XANES and EXAFS Studies of Copper(II) Complexes of 1,4-Dihydrquinoxaline-2,3-dione

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Abstract

Two copper (II) complexes of 1,4-Dihydrquinoxaline -2,3- dione have been prepared. The two complexes are [$CuCl_2.2H_2O$]-L and [$Cu(SO_4)_2.7H_2O$]-L where L = 1,4-Dihydrquinoxaline -2,3- dione . The ligand 1,4-Dihydrquinoxaline -2,3- dione has been preapared by mixing o-phnylenediamine and oxalic acid dihydrate . Synchrotron radiation source which is available at RRCAT(Raja Ramanna Center for Advance Technology), Indore, M.P, India has been used for recording the X-ray k-Absorption Near Edge (XANES) and Extended X-ray K-Absorption Fine Structural (EXAFS) spectra of copper(II) complexes. Various X-ray absorption parameters e.g., chemical shift, edge-width and shift of the principal absorption maximum have been obtained with the help of XANES spectra. The EXAFS data obtained has been used to determine the bond length by using four different methods, i.e., Levy's, Lytle, Lytle, Sayers and Stern's (LSS) and Fourier transformation methods. Data analysis program Athena and the computer software Origin 6.0 professional have been used to processed the obtained data. The results of the study have been reported in this paper.

Keywords: Mixed ligand Copper(II) complexes,RRCAT, XANES, EXAFS,LSS, Athena, , Origin 6.0 professional

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Introduction

Quinoxaline derivatives exhibit a wide variety of biological activities. It has been reported that some quinoxalines demonstrated antibacterial, antifungal, antiviral, antineoplastic, antidepressant, hypoglycemic, anti-inflammatory, excitatory amino acid antagonistic , antiglaucoma, antiparasite, antituberculosis , anticancer , and anti HIV-1 activities [1-13].

Synchrotron radiation source is the intense source of X-rays.It is available on INDUS-2 beamline at RRCAT(Raja Ramanna Center for Advance Technology), Indore, M.P, India. It is used for recording the X-ray K-Absorption Near Edge (XANES) and Fine Structural (EXAFS) spectra of metal and its complexes. XANES has been extensively used to obtain information about the molecular structure of the absorbing atom in compounds and complexes. EXAFS yields information regarding the nearest neighbors of the central metal ions, i.e. bond length. XANES and EXAFS spectra together refers as XAFS spectra.

A search through literature reveals that no work has been done on XAFS study of the transition metal complexes of 1,4-Dihydrquinoxaline -2,3- dione. This gave us the motive to synthesis and characterization of Cu (II) complexes of 1,4-Dihydrquinoxaline -2,3- dione.

Experimental

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 [14], [15], [16]. The experimental data have been analyzed using the available computer software packages Origin 6.0 professional and Athena [17].

The complexes studied in the present investigations are [$CuCl_2.2H_2O$]-L and [$Cu(SO_4)_2.7H_2O$]-L where L = 1,4-Dihydrquinoxaline -2,3- dione . The ligand 1,4-Dihydrquinoxaline -2,3- dione has been preapared by mixing o-phnylenediamine with oxalic acid dihydrate . The complexes were prepared according to the standard method reported in literature and it's purity was checked [18].

Material

All chemicals were of analytical grade purity .Metal salts $Cu(SO_4)_2.7H_2O$, $CuCl_2.2H_2O$ were obtained from E-Merck company while O-phenylendiamine and oxalic acid dihydrate from Systerm..Ethanol absolute 99% (Fluka), NaOH 5%(Fluka), conc.HCl (Merck) and ether (Merck) were used as received from the suppliers.

[A] Synthesis of 1,4-Dihydrquinoxaline -2,3- dione

A solution of oxalic acid dihydrate (0.238mole, 30g) in H2O (100ml) was heated to 100°C and conc.HCl(4.5ml) was added, followed by O-phenylendiamine (0.204 mole, 22g) with stirring .Temperature was maintained at 100°C for 20 min. The mixture was cooled by adding ice in it. The precipitate was formed and washed with water and crystallized from 5% NaOH .

[B] Synthesis of copper(II) complexes

For the Synthesis of copper(II) complexes, hot ethanolic solution of the metal salt(0.01mol) and the ligand (0.02mol) were refluxed for 4h on a water bath at the pH 7.0-7.7 .The precipitate was filtered, washed successively with ethanol and ether and finally dried at 50^0C.

3. Results and Discussion

The curve in the Figure.1 represents the normalized K-absorption spectra. The energies of the copper K-edge (E_K) and the principal absorption maximum (E_A) along with the value of the edge-width (E_A-E_K), the chemical shift (ΔE_K) and effective nuclear charge Z_{eff} are given in Table 1.

The EXAFS spectra converted into k space have been given in Figure 3. The values of energy E and wave vector k corresponding to these maxima and minima have been shown in Table 2,which have been used to evaluate the bond length by Levy method [19]. The slope of energy level Q Vs energy E curve, shown in Figure 4, has been used to evaluate the bond length by Lytle method [20]. The slope of channel number n Vs wave vector k curve, shown in Figure 5, has been used to evaluate the bond length by LSS method [21,22]. The magnitude of Fourier transform of Figure 3 are shown in Figure 6. The bondlengths calculated by all the four methods are tabulated in Table 3.

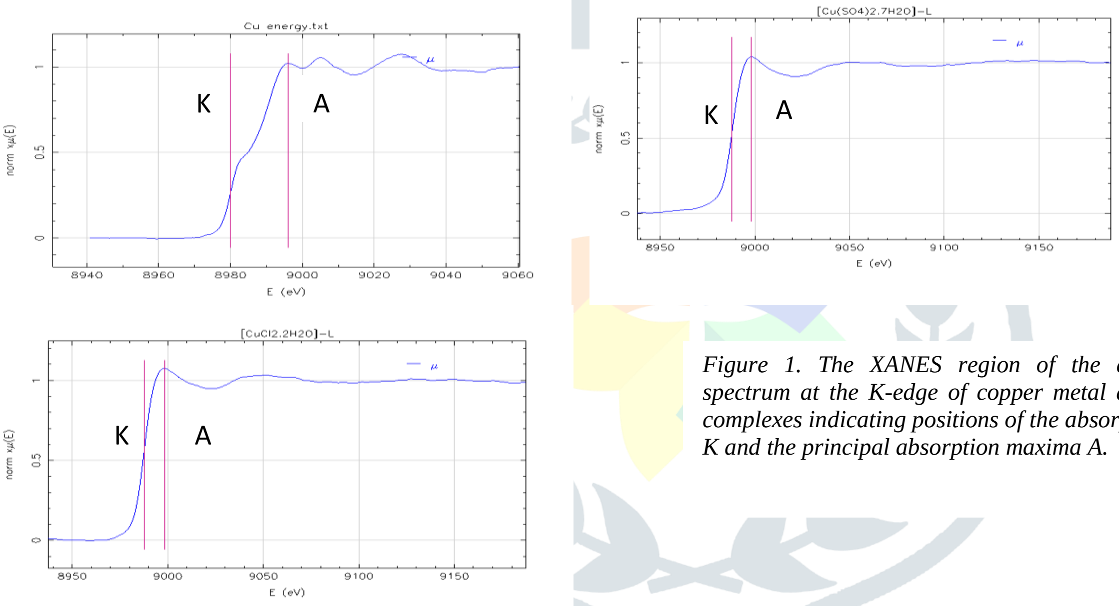

Figure 1. The XANES region of the absorption spectrum at the K-edge of copper metal and in the complexes indicating positions of the absorption edge K and the principal absorption maxima A.

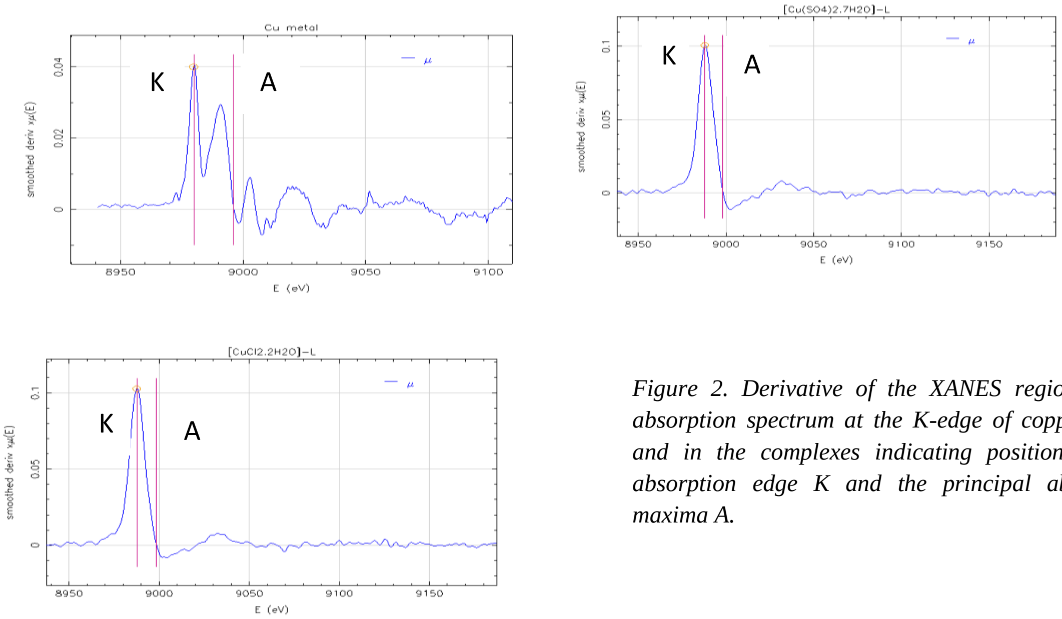

Figure 2. Derivative of the XANES region of the absorption spectrum at the K-edge of copper metal and in the complexes indicating positions of the absorption edge K and the principal absorption maxima A.

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

Complexes	E_K (eV)	E_A (eV)	Chemical shift (eV)	Shift of the principal absorption maximum (eV)	Edge-width (E_A_E_K) (eV)	ENC Electron/ atom	% Covalency
Copper metal	8980.12	8996.21	-	-	16.088	-	-
$[Cu(SO_4)_2.7H_2O]$-L	8988.13	8998.3	8.01	2.09	10.17	0.80	58.68
$[CuCl_2.2H_2O]$-L	8987.77	8998.01	7.65	1.8	10.24	0.77	78.00

1.Shape of the absorption edge

The shape of the K-absorption edges is nearly same in both the copper complexes. None of the complexes show any splitting of the k-edge.Comparing the shapes of the K-absorption edges of these complexes with those establish by Van-Norstrand [23-24] it is concluded that all the complexes have are octahedral structure.

Sinha and Mande [25] also reported the absence of splitting at low energy absorption in octahedral complexes.Katare eta [26] also reported no splitting of the k-edge in copper (II) mixed ligand complexes of aspartic acid. Mishra etal [27] also reported the absence of splitting of the K-edge of copper (II) complexes of amino acids thus indicating octahedral structure of the complexes.

2. Chemical Shift

For computing the chemical shift, the value of E_K (Cu metal) has been taken as 8980.12 eV .The shift of the X-ray absorption edge of copper in a complex with respect to that of the copper metal is written as:

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

In Table 1, the complexes have the value of chemical shift as 8.01 and 7.65 eV. 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 . Hence, on the basis of values of the chemical shift, the complexes are found to have copper in oxidation state +2 [28].

The order in which the ligand contribute to the chemical shift is as follows:

$$[Cu(SO_4)_2.7H_2O]\text{-L} > [CuCl_2.2H_2O]\text{-L}$$

As is well known, an ionic bonding enhances the chemical shift, whereas a covalent bonding suppresses it [29]. Hence, the above order may also be taken as representative of the relative ionic character of the bonding in these complexes. Hence it is clear from the Table 1 that $[Cu(SO_4)_2.7H_2O]$-L is more ionic as compared to $[CuCl_2.2H_2O]$-L.

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 the complexes studied [30].

3. Principal absorption maximum:

The data for the principal absorption maximum E_A for the complexes is also included in Table 1.

The shift of the principal absorption maximum at the K-absorption edge of copper in the complex with respect to that of copper metal has been determined according to the eqn.

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

For computing the principal absorption maximum , the value of E_A(Cu metal) has been taken as 8996.21 eV. It has been observed that the value of E_A is shifted towards the higher energy side with respect to copper metal[30].

4. Edge-width

In Table1, we have reported the values of the edge-width (E_A-E_K). Due to covalent and ionic characters o f complexes edge widths are larger and smaller , respectively.The edge-widths values are 10.17 and 10.24 eV, respectively.It should be noted that, edge widths are relatively smaller, which again support the octahedral structure of the complexes.

5. Effective nuclear charge Z_{eff}

One can define effective nuclear charge as a total charge within a certain molecular volume around the nucleus[31]. For the estimation of effective nuclear charge, various methods have been proposed [32], [33]. 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 [34]. The effective nuclear charge on the copper in the complexes under present study is 0.80 and 0.77 electrons/atom. The results show that chemical shift increases then ENC also increases. It is clearly seen that the copper complexes are more ionic.

6. Percentage covalency

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 [35]. The percentage covalency for the copper complexes under present study are 58.68 and 78.00% .

The percentage covalency in metal ligand bonding increases with decrease in effective charge. It is clear from the Table 1 that chemical shift decreases with increasing covalency.

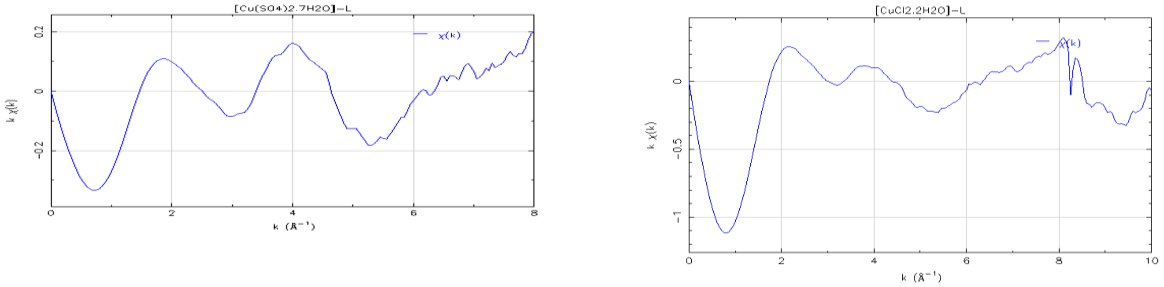

Figure 3. χ (k) versus k curve for the copper complexes

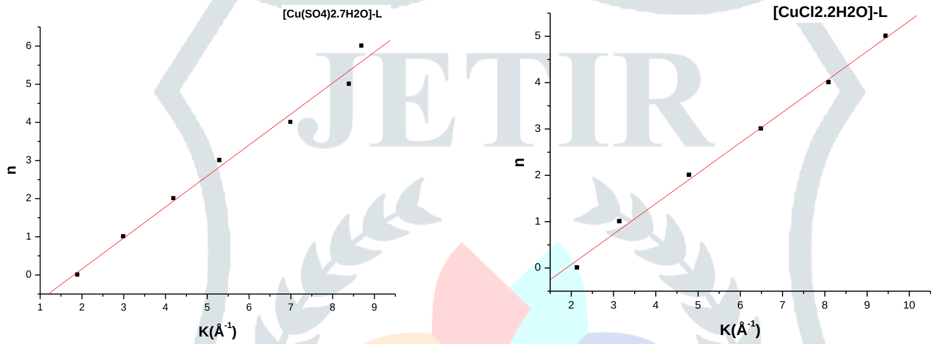

Figure 4. n versus k curve for the copper complexes

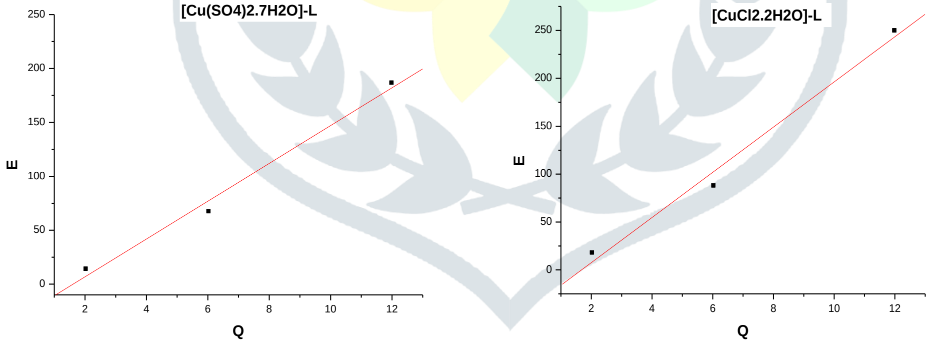

Figure 5. Q versus E curve for the copper complexes

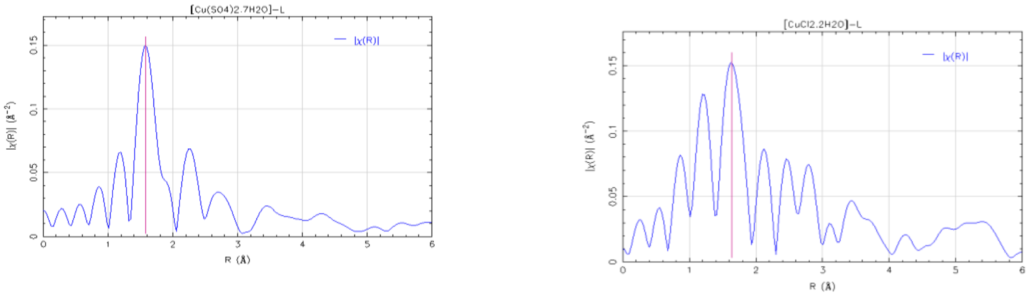

Figure 6. Magnitude of Fourier transform of the χ(k) versus k curve for copper complexes

Table 2.Energy E (eV) and wave vector k (Å^{-1}) for EXAFS maxima and minima at the K absorption edge of copper in the complexes and their corresponding values of n and energy level Q

Structure	n	Q	$[Cu(SO_4)_2.7H_2O]$-L		$[CuCl_2.2H_2O]$-L	
			E	k	E	k
A	0	2.04	13.72	1.9	17.57	2.15
α	1	-	34.22	3.0	37.72	3.15
B	2	6.04	67.07	4.2	87.60	4.8
β	3	-	106.80	5.3	160.64	6.5
C	4	12.0	186.31	7.0	249.46	8.1
γ	5	-	268.28	8.4	339.55	9.45

Table 3.Values of first shell bond lengths (in Å) calculated from Levy's, Lytle's, LSS and Fourier transform methods for the copper complexes

Complexes	Levy's method	Lytle's method	LSS method	Fourier transform
$[Cu(SO_4)_2.7H_2O]$-L	2.24	1.06	1.56	1.59
$[CuCl_2.2H_2O]$-L	2.17	1.65	1.69	1.62

Conclusions

X-ray absorption spectra of mixed ligand copper 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 shape of the K-absorption edges is nearly same in both the copper complexes.But none of the complexes show any splitting of the k-edge, thus indicating octahedral structure of the complexes. The complexes have the value of chemical shift as 8.01 and 7.65 eV.Hence, on the basis of values of the chemical shift, 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 the complexes studied. The chemical shift has been used to determine the effective nuclear charge on the absorbing atom and percentage covalency.

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 value of the chemical shift suggest that copper is in oxidation state +2 in both the complexes. From the positions of the EXAFS maxima and minima, the bond length in the complex has been determined by three different methods viz. Levy's, Lytle's and LSS methods. From the Fourier transforms of the EXAFS spectra, the bond length (uncorrected for phase shift) has been determined. It has been observed that the value of the phase-uncorrected bond length, i.e. R1-α1, as determined from LSS method and that determined from the Fourier transformation method, agree with each other within the limits of experimental error.

5.ACKNOWLEDGMENT

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