligand systems L) is indicated in many studies [45–49]. Among them, the results [49] on the synthesis of the tetranuclear complex $[Cu_4L_2(\mu\text{-}1,1\text{-}N_3)_2] \cdot CH_3CN$ (**XXII**) based on ligand system **XXI** and involving the azide ions of the exchange fragments similar to the described above complex **XX** are worth of special attention. The struc-

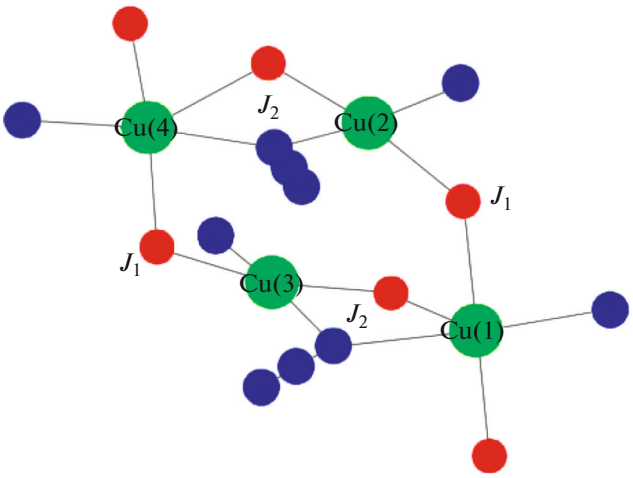
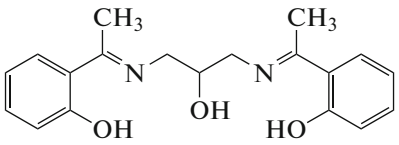


Fig. 21. Structure of the exchange fragment in complex **XXIII**.

ture of the synthesized compound is presented in Fig. 20a, and its simplified view is shown in Fig. 20b.

It is validly mentioned [49] that, in the general case, the exchange fragment of **XXIII** (Fig. 21) that characterizes this complex should contain four different exchange channels. However, taking into account the high degree of symmetry, one can decrease the number of exchange parameters to two.



(XXI)

In this case, the spin-Hamiltonian takes the following form: $\hat{H} = -J_1[(\vec{S}(\text{Cu1})\vec{S}(\text{Cu2}) + \vec{S}(\text{Cu3})\vec{S}(\text{Cu4})] - J_1[(\vec{S}(\text{Cu1})\vec{S}(\text{Cu3}) + \vec{S}(\text{Cu2})\vec{S}(\text{Cu4})]$.

The following values of the exchange parameters were obtained in the framework of this approximation: $J_1 = -153$ cm^{-1} and $J_2 = +191$ cm^{-1}. The former characterizes the exchange channel involving the alkoxide oxygen atom, while the second, ferromagnetic parameter corresponds to the exchange channel involving the azide ion in the $\mu_{1,1}$ coordination, which is completely consistent with the literature data [50] and results [35].

To conclude, the main types and mechanisms of exchange interactions were considered in this review in terms of experimental and theoretical analyses. The electronic and geometric factors exerting a determining effect on the magnetic properties of the bi- and tetranuclear transition metal complexes based on 1,3-diaminopropan-2-ol hydrazones and azomethines were revealed. The authors wittingly restricted their consideration by the description of the magnetic properties of the exchange-bound complexes, whose paramagnetic centers were in the orbital-nondenerate states. Meanwhile, it seems quite evident that the complexation activity of the azomethine, hydrazone, and similar ligands based on 1,3-diaminopropan-2-ol can be restricted in no way by similar systems: there are many published works devoted to studying the complex formation of these ligands with the most part of transition metal ions and many rare-earth elements (see [51, 52] and references cited therein). Obviously, the further theoretical and experimental development of the magnetochemical method in respect of an adequate interpretation of the properties of similar systems is a very urgent task, especially from the viewpoint of the aimed design of supramolecular structures with specified or controlled physicochemical characteristics and for revealing basic regularities of the structure–property relationship in order to obtain novel materials, such as molecular magnetics, for innovative technologies of the nearest future.

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