Extended X-ray absorption fine structure data analysis of copper (II) complexes of 6-methyl-5-arylhydrazono-2-thio-4-oxo-pyridine ligand

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A technique is presented for Extended X-ray absorption fine structure (EXAFS) data analysis for determining the metal-ligand bond length using conventional source. A theoretical EXAFS data analysis is carried out by Fourier analysis of experimental EXAFS data of some copper (II) complexes of 6-methyl-5-arylhydrazono-2-thio-4-oxo-pyridine. The analysis of EXAFS data is presented using MathCad programming and FEFFIT (Fitting of EXAFS by Fast Fourier Inverse Transform) programming. This analysis includes details of the Fourier transform of the data and the extraction of metal-ligand bond length. Bond lengths determined from these two data analysis methods are compared with the bond lengths obtained from several other known techniques.

Keywords: EXAFS, Fourier transform, FEFFIT, Bond length, Copper (II) complexes

1 Introduction

Extended absorption fine structure refers to the oscillatory variation of the X-ray absorption as a function of photon energy beyond the absorption edge. Such fine structure may extend up to 1000 eV above the absorption edge and may have amplitude of up to a few tenths of the edge jump. Synchrotron-based X-ray Absorption Fine Structure (XAFS) spectroscopy becomes a powerful technique providing analytical as well as structural information, with applications in a wide range of scientific fields because of the rapid development of the data treatment techniques. EXAFS has become the technique of choice for local structural investigations in a diverse range of material systems. This technique has also proved very useful, while studying the chemical reactions of matter under extreme conditions of temperature and pressure. The EXAFS oscillations in the absorption spectrum are caused by interference in the final state from backscattering of the outgoing photoelectron wave by neighbours of the excited atom. Hence, it is extremely sensitive to the nearest neighbour bond lengths.

A method for determining the metal-ligand bond length by an appropriate Fourier analysis of the K-edge data has been presented. This is illustrated by a detailed analysis of the data for a series of metal organic based on pyridine ligand systems, which model active centers of natural copper containing metal proteins. The Fourier transform of the experimental EXAFS data is done using the FEFFIT program and metal-ligand bond length is determined. In MathCad programming, EXAFS data is generated for some copper complexes from experimentally determined EXAFS parameters. The noticeable advantage of this technique is that the X-ray absorption spectroscopy may be used as a bulk probe to investigate the surface effects. In particular, the technique permits the analysis of buried interfaces systems that are difficult to be analyzed even with more sophisticated surface investigation equipment. Applications of EXAFS can be found in literature on a variety of fields, namely, chemical reactions at the solid state, surface treatments and structural studies of thin films.

2 Methodology

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. In the present paper, the structural characterization of a series of 6-methyl-5-arylhydrazono-2-thio-4-oxo-pyridine is presented. It is found that pyrimidine heterocyclic has significant influence on the spectra and the results obtained are in agreement with the well-known structure of transition metal complexes. A structural analysis of X-ray absorption fine structure (XAFS) spectroscopy has been used for a local structural refinement on an atom of interest. 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 3d orbital, even though it is a dipole forbidden transition. Since the transition is very sensitive to chemical environment, the pre-edge feature in XAFS 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. In this context, the extended X-ray absorption fine structure (EXAFS) spectra have provided many quantitative structural characterizations such as interatomic distance, coordination number and Debye-Waller factor. 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 work deals with an experimental and theoretical analysis of K-absorption X-ray spectra of copper (II) complexes of 6-methyl-5-arylhydrazono-2-thio-4-oxo-pyridine series. The five reported copper complexes are:

Cu(2-nitro-6-methyl-5-arylhydrazono-2-thio-4-oxo pyridine) or Cu(2N6M5A2T4OPyr)
Cu(3-nitro-6-methyl-5-arylhydrazono-2-thio-4-oxo pyridine) or Cu(3N6M5A2T4OPyr)
Cu (4-nitro-6-methyl-5-arylhydrazono-2-thio-4-oxo pyridine) or Cu (4C6M5A2T4OPyr)
Cu(2-chloro-6-methyl-5-arylhydrazono-2-thio-4-oxo pyridine) or Cu(2C6M5A2T4OPyr)
Cu(3-chloro-6-methyl-5-arylhydrazono-2-thio-4-oxo pyridine) or Cu(3C6M5A2T4OPyr)

With the knowledge of EXAFS, the following explanation has been taken for the analysis of complexes under consideration. It was suggested by Sayers et al. that since $\chi(k)$ can be expressed as:

$$\chi(k) = \sum_j \frac{N_j F_j(k)}{k^2 r_j^2} \exp(-2\sigma^2 k^2) \exp(-2r_j/\lambda) \times \sin[2kr_j + \phi_j(k)]$$

Using Eq. (1) in MathCad programming, $\chi(k)$ can be determined from experimental data. Fig. 1 shows graph of $\chi(k)$ versus $k$ calculated in MathCad programming. 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 neighbours and the extent of disorder, respectively. The Fourier transform method is, thus, a powerful way to determine the local structural information.

Fig. 1 — Calculated EXAFS curves of copper (II) complexes by MathCad programming
Fig. 2 — Magnitude of Fourier transform of copper complexes calculated by MathCad programming

Fig. 3 — EXAFS function for five copper complexes obtained from FEFFIT program

Fig. 4 — Magnitude of Fourier transform of \([k^2\chi(k)]\) for five copper complexes obtained from FEFFIT program

distances \(r'\), which are roughly equal to the true radial distances \(r\). In MathCad programming Fourier transform of the EXAFS data is calculated using Eq. (2) as shown in Fig. 2.

In FEFFIT programming, the EXAFS data were analyzed by the standard procedure\(^\text{12}\). The pre-edge background absorption was subtracted to yield the atomic absorption spectrum of the atom of interest background above the edge was removed from the spectrum using spline fit. The data converted to energy space and then to \(k\) space (Fig. 3). A Fourier transform is applied to these data to convert into the \(r\)-space (Fig. 4).

The bond lengths obtained for copper (II) complexes of 6-methyl-5-arylhydrasono-2-thio-4-oxo-pyridine series from the analysis using MathCad

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Experimental (R_{\text{LSS}})</th>
<th>Experimental (R_{\text{Lytle}})</th>
<th>Experimental (R_{\text{Levy}})</th>
<th>Calculated values by MathCad</th>
<th>Experimental values by FEFFIT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (2N6M5A2T4OPyr)</td>
<td>1.9</td>
<td>2.4</td>
<td>2.1</td>
<td>1.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Cu (3N6M5A2T4OPyr)</td>
<td>1.8</td>
<td>2.2</td>
<td>2.6</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Cu (4N6M5A2T4OPyr)</td>
<td>1.9</td>
<td>2.4</td>
<td>2.4</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Cu (2C6M5A2T4OPyr)</td>
<td>1.8</td>
<td>2.0</td>
<td>2.3</td>
<td>1.3</td>
<td>1.1</td>
</tr>
<tr>
<td>Cu (3C6M5A2T4OPyr)</td>
<td>1.8</td>
<td>2.4</td>
<td>2.1</td>
<td>1.0</td>
<td>1.4</td>
</tr>
</tbody>
</table>

\(R_{\text{LSS}}\) — Bond length by LSS method
\(R_{\text{Lytle}}\) — Bond length by Lytle’s method
\(R_{\text{Levy}}\) — Bond length by Levy’s method
programming and FEFFIT programmings are compared with the bond lengths obtained previously\textsuperscript{4} from LSS method\textsuperscript{13}, Lytle’s method\textsuperscript{14} and Levy’s method\textsuperscript{15}. A comparison of five different Cu-O distances by different methods is presented in Table 1.

3 Conclusions

Fourier transform technique provides results with great accuracy. This method is simple and straightforward, thereby providing a physical picture of the X-ray absorption process. This method appears to have a great potential in studying systems such as crystalline and amorphous materials. The atomic distance of central atom with the first nearest neighbour is not affected very much by changing the various substituents in the ligand. The reason is that the substituents are not directly linked to the central atom.

Results indicate that bond lengths determined by Fourier transforming the calculated data using MathCad programming and FEFFIT programming resembles with the bond lengths obtained by LSS method, Levy’s method and Lytle’s method (Table 1). Thus, the theoretical and experimental values agree well with each other. This means that the parameterized theoretical calculation of the EXAFS spectra describes in good agreement with physical reality. The calculated EXAFS curves for copper complexes of pyridine series are in good agreement with experimental EXAFS curves for all complexes studied within experimental error.

References