Studies of EXAFSSpectra using Copper (II) Schiff Base complexes and Determination of Bond lengths Using Synchrotron Radiation

A Mishra[1], V Vibhute[1], S Ninama[1], N Parsai[1], S N Jha[2], P Sharma[3]
[1]School of Physics Devi Ahilya University, Khandwa Road, Indore [MP]
[2]Applied Spectroscopy Division, Bhabha Atomic Research Centre, Mumbai, India
[3]School of Chemical Sciences, Devi Ahilya University, Khandwa Road, Indore [MP]

Email: vishakhavibhute28@gmail.com, mishraa1960@yahoo.in

Abstract:X-ray absorption fine structure (XAFS) at the K-edge of copper has been studied in some copper (II) complexes with substituted anilines like (2Cl, 4Br, $2NO_2$, $4NO_2$ and pure aniline) with o-PDA (orthophenylenediamine) as ligand. The X-ray absorption measurements have been performed at the recently developed BL-8 dispersive EXAFS beam line at 2.5 GeV Indus-2 Synchrotron Source at RRCAT, Indore, India. The data obtained has been processed using EXAFS data analysis program Athena.The graphical method gives the useful information about bond length and also the environment of the absorbing atom. The theoretical bond lengths of the complexes were calculated by using interactive fitting of EXAFS using fast Fourier inverse transformation (IFEFFIT) method. This method is also called as Fourier transform method. The Lytle, Sayers and Stern method and Levy's method have been used for determination of bond lengths experimentally of the studied complexes. The results of both methods have been compared with theoretical IFEFFIT method.

1. Introduction

Ligand, a metal surrounded by a cluster of ions or molecule, is used for preparation of complex compounds named as Schiff base[1]. Metal complexes of Schiff bases play an essential role in agriculture, pharmaceutical and industrial chemistry and biology. The wide range of uses of o-PDA and its Schiff bases urged us to study its Schiff base. Large number of Schiff bases and their complexes are of significant interest and attention is drawn to them because of their biological activity including anti-tumor, antibacterial, fungicidal and anti-carcinogenic properties. Since the Schiff bases play an important role in the field of science and technology and due to their biological and industrial applications.

X-ray absorption fine structure (XAFS) refers to modulation in X-ray absorption coefficient just above the X-ray absorption edge. XAFS is often divided into two regions, XANES (which lies within the first 30 eV from the edge position) and EXAFS (which lies beyond 30 eV from the absorption edge).EXAFS is applicable to both condensed matter and gases. Single crystal is not required. Information available from EXAFS is average distance between the absorbing atom and its neighboring atoms, mean square variation in the distance and its coordination number and metal- ligand bond length.

In the present paper the bond lengths of the following copper complexes have been calculated experimentally by using Levy's, Lytle's and LSS (Lytle, Sayers and Stern) methods.
1.Copper(II) Pureaniline ($C_{32}H_{28}N_8Cl_2$), namely(Cu1) 2.Copper(II) 2Cl Aniline($C_{32}H_{26}N_8Cl_4$)namely (Cu2) 3.Copper(II)2NO_2aniline($C_{32}H_{26}N_{10}O_4Cl_2$)namely(Cu3) 4.Copper(II)4NO_2aniline($C_{32}H_{26}N_{10}O_4Cl_2$) namely (Cu4)

2. Experimental Techniques

In the present investigations, the X-Ray absorption spectra have been recorded using synchrotron radiation. The X-Ray spectroscopic setup is available at RRCAT and is called beam line. This beam line has been recently commissioned at the 2.5 GeV Indus-2 synchrotron radiation sources [1-3]. The beamline used in the present investigation has been designed in the dispersive mode and is called dispersive EXAFS (DEXAFS) BL-8 beamline. The computer software *Athena* version 0.8.056 has been used for analysis of the digital spectral data. All the complexes were prepared according to the standard methods and their purity was checked. For preparing the pellets, the complexes are mixed uniformly with a binder material like cellulose. Now the pellets of well mixed samples are made using the press (pelletizer).

Sample Preparation:

Preparation of ligand: Takeproperly weighedsubstituted aniline, 16 cc HCland 16 ccwater in a 500 c.c. beaker. Fit a thermometer in the solution and place the beaker in a through of crushed ice. Cool until the temperature of solution has fallen below 5^0c.Dissolve 4 gm of sodium nitrite in 20cc of water and cool it also in ice bath. Add sodium nitrite solution in installments of 2-3 cc. each time to the well cooled solution of aniline and stir the mixture well with keeping the temperature low.The mixture obtained is added to a third beaker containing Acetylacetone, sodium acetate and alcohol by constantly stirring in crushed ice. Reflux this solution for 6 hours and allow it to dry. Again this dried solution is refluxed for 6-7 hours with o-PDA (orthophenylelediamine). Finally, allow it to come in the form of precipitates.

Preparation of metal complex: The metal salt ($CuCl_2.2H_20$) and the above prepared ligand were dissolved in Ethanol and refluxed for 8 - 12 hours. The contents we are then allowed to cool at room temperature for one day. The solution was thendecanted in watch glass andallowed to evaporate. The precipitates were then washed and dried inair [4].

3. Results and Discussion

The bond length in the copper complexes has been calculated with the help of Levy's, Lytle's and LSS (Lytle, Sayers and Stern) methods. The three methods are described as below:

(A)Levy's method (Levy, 1965)

Levy has outlined a simple method of determining bond length (Levy, 1965)[5]. According to this method the bond length R_1 is given by-

$$R_1 = \left(\frac{151}{\Delta E}\right)^{1/2} \text{Å}$$

Where ΔE is energy difference between the first EXAFS maxima B and first EXAFS minima β.

(B) Lytle's method

Lytle employed a "particle in a box" theory to calculate the bond length [6]. In this method the bond length (R_s) is calculated by the radius R_s of equivalent polyhedron through the relation

$$R_s\,(\text{Å}) = \left\{37.60 / M\right\}^{\frac{1}{2}}$$

Where M is slope of E vs Q plot, energy values E is maxima and Q=2.04, 6.04, 12 and 20 are constants. The values of R_s calculated with the help of this method are reported in table 1.

(C)L.S.S. method

In the the LSS method, for determination of the nearest neighbor distances, formula is given 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 [7].

(D)Fourier transforms (FT) method

The magnitude of Fourier transform spectra are shown in Fig 1.The Fourier transform 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 functionof the theoretical expression for EXAFS, known as EXAFS equation[8]. The peaks shifted in the Fourier Transform ar 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 $R_1-\alpha_1$. The distance is given in table 1.

Table1: Values of first shell bond lengths (in Á) calculated from Levy's, Lytle's, L.S.S. and Fourier transform methods for copper (II) complexes.

S. No.	Complex	Phase corrected		Phase uncorrected	
		Levy's method R_1	Lytle's method R_s	L.S.S. method $R_1-\alpha_1$	F.T. method R
1.	Cu1	1.89	1.55	1.40	1.43
2.	Cu2	1.52	1.56	1.34	1.30
3.	Cu3	1.61	1.82	1.30	1.29
4.	Cu4	1.61	1.82	1.34	1.32

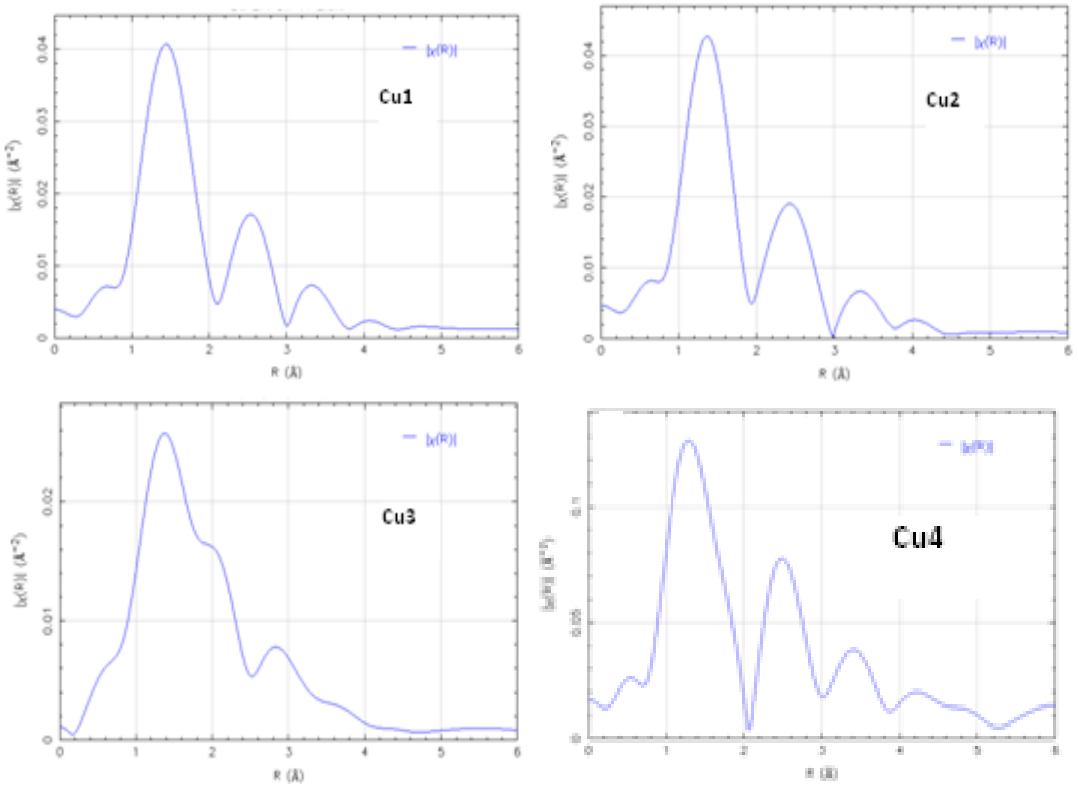

Figure 1 Magnitude of Fourier transform bond length

5. Conclusions

X-ray absorption spectra at the K-edge of copper in copper (II) complexes have been recorded at BL-8 dispersive EXAFS beam line at 2.5 GeV Indus-2 Synchrotron Source at RRCAT, Indore, India.From the positions of EXAFS maxima and minima, the bond lengths in the complexes have been determined by four methods viz. Levy's, Lytle's and LSS methods and the Fourier transforms method. The bond lengths determined by LSS and Fourier transform method are uncorrected for phase shift. It has been observed that the values of R_1-α_1 as determined from the LSS method and that determined from the Fourier transformation method are in good agreement with each other.

Reference

[1] Dhar D N &Taploo C L 1982 *J SciInd Res* **41** 501
[2] Bhattachrya D, Poswal A K, Jha S N, Sangeeta and Sabharwal S C 2009 *Bull mater Sci* **52 (1)** 103
[3] Das N C, Jha S N, Bhattacharyya D, Poswal A K, Sinha A K and Mishra V K 2004 *Sadhana* **29** 545
[4] Raman N, Raja Y P and Kulundaisamy A 2009 Proc. *Indian Acad. Sci* **11 (3)** 183
[5] Levy R M 1965 *J. Chem. Phys.* **43** 1846
[6] Lytle F W 1966 *Advances in X-ray Analysis* **9** 398
[7] Lytle F W, Sayers D E and Stern E A 1975 *Phys. Rev. B.* **11** 4825
[8] Stern E A, Sayers D E and Lytle F W 1975 *Phys. Rev. B.* **11** 4836