Synthesis and Analysis of EXAFS data of Cobalt (II) complexes with 3-[N-Phenyle-thiourea-pentanon-2] as ligand and determination of first shell radial distance

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Abstract: X-ray absorption spectra at the k-edge of cobalt have been studied in cobalt mixed ligand complexes having 3-[N-Phenyle-thiourea-pentanon-2] as ligand. Extended EXAFS spectroscopy provides structural information about a sample by way of the analysis of its X-ray absorption spectrum. It allows determining the chemical environment of a single element in terms of the number and type of its neighbors, inter-atomic distances and structural disorders. The data obtained been processed using EXAFS data analysis program Athena. Theoretical EXAFS has been generated using standard EXAFS equation employing the software MathCad. Fourier transform of calculated EXAFS data has been taken to calculate bond lengths theoretically. The bond lengths are compared with bond lengths obtained using other methods from experimental EXAFS data. The results obtained from theoretical and experimental method are comparable with each other.

Keywords: EXAFS, Cobalt (II) mixed ligand complexes, Thiourea, Bond length

1. Introduction

X-ray absorption spectra at the k-edge of cobalt have been studied in cobalt mixed ligand complexes having 3-[N-Phenylethiourea-pentanon-2] as one of the ligand has been investigated. X-ray absorption fine structure (XAFS) refers to modulations in X-ray absorption coefficient just above an X-ray absorption edge. XAFS is often divided into X-ray absorption near edge structure (XANES), which lies within the first 30 eV of the edge position and extended X-ray absorption fine structure (EXAFS), which lies beyond 30 eV above the absorption edge. The physical origin of EXAFS and XANES is basically same, i.e. the scattering of a photoelectron by its environment. XAFS is an important probe of materials, since it contains atomic information of the local atomic structure, i.e. species of atoms present and their locations, but extracting this information is often complicated¹

EXAFS spectroscopy provides structural information about a sample by way of the analysis of its X-ray absorption spectrum. It allows determining the chemical environment of a single element in terms of the number and type of its neighbors, inter-atomic distances and structural disorders. This determination is confined to a distance given by the mean free path of the photoelectron in the condensed matter, which is between 5 and 10 Å radiuses from the element. Modeling EXAFS spectra to determine the average, local-molecular coordination environment of an absorber atom is a multistep process that is best learned through handson experience. Therefore, we describe here the process of building a structural model by giving examples for certain steps with specific reference to the EXAFS data analysis programs Athena for background removal and Artemis for optimizing the theoretical model to the measured spectrum by Ravel and Newville². These programs are user-friendly GUI interfaces to IFEFFIT Newville³. IFEFFIT is an interactive engine that contains the algorithms for fitting the theoretical FEFF calculations Zabinsky et al⁴ to the measured spectrum, hence the name IFEFFIT. FEFF is the program that calculates the details of the scattering processes from a cluster of atoms. The data-analysis program names used in the examples of present work and give a brief summary of their function. The general approach for determining the average coordination structure around the absorber atom from EXAFS data is to build a structural model for the chemical species being identified, and calculate the theoretical EXAFS spectrum for that model using the FEFF program. Programs such as Artemis adjust the structural parameters in the EXAFS equation (described below) until a least-squares fit is obtained between the theoretical (modeled) and experimental EXAFS spectra. The model is adjusted as needed (e.g., with different atom types) until the best possible fit is obtained between theoretical and experimental spectra.

2. Synthesis and characterization of thiourea:

Thiourea compounds with antimicrobial activity is a term of continuous interest because of increased antimicrobial resistance developed by important pathogen.⁵ Thiourea derivatives have attracted attention of several research groups due to their potential in medicinal chemistry.⁶ The broad spectra of biological activity of thiourea derivatives and their metal complexes have been investigated and diverse bioactivities, such as an antifungal⁷ and anti-malarial⁸, have been reported. Thiourea based non-nucleoside inhibitors of HIV reverse transcriptase have also been described. Although the antimicrobial properties of thiourea have been related⁹⁻¹¹, they are limited in terms of both microorganism strains and structural diversity. To the best of our knowledge, no systematic screening has been reported for this class of compounds. Among the thiourea, the [3-N-(phenyl)-thiourea-pentanone-2] derivatives caught our attention because newly results concerning the low toxicity of these thiourea derivatives¹²⁻¹³ suggested their potential as antibiotic drugs.

2.1 Synthesis of the series 3-(N-phenyl)-thiourea-pentanone-2:

In a round- bottomed flask 6.35gm (2-Cl, 3-Cl, 4-Cl, 3-nitro, 4-nitro) anilines and 3.8gm of ammonium thiocynate were mixed in 10ml of hydrochloric acid, with constant stirring. Content were heated for 2-3 minutes and poured in to beaker. Content 50gm up to white colored precipitate of phenylthiourea with substituted anilines, was obtained in which 90% yield is formed.1-2 pellets of NaOH were added to 2.5ml of pentone-2, 4-dione in 250ml beaker. Now 0.5mol prepared compound of phenylthiourea (with

substituted anilines), added to this solution with constant stirring. After some stirring, 5ml of ethyl alcohol is added. Now the contents were transferred into porcelain dish and then heated up to 30° C with continuous stirring. After heating, now porcelain dish is kept in crushed ice with continuous stirring, after 5minute a pale yellow precipitate of [3-N-(phenyl)-thiourea-pentanone-2], was prepared, in which 85% yield was formed.

2.2 Synthesis of substituted anilines with (Cu and Co) metal for Thiourea Complexation:

2.2.1 Synthesis of the series Cu [3-N(phenyl)-thiourea-pentanone-2]:

In 250ml of beaker, 1.24m mol of 3-N-(phenyl)-thiourea-pentanone-2 was dissolved in 10ml of pure ethyl alcohol. Now, at a room temperature, solution of copper chloride was added drop wise with constant stirring in to five ligands solution. A green precipitate of copper complex is formed. The precipitate was collected by filtration, washed with alcohol and dried under vacuum for overnight. With this method, copper complex of 60% yield is prepared.

2.2.2 Synthesis of the series Co [3-N (phenyl)-thiourea-pentanone-2]:

In 250ml of beaker, 1.24m mol of 3-N- (phenyl)-thiourea-pentanone-2 was dissolved in 10ml of pure ethyl alcohol. Now, at a room temperature, solution of cobalt chloride was added drop wise with constant stirring in to five ligands solution. A pink precipitate of cobalt complex is formed. The precipitate was collected by filtration, washed with alcohol and dried under vacuum for overnight. With this method, cobalt complex of 70% yield is prepared.

Synthetic pathways for the 3-N-(phenyl)-thiourea-pentanone-2 with copper and cobalt metal complexes are shown in figure 1.

3. 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. Here the structural characterization of a series of 3-N-phenyle-thiourea-pentanon-2.is presented. It is found that the thiourea 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 ⁽⁶⁻⁹⁾

The pre-edge background absorption was subtracted to yield the atomic absorption spectrum of the atom of interstate background above the edge was removed from the spectrum using spline fit. The data converted to energy space and then to k space. A Fourier Transform (FT) is applied to these data to convert into the r-space. Bond length of cobalt complexes is calculated by graphical method and bond length calculated by IFEFFIT are approximately same. The present communication deals with a experimental and theoretical analysis of K-absorption X-ray spectra of cobalt (II) complexes of 3-N-phenyle-thiourea-pentanon-2 series shown in Table 1.

With the knowledge of EXAFS, the following explanation has been taken for the analysis of complexes under consideration. It was suggested by Stern E A et al.¹⁵ that since χ (k) can be expressed as:

Using equation (1) in MathCad programming, χ (k) can be determined from experimental data. Figure 2 Shows graph of χ (k) versus k calculated in MathCad programming. The magnitude of the Fourier transform of χ (k) into r-space can yield a radial distribution function whose peaks correspond to the radial distances of different coordination shells 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.

The Fourier transform of the EXAFS function is given as:

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

The magnitude , $\left| \widetilde{\chi}(r) \right| = \{ \widetilde{\chi}_R(r) + \widetilde{\chi}_I(r) \}^{1/2}$ where $\widetilde{\chi}_R(r)$ and $\widetilde{\chi}_I(r)$ 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. In MathCad programming Fourier transform of the EXAFS data is calculated using equation (2) as a shown in figure 3. The pre edge back ground 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 (figure 4). A Fourier transform is applied to these data to convert into the r-space (figure 5). The bond lengths obtained for cobalt (II) complexes of 3-N-phenyle-thiourea-pentanon-2 series from the analysis using MathCad programming and FEFFIT programming are compared with the bond lengths obtained previously¹⁴ from LSS method¹⁵, Lytle Method¹⁶ and Levy's method¹⁷. A comparison of five different Co-O distances by different methods is presented in Table 2.

4. Conclusions

The calculated EXAFS curves for Co (II) complexes of Thiourea series resembles with experimental EXAFS curves for all complexes studied within experimental error. Results indicates that bond lengths determined by Fourier transforming the

calculated data using Mathcad programming resembles with the bond lengths obtained by LSS method, Levy's method and Lytle's method (Table 2). Thus, the theoretical and experimental values agree well with each other. This means that the parameterized theoretical calculation of EXAFS spectra describes in good agreement with physical reality. The calculated EXAFS curves for cobalt complexes of Thiourea series are in good agreement with experimental EXAFS curves for all complexes studied within experimental error.

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Table 1. Name and abbreviation of 3-N-phenyle-thiourea-pentanon-2 series

S. No.	Name of Ligand	Abbreviation	
1	3-N-(3nitro)-thiourea-pentanon-2	(3N3NTU2P)	
2	3-N-(4nitro)-thiourea-pentanon-2	(3N4NTU2P)	
3	3-N-(2chloro)-thiourea-pentanon-2	(3N2CTU2P)	
4	3-N-(3chloro)-thiourea-pentanon-2	(3N3CTU2P)	
5	3-N-(4 chloro)-thiourea-pentanon-2	(3N4CTU2P)	

Table 2 First shell Radial distance in (Å) for cobalt complexes

Complexes	First shell Radial distance using different methods				
	R _{LSS} (Å)	R _{Lytle} (Å)	R _{Levy} (Å)	R _{MathCAD} (Å)	R _{ifeffit} (Å)
Co [3N3NTU2P]	1.01	2.4	2.4	2.1	1.07
Co [3N4NTU2P]	1.04	2.5	2.5	2.7	0.88
Co [3N2CTU2P]	0.89	2.0	2.0	2.2	0.98
Co [3N3CTU2P]	0.90	1.9	2.4	2.4	1.13
Co [3N3CTU2P]	1.02	1.8	1.9	2.5	1.19

R_{LSS} -- First shell Radial distance calculated using LSS method

R_{Lytle} -- First shell Radial distance calculated using Lytle's method

R_{Levy} -- First shell Radial distance calculated using Levy's method

R_{MathCAD}. First shell Radial distance calculated in MathCAD software using Fourier Transform method R_{IFEFFIT}. First shell Radial distance calculated in IFEFFIT software using Fourier Transform method



Figure 1 Synthetic pathways for the 3-N-(phenyl)-thiourea-pentanone-2 with copper and cobalt metal complexes





Figure 2. calculated $\chi(k)$ versus k curves of cobalt (II) complexes calculated using MathCAD software





Figure 3.Magnitude of Fourier transform of calculated $k^2 \chi(k)$ versus k curves of cobalt complexes.





Figure 4. Experimental $\chi(k)$ versus k curves for cobalt complexes.

Figure 5. Magnitude of Fourier Transform of experimental $k^2 \chi(k)$ versus k curves for cobalt complexes.