

**STUDIES ON X-RAY DIFFRACTION AND  
ESTIMATION OF X-RAY K- ABSORPTION EDGE  
OF  
COPPER (II) COMPLEXES**

**A THESIS SUBMITTED TO  
DEVI AHILYA VISHWA VIDYALAYA, INDORE**

**FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY IN PHYSICS**

**BY  
VISHAKHA VIBHUTE**

**SUPERVISOR  
DR. ASHUTOSH MISHRA  
PROFESSOR AND HEAD  
SCHOOL OF PHYSICS**

**DEVI AHILYA VISHWA VIDYALAYA, INDORE  
(M.P.)**

**2014**

## CERTIFICATE

This is to certify that the work entitled “**Studies on X-Ray Diffraction and Estimation of X-Ray K- Absorption Edge of Copper (II) Complexes**” is a piece of research work done by **Vishakha Vibhute** under my guidance and supervision for the degree of Doctor of Philosophy of Devi Ahilya University, Indore and that the candidate has put-in an attendance of more than 200 days with me.

To the best of my knowledge and belief the thesis:

- (i) embodies the work of the candidate :
- (ii) has duly been completed;
- (iii) fulfils the requirements of the Ordinance relating to the Ph.D. degree of the University; and
- (iv) is up to the standard both in respect of contents and language for being referred to the examiner.

December 2014

**(Dr. Ashutosh Mishra)**

Signature of the Supervisor

Forwarded

Professor and Head,  
School of Physics,  
Devi Ahilya University, Indore

The thesis is dedicated to my husband

*Mr. Anand Vibhute*

And my sweet little daughters

*Aditi and Nupur*

## **DECLARATION BY THE CANDIDATE**

I declare that the thesis entitled “**Studies on X-Ray Diffraction and Estimation of X-Ray K- Absorption Edge of Copper (II) Complexes**” is my own work conducted under the supervision of Dr. Ashutosh Mishra, Professor and Head, School of Physics, Devi Ahilya University, Indore (M. P.), approved by Research Degree Committee. I have put in more than 200 days of attendance with the supervisor at the centre.

I further declare that to the best of my knowledge the thesis does not contain any part of any work, which has been submitted for the award of any degree either in this university/Deemed university without proper citation.

**(Dr.Ashutosh Mishra)**

**Vishakha Vibhute**

Signature of the Supervisor

Signature of the candidate

Forwarded

Professor and Head,  
School of Physics,  
Devi Ahilya University, Indore

## **ACKNOWLEDGEMENT**

*I wish to acknowledge my sincere thanks to my supervisor Prof. **Dr. Ashutosh Mishra** Professor and Head, School of Physics, Devi Ahilya University, Indore (M. P.) for giving me this opportunity and confidence to explore my research interests. It is not an exaggeration but a reality that he has provided every facility to carry out my research work. It would not have been possible for me to complete the thesis without his personal interest and guidance during the present work. It is an honour for me to be one of his Ph. D. scholars.*

*I would also like to express my sincere gratitude towards **Dr. B D Shrivastava** Retd. Professor of Physics, School of Studies in Physics, Vikram University, Ujjain for giving me his personal guidance and encouragement during the research work. His selfless perseverance and attention to my work consistently found pearls among my heaps of data. I convey my heartfelt thanks towards Late **Dr. P V Khadikar**, Retd. Professor of Chemistry, School of Chemical Sciences, Devi Ahilya University, Indore. He was not only an eminent educationalist and subject proficient but also has unsurpassable standard of human attributes like benevolence, affection, sympathy, courtesy, enthusiasm and so on. His multifaceted creative intellect manifested in a variety of other things. Therefore the title, "Dear to all the Muses", seems appropriate in this context.*

*I am indebted to **Dr. Pratibha Sharma** and **Dr. Ashok Sharma**, School of Chemical Science, Devi Ahilya University, Indore for their help in the preparation of copper complexes studied in the present investigation. I am also grateful to them for their enthusiastic interest and help in the present work.*

*I am extremely grateful to **Dr. S. K. Deb**, Raja Ramanna Centre for Advanced Technology (RRCAT), Indore and **Dr. S. N. Jha**, **Dr. D. Bhattacharyya**, **Dr. A. Poswal** and **Dr. N. K. Sahoo** and **Mr. Ashok Yadav**, Bhabha Atomic Research Centre (BARC), Mumbai, for providing me the beamline and other necessary facilities at **Indus-2, RRCAT, Indore, India**.*

*I am thankful to **Dr. Mukul Gupta** and **Dr. Uday Deshpande**, IUC, DAE, Indore for providing me the facility of XRD and FTIR measurements and **Mr. Layant** for helping me in taking the measurements.*

*My special thanks are due to Dr. Neetu Parsai, Dr. Samrath Ninama, Dr. Garima Jain, Dr. Abhilasha Bakshi, Dr. Abhijeet Gour( Ujjain) and Dr. Pramod Malviya, without them this research work would not have seen the light of today. Their contributions are remarkable in my research work.*

*I have the pleasure to thank my fellow researchers, Jagruti Dwivedi, Kritika Tiwari, Harsha patil, Supriya Bisen, Pawan Sharma, Nitin Dubey , Aakruti Sisodiya, Ashwini dand and my colleagues Dr. Mohd. Wasim Shaikh, Prof Nanda Page, Prof Teena Pareek, Prof Madhuri Shah, Dr. Amrita Bisen, Prof. Simaran Kaur Bhatia and Prof Shahzadi Noor Khan for their cheerful cooperation and support that created friendly and productive atmosphere during the course of research work.*

*I acknowledge gratefully the help of my friends, well wishers and relatives, whose names have not appeared here, but who helped me directly or indirectly towards the successful completion of this thesis.*

*I express my deep sense of gratitude to my in laws Mr D L Vibhute, Mrs Aruna Vibhute and Mrs. Urmila Deshpande, my sister and brother-in-law Mrs Harshana and Mr. Neeraj Puranik and all my family members for their unconditional, emotional support and constant encouragement, which gave me courage and confidence to materialize my dreams throughout my research work. The sad demise of my brother-in-law Mr. Tushar Vibhute was a big loss of our family during this research work. He will always be remembered for his motivational contributions.*

*I am deeply grateful to my parents Mr Waman Mafidar and Mrs Vaishali Mafidar, for giving me the dream of having the word doctor before my name and for having faith in me. It is their love and support which gave me strength throughout the research work. Their continuous encouragement kept my enthusiasm alive, without which it would have been difficult to complete my thesis.*

*Last but not least I owe my loving thanks to my husband Mr. Anand Vibhute for being by my side always during the tenure of research work. Without his cooperation it would have been difficult to fulfil this dream. My loving thanks is also towards my two sweet little daughters to whom this thesis is dedicated, Aditi and Nupur Vibhute for facing the inconvenience and still showing their love and support during the research work.*

***Vishakha Vibhute***

## **List of Research Papers Published**

**1. “EXAFS data analysis of some cobalt complexes”**

A Mishra, Vishakha Vibhute, Garima Jain and Samrath Ninama, JPCS,365,2012, International Conference on Recent Trends in Physics (ICRTP-2012), IOP, Publishing, Journal of Physics: Conference Series 365 (2012), 012030 doi:10.1088/1742-6596/365/1/012030 ISSN 1742-6596 (online)

**2. “X-ray K-absorption spectroscopic studies of copper complexes”**

A Mishra, Vishakha Vibhute, P Sharma, N Parsai and S Ninama, JPCS,534,2014, International Conference on Recent Trends in Physics (ICRTP-2014), IOP, Publishing, Journal of Physics: Conference Series 534 (2014), 012009 doi:10.1088/1742-6596/534/1/012009 ISSN 1742-6596 (online)

**3. "Theoretical and Experimental Analysis of EXAFS Data and Determination of Bond Lengths"**

A Mishra, Vishakha Vibhute, N Parsai

Communicated in “**International Journal on Innovative Research in Engineering and Sciences**” with ISSN number 2279-0292.

**4. “X-ray Diffraction Studies of some copper complexes”**

A Mishra, Vishakha Vibhute, P Sharma, G Jain, A. Mansoori

National Conference on Nano Science held at Govt.P. G College, Chhindwara.

**5. “EXAFS Spectra Of Copper (II) Schiff Base Complexes And Determination Of Bond Lengths Using Synchrotron Radiation Source”**

A Mishra, Vishakha Vibhute, N. Parsai, S. Ninama, S N Jha, P Sharma

Communicated in Indian Journal of Physics in 2014.

**6. “Analysis of EXAFS Data and Determination of Bond Lengths”**

A.Mishra, Vishakha Vibhute, N. Parsai, S N Jha, P Sharma

Communicated in X-ray spectrometry in 2014.

## PREFACE

X-ray Absorption Fine Structure (XAFS) spectroscopy is a unique tool for studying, at the atomic and molecular scale, the local structure around selected elements that are contained within a material. XAFS can be applied not only to crystals, but also to materials that possess little or no long-range translational order: amorphous systems, glasses, quasicrystals, disordered films, membranes, solutions, liquids, metalloproteins – even molecular gases. This versatility allows it to be used in a wide variety of disciplines: physics, chemistry, biology, biophysics, medicine, engineering, environmental science, materials science, and geology.

X-ray absorption spectroscopy (XAS) has been extensively used in the recent past to obtain information about molecular structure viz., the valency, bond type, ionic charges, coordination stoichiometry etc. in inorganic compounds and complexes. The studies on X-ray absorption fine structure (XAFS), which ultimately yields information regarding the nearest neighbors of the central metal ions, i.e., bond length etc., in an inorganic compound and complex has shown great promise. The use of the X-ray absorption spectroscopy (XAS), to study the coordination compounds has been found to be highly rewarding and far-reaching with regard to an in-depth appraisal of the chemical state and environment of the central metal ion in coordination compounds. A decided advantage of this technique lies in its structural application to complexes biological or chemical system, where single crystals are not available (viz., amorphous, solid, liquid, solution, gas etc.) and other conventional methods fail to provide the desired information.

Many research centres in Indian universities and institutes have been doing extensive research work in this field since 1950 or so. Some of the important centres for X-ray absorption and emission spectroscopic research with principal investigators can be recollected as follows: Pune and Nagpur (Dr. C. Mande), Mumbai ( Dr. B.D. Padalia), Jaipur (Dr. K. B. Garg), Kanpur (Dr. Amarnath Nigam), Allahabad (Dr. G. B. Deodhar, Dr. B. K. Agarwal, Dr. H. L. Nigam), New Delhi ( Dr. V. G. Bhide), Indore (Dr. A. Mishra) and Ujjain (Dr. B. D. Shrivastava). At all of these centres, the laboratory X-ray spectroscopic set-ups were in use which employ photographic method of registration of spectra. These types of set-up comprise of low power (0.5kW - 3kW) X-ray tubes and Cauchoi's-type curved mica crystal spectrographs



employing X-ray films as detectors. After obtaining a number of spectrograms, the analog and digital spectral records are obtained with the help of microphotometers. These analog and digital spectral records were used to be analyzed manually. The results about X-ray absorption edge energies, edge structures, near edge structures and extended fine structures were being reported. The data was used to be generally analyzed qualitatively and empirically to yield useful information about molecular structure. The data was also analyzed through some established relations to yield information about valency, effective nuclear charge, coordination type, average bond length etc. Unfortunately, nearly all of these centres ceased to work in 1980s because research workers around the world had started using X-rays from synchrotron instead of X-ray tubes for recording the X-ray absorption spectra. Unfortunately, the synchrotron was not available in India at that time. Indian synchrotron could become operational only a few years back.

X-ray absorption spectroscopy (XAS) refers to the details of how X-rays are absorbed by an atom at energies near and above the core-level binding energies of that particular atom. The absorption of X-rays on the high energy side of absorption edges does not vary monotonically in condensed matter but has a complicated behaviour which extends past the edge by an amount typically of the order of 1 keV. This non-monotonic variation has received the name of X-ray absorption fine structure (XAFS). The X-ray absorption fine structure is typically divided into two regimes: X-ray absorption near-edge (XANES) structure and extended X-ray absorption fine-structure (EXAFS) structure. The EXAFS has been known for over 80 years. There was a lot of confusion about the theory of EXAFS. The situation changed when Sayers, Stern and Lytle (1971) pointed out, based on a theoretical expression of the EXAFS (Sayers et al., 1971) that a Fourier transform of the EXAFS function with respect to the photoelectron wave number should peak at distances corresponding to nearest neighbour coordination shells of atoms. The introduction of the Fourier transform changed EXAFS from a confusing scientific curiosity to a quantitative tool for structure determination.

The experimental X-ray absorption spectroscopic data obtained from X-ray tube sources is plagued by noise and systematic errors. It wasn't until the 1970s that high brilliance synchrotron radiation began to be used to obtain absorption spectra. Experimental techniques have continued to develop over the years, and due to the

exponential increase in brilliance over time, high quality EXAFS data is now routinely collected at a variety of second and third generation synchrotron sources.

Over the past three decades, the technique of EXAFS has made great strides toward the goal of providing such information. The existence of intense new synchrotron X-ray sources alone was not enough to achieve this goal, even though such facilities spurred considerable progress. In addition, the full success of the EXAFS technique must be attributed in large part to advances in theory, which have led ultimately to a highly quantitative understanding of the phenomena.

In the present thesis, the X-ray absorption fine structure (XAFS) spectroscopy has been used to study copper complexes and copper salts. Studies have been done using both EXAFS and XANES spectroscopies theoretically and experimentally. In the present work a simple and innovative procedure for analysis of EXAFS data was presented. The method was demonstrated to yield satisfactory results for transition metal its complexes and salts. In this procedure, the theoretical EXAFS data was generated, employing computer software MathCAD, for the first coordination shell around the absorbing atom, using EXAFS equation. In this work we have developed a simplified analysis procedure for extracting bond length for the first coordination shell from the experimental EXAFS data. The method is simple and novel because calculations are done using the computer software MathCAD.

### **The thesis is divided into six chapters**

**Chapter I** Introduction.

**Chapter II** Experimental Techniques.

**Chapter III** Preparation and characterization of cu (II) complexes.

**Chapter IV** X-ray K-absorption spectral studies of copper salts.

**Chapter V** X-ray K-absorption spectral studies of copper complexes.

**Chapter VI** Simplified Analysis Method For EXAFS Spectra Using MathCAD Programming.

**Chapter I** describes general introduction to the subject and to the basic phenomenon of absorption of X-rays. The terms used in the X-ray absorption spectroscopy have been explained. The various parameters that can be determined from the X-ray spectroscopic measurements and the information that can be obtained from them have been discussed. In the recent years XAFS has proved to be an important tool in

structure determination. Detailed review articles are now available in literature on XAFS. In the present chapter, a brief theory of EXAFS has been given and the method of extracting parameters has been outlined. It has been pointed out that the parameters determined by XANES and EXAFS (combined called as XAFS) relate to the local environment surrounding the X-ray absorption atom.

Copper is one of the transition elements frequently found at the active site of proteins. Complexation with copper enhances the biological activity of a wide variety of organic ligands. It is important and interesting to understand the physico-chemical properties of copper complexes with newly synthesized Schiff bases which are of biological interest. Hence, for the present study we have chosen a series of Schiff base complexes of copper involving orthophenylenediamine as a ligand. The second series of the study is of copper salts. In this chapter a brief review is given of the work done by earlier workers on K-absorption spectra of copper complexes.

**Chapter II** gives the details of experimental techniques. The Schiff base copper (II) complexes were prepared by chemical root method. Our aim behind the synthesis of this type of ligand was to examine their possible coordination with copper metal. XRD techniques provide the exact idea of structure and activity of coordination compounds. XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. FTIR measurements were also done in the IUC, DAE, Indore. The X-ray absorption fine structure (XAFS) measurements were performed at recently developed BL-8 Dispersive EXAFS beamline at 2.5 GeV INDUS-2 Synchrotron Radiation Source at RRCAT, Indore, India. The beamline described here works in the dispersive mode using a 460 mm long Si (111) crystal mounted on an elliptical bender and a position sensitive CCD detector having 2048 x 2048 pixels. The proposed EXAFS beam-line at INDUS-2 carry out the X-ray absorption measurements in energy dispersive mode involving no time consuming scanning mechanism and thus can be applied to study in-situ fast and time- resolved process. The measurements were carried out in transmission mode at copper K-edge for measuring the absorption spectra of both metals macro cyclic ligand complexes respectively. The plot of sample absorption versus energy was obtained by recording the CCD output with (I) and (I<sub>0</sub>) samples and using the relation,  $I=I_0e^{-\mu x}$ .

**Chapter III** gives details of preparation of Schiff base copper complexes and their characterizations viz X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) measurements. The XRD measurements were carried out using

Bruker D8 Advance X-ray diffractometer. The X-rays were produced using a sealed tube and the wavelength of X-ray was 0.154 nm (Cu K-alpha). The X-rays were detected using a fast counting detector based on Silicon strip technology (Bruker LynxEye detector). XRD gives the information about crystalline nature of copper (II) complexes through calculating lattice parameter and particle size. The lattice parameter has been calculated using well known Bragg relation  $2d \sin\theta = n\lambda$  also the particle size calculated using the Debye Scherer's formula  $t = (0.9 \lambda) / (b \cos\theta_b)$ . FTIR measurements were also taken in IUC, DAE, Indore. Fourier transform infrared (FTIR) spectra were recorded in the frequency range of  $4000-400\text{cm}^{-1}$  employing KBr disc technique using Bruker Germany make Jasco FTIR-300 spectrometer model vertex-70. FT-IR spectroscopy provides information about identifying unknown materials, determine the quality or consistency of a sample and determine the amount of components in a mixture.

**In Chapter IV** the X-ray absorption fine structure (XAFS) studies of some copper salts have been done. The X-ray absorption fine structure measurements were performed at recently developed BL-8 Dispersive EXAFS beamline at 2.5 GeV INDUS-2 Synchrotron Radiation Source at RRCAT, Indore, India. In XANES Measurements have been made to obtain the chemical shift, edge width, shift of principal absorption maximum and effective nuclear charge (ENC) for these compounds have been used to explain the structure of the complexes. The bond lengths called “nearest neighboring distance” have also been obtained by methods of EXAFS data analysis using with computer software IFEFFIT (Athena version 0.8.056).

**In Chapter V** the X-ray absorption fine structure (XAFS) studies of Schiff base copper complexes with legend orthophenylenediamine have been done. The X-ray absorption fine structure measurements were performed at recently developed BL-8 Dispersive EXAFS beamline at 2.5 GeV INDUS-2 Synchrotron Radiation Source at RRCAT, Indore, India. In XANES Measurements have been made to obtain the chemical shift, edge width, shift of principal absorption maximum and effective nuclear charge (ENC) for these compounds have been used to explain the structure of the complexes. The bond lengths called “nearest neighboring distance” have also been obtained by methods of EXAFS data analysis by using computer software IFEFFIT (Athena version 0.8.056).

**In Chapter VI**, a simple and innovative method for analysis of EXAFS data have been presented. The method has been demonstrated to yield satisfactory results for Cu (II) complexes and Cu (II) salts. In this procedure, the theoretical EXAFS data was generated, employing computer software MathCAD, for the first coordination shell around the absorbing atom, using EXAFS equation. In this work a simplified analysis procedure has been developed for extracting bond length for the first coordination shell from the experimental EXAFS data.

Details regarding experiment and analysis of the XAFS data have been given at the appropriate places in the thesis so that anybody who wants to start research work in the field of XAFS may get necessary information at one place.

**The references for all the chapters and publication are given at the end of the thesis.**

**Vishakha Vibhute**

# CONTENTS

CHAPTER – I. ....	1
1 INTRODUCTION.....	1
1.1 X-rays .....	1
1.2 Production of X- rays .....	2
1.2.1 Characteristic X-rays .....	2
1.2.2 Bremsstrahlung X-rays .....	3
1.3 X-rays from Synchrotron .....	4
1.4 Absorption of X-rays .....	6
1.5 X-ray absorption fine structure .....	7
1.5.1 Different features of X-ray absorption spectra.....	13
1.5.2 Applications of XAFS.....	16
1.6 The absorption edge .....	16
1.7 Theory of XANES.....	18
1.7.1 Chemical shift (Edge shift) .....	20
1.7.2 Edge structure .....	22
1.7.3 Applications of XANES spectroscopy.....	25
1.8 Extended X-ray absorption fine structure .....	25
1.8.1 Origin of the EXAFS signal .....	27
1.8.2 Early history of EXAFS .....	29
1.8.3 Analytical expression of the EXAFS signal .....	31
1.9 EXAFS data analysis .....	35
1.9.1 Different methods of determination of bond lengths from EXAFS data .....	36
1.9.2 Fourier Transform (FT) method.....	40
1.9.3 EXAFS analysis using Athena and Artemis softwares.....	41
1.9.4 EXAFS analysis using MathCAD programming .....	43
1.9.5 EXAFS spectroscopy using synchrotron radiation.....	44
1.10 Fourier Transform Infrared Spectroscopy (FTIR) .....	46
1.11 X-ray powder diffraction (XRD) .....	47
1.12 Earlier work done on copper complexes .....	48
1.13 Present work .....	50
CHAPTER – II.....	54
2 EXPERIMENTAL TECHNIQUES .....	54

2.1	Introduction .....	54
2.2	X-ray Diffraction (XRD).....	54
2.3	Fourier Transform Infrared spectroscopy (FTIR).....	59
2.4	X-ray Absorption Fine Structure (XAFS).....	61
2.4.1	Principle of working .....	67
2.4.2	Calibration of CCD channels at copper absorption edges.....	69
2.4.3	Sample preparation for XAS.....	72
2.4.3.1	(a) X-ray absorption calculation .....	72
2.4.3.2	(b) Preparation of absorption screens.....	73
2.4.3.3	(c) Thickness effects or pin whole effects.....	73
2.4.3.4	(d) Particle size effects .....	74
2.5	Obtaining spectra at the EXAFS beamline.....	74
CHAPTER - III.....		78
3	PREPARATION AND CHARACTERIZATION OF Cu (II) COMPLEXES.....	78
3.1	Introduction .....	78
3.2	Synthesis of ligand and its metal complexes .....	80
3.2.1	Synthesis of ligand.....	80
3.2.2	Synthesis of complexes .....	81
3.3	Structural characterization metal complexes .....	84
3.3.1	X-ray Diffraction Study (XRD) .....	84
3.3.1.1	(a) Copper Complexes .....	84
3.3.1.2	(b) Copper Salts .....	88
3.4	Fourier Transform Infrared Spectroscopy (FTIR) .....	90
3.6	Conclusion.....	93
CHAPTER - IV.....		95
4	X-RAY K-ABSORPTION SPECTRAL STUDIES OF COPPER SALTS.....	95
4.1	Introduction .....	95
4.2	Experimental.....	98
4.3	Results and Discussion .....	101
4.3.1	The absorption edge.....	102
4.3.2	Position of the edge .....	102
4.3.3	Chemical shift .....	102
4.3.4	Effective nuclear charge (ENC).....	103
4.3.5	Principal absorption maximum .....	104
4.3.6	Edge-width.....	104
4.3.7	Determination of bond lengths.....	105
4.3.7.1	(i) By graphical methods from EXAFS spectra .....	105

4.3.7.1.1	(a) Levy's method.....	105
4.3.7.1.2	(b) Lytle's method.....	106
4.3.7.1.3	(c) L.S.S. method.....	106
4.3.7.2	(ii) By Fourier transform of EXAFS spectra.....	106
4.4	Conclusions.....	107
CHAPTER - V.....		122
5	X-RAY K-ABSORPTION SPECTRAL STUDIES OF COPPER COMPLEXES USING SYNCHROTRON RADIATION SOURCES.....	122
5.1	Introduction.....	122
5.2	Experimental.....	125
5.3	Results.....	125
5.3.1	The absorption edge.....	126
5.3.2	Position of the edge.....	126
5.3.3	Chemical shift.....	126
5.3.4	Effective nuclear charge and Chemical Shift.....	127
5.3.5	Principal absorption maximum.....	128
5.3.6	Edge-width.....	129
5.3.7	Determination of bond lengths.....	129
5.3.7.1	(i) By graphical methods from EXAFS spectra.....	129
5.3.7.1.1	(a) Levy's method.....	130
5.3.7.1.2	(b) Lytle's method.....	131
5.3.7.1.3	(c) L.S.S. method.....	131
5.3.7.2	(ii) By Fourier transform of EXAFS spectra.....	131
5.4	Conclusions.....	132
CHAPTER - VI.....		154
6	SIMPLIFIED ANALYSIS METHOD FOR EXAFS SPECTRA USING MATHCAD PROGRAMMING.....	154
6.1	Introduction.....	154
6.2	Methodology.....	155
6.2.1	The EXAFS equation.....	156
6.2.2	Values of input parameters.....	157
6.2.3	Fourier transform of the theoretical EXAFS spectrum and determination of first shell bond length.....	157
6.3	Results and discussion.....	159
6.4	Conclusions.....	159
References.....		170



## Figure Captions

Figure 1-3 X-ray production.....	4
Figure 1-4 Absorption processes for X-rays .....	7
Figure 1-5 X-ray absorption coefficient vs photon energy .....	8
Figure 1-7 The normalized K-absorption spectrum of copper metal .....	10
Figure 1-10 Schematic of XAFS experiment .....	12
Figure 1-11 (a) multiple scattering processes responsible for XANES; .....	14
Figure 1-12 XAS Edge result from core ionization .....	17
Figure 1-13 The fundamental processes which contribute to XANES spectra.....	19
Figure 1-14 (A) & (B) Schemes of scattering processes.....	28
Figure 2-3 X-ray Diffractometer viz Bruker D8 Advance X-ray Diffractometer .....	56
Figure 2-4 Braggs law of X-ray diffraction .....	57
Figure 2-5 Photograph of Bruker Germany made Jasco FTIR-300 spectrometer .....	60
Figure 2-6 Path of light in Michelson interferome .....	61
Figure 2-7 Magnetic Layout of Indus-2 ring.....	62
Figure 2-8 Optical lay-out of the dispersive EXAFS beamline .....	63
Figure 2-9 Mechanical lay-out of the dispersive EXAFS beamline .....	64
Figure 2-10 Dispersive EXAFS beam line installed at BL-8 port of Indus-2. ....	65
Figure 2-11 Control consol and shielding hutch of the dispersive EXAFS beamline. ....	66
Figure 2-12 19-axis goniometer developed in collaboration with CDM, BARC. ....	66
Figure 2-13 crystal bender assemblies developed in collaboration with CDM, BARC. ....	67
Figure 2-14 Working principle of the dispersive EXAFS beamline (BL-8) at Indus - 2 Synchrotron facility, Indore, India .....	68
Figure 2-15 Origin curves for Cu foil and $\text{Lu}_2\text{O}_3$ .....	70
Figure 2-16 The method of calibration for Cu metal foil. ....	71
Figure 2-17 The method of calibration, for $\text{Lu}_2\text{O}_3$ .....	71
Figure 2-18 EXAFS spectrum of Cu metal foil in calibrated scale. ....	72
Figure 2-19 Indus - 2 beamlines.....	76
Figure 3-1 Complete synthesis schemes of copper (II) complexes.....	83
Figure 3-2 XRD patterns for copper (II) complexes .....	85
Figure 3-3 XRD patterns for copper (II) complexes .....	89
Figure 3-4 IR spectra of copper complexes. ....	92
Figure 4-1 XAFS data analysis curves for copper metal. ....	112
Figure 4-2 XAFS data analysis curves for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . ....	113
Figure 4-3 XAFS data analysis curves for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . ....	114
Figure 4-4 XAFS data analysis curves for $\text{CuBr}_2$ . ....	115
Figure 4-5 XAFS data analysis curves for $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ .....	116
Figure 4-6 XAFS data analysis curves for $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ .....	117
Figure 4-7 E versus Q curves for the copper salts .....	118
Figure 4-8 n versus k curves for the copper complexes.....	119
Figure 4-9 Plot of oxidation number versus shift in B.E. of 1s electrons as given in table 4.5. ....	120
Figure 5-1 XAFS data analysis curves for copper metal .....	138
Figure 5-2 XAFS data analysis curves for Bisp(4- Nitro) $\text{pdCu}(\text{II})$ bis bd. ....	139
Figure 5-3 XAFS data analysis curves for Bisp(Pure anilene) $\text{pdCu}(\text{II})$ bis bd. ....	140
Figure 5-4 XAFS data analysis curves for Bisp(2-anisidine) $\text{pdCu}(\text{II})$ bis bd. ....	141
Figure 5-5 XAFS data analysis curves Bisp(4-chloroanilene) $\text{pdCu}(\text{II})$ bis bd.....	142
Figure 5-6 XAFS data analysis curves for Bisp(4-bromoanilene) $\text{pdCu}(\text{II})$ bis bd. ....	143
Figure 5-7 XAFS data analysis curves for Bisp(2-chloroanilene) $\text{pdCu}(\text{II})$ bis bd.....	144
Figure 5-8 XAFS data analysis curves for Bisp(3-nitroanilene) $\text{pdCu}(\text{II})$ bis bd.....	145
Figure 5-9 XAFS data analysis curves for Bisp(2-nitroanilene) $\text{pdCu}(\text{II})$ bis bd. ....	146
Figure 5-10 XAFS data analysis curves for Bisp(4-anisidine) $\text{pdCu}(\text{II})$ bis bd. ....	147
Figure 5-11 XAFS data analysis curves for Bisp(Aceto-p-toludine) $\text{pdCu}(\text{II})$ bis bd. ....	148
Figure 5-12 E vs. Q curves for Copper (II) complexes.....	150
Figure 5-13 n versus k curves for the copper complexes.....	152
Figure 6-1 Theoretically calculated $\chi(k)$ versus k curves for the copper (II) complexes. ....	164
Figure 6-2 Magnitude of Fourier transform of the $\chi(k)$ versus k curves of fig. 6.1. ....	166
Figure 6-3 Theoretically calculated $\chi(k)$ versus k curves for the copper (II) Salts.....	168
Figure 6-4 Magnitude of Fourier transforms of the $\chi(k)$ versus k curves of fig. 6.3. ....	169

## Table Captions

Table 2.1. Example calculation to estimate the dilution of copper complex.....	75
Table 3.1 Copper (II) complexes, abbreviation and molecular formula. ....	82
Table 3.2 The observed and the calculated data for X-ray diffraction pattern of the cu (II) complexes .....	86
Table 3.3 Values of unit cell volume, angle $\beta$ and lattice parameters of samples .....	88
Table 3.4 Results of X-ray diffraction studies of Copper Salts .....	90
Table 3.5 FT-IR Spectral data of copper complexes .....	91
Table 4.1 Parameters of DEXAFS beamline (BL-8) at Indus-2.....	99
Table 4.2 Copper Salts and molecular formula. ....	109
Table 4.3 XANES data for the K-absorption edge of copper (II) salts. ....	109
Table 4.4 Values of energy E and wave vector k .....	110
Table 4.5 Values of first shell bond lengths (in Å) .....	110
Table 4.6 Binding energies of 1s electrons of copper atom in different oxidation states. ....	111
Table 5.1 Copper (II) complexes, abbreviation and molecular formula. ....	124
Table 5.2 XANES data for K-absorption edge of Copper (II) complexes. ....	135
Table 5.3 EXAFS Parameter for Cu (II) complex .....	135
Table 5.4 Values of first shell bond lengths (in Å) .....	137
Table 6.1 Copper (II) complexes, abbreviation and molecular formula. ....	161
Table 6.2 Copper (II) salts, abbreviation and molecular formula. ....	162
Table 6.3 First shell metal-ligand bond length in (Å) for copper (II) complexes .....	162
Table 6.4 First shell metal-ligand bond length in (Å) for copper (II) salts .....	163