XANES AND EXAFS STRUCTURAL STUDIES OFBIOLOGICALLY RELEVANT COPPER (II) COMPLEXES OF ARYLHYDRAZONE DERIVATIVES

Pankaj Agrawal[1]*, Pradeep Sharma[2], Ashutosh Mishra[3]

Abstract:
X-Ray absorption fine structure studies of Schiffbase copper(II) complexes were performed. Arylhydrazone derivatives, a primary ligand of copper complexes used in the study, were 5,5-dimethyl-(2-(4-nitrophenyle) hydrazono)cyclohexane-1,3-dione and 5,5-dimethyl-(2-(4-chlorophenyl)hydrazono) cyclohexane-1,3-dione.The crystalline nature and presence of specific functional groups of the copper (II) complexes were confirmed by X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR),respectively. The X-ray absorption near edge structure(XANES) data have been analyzed to calculate the K-edge shift, principal absorption maximum shift, edge width, and chemical shift. The experimental value of chemical shift is in accordance with the principal absorption maximum shift, indicating that the copper is in an oxidation state +2 in the sample. Effective nuclear charge (ENC) and percentage covalency were calculated from chemical shift and edge width, respectively. The first shell bond length was calculated using extended X-ray absorption fine structure (EXAFS) following different graphical methods. Fourier transforms of the normalized spectra have also been used to obtain bond length.

Keywords: XANES, EXAFS, XRD, FTIR, Chemical Shift, Athena, Edge Width

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1. Introduction:

In many different domains, including analytical, biological, and inorganic chemistry, Schiff base copper(II) complexes are among the most frequently utilizedclasses of organic molecules. Due to a wide range of biological actions, including anti-inflammatory,analgesic, antibacterial, anti- convulsant, antitubercular, anticancer,antioxidant, and so forth, Schiff bases have grown in importance in the medical andpharmaceutical industries [1,2]. As building blocks for prospective anti-diabeticmedications, aryl hydrazones of cyclic 1-3 diones have been widely employed [3-6]. Additionally, these complexes were employed as medications for cardiovascular disease,cancer, and anti-inflammation [7-11]. In particular chemical reactions, such as the Hennery reaction, it functions as an active catalyst [12]. Copper (II) complexes are alsothe essential components of supramolecular devices because of their advantageous excited state and quantifiable characteristics. The use of copper complexes is also advantageous in photochemistry, photophysics, and biochemistry. Because of their utility, there is an expanding market for Schiff-base coordinationcomplexes produced by reacting transition metal ions, especially copper. In the present paper, we investigated X-ray absorption fine structure XANES and EXAFS, X-ray diffraction XRD, and FTIR patterns of Cu (II) complexes of 5,5-dimethyl-2-(4-nitrohydrono) cyclohexane-1,3-dione(CL^1) and 5,5- dimethyl-2-(4-chlorohydrono)cyclohexane-1,3-dione(CL^2). X-ray absorption spectroscopy is an excellent tool to determine the electronic and geometrical structure of transition metal complexes. It helps in studying the structure around selected elements contained within a material at the atomic and molecular scales.

It can be applied to materials as well as crystals. This technique is classified into XANES (X-ray absorption near edge spectra) and EXAFS (Extended x-ray absorption finestructure). This study aims to determine the shift of K-edge, a shift of principal absorption maximum, edge width, chemical shift, effective nuclear charge (ENC), and percentage covalency from the XANES study. By EXAFS study, first shell bond lengths of complexes by three graphical methods, viz. Levy's, Lytle's, and LSS were determined. Fourier transforms of the normalized EXAFS spectra were used to calculate bond length. The XRD pattern was investigated to find crystalline structure, space group particle size, etc., and the FTIR pattern was used to confirm functional groups present in the complexes. The purpose of determining the different parameters by XANES and EXAFS is toprovide a better platform to study further biological, chemical, pharmaceutical, andmedicinal properties that will help to predict the chemical behavior of complexes.

2. Experimental:

The samples were prepared by the method reported in the literature [13]. All the chemicals used are in pure grade. The Cu (II) complexes of 5,5- dimethyl-2-(4-nitrohydrazono) cyclohexane-1,3-dione (**CL^1**) and 5,5- dimethyl-2-(4-chlorohydrazono) cyclohexane-1,3-dione(**CL^2**) studied in this paper, has been synthesized by chemical route method at School of Chemistry,DAVV, Indore, India[13,14,15,16]. The chemicals used in the present work are 5,5-dimethylcyclohexane-1,3-dione(dimedone), 4-nitrophenyl, 4-chlorophenyl, ethanol, sodium hydroxide, sodium acetate, sodium nitrate, hydrochloric acid, Calcium chloride, $Cu(Oac)_2.2H_2O$. All the complexes synthesized are in powder form.

X-ray diffraction (XRD) is a resourceful non destructive technique that gives perfect information about the chemical composition and crystallographic structure of materials[17]. The pattern has been indexed using joint committee for power diffraction (JCPDF) software. The XRD pattern is made by using Bruker D-8, an advanced instrument at IUC, DAE-CSR, Indore, India. Complexes were characterized by XRD at room temperature and analyzed by the computer software OriginPro 2016.

Dispersive extended X-ray absorption fine structure (DEXAFS) beamline BL-8 at the 2.5GeV synchrotron Indus-2 at RRCAT Indore, have been utilized for recording the X-ray absorption fine structure (XAFS) spectra according to the procedure outlined in ref.[18].For the XAFS measurements appropriate amount of powder of complexes were thoroughly mixed with cellulose in a gate mortar and pressed in the form of a thin pellet. To select a band of energy from a white synchrotron beam, a bent crystal (Si 111) polychromator is used in this beamline, which is horizontally dispersed and focused on the sample. A position-sensitive CCD detector is used to record the transmitted beam intensity from the sample, thus the whole EXAFS spectrum around the absorption edge takes place in a single shot [18]. For data analysis computer program Athena(Demeter 0.9.25) was used available at the website xafs.org.

In the 4000-500cm^{-1}, the IR spectra were recorded at the School of Pharmacy, SGSITS Indore, India.

3. Result and discussion:

3.1 X-Ray Diffraction: The X-ray diffraction data of the 5,5- dimethyl-2-(4-nitrohydrazono) cyclohexane-1,3-dione (**CL^1**) and 5,5- dimethyl-2-(4-chlorohydrazono) cyclohexane-1,3-dione(**CL^2**) were recorded at room temperature using Cu Kα radiation. XRD patterns of the complexes were shown in figure1and figure2. The pattern indicates poly crysttelline nature of the complexes. The parameters calculated by the diffraction data were listed in Table-1. The diffraction pattern was recorded between 2θ ranging from 0^o to 60^o. The complexes were found in monoclinic crystal lattice with space group P_12_1/n_1 and C_12/n_1. The prominent peaks of the complexes have been identified by JCPDS software.

The average crystalline structuresize was calculated by Debye Scherrer formula-

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

Where K=0.9 geometric factorλ=1.504Åis the wavelength of X-rays, θ is Bragg's angle, β is FWHM Full Width Half Maxima of main diffracted peaks[19] Dislocation density was calculated by the following relation-

$$\delta = \frac{1}{\sigma^2}$$

XRD pattern of complexes **CL^1** and **CL^2** are shown in following figure1.

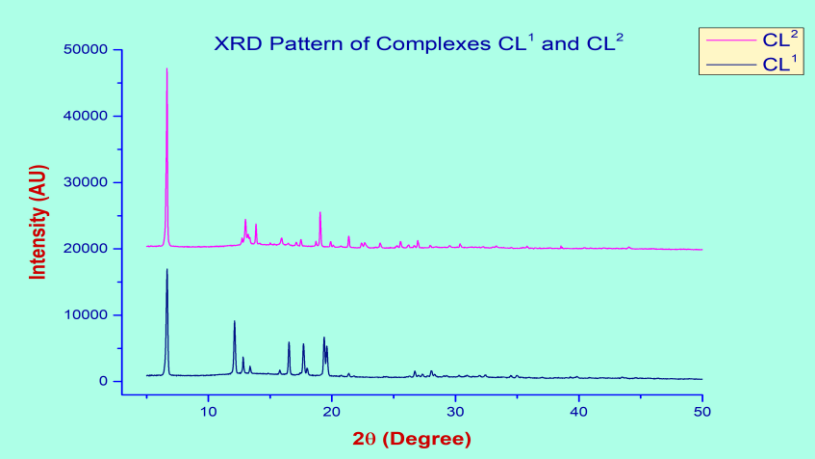


Figure 1. XRD Pattern of Complex **CL^1** and Complex **CL^2**.

Table-01- Crystallographic data for the complexes **CL^1** and **CL^2**

	Complex- **CL^1**	Complex- **CL^2**
Empirical Formula	$C_{16}H_{19}CuN_3O_7$	$C_{16}H_{19}CuClN_2O_5$
Formula weight	428.88	418.33
Crystal System	Monoclinic	Monoclinic
Space group	P1 21/n1	C 1 2/m 1
a (Å)	17.64	17.43
b (Å)	14.63	20.20
c (Å)	17.69	14.26
α°	90.00	90.00
β°	104.46	106.52
γ°	90.00	90.00
Volume (Å^3)	4565.32	5020.75
Density(gram/cm^3)	4.48	2.89
Particle size(nm)	36.67	37.95
Dislocation Density(nm^{-2})	7.43X10^{-4}	6.94X10^{-4}

3.2FTIR : To identify functional groups (chemical bonds) present in compounds, FTIR is an effective investigation technique. In the 4000-500cm^{-1}region,the FTIR spectra of the CL^1 and CL^{2}complexes were recorded. Figure2 presents a comparison of the infrared spectra of the CL^1 complex and the CL^2 complex, measured in the 4000-500cm^{-1} region.

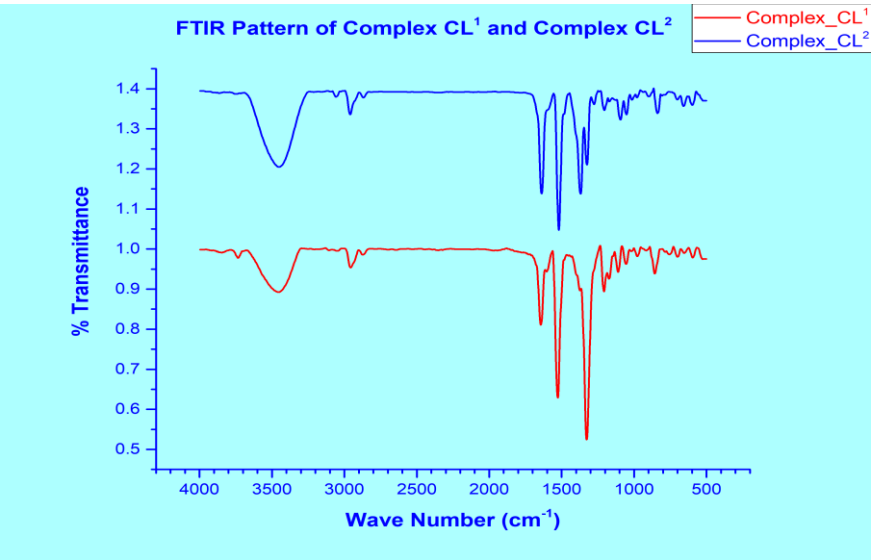


Figure 2. Combined FTIR Pattern of Ligand, Complex C1 and Complex C2.

Hydrated complexes are indicated by the presence of the water molecule indicated by v(OH) group in the broad band of the region 3445–3449cm^{-1} in the FTIR spectrum. The bands attributed tov(C=O andC=O...H) observed in the FTIR at 1674 cm^{-1} and 1620cm^{-1}, respectively. The band in spectral region of 2943cm^{-1} arises from a v(NH) group. Strong bands corresponding to the range 1387-1399cm^{-1} indicate the presence of a v(COO-) coordinated carboxylate group. The peaks between 3043 and 3086 cm^{-1} are depicted as (CH_{arom}) stretching in the spectra of the complexes.

3.3 XANES Study : When a monochromatic beam of X-rays of energy E, passes through a homogeneous sample of the thickness x, then according to Lambert-Beer law –

$$\mu(E)x = log\left(\frac{I_0}{I_t}\right)$$

Where I_0 and I_t are the intensities of incident and transmitted X-rays, $\mu(E)$ is the linear aborption coefficient, which describes how strongly X-rays are absorbed as a function of X-rays energy E. X-ray absorption fine structure are devided in two parts XANES and EXAFS region.[20-25].

XANES occurs in the region from the edge to approximately 40eV above the edge. XANES are the result of multiple scattering [26]. First peak in the derivative spectrum indicates the position of first K-absorption edge E_k. The point where the derivative is zero, gives the position of principal absorption maxima(PAM) E_A.

The XAFS spectra have been plotted for Cu metal, Complexes CL^1 and CL^2 are shown in following figure 3. The curves in the figure 3 correspond to normalized K-absorption spectra.

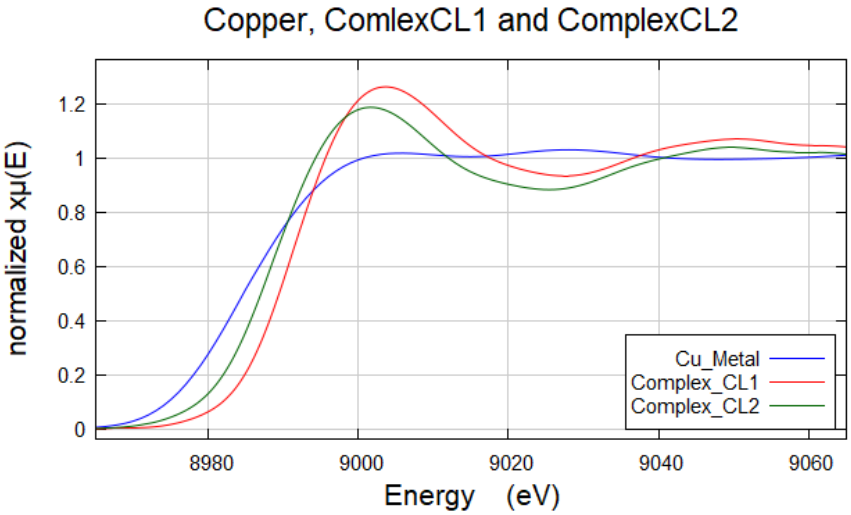


Figure 3. Normalized X-ray absorption spectra of Cu Metal, complexes CL^1 and CL^2.

Derivative spectra shown in figure 4, the initial maxima specified the point of K-absorption edge (E_k), and the initial minimum at zero derivatives match to the position of PAM (E_A).

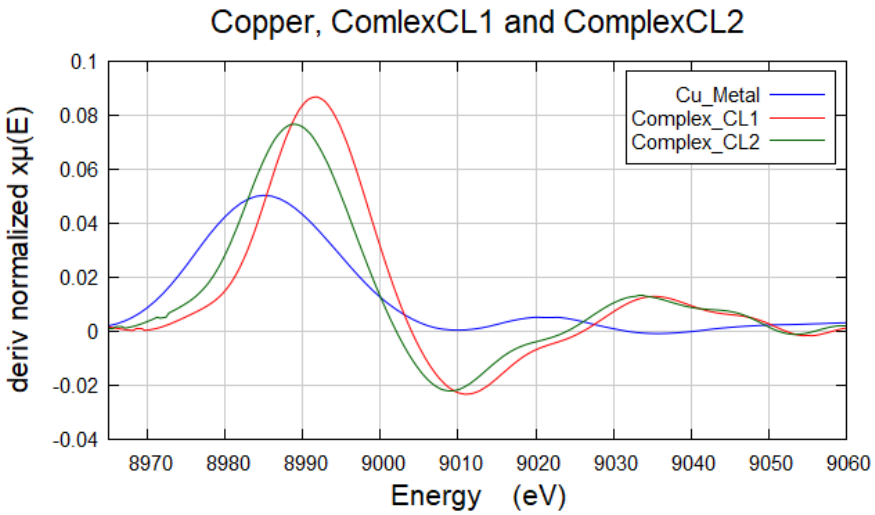


Figure 4. Derivate of XAFS spectra ofCu Metal, complexes CL^1 and CL^2.

The summary of the calculated values of copper K-edge energies (E_k), PAM (E_A), chemical shift, edge width, ENC and percentage covalency of Complexes CL^1 and $CL^2$are given in following table2.

Table 2.XANES data of Cu Metal, complexes CL^1 and CL^2.

S No.	Metal / Complex	E_k (eV)	E_A (eV)	Chemical Shift (eV)	Shift of Principal Absorption Maxima PAM (eV)	Edge Width (eV)	ENC Electron /atom
1	**Cu Metal**	8985.03	9009.32	--	--	24.29	
2	**Complex** CL^1	8991.58	9003.97	6.55	-5.35	12.39	0.45
3	**Complex** CL^2	8988.78	9000.42	3.75	-8.9	11.64	0.26

3.3.1. Chemical Shift:The chemical shift is given as-$\Delta E_k = E_k(\text{Complex}) - E_k(\text{Cu metal})$
Chemical shift data of the complex indicated that the copper metal has a +2 oxidation state in complexes.Chemical shifts of 6.55eV and 3.75eV were found for complexes CL^1 and CL^2, respectively. Ionic bonding extends the chemical shift, while covalent bonding obstructed it [27].

3.3.2. Principal Absorption Maxima(PAM): The PAM is given as-
$\Delta E_A = E_A(\text{Complex}) - E_A(\text{Cu metal})$

Table 2 shows that PAM moved to lower energies [27]. Moreover, the PAM shift of complex CL^2 was greater than that of complex CL^1. As noted in Table 2, PAM shifted by -5.35eV for complex CL^1 and -8.9eV for complex CL^2. The shift of PAM of complexes is in the opposite direction of chemical shifts. These reversible orders demonstrate that the change in the PAM is contrary correlated with the ionic nature of the complexes.It can be concluded that copper is in the +2 oxidation state in this complex.

3.3.3. Edge width: In Table 2, edge width (E_A-E_k) values were evaluated as 24.29eV, 12.39eV and 11.64eV for Cu metal, complex CL^1 and complex CL^2, respectively.

3.3.4. Effective Nuclear Charge(ENC):The ENC of copper in the complexes studied here is calculated to be 0.45 electrons/atom for complex CL^1 and 0.26 electrons/atom for complex CL^2 [28].

3.4 EXAFS Study : Beyond the edge by about 40 eV to 1000 eV, the EXAFS region increases [29]. In the current study, nearest neighbor bond lengths were calculated using Fourier transform methods and Levy's, Lytles, and L.S.S. used to compare results.

3.4.1. Levy's Method: By the Levy's Method, the bond length is given by-

$$R_1 = \left[\frac{151}{\Delta E}\right]^{1/2}$$

Where ΔE is the energy difference between the maximum B and minimum β in the EXAFS spectrum and R_1 is the radius of the initial coordination sphere. Using the data calculated in Table3, bond lengths of 1.74Å and 1.72Å were determined for the complex CL^1 and complex CL^2, respectively, as reported inTable4.[30].

3.4.2. Lytle's Method : In Lytle's Method the bond length is given by-

$$R_s = \left[\frac{37.60}{M}\right]^{1/2}$$

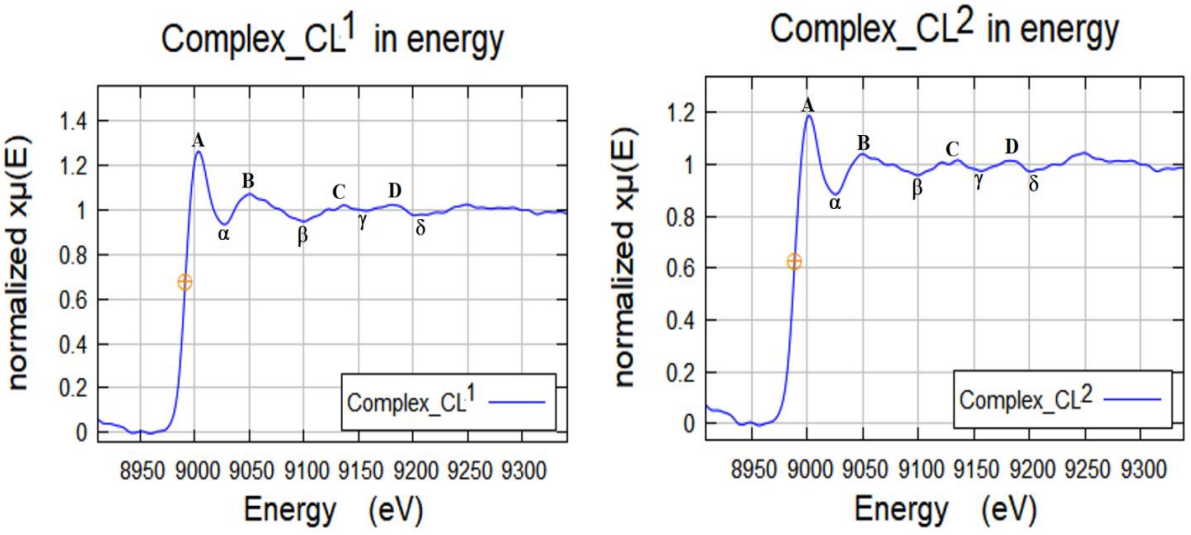
Where M is the gradient of Q-E graph. Using the data calculated in Table3, bond lengths of 1.92Å and 1.90Å were determined for the complex CL^1 and complex CL^2, respectively, as reported in Table4. [31].

3.4.3. L.S.S. Method : The nearest neighbor distance (R_1-α_1) is given by-

$$\frac{2(R_1 - \alpha_1)}{\pi} = Slope\ of\ k - n\ plot$$

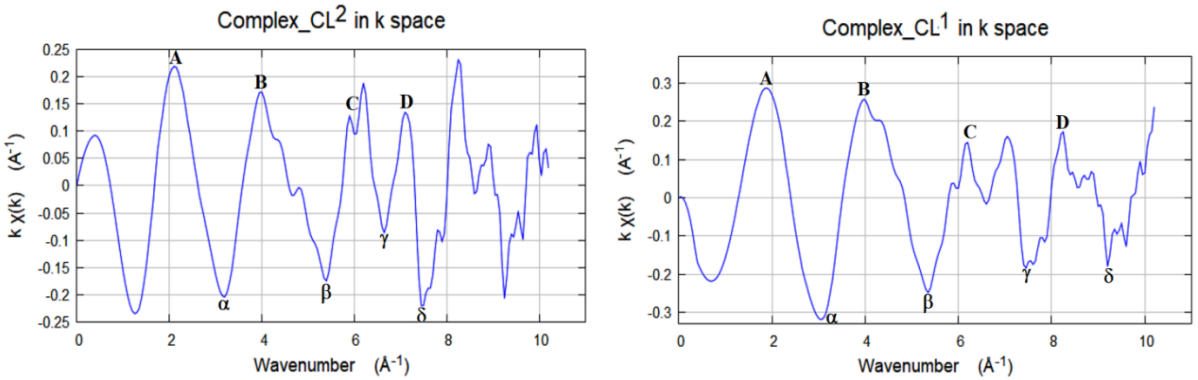
Using the data calculated in Table3, bond lengths of 1.21Å and 1.38Å were determined for the complex CL^1 and complex CL^2, respectively, as reported inTable4.

3.4.4.Fourier transform method : Figure 7 shows the Fourier transform spectra obtained from the χ(k)-k curves of complex CL^1 and complex CL^2. The positions of the first peaks in the Fourier transform spectra provide the phase-corrected bond lengths (R) each for the complexCL^1 andcomplexCL^2, as specified in Table 4. are, 1.35 Å, 1.49Å.



5(a) **5(b)**

Figure 5(a and b). Normalized X-Ray absorption curves of complexes CL^1 and CL^2.

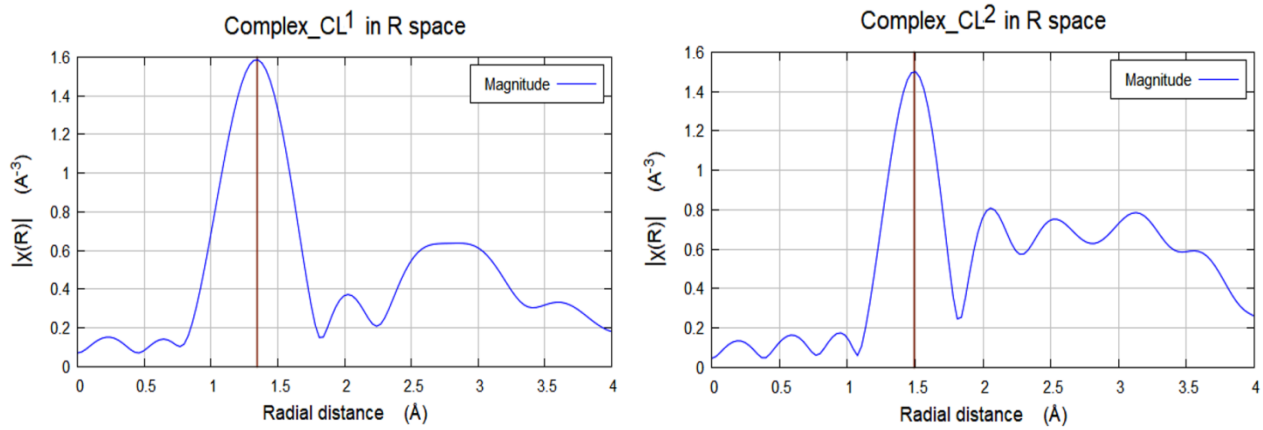


6(a) **6(b)**

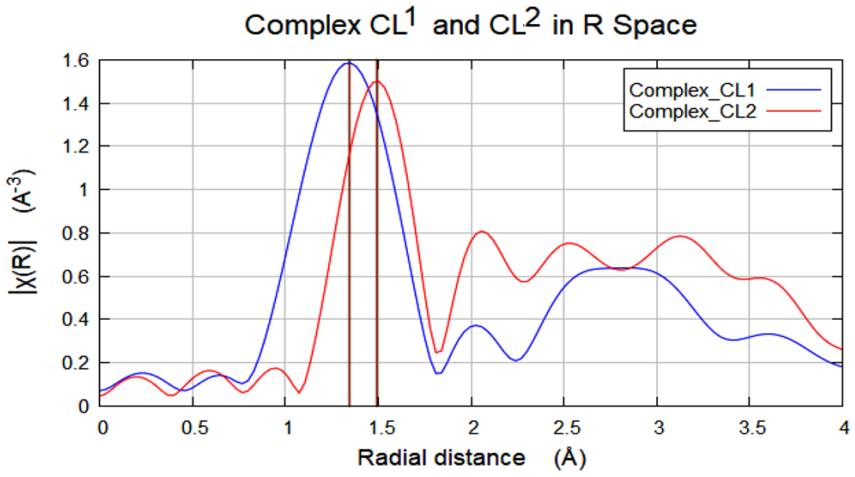
Figure 6 (a and b).χ(k)-k data of complexes CL^1 and CL^2.

Table 3. Energy E(eV), wave vector k(Å^{-1}) of complexes CL^1 and CL^2 obtained fromFigures 5 and 6,the corresponding n values as well as energy level Q.

Structure	n	Q	Complex CL^1		Complex CL^2	
			E (eV)	k(Å^{-1})	E (eV)	k(Å^{-1})
A	**0**	**2.04**	11.88	1.90	12.90	2.10
α	**1**		36.31	3.07	36.39	3.19
B	**2**	**6.04**	58.30	4.07	60.94	4.01
α	**3**		107.98	5.35	111.44	5.40
C	**4**	**12.00**	136.49	6.59	137.68	610.11
α	**5**		167.44	7.65	167.91	6.66
D	**6**	**20.00**	192.24	8.23	196.54	7.11
α	**7**		209.81	9.20	210.06	7.52



7(a) **7(b)**



7(c)

Figure 7(a,b and c). Magnitude of Fourier Transform of Complex CL^1, Complex CL^2 andFouriertransforms of Combined Complex CL^1, Complex CL^2

Table 4. Bond length valuesobtained for the complexes CL^1 and CL^2.

S.No.	Name of Complex	Phase Corrected		Phase uncorrected	
		Levy's method Å	Lytle method Å	L.S.S. Method R1- α1 Å	F.T. method R Å
2.	**Complex** CL^1	1.74	1.92	1.21	1.35
3.	**Complex** CL^2	1.72	1.90	1.38	1.49

4. Conclusion

In the current work, calculations of copper metal and its complexes CL^1 and CL^2 were performed using XRD, FTIR, XANES and EXAFS data [32]. FTIR patterns were used to confirm the presence of functional groups and structural parameters in the investigated complexes. The X-ray diffraction patterns were examined to determine the crystal

structure, space group, particle size, etc. The chemical shifts, PAM shifts and edge widths of the complexes were calculated to be 6.55eV, 5.35eV and 12.39 eV for complex CL^1 and 3.75eV, −8.9eV and 11.64eV for complex CL^2, respectively. Compared to copper metal, PAM is shifted to lower energies. Moreover, PAM from complex CL^2 shows a higher shift than complex CL^1. The PAM shift of the complex is opposite to the chemical shift. These reversible orders demonstrate that PAM changes are inversely proportional to complex ionicity [31–32]. The effective nuclear charge (ENC) values for complexes CL^1 and CL^2 are 0.45 and 0.26 electrons/atom, respectively. According to chemical shift values, copper is present in both complexes in the +2 oxidation state [33]. Three graphics approaches: Levy's, Lytle's and L.S.S. approach was used to determine the bond length of the complex from the maximum and minimum values of EXAFS. Bond lengths were determined using Athena software. The bond lengths calculated using the Lytle, Sayers, and Stern (L.S.S.) method and the results of the Fourier transform method are in strong agreement. Applications in the biological, chemical, and pharmaceutical industries in general can benefit from the results of the studied conjugates.

5. References

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