Identification of different coordination geometries by XAFS in copper(II) complexes with trimesic acid

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ABSTRACT

X-ray absorption spectroscopy (XAS) is very useful in revealing the information about geometric and electronic structure of a transition-metal absorber and thus commonly used for determination of metal-ligand coordination. But XAFS analysis becomes difficult if differently coordinated metal centers are present in a system. In the present investigation, existence of distinct coordination geometries around metal centres have been studied by XAFS in a series of trimesic acid Cu(II) complexes. The complexes studied are: $Cu_3(tma)_2(im)_6$ $8H_2O$ (1), $Cu_3(tma)_2(mim)_6$ $17H_2O$ (2), $Cu_3(tma)_2(tmen)_3$ $8.5H_2O$ (3), $Cu_3(tma)$ $(pmd)_3$ $6H_2O$ $(ClO_4)_3$ (4) and $Cu_3(tma)_2$ $3H_2O$ (5). These complexes have not only Cu metal centres with different coordination but in complexes 1–3, there are multiple coordination geometries present around Cu centres. Using XANES spectra, different coordination geometries present in these complexes have been identified. The variation observed in the pre-edge features and edge features have been correlated with the distortion of the specific coordination environment around Cu centres in the complexes. XANES spectra have been calculated for the distinct metal centres present in the complexes by employing ab-initio calculations. These individual spectra have been used to resolve the spectral contribution of the Cu centres to the particular XANES features exhibited by the experimental spectra of the multinuclear complexes. Also, the variation in the 4p density of states have been calculated for the different Cu centres and then correlated with the features originated from corresponding coordination of Cu. Thus, these spectral features have been successfully utilized to detect the presence of the discrete metal centres in a system. The inferences about the coordination geometry have been supported by EXAFS analysis which has been used to determine the structural parameters for these complexes.

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1. Introduction

Copper plays vital roles in the active sites of several enzymes essential for human health. The coordination geometry of copper at these sites is important as it is related to the biological functions of these enzymes. The two major tools for determining protein structure are X-ray crystallography and nuclear magnetic resonance (NMR) [1]. However, there is often no direct and quantitative structural information on coordination of the metal. The activity of coordination compounds is affected by many factors like the nature of the group substituted to the basic ligand, type of metal and environment around metal cation [2]. Out of these, some properties can be accurately described by combined extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) analysis. The interpretation of both the XANES and EXAFS spectral regions allows complementary evaluation of metal oxidation state, coordination geometry and short range distance information [3]. XAFS is a powerful tool for determining the geometric and electronic structure of a transition-metal absorber and has been successfully applied for the identification of different coordination geometries present in a sample [4–13].

Kau et al. [4] have correlated Cu K-edge XANES features of Cu(I) and Cu(II) model compounds and complexes with oxidation state and geometry. These features have been used to determine quantitatively the oxidation states of the copper sites in type 2 copper-depleted (T2D) and native forms of the multicopper oxidase, Rhus vernicifera laccase. Aquilanti et al. [5] have studied the coordination of metal core of copper(II) complexes containing N_2S_2 macrocyclic

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ligands by EXAFS spectroscopy due to the intrinsic difficulty of growing appropriate crystals for these complexes. For investigating their biological activity, Pellei et al. [6] have reported the synthesis and characterization of copper(II) complexes of nitroimidazole and glucosamine conjugated heteroscorpionate ligands. Gandin et al. [7] have determined the molecular structure of Cu(I) phosphine complexes by EXAFS analysis and also showed a significant in vitro antiproliferative activity for these Cu(I) complexes against several human cancer cell lines derived from solid tumors. In another study, Drzewiecka et al. [8] have used XAFS to determine the geometry of metal–ligand interaction for Cu(II) complexes synthesized from derivatives of benzofuran carboxylic acid. Presence of square planar and tetragonal pyramidal geometry around Cu has been established. Similarly, Klepka et al. [10] have studied three Cu(II) complexes with carboxylic acids using XAFS and found that Cu(II) cation is present in four coordinated square planar, five coordinated tetragonal pyramidal and six coordinated tetragonal-bipyramidal geometries in the three different complexes, respectively. Further, Wolska et al. [11] have studied cobalt and copper complexes prepared with the derivatives of the cinnamic acid. Using XAFS, it has been shown that cobalt complex forms a six fold octahedron coordinated by four carboxylate groups and two water molecules and copper complex has fourfold square-planar geometry with two monodentate carboxylate groups and two aqua ligands. Thus the technique of XAFS has been frequently used for determination of metal-ligand coordination. However, in the case of existence of distinctly coordinated metal centers in a specimen, the XAFS analysis becomes difficult due the averaging of spectral features exhibited by these different coordination.

The present study deals with the XANES analysis of different geometries around copper atoms in five Cu(II) complexes which is supported by EXAFS analysis. Ab-initio XANES computations have been performed with the FEFF code to simulate the electronic structure and the spectral XANES features of Cu atoms. In case of multinuclear complexes having differently coordinated metal centers, the contributions from the two different geometries have been carefully obtained in the samples to provide a convenient reproduction of the experimental spectral features. It has been shown that variation in p-density of states (DOS) of Cu atom due to a peculiar coordination gives rise to specific features observed in the calculated XANES spectra of these Cu centers.

The complexes studied by XAFS at the Cu K-edge are: $Cu_3(tma)_2(im)_6\ 8H_2O$ (**1**), $Cu_3(tma)_2(mim)_6\ 17H_2O$ (**2**), $Cu_3(tma)_2(tmen)_3\ 8.5H_2O$ (**3**), $Cu_3(tma)\ (pmd)_3\ 6H_2O\ (ClO_4)_3$ (**4**) and $Cu_3(tma)_2\ 3H_2O$ (**5**) (where tma, im, mim, tmen, pmd = Trimesic acid, Imidazole, Methy imidazole, Tetramethylethane-1,2-diamine, Pentamethyl diethylene triamine). These complexes have been identified as potential systems for studying differently coordinated Cu centers as the Cu(II) complexes of carboxylic ligands show diverse stereochemistry. The different modes of coordination of carboxylate compounds have been confirmed by the structural studies of their metal complexes [14]. Complex **1** and **2** have Cu^{2+} in distorted trigonal bipyramidal as well as in distorted square pyramidal geometry [15], complex **3** has Cu^{2+} in square pyramidal and distorted octahedral geometry [16], complex **4** has square planar Cu coordination [17] and Complex **5** has Cu^{2+} in pseudo octahedral geometry [18]. Thus, these complexes have not only Cu metal centres with different coordination but in complexes **1**–**3**, there are two types of coordination geometries present around Cu centres. Fig. 1 shows the different coordination geometries present in these complexes.

The aim of the present work is to identify these different coordination geometries with the help of XAFS. For this, the variation in the XANES features (pre-edge and edge features) have been observed with the change in coordination environment of different Cu centres present in the complexes **1**–**5**. Ab-initio calculations

have been used to generate XANES spectra for the complexes **1**–**5**. As the XAFS spectra of complexes **1**, **2** and **3** have contribution from the differently coordinated Cu centres, therefore individual XANES spectra have been generated for these Cu centres present in a single complex. These calculated XANES spectra have been used to check the contribution of Cu centres to the corresponding XANES features observed in the experimental spectra of the complexes. Also, corresponding p-density of states (DOS) have been simultaneously calculated and then correlated with the features observed in calculated spectra due to peculiar coordination of Cu. Further, EXAFS analysis has been done to observe the variation of structural parameters related to the different Cu coordination in these complexes.

2. Experimental

Standard methods cited in the literature [15–18] have been used to prepare and characterize the copper complexes. Complexes in powder form (solid state) were used to prepare absorption screens in the form of pellets. The beamline BL8 of the SLRI, Thailand [19] has been used for recording XANES and EXAFS separately. Synchrotron X-rays photon energy was scanned by a Ge(220) double crystal monochromator to excite the samples in the K-edge XANES and EXAFS regions of copper. XANES spectra of the samples and pure standards (copper foil, CuO, $Cu(CH_3COO)_2$, $CuSO_4$) were collected at Cu K-edge using transmission mode. The X-ray absorption is given by $ln(I_0/I_t)$, where I_t is the transmitted photon intensity after the standard. XANES spectra of Cu metal foil were collected simultaneously for calibration. The energy was calibrated by assigning the first inflection point of the Cu foil spectrum to 8980.3 eV. In order to check the reproducibility of the monochromator position, at least three runs were taken for each sample. The uncertainty in the determination of edge-energy was found to be ±0.1 eV.

3. Data analysis

3.1. Ab-initio calculations using FEFF9

Ab initio XANES calculation have been performed for the complexes **1**–**5** by using computer code FEFF9. In FEFF9 [20,21], ab initio self-consistent real-space Green's function (RSGF) approach has been used including inelastic losses, core-hole effects, vibrational amplitudes, etc. The polarization dependence, core-hole effects, and local field corrections are based on self consistent, spherical muffin-tin scattering potentials. The atomic structure that indicates the position of all the atoms in the lattice is required as input for using FEFF9. For the complexes **1**–**5**, the available crystal structure (Table S1) is used to generate the input file for the FEFF9 calculations. The input files for the FEFF calculations have been generated using the ATOMS module available in the IFEFFIT package [22]. In the present ab-initio calculations, Hedin–Lundqvist potential was chosen and XANES, SCF (Self-Consistent Field) and FMS (Full Multiple Scattering) cards were used.

3.2. EXAFS analysis

The EXAFS data of these five complexes have been analyzed by using the available computer software packages Athena and Artemis [22]. The program Athena was first used in order to process the raw data. The processing included the removal of smooth background from the measured absorption coefficient data, normalization of the X-ray absorption coefficient by the edge step and Fourier transform of the resultant spectrum from k-space (k is photoelectron wave number) to R-space. Artemis program was