Local structure studies of some cobalt (II) complexes using extended X-ray absorption fine structure

Ashutosh Mishra¹, Samrath Ninama¹, Apurva Trivedi²
¹School of Physics, Vigyan Bhawan, Devi Ahilya University, Indore, India
²Shri Vaishnav Institute of Management, Indore, India

E-mail: samrathn@gmail.com, mishraa1960@yahoo.co.in

Abstract: Extended X-ray Absorption Fine Structure (EXAFS) analysis of Cobalt (II) complex as a ligand of 2–methyl-3-[(bis-aniline(R) phenyl]-3H-1,5 benzodiazepine for finding local structure using conventional method. The Co(II) complexes were prepared by chemical root method. The EXAFS spectra were recorded at Cobalt K-edge i.e.; 7709 eV using Dispersive EXFAS beam line at 2.5GeV Indus-2 Synchrotron Radiation Source(SRS) at RRCAT, Indore, India. The recorded EXAFS data were analysed using the computer software Athena for determine the nearest neighbouring distances (bond lengths) of these complexes with conventional methods and it compared with Fourier transform(FT) analysis. The Fourier Transform convert EXAFS data signal into r-space or k-space. This is useful for visualizing the major contributions to the EXAFS spectrum.

1. Introduction

In the present work, the X-ray absorption spectra have been recorded at the K-edge of cobalt in two macro-cyclic complexes. The coordination chemistry of macro-cyclic ligand is a fascinating area of research. 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 [1]. The EXAFS K-edge of Co (II) complexes were recorded at 7709 eV and also determined the bond length between metal-ligand of (a) Co1-Co(II)2-methyl-3-[(bis-ortho nitophenyl)]-3H 1, 5 benzodiazepine chloride, (b) Co2-Co(II)2-methyl-3[(bis-meta nitrophenyl)]-3H 1, 5 benzodiazepine chloride.

A method for determining the metal-ligand bond length by an appropriate Fourier analysis of the EXAFS 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 [1]. The Fourier transform of the experimental EXAFS data is done using the IFEFFIT program [2] and metal-ligand bond length is determined. Applications of EXAFS can be found in literature on a variety of fields, namely, chemical reactions at the solid state [3], surface treatments [4] and structural studies of thin films [5]. A structural analysis of X-ray absorption fine structure (XAFS) spectroscopy has been used for a local structural refinement on an atom of interest [6]. 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 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 [7]. In this context, the extended X-ray absorption fine structure (EXAFS) spectra have provided many quantitative structural characterizations such as inter-atomic distance, coordination number and Debye-Waller factor [8]. 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.

2. Material Synthesis
    Preparation of ligand (L)
Cobalt Complexes have been prepared by chemical root method. The chemicals used are of pure grade. O-phenylenedicarboxylic acid (0.05 mol, 5.0g), substituted aniline(R) (0.05 mol, 6.9g) dissolved in ethanol (25 mL), and ethyl acetoacetate (0.05 mol, 6.7g) dissolved in ethanol (25 mL). The mixtures of both reactants were refluxed for 6 hour. The volume concentrated on the steam bath until white colored crystals began to form. The product was purified by crystallization from hot alcohol. Thus white crystalline pure macro-cyclic ligand was collected.

    Preparation of [Co (II)-L-Cl$_2$]
Hot ethanol solution of ligand (L) (0.01 m. mol, 0.2 g), hot ethanol solution of cobalt chlorides [CuCl$_2$.6H$_2$O] with few drops of hydrochloric acid was added. The solution mixture was then refluxed for 4h. On cooling, colored precipitates were then filtered and washed with cold water and dried in vacuum [8].

3. Experimental
The complexes were finely powdered and then absorption screens were prepared by carefully spreading calculating amount of the powdered on 1 cm area of kapton tape. The cobalt K-edge EXAFS spectra of these absorption screens have been recorded at BL-8 dispersive EXAFS beamline at 2GeV Indus -2 synchrotron radiation source at Raja Ramanna Center for Advanced Technology (RRCAT), Indore, India [9-11]. The energy calibration of beam line for a particular setting of the polychromator can be done by recording the absorption spectra of two standards, whose absorption edge energies are well established. For example for recording the absorption spectra of Co sample, the two standards can be Co metal foil and Ho oxide powder. The absorption spectra of Co K edge and Ho$_2$O$_3$ L$_3$-edge have been recorded under the same setting of crystal bender and goniometer. In the present work we are taking the values of the energies of Co K-edge in metal and Ho L$_3$ –edge in Ho$_2$O$_3$ as 7709 eV and 8074 eV respectively [13].

4. Results and discussion
The X-ray absorption spectra, i.e., normalized μ (E) vs. E curve of Cobalt complexes is shown in figure 2. The bond lengths have been determined using the following four methods, i.e., Levy’s, Lytle, Lytle, Sayers and Stern’s (LSS) and Fourier transformation methods and the results obtained are given in table1.

4.1 Levy’s method
The bond lengths According to Levy’s method [14], are given by Bragg relation $R_1 = [151/\Delta E]^{1/2}$ Å, where $\Delta E$ is the difference in eV of the energies of the EXAFS maximum B and minimum $\beta$ and $R_1$ is the radius of the first coordination sphere.

4.2 Lytle’s method
According to Lytle [15] method the bond length ($R_s$) is evaluate by the radius $R_s$ of equivalent polyhedron through 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 $R_s$ calculated with the help of this method are reported in table 1.
4.3 Lytle, Sayers and Stern’s (LSS) method
In the LSS method [16], 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 shown in table 1. Although, Fourier transform of EXAFS data is a general and powerful technique to determine many physical parameters; however, it is possible to determine nearest-neighbor distances and phase shifts from a simple graphical technique. This is possible because the first shell scattering usually dominates the EXAFS curves; then, if only the major EXAFS peaks are used, the period will be that of the first coordination shell. In this method, the energy positions of the maxima and minima in EXAFS are measured with respect to the inflection point on the main absorption edge, which signifies the Fermi level in metals and the first unoccupied level of suitable symmetry available for the absorption of the ejected electron in the case of compounds.

4.4 Fourier transformation method
The magnitude of Fourier transform spectra are shown in figure 3. 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 by 0.2-0.5 Å 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 [17]. The peaks in the Fourier transform are shifted towards the origin by an amount \(\alpha_j\) 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. There are some subtleties associated with doing the FT of EXAFS data but techniques for dealing with these are well developed. Any signal that is a sum of sine waves can be Fourier transformed to separate each frequency component in distance \(R\), i.e., a Fourier transform separates a signal into its Fourier components. Each Fourier component is defined by an amplitude and phase. The Fourier transform is a complex function containing both real and imaginary parts. The magnitude of the Fourier transform is an envelope of the real and imaginary parts of the Fourier transform.

| Complex   | Levy’s | Lytle | LSS  | F.T.  |
|-----------|--------|-------|------|-------|
| Co foil   | 2.10   | 2.12  | 1.75 | 2.02  |
| Co1       | 2.14   | 1.97  | 1.86 | 2.01  |
| Co2       | 2.18   | 1.95  | 1.72 | 1.99  |

5. Conclusion
Calibration of particular setting of the polychromator has to done and it has been shown by derivative method, and after this EXAFS spectra has been recorded and comparison of the values of bond length \(R_s\) is seen to have slightly lesser values than the corresponding bond lengths obtained by Levy’s method .This may be described to the fact that Levy’s method gives the radius of coordination sphere directly whereas Lytle method does not. In later method, the inter atomic spacing is obtained by multiplying \(R_s\) with a factor Appropriate to the geometry of the system .the value of the bond length obtained from LSS method are closer to obtained by Levy’s method and Fourier transformation method.

Acknowledgement
The authors are thankful to Dr. Shambhu Nath Jha, RRCAT.,Indore for their help in recording the spectra at RRCAT, Indore, India and also thankful to Dr.Pratibha Sharma, school of chemical science, Devi Ahilya University, Indore - 452001, India for their help in preparation of Co(II) complexes.
Figure 1- EXAFS spectra of Co (II) complexes.

Figure 2- Magnitude of Fourier transformation in first shell maxima for Co (II) complexes.

References

[1] Vlasenko V G, Uraev A I, Zubavichus Ya V, Chernyshov A A, Garnovskii A D, & Mamin R K, 2008 Bull. Russian Acad. Sci.: Phys. 72 468.
[2] Newville M 2001 J. Synch. Rad. 8 322.
[3] d’Acapito F, Ghigna P, Alessandri I, Cardelli A, & Davoli I, 2003, Nucl Instrum Methods: Phys Res B 200 421.
[4] Hecht Lutzenkirchen and Frahm R, 2005 Physica B 357 213.
[5] d’Acapito F , Milita S, Satta A, and Colombo L 2007 J Appl Phys 102 043524.
[6] Rehr J J, Leon J M, Zabinsky S I, Albers R C 1991, J Am Chem Soc 113 5135.
[7] Westre T E, Kenepohl P, DeWitt JG, Hedman B, Hodgson K O, Solomon E I 1997 J Am Chem Soc 119 6297.
[8] Mayura Panchbhai A et al. 2008 E-Journal of Chemistry S1 5.
[9] Bhattacharyya D., Poswal A. K., Jha S. N., Sangeeta , Sabharwal S. C.  2009, Bull. Mater. Sci 32 103.
[10] Bhattacharyya D, Poswal A K, Jha S N, Sangeeta , Sabharwal S C, 2009, Nucl. Instrum. Meth. A; 609 286
[11] Das N C, Jha S N, Bhattacharyya D, Poswal A K, Sinha A K and Mishra V K 2004 Sadhana 29 545.
[12] Lee P. L., Beno M. A., Jennings G., Ramanathan M., Knapp G. S., Huang K., Bai J., Montano P. A. 1994 Rev. Sci. Instrum 65.
[13] Matthew A. Marcus, Andrew J. Westphal and Sirine C. Fakra, 2008 J. Synchrotron Rad. 15, 463
[14] Levy R. M. 1965 J. Chem. Phys. 43 1846
[15] Lytle F. W., 1966 Advances in X-ray Analysis 9 398.
[16] Lytle F. W., Sayers D. E. and Stern E. A. 1975 Phys. Rev. B. 11 4825.
[17] Stern E.A., Sayers D. E. and Lytle F. W. 1975 Phys. Rev. B. 11 4836.