Analysis of percentage of covalence, Effective charge and chemical shift of Copper (II) Complexes

Dr. S. Mishra

Department of Engg. Physics
Shri Vaishnav Institute of Tech. & Sc., Indore, M..P., India

Abstract - The present paper deals with the synthesis of transition metal schiff base complexes of copper (II) by chemical root method. 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 .

Keywords – Percentage Covalency, Effective charge, Chemical Sheift.

I. INTRODUCTION

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. XANES reveal to identify the allowed transitions and also the mixing or splitting of the final state orbital. [1, 2] Using known structural data, informative deductions on structure-bonding relations have been made. copper K-edge XANES spectra have been used since they probe 1s→3d, 1s→4p transitions respectively. Since the spectra can be influenced by the state of the d orbital, which is primarily responsible for the bonding with ligands. For Cu-containing complexes, Cu K-edge XANES has been widely used to derive information on the electronic and geometrical structure, and some attempts has succeeded in interpreting the absorption features of Cu K-edge XANES spectra.

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.

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

S.NO.	NAME	MOLECULAR FORMULA	ABBREVIATION
1	Cu[(2-Chloroquinolin-3-yl) Methylene]thiosemicarbezide	C22H16Cl2CuN8S2	Cu[2-chloroquinolin]
2	Cu[(2-chloro-8-methylquinolin-3-methylene)]thiosemicarbazide	C24H20Cl2CuN8S2	Cu[3-methylene]
3	Cu[(2-chloro-8-methylquinolin-4-methylene)]thiosemicarbazide	C24H20Cl2CuN8S2	Cu[4- methylene]

III. RESULT & DISCUSSION

A. Chemical Shift –

The shift of the X-ray absorption edge due to chemical combination has been shown to depend primarily on the valency of the element [7;8]. The edge shift in general shows a marked increase with increase in oxidation state. The edge position moves towards high energy side, when the electronegativity of the ligand increases [9]. Stelling observed that in case of sulpher the edge shifted by about 0.46% in going from S^{2-} to S^{+6} complexes [10].

B. 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 [5] showed in different complexes how the chemical shift is related to the effective charge (EC). Later, Sapre and Mande [6] explained the observed shift on the basis of effective charge calculated from Suchet's empirical formula [7]. It is to be noted that X-ray absorption spectroscopy can also be used to determine the EC on atoms [8, 9] .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 is different complexes are then determined from this plot. [10, 11] The data are presented in Table-2 indicating that EC on copper in its complexes varies between 0.84 to 1.1 electrons/atom. The perusal of Table-2 reveals that the formal oxidation number of copper in these complexes is changed due to chemical combination. to counter the effect of σ 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 [12] and Carver et al. [13] 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-1, the graph plotted against effective charge and the experimental chemical shift of the all six copper 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 reggration analysis. The results, shows that chemical shift increases then EC also increases. It is clearly seen that the copper complexes is ionic .
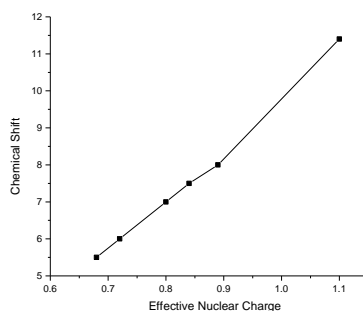

Figure-1 Correlation between chemical shift and ENC.

C. 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 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. 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 42 to 65 and they are reported in Table-2. A graph plotted between percentage covalency and a value of chemical shift of copper complexes (Figure 2). 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.
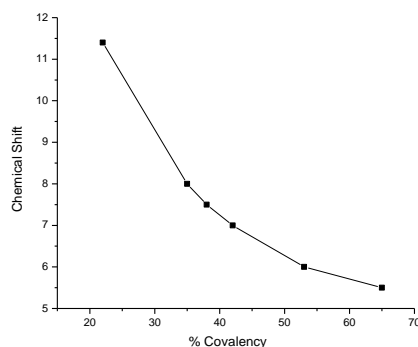

Figure-2 Correlation between % Covalency

Chemical shift for copper (II) complexes

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)	EC electron/atom	% covalency
Cu[2-chloroquinolin]	8985.6	5.5	0.68	65
Cu[3-methylene]	8987	7	0.80	42
Cu[4- methylene]	8986	6	0.72	53

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

IV. CONCLUSION

X-ray K-absorption near edge studies of copper complexes suggests that chemical shift increases then EC also increases. It is clearly seen that the copper complexes is ionic.

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