X-ray absorption fine structure (XAFS) studies of copper (II) mixed ligand complexes having tetramethylethylenediamine as one of the ligands

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Abstract. X-ray absorption fine structure (XAFS) has been studied at the K-edge of copper in copper(II) mixed ligand complexes, having tetramethylethylenediamine (tmen) as one of the ligands, viz., Cu(tmen)(gly)ClO₄, Cu(tmen)(bipy)(ClO₄)₂ and Cu(tmen)(phen)(ClO₄)₂. The spectra have been recorded at the dispersive XAFS beamline (BL-8) at the 2.5 GeV INDUS-2 synchrotron, RRCAT, Indore, India. The data obtained has been processed and analyzed using the computer program Athena. It has been observed that K-edge has been found to split in two edges, K and K', in each of the complex. The chemical shift has been utilized to determine the oxidation state of copper in the complexes and also the effective nuclear charge (ENC). The EXAFS data has been analyzed to obtain the bond lengths in the complexes using Levy’s, Lytle’s and Lytle, Sayers and Stern’s (LSS) methods. The first peak in the Fourier transform of the spectra gives the value of first shell phase uncorrected bond length. The results obtained from the Fourier transformation and LSS methods are in good agreement.

1. Introduction
The X-ray absorption spectroscopy provides information regarding the nature of bonding between the central metal ion and the nearest neighbours. The extended X-ray absorption fine structure (EXAFS) yields information about bond lengths. In the present work, the X-ray K absorption spectra of copper have been studied in the mixed ligand copper(II) complexes having tetramethylethylenediamine as primary ligand, other ligands being – glycine, 2,2'-bipyridine and 1,10-phenanthroline.

2. 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 various aspects of the calibration and the procedure to be followed on this beamline were similar to those described by Gaur et al [1]. The experimental data have been analyzed using the available computer software package Athena.
3. Results
The shapes of the copper K-edge and the near edge structure (XANES) for all the complexes are shown in figures 1(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.

| Complex                  | $E_K$ (eV) | $E_{K'}$ (eV) | $E_A$ (eV) | Chemical shift $\Delta E_K = (E_{complex} - E_{metal})$ (eV) | ENC | Edge-width $(E_A - E_K)$ (eV) |
|--------------------------|------------|---------------|------------|------------------------------------------------------------|-----|-----------------------------|
| Cu metal                 | 8980.5     | 8991.8        | 8995.0     | -                                                          | -   | 14.5                        |
| Cu(tmen)(gly)ClO$_4$     | 8988.4     | 8992.5        | 8999.7     | 7.9                                                        | 0.92| 11.3                        |
| Cu(tmen)(bipy)(ClO$_4$)$_2$ | 8987.6     | 8994.4        | 9001.8     | 7.1                                                        | 0.82| 14.2                        |
| Cu(tmen)(phen)(ClO$_4$)$_2$ | 8989.2     | 8994.9        | 9002.6     | 8.7                                                        | 1.00| 13.4                        |

Figure 1. The XANES region of copper in the complexes indicating absorption edges K and K', shoulder P and the principal absorption maxima A.

Figure 2. Derivative of the XANES region of copper complexes.

Table 2. Values of first shell bond length (in Å).

| S.No. | Complex                  | Levy’s method | Lytle’s method | LSS method | FT method |
|-------|--------------------------|---------------|----------------|------------|-----------|
|       | Phase corrected          | Phase         |                |            |           |
|       |                          | uncorrected   |                |            |           |
| 1     | Cu(tmen)(gly)ClO$_4$     | 1.73          | 1.79           | 1.49       | 1.48      |
| 2     | Cu(tmen)(bipy)(ClO$_4$)$_2$ | 1.75          | 1.58           | 1.44       | 1.45      |
| 3     | Cu(tmen)(phen)(ClO$_4$)$_2$ | 1.73          | 1.65           | 1.41       | 1.42      |

Figure 3. Plot of oxidation number vs binding energy.

4. Discussion
4.1 Splitting of the main edge
The copper K-edge, as shown in figures 1(a–d), 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(a–d).
According to Kau et al.[2] the characteristic feature of Cu(II) is the maximum A at ~9000 eV, which corresponds to 1s→4p transition as well as to the transitions to continuum states. In the absorption edge of the complexes, as seen in figures 2(a–d), apart from shoulder P at ~8985 eV, the feature A at ~9000 eV are present, both of which confirm oxidation state +2 in these complexes.

Figure 4. χ(k) versus k curves for the copper complexes

Figure 5. Magnitude of the Fourier transform of the χ(k) vs k curve for the copper complexes.

4.2 Chemical shift
All the three complexes have the values of chemical shifts between 7.1 to 8.7 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].

4.3 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 the theoretical shift in binding energy of 1s electron is shown in figure 3. The values of ENC so determined have given in table 1.

4.4 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. For the pair of complexes Cu(tmen)(bipy)(ClO_4)_2 and Cu(tmen)(phen)(ClO_4)_2 though the stereochemistry is same, i.e., Cu:N(1:4) but the edge-width values are different, i.e., (bipy) complex(14.2 eV) and (phen) complex(13.4 eV). This may be explained in terms of the higher covalent character in (bipy) complex as compared to (phen) complex as evident from the chemical shift values [6].

4.5 Determination of bond length
In Levy’s method, the bond lengths are calculated by using the relation R_1 = [151/ΔE]^{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 χ(k) versus k curves for copper complexes have been shown in figures 4(a–d). 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 $R_s = \left[ \frac{37.60}{M} \right]^{\frac{1}{2}}$. 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 $R_1$ is the bond length. The parameter $\alpha_1$, depends to a large extent on the central absorbing atom. The values of $(R_1 - \alpha_1)$ thus obtained are given in table 2.

4.6 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 5. 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 $\alpha_j$, and hence, the position of the first peak also determines the distance $(R_1 - \alpha_1)$ [10].

5. 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., $(R_1 - \alpha_1)$, 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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