

Extended X-ray Absorption Fine Structure Data Analysis of Cu (II) Complexes

Kamaljeet S. Sura^{1, a)}, Mahesh Jamod², A. Mishra², B.D. Shrivastava³

¹*Acropolis Institute of Technology and Research Indore (M.P.) India.*

²*School of Physics, DAVV, Indore (M.P), India.*

³*Gov. P. G. College, Dhar (M.P), India.*

^{a)}kamaljeetsura@gmail.com

Abstract. A technique is presented for Extended X-ray absorption fine structure (EXAFS) data analysis for determining the metal-ligand bond length using synchrotron source. In present work a fresh series of Copper complexes have been presented. Cu complexes are synthesized by chemical route method. The synthesized complexes were further characterized by X-ray diffraction (XRD). XRD analysis shows that sample is crystalline in nature and having particle size in the range of nano meters. These complexes have also been characterized by Cu K-Edge EXAFS measurements using the dispersive beam line at 2.5 GeV Indus-2 synchrotron radiation source at RRCAT (Raja Ramanna Centre for Advance Technology), Indore, India. The measured EXAFS data have been analyzed to compute average metal-ligand bond length using Levy's, LSS, Lytle's, Fourier transform methods, with the help of computer software ATHENA.

INTRODUCTION

Synchrotron based X-ray Absorption Fine Structure (XAFS) spectroscopy becomes a powerful technique providing analytical as well as structural information, with applications in a wide range of scientific fields because of the rapid development of the data treatment techniques. Extended X-ray absorption fine structure spectroscopy (EXAFS) refers to the oscillatory variation of the X-ray absorption as a function of photon energy beyond the absorption edge. Such fine structure may extend up to 1000 eV above the absorption edge and may have amplitude of up to a few tenths of the edge jump. EXAFS has become the technique of choice for local structural investigations in a diverse range of material systems. This technique has also proved very useful, while studying the chemical reactions of matter under extreme conditions of temperature and pressure. The EXAFS oscillations in the absorption spectrum are caused by interference in the final state from backscattering of the outgoing photoelectron wave by neighbors of the excited atom. Hence, it is extremely sensitive to the nearest neighbour bond lengths [1]. The bond length was determined by Levy's, Lytle's, Lytle Sayers and Stern's [LSS] and Fourier transformation method.

The Cu complex including *o*-phenylenediamine and malonates have a variety of application in clinical, analytical and biological fields. XRD technique is used to show the details about the particle size, lattice parameter, and to know the crystal structure of these complexes. The XRD patterns were recorded on Bruker D8 Advanced X-ray diffractometer. XRD characterizations were done in IUC, DAE Indore.

METHODOLOGY

- **Chemicals and solvent:** All chemicals (sodium nitrite, sodium acetate, *O*-phenylenediamine, diethyl malonate, ferric chloride and anilines) are of Loba Chemie and solvents (absolute ethyl alcohol) are of Loba Chemie all are laboratory reagent grades and were used without further purifications.
- **Synthesis of Ligand:** In a 100 cc beaker pertinent aniline derivative (0.01M) were dissolved in a mixture of 5.0ml of concentrated hydrochloric acid and 5.0 ml of distilled water. Now the contents kept at freezing temperature in a deep freezer. To this, an aqueous solution of sodium nitrite (0.01, 1.38 g) in 5.0ml of distill

water was added drop wise with continuous stirring keeping the temperature of the reaction in the vicinity of 0-50C. Meanwhile, in another beaker, the particular diethylmalonate (0.01 M), sodium acetate (7.0g) and ethyl alcohol (25ml) were taken, mixed and cooled in an ice bath. Now the diazotized solution was added to this solution in a drop wise manner thorough stirring and maintaining the temperature of the contents below 50C. The reaction mixture was kept for overnight period, filtered through suction, washed with plenty of water and dried in vacuum. Fine crystals of coupled products were obtained in good yield.

- **Synthesis of complex 1:** Diethyl2-(2-(3-chlorophenyl)hydrazono)malonate1,2-Diphenylamine Cu(II) [complex 1] In a 250 ml round bottom flask equimolar ethanol solution of ligands 2-Diphenylamine, Diethyl2-(2-(3-chlorophenyl)hydrazono)malonate and metal salt were taken and this mixture was refluxed for 4 hours. After reflux Solvent was evaporated to afford fine crystal of metal complexes. These metal complexes were recrystallize from ethanol, washed with cold water and dried in vacuum.
- **Synthesis of complex 2:** Diethyln2-(2-o-tolyhydrazono)malonate 1,2-Diphenylamine Cu(II) [complex 2] In a 250 ml round bottom flask equimolar ethanol solution of ligands 2-Diphenylamine, Diethyln2-(2-o-tolyhydrazono)malonate and metal salt were taken and this mixture was refluxed for 4 hours. After reflux Solvent was evaporated to afford fine crystal of metal complexes. These metal complexes were recrystallize from ethanol, washed with cold water and dried in vacuum.
- **Synthesis of complex 3:** Diethyl2-(2-(4-chlorophenyl)hydrazono)malonate1,2-Diphenylamine Cu(II)[complex 3] In a 250 ml round bottom flask equimolar ethanol solution of ligands 2-Diphenylamine, Diethyl2-(2-(4-chlorophenyl)hydrazono)malonate and metal salt were taken and this mixture was refluxed for 4 hours. After reflux Solvent was evaporated to afford fine crystal of metal complexes. These metal complexes were recrystallize from ethanol, washed with cold water and dried in vacuum.

These complexes have been characterized by X-ray diffraction (XRD) and Extended X-ray Absorption Fine Structure (EXAFS).XRD pattern have been recorded by Bruker D8 advance diffractometer at UGC-DAE CSR, Indore. The X-ray absorption fine structure spectra at the K-edge of Copper of these complexes have been recorded at BL-8 Dispersive EXAFS beamline at the 2.5-GeV INDUS-2 Synchrotron Radiation Source at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India .The experimental data have been analyzed using software Origin 8.0 and Athena 0.8.056 [2].

RESULTS AND DISCUSSION

From XRD analysis the crystal structure and lattice parameter were determined by using Bragg's law, $2d\sin\theta=n\lambda$ and particle size is calculated by Debye Scherer's formula, $t=0.9\lambda/B \cos\theta$. Where λ is the wavelength of X-ray, θ is the glancing angle and B is the FWHM (Full width at half maxima).The XRD pattern of the reported complexes is presented in figure 1. The particle size and lattice parameter are given in Table 1. The X-ray analysis shows the complexes are crystalline in nature.

The normalized X-ray absorption spectra of Cu-complexes are reveled in figure 2. The EXAFS spectra transformed into k-space have been shown in figure 3. To convert into R-space a Fourier transform is applied to these data and it is shown in figure 3. The bond lengths of these Cu-complexes have been calculated by different methods. The phase-uncorrected bond length has been calculated by the Fourier transform technique. Before Fourier transform technique was formulated, the bond lengths were extracted from the EXAFS data by the three methods:

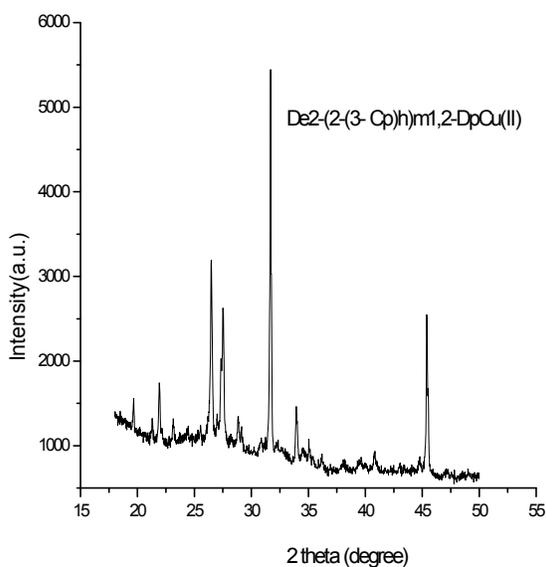
- **Levy's method:** Levy has given a method for obtaining the bond lengths from the analysis of EXAFS [3]. According to Levy, the distance ΔE , from the maximum at B to the minimum at β should be a measure of the radius R_1 of the first coordination sphere through Bragg relation $R_1= (151 /\Delta E)^{1/2}$ Å. The values of R_1 determined by this method are given in table 2. R_1 calculated in this way represents the average bond length. The value of bond length for the complex is available from crystallographic measurements and hence we have compared the crystallographic value, with that determined from Levy's method. It is clear from table 2 that the two values are in agreement with each other in the complex.
- **Lytle's method:** Lytle has proposed a theory in which a nearly spherical polyhedron is constructed in the lattice and approximated by a sphere of equivalent volume with radius R_s [4]. In this method photoelectron ejected as a result of absorption of X-rays are thought of as if they are in a particle in a box. Lytle has found that an absorption maximum will occur whenever E satisfies the equation= $(h^2/ mR_s^2)Q$, where h is Planck's constant, m is the electron mass, and Q represents the zero roots

of the half-order Bessel function. The plots of E vs. Q for the complexes studied are found to be linear. If M is the slope of this straight line, R_s can be determined from the plot using the relation $R_s = (37.60/M)^{1/2} \text{ \AA}$. It may be remarked here that the interatomic distance obtained by this method has to be multiplied by a factor greater than unity and appropriate to the geometry of the system to obtain the correct bond length.

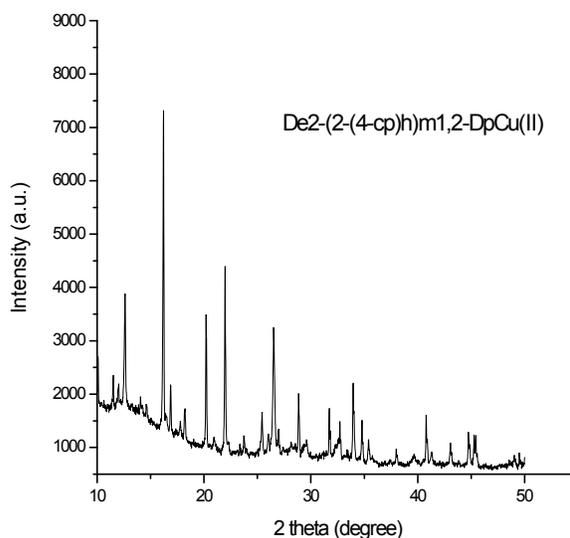
- **L.S.S. method (Lytle, Sayers and Stern)** :According to this method [5], plot of n vs k for the different maxima (n= 0, 2, 4, ...) and minima (n= 1, 3, 5, ...) should results in a straight line. n vs k graphs for the complexes studied are found to be linear. The slope (M') of this line is given by $M' = 2(R_1 - \alpha_1) / \pi$. The value of $(R_1 - \alpha_1)$ can be obtained from the slope of the plot. Once α_1 is evaluated for a standard, R_1 for unknown materials can be determined. It is found that for chemically similar systems, the value of α_1 remains more or less the same. The values of R_1 thus obtained by this method. The distance R_1 obtained from this method is phase uncorrected bond length.
- **Fourier Transform Method:** The position of the first peak in the Fourier transform (figure 4) corresponds to the distance between the absorbing atom and its nearest neighboring atoms, i.e., the radius of first coordination sphere. However, the bond length thus obtained is less than the actual bond length, because it is phase uncorrected. The values for the phase uncorrected bond lengths, as determined from the Fourier transforms, for the three complexes are given in table 2. The phase corrected bond length can be determined by fitting appropriate theoretical model to the experimental Fourier transform curve.

CONCLUSION

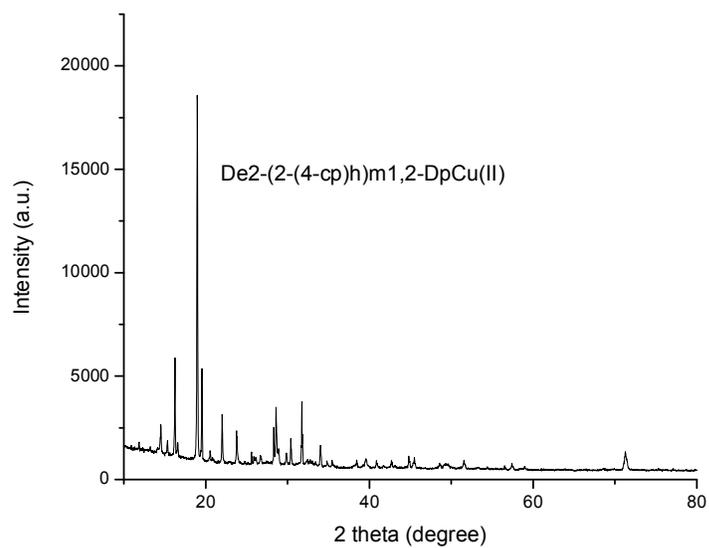
As is evident from the analysis of X-ray diffraction pattern, one can conclude that the samples exhibit crystalline nature and shape of unit cell is simple cubic. From the positions of the EXAFS maxima and minima, the bond lengths of the Copper complexes has been determined by three different methods viz. Levy's, Lytle's and LSS methods. From the Fourier transforms of the EXAFS spectra, the bond length (uncorrected for phase shift) has been determined. It has been observed that the values of the phase-uncorrected bond length, i.e. $R_1 - \alpha_1$ as determined from LSS method and that determined from the Fourier transformation method, are in good agreement with each other.



(a)



(b)



(c)

FIGURE 1. X-ray diffraction pattern for copper complexes

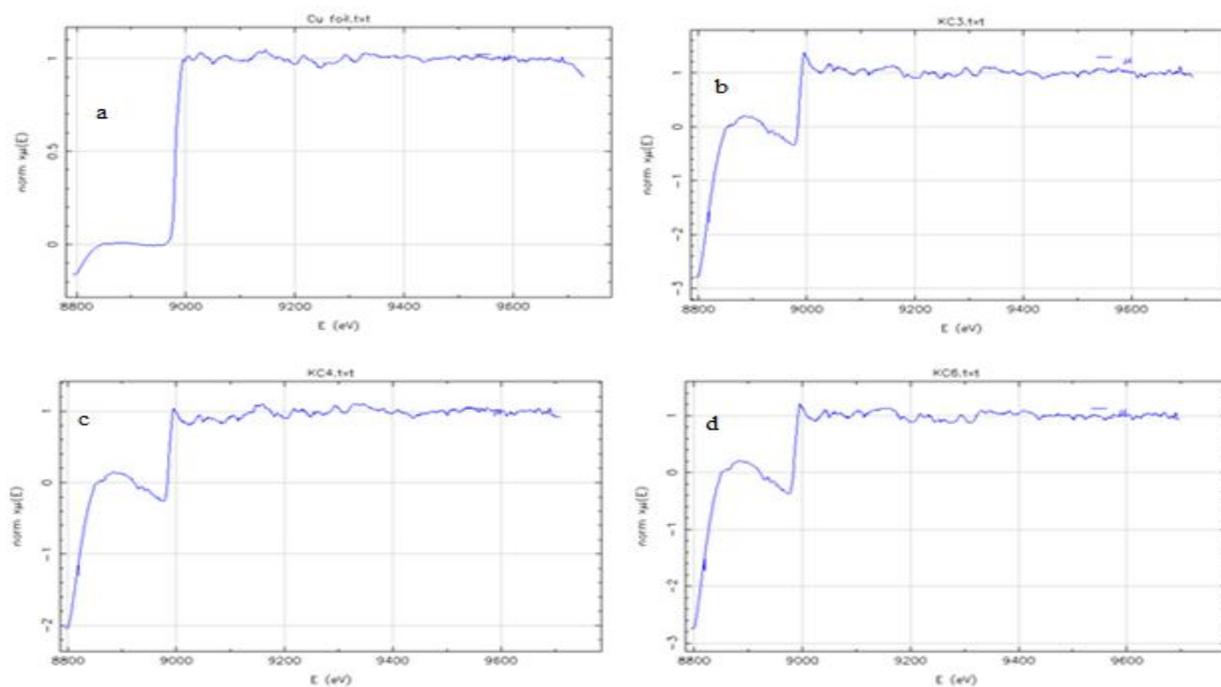


FIGURE 2. EXAFS spectra for copper foil and copper complexes respectively.

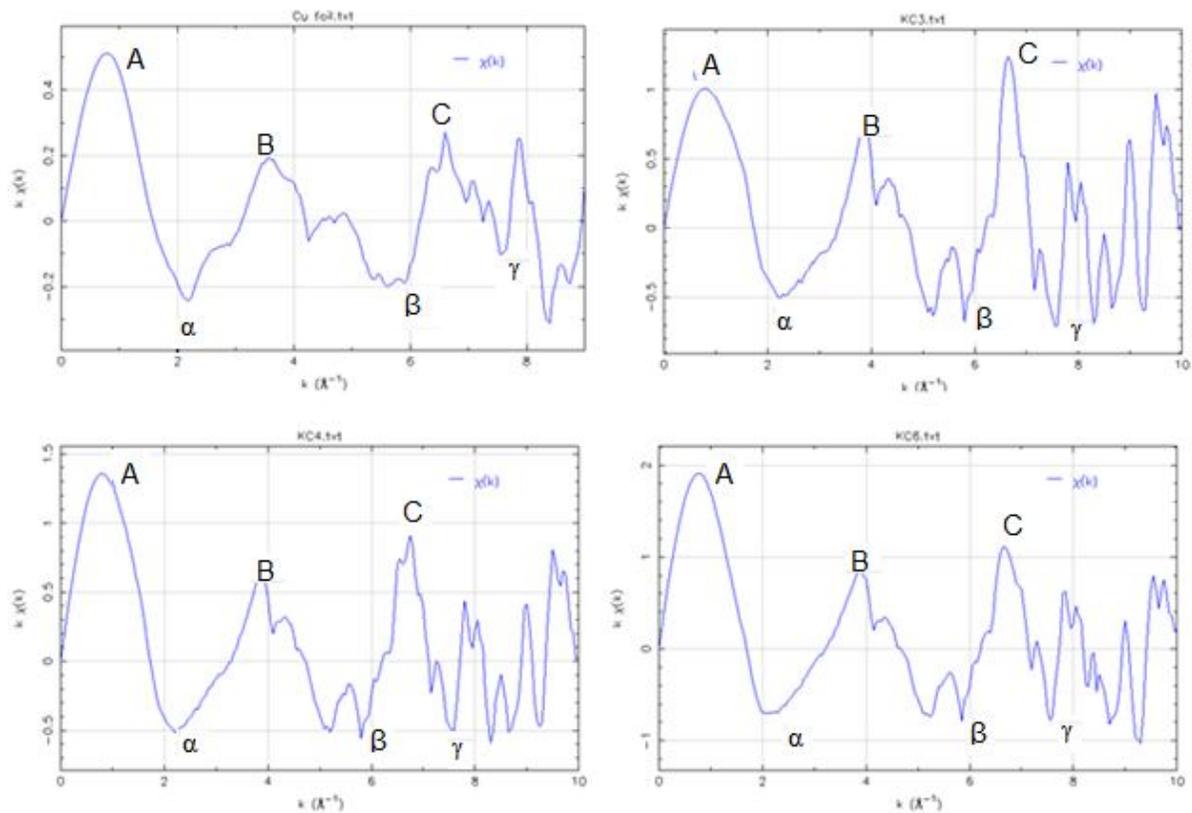


Figure 3. $\chi(k)$ vs. k spectra of copper foil and three complexes.

TABLE 1. Results of X-ray diffraction studies of Copper Complexes

S.No.	Complex	Particle size(in nm)	Lattice Parameter(in nm)
1	Complex 1	49.34	5.64
2	Complex 2	32.61	6.88
3	Complex 3	55.43	12.89

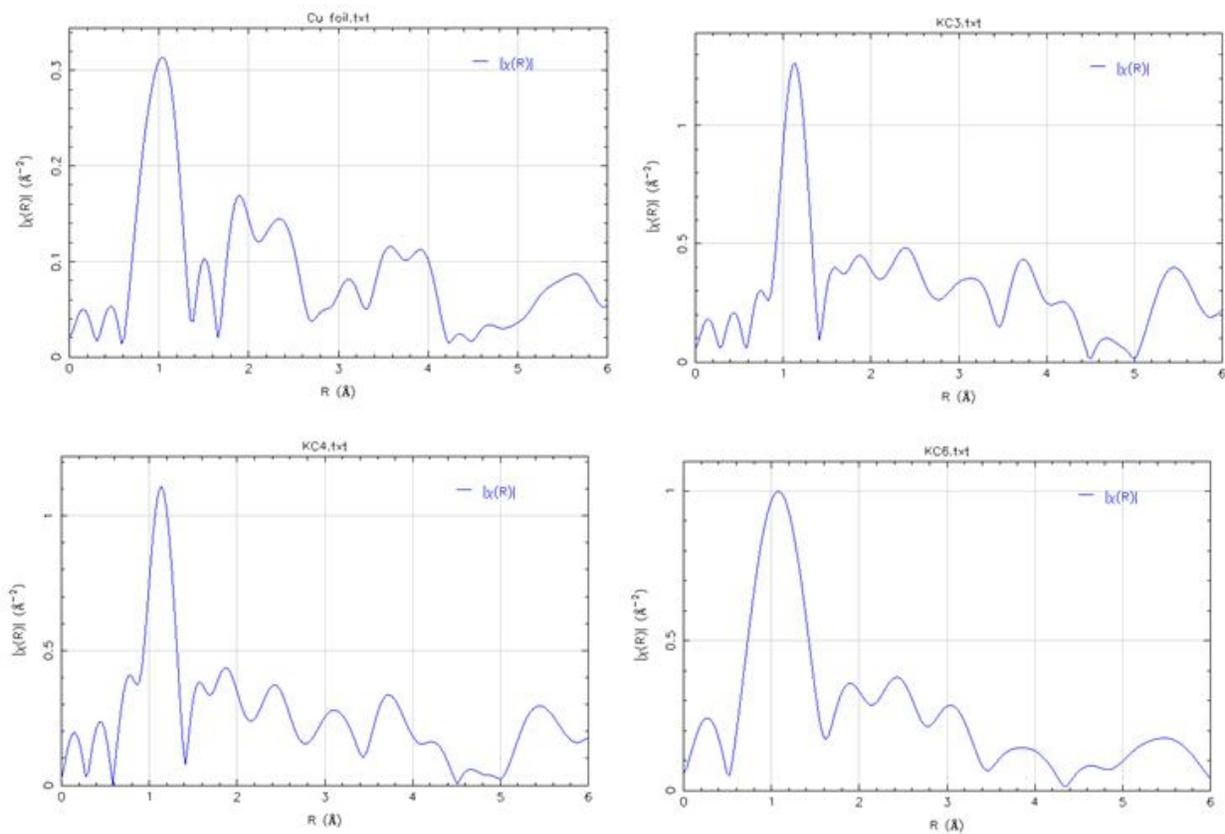


Figure 4. Fourier transformed spectra for copper foil and three complexes.

TABLE 2. Values of first shell bond lengths (in Å) calculated from Levy's, Lytle's, L.S.S. and Fourier transform methods for copper (II) complexes.

S. No.	Cu(II)Complexes	Phase corrected		Phase uncorrected	
		Levy's method $R_1(\text{Å})$	Lytle's method $R_s(\text{Å})$	L.S.S. method $R_1-\sigma_1(\text{Å})$	F.T. method $R(\text{Å})$
1	Complex 1	1.43	1.69	1.33	1.12
2	Complex 2	1.92	2.00	1.64	1.14
3	Complex 3	1.76	2.02	1.60	1.06

ACKNOWLEDGMENT

The authors are thankful to Dr. Shambhunath jha, RRCAT, Indore for their help in recording the spectra at RRCAT, Indore, India.

REFERENCES

1. B. K. Das and R. Chakrabarty 2011 *J. Chem. Sci.* **123** 163.
2. B. Ravel and M. Newville 2005 *J. Synchrotron Rad.* **12** 537
3. R. M. Levy 1965 *J. Chem. Phys.* **43** 1846
4. F. W. Lytle 1966 *Adv. X-ray Annl.* **9** 398
5. F. W. Lytle, Sayers D E and Stern E A 1975 *Phys. Rev. B* **11** 4825