

# X-Ray K-Absorption Near Edge Structural Studies of Mixed Ligand Copper II With Pyridine-2-Carboxamide and Amino Acids

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**Abstract**—This paper describes spectroscopic studied of copper (II) complexes with amino acids as ligands. The samples of mixed ligand Copper II with Pyridine -2-Carboxamide and Amino acids were prepared by chemical root method. X-ray absorption spectra of mixed 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 (M.P). The experimental data has been analysed using XAFS data analysis program Athena and the computer software Origin 6.0 professional. The k-absorption ( $E_K$ ) and the energy of the principal absorption maximum ( $E_A$ ) of copper metal and its complexes, edge width, percentage covalency and effective nuclear charge were determined in the present study.

**Keywords**-Copper complexes, Athena, Origin 6.0 professiona

## I. INTRODUCTION

Copper is widely distributed in nature, as metal, in sulphides, arsenide's, chlorides, carbonates etc. Copper is tough, soft and ductile reddish metal. The electronic configuration of these metals is  $3d^{10} 4s^1$ . It has only one electron outside the filled 4d shell. An important physical property of copper is its colour. A transition metal complex consists of a transition metal (such as Cu) coordinated (bounded to) with one or more ligands (neutral or anionic non metal species). Copper is a moderately active metal. It dissolves in most acids and in alkalis. The present chapter describes spectroscopic studied of copper (II) complexes with amino acids as ligands [1-10]. The amino acid compounds are biologically active, creating considerable interest in their metal complexes [11]. The X-Ray absorption near edge structural studies of mixed ligand Copper II with Pyridine -2-Carboxamide and Amino acids.

## II. EXPERIMENTAL

The X-ray absorption spectra have been recorded using synchrotron radiation. The X-ray spectroscopic setup is available at Raja Ramanna Center for Advanced Technology

(RRCAT), Indore, India and is called dispersive EXAFS beamline BL-8. This beamline has been recently commissioned at the 2.5 GeV Indus-2 synchrotron radiation sources [12]. The transmitted beam intensity from the sample is recorded on a position sensitive CCD detector. The intensities  $I_0$  and  $I_t$ , are obtained as the CCD outputs without and with the sample respectively. Using the relation,  $I_t = I_0 e^{-\mu x}$ , where  $\mu$  is the absorption coefficient and  $x$  is the thickness of the absorber. The experimental data has been analysed using the available computer software package Athena.

### A. Preparation of copper complexes

Sample preparation is carried out by chemical root method .Pyridine and hydrated copper salt was taken in water, the mixture was refluxed on water bath for 3 hours and left in refrigerator overnight, when the complexes crystallised out .The complexes ware recrystallised and dride in air. This copper salt and amino acids was dissolved in warm water and NaOH added in this mixture .Mixture refluxed for 5 hour on water both and left in water both over night in a refrigerator when complexes were crystallised it washed with acetone and dried in air [13], the following complexes were prepared

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| Short name      | Name of the Complexes                                       | Molecular formula   |
|-----------------|---|---|
| S <sub>1</sub>  | Alaninato bis (pyridine -2-carbovamide)copper (II) Bromide  | [Cu(PyC) <sub>2</sub> Ala]Br.2H <sub>2</sub> O                    |
| S <sub>2</sub>  | Alaninato bis (pyridine -2-carbovamide)copper (II) chloride | [Cu(PyC) <sub>2</sub> Ala]Cl.2H <sub>2</sub> O                    |
| S <sub>3</sub>  | Alaninato bis (pyridine -2-carbovamide)copper (II) Nitrate  | [Cu(PyC) <sub>2</sub> Ala](NO <sub>3</sub> ).2H <sub>2</sub> O    |
| S <sub>4</sub>  | Alaninato bis (pyridine -2-carbovamide)copper (II) Sulphate | [Cu(PyC) <sub>2</sub> Ala](SO <sub>4</sub> ).2H <sub>2</sub> O    |
| S <sub>5</sub>  | Alaninato bis (pyridine -2-carbovamide)copper (II) Aceted   | [Cu(PyC) <sub>2</sub> Ala](CH <sub>3</sub> COO).2H <sub>2</sub> O |
| S <sub>6</sub>  | Glycinato bis (pyridine -2-carbovamide)copper (II) Bromide  | [Cu(PyC) <sub>2</sub> Gly]Br.2H <sub>2</sub> O                    |
| S <sub>7</sub>  | Glycinato bis (pyridine -2-carbovamide)copper (II) chloride | [Cu(PyC) <sub>2</sub> Gly]Cl.2H <sub>2</sub> O                    |
| S <sub>8</sub>  | Glycinato bis (pyridine -2-carbovamide)copper (II) Nitrate  | [Cu(PyC) <sub>2</sub> Gly](NO <sub>3</sub> ).2H <sub>2</sub> O    |
| S <sub>9</sub>  | Glycinato bis (pyridine -2-carbovamide)copper (II) Sulphate | [Cu(PyC) <sub>2</sub> Gly](SO <sub>4</sub> ).2H <sub>2</sub> O    |
| S <sub>10</sub> | Glycinato bis (pyridine -2-carbovamide)copper (II) Aceted   | [Cu(PyC) <sub>2</sub> Gly](CH <sub>3</sub> COO).2H <sub>2</sub> O |
| S <sub>11</sub> | Valinato bis (pyridine -2-carbovamide)copper (II) Bromide   | [Cu(PyC) <sub>2</sub> Val]Br.2H <sub>2</sub> O                    |
| S <sub>12</sub> | Valinato bis (pyridine -2-carbovamide)copper (II) chloride  | [Cu(PyC) <sub>2</sub> Val]Cl.2H <sub>2</sub> O                    |
| S <sub>13</sub> | Valinato bis (pyridine -2-carbovamide)copper (II) Nitrate   | [Cu(PyC) <sub>2</sub> Val](NO <sub>3</sub> ).2H <sub>2</sub> O    |
| S <sub>14</sub> | Valinato bis (pyridine -2-carbovamide)copper (II) Sulphate  | [Cu(PyC) <sub>2</sub> Val](SO <sub>4</sub> ).2H <sub>2</sub> O    |
| S <sub>15</sub> | Valinato bis (pyridine -2-carbovamide)copper (II) Aceted    | [Cu(PyC) <sub>2</sub> Val](CH <sub>3</sub> COO).2H <sub>2</sub> O |

### III. RESULT AND DISCUSSION

The copper(II) K-absorption edge in metal, Lu<sub>2</sub>O<sub>3</sub> and the fifteen complexes studies are represented in fig.1. The table 1 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, edge width, percentage covalency and effective nuclear charge.

#### A. Chemical Shifts

The chemical shift in the X-ray absorption spectra is defined as the energy shift of the absorption edge of metal in a complex to the position in the metallic state [13]. The chemical shift is given by  $\Delta E = E_{K(\text{Complex})} - E_{K(\text{Metal})}$ .  $E_{(\text{Complex})}$  = the energy position of the edge of a compound, and  $E(\text{Metal})$  = the energy position of the edge of metal atom.

In the present study, the K-absorption edge of all the copper complexes is found to be higher energy side.

#### B. Shifts of the Principal Absorption Maximum

The shift of the principal absorption maximum depends upon the type of overlap between metal and ligand orbital's. Greater the overlap of the metal ligand orbital, the more stable are bonding molecular orbital's and hence more unstable the anti-bonding orbital's [14]. The principal absorption maximum in transition metal complexes is known to arise due to transition of electron from 1s level to a vacant higher orbital of appropriate symmetry. In table 1, the data for the principal absorption maximum  $E_A$  for the complexes have also been included. It has been observed that with respect metal, the value of  $E_A$  is shifted towards the higher energy side. Shift of principal absorption maximum is between 20.08 to 24.2 eV. Hence, on the basis of the shift of the principal absorption maximum also, it can be inferred that copper is +2 oxidation state in these complexes.

Table-01 -Chemical shift of K-absorption edge of Copper complexes

| S.No | 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 |
|------|-----------|------------------|------------|---------------------|--|----------------|-------------------|----------------------|
| 0    | Cu foil   | 8979.6           | 9004.8     | -                   | 25.2                                     | -              | -                 | -                    |
| 1    | S1        | 8988.5           | 9000.9     | 8.9                 | 21.3                                     | 12.4           | 1.83              | 55.00                |
| 2    | S2        | 8987.4           | 9001.1     | 7.8                 | 21.5                                     | 13.7           | 1.17              | 41.70                |
| 3    | S3        | 8989.5           | 9002.3     | 9.9                 | 22.7                                     | 12.8           | 1.19              | 40.25                |
| 4    | S4        | 8986             | 9001.8     | 6.4                 | 22.2                                     | 15.8           | 1.14              | 39.12                |
| 5    | S5        | 8985.1           | 9002       | 5.5                 | 22.4                                     | 16.9           | 1.11              | 44.57                |

|    |     |         |        |      |      |       |      |       |
|----|-----|---------|--------|------|------|-------|------|-------|
| 6  | S6  | 8987.3  | 9002.3 | 7.7  | 22.7 | 15    | 1.85 | 54.00 |
| 7  | S7  | 8990.5  | 9003   | 10.9 | 23.4 | 12.5  | 1.47 | 47.75 |
| 8  | S8  | 8986.4  | 9003.8 | 6.8  | 24.2 | 17.4  | 1.19 | 49.20 |
| 9  | S9  | 8990.7  | 9000.4 | 11.1 | 20.8 | 9.7   | 1.10 | 39.22 |
| 10 | S10 | 8987.74 | 9001.6 | 8.14 | 22   | 13.86 | 1.11 | 42.50 |
| 11 | S11 | 8988.1  | 9004.5 | 8.5  | 24.9 | 16.4  | 0.83 | 54.00 |
| 12 | S12 | 8989.3  | 9003   | 9.7  | 23.4 | 13.7  | 1.17 | 42.75 |
| 13 | S13 | 8990.2  | 9001.1 | 10.6 | 21.5 | 10.9  | 1.19 | 41.29 |
| 14 | S14 | 8979.6  | 9004.8 | 10   | 25.2 | 25.2  | 1.14 | 31.22 |
| 15 | S15 | 8988.1  | 9001.1 | 8.5  | 21.5 | 13    | 1.11 | 43.50 |
| 16 | S16 | 8988.6  | 9003   | 9    | 23.4 | 14.4  | 1.83 | 52.00 |

### C Edge Width

The edge width of the K-absorption edge increases with the increase of ionic character of metal ligand bonds. In the present work edge width of Cu (II) complexes in Table 1 are ranging from 9.7 eV to 17.04 eV. It represents that the edge width is inversely proportional to covalent character for this series. The reverse trend for these complexes is justified on the basis of the criterion that, in general, edge width of the K-absorption edge increases with covalent character of the bonds. This also agrees with the chemical shift values sequence.

### D Percentage Covalency

The percentage covalency of metal-ligand bonding in copper complexes is in the range 41.70 to 54.00. The results are reported in Table 1. Here one finds that, for each complex, increase in covalent nature of bonding causes a corresponding shift towards the lower energy side.

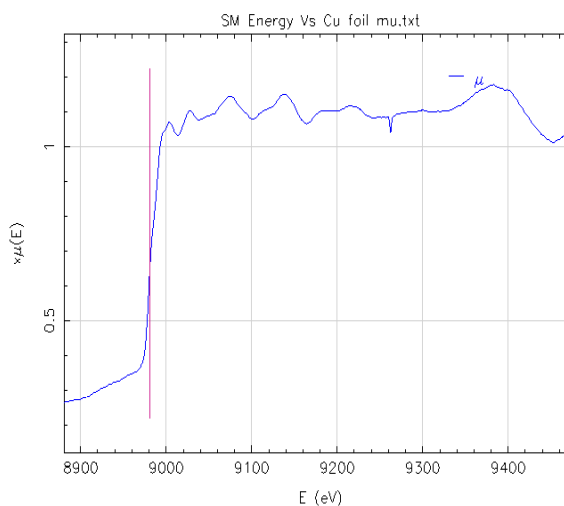
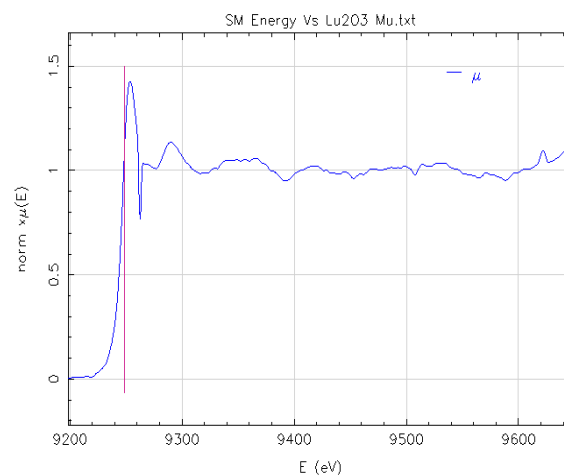
### E Effective Nuclear Charge

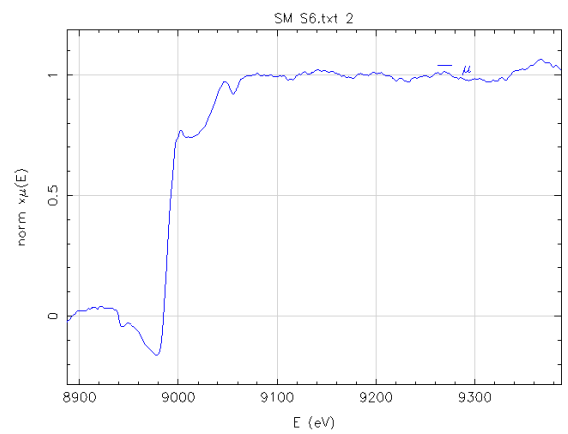
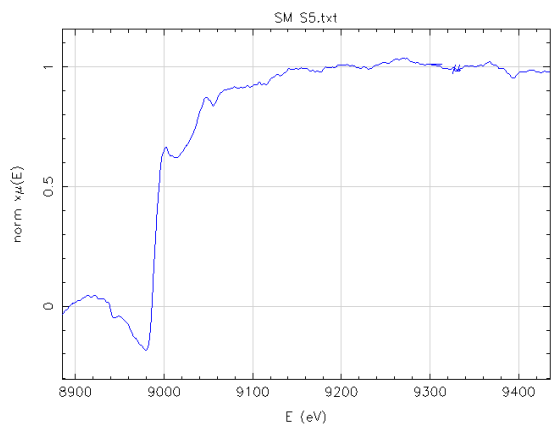
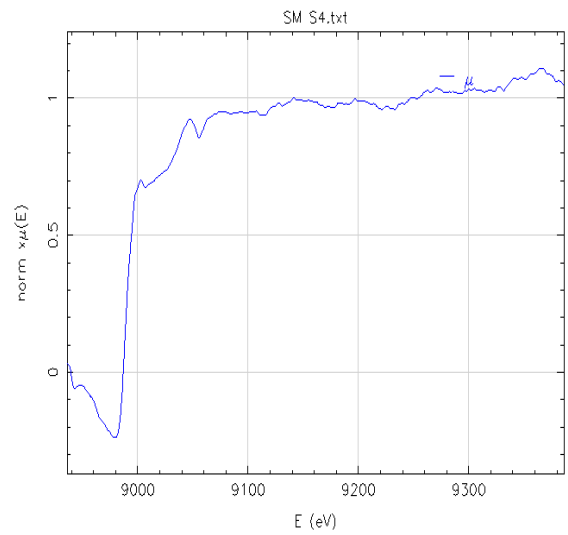
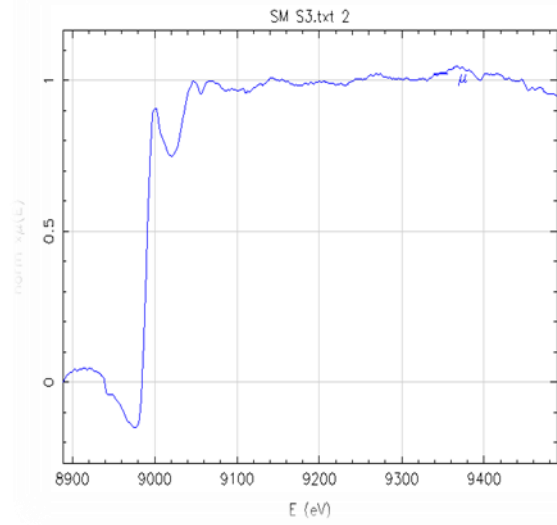
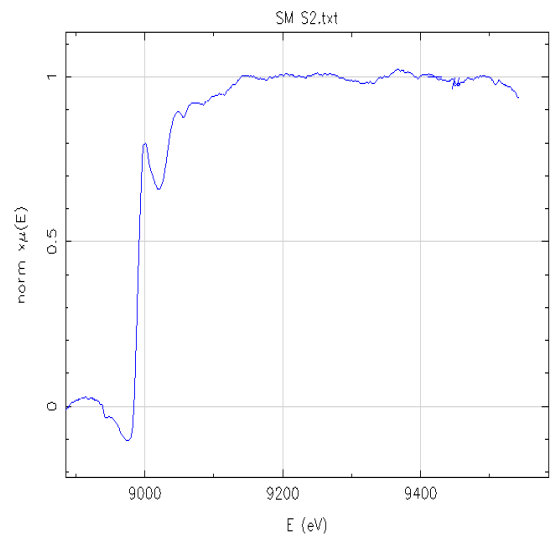
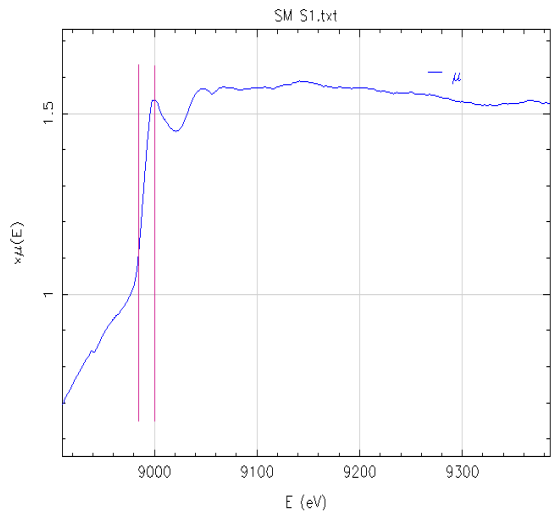
The data reported in Table 1 indicate that the effective charge on copper complexes varies from 1.1 to 1.83 electron/atom, respectively. Table 1 shows that percentage covalency in metal ligand bonding increases with decrease in effective nuclear charge.

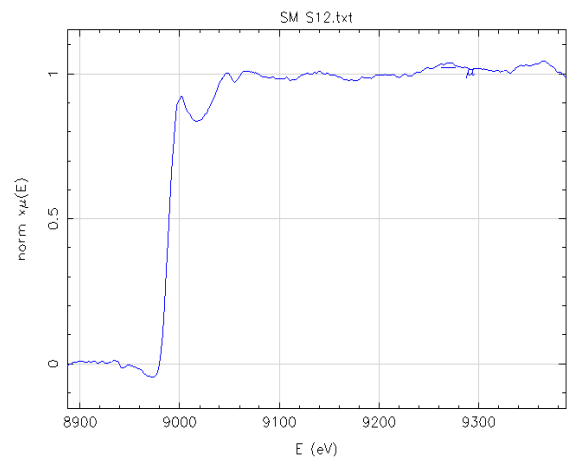
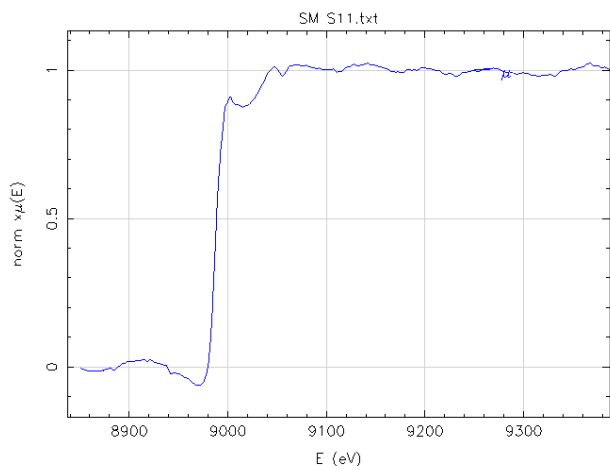
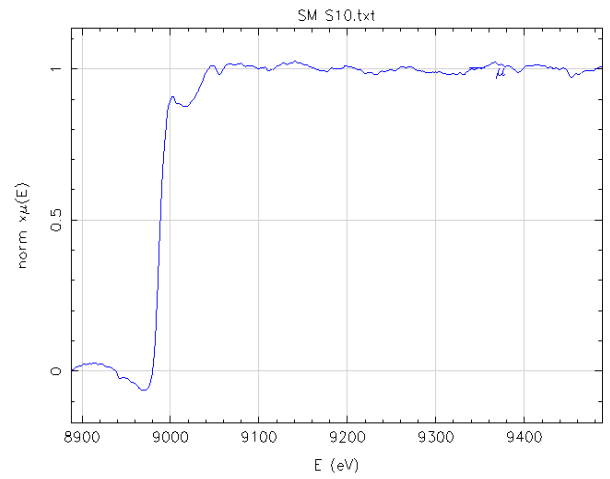
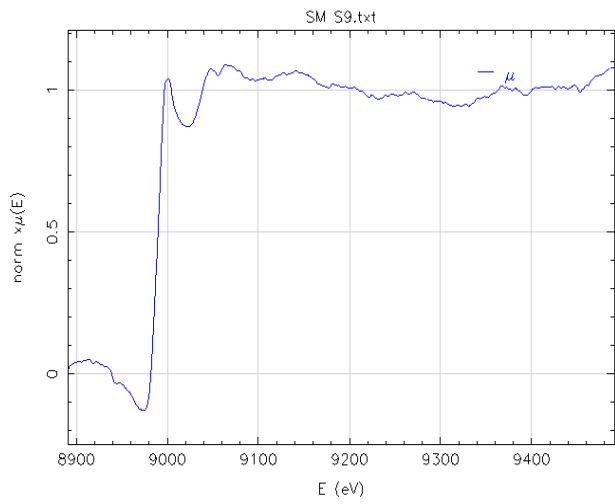
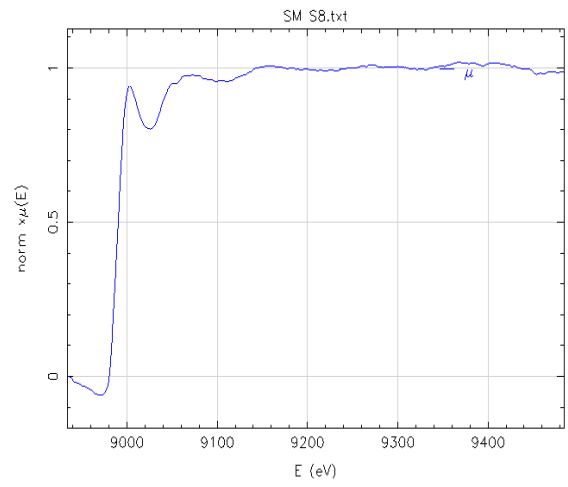
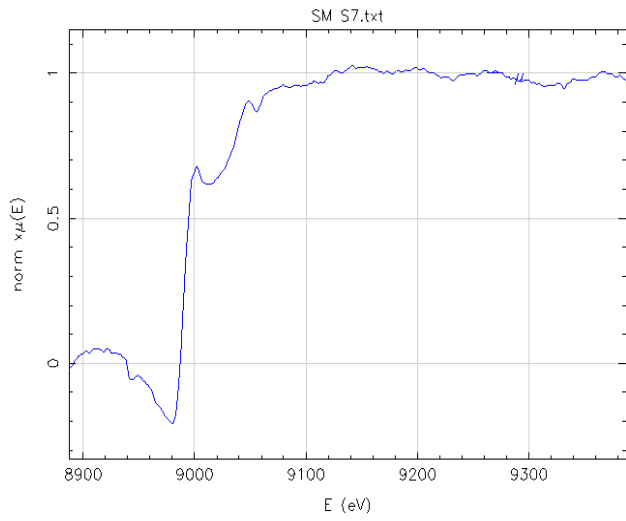
## IV Conclusion

X-ray absorption near edge structure studies of different copper (II) complexes, it can be said that the chemical shift energy values are on the higher energy side. These factors suggest that the geometrical structure of the complexes is cubic. X-ray absorption spectra of mixed 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 (M.P.). The K-edge has been found for all of these complexes. The energies of K-edge ( $E_K$ ), principal absorption maxima ( $E_A$ ) and EXAFS maxima and minima have been reported. From these, the shift of the K-edge, shift of the principal absorption maximum and edge-width has been obtained. The chemical shift has been used to determine the effective nuclear charge

on the absorbing atom. The chemical shift has been used to determine the percentage covalency values on the absorbing atom. The values of the chemical shifts suggest that copper is in oxidation state +2 in all of the complexes.







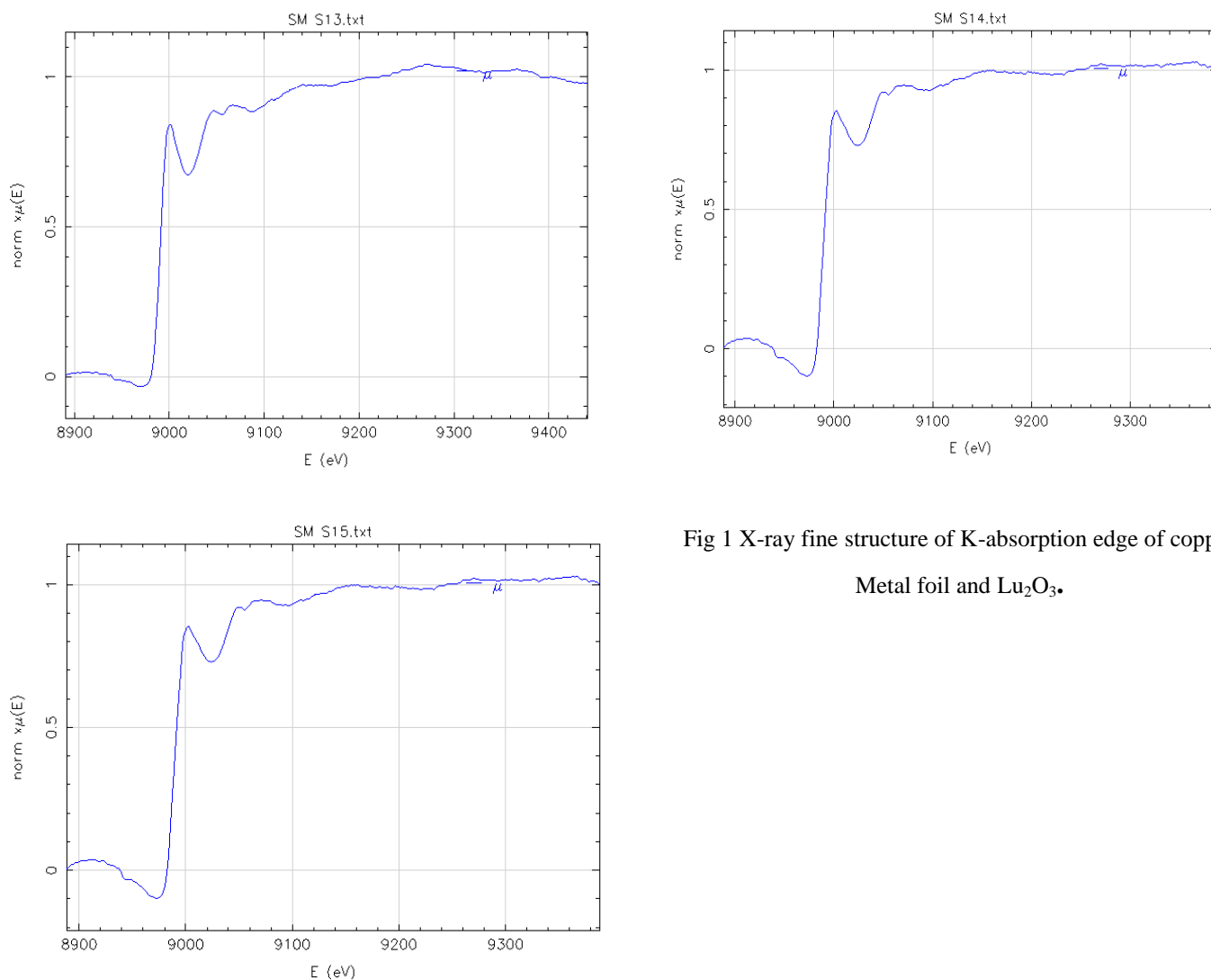


Fig 1 X-ray fine structure of K-absorption edge of copper Metal foil and  $\text{Lu}_2\text{O}_3$ .

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