

Extended X-Ray K-Absorption Spectral Studies of Some Copper (II) Schiff Base Complexes

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Abstract. 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. 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 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*.

Keywords: EXAFS, Copper (II) Schiff Base Complexes, Fourier transform, Bond lengths, XANES.

1. INTRODUCTION

Metal complexes of Schiff bases play an essential role in agriculture, pharmaceutical, industrial chemistry and biology [1]. Since the Schiff bases play important roles in the field of science and technology and due to their biological and industrial applications, some Schiff base complexes have been prepared and their Extended X-ray absorption fine structure (EXAFS) spectra at the K-edge of copper have been studied [2-3]. Schiff bases possess analgesic, anti-inflammatory, antibiotic, antiulcer, and anti- microbial activities. They also exhibit anticancer activity. They have been found to be effective against Mycobacterium tuberculosis [4]. Schiff bases of o-phenylenediamine and its complexes have a variety of applications including biological, clinical and analytical [5-6]. Due to the diverse applications of the Schiff bases, their metal complexes have been synthesized.

2. EXPERIMENTAL DETAIL

The copper complexes have been prepared using o-PDA (orthophenylenediamine) as a ligand [7]. The metal salt (CuCl₂.2H₂O) and the prepared ligand were dissolved in Ethanol and refluxed for 8 - 12 hours. The contents were then allowed to cool at room temperature for one day. The solution was then decanted in watch glass and allowed to evaporate. The precipitates were then washed and dried in air.

The X-ray absorption 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, Indore, according to the procedure described by Gaur et al [8-11]. The Fourier transforms peaks at the radial distances of the neighboring atoms from the absorbing atoms. The Cu (II) Schiff base complexes studied are listed in table 1.

3. RESULTS AND DISCUSSION

Extended X-ray Absorption fine structure: The bond lengths of copper complexes were calculated by using IFEFFIT method, after this process, it has been compared with these three different methods.

1. Levy's method 2. LSS method 3. Lytle method

According to Levy's method [12] bond length given by $R = (151/ \Delta E)^{1/2}$ where, ΔE is the energy separation between first maxima and first minima. The LSS method [13] is a graphical method and according to this method, the simplified equation for wave vector is given by $k = (0.263E)^{1/2}$ where, E is energy position of different maxima and minima in fine structure curve measured from point in K-absorption edge. The total phase

shift $\delta_j(k)$ parameter was also determined using the expression $\delta_j(k) = -\alpha_j k + \beta_j - 1/2\pi$, where notations have their usual meaning. Lytle method [14] is modification of LSS method is given by the expression $R = (37.60/M)^{1/2}$ Where M is slope Between E versus Q plots. The absorption energy maxima are E=A, B, C, D and Q=2.4, 6.4, 12, 20 are constant. In the LSS method, the nearest neighbor distance can be determined by

$$(1/2+n)\pi = 2k(R_1 - \alpha_1) + 2\beta_1,$$

Where R_1 is the bond length. $(R_1 - \alpha_1)$ is the phase uncorrected bond length. The magnitude of Fourier transform spectra are shown in Fig 4(a, b). The Fourier transforms peaks at the radial distances of the neighboring atoms from the absorbing atoms. The distances found in Fourier transform are, However, shorter by 0.2- 0.5Å than the actual distances due to energy dependence of the phase factors in sine function of the theoretical expression for EXAFS, known as EXAFS equation. The peaks shifted in the Fourier transform are shifted towards the origin by an amount α_j and hence the peaks are at distances $R_j - \alpha_j$ [15]. For the first peak $j=1$ and hence the position of the first peak determines the distance $R_1 - \alpha_1$. It is seen that the values of $R_1 - \alpha_1$ as determined from the LSS method and that determined from the Fourier transformation method are in good agreement with each other, i.e. both the LSS method and the Fourier transformation method give nearly same value of the phase uncorrected bond length i.e. $R_1 - \alpha_1$. The normalized Spectra at The K-edge of copper in the complexes is indicated in fig.1(a, b). $\chi(k)$ versus k curve for the complexes are indicated in fig. 2(a, b) The values of n , k , E and Q are listed in table 2 and The values of bond lengths calculated from the above mentioned method are reported in table 3. The E Vs Q plots for the Cu(II) Complexes are indicated in fig.5(a, b) and the n Vs k plots for the Cu(II) Complexes are indicated in fig.6(a, b)

Complexes	Abbreviations	Molecular Formulae
1. Bis-pentanyl R(2-anisidine)-phenyldiazine Cu(II) bis-benzenediamine	Bisp(2anisidine)pdCu(II)bisbd	C ₃₄ H ₃₂ N ₈ O ₂ Cl ₂ Cu
2. Bis-pentanyl R(4-chloro)-phenyldiazine Cu(II) bis-benzenediamine	Bisp(4chloro)pdCu(II)bisbd	C ₃₂ H ₂₆ N ₈ Cl ₄ Cu

Structure	n	Q	Complex 1		Complex 2	
			E	k	E	k
A	0	2.04	13.3	1.87	13.3	1.87
A	1	-	46.5	3.50	45.7	3.50
B	2	6.04	95.8	5.02	97.3	5.02
B	3	-	162.1	6.53	162.1	6.53
C	4	12	191.6	7.10	190.6	7.10
Y	5	-	285.8	8.67	289.1	8.63
D	6	20	443.4	10.8	443.4	10.8

Table 3 Values of first shell bond lengths R (Å) calculated from Levy's, Lytle's, L.S.S. methods and obtained from the Fourier transforms of the experimental EXAFS data for copper (II) complexes.

S. No.	Complex	Phase corrected		Phase uncorrected	
		Levy's method R _l	Lytle's method R _s	L.S.S. method R ₁ -α ₁	F.T. method R
1.	Complex 1	1.50	1.26	1.10	1.17
2.	Complex 2	1.52	1.26	1.10	1.11

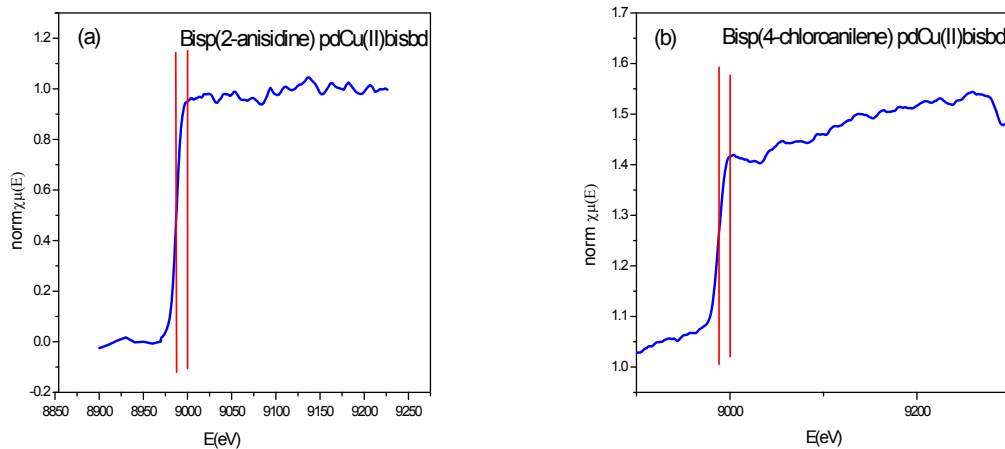


FIGURE 1 The K-edge of copper in the complexes indicating positions of the absorption edge E_K and the principal absorption maximum A.

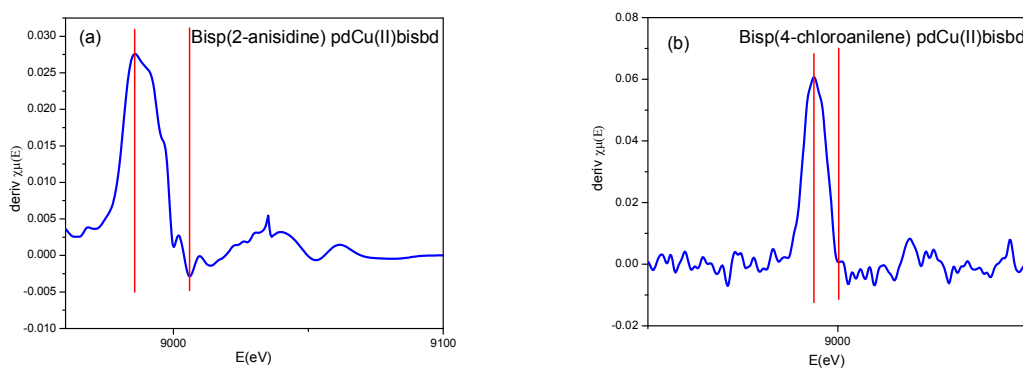


FIGURE 2 Derivative of the absorption spectrum at the K-edge of copper in the complexes indicating positions of the absorption edge E_K and the principal absorption maximum

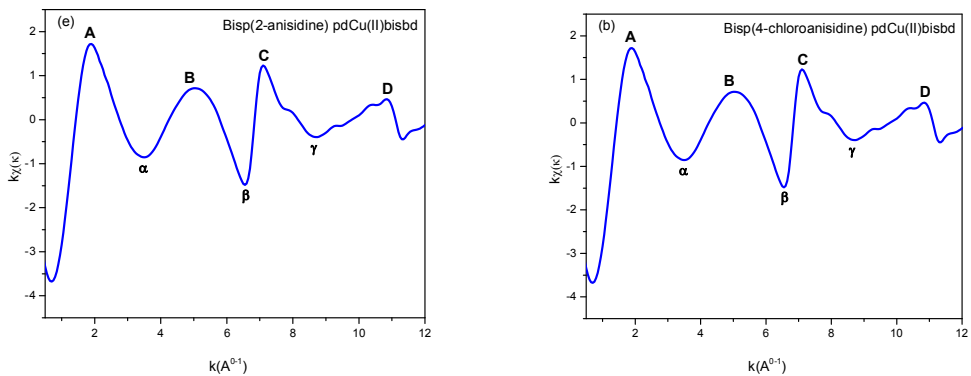


FIGURE 3 $\chi(k)$ versus k curve for the copper complexes

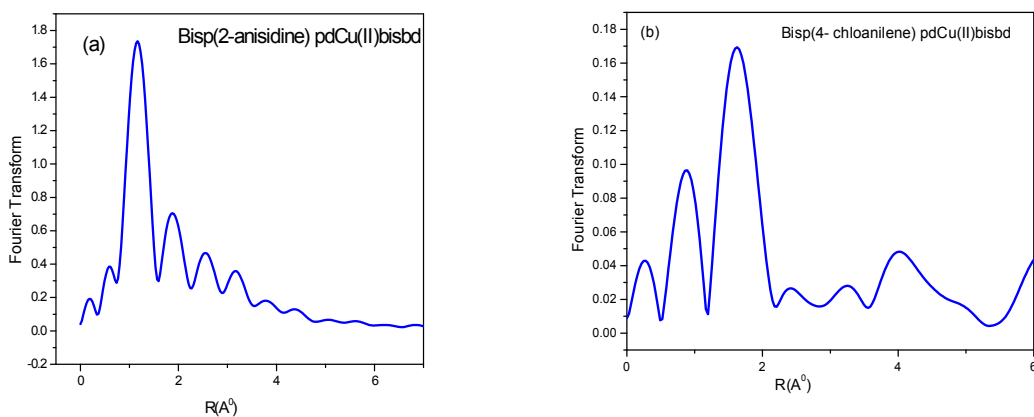


FIGURE 4 Magnitude of Fourier transform of the $\chi(k)$ versus k curve for the Cu(II) complexes

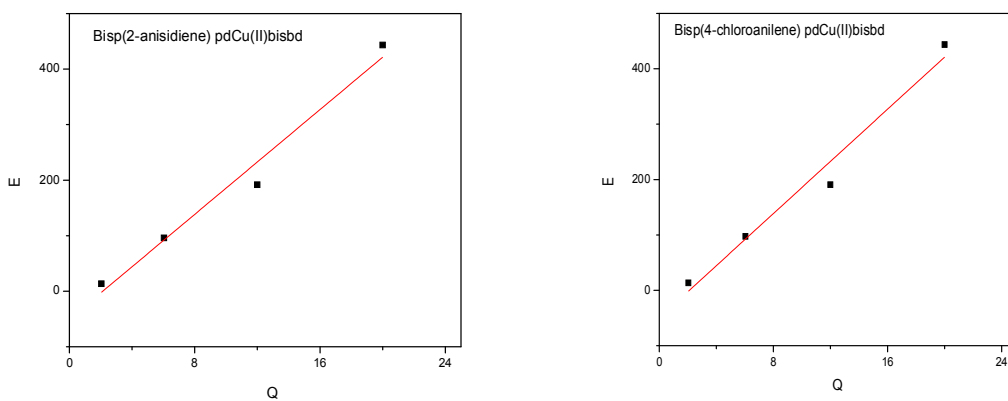


FIGURE 5 E Vs Q plots for the Cu(II) Complexes

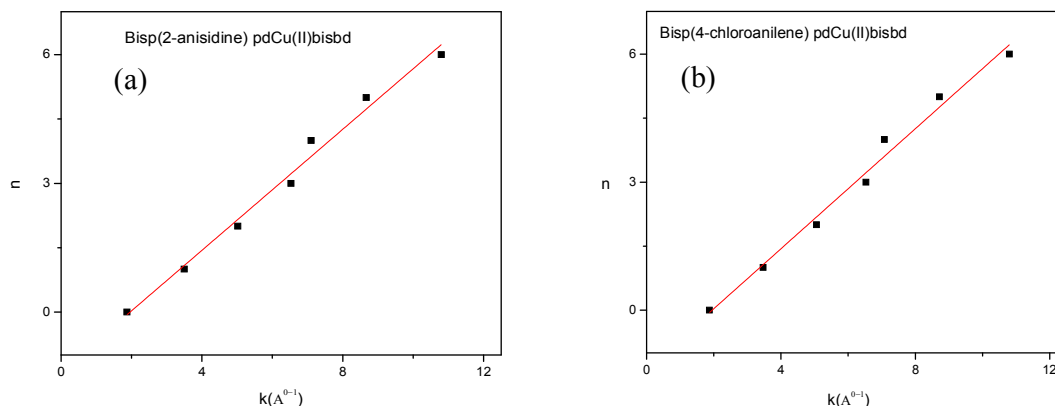


FIGURE 6 n Vs k plots for the Cu(II) Complexes

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