XANES Study of Schiff Base Cu (II) Complex of dimedone couplingwith aniline derivative

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Abstract - X-Ray absorption fine structure of Schiff Base copper (II) complex in which primary ligand was synthesized by dimedone, coupling with aniline derivate. Here aniline derivate is taken as 4-methoxy aniline has been studied. The X-ray diffraction of the complex exhibit the crystalline character of complex, and different lattice parameters were calculated. The X-ray absorption near edge structure (XANES) data have been analyzed to estimate the shift of K-edge, the shift of principal absorption maximum, edge width, and chemical shift. Effective nuclear charge (ENC) and percentage covalency also be calculated. XANES data have been analyzed using the software Athena. Software Origin is used for the graphical representation of XRD Data.

Keywords— XRD, XANES, Chemical Shift, Edge width, Effective nuclear charge, Athena.

I. INTRODUCTION

Schiff base copper(II) complexes exhibit so many interesting and useful biological and pharmaceutical properties such as antibacterial, antiviral, antioxidant, antitumor, and anticancer [1,2]. It also behaves as an active catalyst in some of the specific chemical reactions i.e. Hennery reaction [3]. Copper(II) complexes are also building blocks in supramolecular devices because of its favorable excited states and measurable properties. Copper complexes are also used in photophysics, photochemistry, and biochemistry [4]. In the present paper, we investigated X-ray diffraction XRD and X-ray absorption near edge structure (XANES) patterns of Cu (II) complex of 5,5-dimethyl-2-(4-methoxyhyphenyl)drazono)cyclohexane-1,3-dione(**CL**[1]).

The purpose of determining various parameters by XANES is to provide a better platform for further investigation of their biological, chemical, pharmaceutical, and medicinal properties, and to predict the chemical behavior of complexes
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II. EXPERIMENTAL

The Cu (II) complex of 5,5- dimethyl-2-(4-methoxyphenyl)hydrazono)cyclohexane-1,3-ione(**CL**[1]) studied in this paper, were chemically synthesized at School ofChemistry, DAVV, Indore, India[5,6,7].

X-ray absorption spectroscopy (XAS) in our complex was completed by the EXAFS dispersive beamline BL-8 in a 2.5 GeV synchrotron called Indus-2 established at Raja Ramanna Centre for Advanced Technology (RRCAT) Indore, India was recorded [8]. A complete absorption spectrum was recorded in one scan. Experimental data were analyzed with the software package Athena (Demeter 0.9.25) available on the **xafs.org** website.

The XRD patterns are made using Bruker D-8, an advanced instrument from IUC, DAE-CSR, Indore, India. XRD provides imaginative information about the crystal structure and lattice parameters of complexes. Complexes were characterized by XRD at room temperature and analyzed using the OriginPro 2016 computer software.

III. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction (XRD):
The X-Ray powder diffraction was recorded at room temperature. XRD shows many peaks in the pattern indicating that the complex (**CL**[1]) is polycrystalline. This complex is monoclinic and has a structure of space group $P_1 2_1/c_1$. The average crystalline structure size was calculated by Debye Scherrer formula-

$$\sigma = \frac{0.9\lambda}{\beta cos\theta}$$

Where λ is X-ray wavelength, θ is the Bragg angle, and β is the FWHM (Full Width at Half Maxima of diffraction

peak) Dislocation densities were calculated using the following formula-
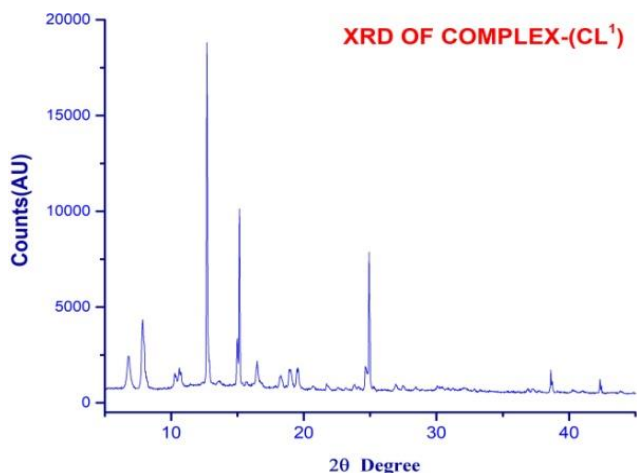
$$\delta = \frac{1}{\sigma^2}$$

Figure1. X-Ray diffraction pattern of Complex (**CL^1**)

Details of crystallographic data collection for the complex (**CL^1**) are summarized in following Table 1.

Table 1. Details of crystallographic data of complex (**CL^1**)**.**

Crystallographic data	Value for Complex (**CL^1**)
Empirical formula	C17O6H22N2Co
Formula weight	409.34
Crystal System	Monoclinic
Space group	P1 21/c1
a (Å)	18.23
b (Å)	14.48
c (Å)	18.63
α°	90.00
β°	94.50
γ°	90.00
Volume (Å^3)	4917.77
Density(gram/m^3)	2.634
Particle size(nm) σ	44.56
Dislocation Density(nm^{-2}) δ	5.04X10^{-4}

3.2 XANES Study:

Using the relation-

$$I_t = I_0 e^{-\mu x}$$

Where μ is the absorption coefficient and x is the absorber thickness.

$\mu(E)$ corresponds to the photon energy of the X-ray radiation used. The XAFS spectra were plotted for the **Cu metal** and complex (**CL^1**)
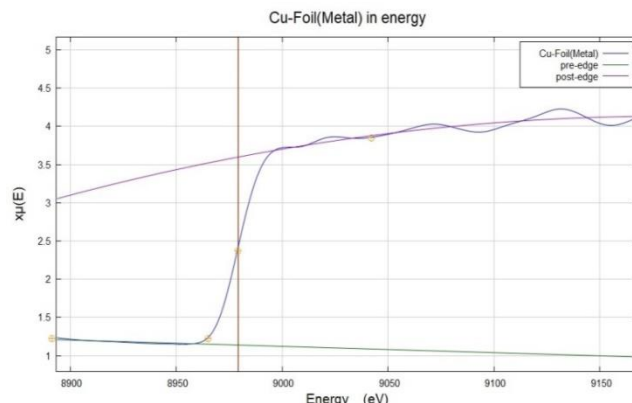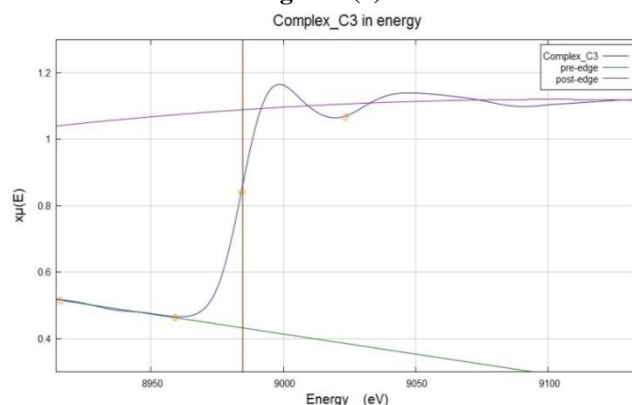

Figure 2(a).

Figure 2(b).

Figure-2. $\mu(E)$ Vs energy plot of Cu metal and Complex (CL^1)

Differential spectra are shown in Figure 4(a) and (b). The first peak in the spectrum marks the position of the K absorption edge (E_k), and the first minimum with zero derivative corresponds to the position of the principal absorption maximum (E_A). The K-edge energies (E_k) and the principal absorption maxima (E_A) of copper are shown in Table2 below, along with the chemical shift value, edge width, effective nuclear charge (ENC), and percentage covalency of complex (**CL^1**).
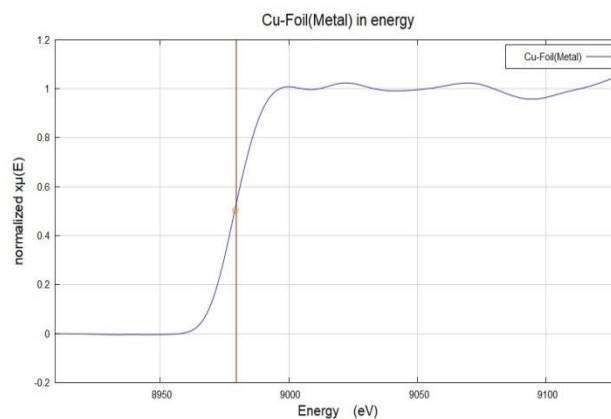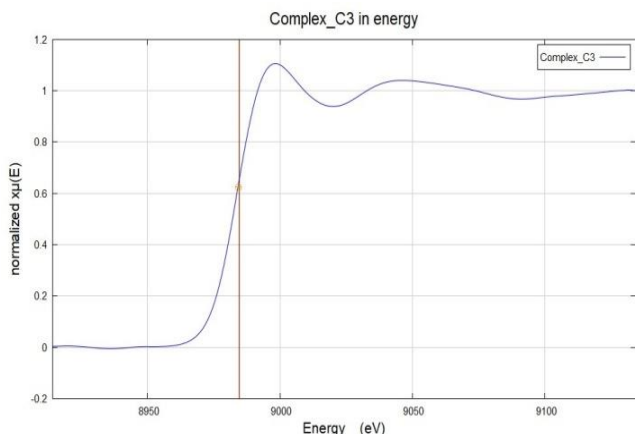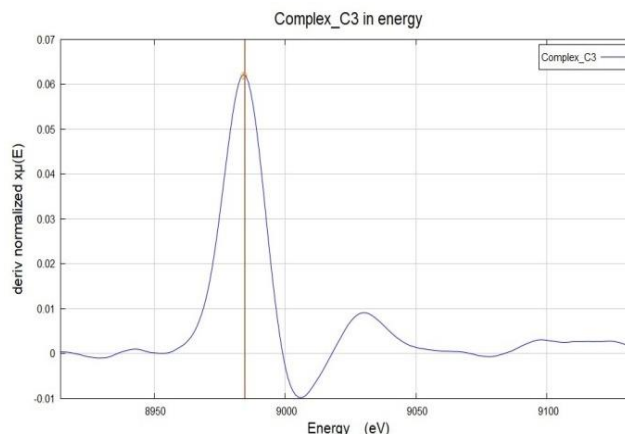

Figure 3(a)
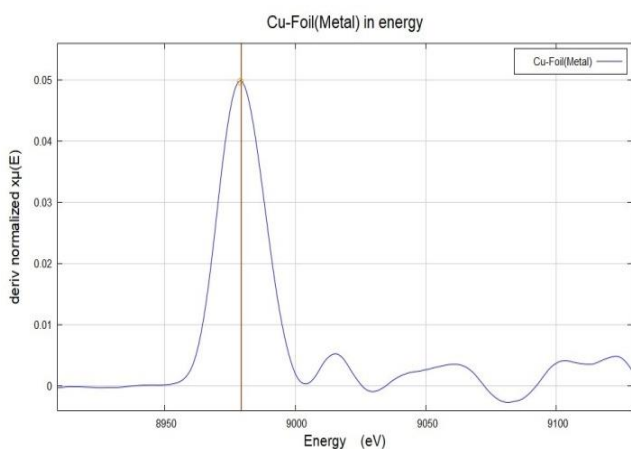
Figure 3(b).

Figure 4(b)

Figure 4(a)

3.2.1 Chemical Shift

The shift from the X-ray absorption edge of the element in a complex to that of the pure element is given by-

$$\Delta E_k = E_k(\text{Complex}) - E_k(\text{Co metal})$$

Based on the chemical shift values, the complex has the +2 oxidation state of copper. The chemical shift value of complex (CL^1) is **5.09eV.** Ionic bonds enhance the chemical shifts, while covalent bonds suppress chemical shifts [9-10].

3.2.2 Principal Absorption Maxima

Table 2 shows that dominant absorption maxima of the complexes are shifted to lower energies compared to Cu metal [11].

Table 2. XANES data for K-absorption edge of Cu metal and studied Complex C1

S. No.	Metal / Complex	E_k (eV)	E_A (eV)	Chemical Shift (eV)	Shift of Principal Absorption Maxima (eV)	Edge Width (eV)	ENC Electron /atom	Percentage Covalency
1	**Cu Metal**	**8979.1**	**9003.9**	-		**24.85**	-	**85.69**
2	**Complex C1**	**8984.2**	**8999.1**	**5.09**	**4.8**	**14.95**	**0.35**	**51.55**

The order of shift of the major absorption maxima of the complex is the reverse order of the chemical shift. This reverse order confirms that the shift in the main absorption maxima is inversely proportional to the ionic properties of the complex. The main absorption maxima were shifted by a value of -4.81 eV for the complex (CL^1) listed in Table 2.

3.2.3Edge width: In Table 2, we calculated the edge width (E_A-E_k) values of **24.85eV** and **14.95eV** for the Cu metal and the complex (CL^1), respectively.

3.2.4.Effective Nuclear Charge: The effective nuclear charge of copper in the complex is calculated at **0.35** electrons/atom for the complex (CL^1) in the current study [12].

IV. CONCLUSION

In the current work XRD and XANES data analysis and calculations were performed for Cu metal and its complex (CL^1). We investigated the XRD patterns to find out the crystal structure, space group, grain size, etc. The chemical shift, the shift of the main absorption maximum, and the edge width of the complex are calculated as 5.09 eV, -4.81 eV, and 14.95 eV [13]. The value of effective nuclear charge (ENC) value is 0.35 for the complex (CL^1). Chemical shift value suggests that copper is in the +2 complex oxidation state [14]. The overall results of the studied complexes may be useful for applications in biomedical, chemical and pharmaceutical fields.

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