XANES Study of Copper((II) Mixed-Ligand Complexes of 8-Hydroxyquinoline

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Abstract

X-ray K-absorption spectroscopic studies have been carried out on three copper (II) mixed-ligand complexes .The complexes are $CuCH_3COO(L)(Q)$, $CuSO_4(L)(Q)$, and $CuNO_3(L)(Q)$ where L= o-hydroxybenzylidene-1-phenyl-2,3-dimethyl-4-amino-3-pyrazolin-5-on and Q=8-hydroxyquinoline . 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 chemical shift data have been utilized to estimate effective nuclear charge on the absorbing atom. Further the observed chemical shifts have been correlated with percentage covalency in these complexes. The data obtained has been processed using data analysis program Athena and the computer software Origin 6.0 professional.

Keywords: Copper complexes, XANES, Athena, Origin 6.0 professional

Introduction

Schiff bases are an important class of ligands in coordination chemistry and find extensive application in different fields [1]. Schiff bases derived from the salicylaldehydes are well known as polydentate ligands coordinating in neutral forms [2] .The interaction of these donors ligands and metal ions give complexes of different geometries and these complexes are potentially biologically active [3]. Thus, in recent years metal complexes of schiff bases have attracted considerable attention due to their remarkable antifungal, antibacterial, antitumor and anticancer activity [4]. Several research papers have been synthesized and characterized on transition metal complexes of Schiff base derived from salicylaldehyde [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. A search through literature reveals that no work has been done on the XANES of transition metal complexes of the Schiff base and 8- hydroxyquinoline . Keeping this in view, the present paper describes the results of an XANES analysis of mixed Schiff base complexes.

Experimental Details

The three complexes studied in the present investigations are $CuCH_3COO(L)(Q)$, $CuSO_4(L)(Q)$

and $CuNO_3(L)(Q)$ where L= o-hydroxybenzylidene-1-phenyl-2,3-dimethyl-4-amino-3-pyrazolin-5-on and Q=8-hydroxyquinoline . All the complexes were prepared according to the standard methods reported in literature and their purity was checked [6]. 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 .On this beamline, the X-ray intensities I_0 and I_t are obtained as the CCD outputs without and with the sample, respectively. Using the relation, $I_t = I_0e^{-\mu x}$, where μ is the absorption coefficient and x is the thickness of the absorber, the absorption μ(E) corresponding to the photon energy (E) are obtained. The experimental data have been analyzed using the available computer software packages Origin 6.0 professional and Athena.

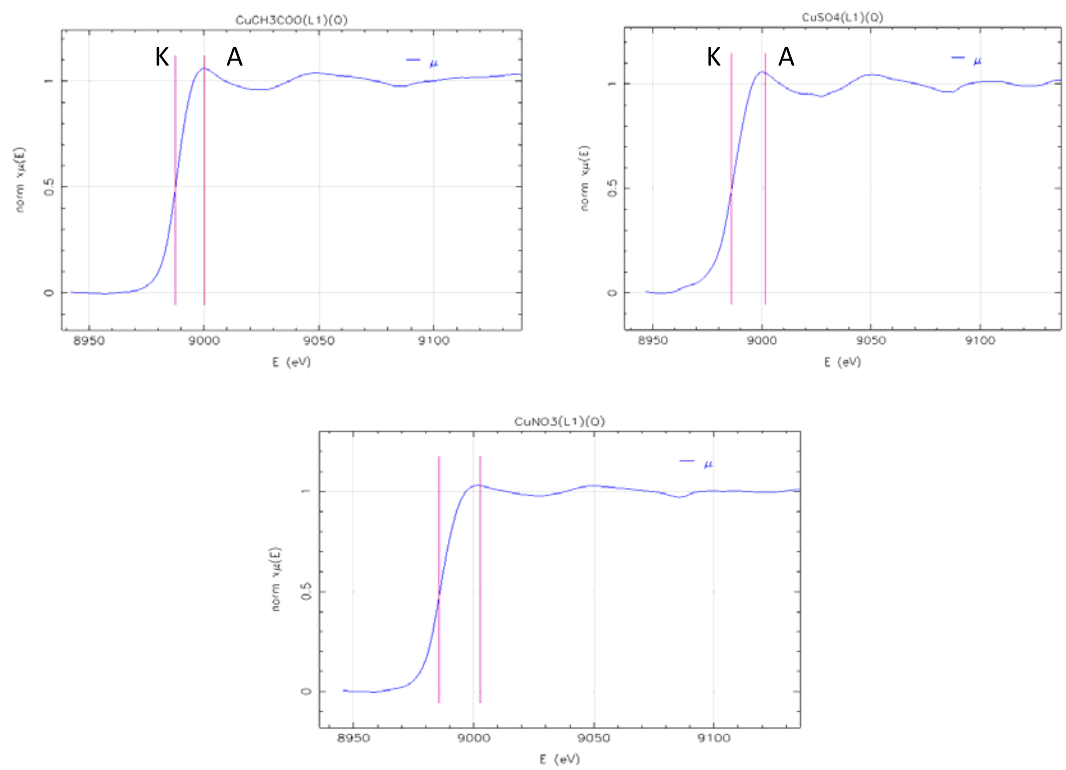

Figure 1. The XANES region of the absorption spectrum at the K-edge of copper in the complexes indicating positions of the absorption edge K and the principal absorption maxima A.

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 1.

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

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principal absorption maximum A (E_A) of copper in metal and its three complexes are presented in Table 1. 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 all the three complexes, as compared with the copper metal K absorption edge

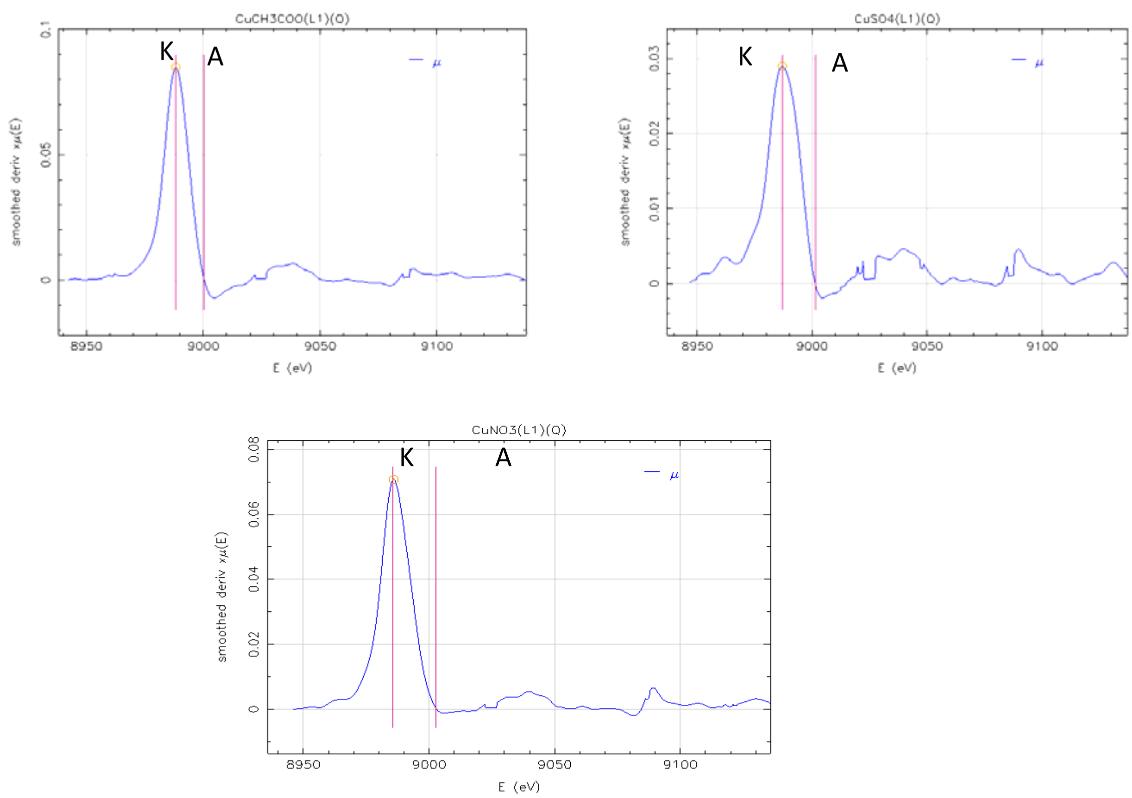

Figure 2. Derivative of the XANES region of the absorption spectrum at the K-edge of copper in the complexes indicating positions of the absorption edge K and the principal absorption maxima A.

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

Complexes	E_K(eV)	E_A(eV)	Chemical shift ΔE_K (eV)	ENC Z_{eff}	Shift of the principal absorption maximum (eV)	Edge-width (E_A_E_K) (eV)	Percentage Covalency
Cu metal	8979.98	8996.00	-	-	-	16.02	-
CuCH3COO(L)(Q)	8988.27	9000.12	8.29	0.82	4.12	11.85	55.85
CuSO4(L)(Q)	8987.07	9001.18	7.09	0.73	5.18	14.11	64.34
CuNO3(L)(Q)	8985.74	9002.71	5.76	0.63	6.71	16.97	68.78

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:

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

For computing the chemical shift, the value of E_K (Cu metal) has been taken as 8979.98 eV. In Table 1,all the three complexes have the values of chemical shifts between 5.76 to 8.29 eV. Hence, on the basis of values of the chemical shifts, all the complexes are found to have copper in oxidation state +2. The order for the three complexes is as follows:

CuCH3COO(L)(Q) > CuSO4(L)(Q) > CuNO3(L)(Q) .

For the complexes under study, the order in which the ligands contribute to the chemical shift is: NO3 < SO4 < CH3COO . 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.

Effective nuclear charge Zeff

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 [7]. A graph was plotted between the theoretical shift in the binding energy and the oxidation number for the copper. The effective nuclear charge Z_{eff} on the copper atom in the complexes studied was then determined from this plot corresponding to the measured values of the edge shifts. The effective nuclear charge on the copper in the complexes under present study varies between 0.63 – 0.82 electrons/atom.

Principal absorption maximum

In Table 1, 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.

For the complexes mentioned in Table 1, the energy range of chemical shift in these complexes is between 5.76 and 8.29 eV, whereas the range for shift of principal absorption maximum is between 4.12 and 6.71 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.

Edge-width

In Table 1, we have reported the values of the edge-width (E_A-E_K). In acceto, sulphato and nitro complexes, the edge-widths values are 11.85, 14.11 and 16.97 eV, respectively. The experimental data of edge-width of Cu(II) complexes (Table 1) show that the edge-width decreases as follows:

$CuCH_3COO(L)(Q)$ < $CuSO_4(L)(Q)$ < $CuNO_3(L)(Q)$

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 that, in general, edge-width of the K absorption edge increases with the increase of covalent character of the bonds provided other factors such as molecular symmetry, etc. remain the same.[8] The reverse trend is justified on this basis.

Percentage Covalency

It is well known that the chemical shifts is also treated as a measure of degree of covalency. Using Clementi's (9) results, a theoretical graph is plotted between shifts in binding energy of 1s electron and percentage covalency. The graph was used to calculate percentage covalency of the complexes and the data are reported in Table 1. The complexes show relatively more ionic character than the covalent ones. It should be noted that increase in covalent character of bonding is associated with shifts towards lower energy side.

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 and percentage covalency. The values of the chemical shifts suggest that copper is in oxidation state +2 in all of the complexes .

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