Theoretical Analysis of Bond Lengths 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

Extended absorption fine structure refers to the oscillatory variation of the X-ray absorption as a function of photon energy beyond the absorption edge. The absorption normally expressed in terms of absorption coefficient (μ) [1,2], can be determined from a measurement of the attenuation of X-rays upon their passage through a material. When the X-ray photon energy (E) is tuned to the binding energy of some core level of an atom in the material, an abrupt increase in the absorption coefficient, known as the absorption edge, occurs. For isolated atoms, the absorption coefficient decreases monoatomoically as a function of energy beyond the edge. For atoms either in a molecule or embedded in a condensed phase, the variation of absorption coefficient at energies above the absorption edge displays a fine structure called EXAFS. Such fine structure may extend up to 1000eV above the absorption edge and may have amplitude of up to a few tenths of the edge jump. Although the extended fine structure has been known for long time, its structural content was not fully recognized until the recent work of Stern, Lytle, and Sayers. Synchrotron-based X-ray Absorption Fine-structure Spectroscopy (XAFS) becomes a powerful technique providing analytical as well as structural information, with applications in a wide range of scientific fields because of the rapid development of the data treatment techniques.

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.
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-Chloroquinolin-3-yl) methylene}thiosemicarbezide	C22H16CL2CUN8S2	2-chloroquinolin
2	1-((2-chloro-8-methylquinolin-3-methylene)thiosemicarbazide	C24H20CL2CUN8S2	3-methylene
3	1-((2-chloro-8-methylquinolin-4-methylene)thiosemicarbazide	C24H20CL2CUN8S2	4- methylene

III. RESULT & DISCUSSION

EXAFS analysis

Bond Length Estimation Methods
There are three experimental methods for the EXAFS data analysis

A. Levy's method (Levy, 1965) –

In Levy's method, the bond lengths are calculated by using the relation (1.11): $R_1 = [151/\Delta E]^{1/2}$ Å, where ΔE is the difference in eV [3,4] of the energies of the EXAFS maximum B and minimum β and R_1 is the radius of the first coordination sphere.

B. Lytle's method (Lytle, 1966) –

The energy values (E) of the EXAFS maxima, given in table 5.3, are plotted against the Q values given by Lytle for p symmetry, i.e., Q = 2.04, 6.0, 12.0, and 20.0. The (E, Q) plots have been found to be linear. The slope M of the E versus Q plots have been used to evaluate the radius R_s of equivalent polyhedron, by using the relation $R_s = [37.60 / M]^{1/2}$. The values of R_s calculated with the help of this method are reported in table 2 for all the complexes.
It may be remarked here that Levy's method gives the radius of coordination sphere directly where as Lytle's method does not. In the later method, the interatomic spacing is obtained by multiplying R_s with a factor appropriate to the geometry of the system.

C. L.S.S. method (Lytle et al., 1975) -

In the Lytle, Sayers and Stern's (L.S.S.) method 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 value of $2(R_1 - \alpha_1) / \pi$ where R_1 is the bond length .The parameter α_1 depends to a large extent on the central absorbing atom [8]. It is found that for chemically similar system, the values of α_1 remains more or less the same.
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
$(1/2+n)\pi=2k\ (R_1- \alpha_1)+2\ \beta_1- \pi$

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-chloroquinolin	2.1	2	1.9
2	3-methylene	1.8	1.8	1.6
3	4-methylene	1.8	1.7	1.8

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

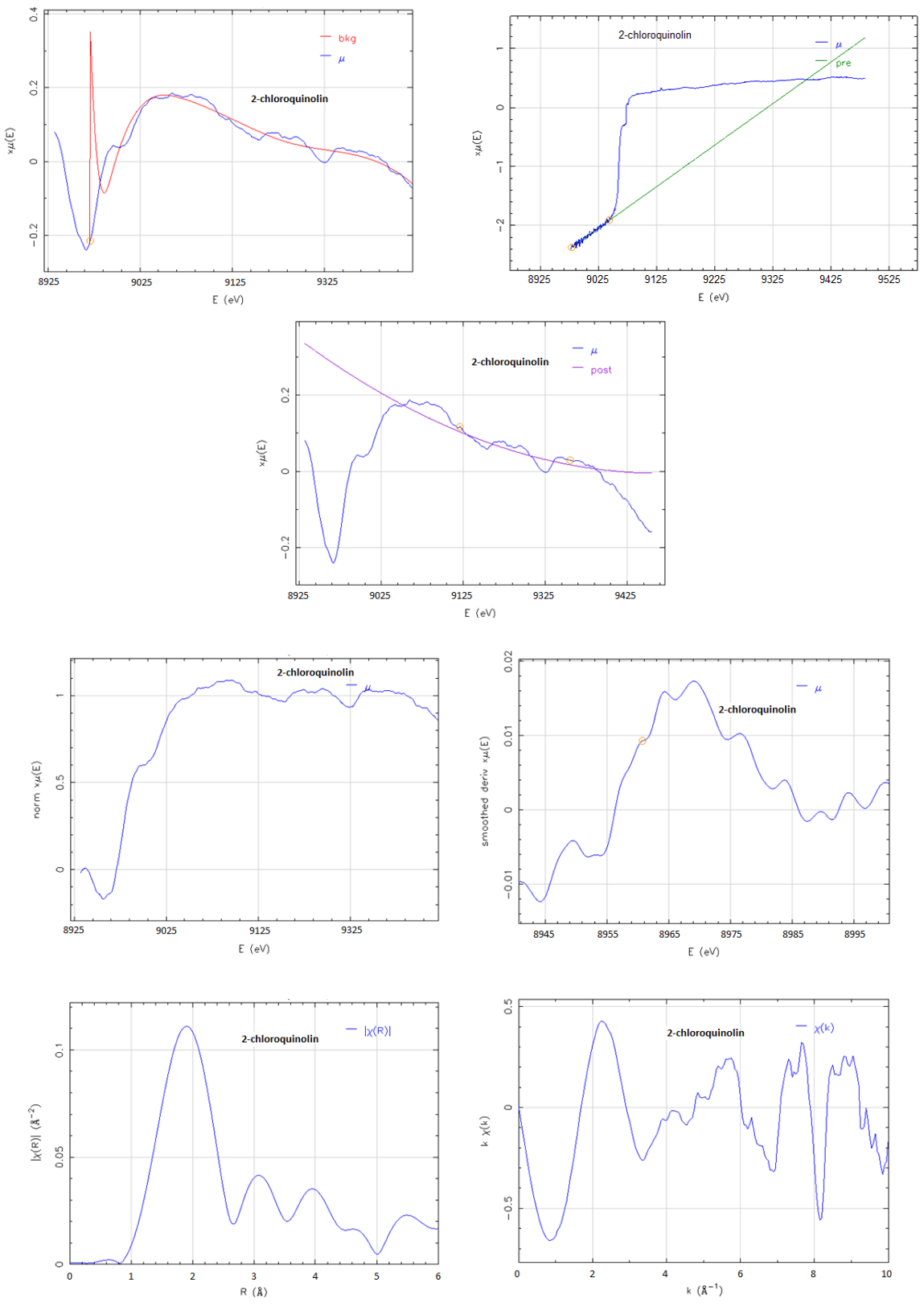

Figure-1 EXAFS curve of 2-chloroquinolin

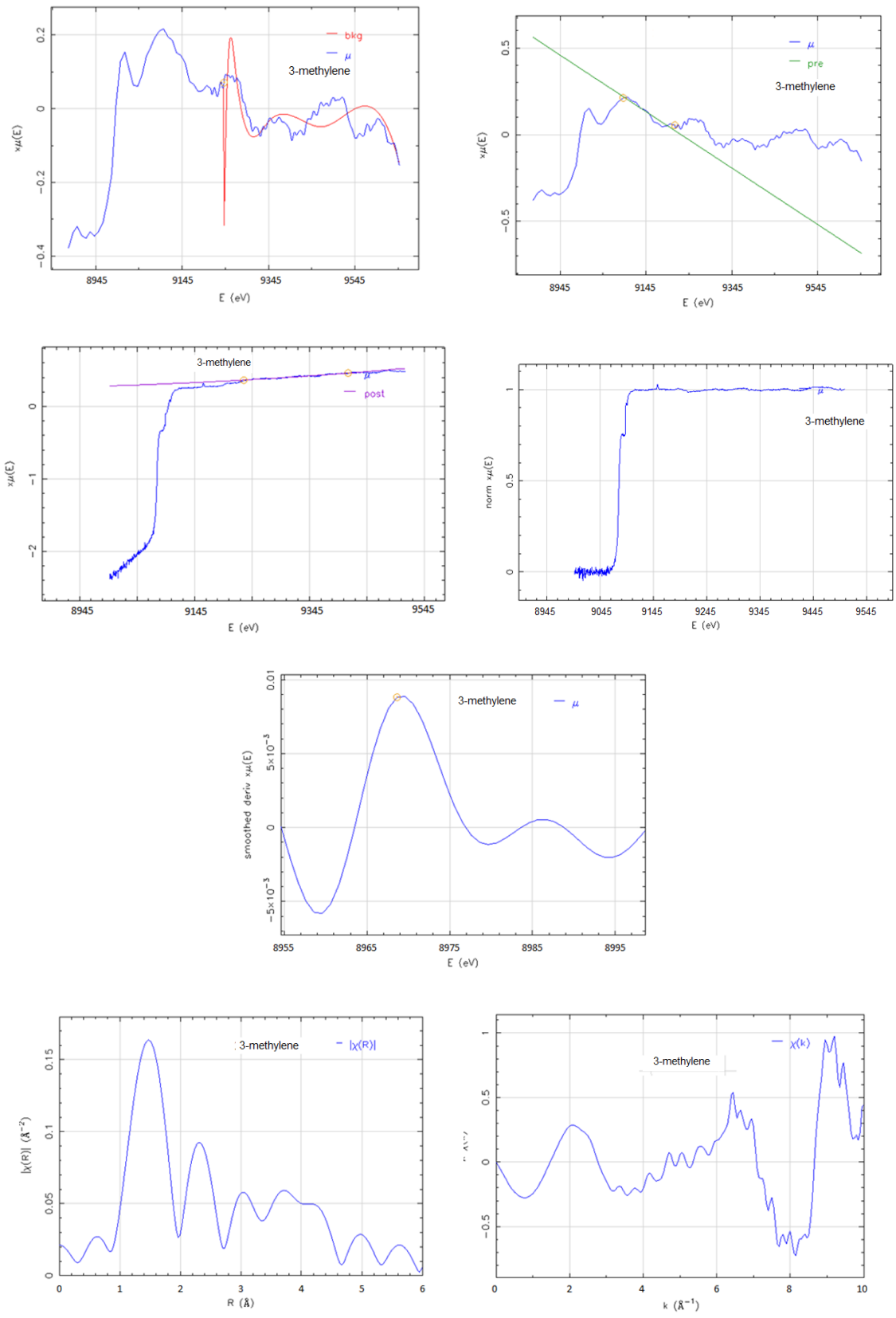

Figure-2 EXAFS curve of 3-methylene

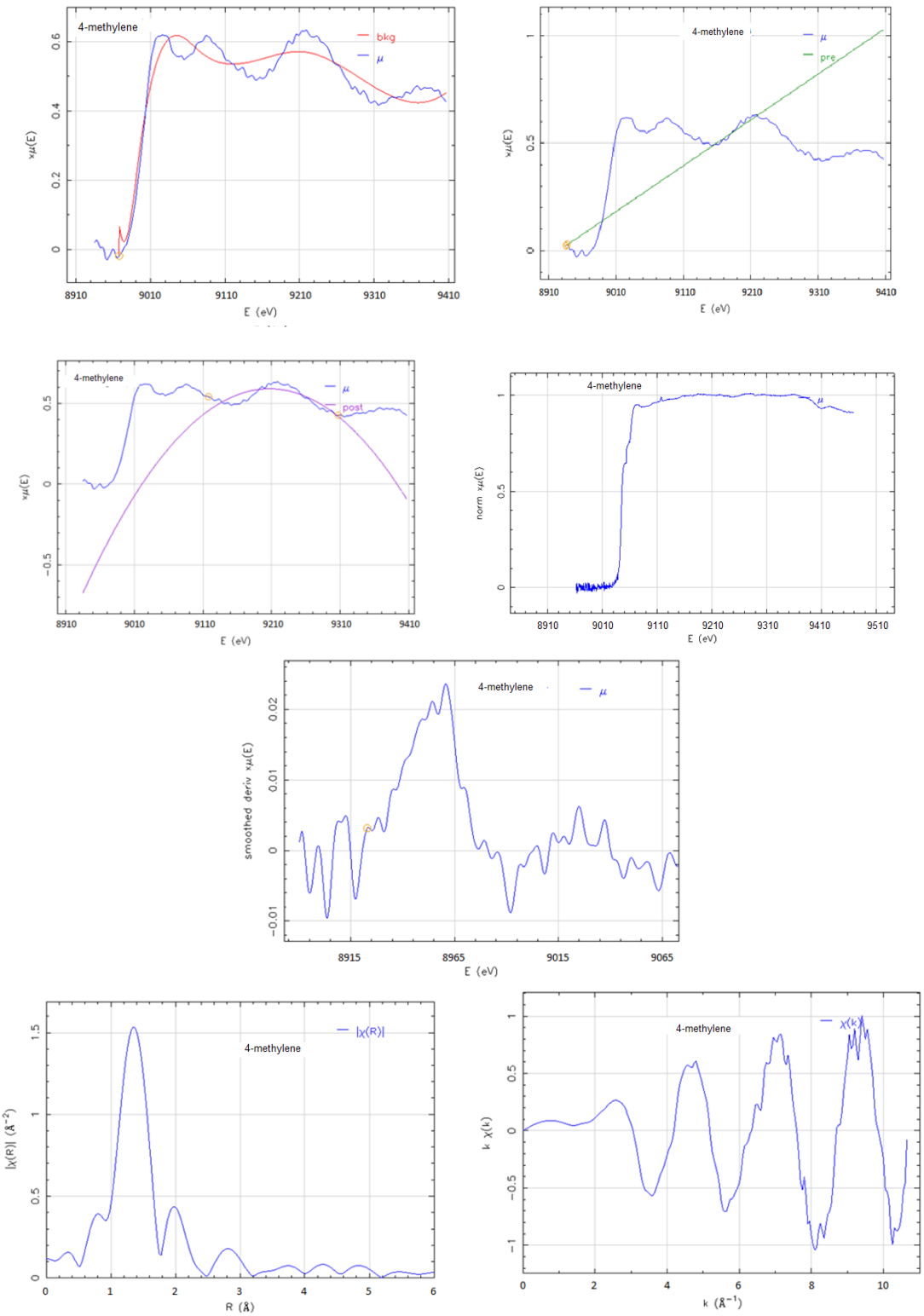

Figure-3 EXAFS curve of 4-methylene

IV. CONCLUSION

The bond lengths determined are comparable. The experimental values agree well with each other. Complexes described here is in good agreement with physical reality

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