Study of XANES Parameters 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 X-ray absorption Near Edge Structure (XANES). The X-ray absorption spectroscopy is a very strong informative experimental approach to study the coordination geometry and bonding relation in metal compounds. The near edge feature involves the transition from some core state to allowed lowest unoccupied empty states in the valance region of a given atomic center.

Keywords – XANES, Chemical Sheift, Shift Of Principal Absorption Maximum, Edge Width

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 beamline BL-8 at RRCAT, Indore .

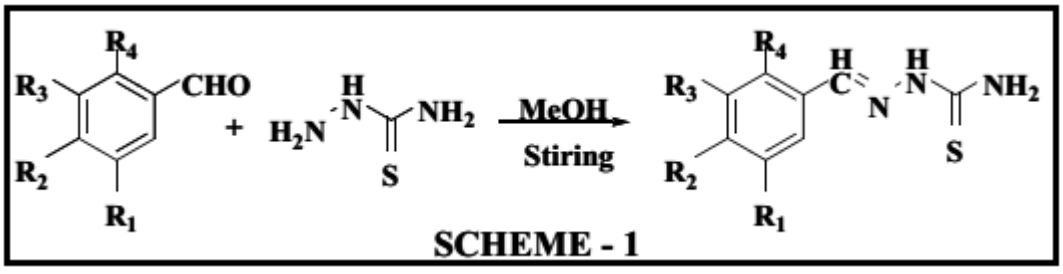
II. PROPOSED ALGORITHM

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) 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.



SCHEME - 1

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 vacuum.

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

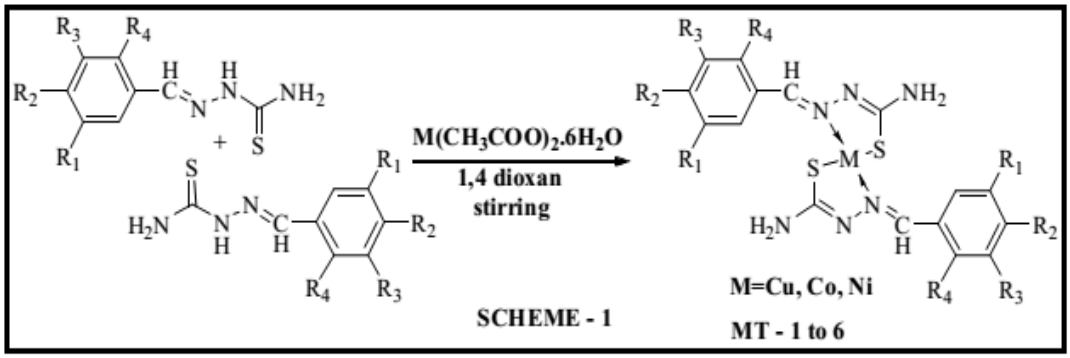


Table – 1 copper(II) complexes with name ,mol. Formulae and abbreviations.

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

A. 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 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.

1. 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
2. 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 were copper metal is present in the same oxidation state but bound to the different ligands, the magnitudes of the observed shifts are different.

B. 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-2 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

The order of the shift of principle absorption maximum in the studied copper complexes is as follows:
3,5-dimethoxy > 4,5–dimethoxy > 2,5-dimethoxy

C. 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 experimental data of edge-widths of copper complexes are given in Table-2 These values are indicating the ionic in nature, looking the values of edge width of the complexes, it is observed that the complex. 3,5 dimethoxy is more ionic compared to others.

Table-2 X-ray absorption near edge parameters copper (II) complexes.

Name of the Complex	Edge Position E_K (eV)	Chemical Shift ΔE_K ~(±0.2)	Shift principal absorption maximum (eV)	Edge Width (eV)
2,5-dimethoxy	**8987.5**	**7.5**	**27**	**19.5**
3,5-dimethoxy	**8991.4**	**11.4**	**38**	**27**
4,5-dimethoxy	**8988**	**8**	**30**	**22**

Energy of copper absorption edge (E_K) present study= 8980 eV [30]

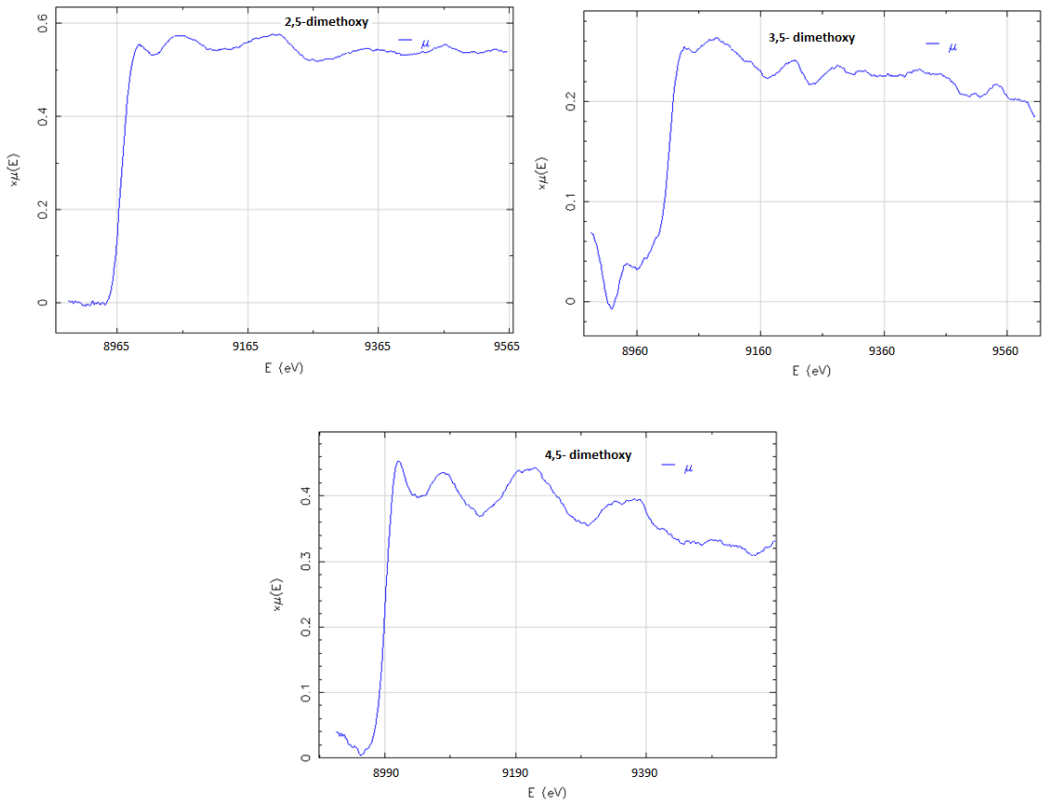


Figure-1 The profile of the K-absorption discontinuity of copper (II) Complexes

IV. CONCLUSION

X-ray K-absorption near edge studies of five 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.

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