APPENDIX
List of publications:

1. XRD and XANES studies of copper complexes using (diethyl 4-amino-1-phenyl-1H-pyrazole-3, 5 dicarboxylate) as ligand, accepted AIP Publication (2013).


8. Synthesis and properties of BaTi$_{0.98}$Cu$_{0.02}$O$_3$, Bhartiya Vigyaan Sammlan, Vol.- 2, (2009).

XRD And XANES Studies Of Copper Complexes Using (diethyl 4-amino-1-phenyl-1H-pyrazole-3,5 dicarboxylate) as Ligand

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Abstract. X-ray diffraction (XRD) and X-ray absorption spectroscopic (XAS) studies have been done on three copper complexes using (diethyl 4-amino-1-phenyl-1H-pyrazole-3,5 dicarboxylate) as ligand. The X-ray diffraction studies of copper complexes have been recorded using Rigaku RINT-2000 X-ray diffractometer equipped with a rotating anode with tube voltage of 40 kV and current of 100 mA. The X-ray absorption spectra of the complexes have been recorded at Raja Ramanna Centre for Advanced Technology (RRCAT),Indore and is called beamline.

Keywords: Copper complex, XRD, XANES.

PACS: 61.05.cp, 78.70.Dm

INTRODUCTION

X-ray diffraction is one of the most important technique used in material science. The structure of copper complexes was determined by X-ray diffraction technique. The parameter like particle size, lattice parameter and volume are calculated with helps of this method.

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. XAFS is often divided into X-ray absorption near edge structure (XANES), which lies within the first 40 eV of the edge position and extended X-ray absorption fine structure (EXAFS), which lies beyond 40 eV above the absorption edge. XANES is strongly sensitive to formal oxidation state and coordination chemistry of the absorbing atom. We have studied X-ray absorption spectra (XAS) at the K-edge of copper copper complexes. XANES parameters, e.g., chemical shift, i.e., shift of K-edge of copper in complex with respect to K-edge of copper metal and edge-width have been determined and discussed.

The present study deals with analysis of X-ray diffraction and X-ray K-absorption spectra of copper (II) complexes i.e. Bis-(diethyl 4-amino-1-(P-nitrophenyl)-1H-pyrazole-3,5 dicarboxylate) copper (II) chloride (Complex-1), Bis-(diethyl 4-amino-1-(3-chlorophenyl)-1H-pyrazole-3,5 dicarboxylate) copper (II) chloride (Complex-2), Bis-(diethyl 4-amino-1-(3-nitrophenyl)-1H-pyrazole-3,5 dicarboxylate) copper (II) chloride (Complex-3).

EXPERIMENTAL

All the complexes have been prepared by chemical root method. The X-ray diffraction patterns of copper complexes have been recorded using Rigaku RINT-2000 X-ray diffractometer with a rotating anode operated at 40 kV and 100 mA. Copper target was used as the source of X-rays at wavelength \( \lambda = 1.54A \).

The X-ray K-absorption near edge spectra of the copper complexes have been recorded using synchrotron radiation. The X-ray spectroscopy setup is available at Raja Ramanna Centre for Advanced Technology (RRCAT),Indore and is called beamline. This beamline BL-8 has been recently commissioned at the 2.5 GeV INDUS-2 Synchrotron radiation source.

RESULTS AND DISCUSSION

X-ray Diffraction:
X-ray diffraction patterns for three copper complexes, were recorded and are shown in Figs 1. Particle size of the complexes was determined with the help of the Scherrer formula in which particle size \( D \) is defined as
Table 1. Results of X-ray diffraction studies of complexes:

<table>
<thead>
<tr>
<th>Complex</th>
<th>Particle size D (nm)</th>
<th>Lattice Parameter</th>
<th>Angle β (Degree)</th>
<th>Unit cell Volume (10^4 cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex-1</td>
<td>50.15</td>
<td>1.42 0.66 1.03</td>
<td>97.72</td>
<td>976.11</td>
</tr>
<tr>
<td>Complex-2</td>
<td>46.84</td>
<td>1.37 0.68 1.02</td>
<td>95.58</td>
<td>959.68</td>
</tr>
<tr>
<td>Complex-3</td>
<td>59.18</td>
<td>1.41 0.66 0.95</td>
<td>95.07</td>
<td>896.09</td>
</tr>
</tbody>
</table>

Average particle sizes of the complexes determined were 50.15, 46.84 and 59.18nm respectively. Diffraction data of the complexes are listed in Tables 1. All the complexes had a monoclinic crystal lattice.

0.9B cosθ, where 0.9 = constant, λ = wavelength, B = angular width and θ = diffraction angle.

Table 2. Results of X-ray absorption near edge spectroscopic studies of complexes:

<table>
<thead>
<tr>
<th>Complex</th>
<th>E_{k1} (eV)</th>
<th>E_{k2} (eV)</th>
<th>E_A (eV)</th>
<th>Chemical Shift (ΔE = E_k(Complex) – E_k(Metal)) (eV)</th>
<th>Edge-width ((E_A-E_k)(eV))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex-1</td>
<td>8986.23</td>
<td>8991.77</td>
<td>8997.15</td>
<td>7.1</td>
<td>10.92</td>
</tr>
<tr>
<td>Complex-2</td>
<td>8986.76</td>
<td>8991.61</td>
<td>8997.46</td>
<td>7.63</td>
<td>10.7</td>
</tr>
<tr>
<td>Complex-3</td>
<td>8987.15</td>
<td>8991.42</td>
<td>8997.46</td>
<td>8.02</td>
<td>10.31</td>
</tr>
</tbody>
</table>

X-ray absorption near edge structure:

The X-ray absorption near edge structure (XANES) parameters i.e., chemical shift and edge-width have been determined. The results are given in table 2.

Chemical Shift:

The K-absorption edge of copper has been found to be shifted towards the high energy side in all the complexes studied as compared to the k-absorption edge in the metal. The shifts of the k-absorption edge of copper in the complexes with respect to that of copper metal have been determined according to the equation:

\[ΔE = E_k(Complex) – E_k(Metal)\]

Where the metal K-edge \(E_k=8979.13\)

The results are given in table 2. The sequence of variation of chemical shifts of the complexes is as follows:

Complex-1 < Complex-2 < Complex-3

Edge width:

In table 2, the value of the edge-width have been reported. The edge-width of copper complexes show that the edge-width decreases as follows:

Complex-1 > Complex-2 > Complex-3

The order of the edge-width is in the reverse order of chemical shift. This represents that the edge width is inversely proportional to ionic character for this series.

CONCLUSION

The XRD studies done on the copper complexes showed that they are monoclinic in nature and it is found that the chemical shift is towards the higher energy side and edge width indicating there ionic character of the complexes.

REFERENCES

X-ray diffraction and absorption spectroscopic studies of copper mixed ligand complexes with aminophenol as one of the ligands

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Abstract. X-ray diffraction (XRD) and X-ray absorption spectroscopic (XAS) studies have been conducted on two copper complexes, i.e., copper macrocyclic complex of succinic acid and ortho aminophenol (complex-1) and copper macrocyclic complex of pthalic acid and ortho aminophenol (complex-2). The diffraction pattern of the complexes have been recorded using Rigaku RINT-2000 X-ray diffractometer equipped with rotating anode X-ray tube operated at 40 kV and 100 mA. The X-ray absorption spectra of the complexes have been recorded at the K-edge of copper on Cauchois type bent crystal spectrograph having radius 0.4 m employing a mica crystal, oriented to reflect from (100) planes, for dispersion. The X-ray absorption near edge structure (XANES) parameters, viz., chemical shift, energy position of the principal absorption maximum and edge-width have been determined and discussed. From the extended X-ray absorption fine structure (EXAFS) data, the bond lengths have been calculated using three methods, namely, Levy’s method, Lytle, Sayers and Stem’s (LSS) method and Fourier transformation method. The results obtained have been compared with each other and discussed.

1. Introduction
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 X-ray absorption spectra is typically divided into two regimes: X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). While XANES refers to the structure on the high energy side of the main edge extending up to ~40 eV from the edge, EXAFS refers to the undulations of the absorption coefficient on the high energy side of the main edge extending from ~40eV to ~1000eV from the edge. XANES is strongly sensitive to formal oxidation state and coordination chemistry of the absorbing atom, while EXAFS is used to determine the distances, coordination number, and species of the neighbors of the absorbing atom. As a result, XAS provides a practical and simple way to determine the chemical state and local atomic structure for a selected atomic species. In the present paper, we have studied X-ray absorption spectra (XAS) at the K-edge of copper in two copper complexes, viz., copper macrocyclic complex of succinic acid and ortho aminophenol (complex-1) and copper macrocyclic complex of pthalic acid and ortho aminophenol (complex-2). XANES parameters, e.g., chemical shift, i.e., shift of K-edge of copper in complex with respect to K-edge of copper metal, energy position of the principal absorption maximum and edge-width have been determined and discussed. The positions of EXAFS maxima and minima have also been determined. Using the EXAFS data, the bond lengths have been calculated using three methods, namely, Levy’s
method, Lytle, Sayers and Stern's (LSS) method and Fourier transformation method. The X-ray diffractometer records of the complexes have been obtained from which the particle size and the lattice parameter have been determined.

2. Experimental

All the complexes have been prepared by chemical root method. The X-ray diffraction patterns of copper complexes have been recorded using Rigaku RINT-2000 X-ray diffractometer with a rotating anode operated at 40 kV and 100 mA. Copper target was used as the source of X-rays at wavelength \( \lambda = 1.54\,\text{Å} \).

The X-ray K-absorption spectra of the copper complexes have been recorded using a Rich Seifert X-ray generator with tungsten target operating at 20 kV and 40 mA. A 0.04 m Cauchois type bent crystal transmission spectrograph employing a mica crystal, oriented to reflect from (100) planes for dispersion, has been used to record the spectra. The spectra were recorded on Kodak X-ray photographic films. The exposure time varied from 2 to 4 hours. Digital records of the spectra were obtained on Carl-Zeiss microphotometer coupled to a computer. The computer software Athena version 0.8.056 has been used for analysis of the digital spectral data.

3. Results and discussion

3.1. X-ray diffraction studies:

The X-ray diffractometer records of the complexes are given in figure 1. Particle size was calculated using Scherer's formula given by:

\[
t = \frac{0.9\lambda}{B \cos \theta}
\]

Here \( t \) is the crystal thickness (in the same units as \( \lambda \)), \( B \) is full width half maxima (in radians) of diffraction line, \( \theta \) is the Bragg angle and \( \lambda \) is the wavelength. The values of particle size and the lattice constant calculated from the diffractometer records are given in table 1.

3.2 X-ray absorption near edge structure:

The X-ray absorption spectra at the K-edge of copper in the complexes are shown in figure 2. The X-ray absorption near edge structure (XANES) parameters, viz., chemical shift, energy position of the principal absorption maximum and edge-width have been determined. The results are given in table 1 and discussed below.

3.2.1 Chemical shift:

The shift of X-ray absorption edge \( i \) (i=K, L, M...) of an element in a complex with respect to that of the pure metal is written as:

\[
\Delta E = E_i (\text{Compound}) - E_i (\text{Element})
\]

The chemical shifts of copper complexes in the present investigation are given in Table 1. The values of shifts are 8.1 and 7.4 eV for complexes 1 and 2 respectively. The compounds studied earlier [1]
Figure 2. X-ray absorption spectra of the complexes from figure 2 for complex 1 and figure 2 for complex 2.

Figure 3(a). Fourier transform of complex 1 from figure 2 for complex 1.

Figure 3(b). Fourier transform of complex 2 from figure 2 for complex 2.

CuO, CuCl₂·2H₂O and CuSO₄·5H₂O have been reported to have chemical shifts 4.3, 5.3 and 6.8 eV respectively, which are all +2 oxidation state compounds. Since the chemical shifts in the present work are less than 10 eV, on this basis, the conclusion is that, the two complexes studied are copper (II) complexes. Therefore, copper exists in oxidation state +2 in the complexes studied in the present investigation. The sequence of variation of chemical shifts of the complexes is as follows: Complex-1 > complex-2.

Recalling that the chemical shift value for a compound is largely dependent on the effective nuclear charge on the central metal ion, the decrease in the chemical shift in complex-2 with respect to complex-1 suggested that phthalic acid has lesser field strength than succinic acid.

3.2.2. Shift of principal absorption maxima:

The values for the shifts of the principal absorption maxima with respect to the absorption edge for the complexes are given in Table 1. The shift in the principal absorption maximum in transition metal complexes is known to arise from the transition of an electron from the 1s level to a vacant orbital of appropriate symmetry. This parameter is sensitive to the valency of the metal ion. It is worth comparing the present values for the shift of principal absorption maxima with the values reported by earlier workers for other copper (II) complexes which lie in range of 17.7 - 25.4 eV. [3,4] Hence on the basis of this comparison, we may say that all the samples in the present investigation possess an oxidation state +2. The order of the shifts of the principal absorption maxima is the same as the order of the chemical shifts indicating that the metal ligand bond is stronger in complex 1 as compared to complex 2.

Table 1. Results of X-ray diffraction and absorption spectroscopic studies of complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>XRD results</th>
<th>XANES results</th>
<th>Bond lengths from EXAFS data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Particle size (nm)</td>
<td>Lattice parameter (nm)</td>
<td>Chemical shift (eV)</td>
</tr>
<tr>
<td>Complex-1</td>
<td>38.64</td>
<td>0.951</td>
<td>8.1</td>
</tr>
<tr>
<td>Complex-2</td>
<td>28.44</td>
<td>0.954</td>
<td>7.4</td>
</tr>
</tbody>
</table>
3.2.3. Edge-width:
The values of the edge width of complexes are given in table 1. Edge-width of the K-absorption edge
increases with the increase of covalent character of the bonds [2]. The relative order of the values of
edge-width are not supported by the values of the chemical shift or the shift in principal absorption
maxima in the present work. The reason may be that the values of edge-width not only depend on the
factors responsible for the chemical shift but also on the geometry of the complexes.

3.3 Bond lengths from extended X-ray absorption fine structure data
From the extended X-ray absorption fine structure (EXAFS) data, the bond lengths have been
calculated using three methods, namely, Levy’s method, Lytle, Sayers and Stern’s (LSS) method and
Fourier transformation method as follows.

3.2.3.1. Levy’s method
In Levy’s method [5], the bond lengths are calculated by using the relation: $R_1 = \left(\frac{151}{\Delta E}\right)^{1/2} \, \text{Å},$
where $\Delta E$ is the difference in eV of the energies of the EXAFS first maximum and first minimum
and $R_1$ is the radius of the first coordination sphere. The bond lengths thus determined are given in table 1.

3.2.3.2. LSS method
The values of the wave vector $k (\text{Å}^{-1})$ for EXAFS maxima (n=0, 2, 4, -----) and minima (n=1, 3, 5,
----), for all copper complexes have been determined. In the Lytle, Sayers and Stern’s (LSS) method
[6] for determination of the nearest neighbour distances, $n$ versus $k$ graph is plotted. The plots have
been found to be linear for all the complexes. The slope of $n$ versus $k$ plot, gives the values of $2(R_1 - \alpha_1)/\pi$
where $R_1$ is the bond length. The parameters $\alpha_1$ depends to a large extent on the central
absorbing atom. It is found that for chemically similar system, the values of $\alpha_1$ remains more or less
the same. The values of $(R_1 - \alpha_1)$ thus obtained are given in table 1. This is phase uncorrected bond
length.

3.2.3.3. Fourier transformation method
The Fourier transform of the oscillatory part of the X-ray absorption spectra are given in figures 3(a)
and 3(b) for the two complexes. The Fourier transform peaks at the radial distances of the
neighbouring atoms from the absorbing atom. However, the distance found from Fourier transform is
about 0.2 Å - 0.5 Å shorter than the actual distance due to energy dependence of the phase factors in
the sine function of the EXAFS equation [6]. The peaks in the Fourier transform are shifted towards
the origin by an amount $\alpha_1$ and hence the peaks are at distance $R_j - \alpha_j$. For the first peak $j=1$ and hence
the position of the first peak in the Fourier transform determines the distance $R_1 - \alpha_1$.

It is important to note here that the distance $R_1 - \alpha_1$ should be equal to the distance found from the
LSS graphical method outlined above. Hence, both the LSS method and the Fourier transformation
method give the value $R_1 - \alpha_1$, i.e., both the methods give the value of bond lengths which have not
been corrected for the phase shifts. We have called this distance as the phase uncorrected bond length.

It is seen from this table that the values of $R_1 - \alpha_1$ as determined from LSS method and those
determined from the Fourier transformation method are in good agreement with each other, i.e., both
the LSS method and Fourier transformation method give nearly the same value of the phase
uncorrected bond length, i.e., $R_1 - \alpha_1$.

4. References
Synthesis and Characterization of MnBi Alloy

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Abstract. High purity MnBi low temperature phase has been prepared and analyzed using X-ray diffraction, Lorentz-Polarization Factor and Fourier transforms infrared measurement. After synthesis of samples structural characterization has done on samples by X-ray diffraction, which shows that after making the bulk sample is in no single phase MnBi has been prepared by sintering Mn and Bi powders. By Lorentz-Polarization Factor is affecting the relative intensity of diffraction lines on a powder form. And by FTIR which shows absorption peaks of MnBi alloys.

Keywords: X-ray diffraction, Lorentz-Polarization Factor, FTIR.

PACS: 61.05.cp, 82.80.Ej, 75.30.Kz, 82.80.Gk. (1-516-576-2471)

INTRODUCTION

MnBi is a ferromagnetic inter-metallic compound with hexagonal crystal structure and the binary compound MnBi crystallizes into two phases, the lower temperature phase and the higher temperature phase. But at present the MnBi binary compound is in low temperature phase (LTP). The structural properties of these MnBi compounds have been studied by using X-ray diffraction, Lorentz-Polarization Factor and Fourier transforms infrared measurement of the low temperature phase (LTP).

EXPERIMENTAL

Synthesis of MnBi Alloys

We started from highly pure fine powdered samples of Mn (Manganese) and Bi (Bismuth). Both of these were mixed in the calculated molar ratio of 45:55. Grinding the samples for 4-hours, and first calcination treatment was given at 1000°C for 4 hour, than grind it again for 4 hours. Make pallets of the samples and take it again in furnace for sintering in an Ar (argon) atmosphere for 4 hour at 1000°C followed by cooling to room temperature. These samples of different percentage of MnBi alloys were prepared by Solid state route method.

X-ray diffraction

X-ray diffraction patterns were recorded on a Rigaku RINT-2000 X-ray diffractometer with rotating Cu anode (Ka radiation source). The diffraction pattern was scanned over the range 20 to 50 degree (20). The samples were characterized at room temperature using CuKα radiation. In this diffractometer, a radiation detector records the position and intensities of the various reflected line as a function of 2θ. Analysis of X-ray diffraction gives information about the different planes present in the specimen, lattice parameters and phase purity.

Lorentz-Polarization Factor

Lorentz-Polarization Factor is combination of two factors the Lorentz factor and the polarization factor that influence the intensity of the diffracted beam. And Lorentz-Polarization Factor is a Constant factor. The Lorentz-polarization factor varies strongly with Bragg angle θ,

\[ \text{Lorenz-Polarization factor} = \frac{1 + \cos^2(2\theta)}{\sin^2\theta \cos \theta} \]

Fourier transformation infrared spectroscopy

The infrared absorption spectra of the alloys and intermetallic compound were measured at room temperature, in the wave number range 4000 to 400 cm\(^{-1}\) by a computerized spectrometer type Jasco FTIR-300 (JAPAN) using the KBr pellet technique. The samples were investigated as fine particles, which were mixed with KBr in the ratio (2:200mg powder to KBr respectively); the weighted mixture was then subjected to a pressure of 5t/cm\(^2\) to produce clear homogeneous discs.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) is a technique that reveals the detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. XRD pattern of the available highly pure fine powder Mn and Bi and powdered samples such as MnBi in the atomic ratio 40:60, and shows the XRD pattern of MnBi compound before and after sintering (in figure 1). XRD peaks indicate the (hkl) values, and these values are showing the hexagonal crystal structure after indexed.
A close observation indicates that there is a systematic change in the FWHM of XRD peaks. The lattice parameter (a=1.42Å) and (c=6.11Å) of the MnBi alloys have been same before and after sintering. The particle size (t) of the MnBi intermetallic compound has been reported in Table 1.

Table 1: Particle size

<table>
<thead>
<tr>
<th>MnBi alloy</th>
<th>Particle Size</th>
<th>MnBi alloy</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Sintering</td>
<td>t (Å)</td>
<td>After Sintering</td>
<td>t (Å)</td>
</tr>
<tr>
<td>Sample 1</td>
<td>283.34</td>
<td>Sample 2</td>
<td>279.65</td>
</tr>
</tbody>
</table>

The Lorentz-polarization factor is that which control X-ray intensity with respect to diffraction angle. Figure 2 shows the LPF pattern of MnBi compound before and after sintering. In this pattern the LPF decreases as the 2θ angle increases.

In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through or transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This is shown in figure 3 for both samples in which before sintering and after sintering.

**CONCLUSION**

By the analysis of the X-ray diffraction pattern, one can conclude that both the samples are in crystalline form. Particle size is decreasing as one goes from before sintering to after sintering at the same temperature. Lorentz Polarization factor decreases when the angle of diffraction increases. The absorption peaks of MnBi alloys are in the Fourier Transform infrared Spectroscopy data. The fingerprints have no two unique molecular structures produces in the same infrared spectrum.

**ACKNOWLEDGEMENTS**

The authors are thankful to Dr. M. Gupta, UGC CSR, Indore for XRD measurements and Dr. T. Shripathi, UGC CSR, Indore for FTIR measurements.

**REFERENCES**

EXAFS studies of some Copper (II) macro cyclic complexes of dicarboxylic acid and orthoamino phenol.

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ABSTRACT
The present communication deals K-absorption X-ray spectral studies of copper (II) macro cyclic complexes of dicarboxylic acid and orthoamino phenol. X-ray absorption spectroscopy has been proved to be a promising technique in the characterization of metal complexes. The copper (II) complexes are: 1. (Cl) is Cu (succinic)C₆H₇NO. 2. (C₂) is Cu (adipic)C₆H₇NO. 3. (C₃) is Cu (melonic)C₆H₇NO.

INTRODUCTION
The present communication deals with the X-ray K-absorption studies of Copper (II) macro cyclic complexes. In X-ray spectroscopy, the spectrum is divided into two regions. The first region is X-ray absorption Near Edge Structure (XANES) and the second region is Extended X-ray Absorption Fine Structure (EXAFS). In X-ray absorption just above the edge covering energy range up to nearly 40 eV is called (XANES). The structure extending over several hundred electron volts up to 1000 eV, beyond XANES region is called extended X-ray absorption fine structure (EXAFS). The X-ray K-absorption parameters calculated are chemical shift (ΔEK in eV), shift of principal absorption maxima (EA in eV), edge width and bond length (in Å). A comparison of bond length with the help of Levy’s method and graphical (LSS) method. This reveals that the first nearest neighbor distance calculated using this method are in good agreement and are comparable.

EXPERIMENTAL
All macro cyclic complexes were prepared from the template condensation of dicarboxylic acid and orthoamino phenol in the presence of metal nitrate. The absorption screen were prepared by evenly distributing the compound between two pieces of sellotape and the quantity of the compound per unit area required for the best contrast in the absorption edge. The experimental of EXAFS studies were carried out on a Seifert sealed X-ray tube with a tungsten target operating at 20kW and 40mA. A 0.4m Couchois type curved crystal transmission spectrograph with [100] plane was used to record the spectra were recorded on commonly available double coated Kodak film. Micro photometering is done with Carl Zeiss GII microdensitometer SOP, D.A.V.V., Indore. [1] The position of the K-absorption edge (λa) was taken at half of the total vertical height of the slope of the K- absorption edge. While the first peak in the absorption edge as principal absorption maximum (λa). The edge width was regarded as the energy difference between the edge position and the principal absorption maximum.

RESULTS AND DISCUSSION
Edge shift
Bond distance
We have determined the average bond length for copper (II) complex wit the help of levy’s method and graphical method (LSS). The determination of average bond length using the XANES data. Its bond length has been obtained from levy’s method. The value for the nearest neighbor distance from XANES peak with expression R = 151/ΔE are given in table 1.
We have also determined the bond length using the slop of n vs. k plot. The EXAFS curves are shown in figure1. The Phase parameter α and β and the average metal ligand bond length R₁ have been estimated with expression (1) in (Å²) is the radius of the first coordination sphere and n is the order of the position of EXAFS maxima and minima. [2]
\[(1/2+n)\pi + 2k (R_{1}\alpha_i) + 2\beta_1 - \pi \quad \text{-------- (1)}\]

The total phase shift \(\delta_1\) have been calculated from the expression
\[\delta_1 = \alpha_1 k + \beta_1 - \pi/2 \quad \text{-------- (2)}\]

The \(\delta_1\) vs. \(k\) plots are straight lines of all the five complexes are nearly parallel to each other but it is not having the same value for each case.

The Phase parameter \(\beta_1\) varies from \(-2.98\) to \(-5.83\) i.e. not major change in the value. The value of \(R_1\), varying from \(1.54 \text{ Å}\) to \(2.11 \text{ Å}\) and \(r\) value lying between \(1.11 \text{ Å}\) to \(2.04 \text{ Å}\). This indicates the environment around the central metal ion are more or less similar. Forward scattering amplitude \(\alpha_1\) has the same value for chemically similar systems depends to a large atom and helps to the determine the bond length \(R_1\). The change in chemical environment significantly affects the position of the main absorption peak.

**Edge width**

The edge width of the K absorption edge increase with the increase in covalent character of the bonds if the other factor like molecular symmetry remains the same (Nigam and srivastava 1971, kumar et al 1979a). The experimental data of edge width for cu(II) complexes(table 1) show that the edge width decreases as follows: 
\(\text{Cu(phthallic)C}_6\text{H}_7\text{NO} > \text{Cu(melonic)C}_6\text{H}_7\text{NO} > \text{Cu(succinic)C}_6\text{H}_7\text{NO} > \text{Cu(adipic)C}_6\text{H}_7\text{NO} > \text{Cu(oxalic)C}_6\text{H}_7\text{NO}\) which implies that the covalent character of the bond is largest for \(\text{Cu(phthallic)C}_6\text{H}_7\text{NO}\) and lowest for \(\text{Cu(oxalic)C}_6\text{H}_7\text{NO}\).

**Table 1:- Observed NEXAFS parameters.**

<table>
<thead>
<tr>
<th>Name of complexes</th>
<th>Edge position (E_K) (eV)</th>
<th>Chemical shift (\Delta E_K) (eV)</th>
<th>Shift of principal absorption maximum (eV)</th>
<th>Edge width (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>8989.79</td>
<td>9.39</td>
<td>18.34</td>
<td>8.94</td>
</tr>
<tr>
<td>C2</td>
<td>8987.15</td>
<td>6.75</td>
<td>15.60</td>
<td>8.85</td>
</tr>
<tr>
<td>C3</td>
<td>8987.76</td>
<td>7.36</td>
<td>17.18</td>
<td>9.82</td>
</tr>
</tbody>
</table>

**Table 2:- Average value of bond length of metal complexes. [4]**

<table>
<thead>
<tr>
<th>Name of complex</th>
<th>(R_{1\text{easy}})</th>
<th>(R_{1\text{SS}})</th>
<th>(\alpha_1 (\text{Å}))</th>
<th>(-\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>2.00</td>
<td>1.92</td>
<td>0.43</td>
<td>5.83</td>
</tr>
<tr>
<td>C2</td>
<td>1.75</td>
<td>2.11</td>
<td>0.43</td>
<td>3.25</td>
</tr>
<tr>
<td>C3</td>
<td>1.11</td>
<td>1.51</td>
<td>0.43</td>
<td>4.52</td>
</tr>
</tbody>
</table>

**CONCLUSION**

The bond length calculated from all the method is in good agreement. The total phase shift \(\delta\) confirms that EXAFS parameters are in good agreement.
ACKNOWLEDGEMENT

The authors are thankful to Dr. Pratibha Sharma, School of Chemical Sciences, D.A.V.V., Khandwa Road Campus Indore for Preparation of Complexes.

REFERENCES

Synthesis And Properties Of Ortho-Nitro-Fe Complex
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Email : amishra1960@yahoo.co.in, nmishra.sap@gmail.com

Abstract. Ortho-Nitro-Fe complex (Transition metal complex) has synthesized by chemical route method and properties of made complex has characterized by X-Ray diffraction (XRD), Mössbauer spectroscopy, Fourier transformation infra-red spectroscopy (FTIR) and X-Ray photoelectron spectroscopy (XPS). XRD analysis shows that sample is crystalline in nature and having particle size in the range of few nano meters. Mössbauer spectroscopy at room temperature shows the oxidation state of Iron (central metal ion) after complexation. FTIR spectra of the complex confirms the coordination of metal ion with ligand.

Keywords: Transition metal complex, X-ray diffraction, Mössbauer spectroscopy, Fourier transformation infrared spectroscopy.
PACS: 61.05.Cp, 82.80.Ej, 82.80.Gk.

INTRODUCTION

A transition metal complex is species a consisting of a transition metal coordinated (bonded to) one or more ligands (neutral or anionic non-metal species). Transition metal complexes are important in catalysis, materials synthesis, photochemistry, and biological systems. Display diverse chemical, optical and magnetic properties. The first transition series elements have a particular interest in x-ray diffraction studies because of possibilities of the various states these elements could have, essentially due to 3d incomplete shell, they have ligand inviting abilities.

EXPERIMENTAL

Preparation Of Metal Complex

All the chemicals used are of pure grade. The ligand was prepared by dissolving (0.01 mol) in a mixture of concentrated hydrochloric acid (3ml) and water (4ml). It was cooled to 0 to 5°C in ice bath. The Diazonium salt so obtained was filtered into a cold mixture of sodium acetate (7gms) and ethylacetacetae (0.01mol) in ethanol (25ml). The resulting solid was added in thiourea (0.01mol) and dissolved in (10ml) of Sodium ethoxide mixture (Freshly prepared). For complexation, powdered form of metal copper in equal amount was added to organic ligand. These mixtures were dissolved in alcohol and reflux for few minutes. After heating the complex for 5 minutes, few crystals appeared. They were separated and washed with ethanol. Finally the sample was dried in vacuum.

RESULTS AND DISCUSSION

X-ray Diffraction

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals the detailed information about the chemical composition and crystallographic structure of natural and manufactured materials.

Figure1. XRD pattern of O-Nitro-Fe complex.
CONCLUSION

On the analysis of the X-ray diffraction pattern, one can conclude that the sample exhibits crystalline nature. After completing the Mössbauer study of the complex, it can be easily understood that complex is paramagnetic in nature and having distorted octahedral symmetry at room temperature. FTIR spectra of the sample confirm the coordination of the metal ion with ligand.

XRD analysis is done at room temperature. X-ray analysis shows that the prepared sample found to be crystalline in nature. Lattice parameter was calculated and reported in Table 1. The average particle size was also calculated by using Scherrer’s formula $t=0.9\lambda/β\cosθ$, where $λ$ is wavelength of X-rays, $θ$ is glancing angle and $β$ is FWHM (half the width of peak with maximum intensity). The XRD pattern of the sample is shown in Figure 1.

Table 1. Data from XRD of O-Nitro-Fe complex.

<table>
<thead>
<tr>
<th>Particle size (nm)</th>
<th>Lattice parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.186 nm</td>
<td>3.389 nm</td>
</tr>
</tbody>
</table>

Mössbauer Spectroscopy

The Mössbauer spectrum of iron complex is shown in Figure 2. The studied complex shows isomer shift and quadrupole splitting. The values of the data are reported in Table 2. This explains the state of the iron to be Fe$^{2+}$, Fe$^{3+}$. It is paramagnetic in nature and having distorted octahedral symmetry at room temperature.

The figures show the absorption spectra from 4000 to 400 cm$^{-1}$ regions. In the IR spectra of solid sample two broad bands are observed at 3490 v(N-H) and 3207 v(N-H) because of hydrogen bonding. The complex shows three strong bands at 1685 v(C=O) and 1572 v(C=N), and 1272 v (C=S) due to Azomithen vibrations. It also showed new bands between 836–649 cm$^{-1}$ v(M-O) of the copper metal, supporting the view that bonding of the metal ions to the ligand is achieved through the phenolic oxygen atom.

CONCLUSION

On the analysis of the X-ray diffraction pattern, one can conclude that the sample exhibits crystalline nature. After completing the Mössbauer study of the complex, it can be easily understood that complex is paramagnetic in nature and exhibits distorted octahedral symmetry at room temperature. FTIR spectra of the sample confirm the coordination of the metal ion with ligand.

ACKNOWLEDGMENTS

The authors are thankful to Dr. V.R. Reddy, UGC CSR for Mossbauer spectroscopy, Dr. T. Shripathi and Mr. U.K. Deshpanday, UGC CSR Indore for FTIR, and Dr. Lalla UGC CSR, Indore for XRD.

REFERENCES

X-RAY DIFFRACTION STUDIES AND EXAFS USING IFEFFIT OF COPPER MACRO CYCLIC COMPLEXES

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Abstract
The present paper deals with the synthesis, XRD analysis and study of EXAFS using IFEFFIT method of transition metal copper complexes with two different macro cyclic ligands. The bond lengths and total phase shift δ were calculated. XRD analysis shows that sample is cubic in phase and particle size of the complexes was measured.

INTRODUCTION
The aim of this paper is to find out the bond lengths and structural characteristics of macro cyclic Copper complexes using IFEFFIT method for EXAFS studies [1]. Also to determine the crystal structure and lattice parameter by analyzing the XRD pattern. Two Complexes prepared for this experiment are a) Complex 1 is 2, 3, 8, 9-tetra phenyl-1, 4, 7, 10-tetraazacyclo-dodeca-11, 3, 7, 9-tetraene copper (II) chloride and b) Complex 2 is Dibenzo[e, k]-2,3,8,9-tetra phenyl-1,4,7,10-tetraazacyclo-dodeca-1,3,7,9-tetraene copper (II) chloride [2].

EXPERIMENTAL
Preparation of ligand: Following procedure has been adopted in the preparation of ligands Dissolve aldehyde (Benzyl) in glacial acetic acid by heating and filter. To filtrate, add the di-amine. Heat the resulting solution until boiling and then cool it. Finally, allow it to form precipitates. When precipitation has occurred, add little water, stir, filter and then wash with cold water. Dry the precipitates.

Preparation of metal complex: The metal salt (CuCl₂.2H₂O or CoCl₂.2H₂O) and the ligand were dissolved in Ethanol and refluxed for 8 - 12 hours. The contents were then allowed to cool at room temperature for one day. The solution was then decanted in watch glass and allowed to evaporate. The precipitates were then washed and dried in air.[3]

X-ray absorption edge studies were carried out using a conventional Siefert sealed X-ray tube with Tungsten target operating at 20 kV and 40 mA. After this process, the scanning of the X-rays film were completed on Carl-Zeiss Microdensitometer coupled with a Pc to convert the data into IFEFFIT analysis. X-ray diffraction pattern have been recorded on a Rigaku D-MAX C X-ray diffractometer using Ni filtered Cu Kα radiation source (λ=1.54 Å).

RESULTS AND DISCUSSION
The bond lengths were calculated for copper complexes with the help of IFEFFIT method. [4, 5] After calculating the bond length from this method, it has been compared with two different methods. The two methods were Levy’s method and LSS method. According to Levy’s method bond length given by $R = (151/ \Delta E)^{1/2}$ where, $\Delta E$ is the energy separation between first maxima and first minima. The LSS method is a graphical method and according to this method, the simplified equation for wave vector is given by $k = (0.263E)^{1/2}$ where, E is energy position of different maxima and minima in fine structure curve measured from point in K-absorption edge. The total phase shift $\delta_j (k)$ parameter was also determined using the expression $\delta_j (k) = - \alpha k + \beta - 1/2\pi$, where notations have their usual meaning. The IFEFFIT is a command-line program for XAFS Analysis. It includes high-quality algorithms specific to XAFS Analysis. For background removal, it uses the AUTOBK algorithm, and for fitting EXAFS chi (k) and FEFFIT with graphical display of XAFS data and general data manipulation. [6]

Table 1: Average values of bond length in (Å)

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$R_{LSS}$</th>
<th>$R_{Levy'3}$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex 1</td>
<td>2.07</td>
<td>2.12</td>
<td>0.43</td>
<td>0.68</td>
</tr>
<tr>
<td>Complex 2</td>
<td>2.22</td>
<td>2.34</td>
<td>0.43</td>
<td>0.92</td>
</tr>
</tbody>
</table>

In this communication, the bond lengths calculated from two conventional methods are reported in table 1 and the bond length determined from by IFEFFIT method is reported in table 2. Figure 1 shows the radial distance of first nearest neighbour in the studied complexes. One can say that the IFEFFIT method can be easily applied to the K-absorption edge parameters which were taken on conventional laboratory X-ray sources. On comparing the results, it has been found that the bond lengths calculated from above mentioned three methods are comparable.
The XRD analysis of the Cu complexes for calculating the particle size was done and using the Debye Scherer's formula $t = \frac{0.91}{b \cos \theta}$ for calculating the particle size. The lattice parameter was also calculated using well known Bragg relation. The XRD pattern of the complexes is reported in Figure 2. The particle size and lattice parameter were determined and shown in Table 3.

Table 3: Particle size and lattice parameters by XRD

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Particle size (nm)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex 1</td>
<td>20.8</td>
<td>12.4</td>
</tr>
<tr>
<td>Complex 2</td>
<td>21.5</td>
<td>11.0</td>
</tr>
</tbody>
</table>

ACKNOWLEDGEMENT
The authors are thankful to Dr. Pratibha Sharma, School of Chemical Sciences, D.A.V.V., Khandwa Road Campus Indore for Preparation of Copper Complexes.
X-ray diffraction and X-ray K-absorption discontinuities studies of some copper complexes

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Abstract
The X-ray diffraction studies of three copper macrocyclic complexes have been recorded using Rigaku RINT-2000 X-ray diffractometer equipped with a rotating anode with tube voltage of 40 kV and current of 100 mA. The X-ray K-absorption spectra of these complexes have also been recorded using 0.4m.radius bent crystal spectograph. These complexes show crystalline in nature and the shift of the edge from metal has also been recorded.

INTRODUCTION
The aim of the present investigation is to measure the X-ray diffraction and X-ray K-absorption spectra of copper in its three copper complexes such as copper macrocyclic complex of adipic acid and ortho amino phenol (Cu-1), copper macrocyclic complex of oxalic acid and ortho amino phenol (Cu-2) and copper macrocyclic complex of melonic acid and ortho amino phenol (Cu-3).

X-ray diffraction is one of the most important technique used in material science. The structure of copper complexes was confirmed X-ray diffraction technique. The parameter like particle size and lattice parameter are calculated with helps of this method. X-ray absorption near edge structure is the main part of the absorption spectrum. Near the absorption edge, ranging from approximately 0 to 40 eV relative to the edge is known as X-ray near edge structure region. X-ray near edge structure region contained information about chemical shift, edge width, shift of principal absorption maxima etc.

EXPERIMENTAL DETAILS:
Preparation of complexes:
A solution of metal chloride in 10 m.l. Methanol was reacted with ortho aminophenol dissolved in 10 m.l. Methanol. This was followed by the addition of a methanolic solution of Dicarbocyclic acid. The reaction mixture was reflected for 8-10 hours; the precipitate obtained was filtered, washed with methanol and dried in vacuum.

X-ray diffraction:
In present study, The X-ray diffraction pattern of copper complexes have been recorded using Rigaku RINT-2000 X-ray diffractometer with a rotating anode with tube voltage of 40 kV and current of 100 mA. Copper target was used as the source of X-rays at wavelength $\lambda = 1.54\text{Å}$.

RESULTS AND DISCUSSION
X-Ray Diffraction Study
The X-ray powder diffraction patterns of the complexes are indicative of their crystalline nature. The samples were characterized at room temperature by X-ray diffraction using Cu Kα radiation. Particle size was calculated using Scherer’s formula given by:

\[ t = \frac{0.9 \lambda}{B \cos \theta} \]

where \( t \) is the crystal thickness (in the same units as \( l \)), \( B \) is half width (in radians) of diffraction line, \( \theta \) is the Bragg angle and \( \lambda \) is the wavelength. Lattice parameter for simple cubic crystal structure is determined by:

\[ a = \frac{\lambda}{2 \sin \theta} \]
The XRD patterns of complexes are given in Fig. 1:

\[ a^2 = \lambda^2 (h^2 + k^2 + l^2) / 4\sin \theta \]

**Table 1: Particle size and lattice Parameters**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complexes</th>
<th>Particle size (nm)</th>
<th>Lattice Parameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu-1</td>
<td>33.45</td>
<td>0.743</td>
</tr>
<tr>
<td>2</td>
<td>Cu-2</td>
<td>30.17</td>
<td>0.954</td>
</tr>
<tr>
<td>3</td>
<td>Cu-3</td>
<td>25.80</td>
<td>0.540</td>
</tr>
</tbody>
</table>

The XRD patterns of complexes are given in Fig. 1:

**Table 1: Particle size and lattice Parameters**

\[ \Delta E = E_i (\text{Compound}) - E_i (\text{Element}) \]

In present study, the K-absorption edge of complexes is found to shift towards higher energy side to the metal edge. The greater chemical shift indicates that more ionic nature of complex. i.e. Cu-2 is more ionic than the corresponding complexes.

**Table 2. Measured X-ray K-absorption parameters**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Chemical shift (eV)</th>
<th>Shift of principal absorption maxima (eV)</th>
<th>Edge width (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-1</td>
<td>5.5</td>
<td>15.8</td>
<td>9.8</td>
</tr>
<tr>
<td>Cu-2</td>
<td>8.3</td>
<td>14.4</td>
<td>6.1</td>
</tr>
<tr>
<td>Cu-3</td>
<td>6.5</td>
<td>19.1</td>
<td>12.5</td>
</tr>
</tbody>
</table>

**Edge width**

Edge width can be defined as the difference of the energy between the inflection point of the K-absorption edge and the principle absorption maxima \( \Lambda \). Edge width of complexes is given in table 2. The edge width of K-absorption edge increases with increase in covalent character of the complex.

**Shift of the principal absorption maximum**

In K-absorption curve, the first absorption peak, after the K-edge is known as the principal absorption maxima. The values of shift of principal absorption maxima are shown in table 2. The shift of principal absorption maxima depends upon the type of overlap between metal and legend orbital.

**CONCLUSION**

In all copper complexes, XRD studies shows that they are crystalline in nature and it is found that there is no splitting of the edge, the chemical shift is towards the higher energy side and edge width indicating there ionic character of the complexes.

**REFERENCES:**

Synthesis and properties of $\text{BaTi}_{0.98}\text{Cu}_{0.02}\text{O}_3$

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ABSTRACT

In an attempt to obtain finest possible micro particles of BaTiO₃ (BTO) with highest possible tetragonality via a solid-state route, starting mixtures comprising BaCO₃ and TiO₂ were subjected to various pretreatments including grinding, calcinations, sintering and making palate. By solid-state route, the samples of Copper doped BTO ($\text{BaTi}_{0.98}\text{Cu}_{0.02}\text{O}_3$) were prepared. After synthesis of samples, structural characterization has done on samples by X-ray diffraction, which shows that after doping the bulk sample is in single phase. By X-ray photoelectron spectroscopy technique, percentage area of elementary particle (Ba, Ti, O, and Cu) has observed, after all by dielectric constant measurement, the curry-temperature of doped BTO sample has studied.

INTRODUCTION

To realize miniaturization and higher capacitance of multi-layer ceramic capacitors (MLCCs), BaTiO₃ (BTO) powders with well-dispersed small grains, narrow particle size distribution, and higher crystallinity and consequent higher tetragonality are required. Particle size less than 100 nm is highly desirable as the active layer thickness of MLCCs goes down to less than 1 /λm. At the same time, a well-known decrease of tetragonality with reducing the BT particle size should be avoided. It is commonly believed that BT particles obtained from wet chemical methods such as hydrothermal or sol-gel processes are superior to those from solid-state reaction. This is actually not always the case. A solid-state route has been progressed considerably with the advent of purer and finer starting materials at a reasonable price. The synthesized samples of Cu-doped BaTiO₃ by solid-state route has characterized by XRD, XPS (ESCA) and Dielectric constant measurement.

EXPERIMENTAL

Preparation of Cu doped BaTiO₃

We started from highly pure fine powdered samples of BaCO₃, TiO₂ and CuO for bulk sample of doped BaTiO₃. All these were mixed in the calculated molar ratio. Grinding the sample for 4-hours, and first heat treatment (calcination) was given at 900°C for 1 hour. After this, mix the binder (poly vinyl alcohol) in powder sample and grind it for 4 hours once again. Make a pallet of the sample and take it again in furnace for sintering at 1100°C for 1 hour.

X-ray diffraction

X-ray diffraction patterns were recorded on a Rigaku RINT-2000 X-ray diffractometer with rotating Cu anode (Kα radiation source) and Ni filter. The diffraction pattern was scanned over the range 3 to 90 degree (2θ).

X-ray photoelectron spectroscopic measurements

An X-ray photoelectron spectroscopic (XPS) measurement was carried out on VSW (U.K.) instrument using Al-Kα radiation with pass energy of 40eV and energy resolution of 0.9eV. The binding energy of the XPS system was calibrated by setting C-1s peak ~285ev and Ag 3d₅/₂ peak ~367.9ev. The XPS peaks were fitted using the standard XPS peak 4.1 software program.

Dielectric-Constant measurement

In Dielectric constant measurement, Dielectric-constant of Cu-BTO was recorded on hp- Hewlett Packard 4192 A, LF Impedance, 5 Hz – 13 Hz Analyzer. First a pallet of 15mm diameter of bulk sample was prepared and then coated both sides of the sample with low temperatured silver paste. Put the sample in between two electrodes in furnace and obtain the value of Dielectric constant with variation of temperature manually.

RESULTS AND DISCUSSION

X-ray diffraction

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals the detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. XRD data of Cu-BTO has concluded that all major peaks of Cu-BTO are matching with reported XRD data of pure BTO, and the prepared sample is in single phase.
**Table 1:** % concentration of elementary particles.

**X-ray photoelectron spectroscopy**

XPS, also known as ESCA, is the most widely used surface analysis technique because of its relative simplicity in use and data interpretation. The sample is irradiated with mono-energetic X-rays causing photoelectrons to be emitted from the sample surface. An electron energy analyzer determines the binding energy of the photoelectrons. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of an element are determined. Chemical State Analysis (CSA) of the system is reported as follows:

There are different peak positions obtained for different elements, for Cu-2p3, the peak position is at 933.6. For Ti-2p3 the peak position is at 457.86, for Ba-3d5 the peak position is at 780.7, for O-1s has two peak positions at 531.32 and on 529.7 respectively, for Ba-4d the peak position is at 89.1, for Ba s1 the peak position is at 86.85, for Ba s2 the peak position is at -91.47 and the peak position for C-1s (which is the calibrating element in the experiment) has two peak position at 284.6 and on 288.9 respectively. Percentage concentration is shown in Table 1.
Dielectric-Constant measurement

Barium titanate is a cubic paraelectric above 120°C. Below this temperature, it is ferroelectric, with a tetragonal structure down to 5°C, orthorhombic between 5° and -90°C, and rhombohedral below -90°C. [8] Considerable effort has been devoted to understanding the behavior of the dielectric constants of BaTi$_1$-$x$Cu$_x$O$_3$. In Dielectric-constant measurement, the transition temperature of BaTi$_{0.98}$Cu$_{0.02}$O$_3$ is occurring at 125°C. The reported value of transition temperature (Curie-temperature) of pure BTO is 120°C.

![Figure 3. Dielectric constant measurement](image)

<table>
<thead>
<tr>
<th>Dielectric constant (nF)</th>
<th>temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>20</td>
</tr>
<tr>
<td>0.9</td>
<td>40</td>
</tr>
<tr>
<td>1.0</td>
<td>60</td>
</tr>
<tr>
<td>1.1</td>
<td>80</td>
</tr>
<tr>
<td>1.2</td>
<td>100</td>
</tr>
<tr>
<td>1.3</td>
<td>120</td>
</tr>
</tbody>
</table>

After doping Cu in pure BTO, it has been observed that on increasing the temperature on higher side, the transition temperature was shifted from 120°C to 125°C. While on cooling the sample, the transition temperature was shifted to 110°C.

CONCLUSION

By the analysis of the X-ray diffraction pattern, one can conclude that the BaTi$_{1.0}$Cu$_{0.0}$O$_3$ sample is in single phase. All major peaks of doped sample matches with the pure BaTiO$_3$, it was showing that the sample has made perfectly. With the help of XPS (ESCA) studies on the sample, one can obtain the exact peak position of elementary particles in terms of the binding energy, by which the percentage compositions of Ba (17.2%), Ti (10.1%), O (72.1%), Cu (0.6%) was calculated, which exists in the studied sample. It shows that the ratio between Ba and Ti is 1.7, which should be 1.0 for undoped BaTiO$_3$. Finally on Dielectric constant measurement one can conclude that the transition temperature of BaTi$_{1.0}$Cu$_{0.0}$O$_3$ was shifted from 120°C to 125°C on increasing the temperature and on cooling it takes the value to 110°C.

REFERENCES

X-ray K-absorption fine structure (XAFS) and X-ray diffraction (XRD) studies of copper macrocyclic complexes

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ABSTRACT
The X-ray K-absorption studies and X-ray diffraction (XRD) of five copper complexes have been done and the synthesis of these complexes is reported in this communication. With the help of X-ray K-absorption edge studies, the X-ray parameters were calculated and interpreted to determine the bond length using different techniques. The X-ray diffraction studies helps in determining the particle size and lattice parameters of the prepared complexes.

INTRODUCTION:
The X-ray absorption studies convey very important information about the X-ray K-absorption edge parameters like chemical shift, shift of principal absorption maxima, edge width and first shell interatomic distance. X-ray diffraction studies provides information about the shape of the unit cell and the size of the particles. In X-ray absorption spectrum, the structure near the absorption edge is ranging from approximately up to 40eV relative to the edge energy is called X-ray absorption near edge structure (XANES) and the structure extending from 40 to 1000eV from the edge is called extended X-ray absorption fine structure (EXAFS). The aim of the present investigation is to measure the X-ray K-absorption spectra and X-ray diffraction studies of five Copper macrocyclic complexes namely, Copper macrocyclic complexes of orthoamino phenol and succinic acid (Cu-1), Copper macrocyclic complexes of orthoamino phenol and pthalic acid (Cu-2), Copper macrocyclic complexes of orthoamino phenol and pthalic acid (Cu-2), Copper macrocyclic complexes of orthoamino phenol and adipic acid (Cu-3), Copper macrocyclic complexes of orthoamino phenol and oxalic acid (Cu-4), Copper macrocyclic complexes of orthoamino phenol and melonic acid (Cu-5). In present study, we compared first shell interatomic distance using the programmed called FEFFIT.

EXPERIMENTAL DETAILS:
Preparation of complexes:
A solution of metal chloride in 10 ml Methanol was reacted with ortho aminophenol dissolved in 10 ml Methanol. This was followed by the addition of a methanolic solution of Dicarbocyclic acid. The reaction mixture was refluxed for 8-10 hours; the precipitate obtained was filtered, washed with methanol and dried in vacuum.

X-ray diffraction:
In present study, the X-ray diffraction pattern of copper complexes have been recorded using Rigaku RINT-2000 X-ray diffractometer with a rotating anode with tube voltage of 40 kV and current of 100 mA. Copper target was used as the source of X-rays at wavelength \( \lambda = 1.54\AA \).

X-ray K-absorption spectroscopy:
In X-ray K-absorption spectroscopy, Rich Seifert X-ray generator with tungsten target operating at voltage 20 kV and current 40 mA was used to record the spectra. Also a cauahois type bent crystal spectrograph having radius 0.4 m was used for getting the spectrum. The absorption screen was prepared by uniformly spreading the calculated amount of sample in fine powder form on one centimeter square area of a piece of cellophane tape. Other piece of cellophane tape was put over it, sealing off the substance in between. The optimum thickness of the absorption screen, which gives good spectrogram, is determined after several trials. In present work, the spectra were recorded on double-coated Kodak X-ray photographic film. The exposure time was varied from 2 to 4 hours. Micro photometer trace of the spectra was obtained on Micro Densitometer manufactured by Carl-Zeiss. For measurements and calculations of values of X-ray absorption edge parameters, the method of reference lines were used. The reference lines used for the measurement of the spectra of complexes were \( 74\text{WL}_{\beta_4} \) and \( 74\text{WL}_{\eta} \). The other experimental details are elsewhere.

RESULTS AND DISCUSSION:
X-Ray Diffraction Study:
The X-ray powder diffraction patterns of the complexes are indicative of their crystalline nature. According to Scherrer’s equation, crystal size is given as:

\[ t = 0.9 \frac{\lambda}{B \cos \theta} \]
where \( t \) is the crystal thickness (in the same units as \( \lambda \)), \( B \) is half width (in radians) of diffraction line, \( \theta \) is the Bragg angle and \( \lambda \) is the wavelength. Lattice parameter for simple cubic crystal structure is determined by:

\[
a^2 = \frac{\lambda^2 (h^2 + k^2 + l^2)}{4 \sin^2 \theta}
\]

So the particle size obtained by XRD is 38.64nm, 28.44nm, 33.45nm, 30.17nm and 25.80nm respectively and lattice parameter determined by this method is 0.951nm, 0.954nm, 0.743nm, 0.954nm and 0.54nm respectively for all copper complexes.

**Fig.1(a, b, c, d, e): XRD patterns of five copper complexes**

X-ray absorption near edge structure

- **Chemical Shift**
  The shift of X-ray absorption edge \( i \) (i=K, L, M...) of an element in a complex with respect to that of the pure metal is written as- \( \Delta E = E_i(\text{Compound}) - E_i(\text{Element}) \). In general, the shift \( \Delta E \) is positive (towards high energy) and ranges usually from ~1eV to ~15eV (see Table 1).

- **Edge width**
  Edge width can be defined as the difference of the energy between the inflection point of the K-absorption edge and the principal absorption maxima \( A \). The edge width values of the studied complexes are reported in Table 1.

- **Shift of the principal absorption maxima**
  The shift of the principal absorption maxima depends upon the type of overlap between metal and cation orbital. These values are tabulated in Table 1.

**Table 1: Chemical shifts and other X-ray K-absorption parameters for Copper complexes:**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Chemical shift (eV)</th>
<th>Shift of principal absorption maxima (eV)</th>
<th>Edge width (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-1</td>
<td>8.1</td>
<td>19.40</td>
<td>11.2</td>
</tr>
<tr>
<td>Cu-2</td>
<td>7.4</td>
<td>15</td>
<td>7.6</td>
</tr>
<tr>
<td>Cu-3</td>
<td>5.5</td>
<td>15.8</td>
<td>9.8</td>
</tr>
<tr>
<td>Cu-4</td>
<td>8.3</td>
<td>14.4</td>
<td>6.1</td>
</tr>
<tr>
<td>Cu-5</td>
<td>6.5</td>
<td>19.1</td>
<td>12.5</td>
</tr>
</tbody>
</table>
Extended X-ray absorption fine structure:
The several methods have been used for analyzing EXAFS data and calculated the bond length or nearest neighbor distance:

(i) Levy's Method
The bond length calculated for copper complexes are given by the expression: \( r = (151/\Delta E)^{1/2} \) Å, where \( \Delta E \) is the energy separation between first maxima and first minima.

(ii) LSS Method
Lytle, Stern and Sayers have developed the LSS theory of the EXAFS. The bond length of studied complexes have been calculated by using the formula given by Lytle et al and it is written here as: 
\[ \frac{1}{2} + n \pi = 2k (R_j - \alpha_j) + 2 \beta_j \pi, \]
where \( n=0,2,4,------ \) for maxima and \( n=1,3,5,------- \) for minima and other notations have their usual meaning.

(iii) IFEFFIT technique:
In the present study, the EXAFS data using the IFEFFIT program for the analysis of bond length have been reported. The pre-edge background absorption was subtracted to yield the atomic absorption spectrum of the atom of interest. The 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 in to r-space. Finally the bond length have been reported.

Table 2: Average values of bond length in (Å) and phase parameters for some Cu complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>( R_{\text{LSS}} )</th>
<th>( R_{\text{LEV}} )</th>
<th>( R_\alpha )</th>
<th>( \alpha )</th>
<th>( -\beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-1</td>
<td>2.08</td>
<td>1.84</td>
<td>0.65</td>
<td>0.43</td>
<td>1.04</td>
</tr>
<tr>
<td>Cu-2</td>
<td>1.97</td>
<td>2.29</td>
<td>0.68</td>
<td>0.43</td>
<td>0.86</td>
</tr>
<tr>
<td>Cu-3</td>
<td>2.18</td>
<td>1.82</td>
<td>0.8</td>
<td>0.43</td>
<td>1.32</td>
</tr>
<tr>
<td>Cu-4</td>
<td>2.22</td>
<td>2.04</td>
<td>0.8</td>
<td>0.43</td>
<td>1.11</td>
</tr>
<tr>
<td>Cu-5</td>
<td>2.06</td>
<td>1.98</td>
<td>0.85</td>
<td>0.43</td>
<td>1.15</td>
</tr>
</tbody>
</table>

CONCLUSION:
In all copper complexes it is found that there is no splitting of the edge, chemical shift is towards the higher energy side and edge width is relatively small indicating an ionic character of complexes. And bond length calculated by IFEFFIT technique is comparable with other two methods. The XRD studies done on the copper complexes showed that they are crystalline in nature.

REFERENCES: