

XAFS Study of the Ferro- and Antiferromagnetic Binuclear Copper(II) Complexes of Azomethine Based Tridentate Ligands

Valery G. Vlasenko^{*†}, Igor S. Vasilchenko[†], Irina V. Pirog^{*}, Tatiana E. Shestakova[†], Ali I. Uraev[†], Anatolii S. Burlov[†], Alexander D. Garnovskii[†]

^{*}*Institute of Physics, Rostov State University, Stachki Ave., 194, 344090, Rostov-on-Don, Russia.*

[†]*Institute of Physical and Organic Chemistry, Rostov State University, Stachki Ave., 194/2, 344090, Rostov-on-Don, Russia.*

Abstract. Binuclear copper complexes are known to be models for metalloenzymes containing copper active sites, and some of them are of considerable interest due to their magnetic and charge transfer properties. The reactions of the complex formation of bibasic tridentate heterocyclic imines with copper acetate leads to two types of chelates with mono deprotonated ligands and with totally deprotonated ligands. Cu *K*-edge EXAFS has been applied to determine the local structure around the metal center in copper(II) azomethine complexes with five tridentate ligands: 1-(salicylideneimino)- or 1-(2-tosylaminobenzilideneimino)-2-amino(oxo, thio)benzimidazoles. It has been found that some of the chelates studied are bridged binuclear copper complexes, and others are mononuclear complexes. The copper-copper interatomic distances in the bridged binuclear copper complexes were found to be 2.85-3.01 Å. Variable temperature magnetic susceptibility data indicate the presence of both ferromagnetic and antiferromagnetic interactions within the dimer, the former is dominating at low temperatures and the latter at high temperatures.

Keywords: binuclear copper complexes, EXAFS, magnetic susceptibility.

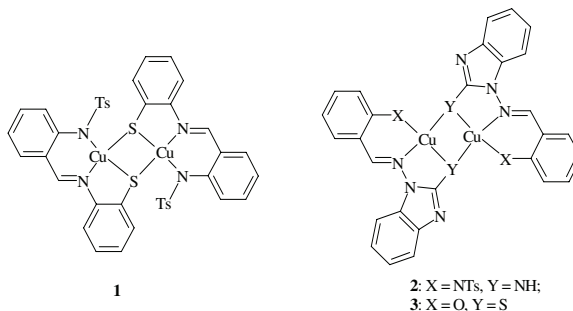
PACS: 61.10.Ht

INTRODUCTION

The binuclear copper active centers are important functional units in metalloproteins. Different members of metalloproteins of the type-3 with binuclear copper sites are known: hemocyanins, tyrosinase, catechol oxidase with bridging oxygen atoms and cytochrome *c* oxidase with bridging sulfur atoms. In most of these, copper is ligated by histidine and cysteine amino acids [1,2].

The binuclear Cu(II) center is diamagnetic due to strong antiferromagnetic coupling associated with a bridging atoms. The modeling of the natural active center of the metalloproteins is a general strategy for the best understanding of the structural details of the natural active sites of the enzymes and their reactivities. Among the model complexes with ferromagnetic exchange, coordination compounds of Schiff bases have an important place [3-5].

In the development of this area we have elaborated methods of synthesis of binuclear copper chelates based on tridentate azomethines containing N₄-, N₂S₂- and N₂OS-ligand environments with aromatic (**1**) or heterocyclic (**2**, **3**) coordination fragments.



In a recent paper [6], we presented the details of syntheses and magnetic characteristics of the complexes **1-3**.

One of the characteristic features of complex **1** is sufficient exchange interaction of antiferromagnetic type which, similar to other complexes containing the Cu₂S₂ fragment, for instance [7], leads to diamagnetism of the whole molecule. Compound **1** is diamagnetic both in the solid state (Faraday method) and in a solution of CDCl₃ (¹H NMR, Evans method). In this connection the ferromagnetic exchange interaction, which was detected for chelate **3** with the same sulfur bridging fragment, is highly unexpected.

Coordination compound **2**, with the bridging group Cu₂N₂, is also ferromagnetic. At the same time the intermolecular interactions in complexes **2** and **3** are also of ferromagnetic character. So, in [6] we for the

first time showed that the type of fragment, annealed to the bridging metallocycle, is the factor affecting the character of exchange interaction in dimeric molecules of copper azomethinic chelates.

In this paper, we present the results of the structural characterization of the binuclear copper complexes **1-3** by analysis of Cu *K*-edge EXAFS data.

EXPERIMENTAL

Synthesis of the above chelates was performed by half hour refluxing the 2-(2-tosylaminophenyl) benzothiazoline, 1-(2-tosylaminobenzilideneimino)-2-aminobenzimidazole or 1-(2-hydroxy benzilidene imino)-2-thiobenzimidazole with $[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]_2$ in methanol (**1**, **2**) or butanol (**3**).

The EXAFS spectra of the Cu *K*-edge for all the samples were obtained at the EXAFS Station of the Siberian Synchrotron Radiation Center (SSRC). The storage ring VEPP-3 with electron beam energy of 2 GeV and average stored current of 70–90 mA was used as the source of radiation. A cut-off monocrystal Si (111) was used as a monochromator. All the spectra were recorded in a transmission mode using two ionization chambers as detectors. EXAFS data were analyzed using the IFEFFIT data analysis package [8]. The radial pair distribution functions around the Cu atoms were obtained by the Fourier transformation of k^3 -weighted spectra over the range of wave numbers 2.8–12.0 Å⁻¹. The structural parameters (the interatomic distances, the coordination numbers and Debye–Waller factors) were determined by non-linear fits of theoretical spectra to experimental ones. Theoretical spectra were simulated by *ab initio* calculations of backscattering amplitudes and phases by means of FEFF7 [9]. Simulation was performed using the crystallographic data for complex **1**. The quality of fit was estimated from discrepancy factors (*Q*-factor).

RESULTS AND DISCUSSION

The Cu *K*-edge XANES spectra and their first derivatives for the binuclear copper complexes **1-3** are shown in Figure 1. The XANES spectra for all three complexes are very similar. It is seen that all the spectra show the pre-edge feature **A** located between 8974 and 8976 eV which is related to the dipole forbidden 1s→3d transition and due to mixing of metal 3d and 4p orbitals. The position and the intensity of features **B**, **C** and **D** are typical for dipole 1s→4p+L transitions and appear in previously published spectra of copper complexes [2]. The splitting of the first

derivative of the XANES spectra has been attributed to the tetragonal symmetry around the atom of the metal.

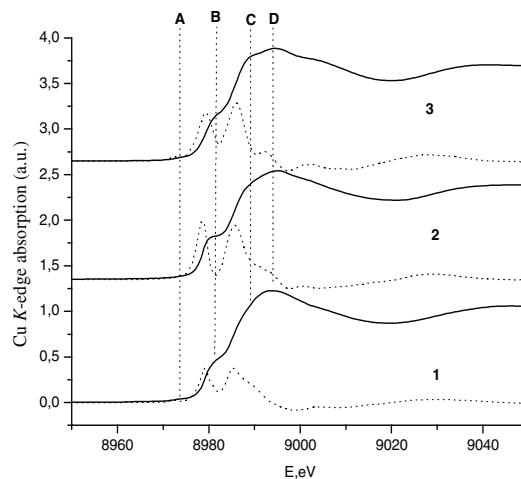


FIGURE 1. The Cu *K*-edge XANES spectra and their first derivatives for the binuclear copper complexes: **1** (**2**), **2** (**3**) and **3** (**1**).

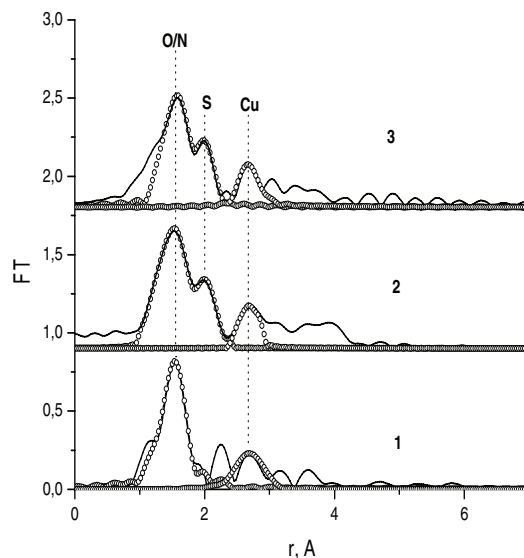


FIGURE 2. Fourier transforms of k^3 -weighted Cu *K*-edge EXAFS data (solid line) and simulations (circles) of the binuclear copper complexes **1** (**2**), **2** (**3**) and **3** (**1**).

TABLE 1. Structural features of the nearest atom environment of copper atom from the EXAFS data (R – interatomic distances, CN – coordination numbers, σ^2 – Debye-Waller factors)

Compound	CN	R, Å	σ^2 , Å ²	Donor atom	Q-factor ²
1	2	1.98 (1.941-1.990) ¹	0.0038	N	0.072
	1	2.19 (2.2086, 2.2188)	0.0043	S	
	1	2.32 (2.3391, 2.3457)	0.0037	S	
	1	2.66 (2.683)	0.0042	O	
	1	2.85 (2.8136)	0.0040	Cu	
2	2	1.97	0.0031	N	0.074
	2	2.00	0.0031	N	
	4	2.79	0.0044	C/N	
	1	3.01	0.0059	Cu	
3	2	1.94	0.0024	N/O	0.084
	1	2.24	0.0073	S	
	1	2.30	0.0079	S	
	1	2.92	0.0063	Cu	

¹Results of X-ray structural determination for complex **1** are given in parentheses

²Q-factor of fit over the range $r=1.0-2.4$ Å

The Fourier Transforms (FT) for free copper chelates over the $k=2.8-12.0$ Å⁻¹ are presented in Figure 2. For all the complexes, the first major peak in the FT is related to the first Cu coordination sphere, which contains four nitrogen atoms for complex **2** and two N/O atoms for complexes **1** and **3**. For the complexes **1** and **3** a second important peak appears at $r=2$ Å, which originates from the backscattering of two sulfur atoms of tridentate ligands coordinated to the copper atom. The smaller peak in the FT of all three complexes at $r=2.6$ Å is due to the presence of a copper atom, that suggests a binuclear structure of these compounds. For the complexes **1-3** the smaller peak in the FT was filtered and fits were performed. The results of these fits are given in Table 1. The bond lengths obtained are in good agreement with the crystallographic data.

Thus, the binuclear copper complexes formation follows from the EXAFS analysis. The presence of two sulfur atoms of the tridentate ligands leads to the short Cu-Cu bond length (2.85-2.92 Å), while the presence of nitrogen atoms in the bridging fragment results in the formation of a longer Cu-Cu bond length (3.01 Å). The Cu-Cu bond lengths found are reasonable for similar copper complexes with N/O or S bridges. The bridging concept has also been suggested as a superexchange path for a ferromagnetic coupling between two Cu(II) ions [6].

ACKNOWLEDGMENTS

Authors are grateful for financial support from the Program of Ministry of Education and Science of the Russian Federation (grant RNP.2.1.1.1875) and RFBR (grant 04-03-32366, 06-03-90892).

REFERENCES

1. E. I. Solomon, U. M. Sundaram and T.E. Machonkin *Chem. Rev.* **96**, 2563-2605 (1996).
2. E. Borghi and P. L. Solari, *J. Synchrotron Rad.* **12**, 102-110 (2005).
3. A. S. Burlov, A. S. Antsyshkina, J. Romero, D. A. Garnovskii, A. Garcia-Vazquez, A. Sousa, and A. D. Garnovskii, *Russ. J. Inorg. Chem.* **40**, 1427 (1995).
4. A. D. Garnovskii, and I. S. Vasilchenko, *Russ. Chem. Rev.* **74**, 193 (2005).
5. A. I. Uraev, V. N. Ikorskii, M. P. Bubnov, K. A. Lysenko, V. G. Vlasenko, I. G. Borodkina, G. S. Borodkin, D. A. Garnovskii and A. D. Garnovskii, *Russ. Journ. Coord. Chem.* **32**, 287-296 (2006).
6. A. I. Uraev, I. S. Vasilchenko *et.al. Mendeleev Commun.* 133-135 (2005).
7. S. Itoh, M. Nagagawa and S. Fukusumi, *J. Am. Chem. Soc.* **123**, 4087 (2001).
8. M. Newville, *J. Synchrotron Rad.* **8**, 322-324 (2001).
9. S. I. Zabinsky, J. J. Rehr, A. Kvik, A. Ankudinov, R. C. Albers and M. J. Eller, *Phys. Rev. B* **52**, 2995 (1995).