

## THEORETICAL MODELING OF THE STRUCTURE OF N-[2-[(HYDROXYALKYLIMINO)METHYL]PHENYL] -4-METHYLBENZENE-SULFAMIDES AND THEIR MONO- AND BINUCLEAR COPPER(II) COMPLEXES

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The paper presents a theoretical DFT UB3LYP/6-311++G(*d,p*) modeling of the structure and magnetic properties of Cu(II) coordination compounds with tridentate Schiff bases derived from 2-tosylaminobenzaldehyde and amino alcohols. It is shown that the elongation of the aliphatic chain in the amine part of ligand systems prevents the formation of binuclear metal-chelate structures. At the same time, mononuclear bis-chelate complexes, as well as mono-adducts containing a coordinated solvent molecule and a tridentate azomethine compound, are formed regardless of the number of methylene units.

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Tridentate azomethine compounds derived from 2-hydroxybenzaldehyde, 2-hydroxynaphthaldehyde, 2-N-tosylaminobenzaldehyde and alkyl amino alcohols are of great scientific interest since they can be used to obtain mono-, bi-, and polynuclear metal complexes. Numerous binuclear compounds of copper [1-8] and nickel [9] have been synthesized and structurally characterized as well as cubane complexes of nickel and copper with ligands containing a hydroxyalkyl imine fragment with deprotonated oxygen atoms of alcohol groups being bridging fragments to form  $M_2N_2O_4$  coordination nodes [3, 10]. These complexes exhibit strong antiferromagnetic or ferromagnetic exchange interactions between paramagnetic centers [1, 10].

There are numerous examples of mononuclear chelate compounds of metals of azomethine ligands where alcohol groups of hydroxyalkyl imine fragments do not coordinate to the metals [11-18], as well as the examples of  $MN_2O_2$  metal cycles being formed. Zinc complexes of azomethine ligands containing hydroxyalkylamine groups demonstrate photo- and electroluminescent properties and biological activity [11, 19-25]. The data concerning metal chelates of such ligands are limited to complexes with  $MN_2O_2$  and  $M_2N_2O_4$  coordination nodes and  $(CH_2)_n$  spacers with  $n = 2, 3$ .

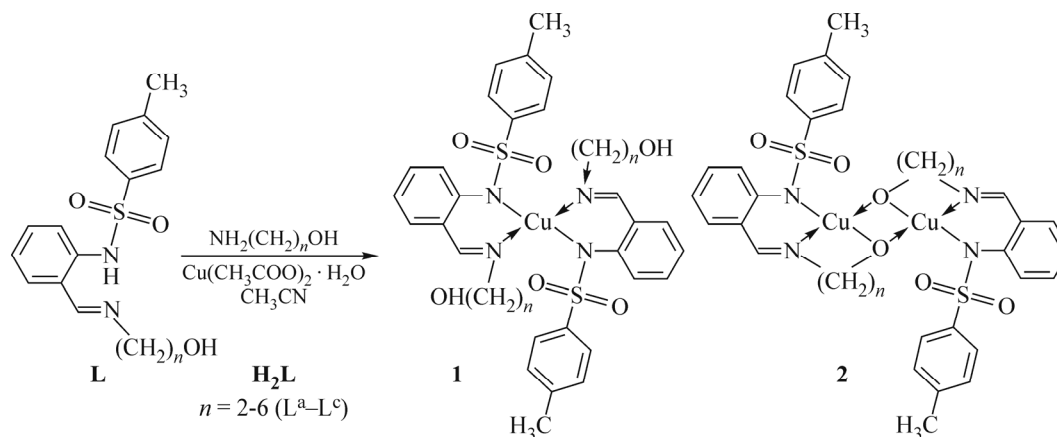
We earlier described the synthesis and structure of azomethine compounds of the derivatives of 2-N-tosylaminobenzaldehyde and aliphatic amino alcohols  $NH_2(CH_2)_nOH$  ( $n = 2-6$ ) and their mono- and binuclear metal complexes [11, 26]. It was established that copper complexes with  $(CH_2)_n$  spacers of the length  $n = 2, 3$  form only binuclear

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structures with antiferromagnetic exchange interaction between metal atoms. In the case of  $(\text{CH}_2)_n$  ( $n = 4-6$ ), mononuclear paramagnetic copper complexes are formed [26].

In the present work, quantum chemical calculations were used to study the effect of the  $(\text{CH}_2)_n$  spacer on the ability of azomethine derivatives of 2-N-tosylaminobenzaldehyde and hydroxyalkylamines (**L**) to constitute chelate cycles during the formation of mono- (**1**) or binuclear copper complexes (**2**).



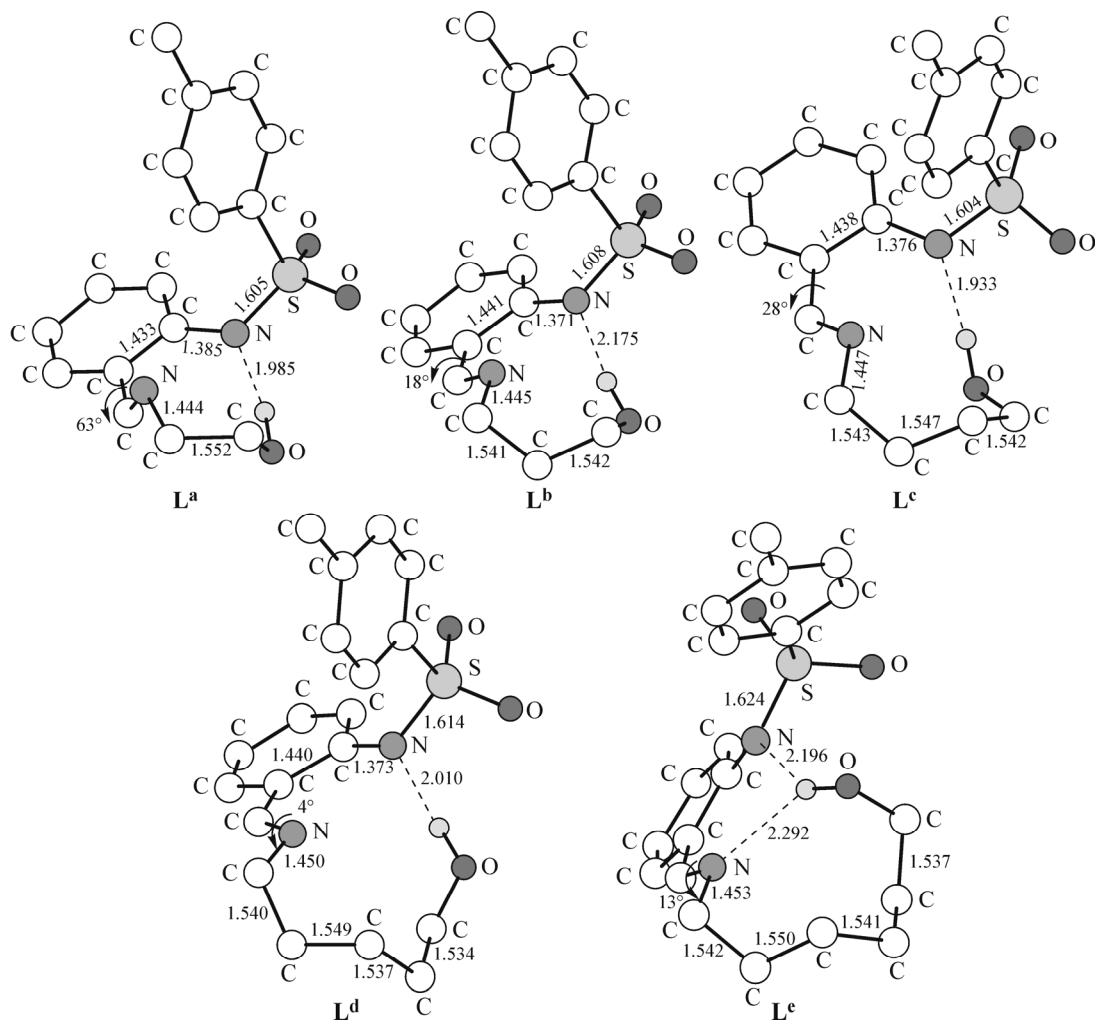
The calculations were performed using the Gaussian 09 software [27] within the density functional theory and the UB3LYP/6-311++G(*d, p*) approximation [28] which was found to reproduce well the characteristics of transition metal bis-chelate coordination compounds [29-31]. The stationary points were located on the potential energy surface by full geometry optimization of molecular structures and subsequent analysis of normal modes. The exchange interactions between unpaired electrons of paramagnetic centers were estimated using the “broken symmetry” (BS) approach [32]. The exchange interaction constants (parameter  $J$ ,  $\text{cm}^{-1}$ ) were calculated by the Yamaguchi formula [33]. The graphical images of molecular structures in Figs. 1-5 were drawn using the ChemCraft program [34] with the input parameters taken from the corresponding Cartesian atomic coordinates obtained from quantum chemical calculations.

## RESULTS AND DISCUSSION

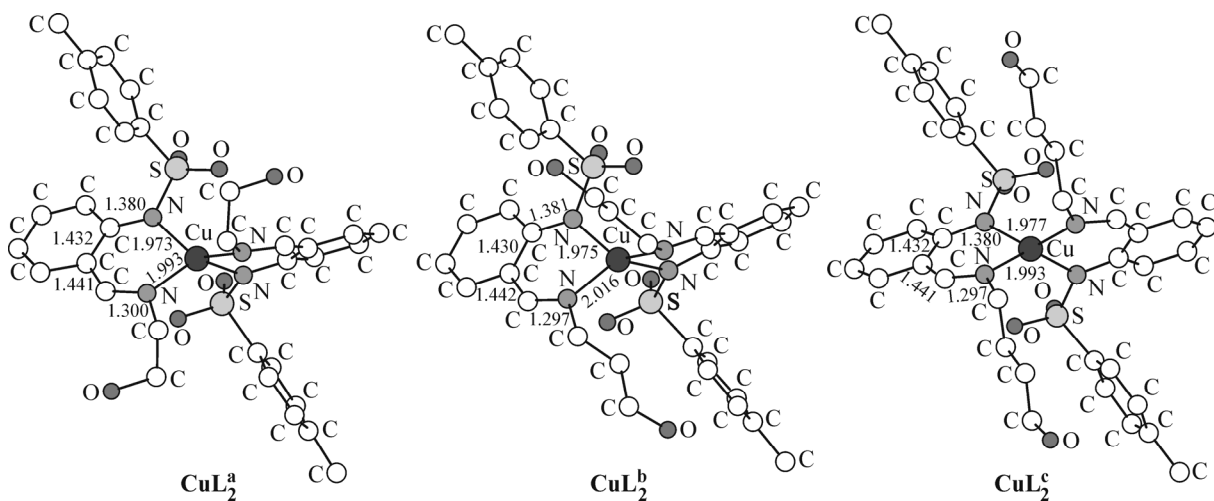
According to the calculation results, the most stable form of the first member of the series is the  $\text{L}^a$  structure ( $n = 2$ ) with a predicted short (1.985 Å) intramolecular dative bond between the hydrogen atom of the hydroxy group and the nitrogen atom linked to the tosyl fragment. The cycle closure makes the azomethine fragment rotate through an angle of  $63^\circ$ . The  $\text{L}^b$  ( $n = 3$ ) structure is characterized by the O...H distance of 2.175 Å and the rotation angle of the azomethine fragment equal to  $18^\circ$  (Fig. 1). The subsequent increase of the number of links in the aliphatic chain leads to the  $\text{L}^c$  ( $n = 4$ ) structure with the hydrogen bond length of 1.933 Å and the rotation angle of the azomethine fragment equal to  $28^\circ$ . The  $\text{L}^d$  ( $n = 5$ ) structure differs from the above structures by insignificant rotation ( $4^\circ$ ) of the azomethine fragment in the opposite direction. The same parameter in the  $\text{L}^e$  ( $n = 6$ ) structure is  $13^\circ$ , and the hydrogen atom of the hydroxyl group forms hydrogen bonds with both nitrogen atoms.

When interacting with metals, potentially tridentate ligand systems  $\text{L}^{a-d}$  can form copper complexes of composition  $\text{CuLL}'$  (where  $\text{L}'$  is a molecule of the solvent or some other additional ligand),  $\text{CuL}_2$ , and  $\text{Cu}_2\text{L}_2$ . The latter type of coordination compounds is of the highest interest, since it provides the possibility of exchange interactions between paramagnetic centers.

Optimized geometries of  $\text{CuL}_2$  complexes show that bis-chelates with  $\text{L}^a$ ,  $\text{L}^b$ , and  $\text{L}^c$  ligands correspond to the  $\text{Cu}_2\text{L}_2^a$ ,  $\text{Cu}_2\text{L}_2^b$ , and  $\text{Cu}_2\text{L}_2^c$  structures characterized by a pseudo-tetrahedral coordination node with the copper atom appearing  $12-15^\circ$  out of the cycle plane (Fig. 2). According to the analysis of coordination bond lengths in optimized bis-chelate structures, the size of the aliphatic chain has almost no effect on the structure of chelate cycles.



**Fig. 1.** Monoanionic structures of  $L^{a-e}$  ligand systems. Hereinafter, bond lengths and angles are given in Å and degrees, respectively; hydrogen atoms, except the hydroxyl atom, are omitted for clarity.



**Fig. 2.** Optimized geometries of  $CuL_2^{a,b,c}$  complexes. Hereinafter, hydrogen atoms are omitted for clarity.

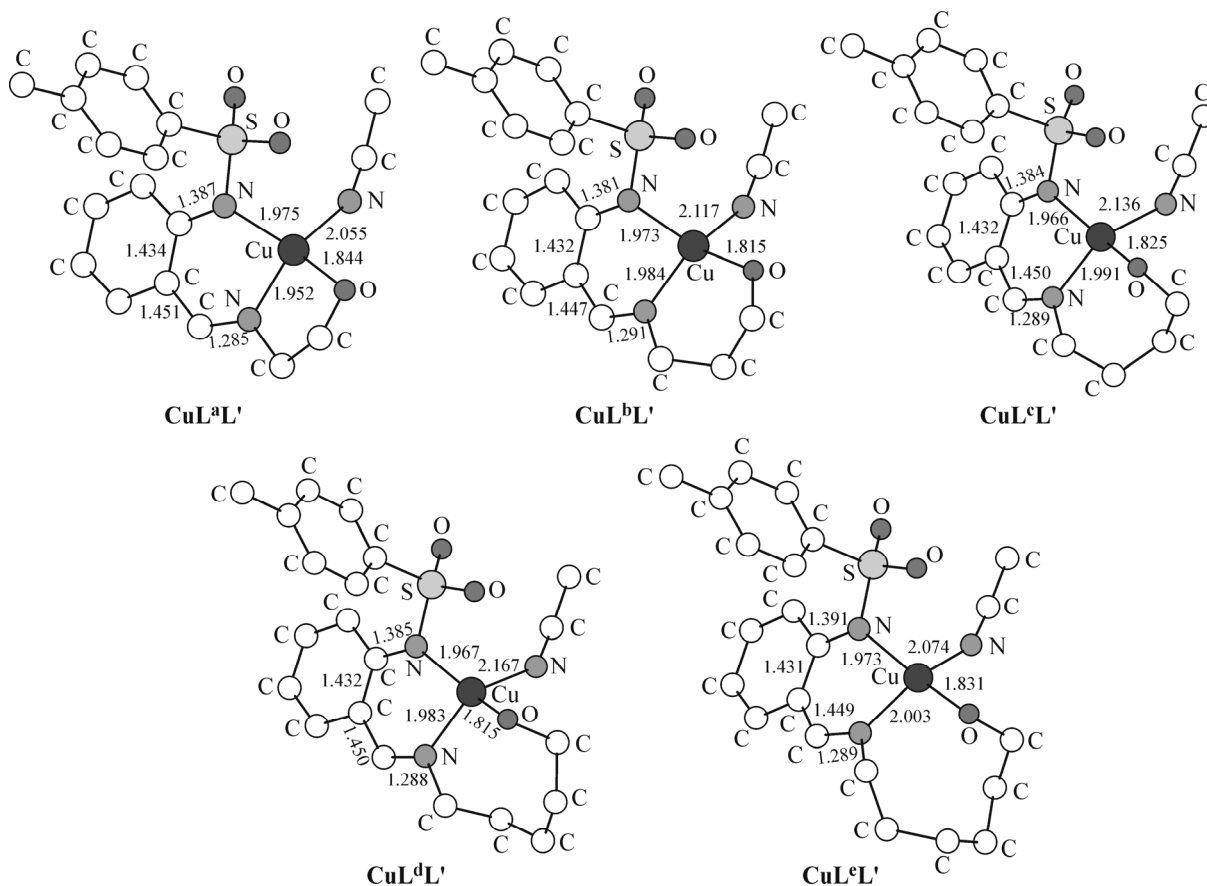


Fig. 3. Optimized geometries of  $\text{CuL}^{a-e}\text{L}'$  complexes.

Fig. 3 shows geometrical parameters of mononuclear  $\text{CuLL}'$  complexes where the fourth coordination site is occupied by an acetonitrile molecule ( $\text{L}'$ ). The Cu–O bond length varies from 1.815 Å (in  $\text{CuL}^b\text{L}'$  ( $n = 3$ ) and  $\text{CuL}^d\text{L}'$  ( $n = 5$ )) to 1.844 Å (in  $\text{CuL}^a\text{L}'$  ( $n = 2$ )). The parameters of the coordination bond between the metal atom and the nitrogen atom of the acetonitrile molecule vary from 2.055 Å (in  $\text{CuL}^a\text{L}'$ ) to 2.167 Å (in  $\text{CuL}^d\text{L}'$ ). Thus, variations of the number of links in the aliphatic chain of the ligand do not prevent the latter from exhibiting tridentate properties in mononuclear  $\text{CuLL}'$  complexes.

Increasing the number of methylene groups in  $\text{L}^{a-d}$  ligands enlarges the volume occupied by the coordination node. On the one hand, such changes can hinder the formation of binuclear structures. On the other hand, they sterically hinder the formation of a planar exchange fragment, so that antiferromagnetic bonding appears in copper complexes with oxygen bridges [35].

According to our calculations,  $\text{L}^a\text{--L}^c$  ligands and copper atoms can form together binuclear *cis*- and *trans*-structures containing intermetallic oxygen bridges. Fig. 4 shows calculated geometries of various forms of  $\text{Cu}_2\text{L}_2^a$ ,  $\text{Cu}_2\text{L}_2^b$ , and  $\text{Cu}_2\text{L}_2^c$  complexes. Interestingly, *trans*-isomers are most energy preferable in  $\text{Cu}_2\text{L}_2^a$  and  $\text{Cu}_2\text{L}_2^b$  compounds, while the  $\text{Cu}_2\text{L}_2^c$ -*cis* isomer becomes the ground state of the  $\text{Cu}_2\text{L}_2^c$  dimer due to the inversion of relative energies (see the Table).

The  $\text{Cu}_2\text{L}_2^d$  ( $n = 5$ ) structure is a loosely bound associate with a distance between metal atoms exceeding 4.00 Å (Fig. 5). According to the quantum chemical study of an adduct containing two acetonitrile molecules, the total energy of the  $\text{Cu}_2\text{L}_2^d \cdot 2\text{L}'$  dimer is 3.3 kcal/mol higher than the sum of energies of two  $\text{CuL}^d\text{L}'$  monomers. Note that the donor atom of the solvent molecule is directed towards the copper ions in the starting geometry of the above mixed-ligand complex whereas acetonitrile molecules in the optimized structure appear beyond the inner coordination sphere of the metal to indicate the

instability of such dimeric associate. This result suggests that the further increase of the number of links in the aliphatic chain of the ligands will prevent the formation of binuclear structures.

The conclusions derived from the above DFT calculations are confirmed by X-ray structural data (Fig. 6) which testify the dimeric structure of the **2b** complex based on the ligand with three methylene linkers [26].

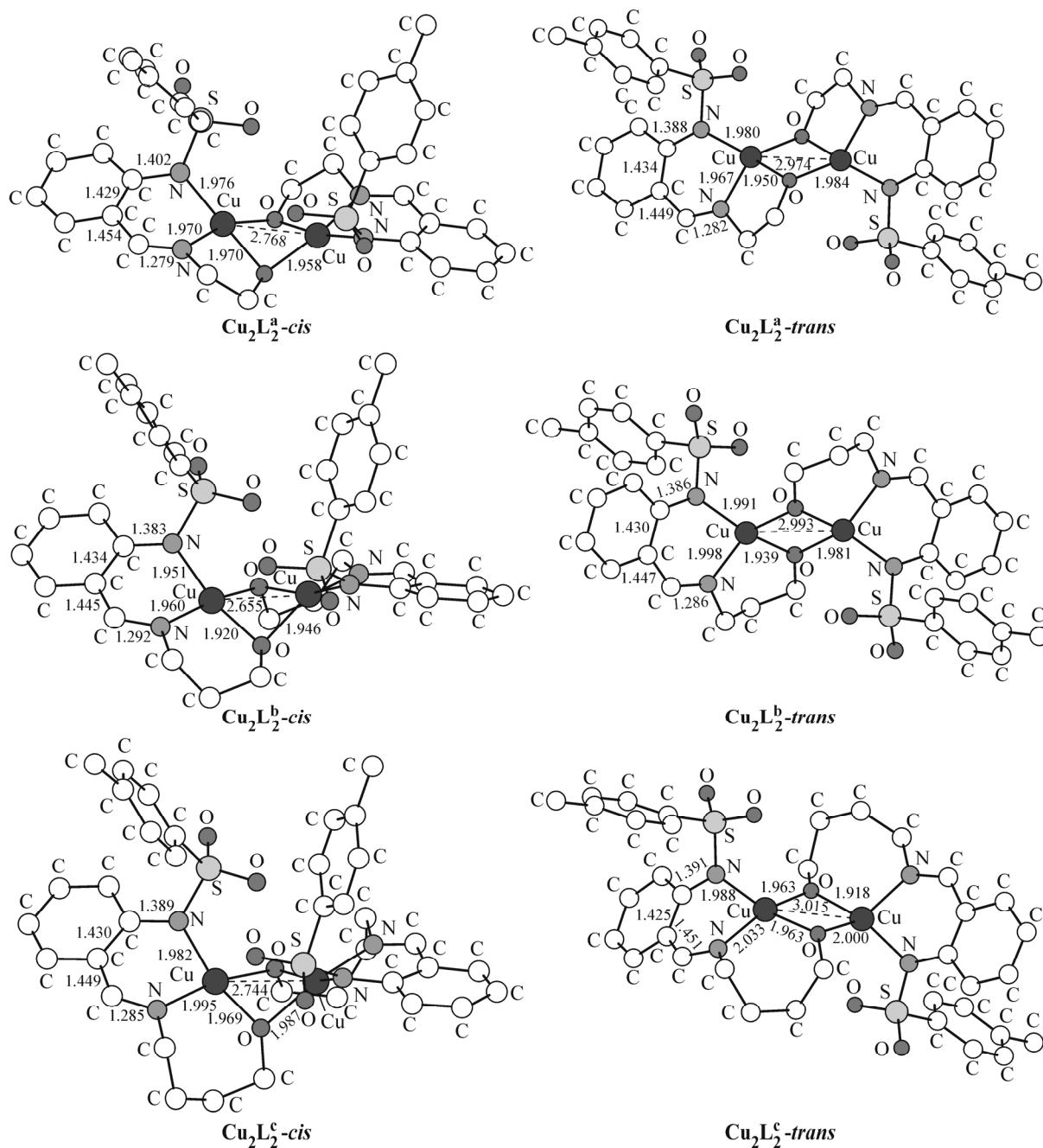
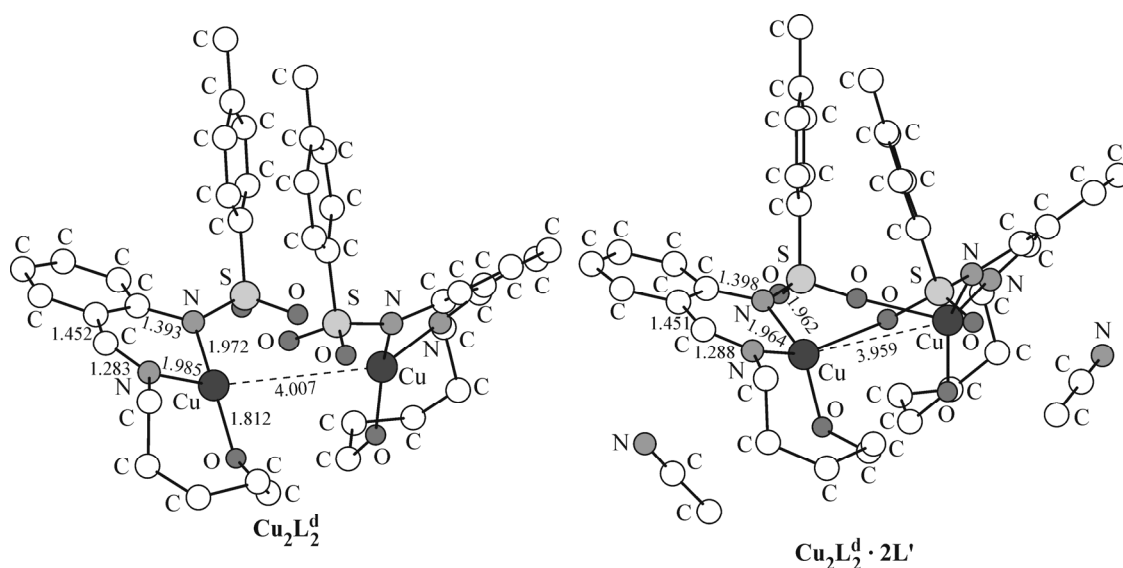


Fig. 4. Optimized geometries of binuclear complexes  $\text{Cu}_2\text{L}_2^a$ ,  $\text{Cu}_2\text{L}_2^b$ , and  $\text{Cu}_2\text{L}_2^c$ .

**TABLE 1.** Spin ( $S$ ), Total Energy ( $E$ , a.u.), Relative Energy ( $\Delta E$ , kcal/mol), Squared Spin Operator ( $S^2$ ), and the Exchange Interaction Parameter ( $J$ , cm<sup>-1</sup>) in  $\text{Cu}_2\text{L}_2$  ( $n = 2-4$ ) Complexes According to the DFT UB3LYP/6-311++G( $d, p$ ) Calculations

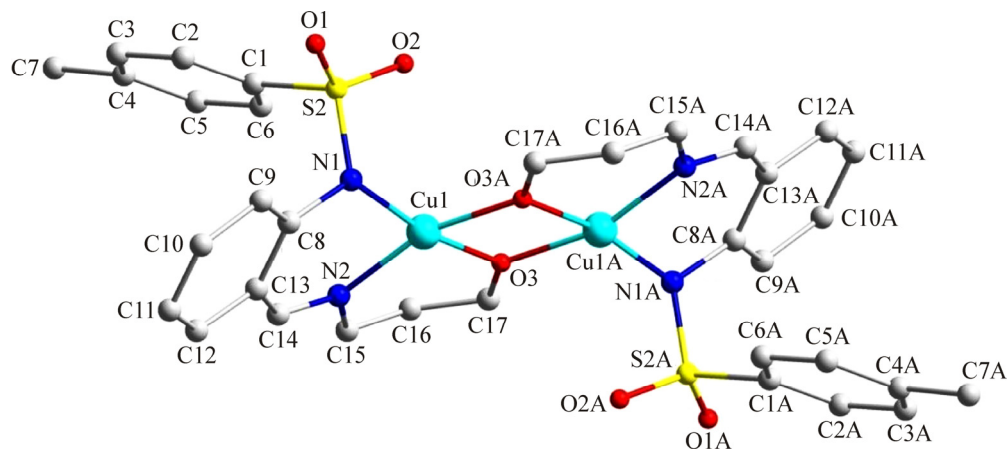
Structure	$S$	$E$	$\Delta E^*$	$S^2$	$J$
$n = 2$					
$\text{Cu}_2\text{L}_2^{\text{a}}\text{-cis}$	2/2	-5986.94025	–	2.007	-678
$\text{Cu}_2\text{L}_2^{\text{a}}\text{-cis BS}$	0	-5986.94351	–	0.950	–
$\text{Cu}_2\text{L}_2^{\text{a}}\text{-trans}$	2/2	-5986.94302	-1.7	2.006	-38
$\text{Cu}_2\text{L}_2^{\text{a}}\text{-trans BS}$	0	-5986.94319	–	0.991	–
$n = 3$					
$\text{Cu}_2\text{L}_2^{\text{b}}\text{-cis}$	2/2	-6065.59423	–	2.006	-150
$\text{Cu}_2\text{L}_2^{\text{b}}\text{-cis BS}$	0	-6065.59470	–	0.976	–
$\text{Cu}_2\text{L}_2^{\text{b}}\text{-trans}$	2/2	-6065.59583	-1.0	2.006	-96
$\text{Cu}_2\text{L}_2^{\text{b}}\text{-trans BS}$	0	-6065.59653	–	0.976	–
$n = 4$					
$\text{Cu}_2\text{L}_2^{\text{c}}\text{-cis}$	2/2	-6144.23090	–	2.006	-17
$\text{Cu}_2\text{L}_2^{\text{c}}\text{-cis BS}$	0	-6144.23098	–	0.992	–
$\text{Cu}_2\text{L}_2^{\text{c}}\text{-trans}$	2/2	-6144.22739	2.2	2.006	-724
$\text{Cu}_2\text{L}_2^{\text{c}}\text{-trans BS}$	0	-6144.22850	–	0.971	–

\*  $\Delta E$  are calculated with respect to the *cis*-isomer.



**Fig. 5.** Optimized geometries of the  $\text{Cu}_2\text{L}_2^{\text{d}}$  associate and the  $\text{Cu}_2\text{L}_2^{\text{d}} \cdot 2\text{L}'$  dimer.

The molecule of the  $\text{Cu}_2\text{L}_2^{\text{b}}$  complex in the crystal is a centrosymmetric structure. Two ligand molecules are tridentate coordinated to two copper(II) ions while two six-membered metallocycles get closed in each of the ligand fragments. The tosyl groups are in the *trans*-position relative to the plane of the  $\text{Cu}_2\text{O}_2$  exchange fragment. Coordination nodes  $\text{CuN}_2\text{O}_2$  are characterized by a highly distorted planar structure: the Cu(1) atom goes 0.0135(1) Å beyond the N(1)N(2)O(3) plane. In the case of a flat square, the largest deviations from the ideal values are exhibited by the O(3)–Cu(1)–



**Fig. 6.** Molecular structure of the binuclear complex  $\text{Cu}_2\text{L}_2^b$  in the smallest overlap projection (hydrogen atoms are omitted for clarity).

O(3A) angle ( $75.97(17)^\circ$ ) and the N(1)–Cu(1)–O(3) angle ( $99.11(18)^\circ$ ). In this case, all atoms of the  $\text{Cu}_2\text{O}_2$  exchange fragment belong exactly to the same plane.

Geometric parameters of the  $\text{Cu}_2\text{L}_2^b$ -*trans* structure calculated with the DFT UB3LYP/6-311++G(*d,p*) method agree well with those measured experimentally for  $\text{Cu}_2\text{L}_2^b$  [26]. The broken symmetry state has a lower total energy than the structure on the triplet PES, which is indicative of the antiferromagnetic nature of exchange interactions in the complex. The calculated value of the parameter  $J$  is  $-150\text{ cm}^{-1}$ . The conducted magnetochemical studies confirmed the predicted antiferromagnetic nature of the exchange interaction in the  $\text{Cu}_2\text{L}_2^b$  complex.

## CONCLUSIONS

Copper complexes of variable chelatability were studied using quantum chemical calculations. The structure of such compounds is shown to depend on the length of the  $(\text{CH}_2)_n$  spacer in azomethine ligands **L**. Binuclear structures  $\text{Cu}_2\text{L}_2$  with tridentate azomethines containing bridging oxygen atoms of alcohol groups are formed for  $n \leq 4$ . The elongation of the aliphatic chain leads to the formation of mononuclear bis-chelate complexes of composition  $\text{Cu}_2\text{L}$  or adducts  $\text{CuLL}'$  with a solvent (acetonitrile) molecule, the azomethine ligand coordinated in the tridentate position to the metal ion. The conclusions drawn from the computer simulation are confirmed by XRD data.

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## CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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