EXAFS 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 (II) 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 synchrotron radiation, i.e., on beamline BL-8 at RRCAT, Indore .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.

Keywords – EXAFS, LSS, Levy's, lytle's methods

I. INTRODUCTION

The transition metal Schiff base complexes 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]. The structure extending from 40 to 1000eV from the edge is called extended X-ray absorption fine structure (EXAFS) and gives information about the local structure of the complexes. The aim of the present investigation is to measure the X-ray K absorption spectra of copper complex , and to compare first shell inter atomic distance.

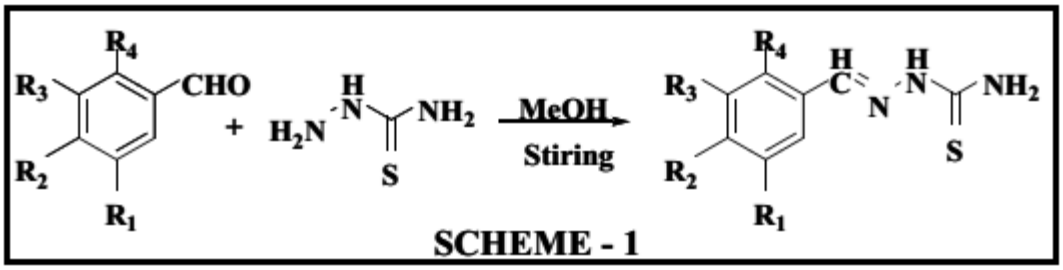
II. PROPOSED ALGORITHM

Experimental Technique –
In the present investigation, the X-ray absorption spectra of Copper(II) complexes of thio- semicarbezide mixed ligands is done using the synchrotron radiation, i.e., on beamline BL-8 at RRCAT, Indore .

Synthesis of complex –
The copper(II) compexes were prepared by chemical root method. The procedure is described below in brief.

A. Synthesis of Ligand –

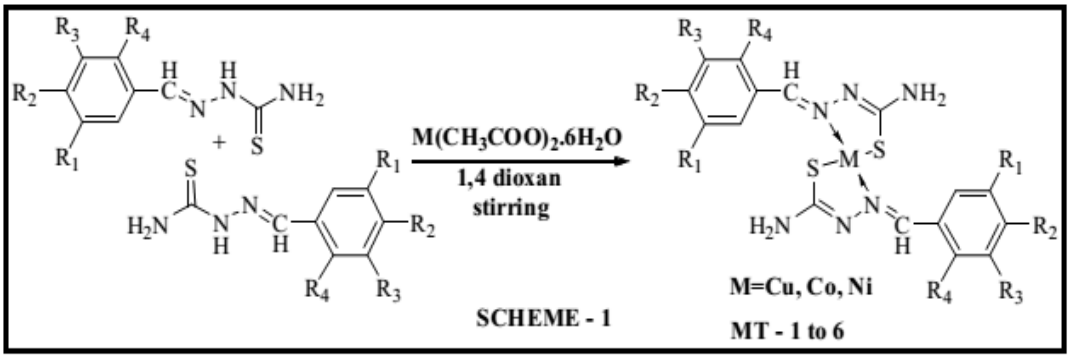
The thiosemicarbazide (0.01M) was dissolved in 10 ml of methanol in a 100 ml round bottom flask, a solution of 0.01M substituted aromatic aldehyde in methanol was added drop wise over a 10 min. period with continues stirring, after addition the reaction mixture was stirred for 3 hours at room temperature, 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 vaccum.



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

Table – 1 copper(II) complexes with name ,mol. Formulae and abbreviations.

S.NO.	NAME	MOLECULAR FORMULA	ABBREVIATION
1	1-(2,5-dimethoxy-2-nitrobenzylidene)thiosemicarbazide	C20H22CL2 CUN8O8S2	2,5-dimethoxy
2	1-(3,5-dimethoxy-2-nitrobenzylidene)thiosemicarbazide	C20H22CL2 CUN8O8S2	3,5- dimethoxy
3	1-(4,5-dimethoxy-2-nitrobenzylidene)thiosemicarbazide	C20H22CL2 CUN8O8S2	4,5- dimethoxy

III. RESULT & DISCUSSION

EXAFS analysis

The bond lengths of copper complexes were calculated using LSS, Levy's, lytle's methods [3, 4, 5]. According to LSS method, the bond lengths can be detrmine using the slope of n vs k plot. The phase parameter $\alpha_1$and β_1, the metal ligandbond 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 [8]. Lytle method is modification of LSS method and the bond length is given by the expression

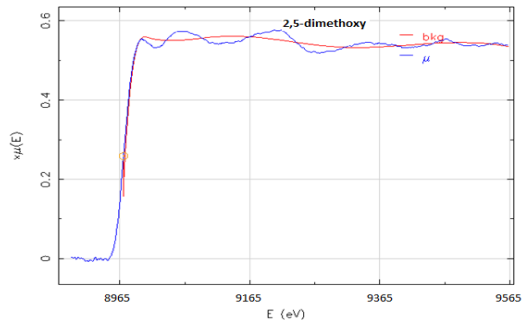
$$R= (37.60/M)^{1/2}$$

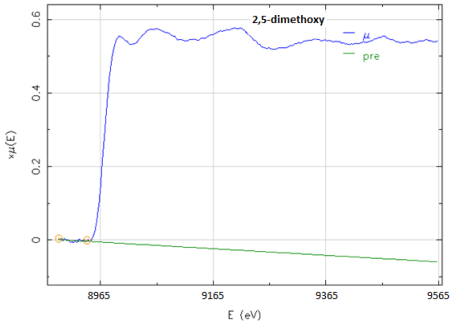
where M is slope between E vs Q plots.

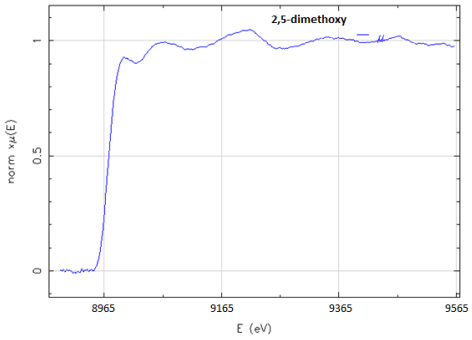
Table – 2 Average value of metal ligand bond length in ($\overset{0}{A}$)$^{-1}$ for Cu complexes R_{LSS}, R_{Lytle}, $R_{Levy's}$

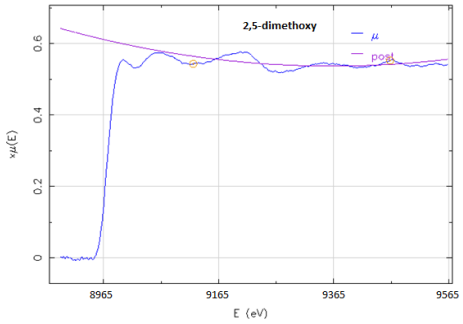
S.No.	Abbreviations	R Levy's	R Lss	R Lytel
1	2,5-dimethoxy	1.2	1.2	1.4
2	3,5- dimethoxy	1.8	1.7	1.9
3	4,5- dimethoxy	1.5	1.2	1.4

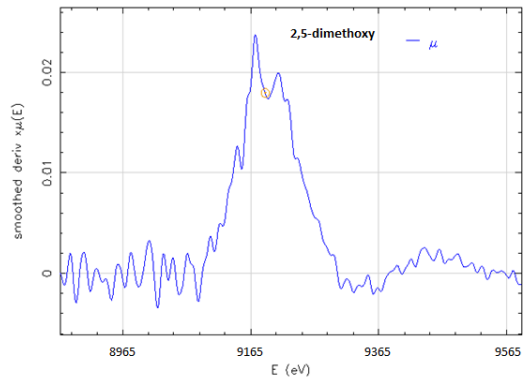
$R_{Levy's}$: *Bond Length by Levy's method*
R_{Lss} : *Bond Length by LSS method*
R_{Lytel} : *Bond Length by Lytel method*

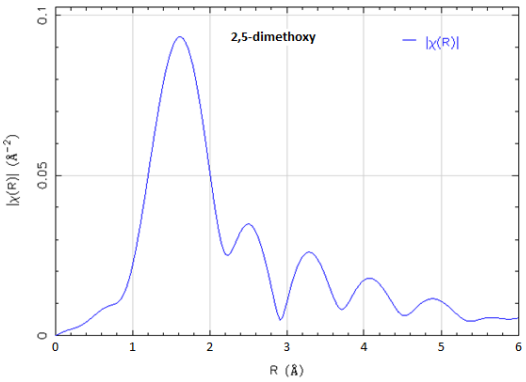












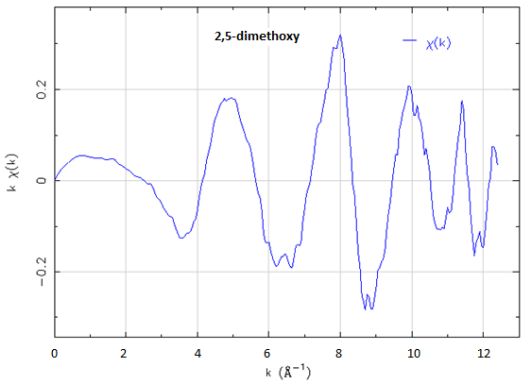
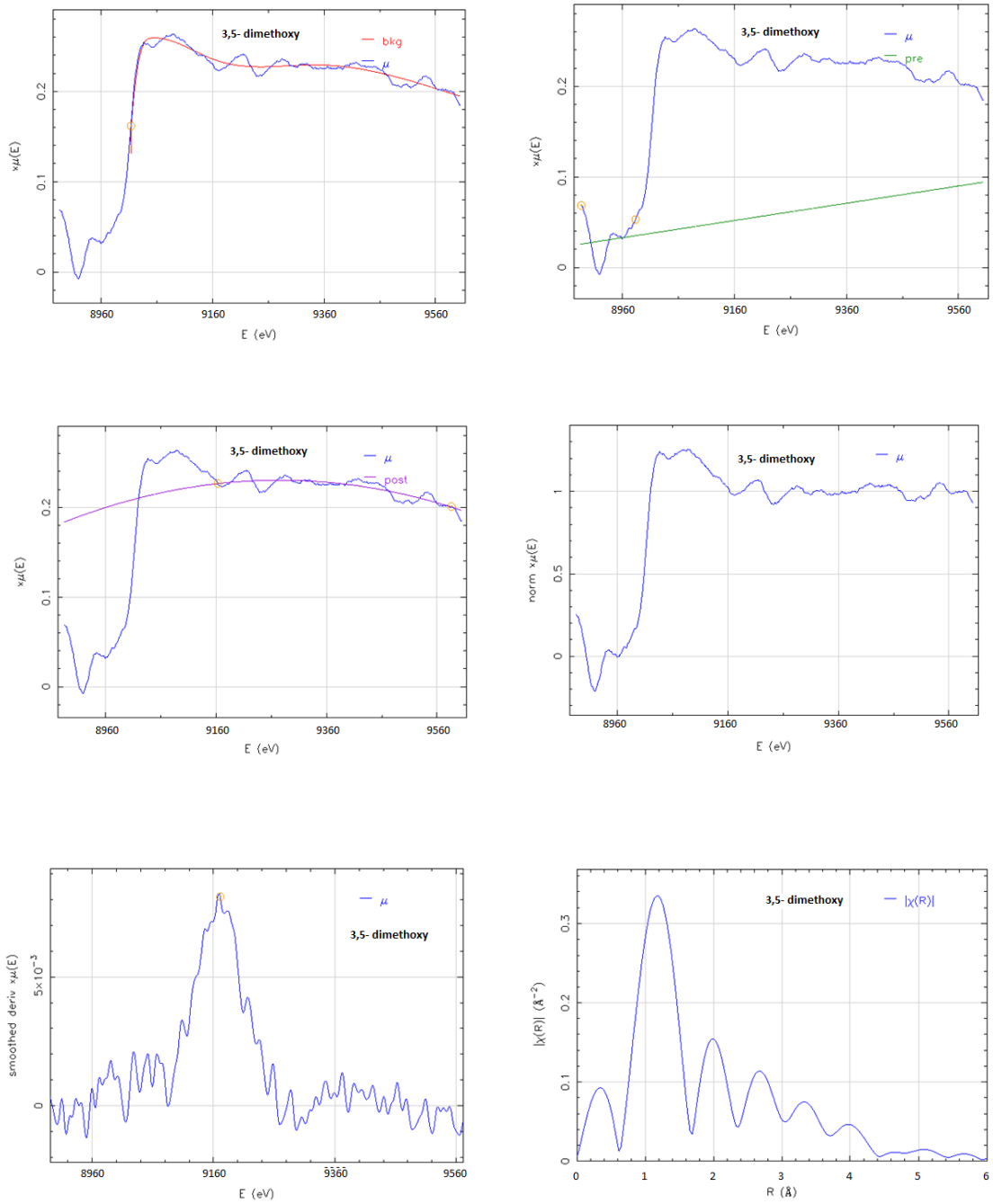


Figure-1 EXAFS curve of 2,5-dimethoxy



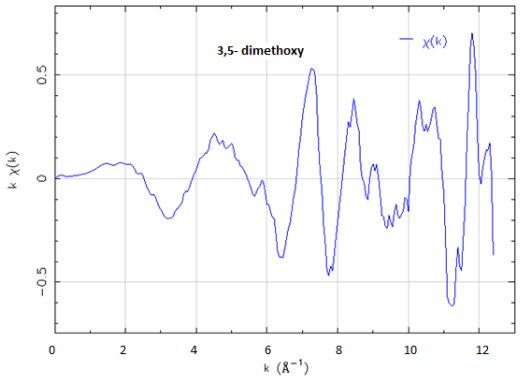
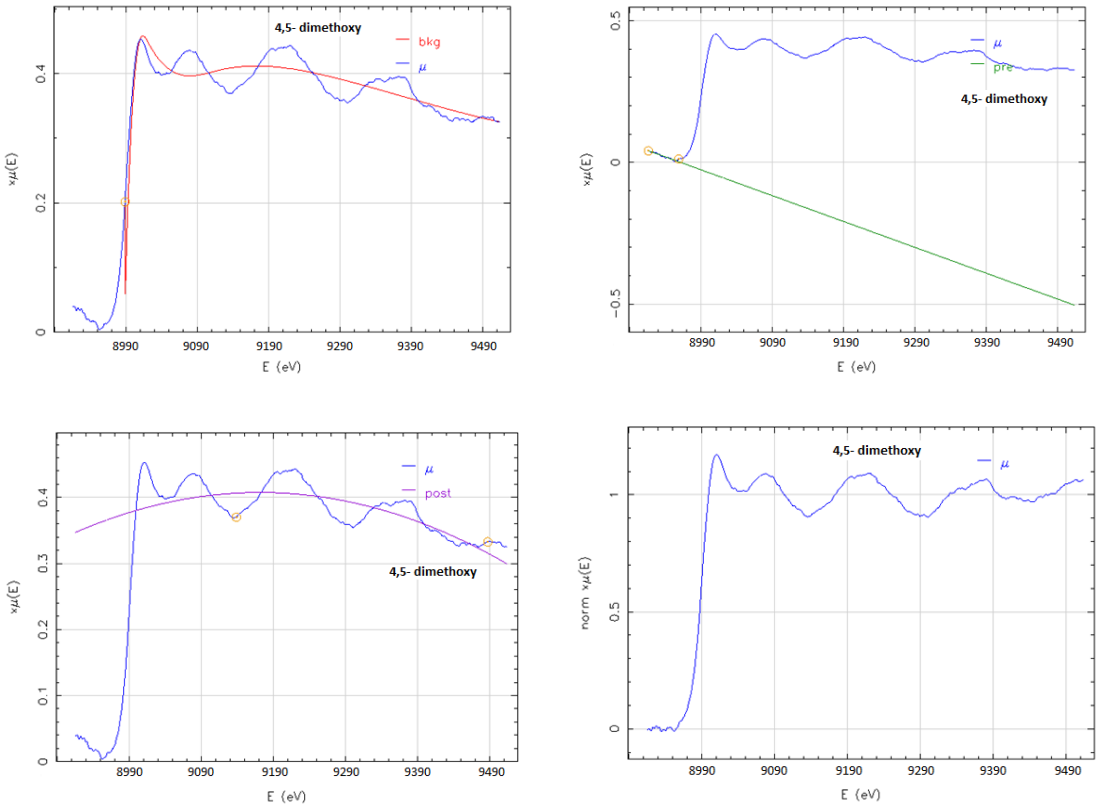


Figure-2 EXAFS curve of 3,5-dimethoxy



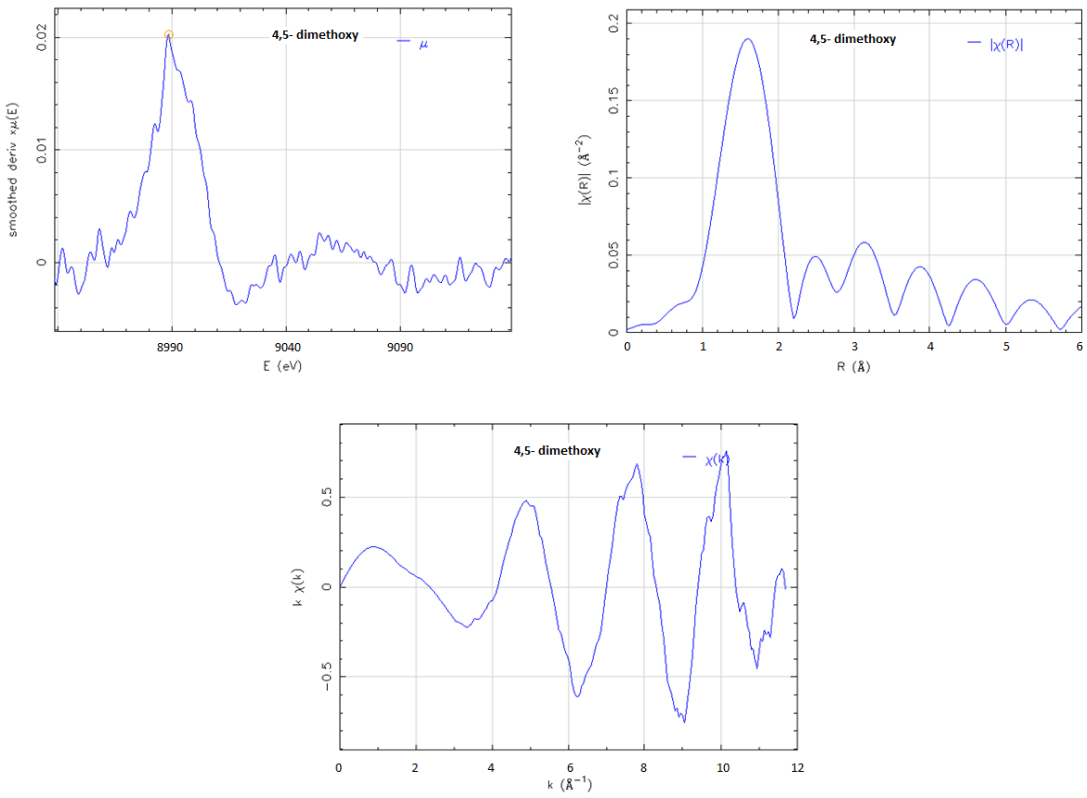


Figure-3 EXAFS curve of 4,5-dimethoxy

IV. CONCLUSION

As is evident from the analysis. that the bond lengths determined are comparable with the bond length obtained by LSS, Levy's and Lytle methods. The experimental values agree well with each other. Complexes described here is in good agreement with physical reality

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