Exafs and comparative studies of copper (II) 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 were characterized by Extended X-ray absorption fine structure (EXAFS) is a technique that has been used for determining the metal ligand bond length using conventional X-ray source and also by EXAFS analysis using IFEFFIT programming. Bond lengths determined from these data analysis methods are compared with the bond lengths obtained from LSS, Levy's and Lytle's methods. Bond lengths of the complexes are in good agreement obtained by theoretical and experimental method.

1. 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 Series of copper (II) complexes thiosemicarbazide as ligand have been taken.

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 thiosemicarbazide as ligand is shown below.

3. Experimental technique

In the present thesis, X-ray absorption spectra at the K-edge have been recorded for series of copper(II) complexes using the dispersive EXAFS beamline (BL-8) at Indus-2 synchrotron at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore.

After this process, the scanning of the X-ray films was completed on Carl-Ziess microdensitometer 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[2].

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 [3, 4, 5]. According to LSS method, the bond lengths can be determine using the slope of n vs k plot. The phase parameter $\alpha_1$and β_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 figure1.1a 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 [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 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 IFEFFIT programming is compared with LSS, Lytle and Levy's methods as depicted in table2.

The theoretical analysis of EXAFS of copper complexes having thiosemicarbazide as ligand has been done and compared with experimental values. The results of the average values of metal ligand bond length are reported in table 2.

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

S. N.	Name	Molecular Formula	Abbreviation
1	Cu[(2,5-dimethoxy-2-nitrobenzylidene)] thiosemicarbazide	C20H22Cl2 CuN8O8S2	Cu[2,5-dimethoxy]
2	Cu[(3,5-dimethoxy-2-nitrobenzylidene)] thiosemicarbazide	C20H22Cl2 CuN8O8S2	Cu[3,5- dimethoxy]
3	Cu[(4,5-dimethoxy-2-nitrobenzylidene)]thiosemicarbazide	C20H22Cl2 CuN8O8S2	Cu[4,5- dimethoxy]

Table 2. The average values of metal-ligand bond length in $(\overset{0}{A})^{-1}$ for copper (II) complexes, thiosemicarbazide as ligand.

S.N.	Abbreviations	R_{Lavy}	R_{Lss}	R_{Lytel}	$R_{IFEFFIT}$
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

$R_{Levy's}$ ***:*** *Bond Length by Levy's method*

R_{Lss} : *Bond Length by LSS method*

R_{Lytel} : *Bond Length by Lytel method*

$R_{IFEFFIT}$: *Bond Length by IFEFFIT*

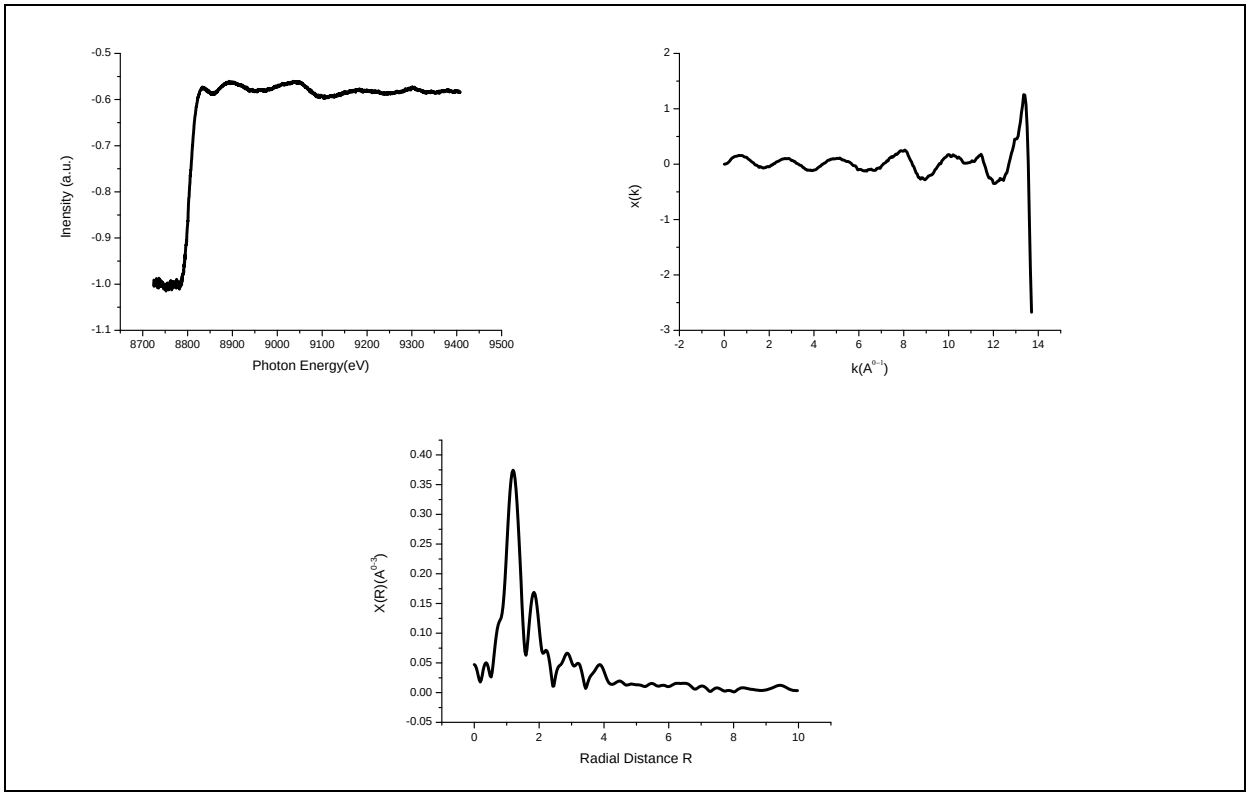

Figure 1. EXAFS curve of Cu[2,5-dimethoxy]

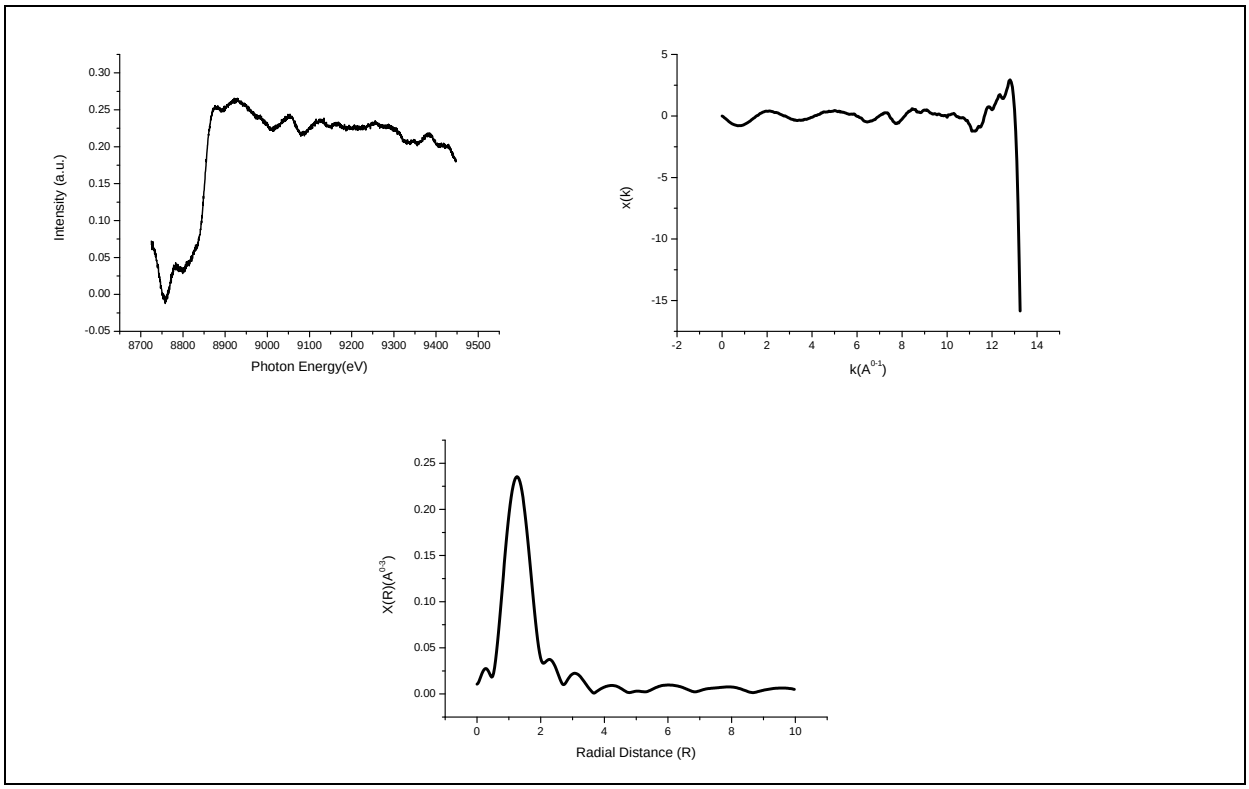

Figure 2. EXAFS curve of Cu[3,5-dimethoxy]

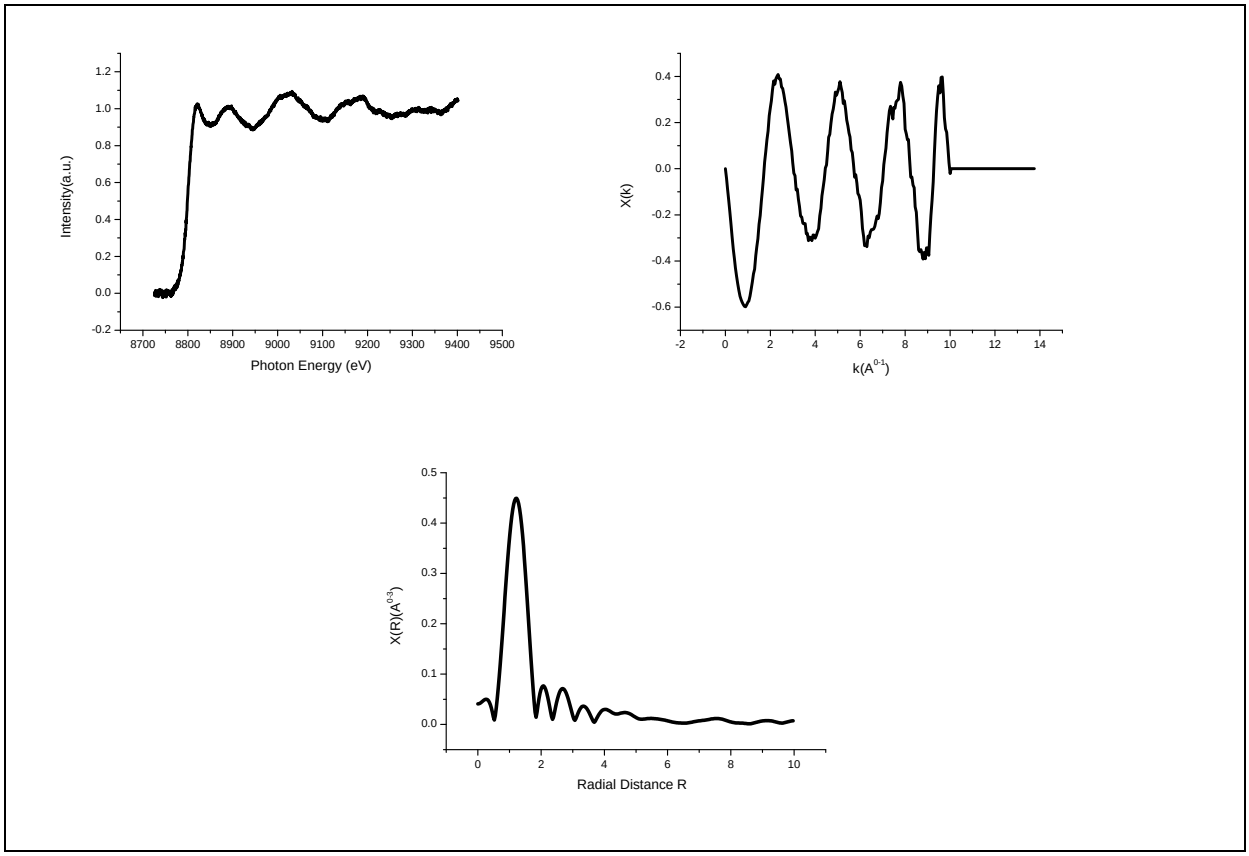

Figure 3. EXAFS curve of Cu[4,5-dimethoxy]

5. Conclusion

As it 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.

References

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