Comparative study of experimental and theoretical analysis of EXAFS data of copper complexes using FT method

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Abstract.
The X-ray absorption spectra at the K-edge for a series of copper mixed ligand, having hydroxypyridine as one of the ligands, have been investigated in the laboratory X-ray spectroscopic set-up. In the series only X-ray absorption near edge structure (XANES) parameters and bond length using modified Lytle, Levy’s and LSS methods were calculated. In the present study the bond lengths are calculated by Fourier Transform method theoretically using IFEFFIT software and compared with experimental results.

Introduction
The transition metal Schiff base complexes of copper have been playing an important role in the development of coordination chemistry. Schiff base metal complexes have been widely studied, because of their antifungal and biological applications. [1]. In the present studies we have taken Schiff base compounds of copper (II) complexes with hydroxypyridine as ligand.
The structure extending from 40 to 1000eV from the edge is called extended X-ray absorption fine structure (EXAFS) and it gives information about the local structure of the complexes. The aim of the present investigation is to measure the spectra of copper complex, and to compare first shell inter atomic distance using the programmed called IFEFFIT.

2. MATERIAL SYNTHESIS
Preparation of Schiff Base Ligand
Standard method was adopted for the preparation of the complexes. The series of the copper (II) complexes with hydroxypyridine as ligand is shown in table 1 below.

| S.N. | Name Of Complexes | Abbreviations | Mol. Formulae          |
|------|-------------------|---------------|------------------------|
| 1    | Copper (II) sulphasothiazole salicylaldimine | CU(SUTSA) | (C_{16}H_{12}N_{3}O_{3}S_{2})_{2}Cu |
| 2    | Copper(II) Sulphadiazine salicylaldimine | CU(SUDSA) | (C_{17}H_{13}N_{2}O_{3}S)_{2}Cu |
| 3    | Copper(II) sulphamethoxy salicylaldimine | Cu(SUMSA) | (C_{17}H_{14}N_{2}O_{4}S)_{2}Cu |
| 4    | Copper(2,3-dihydroxy pyridine) | Cu(DHP) | (C_{9}H_{8}NO_{2})_{2}Cu |
| 5    | Copper(2-amino,3-hydroxy pyridine) | Cu(AHP) | (C_{9}H_{8}N_{2}O_{2})Cu |
| 6    | Copper(3-hydroxy pyridine 2-carboxylic acid) | Cu(HPA) | (C_{9}H_{8}NO_{3})_{2}Cu |

Table 1: Series of copper (II) complexes hydroxypyridine as ligand.

3. EXPERIMENTAL TECHNIQUE
X-ray absorption fine structure studies were carried out using a conventional Siefert sealed X-ray Tube with Tungsten target operating 20 kV and 40 mA. After this process, the scanning of the X-ray films was completed on Carl-Ziess microdensitometer coupled with computer to convert the data into FT
format. The FEFF series of programs for the calculation of x-ray absorption spectra has had a
transformative impact on EXAFS analysis because of its accuracy, flexibility, and portability. Its
primary use has been in supporting a path by path analysis of experimental data using auxiliary
programs such as IFEFFIT, Artemis, Six Pack, etc. In this paper alternative strategies for XAFS
analysis that combine FEFF are described [2]. IFEFFIT is an interactive program for XAFS Data Analysis.
It runs like a command-line 'shell' in which commands are entered to process and manipulate data. IFEFFIT has
a fairly high-level command language so that one can do the complex manipulation needed for XAFS analysis
(such as background subtraction and Fourier transforms) with simple commands [3,4].

The EXAFS data usually analyzed on following steps.
(a) Pre edge background removal from raw data.
(b) Isolation of EXAS oscillations from the post edge data.
(c) Conversion of EXAFS oscillations from energy space to photoelectron wave vector space.
(d) Fourier Transform of the EXAFS oscillations into r-space.
(e) Extraction of individual shell contributions to EXAFS by inverse Fourier Transform.

4. RESULTS AND DISCUSSION

EXAFS analysis
The bond lengths of copper complexes were calculated using IFEFFIT method and compared with
LSS, Levy’s, Lytle’s methods [5, 6, 7]. According to LSS method, we have determined the bond
length using the slope of n vs k plot. The phase parameter $\alpha_1$ and $\beta_1$, the metal ligand bond length $R_1$
have been estimated with expression

$$(1/2+n) \pi = 2k(R_1 - \alpha_1) + 2 \beta_1 - \pi$$

The EXAFS curves are shown in figure 1. By using the Levy’s method, the bond length has been
obtained from the expression

$$r = (151/\Delta E)^{1/2}$$

where, $\Delta E$ is the energy difference between first maxima and first minima [7]. Lytle method is
modification of LSS method and the bond length is given by the expression

$$R = (37.60/M)^{1/2}$$

where M is slope between E vs Q plots. In FEFFIT programming the EXAFS data were analyzed by
the standard procedure. The preedge background absorption was subtracted to yield the atomic
absorption spectrum of the atom of interest background above the edge was removed from the
spectrum using sp line fit. The data converted to energy space and then to k space. A Fourier transform
is applied to these data to convert into the r-space. The bond lengths of copper complexes calculated
by IFEFFIT programming is compared with LSS, Lytle and Levy’s methods as depicted in table 2.
The theoretical analysis of EXAFS of copper complexes having hydroxypyridine as ligand has been
done and compared with experimental values. Following table shows the results.
| S.N. | Complexes     | $R^a_{\text{Levy}}$ | $R^a_{\text{Lytle}}$ | $R^a_{\text{LSS}}$ | $R^a_{\text{IEFFIT}}$ |
|------|---------------|---------------------|----------------------|-------------------|---------------------|
| 1    | Cu(SU\text{TSA}) | 2.4                 | 2.2                  | 2.5               | 1.2                 |
| 2    | Cu(SUDSA)     | 2.1                 | 2                    | 2.6               | 1.7                 |
| 3    | Cu(SUMSA)     | 1.8                 | 1.8                  | 2.5               | 1.5                 |
| 4    | Cu(DHP)       | 2                    | 2                    | 2.1               | 1.7                 |
| 5    | Cu(AHP)       | 2.2                 | 2.4                  | 2.6               | 2.5                 |
| 6    | Cu(HPA)       | 2.2                 | 2.1                  | 2.4               | 2.6                 |

$R_{\text{Levy}}$: Bond Length by Levy’s method  
$R_{\text{LSS}}$: Bond Length by LSS method  
$R_{\text{Lytle}}$: Bond Length by Lytel method  
$R_{\text{IEFFIT}}$: Bond Length by FT method

Table 2: The average values of metal-ligand bond length in ($\text{Å}^{-1}$) for copper (II) complexes, hydroxypyridine as ligand.

Figure 1 Shows EXAFS spectra of Cu (II) complexes

Figure 2 Magnitude of F.T. of $k^2\chi(k)$ for six copper (II) complexes hydroxypyridine as ligand
5. CONCLUSION
As is evident from the analysis that the bond lengths determined by Fourier transforming the FEFFIT programming are comparable with the bond length obtained by LSS, Levy’s and Lytle methods. The theoretical and experimental values agree well with each other. This means that the parameterized theoretical calculation of the EXAFS spectra of copper complexes described here is in good agreement with physical reality.

6. REFERENCES
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