XANES and EXAFS Studies of Copper (II) Micro Cyclic Carbamide complexes

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Abstract- Synthesis of metal complexes [Cu (Carbamide) X_2] (X = Br, Cl, NO_3, SO_4, CH_3COO) by the chemical root method. 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. XANES and EXAFS data have been analyzed using the computer software Athena.

Keywords- EANES, EXAFS, Copper (II), Carbamide

Introduction

The present paper includes 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].The metal complex with ligand systems containing oxygen and nitrogen donor atoms are very important class of coordination compound. It is known that the carbamide complex of copper plays an important role [6-13].

Experimental

The X-ray absorption spectra at the K-edge of copper of the complexes listed in table 1 have been recorded at BL-8 EXAFS beamline at the Indus-2 Synchrotron Source, Indore, India. The experimental data have been analyzed using the available computer software package Athena.

Results

Copper K-edge and the near edge structure (XANES) for all the complexes are shown in figures1 (a-d). The energies of the various absorption features are given in table 1.

Table 1. XANES data for the K-absorption edge of copper in the 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 foil	8980.5	9003.7	-	-	23.2	-	-
[Cu(II)Carbamide)](NO_3)	8992.8	8999.2	12	18	6	1.53	36.34
[Cu(II)Carbamide)] (Br)	8990.8	8996.8	10	16	5	1.03	42.75
[Cu(II)Carbamide)](Cl)	8989.8	9002.5	9	22	12	0.96	45.00
[Cu(II)Carbamide)] (CH_3COO)	8988.8	8999.7	8	19	10	0.93	47.25
[Cu(II)Carbamide)](SO_4)	8988.5	8998.5	8	18	9	0.90	49.29
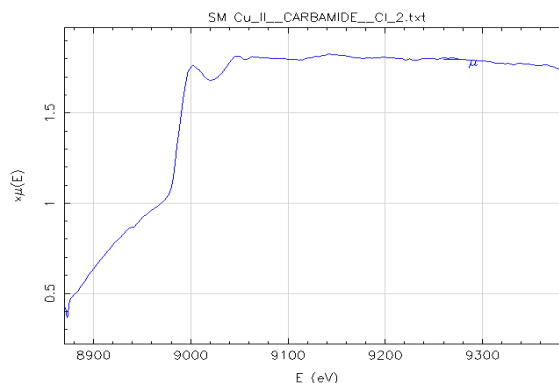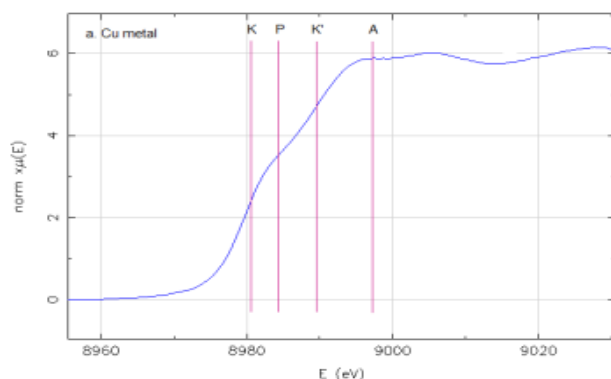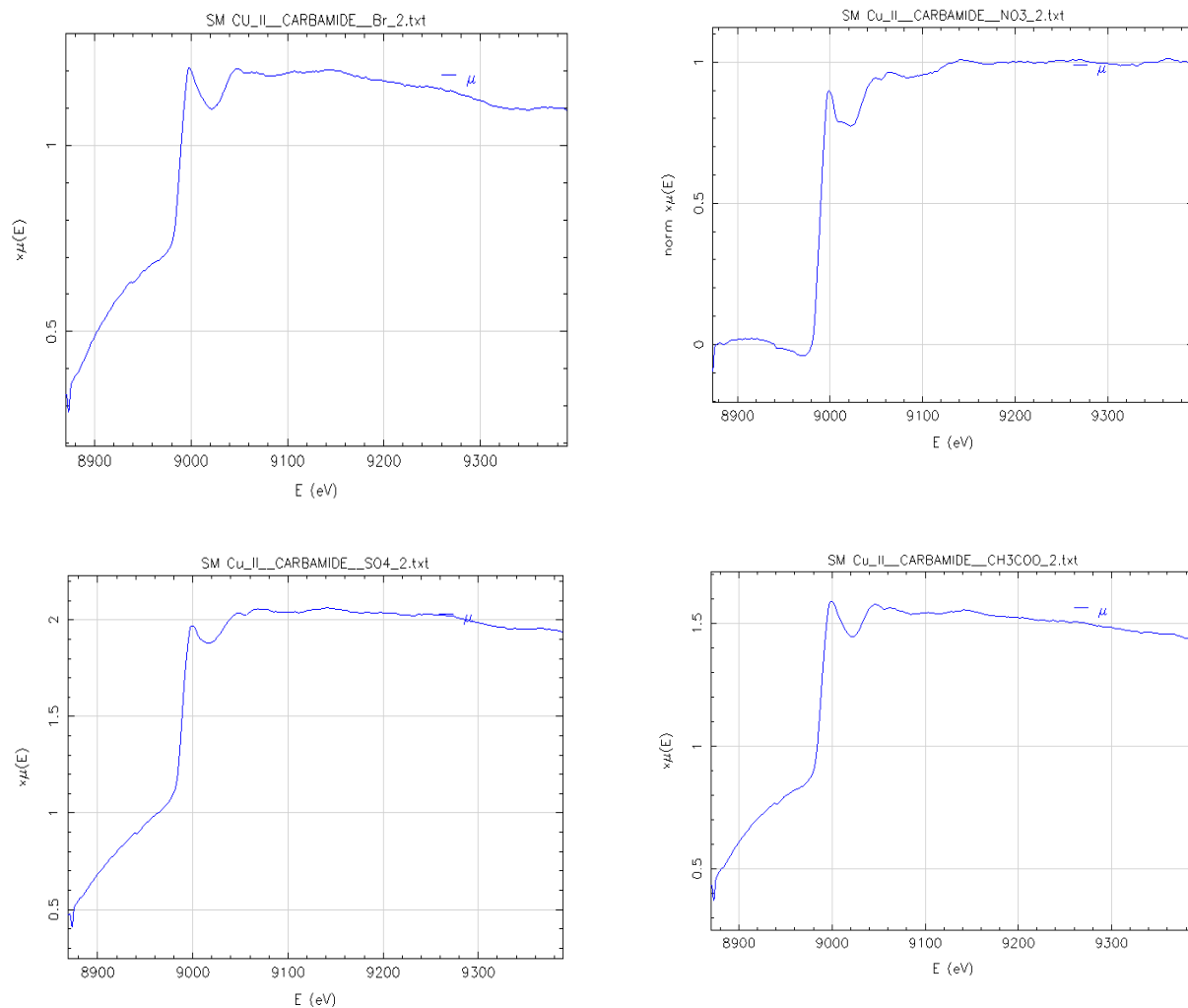
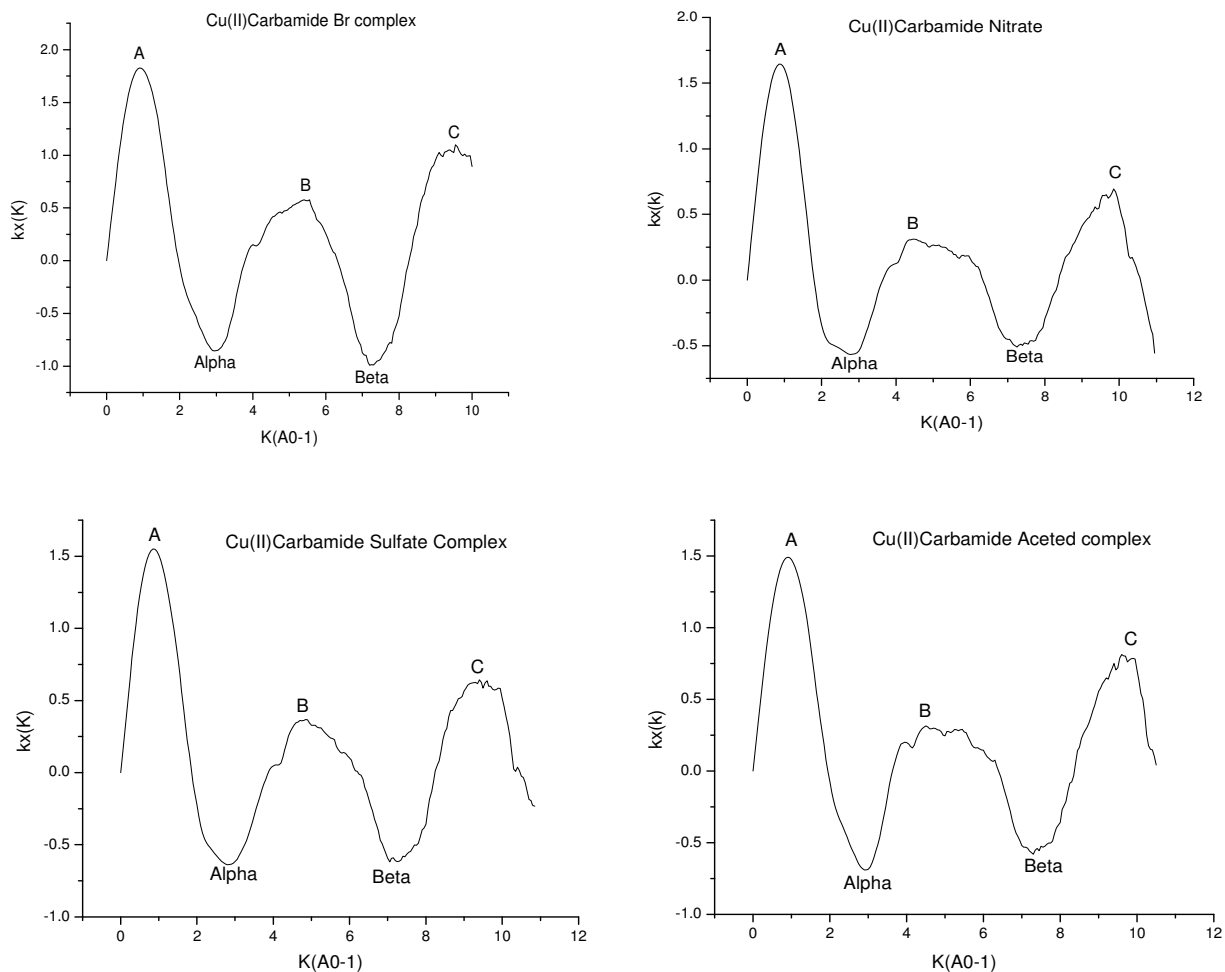**Figure 1**. The XANES region of copper in the complexes
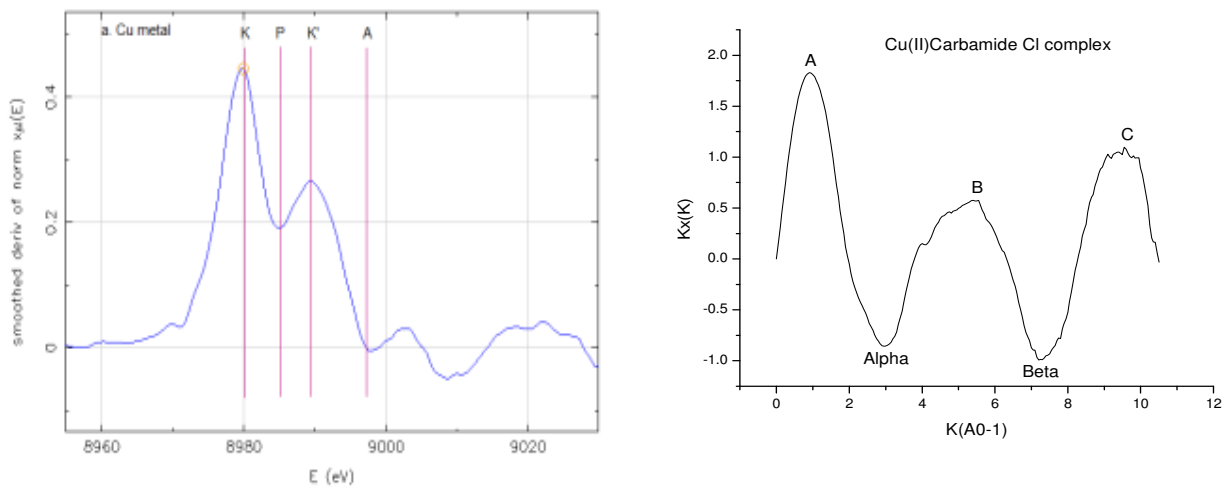
Figure 2. Derivative of the XANES region of copper complexes χ(k) versus k curves for the copper complexes

Table 2 Values of bond lengths calculated from Levy's, Lytle's LSS and F.T

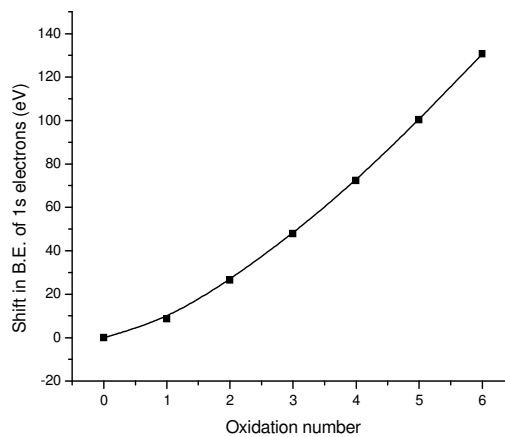| S.No.	Complex	Phase corrected		Phase uncorrected	
		Levy's method R(Å)	Lytle's Method R(Å)	L.S.S. Method R(Å)	F.T. method R(Å)
1	I	1.63	1.96	2.09	1.91
2	II	1.92	2.01	2.12	1.88
3	III	1.81	1.97	2.70	1.91
4	IV	1.82	1.96	2.67	1.92
5	V	1.61	1.95	2.08	1.88

Figure 3. Plot of oxidation number Vs binding energy

Discussion (a) Splitting of the main edge-The copper K-edge, as shown in figures 1, has been found to split into two components, i.e. K and K′. The splitting is seen clearly in the first derivative of these spectra, given in figures 2. According to Gaur et al., [1] the characteristic feature of Cu (II) is the maximum A at ~9003 eV, which corresponds to $1s{\rightarrow}4p_z$ transition as well as to the transitions to continuum states. In the absorption edge of the complexes, as seen in figures 2 apart from absorption edge at ~8988 eV, the feature A at ~8999 eV are present, both of which confirm oxidation state +2 in these complexes.
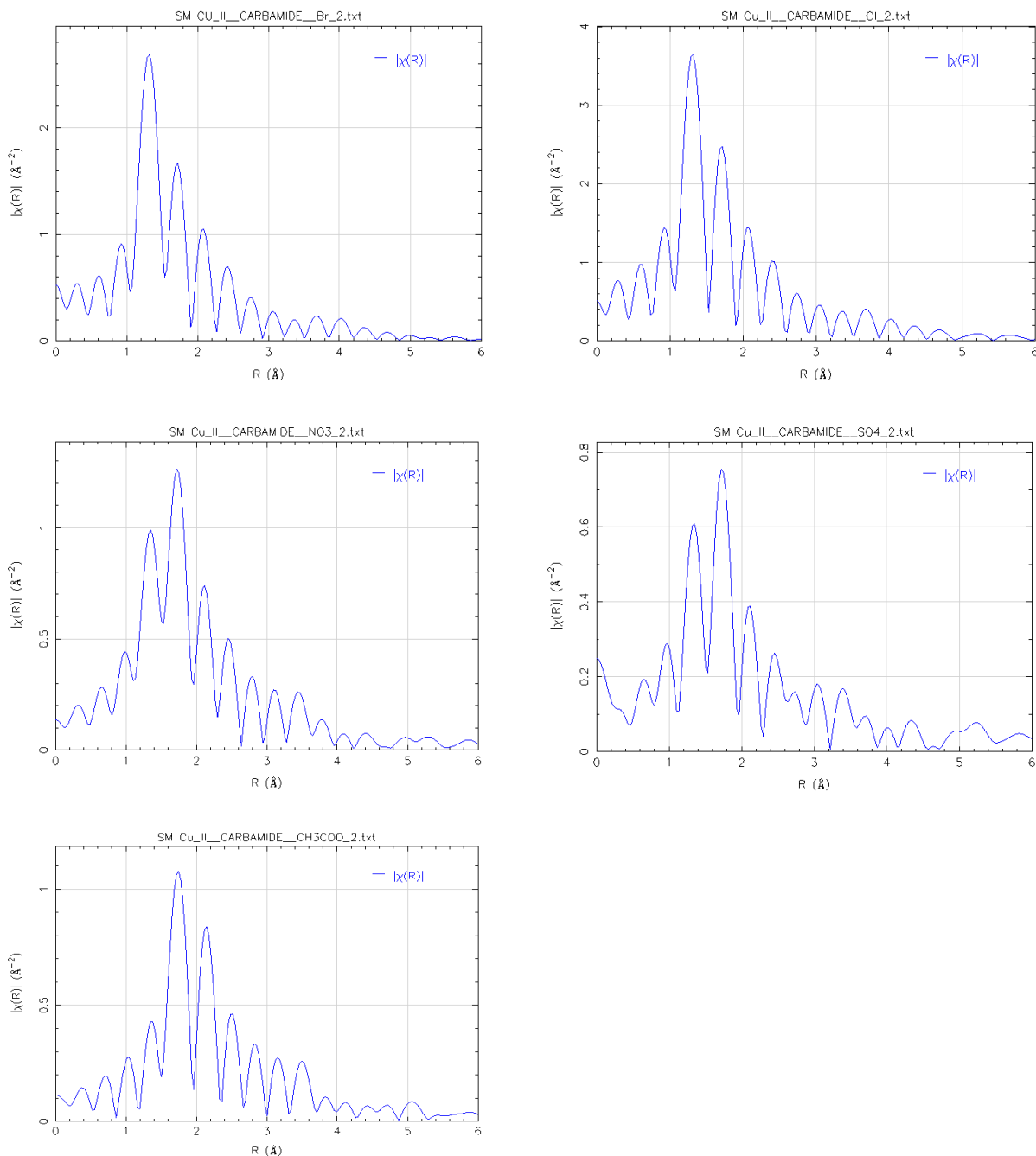

Figure 3. Magnitude of the Fourier transform of the $\chi(k)$ vs k curve for the copper complexes

(b) Chemical shift -All the three complexes have the values of chemical shifts between 8 to 12 eV (table 1). Hence, on the basis of values of the chemical shifts, all the complexes are found to have copper in oxidation state +2 [3].

(c) Effective nuclear charge (ENC)-If the binding energies of K-electron of copper in different oxidation states are determined, one can find from the difference in binding

energies of the neutral atom and the ionized atom, the so called theoretical shifts in the X-ray absorption edge. In the present work, the theoretical values of binding energies have been taken from the tables of Clementi and Roetti[4]. A plot of oxidation number versus theoretical shift in binding energy of 1s electron is shown in figure 3. The values of ENC so determined have given in table 1.

(d)Edge-width-In general, the edge-width of the K-absorption edge (E_A - E_k) increases with the increase of covalent character of the bonds provided other factors like molecular symmetry etc. remain the same [5]. The edge-width values depend on stereochemistry and on the nature of bonding, i.e., ionic/ covalent. The edge width of Cl complex (12 eV) ,Aceted(10 eV) ,SO_4 (9eV) NO_3(6eV) and Br(5 eV) complex(13.4 eV). This may be explained in terms of the higher covalent character in Cl complex as compared to Br complex as evident from the chemical shift values [6].

(e) Determination of bond length-In Levy's method, the bond lengths are calculated by using the relation $R_1 = [151/\Delta E]^{1/2}$ Å, where ΔE is the difference in eV of the energies of the EXAFS maximum B and minimum β [7]. The bond lengths estimated in this way are tabulated in Table 2.

The $\chi(k)$ versus k curves for copper complexes have been shown in figures 2. In Lytle's method [8], the energy values (E) of the absorption maxima as obtained from the measurements are plotted, against the Q values for p symmetry, i.e., Q = 2.04, 6.04, 12.00 and 20.00. The slope M of the E vs Q plots are used to evaluate the radius R_s by using the relation $R_s = [37.60/M]^{1/2}$. The values of R_s calculated with the help of this method are reported in table 2.

Lytle, Sayers and Stern's (L.S.S.) have given a simple method to determine the nearest neighbour distances [9]. To estimate the bond length by this method, n vs k graph for the complexes studied have been plotted. The slope of n vs k plot gives the value of $2(R_1 - \alpha_1)/\pi$ where R1 is the bond length. The parameter α_1, depends to a large extent on the central absorbing atom. The values of $(R_1 - \alpha1)$ thus obtained are given in table 2. It has been observed that the value of the phase uncorrected bond length, i.e., R_1-α_1 as determined from L.S.S. method and that determined from the Fourier transformation method are in good agreement with each other, i.e., both the L.S.S. method and Fourier transformation method give nearly the same value of the phase uncorrected bond length.

(f)By Fourier transform of EXAFS spectra-The Fourier transform of the $\chi(k)$ vs k spectra peaks at the radial distances of the neighbouring atoms from the absorbing atom. The magnitude of the Fourier transform of the $\chi(k)$ vs k curve for the copper complexes is shown in figure 3. However, the distance found from Fourier transform is shorter than the actual distance as a result of energy dependence of the phase factors in the sine function of the EXAFS equation. The peaks in the Fourier transform are shifted towards the origin by an amount α_j, and hence, the position of the first peak also determines the distance (R_1-α_1) [10-12]. The normalized spectra, i.e., μ (E) versus E curves have been obtained. From these curves, χ (k) versus k curves have been obtained, which has then been Fourier transformed using the software Athena. From the Fourier transforms of the EXAFS spectra the bond lengths (uncorrected for phase shift) have been determined.

Conclusions
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. The bond lengths have been determined. It has been observed that the values of the phase uncorrected bond length, i.e., (R1-α1), as determined from LSS method and that determined from the Fourier transformation method, are in good agreement with each other. The present work shows that the methods outlined above provide reliable results for the first coordination shell bond lengths.

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