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ATOMIC STRUCTURE OF THE COPPER BROMIDE COMPLEX BASED ON BENZOIN 1′-PHTHALAZINYLHYDRAZONE: DFT AND X-RAY ABSORPTION SPECTROSCOPY ANALYSIS

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A copper bromide complex based on benzoin 1′-phthalazinylhydrazone is synthesized. Within density functional theory (OPBE/TZP) the optimal structural parameters of the complex are determined. X-ray Absorption Near-Edge Structure (XANES) spectra above the *K* absorption edge of copper are measured in the copper bromide complex. Theoretical XANES spectra of the *K* absorption edge of copper are calculated based on the full multiple scattering method and in the full potential of the finite difference method. Good agreement between the theoretical XANES spectrum and the experimental data is obtained.
Keywords: atomic structure, density functional theory, XANES spectroscopy.

INTRODUCTION

Constant interest to hetarylhydrazones and transition metal complexes based on them is due to the possibility of the practical use of these compounds. Hydrazones and their complexes are widely applied, in particular, as catalysts, dyes, analytical reagents and pesticides [1-4]. We should specially note high biological activity that the compounds of this class show: hypotensive, antituberculous, antitumoral, antiviral, antibacterial, and psychotropic [5-10]. Owing to the structural features of hetarylhydrazones, it is easy to vary their structure, and a large number of donor centers allow the targeted synthesis of both mono- and polynuclear complexes of different composition and structure depending on conditions.

We have previously obtained and described copper(II) complexes based on benzoin(1′-phthalazinyl)hydrazone of type *1* [11] (Fig. 1).

In this work, we show that in the interaction of hydrazone *1* with copper(II) acetate, a binuclear complex of the composition Cu_2L_2 forms, where L is the twice deprotonated form of the ligand. In the presence of copper(II) halides, the ligand is oxidized by metal ions with the formation of complexes of monovalent copper of type *2* (X = Cl, Br) with the general formula $C_{15}H_{10}ClCuN_4O$ and $C_{15}H_{10}BrCuN_4O$ respectively.

The present work is devoted to the analysis of the structure of type *2* compound (X = Br) within density functional theory and X-ray absorption near-edge structure (XANES) spectroscopy.

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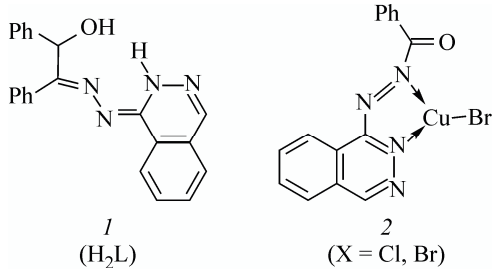

Fig. 1. Chemical formula of type *1* hydrazone and type *2* complexes.

EXPERIMENTAL

Benzoin 1′-phthalazinylhydrazone *1* was synthesized by the following procedure [11]: to a hot 0.01 mol 1-hydrazinophthalazine hydrochloride suspension in 50 ml of methanol a hot 0.01 mol benzoin solution was added. In 5 min an equivalent amount of sodium acetate was added to the mixture, after which a bright yellow precipitate started to form. The reaction mixture was boiled for 3 h and left overnight. The formed precipitate was filtered off, twice washed with warm water and then by hot methanol. It was recrystallized from a methanol–DMF mixture (2:1).

Yield 65%. Amorphous bright yellow powder. $T_m = 218°C$. Elemental analysis: gross formula $C_{22}H_{18}N_4O$; calculated (%): C 74.6, H 5.12, N 15.8; found (%): C 73.7, H 4.99, N 16.1.

Copper bromide complex based on benzoin 1′-phthalazinylhydrazone *2*. To a hot 0.001 mol hydrazone *1* suspension in 5 ml of methanol a hot metal salt solution of 0.001 mol $CuBr_2$ was added. The reaction mixture was boiled for 4 h. The formed precipitate was filtered off, washed with hot methanol.

Yield 42%. Yellow precipitate. $T_m > 250°C$. Elemental analysis: gross formula $C_{15}H_{10}BrCuN_4O$; calculated (%): C 44.4, H 2.48, N 13.8; Cu, 15.7; found (%): C 43.9, H 2.7, N 14.2, Cu 15.4.

^{1}H NMR and IR spectroscopy data for compounds *1* and *2* are given in the work [11].

In this work, we first measured the XANES spectrum above the *K* absorption edge of copper of the title compound. Measurements were performed on the Structural Material Science Station of the Kurchatov Center of Synchrotron Radiation and Nanotechnologies [12]. The Sibir'-2 storage ring worked with the energy of 2.5 GeV with an average current of 70 mA. For monochromatization of the synchrotron radiation (SR) beam a single crystal Si[111] monochromator was used. The absorption spectra were measured in transmission mode. A fine layer of the sample powder was uniformly spread over adhesive film that was several times folded to achieve the optimal absorption coefficient and a jump on the corresponding absorption edge. X-ray beam intensities before and after the sample were measured by means of two ionization chambers filled with nitrogen and argon and connected to Keithley digital picoampermeters. The energy scanning step in the XANES region was 0.3-0.4 eV; point integration time was 2 s.

CALCULATION PROCEDURE

The geometric structure of the copper bromide complex based on benzoin 1′-phthalazinylhydrazone was optimized using the ADF2009 program package [13-18] resting upon Kohn–Sham density functional theory (DFT). The initial structure of the $C_{15}H_{10}BrCuN_4O$ copper complex was obtained as a result of the geometric modeling with the use of standard bond lengths and bond angles.

Calculations were made in the generalized gradient approximation (GGA) with the OPBE exchange-correlation functional [19] involving the OPTX exchange [20] and PBEc correlation [21] parts. This functional was selected because as recently shown [22], its application results in the correct prediction of the properties of transition metal compounds. The calculations were performed with the use of a triple-zeta basis set of the Slater type extended by polarization functions.

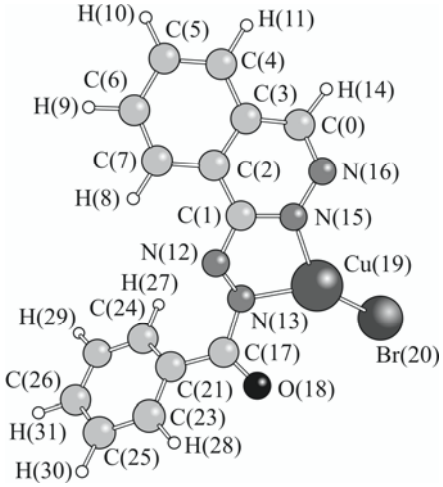

Fig. 2. Spatial structure of the $C_{15}H_{10}BrCuN_4O$ complex.

The ADF package has previously been successfully used to analyze the atomic structure and electronic properties of compounds based on copper (see, for instance, the works [23, 24]).

A theoretical analysis of the XANES spectrum above the *K* absorption edge of the $C_{15}H_{10}BrCuN_4O$ complex was carried out by the finite difference method using the FDMNES2009 program package [25]. One of the advantages of this method is the possibility to perform calculations in the full potential without the *muffin-tin* approximation [26] for the shape of the molecular potential, which is used in a number of modern program packages for calculations of X-ray absorption spectra (e.g., in the FEFF8.4 program package [27, 28]). At the same time, the importance of computations being performed in the full potential (beyond the *muffin-tin*-approximation for the potential shape) in calculating XANES spectra has been shown for some nickel and cobalt complexes [29-31].

Cu *K*-XANES spectra were calculated with the use of the exchange-correlation potential of the Hedin–Lundqvist type. Calculations were carried out with allowance for a core vacancy induced by the electronic transition.

RESULTS AND DISCUSSION

As noted above, the initial structure of the copper bromide complex based on benzoin 1′-phthalazinylhydrazone was selected by the geometric modeling. In the next stage of the study, the full optimization of the geometric structure of the complex was performed using the ADF2009 program. The spatial structure of the $C_{15}H_{10}BrCuN_4O$ complex is shown in Fig. 2. Table 1 lists the Cartesian atomic coordinates of the complex obtained as a result of the optimization. Tables 2 and 3 summarize the information on the selected geometric parameters of the complex: bond lengths and bond angles respectively.

The obtained structure of the copper bromide complex based on benzoin 1′-phthalazinylhydrazone was then used to calculate the XANES spectra. The theoretical X-ray absorption spectrum above the *K* absorption edge of copper were calculated based on the full multiple scattering method within the *muffin-tin* approximation for the shape of the molecular potential (FEFF8.4 program) and the full potential finite difference method (FDMNES2009 program). A molecule of the title complex consists of 32 atoms. The XANES spectrum was modeled using the FEFF8.4 program for a cluster involving all 32 atoms (cluster radius of 8 Å). Since the calculations based on the full potential finite difference method require substantially larger computational resources, the Cu *K*-XANES spectrum was calculated using the FDMNES2009 program code for the atomic cluster surrounding the copper atom, which consisted of 16 atoms (the cluster radius around the absorbing copper atom was 5 Å).

Fig. 3 illustrates a comparison of the experimental XANES spectrum above the *K* absorption edge of copper of the title complex (curve *1*) with the theoretical spectra calculated using two program codes: FEFF8.4 (curve *3*) and

TABLE 1. Cartesian Atomic Coordinates of the $C_{15}H_{10}BrCuN_4O$ Complex Obtained as a Result of the Geometric Optimization

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(0)	0.2621	2.9147	0.9497	H(11)	–1.0346	5.3103	1.2864	C(22)	–3.9488	–2.6985	1.2797
C(1)	–1.1969	0.7445	1.5321	N(12)	–1.8082	–0.4056	1.9128	C(23)	–3.3827	–3.9541	3.2716
C(2)	–1.8731	2.0027	1.6104	N(13)	–1.2176	–1.4648	1.4719	C(24)	–5.2456	–3.1971	1.3420
C(3)	–1.0773	3.1476	1.3646	H(14)	0.9054	3.7434	0.6552	C(25)	–4.6856	–4.4274	3.3437
C(4)	–1.6483	4.4308	1.4759	N(15)	0.1258	0.6631	1.2567	C(26)	–5.6173	–4.0554	2.3749
C(5)	–2.9785	4.5602	1.8173	N(16)	0.8183	1.7286	0.8811	H(27)	–3.6639	–2.0371	0.4648
C(6)	–3.7671	3.4198	2.0532	C(17)	–1.5924	–2.6475	2.2039	H(28)	–2.6385	–4.2520	4.0065
C(7)	–3.2316	2.1522	1.9438	O(18)	–0.6758	–3.2530	2.7251	H(29)	–5.9684	–2.9189	0.5764
H(8)	–3.8351	1.2709	2.1435	Cu(19)	0.6981	–1.2124	0.8977	H(30)	–4.9743	–5.0971	4.1530
H(9)	–4.8124	3.5396	2.3346	Br(20)	2.4558	–2.3826	0.0345	H(31)	–6.6359	–4.4397	2.4228
H(10)	–3.4236	5.5501	1.9048	C(21)	–3.0068	–3.0789	2.2430				

TABLE 2. Selected Optimal Bond Angles in the Type *2* Complex (X = Br)

Bond angle	Deg
N(13)–Cu(19)–Br(20)	140.9
N(15)–Cu(19)–Br(20)	140.5
N(13)–Cu(19)–N(15)	78.1
C(1)–N(15)–Cu(19)	112.0
N(12)–C(1)–N(15)	116.5
C(1)–N(12)–N(13)	113.2
N(13)–C(17)–O(18)	115.5
C(21)–C(17)–N(13)	120.1
N(12)–N(13)–Cu(19)	115.4

TABLE 3. Selected Optimal Bond Lengths in the Type *2* Complex (X = Br)

Bond length	Å	Bond length	Å
Cu(19)–Br(20)	2.281	N(12)–N(13)	1.290
Cu(19)–N(15)	1.993	C(1)–N(15)	1.353
N(13)–Cu(19)	2.015	N(12)–C(1)	1.356
Cu(19)–O(18)	3.065	N(13)–C(17)	1.441
N(15)–N(16)	1.325	C(17)–O(18)	1.216

FDMNES2009 (curve *2*). It is seen that the spectrum calculated using the FEFF8.4 code is not consistent with the experiment: the theoretical spectrum does not reproduce, for instance, a feature designated as *A* in the low energy region. At the same time, the calculations performed by the FDMNES2009 code well agree with the experimental data. A reason for the unsatisfactory agreement between the experiment and the theoretical spectrum calculated using FEFF8.4 is the *muffin-tin* approximation implemented in this program for the shape of the molecular potential. Similar results have recently been obtained in the analysis of the X-ray absorption spectra above the *K* absorption edge of nickel in some planar nickel complexes, e.g. $Ni(EtOCS_2)_2$ [29]. In the Ni *K*-XANES spectra calculated with allowance for the *muffin-tin* approximation for the potential shape, the fine features of the low-energy regions of XANES spectra were not reproduced. The analysis performed in this work once again shows the importance of calculating XANES spectra for loosely packed structures

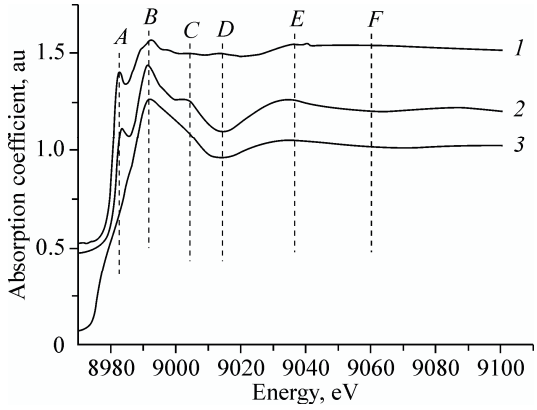

Fig. 3. Comparison of the experimental X-ray absorption spectrum above the *K* absorption edge of copper in the $C_{15}H_{10}BrCuN_4O$ complex (*1*) with the theoretical spectra calculated in the full potential (*2*) and with allowance for the *muffin-tin* potential shape (*3*).

(to which the copper bromide complex based on benzoin 1′-phthalazinylhydrazone belongs) in the full potential (above the *muffin-tin* approximation for the shape of the molecular potential).

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