X-Ray, K-Absorption Spectroscopic Studies of Mixed Ligand Copper (II) Complexes of Benzaldehyde

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Abstract

X-ray K-absorption spectroscopic studies have been carried out on three biologically important copper (II) mixed-ligand complexes. The complexes are: I Cu(ben)(p-Tol)(Br), II Cu(ben)(p-Tol)(Cl), and III Cu(ben)(p-Tol)(NO₃) in which benzaldehyde has been used as a primary ligand and p-toluidine has been used as a secondary ligand. XANES spectra have been recorded at the K-edge of Cu using the dispersive beam line at 2.5gev Indus-2 ynchrotron radiation source RRCAT (Raja Ramanna Center for Advance Technology), Indore, and India. The XANES data have been analysed using the computer softwares Athena and Origin 6.0. Various X-ray absorption parameters e.g., chemical shift, edge-width and shift of the principal absorption maximum have been determined in the present study. From these XANES data the effective nuclear charge on copper and percentage covalency in these complexes have been estimated. Further, the observed chemical shifts have been correlated with ENC and percentage covalency in these complexes. The studies establish significant correlation between various parameters for these complexes.

Keywords: XANES, Athena, Origin 6.0, ENC

Introduction

The X-ray absorption fine structure analysis can give details about the electronic structure and the local arrangement of atoms around the absorbing atom. X-ray absorption near edge structure (XANES) is a powerful and promising tool for determination of the local structure of samples. Aminonitrile is potentially a chelating ligand [1, 2]. A chelating agent is a substance whose molecules can form several bonds to a single metal ion. In other words, a chelating agent is a multidentate ligand. A single molecule of aminonitrile can form two bonds to a transition-metal ion such as Cu2+. The bonds are formed between the metal ion and the nitrogen atoms of aminonitrile.

Chemical shifts as obtained by X-ray absorption spectroscopic studies have yielded useful information in various kinds of samples having biological relevance and utility in pharmacology (3-7). In the present paper, we have studied X-ray absorption near edge structure (XANES) at the K-edge of copper and have also measured various X-ray absorption parameters in some copper complexes involving benzaldehyde and p-toluidine.

Experimental details

The three complexes studied in the present investigations are Cu(ben)(p-Tol)(Br) , Cu(ben)(p-Tol)(Cl) and Cu(ben)(p-Tol)(NO₃) where ben = benzaldehyde and p-Tol = p-toluidine . These three

complexes were synthesized according to the standard methods reported in literature and their purity was checked [8]. In these complexes benzaldehyde has been used as a primary ligand and p-toluidine has been used as a secondary ligand. The ligand L= (p-methyl anilino) phenyl acetonitrile was synthesized by Strecker's procedure [9,10] which included the reaction of benzaldehyde with p-toluidine. 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 [11-13]. The digital records were analyzed using computer programs Origin and Athena [14]. Derivative spectra were used for obtaining the K-edge position.
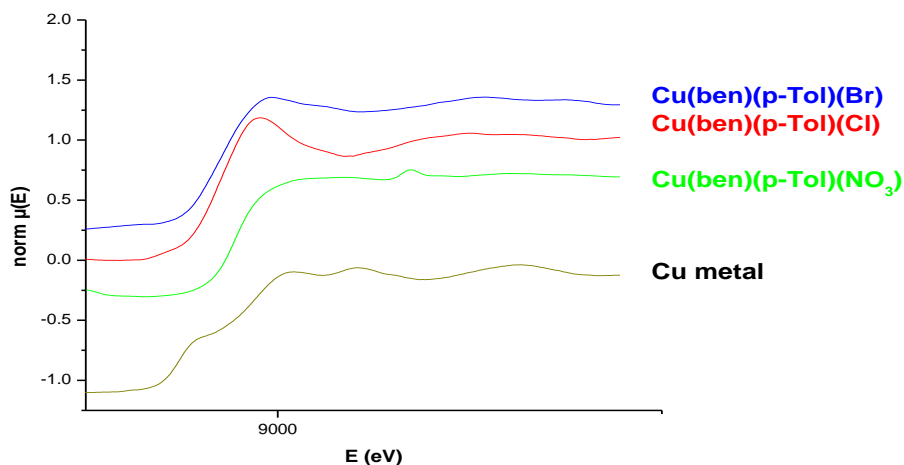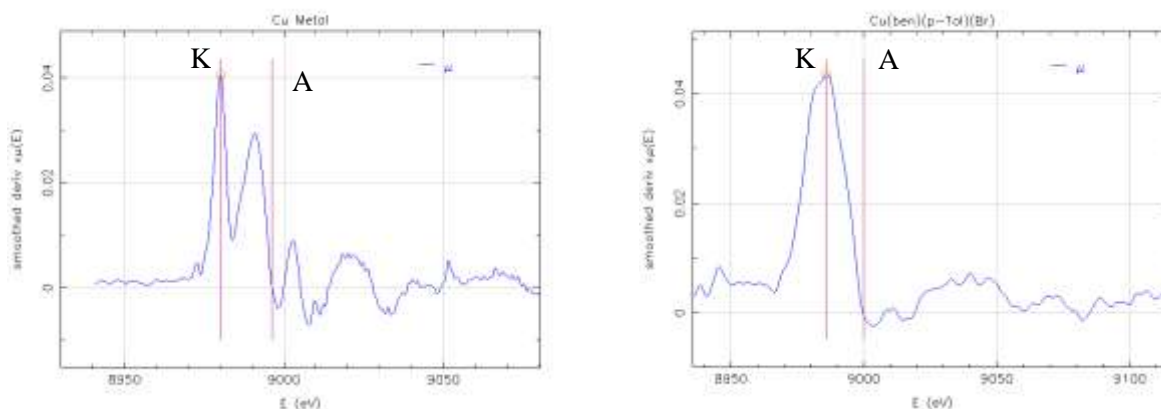

Figure 1: The XANES region of the absorption spectrum at the K-edge of copper metal and in it's complexes. The different spectra have been shifted vertically for better presentation.
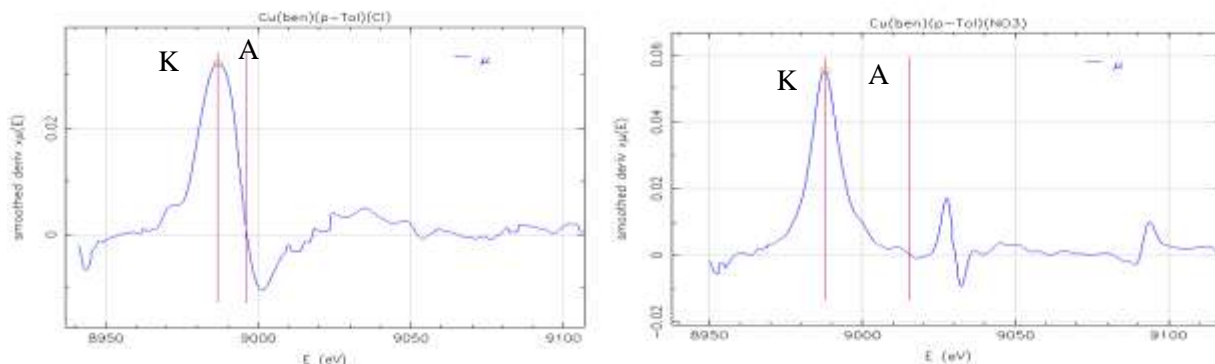
Figure 2: Derivative of the XANES region of the absorption spectrum at the K- edge of copper in the complexes indicating positions of the absorption edge K and the principal absorption maxima A.

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 Figure 1. The curves in this figure represent the normalized K absorption spectra. The energy 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) and the chemical shift ΔE_K are given in Table 1.

Position of the edge

The first derivatives of the XAFS spectra indicating positions of the absorption edge E_k and principal absorption maximum E_A are shown in Figure 2. The inflection point of the first rise in the absorption edge corresponds to the binding energy corresponding to that edge, i.e., the inflection point on the K edge corresponds to the binding energy E_o or E_K of the K level.

For the K-absorption edge, the position of the edge is written as E_K in eV. The values of E_K for the K-absorption edge of copper in its complexes studied are given in Table 1.

Chemical shift

In various kinds of samples having biological relevance and utility in pharmacology chemical shifts as obtained by XAS studied have yielded useful information The shifts of the K-absorption edge of copper in the complexes with respect to that of copper metal have been determined according to the eqn.

$$\Delta E_K = E_K(complex) - E_K(metal)$$

The results are given in Table 1. For computing the chemical shift, the value of E_K(Cu metal) has been taken as 8980.12 eV.

For the complexes under study, the order in which the ligands contribute to the chemical shift is:

$$Br < Cl < NO_3$$

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 .In Table 1 all the complexes have the values of chemical shifts between 5.83 to 9.49 eV. Hence, on the basis of values of the chemical shifts, all the complexes are found to have copper in oxidation state +2.

As compared to the K-absorption edge in the metal, the K-absorption edge of copper has been found to be shifted towards the high-energy side in all the complexes studied.

Complexes	E_K (eV)	E_A (eV)	Chemical shift (eV)	Shift of principal absorption maxima (eV)	Edge-width ($E_A - E_K$) (eV)	ENC Electron/atom	% Co-valency
Copper metal	8980.12	8996.21	-	-	16.088	-	-
Cu(ben)(p-Tol)(Br)	8985.95	9000.03	5.83	3.82	14.08	0.63	68.38
Cu(ben)(p-Tol)(Cl)	8987.00	8999.05	6.88	2.84	12.05	0.71	65.15
Cu(ben)(p-Tol)(NO₃)	8988.44	9016.08	8.32	19.87	27.64	0.82	55.45

Table 1: XANES data for the K absorption edge of copper in the complexes

Effective nuclear charge and chemical shift

Gianturco and Coulson [15] showed in different complexes how the chemical shift is related to the effective charge (EC). On the basis of effective charge calculated from Suchet's empirical formula [16], Sapre and Mande [17] explained the observed shift. It is to be noted that X-ray absorption spectroscopy can also be used to determine the EC on atoms [18, 19]. 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. From this plot, the effective charge on the copper atom is different complexes are then determined [20].The data is presented in Table 1. Mande and Kondawar showed chemical shift to be directly proportional to the effective charge on the absorbing atom. Siegbahn [21] and Carver *et* al. [22] also justify the linear fit of chemical shift with EC. In Figure 3, the graph is plotted against effective charge and the experimental chemical shift of the four copper complexes studied. The results show that chemical shift increases then EC also increases. It is clearly seen that the copper complexes is more ionic.
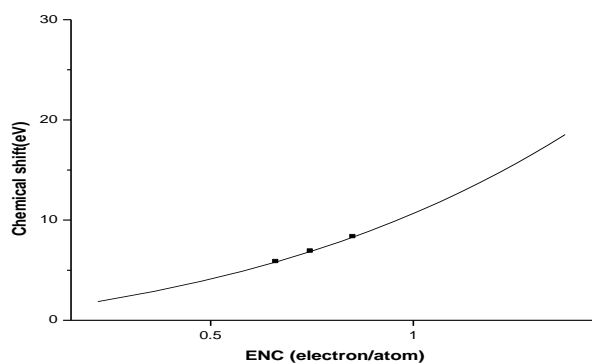

Figure 3: Co-relation between chemical shift and ENC

Percentage covalency and chemical shift

The chemical shift is also treated as a measure of covalency. A graph is plotted between percentage covalency and a value of chemical shift of copper complexes (Figure 4). It is clear from the graph that the chemical shift decreases as the percentage covalency increases. 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 results of atomic function and percentage covalency for copper [23].
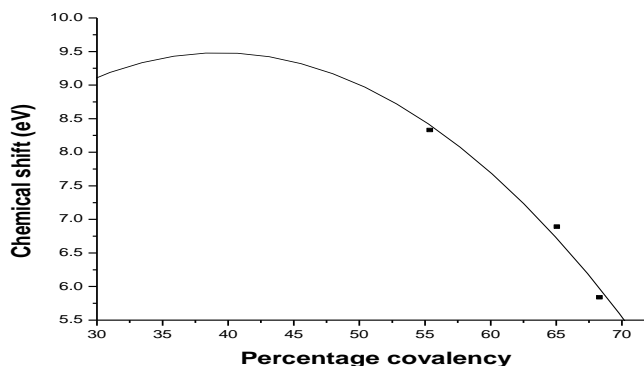

Figure 4: Co-relation between chemical shift and percentage covalency

Percentage covalency and ENC

Finally, the reported values as mentioned above are used for plotting the graph between percentage covalency and ENC for copper (II) complexes. It is clear from the graph that the percentage covalency increases as effective charge decreases. Figure 5 shows parabolic correlation between ENC and percentage covalency. A.Mishra [24] also observed similar type of correlation.
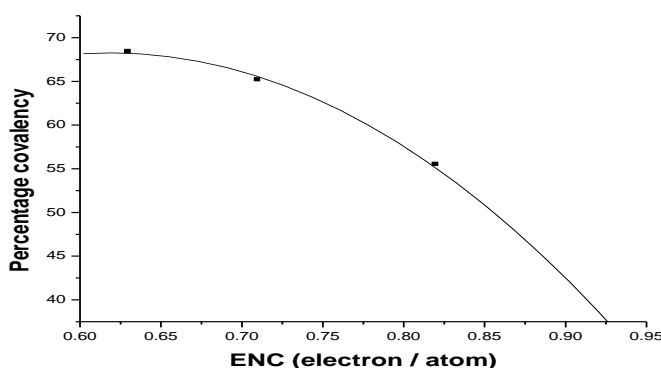

Figure 5: Co-relation of effective nuclear charge with percentage covalency for copper (II) complexes

Principal absorption maximum

The data for the principal absorption maximum E_A for the complexes is also included in Table 1. It has been observed that the value of E_A is shifted towards the higher energy side with respect to copper metal. The shifts of the principal absorption maximum at the K-absorption edge of copper in the complexes with respect to that of copper metal have been determined according to the eqn.

$$\Delta E_A = E_A(\text{complex}) - E_A(\text{metal})$$

For computing the chemical shift the value of E_A(Cu metal) has been taken as 8996.21 eV.

Edge-width

In Table.1 the values of the edge-width (E_A-E_K) have been reported. The order of the edge width in each series of complexes does not match with the order of chemical shift because the edge width does not only depend on those factors that are responsible for chemical shift. This represents that the edge-width is inversely proportional to ionic character for this series. The reverse trend for these complexes is justified on the basis of the criterion that, in general, edge-width of the K-absorption edge increases with the increase of covalent character of the bonds provided other factors like molecular symmetry etc., remain the same [25].

Conclusions

X-ray absorption spectra of mixed ligand copper (II) complexes at the K-edge of copper have been recorded at the EXAFS beamline setup at the Indus-2 synchrotron source at RRCAT, Indore. The energy of K-edge (EK) and principal absorption maxima (EA) 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.

Acknowledgement

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