XANES Studies of Cu(II) Complexes derived from Benzil 2,4-dinitrophenylhydrazone with anilines

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Abstract— This paper deals with the X-ray absorption near edge structural studies of transition metal Schiff base complexes of Cu(II), derived from benzil-2,4-dinitrophenylhydrazone with different anilines, that have been prepared by chemical root method. These synthesized complexes have been characterized by Cu K-Edge XANES measurements using the BL-8 Dispersive EXAFS beamline at 2.5 GeV Indus-2 synchrotron radiation source at RRCAT (Raja Ramanna Centre for Advance Technology), Indore, India. The measured XANES data have been analyzed to compute the energies of the K absorption edge, chemical shifts, shifts of the principal absorption maximum and edge-widths. The values of the chemical shift suggest that copper is in oxidation state +2 in all of the complexes. By calculating the chemical shift effective nuclear charge on copper atom has been estimated. All these calculation has been done with computer software ATHENA.

I. INTRODUCTION

Schiff base ligands containing azomethine group (>C=N-) are easily prepared by the condensation among aldehydes and amines and therefore are considered 'privileged ligands' [1]. In the present studies the complexes of Cu(II) with Schiff bases ligand derived from 2,4 dinitrophynylhydrazon with different anilines have been characterized by X-ray absorption spectroscopy. X-ray absorption spectroscopy has emerged as a leading technique for local structure determination, with the manifestation of modern bright synchrotron radiation sources, which can be applied to any kind of material. It is 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. The XANES characterization of the mentioned complexes had been carried out and their results have been reported in this paper. [2,3].

II. EXPERIMENTAL

In the present study, the X-ray absorption spectra have been recorded using synchrotron radiation source available at Raja Ramanna Center for Advaced Technology (RRCAT), Indore, India called dispersive EXAFS beamline BL-8. This beamline has been specially made at the 2.5 GeV Indus-2 synchrotron radiation source [4]. In this beamline a bent crystal (Si 111) polychromator is used to opt for a band of energy from the white synchrotron beam which is horizontally dispersed and focused on the sample. The whole EXAFS spectrum around an absorption edge in a single shot has been recorded (typical acquisition time of one spectrum is ~300 msec). The incident and transmitted intensities I0 and It, are obtained as the CCD outputs without and with the sample respectively. Using the relation, $I_t = I_0 e^{-\mu x}$, 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 has been analyzed using the available computer software package Athena0.8.056 and Origin 8.0.[5].

All the complexes studied in this paper have been prepared by standard method reported in litreture.[6].

III. RESULTS AND DISCUSSION

The shapes of the Cu- K-absorption discontinuity and the associated near edge structure in the region -50 < E < 50 eV (XANES) for Cu metal and all the complexes are shown in Fig 1-4.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 (ENC) and the chemical shift are given in Table 1. 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 (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. Following XANES parameter has been calculated and results are reported in Table 1:

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:

$$\Delta E_K = E_K(complex) - E_K(metal) \qquad (1)$$

For computing the chemical shift, the value of E_K (Cu metal) has been taken as 8980.04 eV. In Table 1 , the complexes have the values of chemical shifts between 6.65 to 6.88 eV. Hence, on the basis of values of the chemical shifts, the complexes are found to have copper in oxidation state +2 [7]. The order for these complexes is as follows:

Complex 3 < Complex 1 < Complex 2.

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 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 8994.36 eV and for all the complexes it is shifted towards the higher energy side [8].

For the complexes mentioned in Table 1, the energy range of chemical shift in these complexes is between 6.65 to 6.88 eV whereas the range for shift of principal absorption maximum is between 3.02 and 4.25 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 1, we have reported the values of the edge-width (E_A-E_K). The edge-width is between 10.45 to 11.93 eV. The experimental data of edge-width of Cu(II) complexes (Table 1) show that the order of edge-width is as follows:

Complex 2 < Complex 1 < Complex 3.

D. Effective Nuclear Charge (ENC)

For the estimation of effective nuclear charge, various methods have been proposed [9].

In the present work, ENC has been obtained from the measured chemical shift by using the semi-experimental method by employing the procedure suggested by Nigam and Gupta [10,11]. The effective nuclear charge on the copper in the complexes under present study varies between 0.76 – .78 electrons/atom. The results show that chemical shift increases then ENC also increases.

IV. CONCLUSION

From the X-ray absorption spectra of copper complexes at the K-edge of copper, recorded at EXAFS beamline setup at the Indus-2 synchrotron source at RRCAT, Indore, the energy of Kedge (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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Figures and Tables:
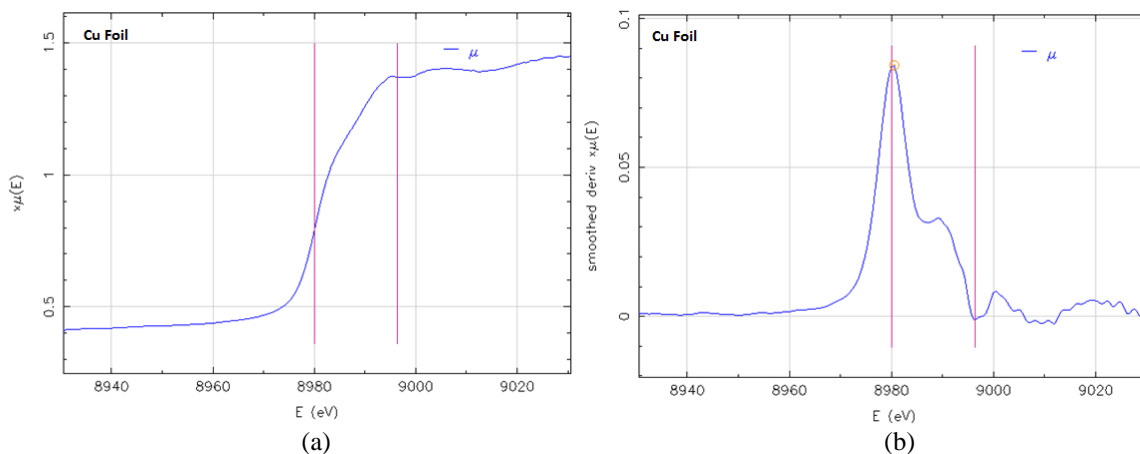

(a)   (b)

Fig. 1 (a) XAFS spectrum and (b) Derivative of XAFS spectrum for copper Foil indicating position of absorption edges K and principal absorption maxima A.
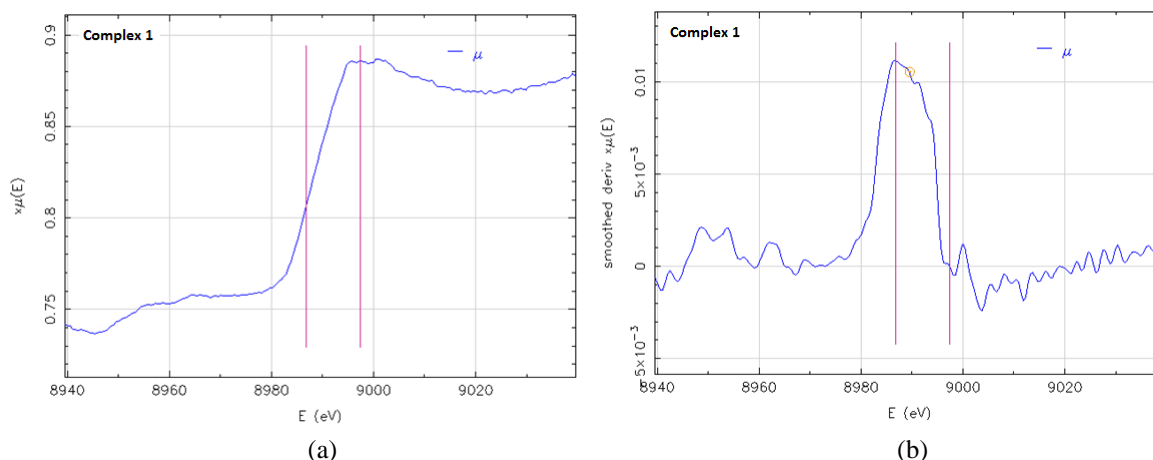

(a)   (b)

Fig. 2 (a) XAFS spectrum and (b) Derivative of XAFS spectrum for Complex 1 indicating position of absorption edges K and principal absorption maxima A.
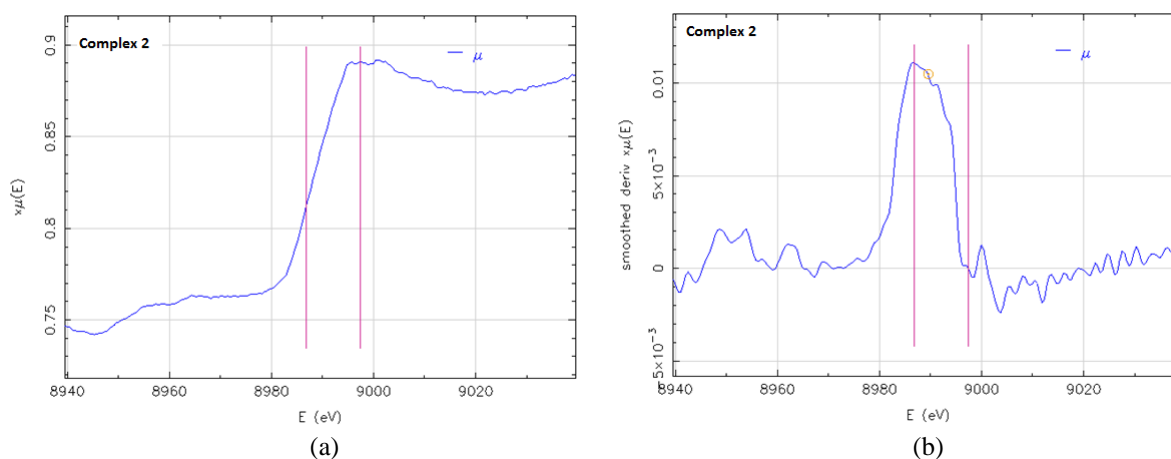

(a)   (b)

Fig. 3 (a) XAFS spectrum and (b) Derivative of XAFS spectrum for Complex 2 indicating position of absorption edges K and principal absorption maxima A.
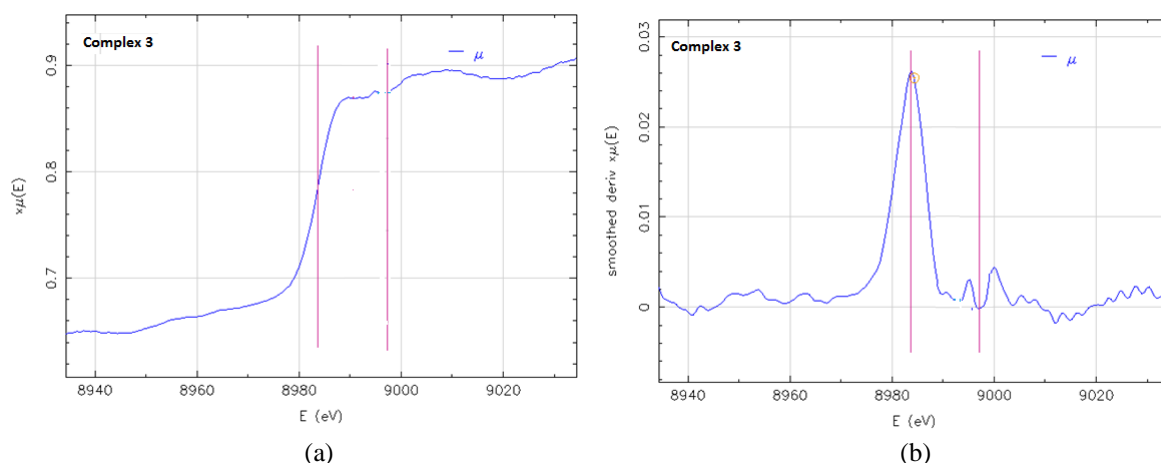
(a)   (b)

Fig. 4 (a) XAFS spectrum and (b) Derivative of XAFS spectrum for Complex 3 indicating position of absorption edges K and principal absorption maxima A.

Table 1. XANES data for K-absorption edge of Copper(II) complexes.

S.No.	Complex	E_K (eV)	E_A (eV)	Chemical shift $\Delta E_K =$ ($E_K$complex - $E_K$metal) (eV)	ENC	Shift of Principal Absorption Maxima (eV)	Edge-width (E_A-E_K) (eV)
1	Cu_Foil	8980.04	8994.36	--	--	--	14.32
2	Complex 1	8986.79	8998.22	6.75	0.77	3.86	11.43
3	Complex2	8986.92	8997.37	6.88	0.78	3.02	10.45
4	Complex 3	8986.68	8998.61	6.65	0.76	4.25	11.93

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