

Comparative Analysis of Bond Lengths of EXAFS Data of Copper (II) Complexes Using IFEFFIT Method

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Abstract - In the present study the bond lengths are calculated by Fourier Transform method theoretically using IFEFFIT software and have also been compared with experimental results. IFEFFIT is an interactive program for XAFS Data Analysis. It runs like a command-line 'shell' in which commands are entered to process and manipulate data. IFEFFIT has a fairly high-level command language so that one can do the complex manipulation needed for XAFS analysis (such as background subtraction and Fourier transforms) with simple commands.

Keywords – EXAFS, IEEFFIT Method.

I. INTRODUCTION

In the present paper the already available EXAFS spectra were analyzed and the bond lengths are calculated by Fourier Transform method theoretically using IFEFFIT software and compared with experimental results.

IFEFFIT is an interactive program for XAFS Data Analysis. It runs like a command-line 'shell' in which you enter commands to process and manipulate data. IFEFFIT has a fairly high-level command language so that one can do the complex manipulation needed for XAFS analysis (such as background subtraction and Fourier transforms) with simple commands. One of the principle features of IFEFFIT is that it's command-line functionality can be run in either interactively, from files of commands (i.e., batch files), or accessed from within other programming and high-level scripting languages like Tcl, Perl, and Python. While the full details of this are beyond the scope of this tutorial, IFEFFIT is not just a single program, but a family of related programs and libraries.

II. PROPOSED ALGORITHM

Experimental Technique –

Material Synthesis –

Preparation of Schiff Base Ligand-

Standard method was adopted for the preparation of the complexes. The series of the copper (II) complexes with Coumarine as ligand is shown below.

Table-1 Series of Copper Complexes Coumarine as Ligand.

S. No.	Name of Ligand	Abbreviation	Mol. Formula
1	3-(4-nitro) phenylazo-7-hydroxy 4-methyl coumarine	34NPA7H4MC	C ₁₆ H ₁₁ N ₃ O ₅
2	3-(4-nitro) phenylazo-7-hydroxy 4-methyl coumarine	32NPA7H4MC	C ₁₆ H ₁₁ N ₃ O ₅
3	3-(4-nitro) phenylazo-7-hydroxy 4-methyl coumarine	33NPA7H4MC	C ₁₆ H ₁₁ N ₃ O ₅

III. RESULT & DISCUSSION

A. Bond length estimation by IFEFFIT –

EXAFS spectroscopy is a useful method for determining the local structure around a specific atom in disordered systems. This technique provides information about the coordination number, the nature of the scattering atoms

surrounding a particular absorbing atom, the interatomic distance between the absorbing atom and the backscattering atoms, and Debye–Waller factor. The measurements are done with high energy X-rays, which are normally generated by synchrotron radiation sources. The data analysis is facilitated by specially developed program packages suitable for evaluation purposes. EXAFS spectroscopy is employed in several fields for a variety of applications. Here the structural characterization of a series of is presented. It is found that the pyrimidine heterocyclic has significant influence in the spectra and the results obtained are in agreement with the well-known structure of transition metal complexes. Recently, a new structural analysis of X-ray absorption (XANES/EXAFS) spectroscopy has been used for a local structure refinement on an interesting atom. The absorption peak features in the X-ray absorption near-edge structure (XANES) give useful structural information such as oxidation state of chemical species, site symmetry, and covalent bond strength.[1-4] In general, the small pre-edge peaks of the K-edge absorption spectra for transition metal compounds have been assigned to the transition from 1s to nd orbital, even though it is a dipole forbidden transition. Since the transition is very sensitive to chemical environments, the pre-edge feature in XANES studies has been used to infer the local structure around the central atom. Some molecular orbital calculation studies have been reported that the pre-edge peak intensity is related to 3d and 4p orbital mixing by perturbation of site symmetry and increases gradually with the departure from a centro symmetric environment.[5-7] On the other hand, extended X-ray absorption fine structure (EXAFS) spectra have provided many quantitative structural characterizations such as interatomic distance, coordination number, and Debye-Waller factor.[8-12] Since the EXAFS refinement does not depend on the long-range order of atomic arrangement and is very sensitive to atomic local sites, it is a powerful technique for local structural analysis of partially substituted inorganic compounds. The present communication deals with theoretical analysis of K-absorption X-ray spectra of copper (II) complexes of series.

B. Fourier Transform of the EXAFS oscillations into r-space –

It was suggested by Sayers et al that since $\chi(k)$ can be expressed

$$\chi(k) = \sum_j \frac{N_j F_j(k)}{k r_j^2} \exp(-2\sigma_j^2 k^2) \exp(-2r_j / \lambda) \sin(2kr_j + \phi_j(k)) \quad (1)$$

as a sum of sine waves in above equation the magnitude of the Fourier, transform of $\chi(k)$ into r-space can yield a radial distribution function whose peaks correspond to the radial distances of different coordination shells around the absorbing atom, and the peak amplitude and width indicate the number of nearest neighbors and the extent of disorder, respectively. The Fourier transform method is thus a powerful way to determine the local structural information. The Fourier transform of the EXAFS function is given as

$$\tilde{\chi}(r) = \left(\frac{1}{2\pi} \right)^{1/2} \int_{k_{\min}}^{k_{\max}} k^n \chi(k) \exp(i2kr) dk \quad (2)$$

The magnitude $\left| \tilde{\chi}(r) \right| = \{ \tilde{\chi}_R(r) + \tilde{\chi}_I(r) \}^{1/2}$, where $\tilde{\chi}_R(r)$ and $\tilde{\chi}_I(r)$ are the real and imaginary

parts of the Fourier transform, respectively, shows peaks at distances r_j' which are roughly equal to the true radial distances r_j . The Fourier transform of the function of Figure 1 is shown in figure 2. The small shift in the position of each peak is caused by the phase shifts $\phi_j(k)$. This can be easily understood if one assumes $\phi_j(k)$ to be linear function of k . Which is a very good approximation. Then, the argument of the sine function in equation (1) is

$$2kr_j + \phi_j(k) = 2kr_j(k) - \alpha_j k + \beta_j = 2k(r_j - \alpha_j / 2) + \beta_j \quad (3)$$

which implies that the Fourier transform peaks occur at $r_j' = r_j - \alpha_j / 2$. The range of Fourier transform is

so chosen that k_{\min} is about $2 \text{ to } 9 (\text{\AA})^{-1}$, to exclude the multiple scattering effects, which dominates the near structure and since equation (2) is valid at k values above this. Before, Fourier transforming, $\chi(k)$ is multiplied by k^n where n=1, 2 or 3, in order to get almost equal amplitude of the transformed function over the complete k-range. This type of weighing prevents the large amplitude oscillations from dominating the smaller

ones when determining distances, which are dependent upon the frequency and not the amplitude of $\chi(k)$. Higher powers of k , also make the transform less sensitive to chemical effects, which are significant at low k values. The k^3 weighting roughly cancels the k^{-2} dependence of $F(k)$ and the k^{-2} term in equation (2). However, the backscattering amplitude of low-Z scatterers dies out much faster with k and hence a higher power of k may only amplify the noise. In such cases a lower of k may have to be used. The weighting of $\chi(k)$ is justified provided all materials that are being compared are treated similarly.

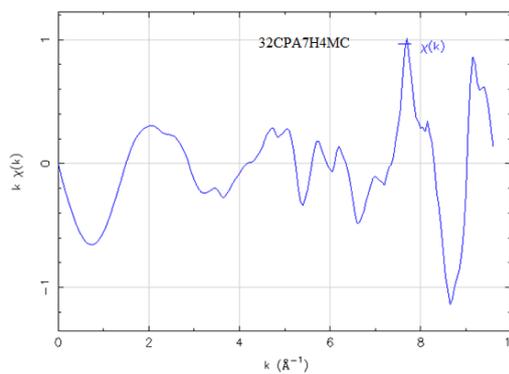
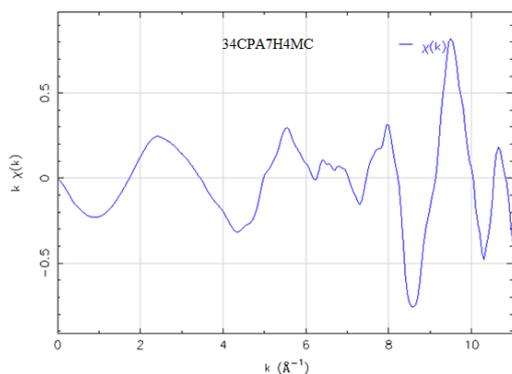
C. Data analysis –

The analysis of Fourier transformation of $k^n \chi(k)$ into r-space was carried out using the IFEFFIT. This will ensure that the FT gives the correct contribution due to all constituent frequencies in $\chi(k)$. This is important for accurate determination of local structure. The k range for Fourier transform was $2 \leq k \leq 9(\text{\AA})^{-1}$. The first strong peak at 1.7\AA for complex in the magnitude of the Fourier transform is due to the oxygen nearest neighbors around the copper ions the peaks are shifted towards smaller distances because of the phase shifts. The inverse Fourier transform of this peak in k -space gives the contribution to EXAFS from the oxygen nearest neighbors. The transform range was $r_1 = 1.1$ to $r_2 = 2.5$ for copper complexes. In contrast to conventional EXAFS fitting analysis, other kinds of EXAFS analysis computation originated from the Tikhonov regularization method is the iterative solution projection method using numerical algorithm of manipulating matrix inversion computation under the ill-posed mathematical problem. The EXAFS spectra obtained using equation (2) in IFEFFIT programming for copper (II) complexes of coumarine are shown in figure 1 and 2. Fourier Transform of the EXAFS data of copper (II) complexes is carried out using equation (3). The imaginary, real and magnitude part of Fourier Transform of EXAFS data are calculated for Cu complexes. The bond length is measured from magnitude of Fourier Transform shown in figure 2 for copper (II) complexes series.

Table-2 The average values of metal-ligand bond length in $(\text{\AA})^{-1}$ for copper complexes

S.No	Complexes	R_{Levy}^a	R_{Lytle}^a	R_{LSS}^a	$R_{IFEFFIT}^d$
1	34NPA7H4MC	2.7	2.7	2.8	1.7
2	32NPA7H4MC	2.7	2.4	2.5	1.6
3	33NPA7H4MC	3.4	2.2	1.9	1.1

- a) Bond Length by LSS
- b) Bond Length by Lytle method
- c) Bond Length by Lytle method
- d) Bond Length by IFEFFIT.



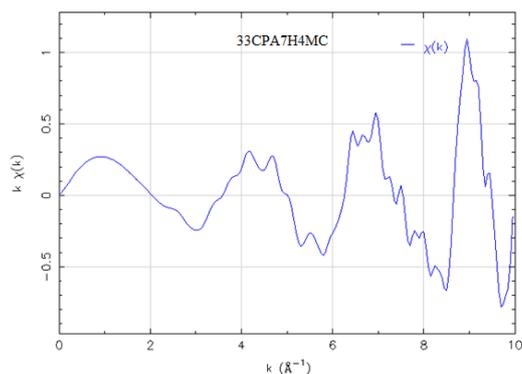


Figure-1 Shows EXAFS spectra of Cu(II) complexes.

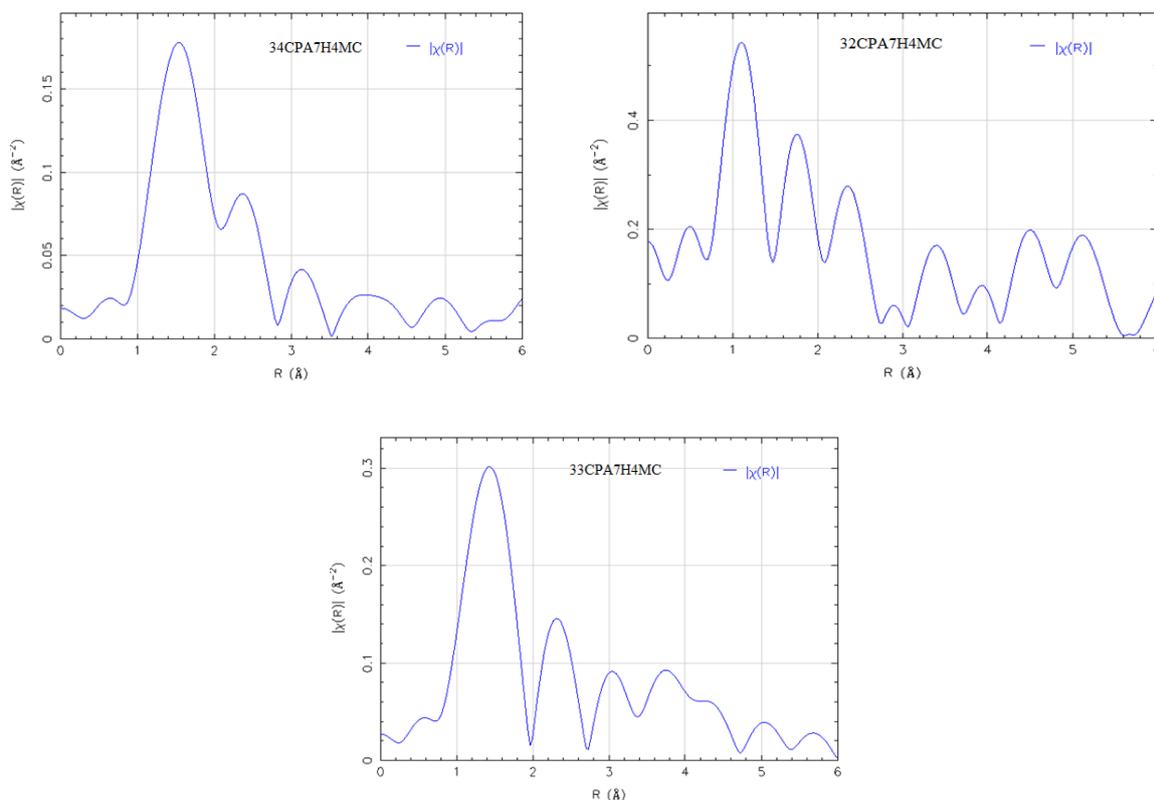


Figure-2 Magnitude of F.T of $k^2\chi(k)$ for copper (II) complexes

IV. CONCLUSION

The above study shows that theoretical calculation of the EXAFS spectra of copper complexes described here is in good agreement with physical reality.

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