

## X-ray Spectral Study by EXAFS of Some Copper (II) Complexes using Synchrotron Radiation Source

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### Abstract

Bond length determination by Extended X-ray absorption fine structure (EXAFS) has been studied at the K-edge of copper in copper (II) mixed ligand complexes. The prepared mixed ligand is p-methoxy anilino-p-methoxy phenyl acetonitrile (L). The ligand was prepared which included the reaction of p-methoxybenzaldehyde with and p-anisidine. Four prepared complexes are I.  $[Cu_2(L)_2(H_2O)_8](SO_4)_2$ , II.  $[Cu_2(L)_2(H_2O)_8](Br)_2$ , III.  $[Cu_2(L)_2(H_2O)_8](Cl)_2$ , and IV.  $[Cu_2(L)_2(H_2O)_8](NO_3)_2$ . The spectra have been recorded at the dispersive XAFS beamline (BL-8) at the 2.5 GeV INDUS-2 synchrotron, RRCAT, Indore, India. The data obtained has been processed and analysed using the computer program Athena and Origin 6.0. The EXAFS data has been analysed to obtain the bond lengths in the complexes using Levy's, Lytle's and Lytle, Sayers and Stern's (LSS) methods. The first peak in the Fourier transform of the spectra gives the value of first shell phase uncorrected bond length. The results obtained from the Fourier transformation and LSS methods are in good agreement.

**Keywords:** Copper complexes, EXAFS, Athena, RRCAT, LSS

### Introduction

The Extended X-ray Absorption Fine Structure (EXAFS) yields information regarding the nearest neighbors of the central metal ions, i.e. bond length. The Fourier transform of an EXAFS spectrum provides information on the distribution of atomic shells as a function of distance from the target absorber. These distances are called phase uncorrected bond lengths. The bond lengths can also be determined by three other methods, namely, Levy's, Lytle's, and Lytle, Sayers and Stern's (LSS) methods. The LSS method also gives phase uncorrected bond length of the first shell. Hence, it is worth comparing the bond lengths obtained from LSS method with those obtained from Fourier transformation method. A search through literature reveals that no work has been done on the EXAFS of copper (II) complexes of ligand p-methoxy anilino-p-methoxy phenyl acetonitrile(L). Keeping this in view, we have studied X-ray K absorption spectra of copper in the mixed ligand copper complexes. The results of the study have been reported in this paper.

### Experimental Details

Four complexes studied in the present investigations I.  $[Cu_2(L)_2(H_2O)_8](SO_4)_2$ , II.  $[Cu_2(L)_2(H_2O)_8](Br)_2$ , III.  $[Cu_2(L)_2(H_2O)_8](Cl)_2$  and IV.  $[Cu_2(L)_2(H_2O)_8](NO_3)_2$ , in which p-methoxybenzaldehyde has been used as a primary ligand and p-anisidine has been used as a secondary ligand. The ligand L= (p-methoxy anilino)-p- methoxy phenyl acetonitrile was synthesized by Stecker's

procedure [1,2] which included the reaction of p-methoxybenzaldehyde with p-anisidine[3]. The four mixed ligand copper complexes are listed in Table 1 along with their molecular formulae.

The X-ray absorption spectra at the K-edge of copper of the complexes listed in Table 1 have been recorded at BL-8 EXAFS beamline at the Indus-2 Synchrotron Source, Indore, India. The various aspects of the calibration and the procedure to be followed on this beamline were similar to those described by Gaur et al [4]. The experimental data have been analysed using the available computer software packages Origin 6.0 professional and Athena[5].

Table 1 List of all Complexes

S.NO	Abbreviation	Molecular formula
1.	$[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_8](\text{SO}_4)_2$	$[\text{Cu}_2(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_8](\text{SO}_4)_2$
2.	$[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_8](\text{Br})_2$	$[\text{Cu}_2(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_8](\text{Br})_2$
3.	$[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_8](\text{Cl})_2$	$[\text{Cu}_2(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_8](\text{Cl})_2$
4.	$[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_8](\text{NO}_3)_2$	$[\text{Cu}_2(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_8](\text{NO}_3)_2$

## Material and Methods

### Material

All reagent used were analytical grade purity. All Metal salts of copper (II) were obtained from E-Merck/ Sigma/Adrich company, p-methoxy benzaldehyde, glacial acetic acid 99 % (Merck), concentrated  $\text{H}_2\text{SO}_4$  99 % (Merck), ethanol absolute 99% (Fluka) were used as received from the suppliers. p-anisidine and p-anisidine sulfonic acid were supplied by Prasand group of industries.

### Synthesis of Cu (II) complexes of ligand L

#### [A] Preparation of ligand L= [(p- methoxy anilino)-p-methoxy phenyl acetonitrile]

The aldehyde, p-methoxy benzaldehyde 0.05 mole was dissolved in 50 ml of glacial acetic acid. In order to bring the pH to 2, p-anisidine sulfonic acid was added in small portions. Then 0.05 mole of the amine p-anisidine is added in it. Concentrated  $\text{H}_2\text{SO}_4$  is added drop wise in order to adjust the pH to 3-4. KSCN 0.05 mole was added to the mixture which was kept stirring. The disappearance of the starting material (the amine) and development of a higher spot on T.L.C was checked at the end of the reaction. The reaction mixture was poured on ice so that immediate precipitation takes place. By adding ammonia, compound is made slightly alkaline. The solid product was filtered, washed with water and dried.

#### [B] General method for preparation of the complexes of ligand L

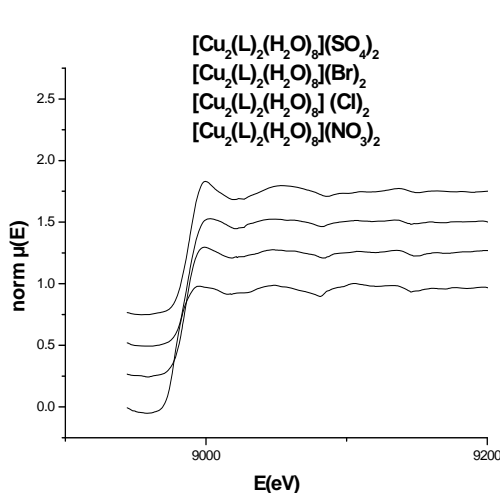
A solution of a metal salt of Cu (II) in absolute ethanol was added to ethanolic solution of the ligand with a continuous stirring. The molar ratio of the reactants was 2:1. Precipitation took place immediately. Each mixture is heated under reflux for 30 minutes for complete precipitation. The products were filtered off, washed several times with ethanol and dried under vacuum.

**Table 2.** Energy E (eV) and wave vector k ( $\text{\AA}^{-1}$ ) for EXAFS maxima and minima at the K absorption edge of copper in the complexes and their corresponding values of n and energy level Q.

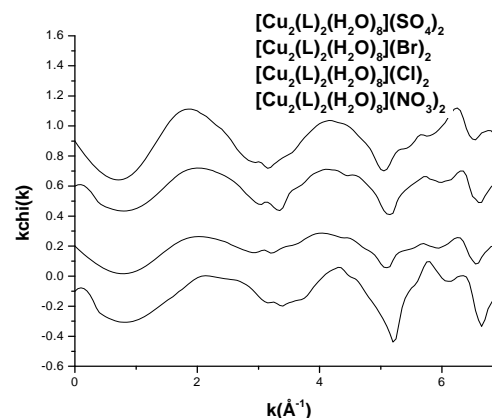
Structure	n	Q	$[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_8](\text{SO}_4)_2$		$\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_8(\text{Br})_2$		$\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_8(\text{Cl})_2$		$\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_8(\text{NO}_3)_2$	
			E (eV)	k ( $\text{\AA}^{-1}$ )	E (eV)	k ( $\text{\AA}^{-1}$ )	E (eV)	k ( $\text{\AA}^{-1}$ )	E (eV)	k ( $\text{\AA}^{-1}$ )
A	0	2.04	10.35	1.65	15.97	2.05	18.40	2.2	19.24	2.25
$\alpha$	1	-	37.72	3.15	92.67	3.35	52.05	3.7	43.95	3.4
B	2	6.04	65.48	4.15	63.9	4.1	146.15	6.2	70.30	4.3
$\beta$	3	-	96.96	5.05	100.84	5.15	237.30	7.9	100.84	5.0
C	4	12.0	148.52	6.25	153.31	6.35	294.49	8.8	127.90	5.8
$\gamma$	5	-	219.61	7.6	165.62	6.6	18.40		170.68	6.7

## Results and Discussion

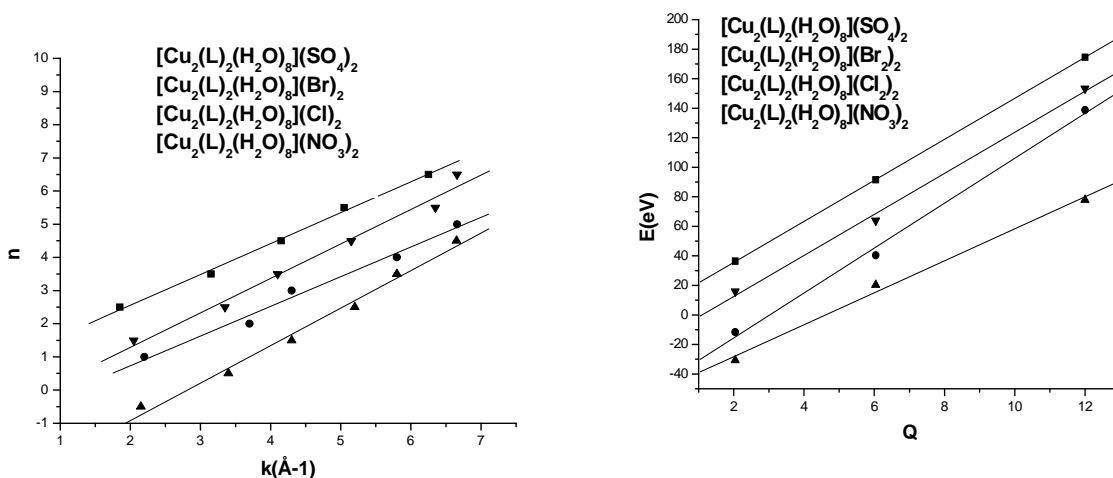
The normalized X-ray absorption spectra of copper complexes are shown in Fig.1. Following the principal absorption maximum, there are distinct EXAFS features extending up to 350 eV on the high-energy side of the K absorption edge. The EXAFS spectra converted into k space have been given in Fig. 2. The slope of channel No n verses wave vector k curves, shown in Fig.3, have been used to evaluate the bond length by LSS method. The slope of energy level Q verses energy E curves, shown in Fig.4, have been used to evaluate the bond length by Lytle method. The values of energy E and wave vector k corresponding to these maxima and minima have been shown in Table 2. The magnitudes of Fourier transform of Fig. 2 are shown in Fig. 5.



**Figure 1.** The normalized XAFS spectrum of copper complexes

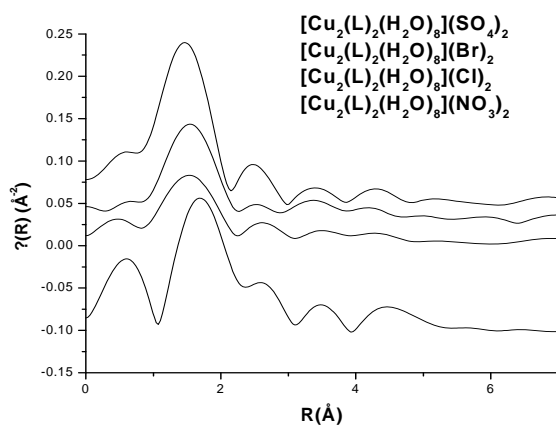


**Figure 2.**  $\chi(k)$  versus k curves for the copper complexes



**Figure 3.**  $n$  versus  $k$  curves for the copper complexes

**Figure 4.**  $Q$  versus  $E$  curves for the copper complexes



**Table 3.** Values of first shell bond lengths (in  $\text{\AA}$ ) calculated from Levy's,[6] Lytle's,[7] LSS[8] and Fourier transform methods for the complexes

S.No.	Complex	Phase corrected		Phase uncorrected	
		Levy's Method $R_L$	Lytle's Method $R_S$	LSS Method $(R_1 - \alpha_1)$	FT Method $R$
01.	$[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_8](\text{SO}_4)_2$	2.24	1.64	1.41	1.40
02.	$[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_8](\text{Br})_2$	2.17	1.64	1.50	1.50
03.	$[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_8](\text{Cl})_2$	2.18	1.08	1.74	1.52
04.	$[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_8](\text{NO}_3)_2$	2.20	1.86	1.69	1.62

## Discussion

### Determination of bond length by Levy's, Lytle's and L.S.S

In Levy's method, the bond lengths are calculated by using the relation  $R_1 = [151/\Delta E]^{1/2} \text{ \AA}$ , where  $\Delta E$  is the difference in eV of the energies of the EXAFS maximum B and minimum  $\beta$  [6]. The bond lengths estimated in this way are tabulated in Table 3.

The normalized spectra of all Cu(II) complexes have been shown in Fig.1 and the  $\chi(k)$  Vs  $k$  curves for copper complexes have been also shown in Fig.2. In Lytle's method [7], the energy values (E) of the absorption maxima as obtained from the measurements are plotted, against the Q values for p symmetry, i.e., Q = 2.04, 6.04, 12.00 and 20.00. The slope M of the E Vs Q plots shown in Fig.3 are used to evaluate the radius  $R_s$  by using the relation  $R_s = [37.60/M]^{1/2}$ . The values of  $R_s$  calculated with the help of this method are reported in the same Table 3.

Lytle, Sayers and Stern's (L.S.S.) have given a simple method to determine the nearest neighbour distances [8]. To estimate the bond length by this method,  $n$  Vs  $k$  graph shown in figure 4, have been plotted. The slope of  $n$  Vs  $k$  plot gives the value of  $2(R_1 - \alpha_1)/\pi$  where  $R_1$  is the bond length. The parameter  $\alpha_1$ , depends to a large extent on the central absorbing atom. The values of  $(R_1 - \alpha_1)$  thus obtained are given in the same Table 3.

### Determination of bond length by Fourier transform of EXAFS spectra

The normalized EXAFS spectra have been Fourier transformed and are given in figure 3. The position of the first peak in the Fourier transform gives the value of first shell bond length, which is shorter than the actual bond length because of energy dependence of the phase factors in the sine function of the EXAFS equation. This distance is thus the phase-uncorrected bond length. The peaks in the Fourier transform are shifted towards the origin by an amount  $\alpha_j$ , and hence, the peaks are at distances  $R_j - \alpha_j$  [9]. For the first peak,  $j = 1$  and, hence, the position of the first peak determines the distance  $R_1 - \alpha_1$ . The distance  $R_1 - \alpha_1$  should be equal to the distance found from the LSS graphical method. Hence, both the LSS method and the Fourier transformation (FT) method give the value  $R_1 - \alpha_1$ , i.e. both the methods give the value of bond lengths, which have not been corrected for the phase shifts. This distance is called as the phase-uncorrected bond length. The position of the first peak in the Fourier transform which gives the value of  $R_1 - \alpha_1$ , are given in table 3 for all the complexes. It is seen from table 3 that the values of  $R_1 - \alpha_1$  as determined from LSS method and those determined from the Fourier transformation method are in good agreement with each other, i.e. both the LSS method and Fourier transformation method give nearly the same value of the phase-uncorrected bond length, i.e.  $R_1 - \alpha_1$ .

## Conclusions

The bond lengths have 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. The present work shows that the methods outlined above provide reliable results for the first coordination shell bond lengths.

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