EXAFS study of copper thiosemicarbazide complexes

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Abstract. The present paper deals with the synthesis of transition metal Schiff base complexes of copper by chemical root method. The synthesized metal complexes have been studied by extended X-ray absorption fine structure (EXAFS) technique. The metal ligand bond length have been determined using LSS, Levy’s and Lytle’s methods. Bond-lengths have also been determined from the Fourier transform of the EXAFS data. Bond lengths determined from these methods are comparable to each other.

1. Introduction
In the present investigation, the X-ray absorption spectra of Copper(II) complexes of thiosemicarbazide mixed ligands is done using the synchrotron radiation, i.e., on beamline BL-8 at RRCAT, Indore [1 – 3]. In organic chemistry, semicarbazide is a derivative of urea, where NH₂ on one side has been replaced with H₂NNH hydrazine, yielding H₂NNHC(=O)NH₂. A thiosemicarbazide is an analog with a sulfur atom in place of the oxygen atom. Semicarbazone is a ketone form of semicarbazide which is derived by the condensation reaction between a ketone (or aldehyde) and a semicarbazide. Semicarbazide products (semicarbazones and thiosemicarbazones) are known to have an activity of antiviral, antiinfective and antineoplastic through binding to copper or iron in cells.

X-ray absorption fine structure (EXAFS) refers to small amplitude oscillations in the X-ray absorption coefficient that can extend hundreds of electron volts above a core-level absorption edge. These oscillations arise from final state interference effects of backscattered photoelectrons from neighboring atoms. In contrast, an isolated atom exhibits a smooth and essentially structure less absorption background corresponding to the photoionization process induced by a core-level excitation. EXAFS features on the high-energy side of the k absorption edge, up to several hundred eV have been observed in the copper and cobalt metal complexes. Different theories developed to explain the EXAFS have already been studied.

2. Material synthesis
The copper(II) complexes were prepared by chemical root method. The procedure is described below in brief.

(a) Synthesis of ligand:
The thiosemicarbazide (0.01M) was dissolved in 10 ml of methanol in a 100 ml round bottom flask, a solution of 0.01M substituted aromatic aldehyde in methanol was added drop wise over a 10 min. period with continues stirring, after addition the reaction mixture was stirred for 3 hours at room temperature, reaction was monitored by TLC. After completion solvent was evaporated and residue was washed with cold methanol and dried at room temperature.
In the ligands, substituted methoxy group and anilines are at different positions.

(b) Preparation of metal complexes:

Corresponding metal acetate (0.01mol) was dissolved in min. quantity of water and then was added to the hot solution of ligand (0.02mol) in methanol (50-60 ml). The reaction mixture was heated on 80 – 90°C for 1 hr. with constant stirring and then the reaction mixture stirred for 3 days, until a colored solid mass separated out. The ppt was filtered, washed with methanol and finally with diethyl ether and dried in vacum.

Here the series of copper(II) compounds are mentioned in table 1 which are under study.

**Table 1 Copper(II) complexes with name, mol. formulae and abbreviations.**

| S. No. | Complex | Molecular formula | Abbreviation |
|--------|---------|-------------------|--------------|
| 1      | Cu[(2,5-dimethoxy-2-nitrobenzylidene)]thiosemicarbazide | C_{20}H_{22}Cl_{2}CuN_{8}O_{8}S_{2} | Cu[2,5-dimethoxy] |
| 2      | Cu[(3,5-dimethoxy-2-nitrobenzylidene)]thiosemicarbazide | C_{20}H_{22}Cl_{2}CuN_{8}O_{8}S_{2} | Cu[3,5-dimethoxy] |
| 3      | Cu[(4,5-dimethoxy-2-nitrobenzylidene)]thiosemicarbazide | C_{20}H_{22}Cl_{2}CuN_{8}O_{8}S_{2} | Cu[4,5-dimethoxy] |
| 4      | Cu[(2-Chloroquinolin-3-yl)Methylene]thiosemicarbazide | C_{22}H_{16}Cl_{2}CuN_{8}S_{2} | Cu[2-chloroquinolin] |
| 5      | Cu[(2-chloro-8-methylquinolin-3-methylene)]thiosemicarbazide | C_{24}H_{20}Cl_{2}CuN_{8}S_{2} | Cu[3-methylene] |
| 6      | Cu[(2-chloro-8-methylquinolin-4-methylene)]thiosemicarbazide | C_{24}H_{20}Cl_{2}CuN_{8}S_{2} | Cu[4-methylene] |

3. Experimental

X-ray absorption fine structure studies were carried out on beamline BL-8 coupled with computer to convert the data into IFEFFIT. 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[4].
4. Results and discussion
The EXAFS curves are shown in figure 1 and the Fourier transforms are given in figure 2. The bond lengths of copper complexes were calculated using Fourier transform 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 α and β, the metal ligand bond length R have been estimated with expression

\[(n+1/2)\pi=2k (R_1-\alpha)+2 \beta -\pi\]

Using the Levy’s method, the bond length has been obtained from the expression

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

where, ΔE is the energy difference between first maxima and first minim [8].

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 pre-edge 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 spline 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 Fourier transform is compared with LSS, Lytle and Levy’s methods as depicted in table 2 given below.

| S.N. | Abbreviations       | R_{Levy} | R_{LSS} | R_{Lytle} | R_{FT} |
|------|---------------------|----------|---------|-----------|--------|
| 1    | Cu[2,5-dimethoxy]   | 1.2      | 1.2     | 1.4       | 1.5    |
| 2    | Cu[3,5- dimethoxy]  | 1.8      | 1.7     | 1.9       | 1.1    |
| 3    | Cu[4,5- dimethoxy]  | 1.5      | 1.2     | 1.4       | 1.6    |
| 4    | Cu[2-chloroquinolin| 2.1      | 2       | 1.9       | 1.9    |
| 5    | Cu[3-methylene]     | 1.8      | 1.8     | 1.6       | 1.4    |
| 6    | Cu[4- methylene]    | 1.8      | 1.7     | 1.8       | 1.3    |

R_{Levy} : Bond length by Levy’s method, R_{LSS} : Bond length by LSS method
R_{Lytle} : Bond length by Lytle method and R_{FT} : Bond length by Fourier transform

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.

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Figure 1 Shows EXAFS spectra of Cu(II) complexes.

Figure 2 Magnitude of Fourier transform of $k^2\chi(k)$ for Cu(II) complexes.