X-ray Diffraction and Extended X-ray Absorption Fine Structure (EXAFS) Studies of Copper (II) Complexes with Ligands 2-methyl-3-[(bis-aniline(R) phenyl]-3H-1, 5 Benzodiazepine using Synchrotron Radiation Source

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An X-ray diffraction (XRD) analysis of Copper (II) complex as a ligand of 2-methyl-3-[(bis-aniline(R) phenyl]-3H-1, 5 benzodiazepine revealed the existence of a single phase and cubic structure of copper. Lattice parameter and particle size have been calculated by XRD. Extended X-ray absorption fine structure (EXAFS) spectra have been recorded at Copper (II) K-edge using the energy dispersive EXAFS beam line at 2.5GeV Indus -2 synchrotron source at RRCAT, Indore, India. These data have been calibrated by derivative method and also used to determine the bond lengths with the help of three different methods, namely, Levy's, Lytle's and Lytle, Sayers and Stern's (LSS) methods. 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

The X-ray diffraction (XRD) is a resourceful and non-destructive technique that can explain the perfect information about the chemical composition and crystallographic structure of natural and manufactured materials. In the present work, the XRD technique has been used to give information regarding the complexes involved in the present communication. The X-ray absorption spectra of the complexes have also been taken into consideration for the study and the X-ray absorption spectra have been recorded at the K-edge of Copper (II) complexes in five macro-cyclic complexes. The coordination chemistry of macro-cyclic ligands is a fascinating area of research. The synthetic, kinetic and structural aspects [1-2] of poly-aza macro-cyclic complexes have received considerable attention and a variety of such systems have been synthesized [3-9]. With the help of X-ray absorption spectra, the extended X-ray absorption fine structure (EXAFS) spectroscopy has been explained and it is an effective technique for selectively investigating the local coordination environment around the metal active site of complexes [10]. The X-ray absorption edge study of the complexes has been carried out using synchrotron radiation source for X-ray. This facility is available at dispersive EXAFS (DEXAFS) beam line BL8 at RRCAT Indore, India. The extended X-ray absorption fine structure (EXAFS) K-edge of Cu (II) complexes were recorded at 8980.5eV and also determined the bond length between metal-ligand of following complexes.

1. Cu (II)-2-methyl-3-[(bis-2nitroaniline phenyl)]-3H-1, 5 benzodiazepine chloride. (Cu2M3bis2Nap3H15BdCl)
2. Cu (II)-2-methyl-3-[(bis-3nitroaniline phenyl)]-3H-1, 5 benzodiazepine chloride. (Cu2M3bis3Nap3H15BdCl)
3. Cu (II)-2-methyl-3-[(bis-4nitroaniline phenyl)]-3H-1, 5 benzodiazepine chloride. (Cu2M3bis4Nap3H15BdCl)
4. Cu (II)-2-methyl-3-[(bis-2chloroaniline phenyl] -3H-1, 5 benzodiazepine chloride. (Cu2M3bis2Clap3H15BdCl)
5. Cu (II)-2-methyl-3-[(bis-3chloroaniline phenyl] -3H-1, 5 benzodiazepine chloride. (Cu2M3bis3Clap3H15BdCl)

Basically EXAFS analysis is applicable to the determination of the radial distribution of atoms around a particular absorbing atom, thus providing a probe for the structure in the vicinity of the absorbing atom. It gives structural information about the numbers, types, and distances to neighbouring atoms from absorbing elements. In this article, bond lengths shall also be determined from EXAFS maxima and minima with the help of three different methods, namely Levy's method [11], Lytle's method [12] and LSS (Lytle, Stern, Sayer's) method [13] and also compared with the Fourier transform method. There is a comparative study of theoretical and experimental values of

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bond lengths of the studied complexes and the values have also been reported in the tabular form. In this communication, a method of determining the metal ligand bond length by an appropriate Fourier analysis of the K-edge data has been presented theoretically to analyse the experimental values. This is illustrated by a detailed analysis of the data for a series of poly-aza macro cyclic ligand. The noticeable advantage of EXAFS 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 analysed even with more sophisticated surface investigation equipment. Application of EXAFS can be found in literature on a variety of fields, namely chemical reactions in the solid state, surface treatments and the structural studies of thin films [14,15].

2. Experimental Technique

2.1. Material synthesis

Preparation of ligand (L)
The Copper complexes were prepared by chemical root method using the pure grade chemicals. A mixture of reactants O-phenylenediemine (.05 mol, 5.0g), substituted aniline(R) (.05 mol,6.9g) in ethanol (25 mL) and ethyl acetoacetate (.05 mol, 6.7g) dissolved in ethanol (25 mL) were refluxed for 6 hour. The volume concentrated on the steam bath until white colored crystals began to form. The product was purified by crystallization from hot alcohol. Thus white crystalline pure macro cyclic ligand was collected.

Preparation of [Cu (II)-L-Cl$_2$]
A solution mixture of hot ethanol solution of ligand (L) (0.01m.mol, 0.2 g) and hot ethanol solution of Copper chlorides [$CuCl_2.6H_2O$] with few drops of hydrochloric acid was then refluxed for 4 hours. On cooling, colored precipitates were then filtered and washed with cold water and dried in vacuum [16].

3. EXAFS Spectra Recording at Indus-2

The complexes were finely powdered and then absorption screens were prepared by carefully calculating the amount of powder for spreading 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 beam line at 2GeV Indus-2 synchrotron radiation source at Raja Ramanna Center for Advanced Technology (RRCAT), Indore, India [17-19]. 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 [20]. The elliptical optics offer 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 a few microseconds for a rich sample. The beam-line has a resolution of 1eV at the photon energies of 10keV. The plot of absorption *versus* photon energy was obtained by recording intensities I_o and I_t as the CCD outputs, with and without sample, respectively, and using the relation $I_t=I_oe^{-\mu x}$, where μ is the absorption coefficient and x is thickness of the absorber. For recording the EXAFS spectrum on the dispersive EXAFS beam-line, the crystal bender and the goniometer have been set to cover the energy range of the Copper K-edge absorption spectra.

4. Results and Discussion

X-ray diffraction

The X-ray diffraction technique is useful for the structural analysis. All five Cu complexes were found in single phases. The XRD patterns are shown in Fig. 1 after indexing the simple cubic structure that was found. Table 1 indicates the particle size (in nm) and the lattice parameter (in Å) for the entire samples The pattern has been indexed using JCPDF software and lattice parameter have been using the Bragg's law [21]. The Braggs condition is $2d\sin\theta=n\lambda$, where d is the lattice spacing. The particle size are determined by Debye formula

$t=0.9\lambda/(\beta\cos\theta)$, where, $\lambda=1.54A^0$, β=Angular width

Extended X-ray absorption fine structure

The X-ray absorption spectra, i.e., normalized $\mu(E)$ versus E curve of all five Cu complexes are shown in Fig. 2. The $\chi(k)$ versus K spectra are shown in Fig. 3(a-e) of all five Cu complexes. The bond lengths have been determined using the following four methods: a) Levy's, b) Lytle, c) Lytle, Sayers and Stern's (LSS), and d) Fourier transformation. The results obtained are reported in Table 2.

a) Levy's method
The bond lengths, according to Levy's method [11], 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. The bond length of these samples was raging from 1.67

Å to 2.44 Å. The variation in the bond length is due to a change in metal ligation with a ligand.

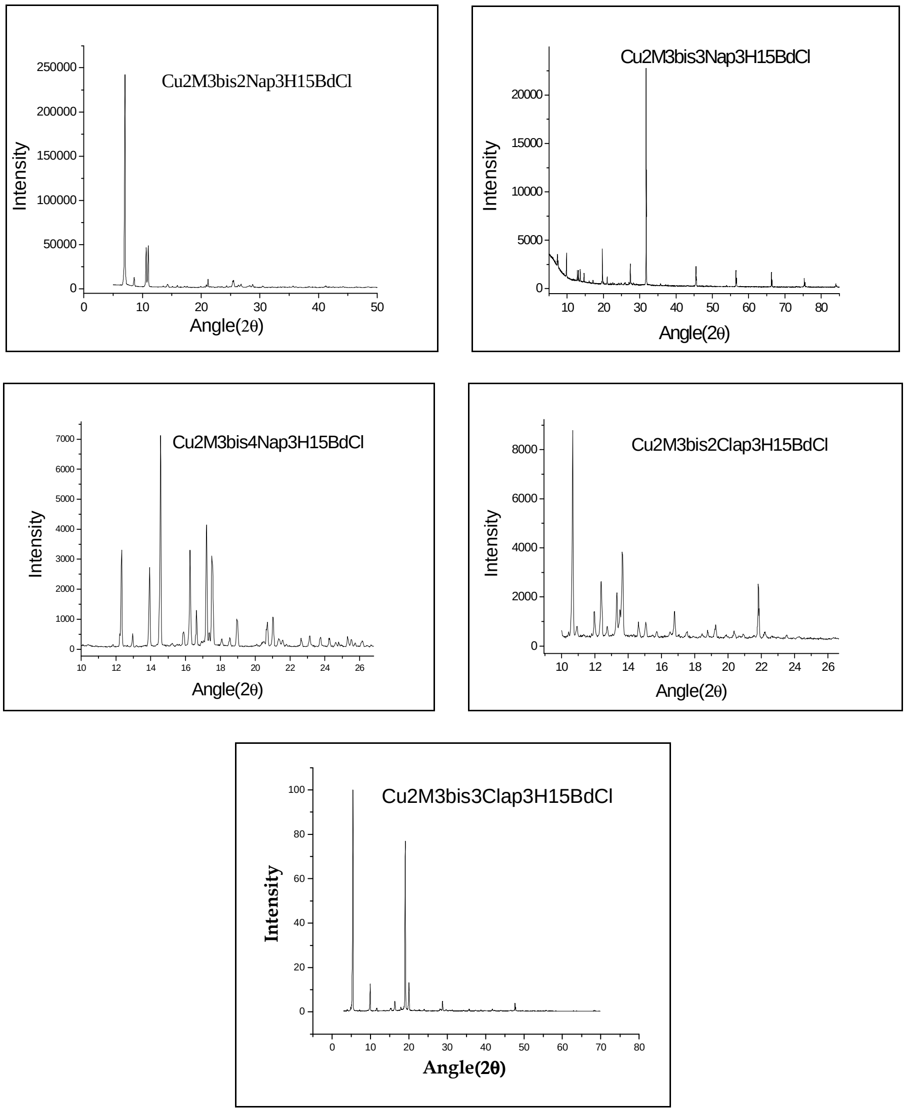

Fig.1: XRD pattern for all five Cu (II) complexes.

Table 1: Particle size and lattice parameter of calculated Cu (II) complexes.

S. No.	Name of Complexes	Particle size(nm)	Lattice parameter (Å)
1	Cu2M3bis2Nap3H15BdCl	21.20	8.27
2	Cu2M3bis3Nap3H15BdCl	24.41	9.10
3	Cu2M3bis4Nap3H15BdCl	27.18	9.21
4	Cu2M3bis2Clap3H15BdCl	27.87	10.10
5	Cu2M3bis3Clap3H15BdCl	28.51	10.24

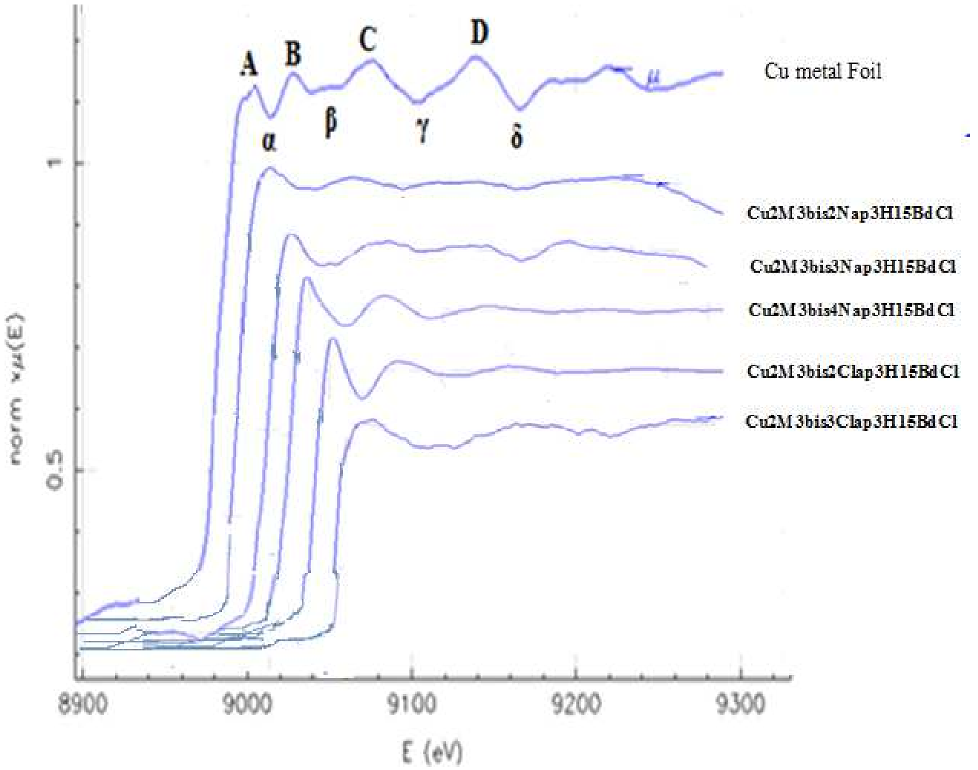

Fig.2: Normalized spectra for all Cu (II) complexes.

Table 2: Bond length (R in A^0) by Levy's, Lytle's and L.S.S., and Fourier transform method of (F.T.) for Copper (II) complexes.

S.No.	Complex	Phase Corrected		Phase uncorrected	
		Levy's method R_1	Lytle method R_s	L.S.S.method R1-α1	F.T. method R
1.	Cu2M3bis2Nap3H15BdCl	1.67	1.57	1.44	1.42
2.	Cu2M3bis3Nap3H15BdCl	2.16	1.76	1.68	1.70
3.	Cu2M3bis4Nap3H15BdCl	2.44	1.80	1.55	1.58
4.	Cu2M3bis2Clap3H15BdCl	1.78	1.73	1.57	1.60
5.	Cu2M3bis3Clap3H15BdCl	1.97	1.41	1.50	1.51

b) Lytle's method

According to the Lytle [12] method, the bond length (R_s) is evaluated by radius R_s of equivalent polyhedron through the relation $R_s = [37.60/M]^{1/2}$, where M is slope of the E - Q plot, energy values (E) is EXAFS maxima and Q = 2.04, 6.04, 12.0, and 20.0 are constants. The values of R_s calculated with the help of this method are reported in Table 2. The bond length is given, which varies for samples. The order matches with Levy's method.

c) The method of Lytle, Sayers and Stern (LSS)

In the LSS method [13], the determination of nearest neighbour distances gives the value $(1/2+n)\pi = 2k(R_1 - \alpha_1) + 2\beta_1$, where R_1 is the bond length, and $(R_1 - \alpha_1)$ is the phase uncorrected bond length. The k versus chi χ (k) graph is shown in Fig. 3(a-e) for all complexes.

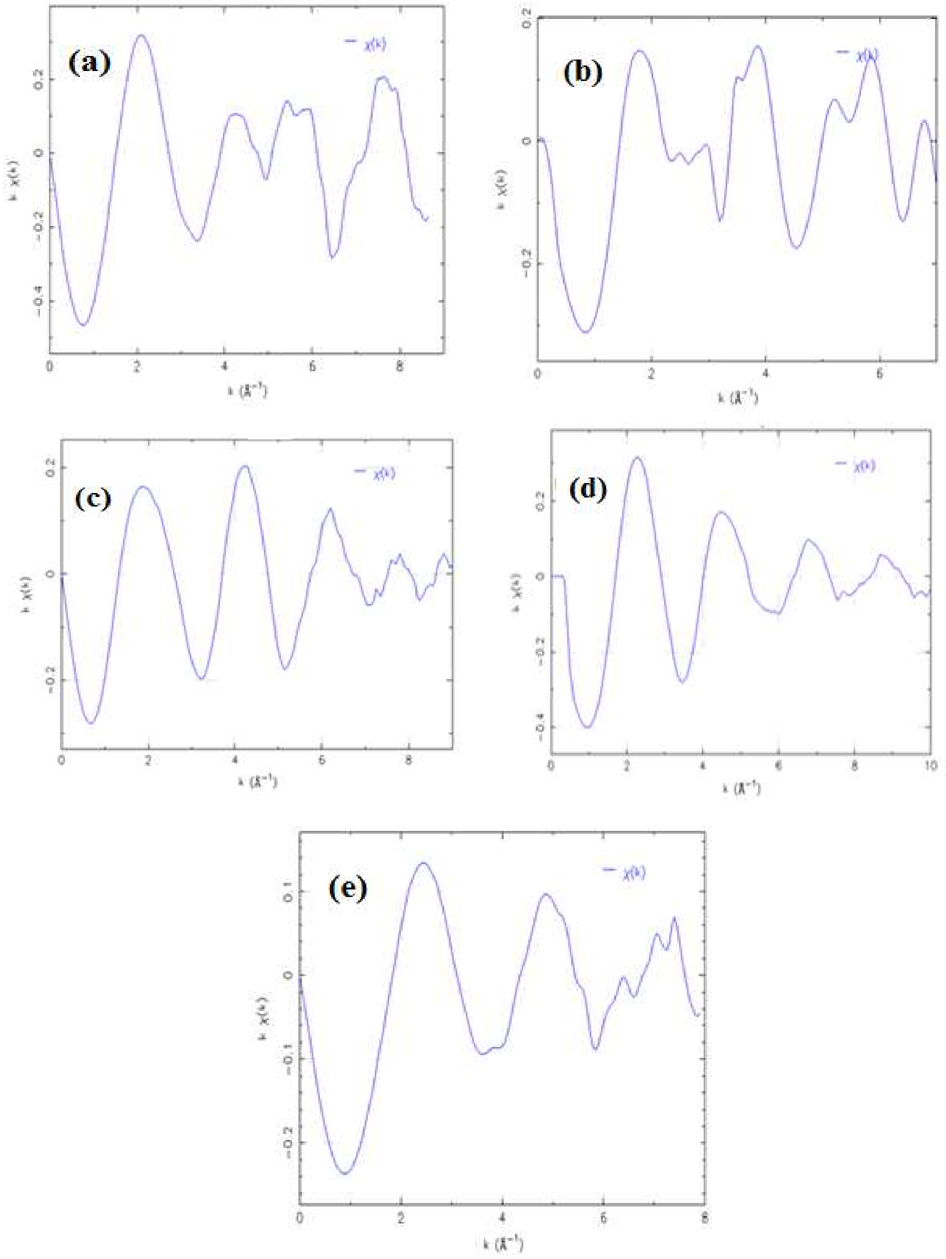

Fig.3(a-e): k versus χ(k) curve for Cu (II)complexes.

d) Fourier transformation method

In the present communication, bond length has been determined by the Fourier transformation method for copper complexes studied here with detailed information as mentioned below. In this case, only the phase uncorrected bond lengths were determined by this method. One of the analyses of EXAFS was based on the Fourier transform (FT) of the data expressed in momentum space. The absolute value of the transform was found to peak at distances shifted from the known values by 0.2 - 0.5Å. By correcting for these shifts using systems with known distances the bond length information can be extracted [22-25].

The Fourier transformation of k^n χ(k) in momentum (k) space over the finite k range k_{min} to k_{max} gives rise to a modified radial distribution function $\phi_n(R')$ in distance (R') space.

$$\phi_n(R') = \frac{1}{\sqrt{2\pi}} \int_{k_{min}}^{k_{max}} w(k)k^n\chi(k)e^{2ikR'}dk \qquad (1)$$

To locate the position of each peak in $\phi_n(R')$, it is necessary to understand the phase shift fully. The linear k dependent term shifts the frequency of sine wave of EXAFS equation from R_i to $(R_i - \alpha_i)$. In the Fourier transform, this has the effect of shifting all the peaks towards the origin by α, E_0 and the weighting scheme chosen. α can be obtained from model compounds and transferred to unknown systems in order to predict distances.

Also included in the Fourier transform is a window function w(k), which selects the *k* range to be transformed. w(k) can be the square window if care is taken to choose the cut off to be where χ(k) is small, or a smooth window such as the following Hanning function can be applied.

$$w(k) = \frac{1}{2}\left[1 - \cos 2\pi\left(\frac{k - k_{min}}{k_{max} - k_{min}}\right)\right] \qquad (2)$$

It is clear that w(k) = 0 at k = k_{min} and $k_{max.}$ This window is normally applied to the first and the last 5 - 10% of the data while keeping w(k) = 1 for the remaining data set. It is clear that this window smoothly sets the data to zero (w(k) = 0) at k_{min} and at $k_{max.}$

In general, this method works well for systems with well separated peaks. The weakness of it is that since the amplitude F(k) and the phase Φ(k) functions have characteristic k dependence, the Fourier transform peak magnitude and phase shift α in the distance space depends on E_0, the weighting of the data, the data range in k space and the Debye-Waller factors etc. The modelling EXAFS spectra to determine the average, local-molecular coordination environment of an absorber atom is a multi-step process that is learned through hands-on experience. The process of building a structural model is described with specific references to the EXAFS data analysis programs Athena for background removal and Artemis for optimizing the theoretical model to the measured spectrum [26].

The EXAFS equation contains structural parameters (N, R, σ^2) as well as functions that are characteristic of atoms in the sample (f(k), δ_1(k), λ(k)). These scattering amplitudes and phases can be obtained to a good approximation by comparing the unknown sample with standard compounds of known structure; the scattering amplitudes and phases are said to be transferable. The reason that the transferability concept works well is that the backscattering amplitude is relatively insensitive to the potential in the periphery of the backscatterer (one way to see this is that the large momentum transfer involved in backscattering can only be caused by high spatial Fourier components of the scattering potential, which occur in the core region of the backscatterer). Since it is the outer regions of the scatterer that are affected most by chemical bonding and solid state effects, the scattering amplitudes and phases are not strongly sensitive to chemical effects in the EXAFS region. The traditional method of data analysis involves a sequence of steps as correction for instrumental effects such as detector dead time losses and energy resolution; spectrum averaging and removal of monochromator glitches; normalization of the spectrum to unit edge step to compensate for variations in sample thickness or concentration; selection of the energy threshold E_0 and interpolation to k-space; subtraction of smooth background (typically using cubic spline functions) to generate χ(k); Fourier transformation and filtering to produce single shell amplitude and phase; determination of model parameters using the ratio method or nonlinear least squares fitting of data using empirical or theoretical standards. None of the numerical operations is particularly difficult; they are straightforward to implement using standard subroutine libraries. Presently, the EXAFS data is analysed to yield structural information using the available computer softwares Athena and Artemis or similar softwares [26]. Theoretical model is generated using Artemis, which requires crystallographic data of standards, i.e., of the compound itself or of a similar compound. Experimental standards are also sometimes used for generating models. In the present work, we have shown this by using sophisticated software. The magnitude of Fourier transform spectra are shown in Fig. 4(a-e). The Fourier transforms peaks at the radial distances of the neighbouring atoms from the absorbing atom. The distances found in Fourier transform are, however, shorter by distance in few 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 [22]. 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-α_j. For the first peak j=1 and hence the position of the first peak determines the distance R_1-α_1. This distance is given in table 2. One can compare the values with LSS method. The order of values is same as in LSS method and it has been found that the values are much closed to values of LSS method.

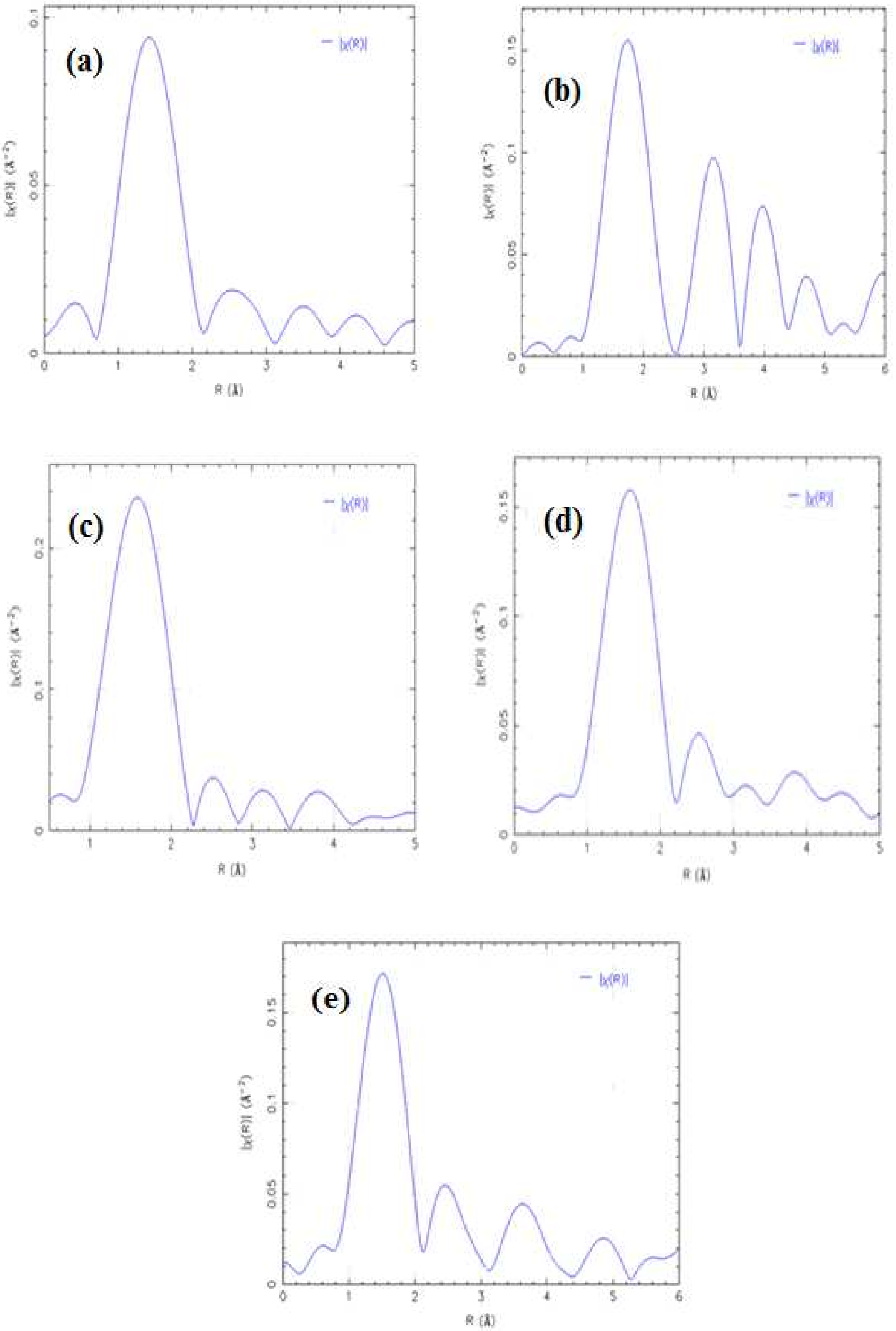

Fig.4(a-e): Magnitude of Fourier transform of the χ(k) versus k curve for Cu(II)complexes.

5. Conclusion

The XRD method clearly showed the crystalline nature of copper complexes. A calibration of particular setting of the polychromator has to be done and it has been shown by the derivative method. After this, the EXAFS spectra have been recorded and compared to 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 ascribed to the fact that Levy's method gives the radius of coordination sphere directly whereas Lytle method does not. In the 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 that obtained by Levy's method and the Fourier transformation method.

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