



Extended X-ray absorption fine structure (EXAFS) and (XANES) studies of zinc complex with Schiff base using synchrotron radiation source

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Abstract: The present work deals with synthesis of zinc complexes with Schiff base which were prepared by using chemical root method. The Schiff base was prepared by condensation process. The X-ray absorption spectra have been recorded at BL-9 scanning Extended X-ray Absorption Fine Structure (EXAFS) beam line at the 2.5-GeV INDUS-2 Synchrotron Source, RRCAT, Indore, India. The data analysis has been done using EXAFS software Athena. The normalized EXAFS spectra have been Fourier transformed. 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. The bond length has been measured using Levy's, Lytle's and Lytle, Sayer's (LSS) graphical method. The values of bond length obtained using various methods are in good agreement to each other. The values of chemical shift, Shift of principal maxima and value of edge width is obtained by analysing XANES spectrum.

Introduction

The transition metal complexes with Schiff base are very important because they have so many applications in industry and medicine. X-ray absorption spectroscopy has been widely used to obtain information about the molecular structure of compounds and complexes. We can get information regarding the nearest neighbours of the central metal ions using the extended X-ray Absorption fine structure [1]. Hence, we have studied X-ray K absorption spectra of zinc complex with Schiff base. In X-ray absorption spectroscopy absorption of X-rays is measured as a function of incident X-ray energy. Variation of the X-ray absorption coefficient near the absorption edge is termed as X-ray absorption fine structure. Absorption edge is formed in the graph because at a particular energy, the

absorption increases suddenly and drastically. The fine structure is based on X-ray photoelectric effect. 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 [2]. In order to find radial distribution of atoms around a particular absorbing atom and structural information we have used EXAFS analysis. EXAFS is used to calculate bond length i.e. distances of the neighboring atoms from absorbing elements. In this article bond lengths have been determined from EXAFS maxima and minima with the help of three different graphical methods. The values obtained are compared with the Fourier transform method. The XANES (X ray absorption near edge

structure) parameters have also been calculated using the spectrum.

Experimental :

(A) Synthesis of Schiff base:

All the chemicals used are of pure grade. The Schiff base was prepared by reaction of (E)-3-(P-tolyldiazenyl) pentane-2,4-dione with Ethylene diamine (EDA) and the mixture was refluxed for 8 hours. After the reaction was complete the reaction mixture was poured over crushed ice. The separated solid product was filtered and dried.

(B) Synthesis of zinc complex:

The zinc complex with Schiff base was prepared by chemical route method. A solution of metal salt zinc acetate (0.005 mol) was mixed drop wise with the solution of Schiff base (0.01 mol) in 20 ml of ethanol. The mixture was refluxed for 8 hours in 70-80 °C on water bath. On cooling, colored solid product was formed which was collected by filtration and dried and stored in desiccators.

EXAFS Spectra Recording at INDUS 2

The complexes were finely powdered and then absorption sheets were prepared. The zinc K edge spectra were obtained from BL 9 scanning EXAFS beam line at 2.5 GeV INDUS 2 synchrotron radiation source at Raja Ramanna Center for Advanced Technology (RRCAT) Indore, India [3-5]. On this beam line, the X-ray intensities I_0 and I_t are obtained as the CCD outputs. Using the relation, $I_t = I_0 e^{-\mu x}$, where μ is the absorption coefficient and x is the thickness of the absorber. The experimental data have been analysed using the available computer software package Athena. First the normalized $\mu(E)$ versus E spectra are obtained, then $\chi(k)$ versus k spectra are obtained, and finally, the Fourier transforms of the latter are obtained. For recording the spectrum on scanning EXAFS beamline, the crystal bender and the goniometer are set to cover the energy range of the zinc K-edge absorption spectra. From figure 1 and figure 2 it is clear the value of energy at which K absorption edge is obtained in zinc complex is comparable to the value of energy (9659 eV) at which K absorption edge is obtained in zinc metal foil.

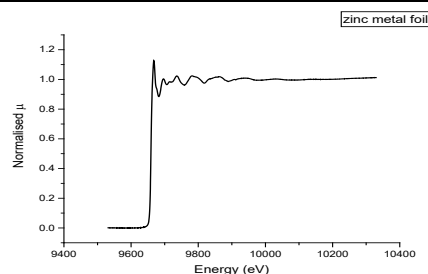


Figure 1 Normalized μ versus energy graph for zinc foil.

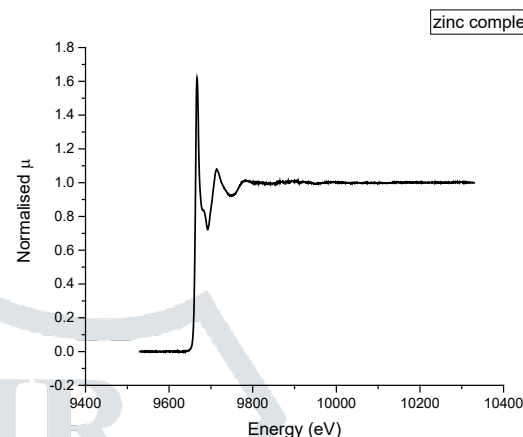


Figure 2 Normalized μ versus energy graph for zinc complex.

XANES Parameters calculation:

Chemical shift

The K absorption edge of zinc has been found to be shifted towards the high-energy side as compared to the K absorption edge in the metal. The value of E_K for zinc complex is 9661.49 eV. The shifts of the K absorption edge of zinc in the complexes with respect to that of zinc metal have been determined according to the formula $\text{Chemical shift} = E_K - \text{Standard}$. The value of chemical shift for zinc complex is 2.49 eV. For computing the chemical shift, the value of E_K (zinc metal) has been taken as 9659 eV.

Shift of Principal absorption maximum

The principal absorption maximum E_A for the zinc complex has been shifted by 7.5 eV with respect to zinc metal, the value of E_A is shifted towards the higher energy side.

Edge-width

The values of the edge-width ($E_A - E_K$) for the zinc complex is found to be 5.01 eV.

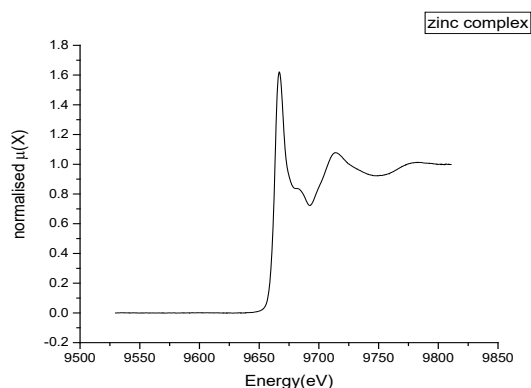


Figure 3 XANES graph for zinc complex

Determination of bond lengths:

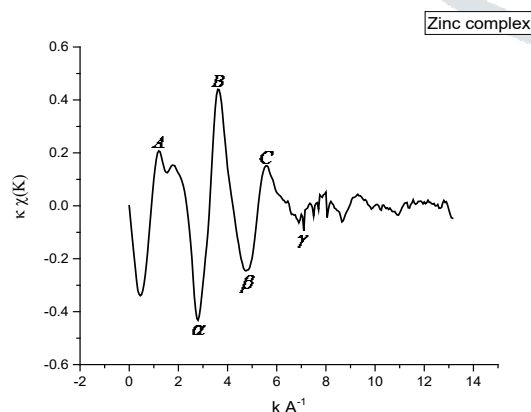
By graphical methods from EXAFS spectra

The X-ray absorption spectra, i.e., normalized $\mu(E)$ vs. E curve of zinc complex has been plotted. The $k\chi(k)$ vs. k spectra are shown in figure 4 of zinc complex. The bond lengths have been determined using the following four methods, i.e.: a) Levy's, b) Lytle, c) Lytle, Sayers and Stern's (LSS) and d) Fourier transformation.

Values of first shell bond lengths (in Å) calculated from Levy's, Lytle's, LSS and Fourier transform methods.

Zinc complex with Schiff base	Phase corrected		Phase uncorrected	
	R_{Levy}	R_{Lytle}	R_{LSS}	R_{FT}
	2.0	1.63	1.61	1.56

Table 1: Value of bond length obtained by various methods.

Figure 4 The $k\chi(k)$ vs. k spectra of zinc complex

a) Levy's method

The bond lengths according to Levy's method [8], 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.

Table 2 : Energy E (eV) and wave vector k (\AA^{-1}) for EXAFS maxima and minima at the K absorption edge of zinc complex and their corresponding values of n and energy level.

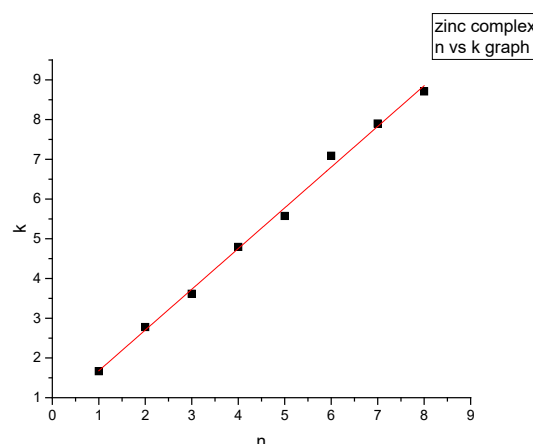
Zinc complex with Schiff base	Structure	n	Q	E	K
	A	0	2.04	10.55	1.66
	α	1	-	29.36	2.77
	B	2	6	49.71	3.61
	β	3	-	87.38	4.79
	C	4	12	118.09	5.57
	γ	5	-	191.45	7.09

b) Lytle's method

According to Lytle [9] method the bond length is calculated by 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 bond length are shown in the table 1.

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

The values of the wave vector k (\AA^{-1}) for EXAFS maxima ($n=0, 2, 4, \dots$) and minima ($n=1, 3, 5, \dots$), for all the zinc complexes are presented in Table 2. In the LSS method for determination of the nearest neighbour distances, n versus k graph is plotted fig5. The plots have been found to be linear for all the complexes. The slope of n versus k plot gives the value of $2(R_1 - \alpha_1)/\pi$ where R_1 is the bond length. In the LSS method [10], for determination of the nearest neighbor distances, gives the value of $(1/2 + n)\pi = 2k(R_1 - \alpha_1) + 2\beta_1$, where R_1 is the bond length. $(R_1 - \alpha_1)$ is the phase uncorrected bond length.

Fig:5 n vs k graph for zinc complex

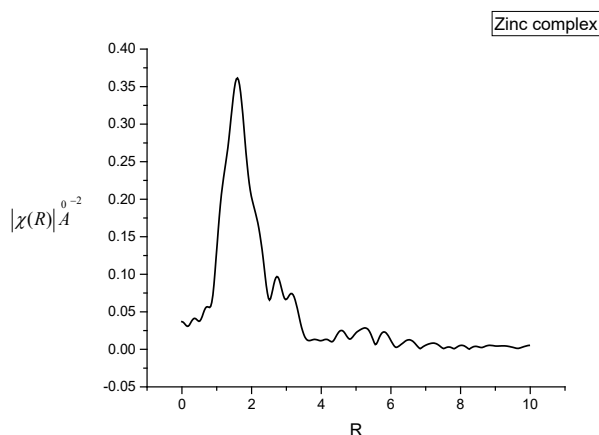


Figure 6 Graph between Fourier transform $\chi(k)$ and radial distance R.

d) Fourier transformation method

The magnitude of Fourier transform spectra are shown in figure 6. 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 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 [11]. 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. We can compare the values with LSS method.

Conclusion:

X-ray absorption spectra of zinc complex at the K-edge of zinc have been recorded and shift of the K-edge (chemical shift), shift of the principal absorption maximum and edge-width has been obtained. From the positions of the EXAFS maxima and minima, the bond lengths in the complex have been determined by three different methods viz. Levy's, Lytle's and LSS methods. From the Fourier transforms of the EXAFS spectra, the bond lengths (uncorrected for phase shift) 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 distances found in Fourier transform are, however, shorter than the actual distances due to energy dependence of the phase factors in sine function of the theoretical expression for EXAFS.

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