

Investigation of Polycrystalline Copper(II) Chloride–1.5-Dimethyltetrazole Complex Compound with X-ray Absorption Spectroscopy

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Abstract—The polycrystalline copper(II) chloride–1.5-dimethyltetrazole (CuCl_2L , where L is 1.5-dimethyltetrazole) complex compound is investigated with the methods of extended x-ray absorption fine-structure (EXAFS) and x-ray absorption near-edge structure (XANES) spectroscopy at the *K* absorption edge. The data on the complex structure are compared to the results of x-ray diffraction study.

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INTRODUCTION

This study is only a part of the systematic investigation into complex compounds of the transition metals with substituted tetrazoles. These compounds are of interest by and a large due to their thermodynamic, photochromic, ferromagnetic, and other properties; they can be employed in many uses [1]. To predict their properties and to find methods of their synthesis, one needs to investigate their spatial and electronic structures. X-ray diffraction study and wave-mechanical computations are the principal ways of structural investigations. However, in a number of cases, of interest is the employment of x-ray absorption spectroscopy, viz., EXAFS and XANES spectra, which provide data on the local electronic structure of an adopted type [2]. The EXAFS spectra make it possible to obtain such structural parameters as interatomic distances, coordination number, and the Debye–Waller temperature factor and to determine the type of atoms adjacent to an absorbing atom. The fine structure of absorption spectra within an XANES region provides a way of investigation into the nature of a chemical bond in a compound. The analysis of these spectra is of considerable importance in investigating solutions, amorphous substances, and chemical compounds when single crystals of them suited for the x-ray diffraction study are difficult to produce.

In this paper, copper(II) chloride–1.5-dimethyltetrazole (CuCl_2L , where L is methyltetrazole) complex compound (complex I) is studied by the methods of

EXAFS and XANES spectroscopy. Its space group shown in Fig. 1 was studied with x-ray powder diffraction [3, 4]. The need for the storage, analysis, and generalization for the data on investigation of complex compounds with transition metals and substituted tetrazoles has arisen due to the lack of data on x-ray absorption spectra of these compounds in the literature.

EXPERIMENTAL

Synthesis of Complex I

The compound was synthesized by the interaction of solutions of 1.5-dimethyltetrazole in methanol–diethyl ether mixture and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in methanol. This procedure is fully considered in [3]. To control the presence of crystalline and amorphous impurities, the synthesized finely crystalline powder specimen of complex I was analyzed by x-ray diffraction analysis, infrared spectroscopy, and elementary analysis.

Recording and Processing of EXAFS and XANES Spectra

The x-ray absorption spectrum of the complex I was recorded at room temperature in the range of the CuK absorption edge with the use of the VEPP-3-type storage ring created at the Siberian Center of Synchrotron Radiation in the Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences.

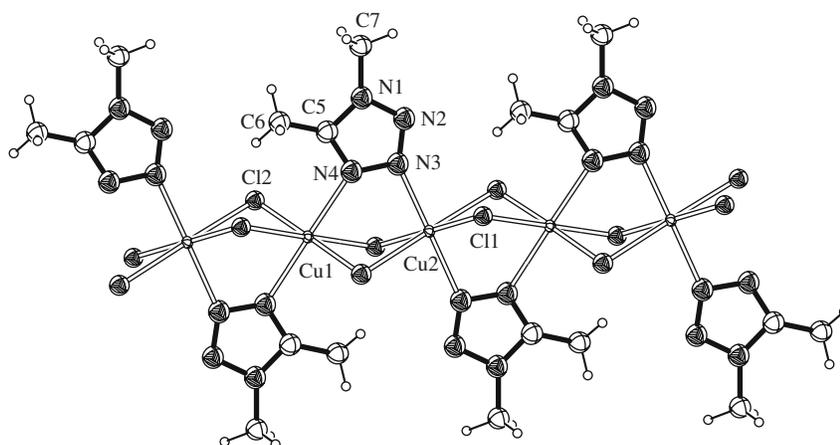


Fig. 1. Structural fragment of complex I. Atoms of an asymmetrical cell are numbered.

In the process of measurements, the operation conditions were as follows: energy of 2 GeV and current of 80 mA. X-ray radiation intensity was measured in front of and back of a specimen with two ionization chambers filled by a Ar–He mixture; the hatched monolithic silicon Si(111) single crystal was employed as a monochromator. The test specimen was prepared in the form of a homogeneous pressed pellet. The specimen thickness was arranged in line with the x-ray absorption jump equal to 0.8–1.0. The x-ray absorption spectrum was recorded within the energy range between 8920.0 and 9818.6 eV scanning by a step of 1.5 eV. An EDA software package [5, 6] was used to process the obtained experimental results.

The near fine structure of x-ray absorption (XANES) was found by subtracting the background $\mu_{\text{bgd}}(E)$ from the experimentally found absorption coefficient $\mu_{\text{exp}}(E)$. The background was obtained for the short-wave spectral region from the *K* absorption edge and extrapolated into the long-wave region, and then the absorption coefficient was normalized on the side of the long-wave region. The XANES spectrum

obtained and its energy derivative $d\mu_{\text{exp}}(E)/dE$ are presented in Fig. 2.

The partial densities of *p* and *d* states of two structural fragments for complex I related to two nonequivalent positions of copper atoms Cu1 and Cu2 were calculated to interpret the XANES spectrum. The calculations were performed with the use of a FEFF8.2 software package [7] in the approximation of the total multiple scattering for clusters of size down to 6.81 Å. They comprise the fragments of the crystalline structure of the copper(II) chloride–1.5-dimethyltetrazol complex compound (that is, CuCl_2L) [3, 4]. A cluster of the maximum size includes 68 atoms positioned around an absorbing atom of copper (Cu1 or Cu2). The self-consistent potential of the clusters was calculated in the muffin-tin approximation with 15-percentage overlapping for the potentials of adjacent atoms. The exchange-correlation effects were taken into account through the utilization of the Hedín–Lundquist complex potential [8]. The process of absorption of an x-ray quantum by a copper atom was calculated in the dipole approximation for the transition $1s \rightarrow np$ ($\Delta l = 1$); the total relaxation of all electronic levels in the presence of a hole at ground state $1s$ was taken into account. The obtained results are given in Fig. 3.

The EXAFS component $\chi(k)$ (Fig. 4a) was determined [2] from the equation given by

$$\chi(k) = [\mu_{\text{exp}}(E) - \mu_{\text{bgd}}(E) - \mu_0(E)]/\mu_0(E),$$

where $\mu_0(E)$ is the atomic absorption coefficient for a long-wave region from the absorption edge, $k = [2m_e(E - E_0)/\hbar^2]^{1/2}$ is the wave number of a photoelectron, m_e is the electron mass, \hbar is Planck's constant, and E_0 is the reference point for the kinetic energy of a photoelectron. The value of E_0 defines a zero energy of a photoelectron ($k = 0$); therefore, the choice of E_0 is the key point, because it exerts an influence on the accuracy of determination of interatomic distances. In this paper, the value of E_0 is taken to be equal to 8989.83 eV, which

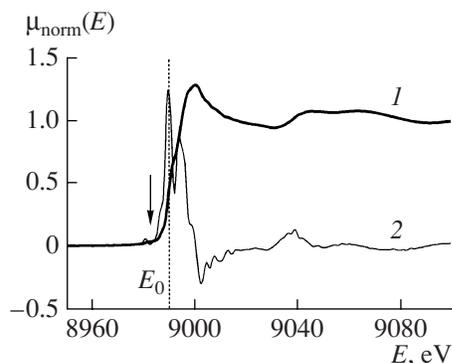


Fig. 2. Experimentally obtained XANES spectrum with CuK edge of complex I (1) and its first derivative $d\mu/dE$ (2). The position of the preedge peak is shown by the arrow.

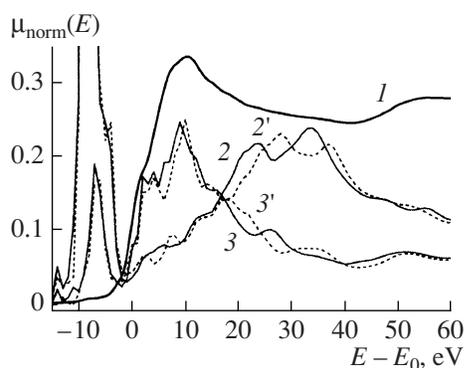


Fig. 3. Experimentally obtained XANES spectrum in the vicinity of CuK edge for complex I (1) and calculated partial densities of d states (2, 2') and p states (curves 3, 3') for copper. Curves 2 and 3 are calculated for Cu1 atom, curves 2' and 3' are calculated for Cu2 atom.

is in agreement with the maximum value of the first derivative of the absorption coefficient and shows the best agreement between the calculated and experimentally found EXAFS spectra.

The separated EXAFS component $\chi(k)k^2$ and its Fourier transform calculated within the range of $k = 0.3\text{--}13.0 \text{ \AA}^{-1}$ with the use of the Keizer–Bessel (window) function are shown in Fig. 4b. Note that the peak positions in the Fourier transform differ from the crystallographic values by the value of the phase shift, depending on the sort of absorbing and scattering atoms. Next, the contribution of atoms of the first coordination sphere around the copper atom, that is, two nitrogen atoms and four chlorine atoms, was estimated with the procedure of the inverse Fourier transform within the range of $R = 0.6\text{--}2.7 \text{ \AA}$ (Fig. 4b).

Simulating the EXAFS spectrum with allowance made for the first coordination sphere around a copper atom was performed in the range of $k = 2.5\text{--}11.0 \text{ \AA}^{-1}$ in the single-scattering approximation [2] in the form of

$$\chi(k) = \sum_i N_i S_0^2 (kR_i)^{-1} f(k, R_i)$$

$$\times \exp(-2\sigma_i^2 k^2) \sin[2kR_i + \varphi(k, R_i)],$$

where notation i denotes the group of N_i atoms spaced at an interval of R_i ; σ_i is the Debye–Waller factor, equal to the root-mean-square (rms) relative displacement of atoms; S_0^2 is the scale factor, allowed for the many-electron effects (in this paper, $S_0^2 = 1$); and $f(k, R_i)$ and $\varphi(k, R_i)$ are the rms scattering amplitude and the phase shift, respectively, which were calculated with the use of the FEFF8.2 software package [7]. The structure parameters R_i and σ_i were found with the nonlinear optimization technique [5, 6]: we were striving to achieve the best agreement between the theoretical and experimental EXAFS spectra (Fig. 5). The obtained data are presented in the table.

RESULTS AND DISCUSSION

The investigations performed using x-ray diffraction analysis reveal that complex I is a chain coordination polymer [3, 4]. Figure 1 presents the structure of a polymer chain and numbering of atoms in an asymmetric cell that comprises two nonequivalent copper atoms Cu1 and Cu2. They both are positioned in the center of symmetry. The coordination polyhedrons with copper atoms are extended octahedrons with chlorine atoms in axial sites; two chlorine atoms and two nitrogen atoms occupy equatorial sites. Copper atom Cu1 is linked only to atoms N4 of the tetrazole row, copper atom Cu2 is linked only to atoms N3. The table lists data [3, 4] on the copper atom coordination environment.

XANES Spectra

A normalized XANES spectrum of the CuK edge for complex I is presented in Fig. 2. A plot of the derivative $d\mu/dE$ shows a weak preedge peak at $E = 8983 \text{ eV}$.

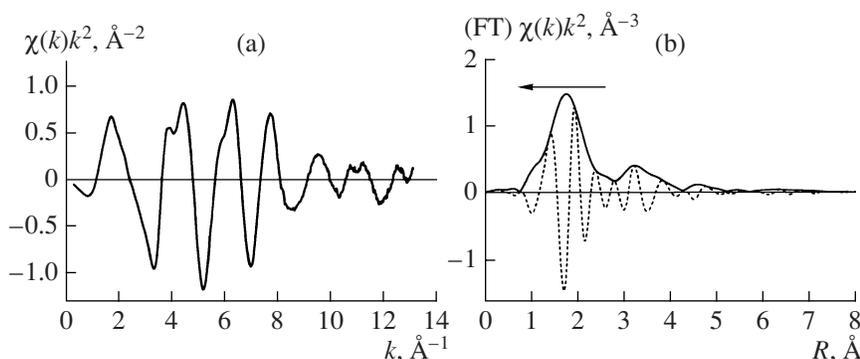


Fig. 4. Experimentally obtained EXAFS spectrum $\chi(k)k^2$ with CuK absorption edge of complex I (a) and its Fourier transform (FT) $\chi(k)k^2$ (b); module of the Fourier transform is depicted by a solid line, its imaginary part is depicted by a dashed line. The region of the first coordination sphere is shown by a horizontal line.

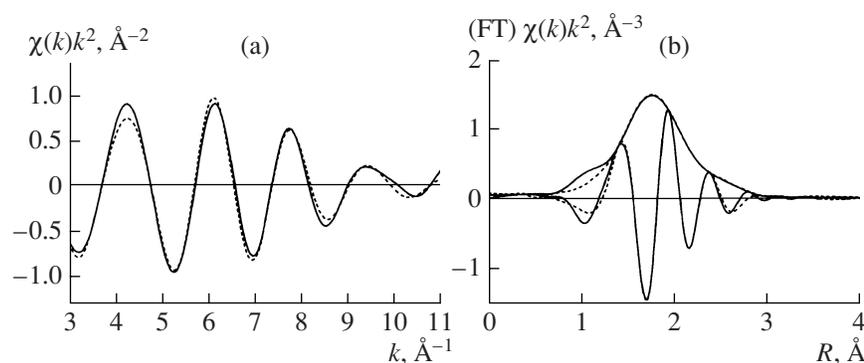


Fig. 5. A comparison between experimentally obtained EXAFS spectrum for the first coordination sphere of copper atom in complex I in terms of $\chi(k)k^2$ (solid lines) and the same spectrum calculated for optimized parameters (dashed lines) (a); and (b) a comparison between their Fourier transforms (FT) in terms of $\chi(k)k^2$ (module and imaginary part of FT are shown).

This peak may be assigned to the electron transition from the $1s$ energy level of copper to a free energy level of the complex, which is formed with the participation of $3d$ state of a copper atom ($1s \rightarrow 3d$ transition). Low intensity of the preedge peak derives from the fact that this transition is forbidden in the dipole approximation; this situation is in agreement with a distorted centrosymmetrical octahedral coordination of copper atoms in the complex crystal structure [3, 4].

We calculated the partial densities for p and d states of copper in complex I for clusters of two sizes with a center at the copper atom. A large-sized cluster involves 69 atoms, and a small-sized one involves six atoms of the first coordination sphere. According to the calculations, a consideration of the first coordination sphere only makes it possible to reproduce the general shape of the XANES spectrum in the vicinity of the absorption edge; however, to simulate the spectrum in more detail, one should take into consideration a cluster of a greater size. The experimental XANES spectrum of the CuK edge for complex I is related to the calculated partial densities of the p and d states of a copper for two large-sized clusters corresponding to copper atoms Cu1 and Cu2 (Fig. 3). As is seen, the p state density reproduces the main features of the experimental XANES spectrum. This correlates with the universally accepted

explanation of the spectrum when the $1s \rightarrow 4p$ transition is invoked. The difference in contribution from two nonequivalent copper atoms Cu1 and Cu2 is seen at an energy of about 20 eV above the absorption edge.

Comparing the densities of the p and d states in the region of the preedge peak (Fig. 3), one can notice their severe overlapping. This is expressed in the partial removal of prohibition on the transition $1s \rightarrow 3d$. Thus, the origin of the preedge peak is an involved question and correlated, just as with the true quadrupole transition $1s \rightarrow 3d$, with the dipole one into a hybridized pd state. In addition, the intensity of the preedge peak is a function of the extent to which the $3d$ state of copper atom Cu(II) is completed. One may expect that a charge transfer from ligands to a copper atom out of the covalent bonds Cu–Cl and Cu–N results in a decrease of the number of the free $3d$ states and a drop in the intensity of the preedge peak.

EXAFS Spectra

The experimentally obtained EXAFS spectrum $\chi(k)k^2$ and its Fourier transform (FT) $\chi(k)k^2$, calculated in the range of $k = 0.3\text{--}13.0 \text{ \AA}^{-1}$, are shown in Fig. 4. Three peaks with rapidly declining amplitude are visible in the Fourier-transform curve, which suggests that

A comparison between the structural parameters of complex I obtained from EXAFS spectrum and those from the results of x-ray diffraction analysis

Data from [3, 4]		Results of simulation of EXAFS spectrum			
Bond	$R, \text{ \AA}$	Bond	N	$R, \text{ \AA}$	$\sigma^2, \text{ \AA}^2$
Cu1–N4	2.248(10)	Cu–N	2	2.08 ± 0.02	0.005 ± 0.001
Cu2–N3	2.155(12)				
Cu1–Cl2	2.233(5)	Cu–Cl _{eq}	2	2.27 ± 0.02	0.008 ± 0.001
Cu2–Cl1	2.231(5)				
Cu1–Cl1	2.768(5)	Cu–Cl _{ax}	2	2.69 ± 0.02	0.014 ± 0.002
Cu2–Cl2	2.829(5)				

intense static and/or thermal disordering occurs. The first peak in the vicinity of 1.8 Å corresponds to the structural contributions of six atoms of the nearest surrounding, namely, two nitrogen atoms and four chlorine ones, which are immediately bound to an absorbing copper atom [1, 2]. The isolated contribution of the first coordination sphere with copper atoms to the EXAFS spectrum and its theoretical analog corresponding to the values of the optimized parameters of R_i and σ_i (see table) are presented in Fig. 5a; the corresponding Fourier transforms are shown in Fig. 5b.

As a whole, the values of interatomic distances obtained from the EXAFS spectrum are close to these of x-ray diffraction analysis. The best agreement is observed for the distances between Cu and Cl_{eq} in the equatorial plane of the coordinate octahedron; the values obtained by the two methods agree within 3σ . The Cu–Cl_{ax} distances and the Cu–N distances show worse agreement, namely, within about 6σ . Overlapping of the first and second peaks in the experimental curves of the Fourier-transform may be among the reasons for the observed discrepancy. The overlapping makes difficult their correct separation: the accuracy of revealing the contribution of the first coordination sphere to the function $\chi(k)k^2$ is lowered. Moreover, the presence of two nonequivalent copper atoms Cu1 and Cu2 adds complexity to the situation as well.

CONCLUSIONS

As a whole, the results of the investigations into the EXAFS and XANES spectra in the region of the CuK absorption edge for complex I are consistent with the x-ray diffractometry data. Peak positions and intensities in the spectra correlate with the structure characteristics and the nature of surrounding atoms. The subsequent

accumulation and generalization of the data on x-ray absorption spectra of tetrazole complex compounds will make it possible to extend the application of this information in chemistry and structure chemistry of this type of compounds.

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