

XANES Study of Copper (II) Complexes of Aeromatic Amines

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Abstract— X-ray K-absorption spectroscopic studies have been carried out on two copper (II) mixed-ligand complexes .The complexes are: $[\text{Cu}(\text{L}2)_2](\text{CH}_3\text{COO})_2$ and $[\text{Cu}_2(\text{L}3)_2(\text{H}_2\text{O})_8](\text{CH}_3\text{COO})_2$. The ligand $\text{L}2=(\text{P-methyl anilino})-\text{P-methoxy phenyl acetonitrile}$ and $\text{L}3=(\text{P-methoxy anilino})-\text{P-methoxy phenyl acetonitrile}$ were synthesized. The two ligands were prepared by Strecker's procedure which included the reaction of p-methoxybenzaldehyde with p-toluidine and p-anisidine respectively. 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, 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. The studies establish significant correlation between various parameters for these complexes. XANES data have been analysed using the computer software Origin 6.0 professional and Athena.

Key words: Copper complexes, Aeromatic Amines, Athena

I. INTRODUCTION

The chemistry of nitrile and α -aminonitrile compounds and their derivatives has received special attention because of their application as potential ligands for a large number of metal ions [1].Nitriles and α -aminonitrile derivatives had a biological activities [2] as herbicides [3] , pharmacological agents [4] and biological synthesis of chemical compounds by it's microbial metabolism in some organisms [5].

X-ray absorption spectroscopy has been extensively used to obtain information about the molecular structure viz. the oxidation state and the effective nuclear charge of the absorbing atom in compounds and complexes. XANES and EXAFS studies of some of the Cu(II) complexes of p-toluidine and p-anisidine have been already discussed in previous literature [6]- [11]. The XANES characterization of some more complexes had been carried out and their results have been reported in this paper.

II. EXPERIMENTAL DETAILS

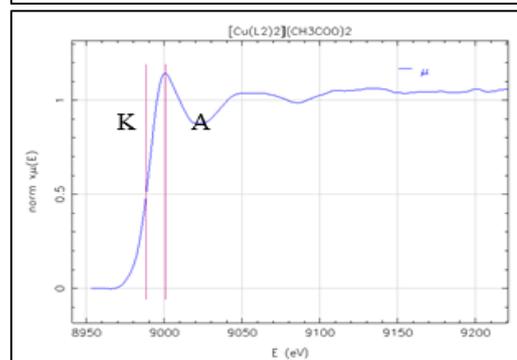
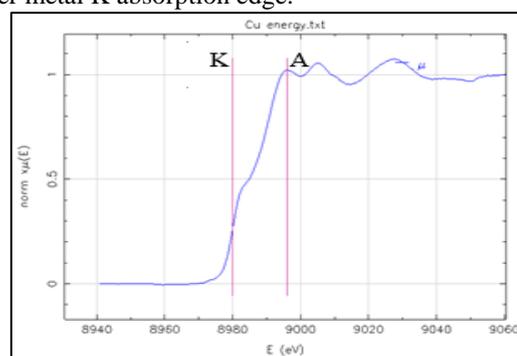
The two complexes studied in the present investigations are $[\text{Cu}(\text{L}2)_2](\text{CH}_3\text{COO})_2$ and $[\text{Cu}_2(\text{L}3)_2(\text{H}_2\text{O})_8](\text{CH}_3\text{COO})_2$. The ligand $\text{L}2=(\text{P-methyl anilino})-\text{P-methoxy phenyl acetonitrile}$ and $\text{L}3=(\text{P-methoxy anilino})-\text{P-methoxy phenyl acetonitrile}$ were synthesized. The two ligands were prepared by Strecker's procedure [12], [13]which included the reaction of p-methoxybenzaldehyde with p-toluidine and p-anisidine respectively. All the complexes were prepared according to the standard methods reported in literature and their purity was checked [14]. 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 [15], [16], [17]. The experimental data have been analyzed using

the available computer software packages Origin 6.0 professional and Athena [18].

III. RESULTS AND DISCUSSION

The shapes of the copper K-absorption discontinuity and the associated near edge structure (XANES) for all the complexes are shown in Fig 1.The curves in this figure represent the normalized K absorption spectra. The energies of the copper K-edge(E_K)and the principal absorption maximum (E_A) along with the values of the edge-width (E_A-E_K),effective nuclear charge Z_{eff} and the chemical shift ΔE_K are given in Table 2.

The first derivative of the spectra, indicating positions of the absorption edge K and principal absorption maximum A are shown in Fig. 2.The first peak in the derivative spectra gives the position of the K absorption edge (E_K). The position where the derivative is zero, gives the position of principal absorption maxima (E_A). The results of the energy of the K absorption edges (E_K) and the energies of principal absorption maximum A (E_A) of copper in metal and its three 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 table that copper K-edge is found to be shifted towards the high-energy side in the two complexes, as compared with the copper metal K absorption edge.



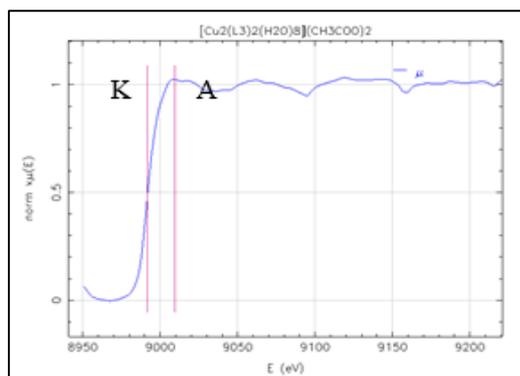


Fig. 1: The XANES region of the absorption spectrum at the K-edge of copper in the complexes indicating positions of the absorption edge K and the principal absorption maxima A.

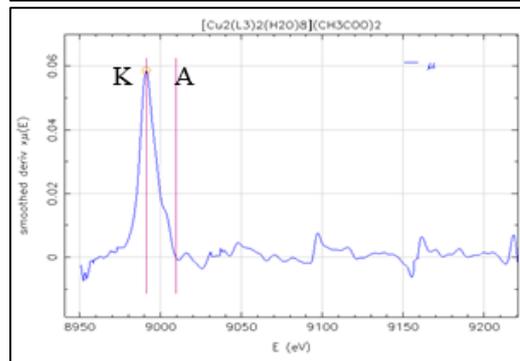
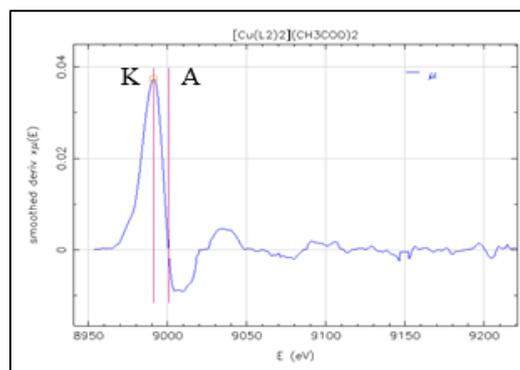
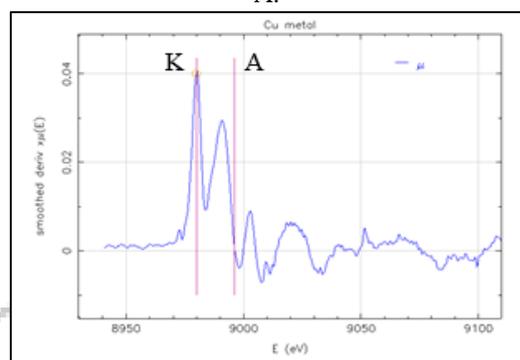


Fig. 2: Derivative of the XANES region of the absorption spectrum at the K-edge of copper in the complexes indicating positions of the absorption edge K and the principal absorption maxima A.



| Complexes | Abbreviation | Molecular formulae |
|---|--|--|
| [bis{(p-methyl anilino)-p-methoxyphenyl acetonitrile} copper(II)] acetate | [Cu(L2) ₂](CH ₃ COO) ₂ | [Cu(C ₁₆ H ₁₆ N ₂ O) ₂](CH ₃ COO) ₂ |
| [Octaaqua-di-α-(p-methoxy anilino)-p-methoxy phenyl acetonitrile] dicopper(II)] acetate | [Cu(L3) ₂ (H ₂ O) ₈](CH ₃ COO) ₂ | [Cu ₂ (C ₁₆ H ₁₆ N ₂ O) ₂ (H ₂ O) ₈](CH ₃ COO) ₂ |

Table 1: Abbreviation and Molecular Formulae of Cu (Ii) Complexes

| Complexes | E _K (eV) | E _A (eV) | Chemical shift (eV) | Shift of the principal absorption maximum (eV) | Edge-width (E _A -E _K) (eV) | ENC Electron / atom | % Covalency |
|--|---------------------|---------------------|---------------------|--|---|---------------------|-------------|
| Copper metal | 8980.12 | 8996.21 | - | - | 16.088 | - | |
| [Cu(L2) ₂](CH ₃ COO) ₂ | 8989.56 | 9000.47 | 9.44 | 4.26 | 10.91 | 0.90 | 40.90 |
| [Cu(L3) ₂ (H ₂ O) ₈](CH ₃ COO) ₂ | 8990.96 | 9010.00 | 10.84 | 13.79 | 19.04 | 1.00 | 30.80 |

Table 2: Xanes Data for the K Absorption Edge of Copper in the Complexes.

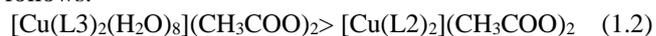
A. Chemical Shift

The shift of the X-ray absorption edge of an element in a compound/complex with respect to that of the pure element is written as:

$$\Delta E_K = E_{K(\text{complex})} - E_{K(\text{metal})} \quad (1.1)$$

For computing the chemical shift, the value of E_K (Cu metal) has been taken as 8980.12 eV. In Table 2, the two complexes have the values of chemical shifts between 4.44 to 10.84 eV. Hence, on the basis of values of the chemical shifts, the complexes are found to have copper in

oxidation state +2 [19]. The order for these complexes is as follows:



As is well known, an ionic bonding enhances the chemical shift, whereas a covalent bonding suppresses it. Hence, the above order may also be taken as representative of the relative ionic character of the bonding in these complexes.

B. Principal Absorption Maximum

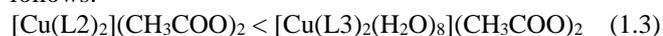
In Table 2, we have also included the data for the principal absorption maximum E_A in the complexes and in the metal. It has been observed that for copper metal, the value of E_A is 8996.0 eV and for all the complexes it is shifted towards the higher energy side [20].

For the complexes mentioned in Table 2, the energy range of chemical shift in these complexes is between 9.44 and 10.84, whereas the range for shift of principal absorption maximum is between 4.26 and 13.79 eV. Hence, on the basis of the shift of the principal absorption maximum, in addition, it can be inferred that copper is in +2 oxidation state in these complexes.

C. Edge-Width

In Table 2, we have reported the values of the edge-width ($E_A - E_K$). The edge-widths values are 10.91 and 19.04 eV, respectively.

The experimental data of edge-width of Cu(II) complexes (Table 2) show that the edge-width decreases as follows:



D. Effective Nuclear Charge [Z_{eff}]

For the estimation of effective nuclear charge, various methods have been proposed [21], [22].

In the present work, Z_{eff} has been obtained from the measured chemical shift by using the semi-experimental method by employing the procedure suggested by Nigam and Gupta [23]. The effective nuclear charge on the copper in the complexes under present study varies between 0.52 – 1.00 electrons/atom. The results show that chemical shift increases then ENC also increases.

E. Percentage Covalency

It is clear from the data that the percentage covalency increases as effective charge decreases. A.Mishra [24] also observed similar type of correlation.

IV. CONCLUSIONS

X-ray absorption spectra of mixed ligand copper 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. 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 order of the chemical shift may also be taken as representative of the relative ionic character of the bonding in these complexes. 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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