X-ray near edge studies on copper (II) carbamide complexes

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Abstract: Synthesis of metal copper (II) complexes have been carried out by the chemical root method. The X-ray K- absorption near edge measurements were carried out and the 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.

1. 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]. 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]. In this paper describes X-ray studies of the five copper (II) Carbamide complexes : Copper (II) Carbamide Bromide {Cu (II) UBr} [Cu (NH\textsubscript{2}CONH\textsubscript{2})]Br\textsubscript{2}, Copper (II) Carbamide Chloride {Cu (II) UC} [Cu (NH\textsubscript{2}CONH\textsubscript{2})]Cl\textsubscript{2}, Copper (II) Carbamide Nitrate {Cu (II) UN} [Cu (NH\textsubscript{2}CONH\textsubscript{2})] (NO\textsubscript{3})\textsubscript{2}, Copper (II) Carbamide Sulphate {Cu (II) US} [Cu(NH\textsubscript{2}CONH\textsubscript{2})] (SO\textsubscript{4})\textsubscript{2} and Copper (II) Carbamide Acetate {Cu (II) UA} [Cu(NH\textsubscript{2}CONH\textsubscript{2})] (CH\textsubscript{3}COO)\textsubscript{2}.

2. Experimental
All complexes are prepared by chemical root method. X-ray absorption spectra of carbamide ligand copper complexes at the K-edge of copper have been recorded at the recently developed EXAFS beam line set-up at the Indus-2 synchrotron source at RRCAT, Indore, India.

3. Results and discussion
Fig. 1 shows that copper K –absorption edges and for five complexes studied. The energy of the K- absorption edge \( E_K \) and the energies of the principal absorption maximum \( E_A \) of copper in the various complexes are given in Table 1. The chemical shifts (in eV) of the K-absorption edge of copper in these complexes with respect to the metal edge are also given in Table 1 and it has been found that. K- absorption edge of copper is shifted towards the high energy side in the five complexes.

3.1 Chemical shifts
The shift of the X-ray absorption edge \( (i=K, L, M…) \) [7] of an element in a compound /complex with respect to that element is written as: \( \Delta E_K = E_{K(\text{complex})} - E_{K(\text{metal})} \).

The chemical shift values of the present work are ranging from 8.3 to 12.3 eV. Shift for the nitro complex is greater than the shift for the sulphate complex .This has been attributed to the large polarizability of nitro as compared to the sulphate. Thus; the contribution due to such a bonding towards
chemical shift in the sulphate complex is more than that of nitro complex. It has been found that shift in copper complexes under investigation is towards high energy side. The chemical shift in the studied samples is of the order- [Copper(II)(Carbamide)]Dinitrate > [Copper(II)(Carbamide)]Dibromide > [Copper(II)(Carbamide)] Dichloride > [Copper(II)(Carbamide)] Diacetate > [Copper (II) (Carbamide)] Disulphate. Earlier researchers V.K. Hinge et al [8] have reported the chemical shift value of various copper (II) complexes between 8.3 to 12.3 eV. Hence on comparing values of chemical shifts of all complexes are found to have copper in oxidation state +2.

![Fig.1 (a, b, c, d, e, f). X-ray K-absorption edge of copper metal and in its complexes](image)

### 3.2 Shift of the Principal Absorption Maximum and Edge Width

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→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]. 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. In the present work edge width of Cu (II) complexes in Table 1 are ranging from 5 to 12 eV. Further, it may be seen that as the co-ordination stoichiometry varies as a results of gradual replacement of metal –oxygen by metal –halogen bonds in the complexes, the edge width shows a marked decrease .In fact; edge width has decreases with decreasing covalent character of the metal –ligand bond.

### 3.3 Effective Nuclear Charge and Percentage Covalency

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 Guta
ENC on the copper in the complexes under present study varies between 0.90 to 1.53 electrons/atom. Chemical shift is also a measure of degree of covalency [11]. Clementi’s [12] results of 1s orbital energies for different oxidation states of copper are available. Shift in 1s orbital energy has been calculated [13]. 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 1.

4. Conclusion
From these, the shift of the K-edge (chemical shift), shift of the principal absorption maximum and edge-width has been obtained. The order of chemical shift may also be taken as representative of the relative ionic character of the bonding in these complexes. The values of the chemical shifts suggest that copper is in oxidation state +2 in all of the complexes.

Table 1 - Chemical shift and other parameters 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     | -                   | -                                       | -              | -                 | -                      |
| [Cu(II)Carbamide](NO$_3$) | 8992.8          | 8999.2     | 12.3                | 18                                      | 6              | 1.53              | 36.34                  |
| [Cu(II)Carbamide](Br)     | 8990.8          | 8996.8     | 10.3                | 16                                      | 5              | 1.03              | 42.75                  |
| [Cu(II)Carbamide](Cl)     | 8989.8          | 9002.5     | 9.3                 | 22                                      | 12             | 0.96              | 45.00                  |
| [Cu(II)Carbamide](CH$_3$COO) | 8988.8      | 8999.7     | 8.3                 | 19                                      | 10             | 0.93              | 47.25                  |
| [Cu(II)Carbamide](SO$_4$) | 8988.5          | 8998.5     | 8.3                 | 18                                      | 9              | 0.90              | 49.29                  |

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