

# XANES Parameters Studies of Copper [Cu(II)] Complexes of Schiff Bases Ligand

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**Abstract-** The present paper deals with the synthesis of complexes of Cu (II) of schiff bases by chemical root method. The synthesized metal complexes were characterized by the synchrotron radiation source and X-ray K-absorption parameters such as Chemical shift, Edge Width, Percentage Covalency, Effective charge, Shift of Principal absorption maxima are determined.

**Keywords –** XANES, Chemical shift, Edge Width, Percentage Co valency, Effective charge etc.

## I. INTRODUCTION

The nature of the electronic structure and bonding in transition metal compounds is matter of intrinsic interest. High-energy spectroscopic are well suited to provide information on these points. Among them, X-ray absorption spectroscopy (XAS) has been revealed to be a potential tool for determining the electronic and geometrical structure of complex compounds. In particular, K edge and XANES spectra of transition metal complexes have been the topic of several studies. The position and shape of X-ray absorption discontinuities have been used to deduce structural and chemical bonding information on transition metal complexes. The K-absorption spectra were recorded on the synchrotron radiation, i.e., on beam line BL-8 at RRCAT, Indore .

## II. PROPOSED ALGORITHM

A. *synthesis of the complexes .*

B. physicochemical investigation: methods used synchrotron radiation source and X-ray K-absorption.

## III. RESULTS AND DISCUSSION

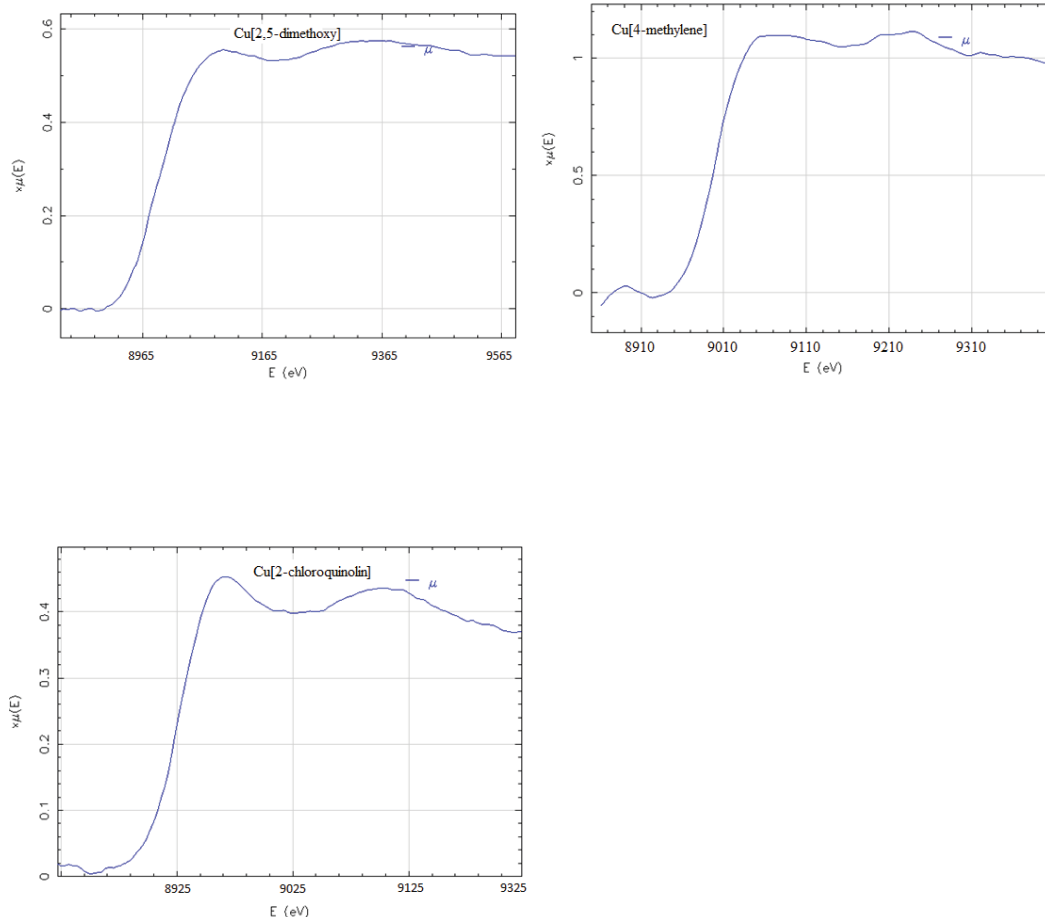
A. *Synthesis of the complexes :*

Reported complexes are synthesized by chemical root methods.

Table :1 Name of the reported compounds:

S. No.	NAME	MOLECULAR FORMULA	ABBREVIATION
1	Cu[(2,5-dimethoxy-2-nitrobenzylidene)]thiosemicarbazide	C <sub>20</sub> H <sub>22</sub> Cl <sub>2</sub> CuN <sub>8</sub> O <sub>8</sub> S <sub>2</sub>	Cu[2,5-dimethoxy]
2	Cu[ (2-Chloroquinolin-3-yl) Methylene]thiosemicarbazide	C <sub>22</sub> H <sub>16</sub> Cl <sub>2</sub> CuN <sub>8</sub> S <sub>2</sub>	Cu[2-chloroquinolin]
3	Cu[ (2-chloro-8-methylquinolin-3-methylene)]thiosemicarbazide	C <sub>24</sub> H <sub>20</sub> Cl <sub>2</sub> CuN <sub>8</sub> S <sub>2</sub>	Cu[3-methylene]

Figures: 1 shown below are XANES characteristics of the synthesized compounds:



#### B. physicochemical investigation:

- *Chemical Shift*

When an atom irradiated by an energetic beam of particles or photons, an electron from an inner shell can be expelled. When an electron from an outer electronic shell fills the vacancy, it is called characteristic X-ray radiation can be emitted. The energy of the radiation depends on the energy levels of the atom. If continuous X-rays irradiate an atom, then the radiation can be absorbed. If the radiation can be absorbed, the energy of the incoming photon is sufficient to ionize the atom or to excite the inner electron to an unoccupied level. This gives rise to an absorption edge in the spectrum for each inner level. The position of the absorption edge gives information about the electron binding energy, i.e., the energy needed to remove the electron from the atom. For several decades, X-ray spectroscopy was the main source of information regarding the atomic structure.

Chemical shift of X-ray K-absorption edges of complexes and compounds, which are shift of high energy of K-edge, are affected by two factors.

I. The tighter binding of the core level because of the change of the effective charge (or screening) of the nucleolus caused by the participation of the valance electron in the chemical bond formation and

II. The appearance of the energy gap going from metal to compound, which is related to phenomenon such as covalence, effective charge, coordination number, crystal structure etc. When bonding takes place, the shift in the X-ray absorption edge energy provides valuable information [1, 2] on changes that occurs in the conduction band.

The shift due to chemical combination is on the high-energy side following Agrawal and Verma's rule. [3,4]. Here copper complexes have showed different chemical shift. In complexes also where copper metal is present in the same oxidation state but bound to the different ligands, the magnitudes of the observed shifts are different. The

edge shifts depends on the magnitude of the final levels involved in the formation of chemical bonds and is mainly responsible for the observed chemical shifts. The chemical shift [5-9] and XAS studies [10-11] have been utilized to obtain important chemical information regarding the coordination in the complexes belonging to transitional metals. The edge shift  $\Delta E_K$  (known as chemical shift) is defined as follows

$$\Delta E = E_{K(\text{compound})} - E_{K(\text{metal})}$$

The position of the X-ray K absorption edge depends on the valence of the absorbing ion. But valence state is not the only factor that governs the magnitude of the chemical shift. At least four factors that must be considered to explain the chemical shift values in metal complexes as valence state, the effective charge on the central metal ion [26,27], Stereochemistry and ionic bonding. Chemical shift is towards the higher energy side of the metal edge this trend is similar to the results in earlier compounds [6-9] and it increases progressively with increases in the valence cation, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of metal-ligand bonding. When the ligand is attached to the metal, the complex is formed and the chemical shift is higher and positive on all the metal complexes. Herein, the present study one observed the chemical shifts are positive and lay in the range 5.5 to 11.4eV for copper complexes, The order of the chemical shift of the K edge (difference of metal K-edge and the corresponding K-edge of the complex) of copper complex as show that the complex( [Cu(3,5-dimethoxy)] having larger value of chemical shift as compared to other studied complexes. It is well known that the edge shift is proportional to the ionicity, therefore large chemical shift indicating that complexes are more ionic in nature. The values of chemical shift of all the copper complexes show the ionic character. Also here in, the positive shift in the absorption energies could be explained by an increase in the highest unoccupied d level due to an increase in the ligand field splitting. It is clear indicates that the positive shifts in the  $1s \rightarrow 3d$  transition peaks are systematically correlated to the increase in the ligand field splitting. The binding energy of the electron at core levels could depend on the ligands. From the above discussion, it has been concluded that the ligand field change is a primary factor in determining the chemical shifts. The positive shift is attributed to an increase in the ligand field splitting. It should be noted that the present conclusion is consistent with results obtained by the group of coworkers [6-9]. They observed a positive shift in the  $1s \rightarrow 3d$  peaks due to a ligand field change. Since the outermost atomic orbital directly participates in chemical bonding and is modified considerably in the condensed phase, these spectra would be very informative for identifying the structure, electronic state and bonding of Cu (II) in unknown materials. Note that there is a significant edge feature near the pre edge peak in the Cu K edge spectra. Finally the chemical shift concept obtained should be useful for an improved understanding of X-ray absorption spectra. The role of various bonds attached to the central atom copper ion is prominent in determining the overall chemical shift in metal complexes. Further not only ligations of particular type Cu-O is responsible in imparting ionic or covalent character to the complexes, but their planer/axial positions also contributes to the ionic or covalent character. The values reported here reveal that the copper complexes are ionic in nature.. The sample is octahedral. Larger chemical shift value in this case suggests larger effective charge of the central metal ion resulting due to the change in geometry. The positive shifts are attributed to an increase in the unoccupied level of the ligand field, which is due to an increase in the ligand field splitting. It should be noted that the present explanation is consistent with results by the group of Shivastava et al, who observed a positive shift in the  $1s \rightarrow 3d$  and  $2p \rightarrow 3d$  peaks due to a ligand field change. Additionally, it appears that the pre-edge features ( $1s \rightarrow 3d$  peaks) varies in both position and intensity as a function of the ligand field strength. As the ligand field strength increases, the intensity of the pre-edge peak decreases and the peak position shift to higher energy. Since the outermost atomic orbital directly participates in chemical bonding and is modified considerably in the condensed phase, these spectra would be very informative for identifying the structure, electronic state and bonding of copper metal in unknown materials.

- *Shift of Principal absorption maximum*

The shift of the principal absorption maximum depends upon the type of overlap between metal and the ligand orbitals. Greater the overlap of metal d orbitals, the more stable are bonding molecular orbitals. Since transition of principal absorption maximum occurs from  $1s$  to the unoccupied orbitals ( $1s \rightarrow T_{1u}$ ) in octahedral complexes the principal absorption maximum shifts to the higher energy. Our value of shift of A in Table 3.1 in case

of copper complexes they are ranging from 24 to 38 eV. The principal absorption maximum (A) for octahedral complexes of 3d transition metals is assigned to the  $(1s \rightarrow T(\sigma, \pi))$  transition. In general, the greater the overlap of metal and ligand orbitals, the greater is the strength of the bond. Since strengthening of the Metal-Ligand bond would lead to a greater stabilization of antibonding MOs, and a corresponding destabilization of bonding MOs, the shift in the principal absorption maximum towards the high energy side values with increasing Metal-Ligand bond strength would be expected. It has been argued that a more oxidized metal forms a stronger bond with the ligand-giving rise to more stable bonding orbitals. These antibonding orbitals are, however, raised in energy due to stronger repulsive forces and hence the principal absorption maximum shifts towards the high-energy side with increasing M-L, bond strength would be expected. On the higher energy side of the K-edge, there appears a pronounced absorption peak and this is referred to as the principal absorption maximum. The shift of the principal absorption maximum in a complex can be defined as the energy difference between the principal absorption maximum ( $E_A$ ) and the corresponding energy of the metal edge  $E_K$  this parameter is sensitive to metal ion. The shift of main peak towards high energy side with increase in oxidation states has been explained. In terms of a similar shift of unoccupied  $4p^*$  (antibonding) orbitals. It has been argued that a more oxidized metal forms a stronger bond with the ligand giving rise to more stable bonding orbitals. These antibonding orbitals are however, raised in energy due to stronger repulsive forces, and hence, the principal absorption maximum shifts towards the high-energy side. The shift of principal absorption maximum for Cu (II) complexes shows less value. From this, it can be inferred that the copper complex show more ionic character. Structure of the K-absorption edge of transition metals in variety of solids has been investigated. Based on these studies, a criterion of coordination symmetry was suggested. It has been reported that the low energy absorption occurs predominantly in the complex having tetrahedral or low symmetry, and no such absorption is noticed in octahedral complexes. None of our complexes under investigation shows any splitting of the K-absorption edge, indicating octahedral geometry. Earlier X-ray absorption spectroscopic studies on transition metals have also been yielded useful information.

- *Edge Width*

The edge width of the K-absorption edges increase with the increase in covalent character of the bonds provided other factors like molecular geometry etc remain the same. The values of edge width reported here for copper complexes, indicative of the octahedral structure. This can also be confirmed when there is no splitting of the main edge in the complexes (Figure 1).

- *Effective charge and Chemical Shift*

The X-ray K absorption process involves the ionization of 1s electrons. The energies of inner shell electrons of an atom are often shifted by a small extent due to the change in chemical or crystallographic environment of the atom. This is experimentally observed as the 'chemical shift' of absorption edge of the atom in compounds. Gianturco and Coulson showed in different complexes how the chemical shift is related to the effective charge (EC). Later, Sapre and Mande explained the observed shift on the basis of effective charge calculated from Suchet's empirical formula. It is to be noted that X-ray absorption spectroscopy can also be used to determine the EC on atoms. In this approach Hartree-Fock (H-F) 1s electron energies in different oxidation states of an atom are used and graph is plotted between the theoretical chemical shift and oxidation number for copper. The effective charge on the copper atom in different complexes are then determined from this plot. The data recorded indicate that EC on copper in its complexes varies between 0.68 to 1.1 electrons/atom. The perusal reveals that the formal oxidation number of copper in these complexes is changed due to chemical combination, to counter the effect of  $\sigma$  bonding. Mande and Kondawar showed chemical shift to be directly proportional to the effective charge on the absorbing atom. Justification of the linear fit of chemical shift with EC were also given by Siegbahn and Carver *et al.* According to these researchers, the difference ion potential felt by an electron in the valence level in a compound and the reference metal was proportional to EC. They assumed this difference in potential itself to be the difference in energy of the valence levels. In figure 2, the graph plotted against effective charge and the experimental chemical shift of the complexes studied.

By knowing effective charge, one estimated different parameters. These Table shows that the percentage covalency in metal ligand bonding increase with decrease with effective charge. It is revealed from the graph that shift decrease with increasing covalency. These supporting the empirical rule. The graph plotted between EC and chemical shift for copper complexes shows a linear relationship, which provides a linear regression analysis. The

results, shows that chemical shift increases then EC also increases. It is clearly seen that the copper(II) complexes are ionic .

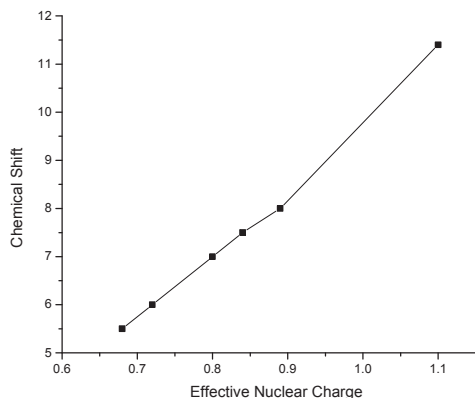


Fig. 2 Correlation between chemical shift and ENC.

- *Percentage Covalency and Chemical Shift*

The chemical shift is also treated as a measure of covalency. The chemical shift is governed by covalent character of the bond [3] as the chemical shift goes on increasing, it has been found that this causes a decrease in the covalency. A theoretical graph is plotted between the calculated value of binding energy of 1s electron using Clementi's results of atomic function and percentage covalency for copper and cobalt. This graph is used to calculate the percentage covalency of the bonds. The percentage covalency of metal-ligand bonding in copper complexes is the range 22 to 65 and they are reported in Table 3.2. A graph plotted between percentage covalency and a value of chemical shift of copper complexes (figure 3). This graph shows that the chemical shift decreases as the percentage covalency increases. Finally, the reported values and the plots as mentioned above are also confirmed by plotting the graphs. between percentage covalency and EC for copper complexes. This graph shows that the percentage covalency increases as effective charge decreases.

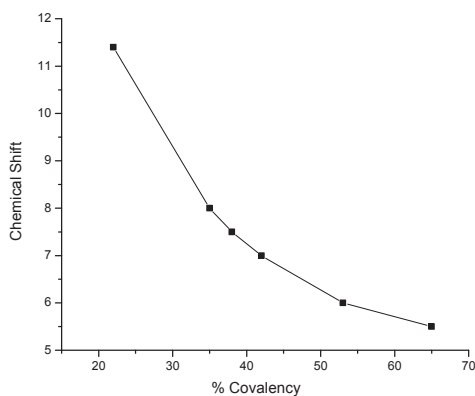


Figure 3 Correlation between % Covalency Chemical shift for copper (II) complexes

Table :2

Name of the Complex	Edge Position $E_K$ (eV)	Chemical Shift $\Delta E_K$ $\sim(\pm 0.2)$	Shift principal absorption maximam (eV)	Edge Width (eV)	EC electron/ atom	% covalency
2,5-dimethoxy	8987.5	7.5	27	19.5	0.84	38
2-chloroquinolin	8985.6	5.5	24	19	0.68	65
3-methylene	8987	7	29	32	0.80	42

#### IV.CONCLUSION

X-ray K-absorption near edge studies of six copper complexes suggests that the chemical shifts values are on the higher energy side. The values reported for copper complexes confirm that these complexes are ionic in nature. The edge width values are found to be on the high energy side. There is no splitting on the main edges of the complexes. These factors suggest the geometrical structure of the complexes to be octahedral. The other important result obtained is that the effective charge is correlated with percentage covalency and chemical shift.

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