

## X-ray absorption spectral studies of copper (II) mixed ligand complexes

B Soni<sup>1</sup>, Davood Ah Dar<sup>1</sup>, B D Shrivastava<sup>1\*</sup>, J Prasad<sup>2</sup>, K Srivastava<sup>2</sup>

<sup>1</sup>School of Studies in Physics, Vikram University, Ujjain-452001, India

<sup>2</sup>Department of Chemistry, University of Allahabad, Allahabad 211002, India.

email: rashmibasant@gmail.com

**Abstract.** X-ray absorption spectra at the K-edge of copper have been studied in two copper mixed ligand complexes, one having tetramethylethylenediamine (tmen) and the other having tetraethylethylenediamine (teen) as one of the ligands. The spectra have been recorded at BL-8 dispersive extended X-ray absorption fine structure (EXAFS) beamline at the 2.5 GeV INDUS-2 synchrotron, RRCAT, Indore, India. The data obtained has been processed using the data analysis program *Athena*. The energy of the K-absorption edge, chemical shift, edge-width and shift of the principal absorption maximum in the complexes have been determined and discussed. The values of these parameters have been found to be approximately the same in both the complexes indicating that the two complexes possess similar chemical environment around the copper metal atom. The chemical shift has been utilized to estimate effective nuclear charge on the absorbing atom. The normalized EXAFS spectra have been Fourier transformed. The position of the first peak in the Fourier transform gives the value of first shell bond length, which is shorter than the actual bond length because of energy dependence of the phase factors in the sine function of the EXAFS equation. This distance is thus the phase-uncorrected bond length. Bond length has also been determined by Levy's, Lytle's and Lytle, Sayers and Stern's (LSS) methods. The results obtained from LSS and the Fourier transformation methods are comparable with each other, since both are phase uncorrected bond lengths.

### 1. Introduction

Chelating diamine ligands form a variety of complexes with transition metal ions. Biological as well as catalytic activity of copper(II) complexes having ethylenediamine as a ligand has also been studied [1]. Tetramethylethylenediamine (tmen) can be classified as an organic base like amines and amidines that are regarded as the strong base due to the resonance stability of their conjugate acid. Nishiyama *et al.* [2] have shown that tmen acts as a powerful ligand for the hydrosilylation of ketones. Sano *et al.* [3] have demonstrated that tmen could induce the acylation of alcohol with benzoyl chloride.

X-ray absorption spectra at the K-edge of copper have been studied in two copper mixed ligand complexes,  $\text{Cu}_2(\text{teen})_4(\text{OH})_2(\text{ClO}_4)_2$  (**1**) and  $\text{Cu}_2(\text{tmen})_4(\text{OH})_2(\text{ClO}_4)_2$  (**2**) (tmen = tetramethylethylenediamine and teen = tetraethylethylenediamine).

### 2. Experimental details

The X-ray absorption spectra have been recorded at the BL-8 dispersive extended X-ray absorption fine structure (EXAFS) beamline at the 2.5 GeV Indus-2 synchrotron at RRCAT, Indore, India [4]. The energy calibration of the spectra has been done following the procedure outlined in reference [5].



### 3. Results and discussion

The spectral data has been analyzed using the computer program *Athena* [6]. Normalized  $\mu(E)x$  (absorption) vs.  $E$  (energy) curves and  $\chi(k)$  (oscillations) vs.  $k$  (wave vector) curves for the complexes are shown in figures 1 and 2 respectively. From the first derivative of figure 1, shown in figure 3, it has been observed that K-edge has been found to split in two edges, K and K', with a shoulder P in between, in each complex. The spectra in figures 1,2 and 3 have been shifted vertically by suitable values so that the spectra may be easily compared with each other. The values of the energies of the K-absorption edges ( $E_K$  and  $E_{K'}$ ), shoulder P and principal absorption maximum A ( $E_A$ ) are presented in table 1.

**3.1. Splitting of the edge.** The maximum A at ~9000 eV corresponds to  $1s \rightarrow 4p_z$  transition as well as to the transitions to continuum states. Both of the features, i.e., shoulder P at ~8988 eV and maximum A at ~9000 eV are characteristics of Cu(II). Thus, copper has been found to have oxidation state +2 in these complexes.

**3.2. Chemical shift.** Taking the energy of copper metal K-edge as 8980.5 eV, the chemical shift, i.e., the shift of the K-edge in the complex with respect to that in the metal has been found to be the same in both the complexes, i.e., 5.7 eV. Since +2 oxidation state of copper is known to give chemical shift of the K-absorption edge of copper of the order of 5 eV or more, hence the obtained values of the chemical shift suggest that copper is in +2 oxidation state in both the complexes [7].

**3.3. Principal absorption maximum.** The principal absorption maximum (A) has been found to be shifted towards the higher energy side with respect to copper metal by 3.4 eV in both the complexes. Hence, on the basis of this shift also, it can be inferred that copper is in +2 oxidation state in these complexes. Thus, the relative ionic character has been found to be the same in both the complexes.

**3.4. Edge-width.** In general, edge-width ( $E_A - E_K$ ) of the K absorption edge increases with the increase of covalent character of the bonds provided other factors like molecular symmetry etc., remain the same [8]. In the present study, the edge-width is found to be the same in both the complexes showing that both the complexes have similar molecular symmetry.

**3.5. Effective nuclear charge ( $Z_{eff}$ ).** The effective nuclear charge ( $Z_{eff}$ ) has been obtained from the measured chemical shift by using the method outlined by Nigam and Gupta [9] and Parsai *et al.* [10]. The effective nuclear charge on the copper in both the complexes has been found to be 0.57 electrons/atom.

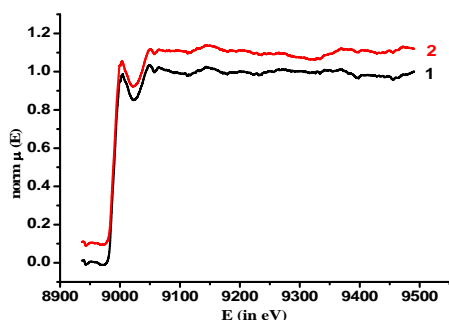
**3.6. Determination of bond lengths.** The bond length has been determined from the extended X-ray absorption fine structure (EXAFS) data by Levy's [11], Lytle's [12] and Lytle, Sayers and Stern's (LSS) [13] methods. These methods are well known methods and have been described recently by Parsai *et al.* [10]. In fact, before the Fourier transformation followed by the fitting of theoretical spectrum to the experimental spectrum became a standard and routine technique, the bond length used to be extracted from the EXAFS data by these three methods. The results obtained for the complexes by these methods are given in table 3. Levy's method gives the radius of coordination sphere ( $R_1$ ) directly, where as Lytle's method does not. In the latter method, the interatomic spacing is obtained by multiplying the obtained bond length ( $R_s$ ) with a factor appropriate to the geometry of the system. The LSS method gives the value of  $(R_1 - \alpha_1)$  where  $R_1$  is the bond length and the parameter  $\alpha_1$  depends to a large extent on the central absorbing atom [9]. For chemically similar system, the value of  $\alpha_1$  remains more or less the same.

The normalized EXAFS spectra of figure 3 have been Fourier transformed and are given in figure 4. The position of the first peak in the Fourier transform gives the value of first shell bond length, which is shorter than the actual bond length because of energy dependence of the phase factors in the

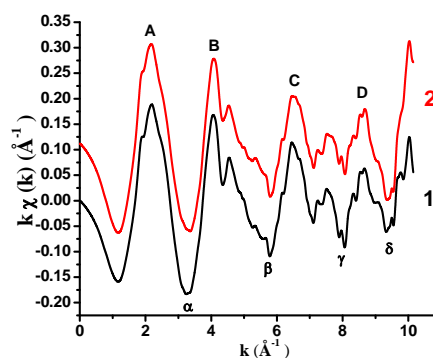
sine function of the EXAFS equation. This distance is thus the phase-uncorrected bond length. The peaks in the Fourier transform are shifted towards the origin by an amount  $\alpha_j$ , and hence, the peaks are at distances  $R_j - \alpha_j$  [14]. For the first peak,  $j = 1$  and, hence, the position of the first peak determines the distance  $R_1 - \alpha_1$ . The distance  $R_1 - \alpha_1$  should be equal to the distance found from the LSS graphical method. Hence, both the LSS method and the Fourier transformation (FT) method give the value  $R_1 - \alpha_1$ , i.e. both the methods give the value of bond lengths, which have not been corrected for the phase shifts. This distance is called as the phase-uncorrected bond length. The position of the first peak in the Fourier transform which gives the value of  $R_1 - \alpha_1$ , are given in table 3 for both the complexes. It is seen from table 3 that the values of  $R_1 - \alpha_1$  as determined from LSS method and those determined from the Fourier transformation method are in good agreement with each other, i.e. both the LSS method and Fourier transformation method give nearly the same value of the phase-uncorrected bond length, i.e.  $R_1 - \alpha_1$ .

#### 4. Conclusion

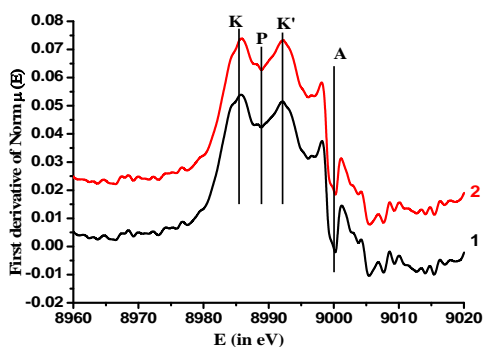
The edge features, chemical shift, edge-width and shift of the principal absorption maximum in the complexes have been found to be approximately same in both the complexes. Copper has been found to be in oxidation state +2 in both the complexes. The effective nuclear charge on the copper in the complexes has been reported. The present study indicates that the two complexes possess similar chemical environment around the copper metal atom. Bond length has also been determined by Levy's, Lytle's and Lytle, Sayers and Stern's (LSS) methods. The results obtained from LSS and the Fourier transformation methods are comparable with each other, since both are phase uncorrected bond lengths.



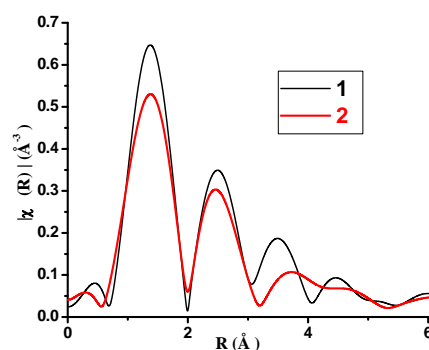
**Figure 1.** Normalized  $\mu(E)$  vs.  $E$  curves for complexes **1** and **2**



**Figure 2.**  $|\chi(k)|$  vs.  $k$  spectra of complexes **1** and **2**



**Figure 3.** Derivative spectra for the complexes **1** and **2**.



**Figure 4.** Fourier transformed data of figure 2.

Table 1. Data for the K-edge of copper in the complexes

Complex	$E_K$ (eV)	$E_{K'}$ (eV)	$E_A$ (eV)	Chemical shift ( $E_K - 8980.5$ )	ENC	Shift of the principal absorption maximum	Edge width ( $E_A - E_K$ )
<b>Cu foil</b>	8980.5	8992.3	8997.0	-	-	-	16.5
<b>1</b>	8985.7	8992.2	9000.4	5.2	0.57	3.4	14.7
<b>2</b>	8985.7	8992.2	9000.4	5.2	0.57	3.4	14.7

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

Structure	$n$	$Q$	Complex 1		Complex 2	
			$E$ (eV)	$k$ ( $\text{\AA}^{-1}$ )	$E$ (eV)	$k$ ( $\text{\AA}^{-1}$ )
A	0	2.04	18.4	2.2	18.4	2.2
$\alpha$	1	-	41.4	3.3	41.4	3.3
B	2	6.04	63.9	4.1	63.9	4.1
$\beta$	3	-	127.9	5.8	127.9	5.8
C	4	12.00	155.7	6.4	160.6	6.5
$\gamma$	5	-	249.5	8.1	249.5	8.1
D	6	20.00	287.8	8.7	287.8	8.7
$\delta$	7	-	328.9	9.3	336.0	9.4

Table 3. Values of first shell bond lengths (in  $\text{\AA}$ ) calculated from Levy's [11], Lytle's [12], LSS[13] and Fourier transform methods for the complexes.

	Levy's method	Lytle's method	LSS method	FT method
	$R_1$	$R_s$	$R_1 - \alpha_1$	$R$
<b>Complex 1</b>	1.97	1.68	1.36	1.37
<b>Complex 2</b>	1.97	1.68	1.36	1.38

## References

- [1] Samrah P, Singha S, Chakrabarty R, Bora S J, Das B K 2007 *Ind J Chem.* **46A** 1929.
- [2] Nishiyama H, Furuta A 2007 *Chem. Commun.* 760.
- [3] Sano T, Ohashi K, Oriyama T 1999 *Synthesis* 1141.
- [4] Das N C, Jha S N, Bhattacharyya D, Poswal A K, Sinha A K and Mishra V K 2004 *Sadhana* **29** 545.
- [5] Gaur A, Johari A, Shrivastava B D, Gaur D C, Jha S N, Bhattacharyya D, Poswal A, Deb S K 2011 *Sadhana* **36** 339.
- [6] Ravel B and Newville M 2005 *J. Synchrotron Rad.* **12** 537.
- [7] Kau L S, Spira-Solomon D J, Penner-Hahn J E, Hodgson K O, Solomon E I, 1987 *J. Am. Chem. Soc.* **109** 6433.
- [8] Kumar A, Nigam A N and Shrivastava B D 1981 *X-ray Spectrom.* **10** 25.
- [9] Nigam A K and Gupta M K 1974 *J. Phys. F: Metal Physics* **4** 1084
- [10] Parsai N, Mishra A, Shrivastava B D 2014 *X-ray Spectrom.* **43** 157
- [11] Levy R M 1965 *J. Chem. Phys.* **43** 1846.
- [12] Lytle F W 1966 *Adv. X-Ray Anal.* **9** 398.
- [13] Lytle F W, Sayers D E, Stern E A 1975 *Phys. Rev. B* **11** 4825.
- [14] Stern E A, Sayers D E, Lytle F W 1975 *Phys. Rev. B* **11** 4836