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EXAFS spectra using synchrotron radiation of Cu (II) complexes

Samrath Ninama[1], A Mishra[2]

[1]Kasturbagram Rural Institute, Kasurbagranm Indore [MP] 452020, India
[2]School of Physics, Vigyan Bhawan, Devi Ahilya University, Indore - 452001, India

E-mail: samrathn@gmail.com

Abstract: EXAFS analysis of Cu (II) complex as a ligand of 2-methyl-3-[(bis-aniline(R) phenyl]-3H-1, 5 benzodiazepine. Extended X-ray absorption fine structure (EXAFS) spectra have been recorded at the K-edge of Cu (II) using the energy dispersive EXAFS beam line at 2.5GeV Indus - 2 synchrotron source at RRCAT, Indore, India. A theoretical EXAFS data analysis is also carried out by Fourier analysis of experimental EXAFS data of the copper (II) complexes. This analysis includes details of the Fourier transform of the data and the extraction of metal-ligand bond length. Bond lengths determined from data analysis methods are compared with the bond lengths obtained from several other known techniques, namely, Levy's, Lytle's and Lytle, Sayers and Stern's (LSS) methods. These data have also been calibrated by derivative method and bond lengths have also been obtained from Fourier transformation method and the results have been compared with the each other. The EXAFS data have been analyzed using the computer software *Athena*.

1 Introduction

In the present work, the X-ray absorption spectra have been recorded at the K-edge of copper macro-cyclic complexes. The coordination chemistry of macro-cyclic ligand is a fascinating area of research. The extended X-ray absorption fine structure (EXAFS) spectroscopy is an effective technique for selectively investigating the local coordination environment around the metal active site of complexes. The EXAFS K-edge of Cu (II) complexes were recorded at 8980 eV and also determined the bond length between metal-ligand of four complexes namely

(a)Cu1- Cu(II)2-methyl-3[(bis-ortho nitophenyl)]-3H 1, 5 benzodiazepine chloride.
(b)Cu2-Cu(II)2-methyl-3[(bis-meta nitrophenyl)]-3H 1, 5 benzodiazepine chloride.

A method for determining the metal-ligand bond length by an appropriate Fourier analysis of the K-edge data has been presented. This is illustrated by a detailed analysis of the data for a series of metal organic based on pyridine ligand systems, which model active centers of natural copper containing metal proteins [1]. The Fourier transform of the experimental EXAFS data is done using the FEFFIT program [2] and metal-ligand bond length is determined. This is open source program for flexible data reduction/fitting engine that can be used directly in command line mode or called by external programs. *Athena* has nine integrated graphical interfaces that use IFEFFIT for most of the numerical calculations. The noticeable advantage of this technique is that the X-ray absorption spectroscopy may be used as a bulk probe to investigate the surface effects. In particular, the technique permits the analysis of buried interfaces systems that are difficult to be analyzed even with more sophisticated surface investigation equipment. Applications of EXAFS can be found in literature on a variety of fields, namely, chemical reactions at the solid state [3], surface treatments [4] and structural studies of thin films [5].A structural analysis of X-ray

absorption fine structure (XAFS) spectroscopy has been used for a local structural refinement on an atom of interest [6]. In general, the small pre-edge peaks of the K-edge absorption spectra for transition metal compounds have been assigned to the transition from 1s to nd orbital, even though it is a dipole forbidden transition. Since the transition is very sensitive to chemical environment, the pre-edge feature in XAFS studies has been used to infer the local structure around the central atom. Some molecular orbital calculation studies have been reported that the pre-edge peak intensity is related to 3d and 4p orbital mixing by perturbation of site symmetry and increases gradually with the departure from a centro-symmetric environment [7]. In this context, the extended X-ray absorption fine structure (EXAFS) spectra have provided many quantitative structural characterizations such as inter-atomic distance, coordination number and Debye-Waller factor [8]. Since the EXAFS refinement does not depend on the long-range order of atomic arrangement and is very sensitive to atomic local sites, it is a powerful technique for local structural analysis of partially substituted inorganic compounds.

EXAFS spectroscopy is a useful method for determining the local structure around a specific atom in disordered systems. This technique provides information about the coordination number, the nature of the scattering atoms surrounding a particular absorbing atom, the inter-atomic distance between the absorbing atom and the backscattering atoms and Debye–Waller factor. The measurements are done with high energy X-rays, which are normally generated by synchrotron radiation sources. The data analysis is facilitated by specially developed program packages suitable for evaluation purposes. EXAFS spectroscopy is employed in several fields for a variety of applications [9-10].

2.1 Methodology
Copper Complexes have been prepared by chemical root method. The chemicals used are of pure grade.
2.2. EXAFS Spectra Recording at Indus-2 Beamline
The complexes were finely powdered and then absorption screens were prepared by carefully spreading calculating amount of the powdered on 1 cm area of kapton tape. The Copper K-edge EXAFS spectra of these absorption screens have been recorded at BL-8 dispersive EXAFS beamline at 2GeV Indus -2 synchrotron radiation source at Raja Ramanna Center for Advanced Technology (RRCAT), Indore, India [12-14]. Schematic diagram describing basic principal of the beam line is shown in figure 1. The beam line has 460 mm long Si (111) crystal having 2d value equal to 6.2709A^o mounted on an elliptical bender, which can bend the crystal to take shape of an ellipse [15].The elliptical optics offers maximum aberration. The radiation transmitted through the sample is detected by a positive-sensitive CCD detector having 2048×2048 pixels. The whole absorption spectrum can be recorded simultaneously in even a few microseconds for a rich sample. The beamline has a resolution of 1 eV at the photon energies of 10keV. The plot of absorption *versus* photon energy is obtained by recording intensities I_o and I_t, as the CCD outputs, without and with sample, respectively. Using the relation $I_t=I_o\,e^{-\mu x}$, where μ is the absorption coefficient and x is thickness of the absorber. For recording the EXAFS spectrum on the dispersive EXAFS beamline, the crystal bender and the goniometer have been set to cover the energy range of the Copper K-edge absorption spectra.
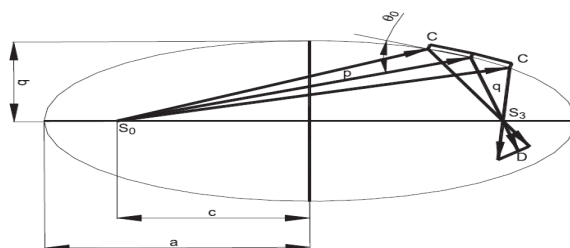
Figure 1 Schematic showing the working principle of the dispersive EXAFS beamline   (BL-8) at Indus - 2 Synchrotron facilities, Indore, India.

Table 1. Values of first shell bond length (in Å) for copper complexes

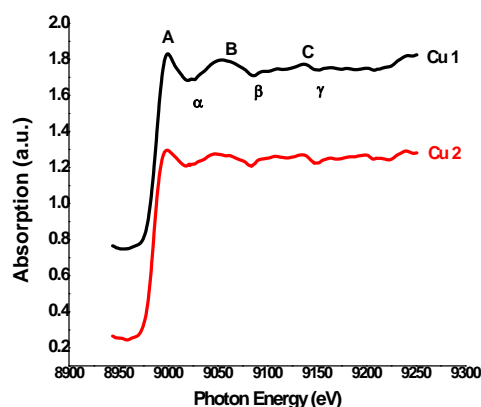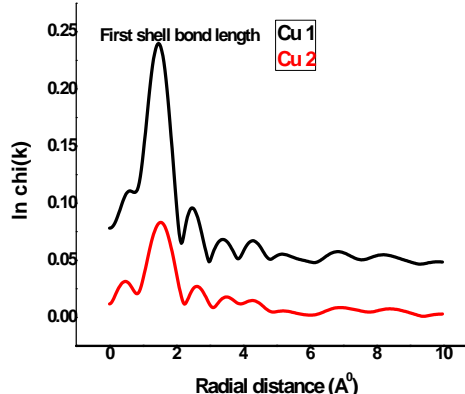| Complex	Levy's	Lytle	LSS	F.T.
Cu1	2.48	2.17	1.55	1.71
Cu2	2.17	1.97	1.76	1.75

Figure 2 μ (E) vs. E curve of Copper complexes

Figure 3 Bond length by FT method

3. Results and discussion

Extended X-ray Absorption fine Structure (EXAFS)

Although, Fourier transform of EXAFS data is a general and powerful technique to determine many physical parameters; however, it is possible to determine nearest-neighbor distances and phase shifts from a simple graphical technique. This is possible because the first shell scattering usually dominates the EXAFS curves; then, if only the major EXAFS peaks are used, the period will be that of the first coordination shell. In this method, the energy positions of the maxima and minima in EXAFS are measured with respect to the inflection point on the main absorption edge, which signifies the Fermi level in metals and the first unoccupied level of suitable symmetry available for the absorption of the ejected electron in the case of compounds.

The X-ray absorption spectra, i.e., normalized μ (E) vs. E curve of Copper is shown in figure 2. The bond lengths have been determined using the following four methods, i.e., Levy's, Lytle, Lytle, Sayers and Stern's (LSS) and Fourier transformation methods and the results obtained are given in table1.

3.1 Levy's method

The bond lengths According to Levy's method [17], are given by Bragg relation $R_1 = [151/\Delta E]^{1/2}$ Å, where ΔE is the difference in eV of the energies of the EXAFS maximum B and minimum β and R_1 is the radius of the first coordination sphere.

3.2 Lytle's method

According to Lytle [18] method the bond length (R_s) is evaluate by the radius R_s of equivalent polyhedron through the relation $R_s = [37.60 / M]^{1/2}$.where M is slope of E vs Q plot ,energy values (E) is EXAFS maxima and Q = 2.04, 6.04, 12.0, and 20.0 are constant . The values of R_s calculated with the help of this method are reported in table 1.

3.3 Lytle, Sayers and Stern's (LSS) method

In the LSS method [19], for determination of the nearest neighbor distances, gives the value of $(1/2+n)$ π= $2k(R_1 - \alpha_1)+2\beta_1$,where R_1 is the bond length. $(R_1 - \alpha_1)$ is the phase uncorrected bond length shown in table 1.

3.4 Fourier transformation method

The X-ray absorption spectra were recorded and calculated of copper complexes Fourier transformation is shown in figure 3. The bond lengths of first successive maxima had been determined using Fourier transformation methods and the results obtained are given 1.71 and 1.75 respectively.

The Fourier transforms peaks at the radial distances of the neighboring atoms from the absorbing atom. The distances found in Fourier transform are, however, shorter by 0.2-0.5 Å than the actual distances due to energy dependence of the phase factors in sine function of the theoretical expression for EXAFS, which is known as the EXAFS equation [20]. The peaks in the Fourier transform are shifted towards the origin by an amount α_j and hence the peaks are at distances $R_j-\alpha_j$. For the first peak j=1 and hence the position of the first peak determines the distance $R_1-\alpha_1$. This distance is given in table 1.

4. Conclusion

Calibration of particular setting of the polychromator has to done and it has been shown by derivative method, and after this EXAFS spectrum has been recorded and comparison of the values of bond length R_s is seen to have slightly lesser values than the corresponding bond lengths obtained by Levy's method. This may be described to the fact that Levy's method gives the radius of coordination sphere directly where as Lytle method does not. In later method, the inter atomic spacing is obtained by multiplying R_s with a factor Appropriate to the geometry of the system .the value of the bond length obtained from LSS method are closer to obtained by Levy's method and Fourier transformation method.

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