Analysis of Chemical Shift, Shift of Principal Absorption Maxima, Edge Width, Percentage of Covalency of Cu(II) Complexes

A Mishra[a)], S. Mishra and R. Bhatt

School of physics, Devi Ahilya University, Khandwa Road, Indore 452001
[a)]Email: amishra1960@yahoo.co.in

Abstract: The present paper deals with the synthesis of transition metal Schiff base complexes of copper by chemical root method. 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 . Complexes of Cu(II) complexes with thiosemicarbezide as legand have been taken in to consideration and analysis of chemical shift, shift of principal absorption maxima, edge width, percentage of covalency were done.

INTRODUCTION

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

Table 1: Series of Copper (II) Complexes thiosemicarbezide as Ligand.

S. No.	Name of Ligand	Abbreviation	Mol. Formula
1	Cu[(2-Chloroquinolin-3-yl) Methylene]thiosemicarbezide	$C_{22}H_{16}Cl_2CuN_8S_2$	Cu[2-chloroquinolin]
2	Cu[(2-chloro-8-methylquinolin-3-methylene)]thiosemicarbazide	$C_{24}H_{20}Cl_2CuN_8S_2$	Cu[3-methylene]
3	Cu[(2-chloro-8-methylquinolin-4-methylene)]thiosemicarbazide	$C_{24}H_{20}Cl_2CuN_8S_2$	Cu[4- methylene]

RESULT & DISCUSSION

Chemical shift

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.

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

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 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. 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.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 and XAS studies have been utilized to obtain important chemical information regarding the coordination in the complexes belonging to transitional metals. The edge shift ΔE_K (known as chemical shift) is defined as follows

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

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, Stereochemistry and ionic bonding.

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.

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 3.2. These values are indicating the ionic in nature.

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 [16] 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.

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 maxima m (eV)	Edge Width (eV)	EC electron/ atom
$C_{22}H_{16}Cl_2CuN_8S_2$	8987.5	7.5	27	19.5	0.84
$C_{24}H_{20}Cl_2CuN_8S_2$	8991.4	11.4	38	27	1.10
$C_{24}H_{20}Cl_2CuN_8S_2$	8988	8	30	22	0.89

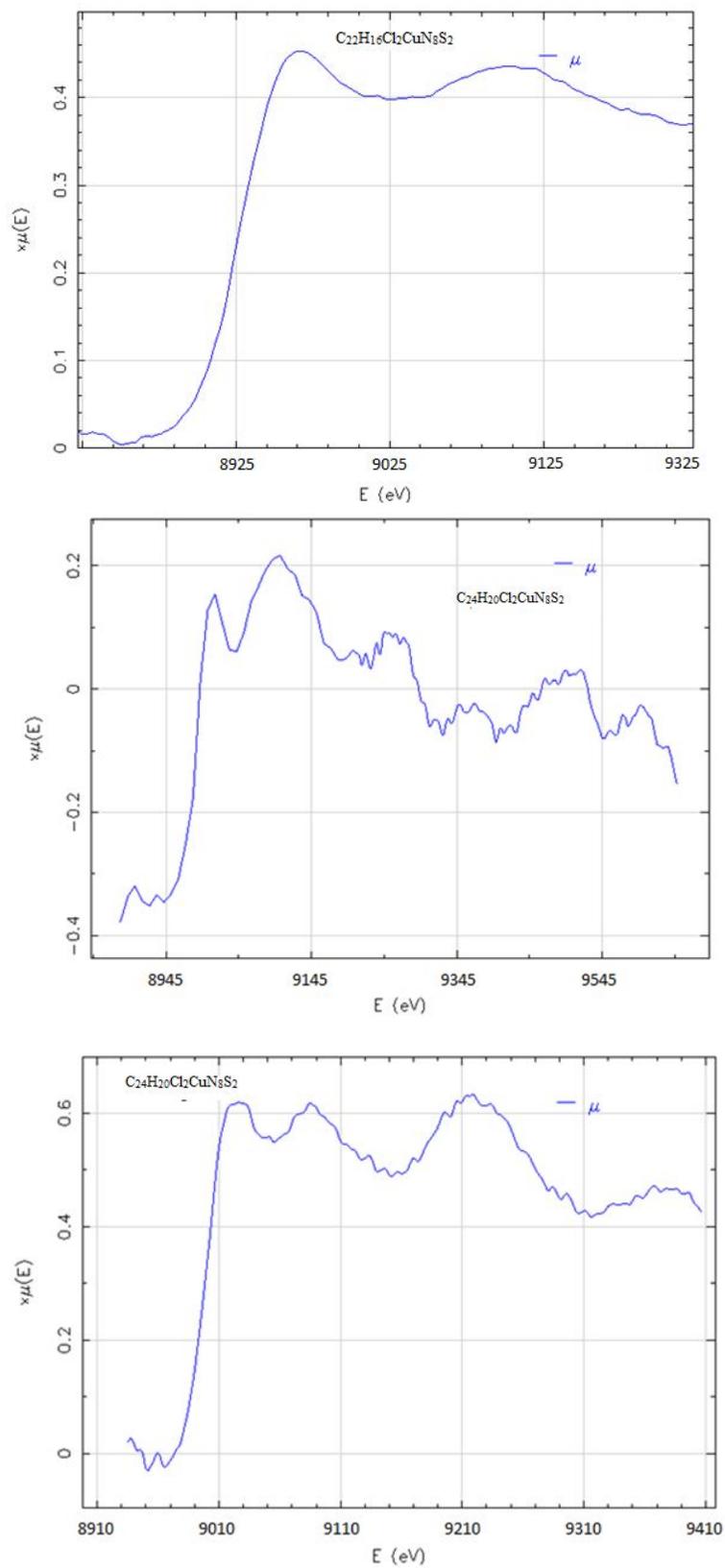Energy of copper absorption edge (E_K) present study= 8980 eV [30]

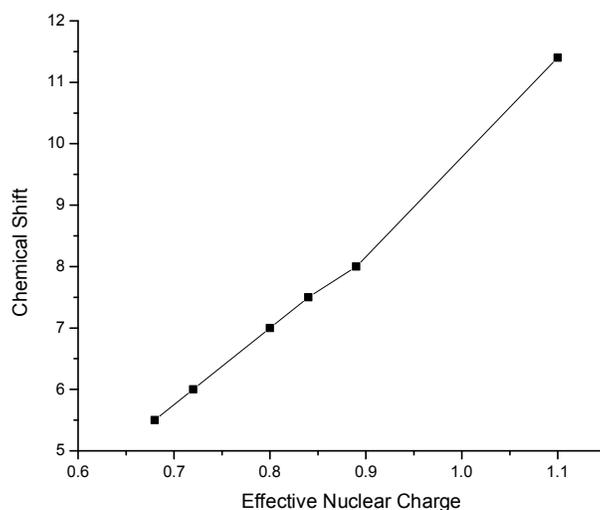**Figure 1** The profile of the K-absorption discontinuity of six copper (II) Complexes

Figure 2. Correlation between chemical shift and ENC.

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