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X-ray Diffraction and X-ray K-absorption Near Edge Studies of Copper (II) Micro Cyclic Carbamide Complexes

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Abstract:-Synthesis of metal complexes [Cu (Carbamide)] (X = Br, Cl, NO_3, SO_4, CH_3COO) by the chemical root method. The XRD data have been recorded at DAE, IUC Indore. 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. XRD and XANES data have been analysed using the computer software Origin 8.0 professional and Athena. X-ray diffraction studies of all the complexes are indicative of their crystalline nature. The crystalline size of the samples is estimated using the Scherer's formula. The values of the chemical shifts suggest that copper is in oxidation state +2 in all of the complexes.

Key words – Cu (II) Carbamide complex, XRD, XANES, etc.

Introduction

The present paper includes XRD and the X-ray absorption of copper (II) micro cyclic carbamide complexes. There has been a lot of interest in synthesis structure and properties of nitrogen donor ligands particularly carbamide, thiocarbamide and its derivatives due to their wide application as pharmaceuticals [1] and in wood protection [2-5].Metal complex with ligand systems containing oxygen and nitrogen donor atoms are very important class of coordination compound and complexes. It is known that the carbamide complex of copper plays important role [6-19] .

X-ray studies of the following five copper (II) Carbamide complexes-$[Cu(NH_2CONH_2)]Br_2$, $[Cu(NH_2CONH_2)]Cl_2$, $[Cu(NH_2CONH_2)](NO_3)_2$, $[Cu(NH_2CONH_2)](SO_4)_2$ and $[Cu(NH_2CONH_2)](CH_3COO)_2$

Experimental

(a) Synthesis of copper (II) carbamide with malonic acid

Reflexed solution of Carbamide (0.002 moles) and Cu metal salt (0.002 moles) in methanol (10 mL) was added drop wise to malonic acid (0.002 moles) in methanol (40 mL). After the addition was completed; the refluxing was continued for 12 h. The precipitate was filtered and washed with methanol, then dried in air.For Carbamide

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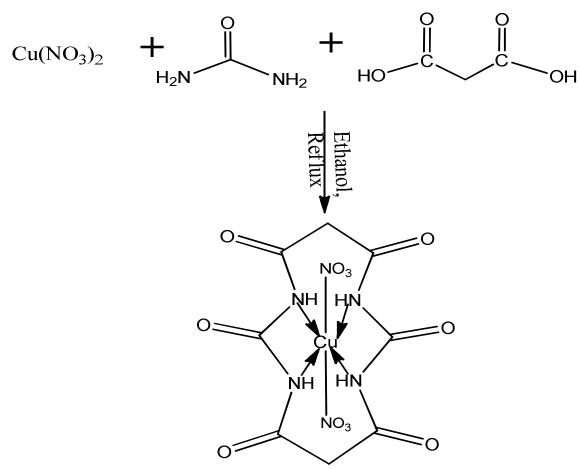


Fig 1- Chemical Scheme for copper (II) (Carbamide) Complexes.

In the present investigation, the preparation of complexes by chemical root methods, the X-ray diffraction have been recorded using bucker D8 DAE, IUC Indore, absorption spectra have been recorded using synchrotron radiation. The X-ray spectroscopic setup is available at Raja Ramanna Center for Advaced Technology (RRCAT) and is called BL-8 beamline. This beamline BL-8 has been recently commissioned at the 2.5 GeV Indus-2 synchrotron radiation sources.

Results and Discussion

The sample was characterized at room temperature by X-ray diffraction using CuKα radiation. X-ray diffraction studies of all the complexes are indicative of their crystalline nature. The diffraction pattern of complexes recorded between 2θ ranging from 10° to 80°.The particle size and lattice parameter shown in the table 1 and XANES Parameter shown in table 2.

The table 2 presents the results for the K-absorption (E_K) and the energy of the principal absorption maximum (E_A) of copper metal and its complexes .The chemical shifts (eV) of the K-absorption edge of copper in the complexes are also given in Table 2 For all the complexes the distances (in eV)of principal absorption maximum E_A with respect to the respective K –absorption edge have been computed and are collected in Table 2 .It can be readily seen from Table 2 that copper K-edge is found to be shifted towards the high energy side in all the five complexes as compared to the copper metal K- absorption edge .

Table1-Value of particle size and lattice parameter by XRD for copper (II) (Carbamide) complexes

Complexes	2θ	hkl	Particle size(nm)	Lattice parameter in Å
Copper(II)Carbamide Bromide	27.04	1,1,1	9.21	5.70
Copper(II)Carbamide Chloride	12.56	2,2,2	8.46	12.15
Copper(II)Carbamide nitrate	12.12	1,1,1	9.87	12.70
Copper(II)Carbamide sulphate	18.77	1,1,1	11.04	11.94
Copper(II)Carbamide acetate	13.76	1,1,1	10.61	11.03

Table-2 Chemical shift of K-absorption edge of Copper (II) Carbamide complexes

Complexes	E_K-Edge (eV)	E_A(eV)	Chemical Shift (eV)	Shift of principal absorption maxima (eV)	Edge width (eV)	ENC Electron/ atom	Percentage covalency (%)
Copper metal	8980.5	9003.7	-	-	23.2	-	-
[Cu(II)U](NO_3)	8992.8	8999.2	12	18	6	1.53	36.34
[Cu(II)U)] (Br)	8990.8	8996.8	10	16	5	1.03	42.75
[Cu(II)U)](Cl)	8989.8	9002.5	9	22	12	0.96	45.00
[Cu(II)U)] (CH_3COO)	8988.8	8999.7	8	19	10	0.93	47.25
[Cu(II)U)](SO_4)	8988.5	8998.5	8	18	9	0.90	49.29

Energy of copper K-edge (Practical E_K) present study =8980.5eV

Chemical Shift:-The shift of the X-ray absorption edge (i=K, L, M…..) of an element in a compound/complex with respect to that pure element is written as:

$$\Delta E_k = E_{k\,(complex)} - E_{k\,(metal)}$$

The values of chemical shifts obtained for all the complexes are tabulated in Table 1.for the present complexes, the chemical shifts values lie in the **range 8 to 12 eV.** Hence on the basis of the values of the chemical shifts, all our complexes are found to have copper in oxidation state +2.

Shift of the Principal Absorption Maxima:-In the Table 2, we have also included the data for the principal absorption maximum E_A in the complexes and metal .it has been observed that for copper metal, the value of E_A is 9003.7 eV.

The shift of principal absorption maximum depends upon the type of overlap between metal atom and the ligand orbital's. The greater the overlaps of the metal and the ligand orbital, the more stable are bonding molecular orbitals and hence the corresponding antibonding molecular orbitals are more unstable. Since the principal absorption maxima occurs due to the transitions from 1s orbital to the unoccupied antibonding molecular ($1s \rightarrow 5t_{1u^*}$ in octahedral), the principal absorption maxima, therefore, shifts to the higher energy side is towards the high energy side of the edge [9].

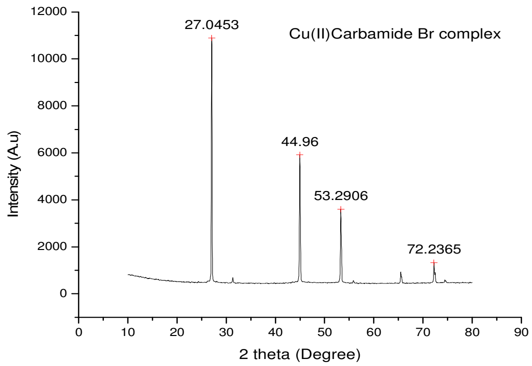
Edge Width:-The edge widths are shown in Table 1 and related to the electro negativity differences between the central metal ion and its surrounding neighbours in the co-ordination sphere according to a semi-empirical correlation proposed by Nigam and Shrivastava [9] Equation [$E_w\Sigma(X_M-X_L)]^{1/2}$= constant for given metal in given region}.Table 1 shown that the measured edge widths for the all complexes are similar. In the present work edge width of Cu (II) complexes in Table 1 are ranging from **5 to 12 eV**

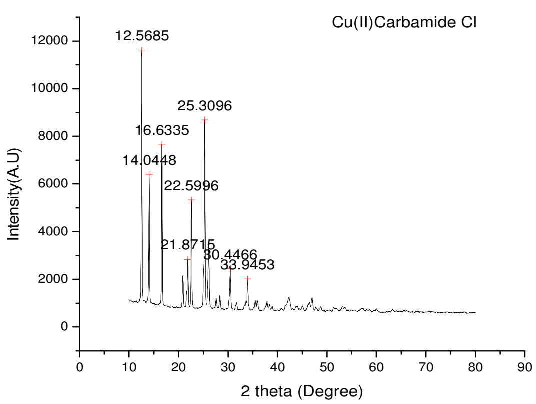
Effective Nuclear Charge:-Effective charge can be defined as a total charge within a specified volume around the nucleus. Various theoretical and phenomenological methods have been proposed for the estimation of the effective nuclear charge .In the present work effective nuclear charge has been obtained from the measured chemical shift by using the semi- experimental methods by employing the procedure suggested by Nigam and Gutpa [10].ENC on the copper in the complexes under present study varies **between 0.90 to 1.53 electrons /atom.**

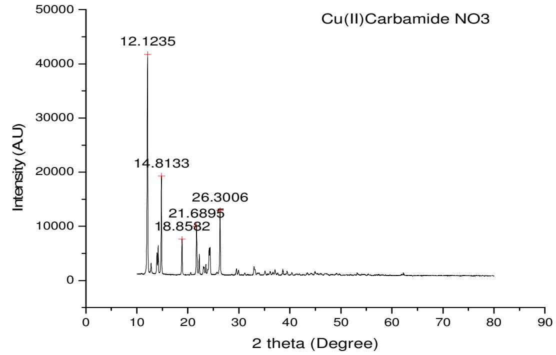
Percentage Covalency:-. The percentage covalency of metal ligand bonding in copper complexes is the ranging from **36.34 to 49.29 and they are reported in table 2.**

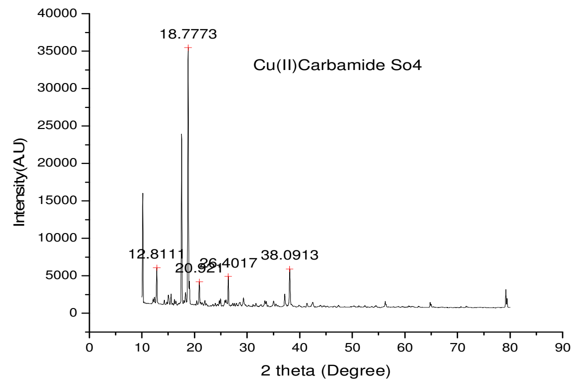
Conclusion

All the copper (II) complexes are crystalline in nature and the analysis of X-ray diffraction pattern shows that the samples exhibit simple cubic phase. The chemical shift values between 8 to 12 eV, shift of the principal maximum values between 16 to 22 eV and edge width values between 5 to12eV .The effective nuclear charges ranging from 0.90 to 1.53 electron/atom. The percentage covalency values ranging from **36.34 to49.29 %.**The values of the chemical shifts suggest that copper is in oxidation state +2 in all of the complexes.









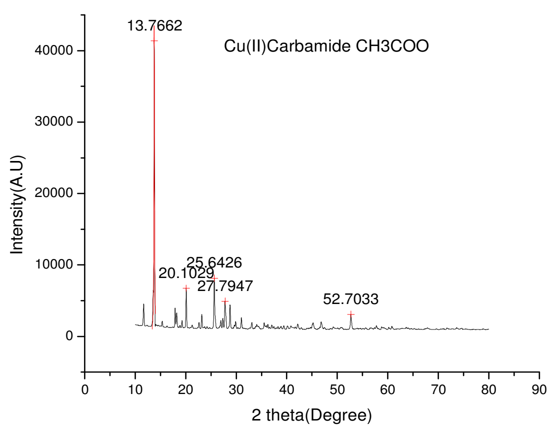


Fig.:-2 XRD pattern for Cu (Carbamide) complexes.

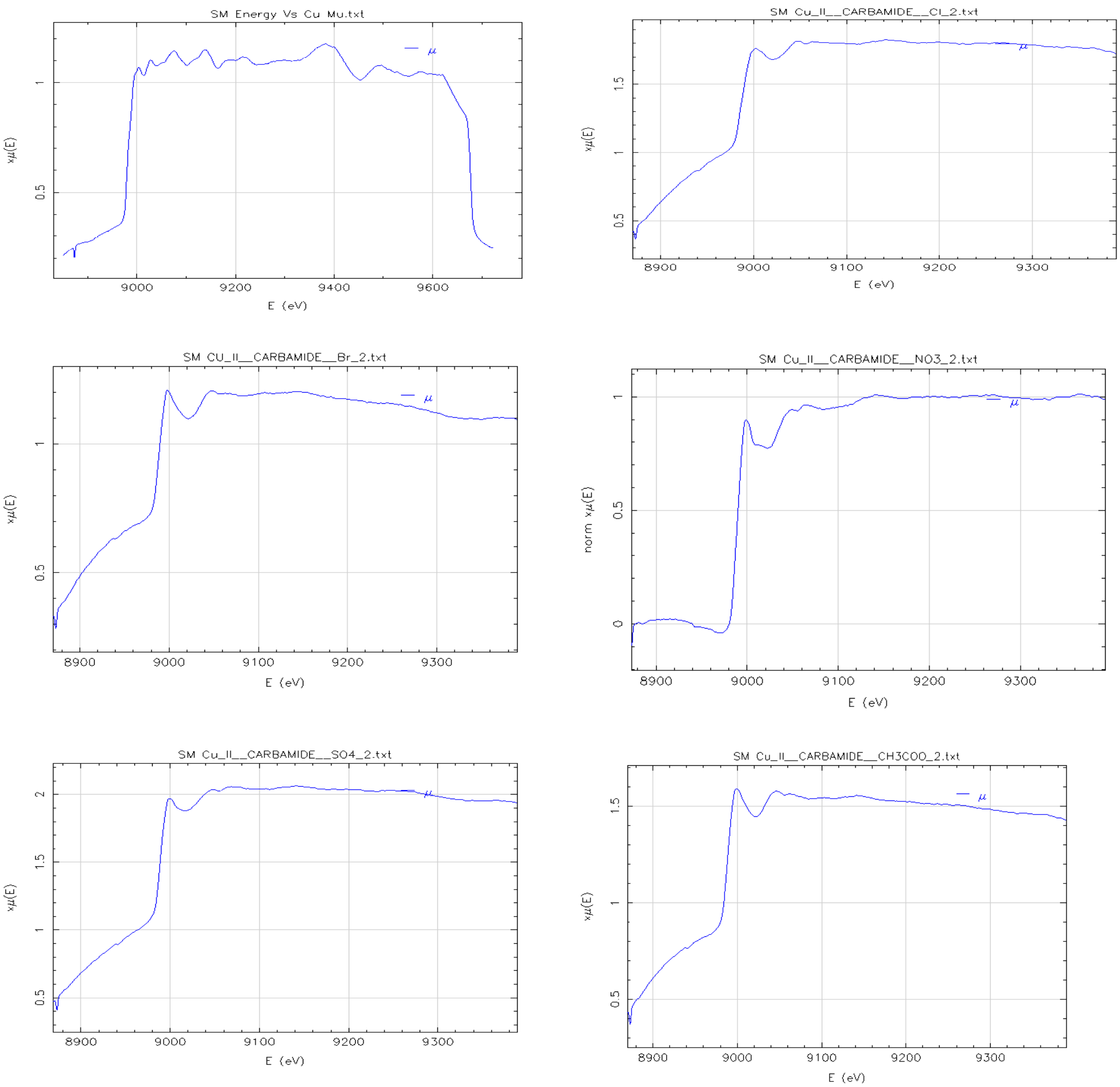


Fig2. X-ray absorption near edge structure of copper II complexes and metal foil.

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