

XANES Study of Copper (II) Mixed Ligand Complexes of alpha-Aminonitrile

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Abstract: X-ray K-absorption near edge spectroscopic studies have been carried out on four copper (II) mixed-ligand complexes. The complexes are: I-[CuCH₃COO(ben)(p-Tol)], II-[CuCH₃COO(ben)(p-Ani)], III-[CuCH₃COO(p-Chloroben)(p-Tol)] and IV-[CuCH₃COO(p-Chloroben)(p-Ani)] in which benzaldehyde and P-chlorobenzaldehyde act as primary ligands while P-toluidine and P-anisidine act as secondary ligands. XANES spectra have been recorded at the K-edge of Cu using the dispersive beam line at 2.5GeV Indus-2 synchrotron radiation source RRCAT (Raja Ramanna Center for Advance Technology), Indore, and India. Various X-ray absorption parameters e.g., chemical shift, edge-width and shift of the principal absorption maximum have been obtained in the present study. These parameters have been utilized to explain the structure of the complexes. The studies establish significant correlation between various parameters for these complexes. XANES data have been analyzed using the computer software Origin 6.0 professional and Athena.

Keywords: XANES, Copper (II) mixed ligand complexes, alpha-Aminonitrile, Origin 6.0, Athena.

I. INTRODUCTION

Because of their application as potential ligands for a large number of metal ions, nitrile and alpha -aminonitrile compounds and their derivatives has received special attention. [1],[2],[3]. By its microbial metabolism in some organisms [4], nitriles and alpha -aminonitrile derivatives had biological activities [5] as herbicides [6], pharmacological agents [7] and biological synthesis of chemical compounds.

To probe the structure of condensed matter on a microscopic scale, many methods have been developed over the past century. X-ray absorption spectroscopy is one of such methods. The X-ray absorption coefficient is measured as a function of X-ray energy in this technique. X-ray absorption near edge structure or XANES is a fine structure, observed in the X-ray absorption coefficient immediately above an X-ray absorption edge and extending up to 50 eV beyond the edge. To obtain information about the molecular structure viz. the oxidation state and the effective nuclear charge of the absorbing atom in compounds and complexes, X-ray absorption spectroscopy has been extensively used. Therefore, to measure the change in the position of the main edge and to calculate the chemical shift, much attention has been paid by different workers [8], [9], [10] on XANES studies of metal complexes. While studying the shift in X-ray absorption spectra of metal complexes, it is observed by different workers [11],[12] that, chemical shift not only depends upon valency but also depends upon coordination number [13], ionocity [14], nature of the chemical bond and effective nuclear charge [15].

All above gave us the motives for XANES characterization of Cu (II) complexes of benzaldehyde and p-Chlorobenzaldehyde by their reaction with p-Toluidine and p-Anisidine.

TABLE I. Copper (II) mixed ligand complexes and molecular formulae

Complex	Abbreviation	Molecular formula
I	CuCH ₃ COO(ben)(p-Tol)	[Cu(C ₁₅ H ₁₄ N ₂)(CH ₃ COO)]
II	CuCH ₃ COO(ben)(p-Ani)	[Cu(C ₁₅ H ₁₄ N ₂ O)(CH ₃ COO)]
III	CuCH ₃ COO(p-Chloroben)(p-Tol)	[Cu(C ₁₅ H ₁₃ N ₂ Cl)(CH ₃ COO)]
IV	CuCH ₃ COO(p-Chloroben)(P-Ani)	[Cu(C ₁₅ H ₁₃ N ₂ OCl)(CH ₃ COO)]

II. EXPERIMENTAL DETAILS

All the complexes were prepared according to the standard method and their purity was checked. All experiments were conducted at room temperature and atmospheric pressure.

The four mixed ligand copper (II) complexes are listed in Table.1 along with their abbreviations and molecular formulae. The X-ray absorption spectra at the K-edge of copper of these complexes have been recorded at BL-8 Dispersive EXAFS beamline at the 2.5-GeV INDUS-2 Synchrotron Source, Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. The various aspects of the calibration and the procedure to be followed on this beamline have been given by Gaur et al [16]. Derivative spectra were used for obtaining the k-edge position. Softwares Origin 6.0 and Athena version 0.8.056 [17] were used for data analysis.

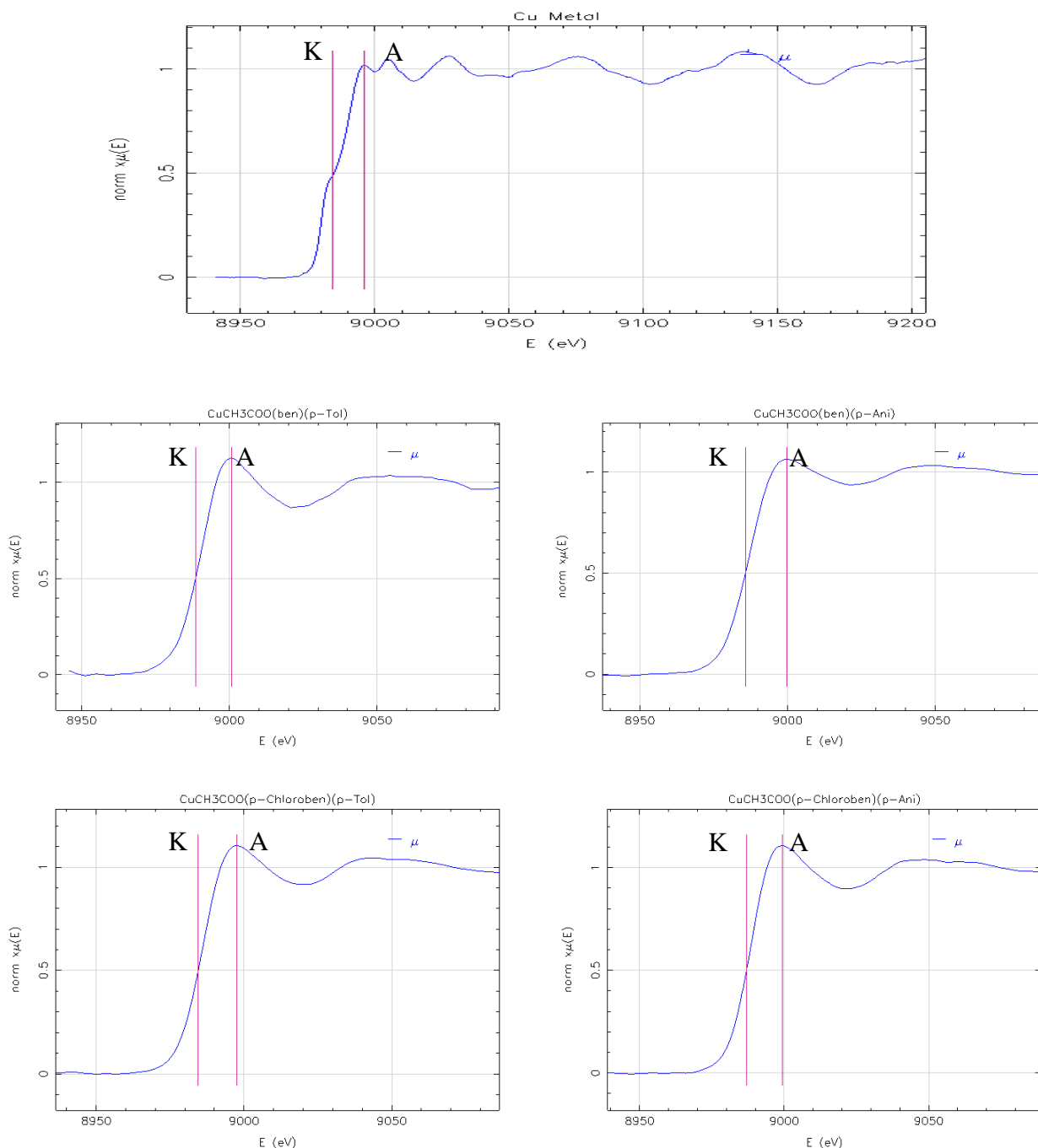


Fig.1. The XANES region of the absorption spectrum at the K-edge of copper metal and in it's complexes indicating positions of the absorption edge K and the principal absorption maxima A

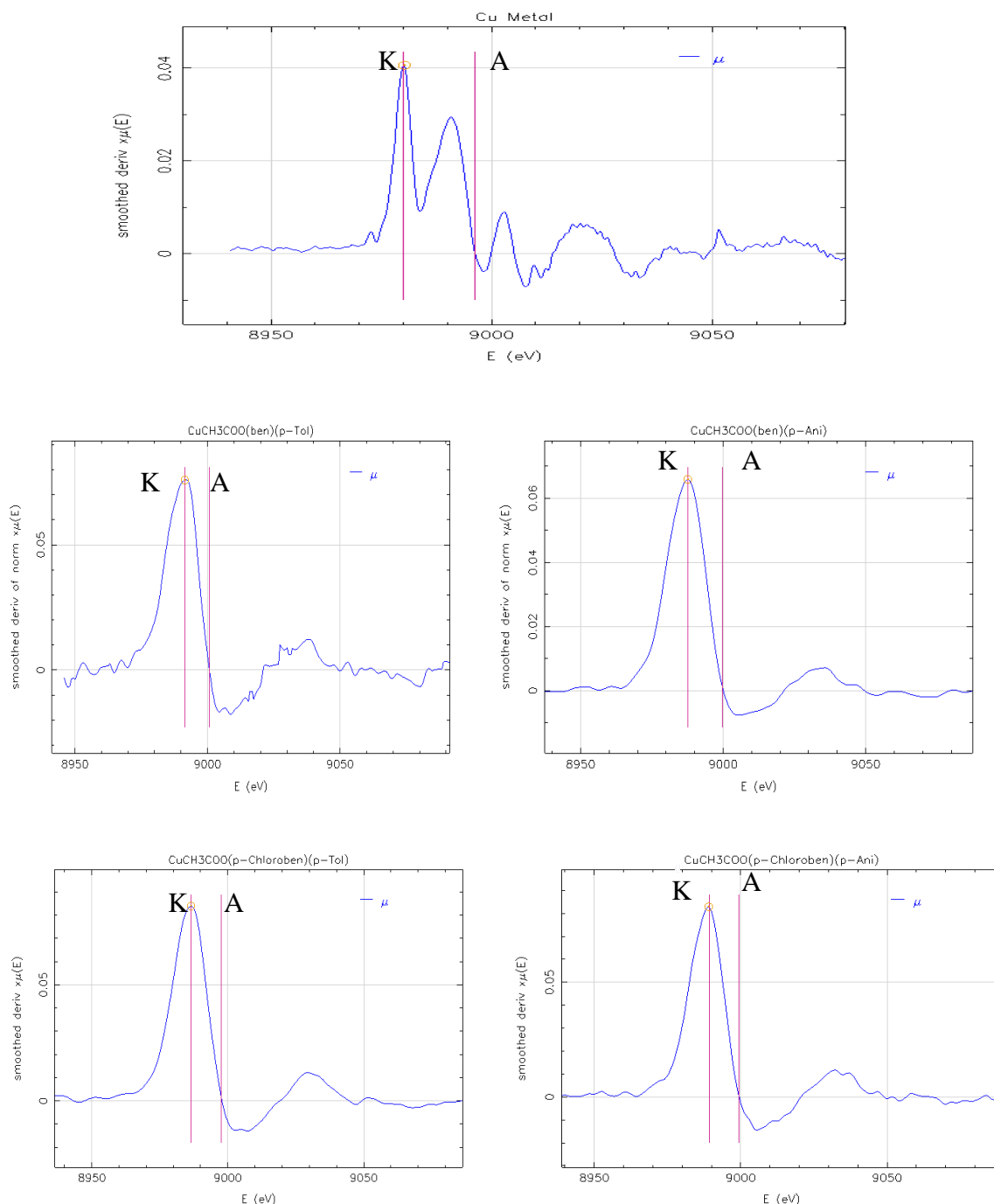


Fig. 2 Derivative of the XANES region of the absorption spectrum at the K-edge of copper in the complexes indicating positions of the absorption edge K and the principal absorption maxima A

III. RESULTS

The shapes of the copper K-edge and the associated near edge structure (XANES) for all the complexes are shown in Fig. 1. The curves in this figure represent the normalized X-ray absorption spectra. The first derivative of the spectra, shown in Fig. 2, indicating positions of the absorption edges K and principal absorption maximum A. The results of the energy of the K absorption edges (E_K) and the energy of principal absorption maximum A (E_A) of copper in metal and its four complexes are presented in Table 2. The chemical shifts (in eV) of the K-absorption edge of copper in the complexes are also given in this Table. For all the complexes, the distances (in eV) of the principal absorption maximum A with respect to the respective K absorption edge have also been computed and are collected in the same table. It can be readily

seen from the table that copper K-edge is found to be shifted towards the higher-energy side in all the four complexes, as compared with the copper metal K-absorption edge.

TABLE 2. XANES data for the K absorption edge of copper in the complexes

Complexes	EK (eV)	EA (eV)	Chemical shift (eV)	Shift of the principal absorption maximum (eV)	Edge-width (EA-EK) (eV)	ENC Electron / atom	% Covalency
Copper metal	8980.12	8996.21	-	-	16.09	-	-
CuCH ₃ COO(ben)(p-tol)	8990.92	9000.93	10.80	4.72	10.01	1.00	31.27
CuCH ₃ COO(ben)(p-ani)	8987.51	9000.10	7.39	3.89	12.59	0.75	62.72
CuCH ₃ COO(p-Chloroben)(P-tol)	8985.50	8998.58	5.38	2.37	13.08	0.60	69.59
CuCH ₃ COO(p-Chloroben)(p-ani)	8989.17	8999.30	9.05	3.09	10.13	0.88	45.35

IV. DISCUSSION

1. SHAPE OF THE k-ABSORPTION EDGE:

The shape of the K-absorption edges is nearly same in all four complexes. The shapes of the K-absorption edges of these complexes are compared with those established by Van-Norstrand [18],[19]. It is concluded that all the complexes have octahedral structure. It is observed that, mixed valency systems exhibit splitting of the X-ray absorption edge. None of the complexes show any splitting of the k-edge. Katare et al [10] also reported no splitting of the k-edge in copper (II) mixed ligand complexes of aspartic acid. Mishra et al [20] also reported the absence of splitting of the k-edge of copper (II) complexes of amino acids thus indicating octahedral structure of the complexes.

2. CHEMICAL SHIFTS:

In various kinds of samples having biological relevance and utility in pharmacology [21],[22],[23], chemical shifts as obtained by XAS studies have yielded useful information. The shift of X-ray absorption edge i ($i=K, L, M$) of an element in a complex with respect to that of pure element has been written as

$$\Delta E_i = E_i(\text{complex}) - E_i(\text{element})$$

The results are given in Table 2. For computing the chemical shift, the value of $E_i(\text{element})$ has been taken as 8980.12 eV.

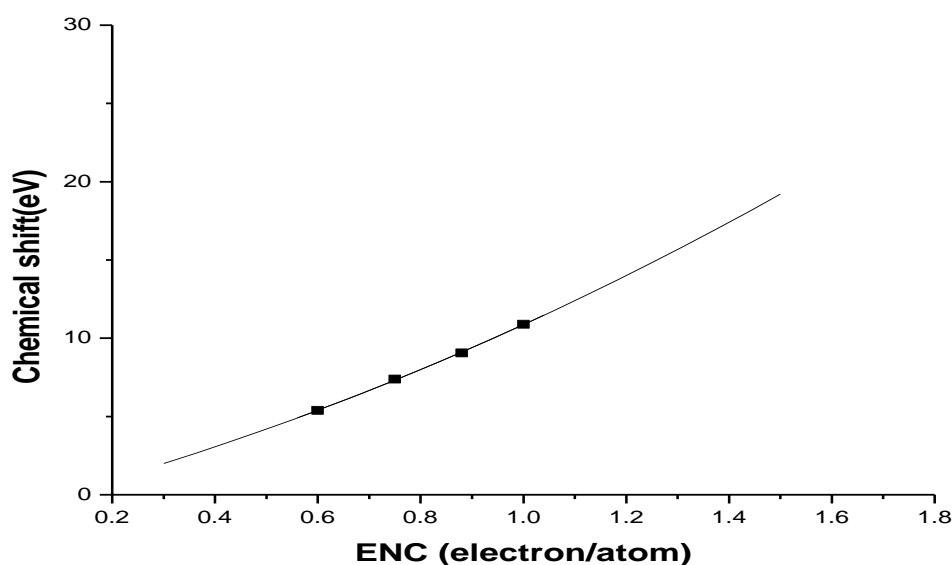
The experimental data of chemical shift of Cu (II) complexes show that the chemical shift decreases. The order is as follows:

$$\text{Complex I} > \text{Complex IV} > \text{Complex II} > \text{Complex III}$$

The compounds having copper in oxidation state in +1 show chemical shifts less than 5 eV while those having copper in oxidation state in +2 show chemical shifts more than 5 eV [24]. In Table.2, all the four complexes have the values of chemical shifts between 5.38 to 10.80 eV. Hence, on the basis of values of the chemical shifts, all the complexes are found to have copper in oxidation state +2. The K-absorption edge of copper has been found to be shifted towards the higher-energy side in all the complexes studied as compared to the K-absorption edge in the metal.

2.1 CHEMICAL SHIFTS AND EFFECTIVE NUCLEAR CHARGE (ENC):

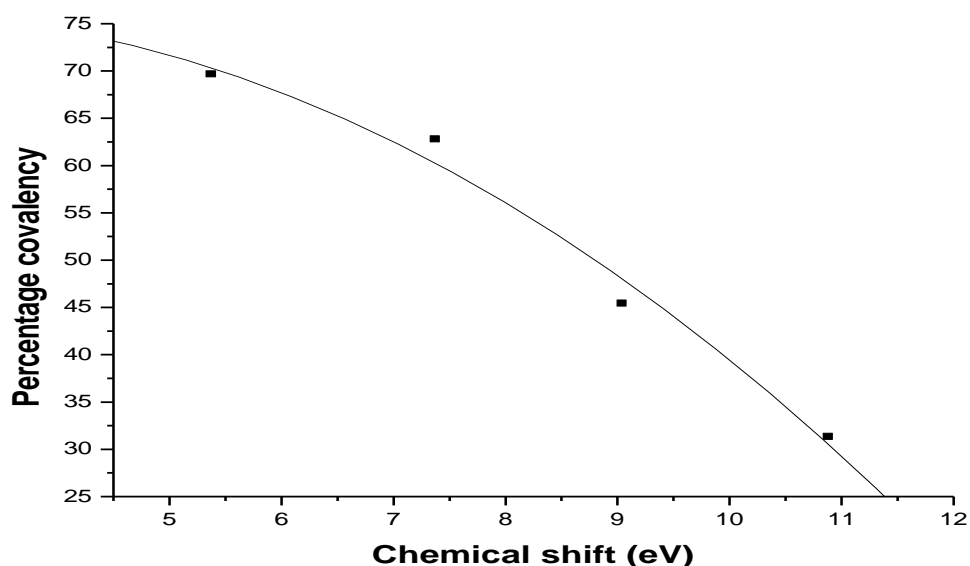
For the estimation of effective nuclear charge, various methods have been proposed [25], [26]. Here, by employing the procedure suggested by Gupta and Nigam [27], the ENC has been estimated from measured chemical shifts. The ENC of the copper atom in the complexes are found to be in the range 1.39 to 1.69 electrons/atom as shown in Table.2. An attempt was made to establish graphical correlation of ENC with chemical shift for copper complexes. The data points are consistent with a parabolic relationship between the chemical shift and ENC as shown in Graph.1. A.Mishra [28] also established the correlation of effective nuclear charge with chemical shift for copper complexes of 3-arylazo-7-hydroxy-4-methylcoumarin.



Graph .1 Correlation of effective nuclear charge with chemical shift (ΔE) for copper complexes

2.2 CHEMICAL SHIFTS AND PERCENTAGE COVALENCY:

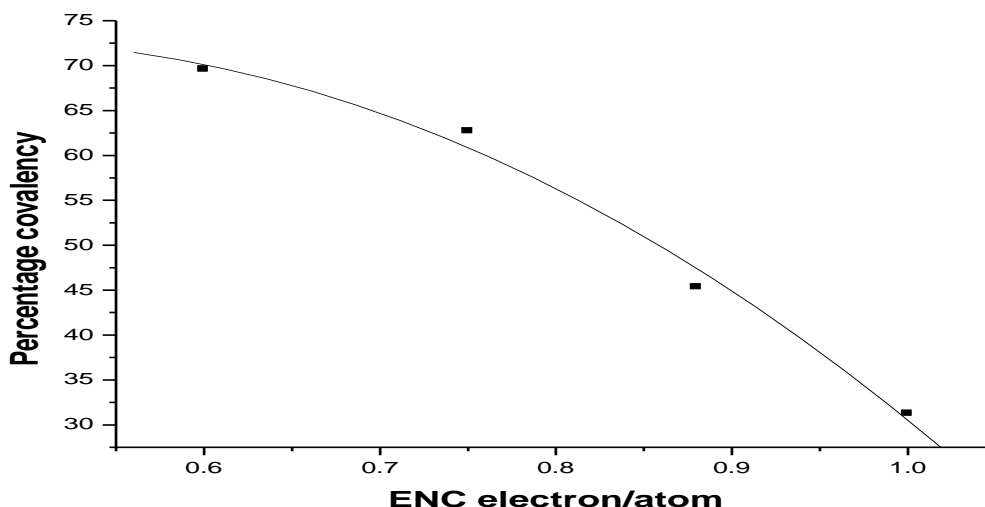
The chemical shift is also treated as a measure of degree of covalency [29],[30]. To calculate the percentage covalency of the bonds, a theoretical graph is plotted between the calculated value of binding energy of 1s electron using Clementi's [31] results of atomic function and percentage covalency for copper. The results reported in Table.2 show that, for each complex, increase in percentage covalency in metal-ligand bond causes corresponding shifts towards the lower energy side, which is in accordance with the results of Agarwal et al [13]. An attempt was made to establish graphical correlation of percentage covalency with chemical shift for copper complexes. The data points are consistent with a parabolic relationship and are shown in Graph .2. It is clear from the graph that the chemical shift decreases as the percentage covalency increases.



Graph .2 Correlation of percentage covalency with chemical shift (ΔE) for copper complexes

2.3 PERCENTAGE COVALENCY AND ENC:

Observations in Table.2 show that the percentage covalency in metal-ligand bond increases with decreases in ENC. Graph.3 show parabolic correlation between ENC and percentage covalency. A.Mishra [28] also observed similar type of correlation.



Graph. 3 Correlation of effective nuclear charge with Percentage covalency for copper complexes

3. PRINCIPAL ABSORPTION MAXIMUM:

Table.2 also presents the data for the principal absorption maximum E_A in the complexes and in the metal. It depends on the type of overlap in between metal and ligand orbitals. If overlap is more, then the bonding orbitals are stable and anti-bonding orbitals are unstable. For the complexes mentioned in Table.1, the range for shift of principal absorption maximum is between 2.37 - 4.72 eV. In the complexes, the principal absorption maxima are found to be shifted towards higher energy side [32]. The shifting of principal absorption maxima towards higher energy side are also reported by Mishra et al [20] and Hinge et al [9].

4. EDGE-WIDTH:

In Table.2, the values of the edge-width ($E_A - E_K$) have been reported. The experimental data of edge-width of Cu (II) complexes (Table.2) show that the edge-width decreases as follows:

$$\text{Complex I} < \text{Complex IV} < \text{Complex II} < \text{Complex III}$$

The order of the edge-width is in the reverse order of chemical shift of the same complexes. The reverse trend for these complexes is justified on the basis of the criterion suggested by Nigam et al [33]. According to Nigam et.al, the edge width of the K-absorption edge increases with the increase of covalent character of the bonds provided other factors like molecular symmetry etc. remains the same.

V. CONCLUSIONS

X-ray absorption spectra of mixed ligand copper (II) complexes at the K-edge of copper have been recorded at the recently developed EXAFS beamline setup at the Indus-2 synchrotron source at RRCAT, Indore. In all the four copper (II) complexes it is found that, there is no splitting of edge suggesting the octahedral structure of the copper (II) complexes. The energy of K-edge (E_K) and principal absorption maxima (E_A) have been reported. From these, the shift of the K-edge (chemical shift), shift of the principal absorption maximum and edge-width has been obtained. The chemical shift is towards the higher energy side and edge width is relatively small. The chemical shift has been used to determine the effective nuclear charge on the absorbing atom. The values of the chemical shifts suggest that copper is in oxidation state +2 in all of the complexes.

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