ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 8, pp. 616–620. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.G. Starikov, V.A. Kogan, V.V. Lukov, V.I. Minkin, R.M. Minyaev, 2009, published in Koordinatsionnaya Khimiya, 2009, Vol. 35, No. 8, pp. 625–629.

Influence of Structural Factors on the Magnetic Properties of the Binuclear Copper Complexes with Salicylaldehyde Hydrazone and Bis(hydrazone)-2,6-Diformylphenol: Quantum-Chemical Calculations

A. G. Starikov[a]*, V. A. Kogan[b], V. V. Lukov[b], V. I. Minkin[a,c], and R. M. Minyaev[c]

[a] *Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, Russia*

[b] *Southern Federal University, Rostov-on-Don, Russia*

[c] *Research Institute of Physical and Organic Chemistry, Southern Federal University, Rostov-on-Don, Russia*

** E-mail: andr@ipoc.rsu.ru*

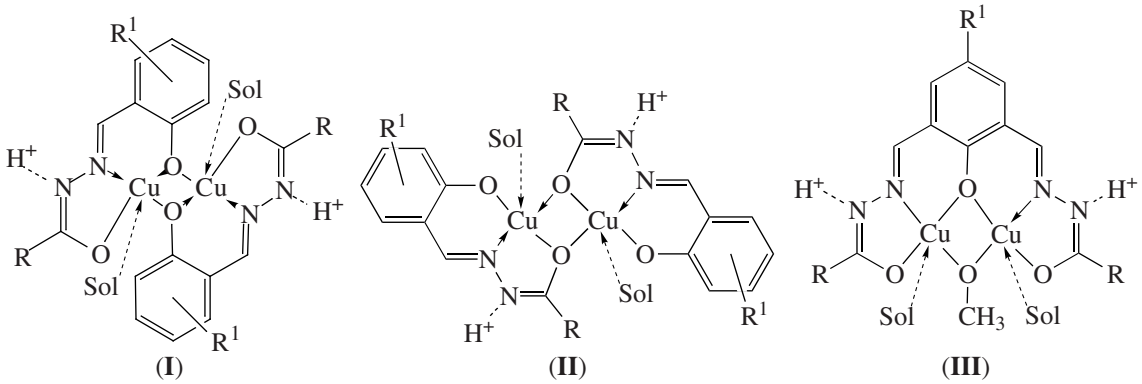
Received December 3, 2008

Abstract—The structures and magnetic properties of the binuclear copper complexes of salicylaldehyde mono- and bis(hydrazone) derivatives were studied by the quantum-chemical density functional theory (B3LYP/6-311^{++}g(*d,p*)) using the broken-symmetry technique. The change in the degree of deprotonation of the ligands was found to exert an insignificant effect on the magnetic properties, whereas the coordination of solvent molecules substantially weakened the antiferromagnetic interaction.

DOI: 10.1134/S1070328409080090

Investigation of magnetostructural correlations of polynuclear systems has recently attracted attention of researchers due to the development of new molecular magnetic materials [1, 2]. However, the theoretical study of the magnetic properties of these systems is difficult because of complicated quantum-chemical calculations, which is caused by the existence of many near-lying electron states. It has previously been shown [3] that the density functional theory (DFT) using the broken-symmetry technique [4] well describes the magnetostructural correlations and predicts rather reliably the influence of structural factors on the character of exchange interactions in these complexes. For instance, the magnetic behavior of the Cu(II) binuclear complexes with the hydroxo and alkoxo bridging groups was studied in detail [5, 6], and dependences were observed between the exchange interaction constant (**J**) and such parameters as the angle of the CuOCu bridging fragment, the Cu–O distance, and the shift of the substituents at the bridging oxygen atoms from the plane.

The experimental studies indicate [7, 8] that the binuclear copper complexes with salicylaldehyde mono- (**I**, **II**) and bis(hydrazone) (**III**) derivatives are characterized by the considerable antiferromagnetic exchange interaction



(**I**) (**II**) (**III**)

R = Alk, Ar; R^1 = Alk, Hal.

In this case, the ligands of the first type can form complexes that exist in two conformations and differ by the fact whether the phenoxide (**I**) or hydrazide (**II**) oxygen atom is included into the exchange fragment. An interesting feature of these complexes is the ability to coordinate solvent molecules and form both neutral and cationic complexes due to a change in the degree of deprotonation of the ligands, which can substantially change the magnetic properties.

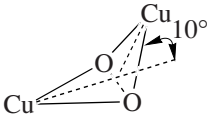
The purpose of this work is to study the influence of solvent coordination and the degree of deprotonation on the magnetic properties of the binuclear copper complexes with the salicylaldehyde mono- and bis(hydrazone) derivatives using the DFT B3LYP/6-311^{++}g(*d*,*p*) quantum chemical calculations [9] and the broken-symmetry technique. All simulations were performed using the Gaussian 03 program [10]. The geometry of molecular structures was completely optimized in order to find stationary points on the potential energy surface. The character of stationary points was determined by the calculation of the eigenvalues of the Hesse matrix. The structures related to the energy minima on the potential energy surface were determined by the fastest descent method (motion along the gradient line) from the saddle point to the adjacent stationary point [11].

The exchange interaction constant (***J***) were calculated using the broken-symmetry technique by the formula [12]

$$E_T - E_{BS} = -2J,$$

where E_T is the energy of the triplet state, and E_{BS} is the energy of the broken-symmetry state. The binuclear Cu(II) complexes with salicylaldehyde hydrazone are shown in Fig. 1.

The results of calculations for unsubstituted (R = R^1 = H) neutral complexes **I** and **II** with the doubly protonated ligands show that structure **IV** corresponds to he global minimum on the triplet potential energy surface (Fig. 1), and structure **V** isomeric to structure **IV** is destabilized by 4.8 kcal/mol (Table 1). The calculated 2*J* constant values for structures **IV** and **V** are –347 and –57 cm^{-1}, respectively, indicating the antiferromagnetic character of the exchange interaction. Structure **IV** is considerably bent along the O–O line of the exchange fragment, whose angle is 10°



The optimization of the geometry of the isomeric forms of the cationic complexes with the monodeprotonated ligand results in structure **VI** (Fig. 1), which is characterized by the turn of two parts of the molecule by an angle of 16° (along the O–O line of the exchange fragment) and destabilized (by 19.5 kcal/mol) with respect to planar structure **VII** (Fig. 1). The comparison

Table 1. Total energy (E_{tot}) of the triplet state, relative energy (ΔE), state energy (E_{BS}), and exchange interaction constant (2*J*) in structures **IV**–**IX** calculated by the DFT B3LYP/6-311^{++}g(*d*,*p*) method

Structure, symmetry	E_{tot}, au	ΔE, kcal/mol	E_{BS}, au.	2*J*, cm^{-1}
IV, C_2	–4418.23063	4.8	–4418.23221	–347
V, C_2	–4418.22300		–4418.22326	–57
VI, C_2	–4418.89270	19.5	–4418.89456	–408
VII, C_2	–4418.86170		–4418.86213	–94
VIII, C_2	–4649.77677		–4649.77799	–268
IX, C_i	–4650.46789		–4650.46900	–244
Experiment				–332

of the 2*J* values for the pairs of structures **IV**, **VI** and **V**, **VII** indicates a weak dependence of the magnetic properties of the complexes on their charges. The results obtained suggest that the formation of the complexes with the inclusion of the phenoxide oxygen atom into the exchange fragment is preferential regardless of the degree of protonation of the ligand. This coordination mode is confirmed by the X-ray diffraction data [13, 14], according to which solvent molecules are incorporated into the internal coordination sphere of these complexes. Solvates **VIII** and **IX** including two methanol molecules were calculated to study the influence of this process on the magnetic properties of the most stable forms **IV** and **VI**. The stabilization energy of structures **VIII** and **IX** is 10.1 and 28.4 kcal/mol, respectively. The complex formation is accompanied by the pyramidalization of the copper atoms and planarization of the exchange fragment, resulting in a substantial (more than by 100 cm^{-1}) decrease in the exchange interaction constants. The binuclear Cu(II) complexes with 2,6-diformylphenol bis(hydrazone) are shown in Fig. 2.

As shown by the results of calculations of complexes **III** (R = R^1 = H), structures **X** and **XI**, which differ only by the degree of deprotonation of the ligand, correspond to the minima on the triplet potential energy surface (Fig. 2). Their geometric characteristics indicate the predominantly planar structure of the considered complexes, except for the methoxy group shifting from the plane, which is consistent with the X-ray diffraction studies of similar structures [16]. It is noteworthy that the difference in the total charges of complexes **X** and **XI** does not affect their structural and electronic characteristics (Table 2, Fig. 2). The greatest changes are observed for the Cu–O bond lengths of the hydrazide fragment, being 0.04 Å.

The analysis of the NBO charges and spin density on the copper atoms and nitrogen and oxygen atoms that are adjacent to the copper atoms revealed no dependence of their values on the total charge of the complex. The calculated magnetic interaction constants

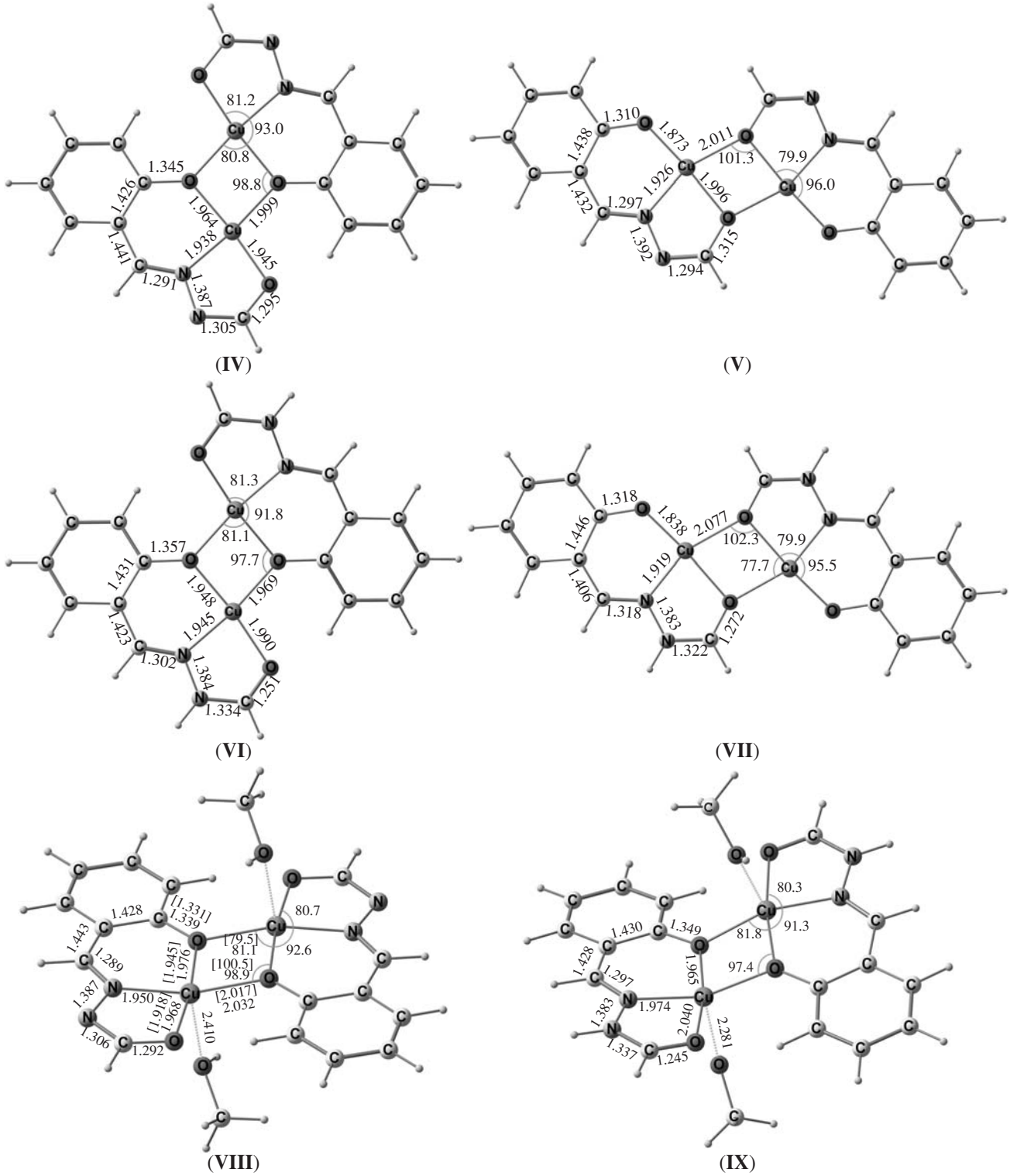


Fig. 1. Geometric characteristics of structures **IV–IX** (bond lengths are given in angström, angles are given in degrees, and the X-ray diffraction data [13] are presented in brackets).

of complexes **X** and **XI** are –500 and–564 cm^{-1}, which substantially exceeds the experimental value (–336 cm^{-1}) [17]. Evidently, the calculation of isolated structures **X** and **XI** does not allow their correct comparison with the X-ray diffraction data, according to which the complex includes two solvent molecules [15]. Structures **XII** and **XIII** were calculated to estimate the influence of methane molecule coordination

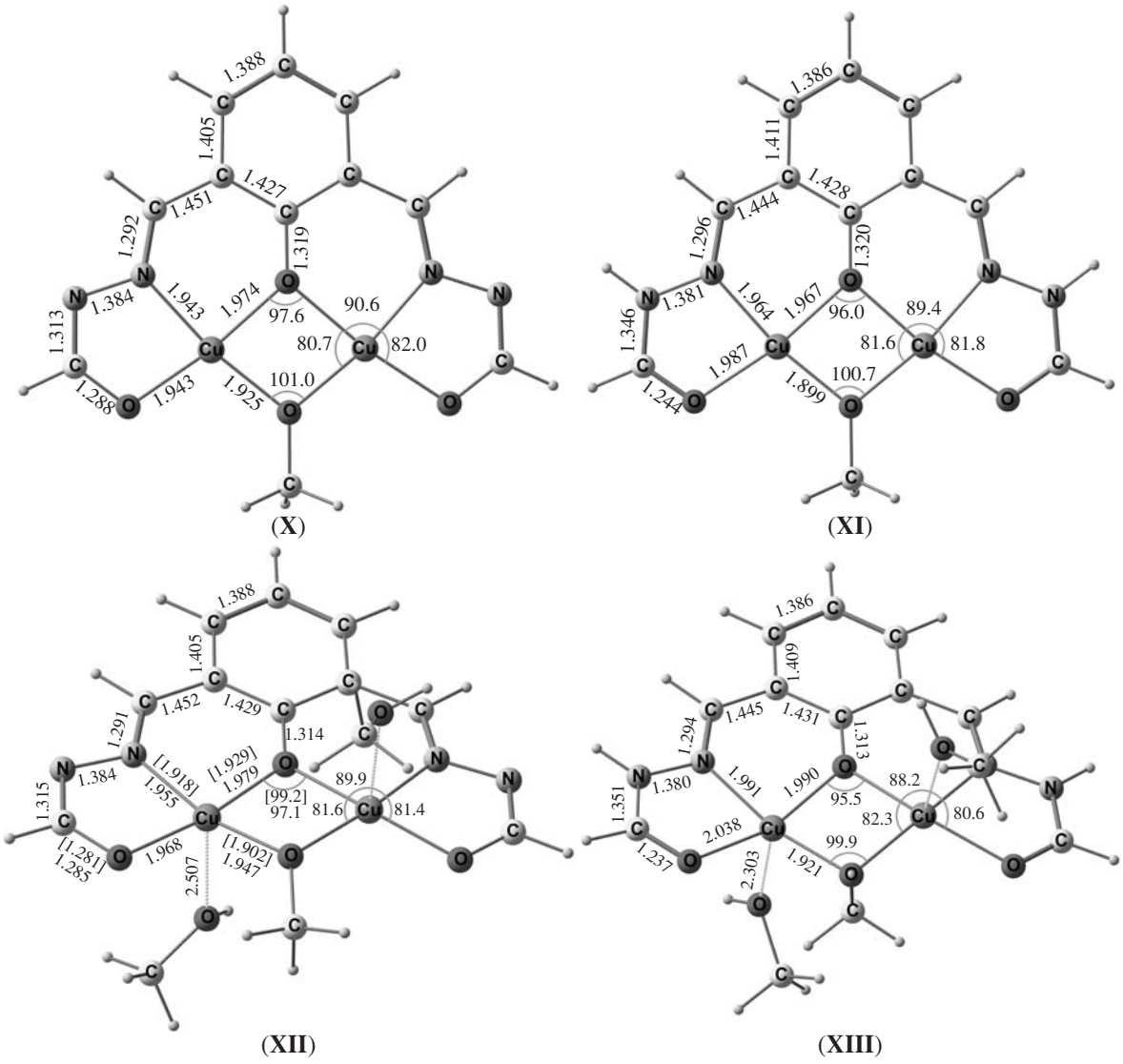


Fig. 2. Geometric characteristics of structures **X–XIII** (X-ray diffraction data [15] are presented in brackets).

on the magnetic properties of complexes **X** and **XI**. The energies of complex formation of structures **XII** and **XIII** are 8.6 and 28.9 kcal/mol, respectively, and this process is accompanied by the pyramidalization of the copper atoms due to an increase in the coordination number. These changes in the geometric characteristics of the complexes decrease the exchange interaction constants of structures **XII** and **XIII** to –342 cm^{-1}. This value agrees completely with the magnetochemical measurements.

Thus, the quantum-chemical DFT (B3LYP/6-31^{++}g(*d,p*)) study using the broken-symmetry technique of the structures and the magnetic properties of the binuclear copper complexes of the salicylaldehyde mono- and bis(hydrazone) derivatives suggests that the change in the degree of deprotonation of the ligands insignificantly affects the magnetic properties, whereas the coordination of solvent molecules substantially weakens the antiferromagnetic interaction. The calculation results are well consistent with the physicochemical data and confirm that they are adequate to the geometric model [18] developed earlier to predict the char-

Table 2. Total energy (E_{tot}) of the triplet state, state energy (E_{BS}), and exchange interaction constant (2*J*) in structures **X–XIII** calculated by the DFT B3LYP/6-311^{++}J(*d*, *p*) method

Structure, symmetry	E_{tot}, au	E_{BS}, au	2*J*, cm^{-1}
X, C_s	–4226.43138	–4226.43366	–500
XI, C_s	–4227.08440	–4227.08697	–564
XII, C_1	–4457.97503	–4457.97659	–342
XIII, C_1	–4458.66048	–4458.66204	–342
Experiment			–336

acter of the exchange interaction in the complexes of the considered type.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 09-03-00684) and the president of the Russian Federation (grant no. NSh 363.2008.3).

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