X-ray absorption spectral studies of copper(II) mixed ligand complexes having ethylenediamine as one of the ligands

Shikha Dwivedi 1, S K Joshi 2, V K Hinge 3, B D Shrivastava 4, J Prasad 4 and K Srivastava 4
1 School of Studies in Physics, Vikram University, Ujjain 456001, India
2 S. V. Govt. Commerce College, Ratlam 457001, India
3 Physics Department, Ujjain Engineering College, Ujjain 456010, India.
4 Department of Chemistry, University of Allahabad, Allahabad 211002, India

Email: shi.dwivedi@gmail.com

Abstract. X-ray absorption spectra of copper(II) mixed ligand complexes, having ethylenediamine (en) as one of the ligands, have been recorded at the K-edge of copper at the dispersive extended X-ray absorption fine structure (EXAFS) beamline (BL-8) at the 2.5 GeV INDUS-2 Synchrotron, RRCAT, Indore, India. The samples studied are: Cu(en)2(ClO4)2, Cu(en)2Br2.H2O and Cu(en)2SO4. The data obtained has been processed using EXAFS data analysis program Athena. The K-edge has been found to split in two edges $K$ and $K'$ in each of the complex. The energies of the edges $K(E_K)$ and $K'(E_K')$ and the principal absorption maximum $A(E_A)$ have been determined from the derivative spectra. The chemical shift has been utilized to determine the oxidation state of copper in the complexes and to estimate effective nuclear charge (ENC) on the absorbing atom. The EXAFS data has been used to determine the bond lengths in the complexes using three different graphical methods. The bond lengths, obtained from one of these methods and the Fourier transformation method, are comparable with each other, showing that both of these methods give phase uncorrected bond lengths.

1. Introduction
In the present paper, the X-ray absorption spectra of three mixed ligand complexes of Cu(II) having ethylenediamine (en) as one of the ligands, viz., Cu(en)2(ClO4)2, Cu(en)2Br2.H2O and Cu(en)2SO4 have been investigated. Earlier these samples have been studied using laboratory X-ray spectrometer setup [1]. In the present work the spectra have been studied using synchrotron source.

2. Experimental
The complexes have been prepared and characterized using standard methods [2]. The absorption spectra at the K-edge of copper of these complexes have been recorded at BL-8 EXAFS beamline at INDUS-2 synchrotron source at RRCAT, Indore, India. The experimental data have been analyzed using the available computer software Athena.
3. Results

Various XANES features indicating absorption edge K and K’ and A are shown in figures 1(a-d). The derivative spectra for all the three complexes are depicted in figures 2(a-d). The values of the energies of the edges K (E_K) and K’ (E_K’) and the principal absorption maximum A (E_A) have been determined from the derivative spectra and are given in table 1. The magnitudes of Fourier transform of figures 4(a-d) are shown in figures 5(a-d).

**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 |
|--------------------------|----------|-----------|----------|---------------------------------------------------------------|-----|
| Cu metal                 | 8980.5   | 8991.8    | 8995.0   | -                                                             | -   |
| Cu(en)\(_2\)(ClO\(_4\))\(_2\) | 8986.4   | 8991.7    | 9000.8   | 5.9                                                           | 0.62 |
| Cu(en)\(_2\)Br\(_2\)H\(_2\)O | 8986.1   | 8991.2    | 9000.3   | 5.6                                                           | 0.58 |
| Cu(en)\(_2\)SO\(_4\)     | 8987.6   | 8991.2    | 9002.7   | 7.1                                                           | 0.82 |

**Figure 1.** The XANES region of copper in the complexes indicating K and K’, shoulder P and A.

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’ in all the complexes with a shoulder P in between as shown in figures 2(a-d). According to Kau et al.,[3] the characteristic feature of Cu(II) is the maximum A at ~ 9000eV, which also corresponds to 1s→4p\(_z\) transition as well as to the transitions to continuum states. In the absorption edge of the complexes, apart from shoulder P at ~ 8985eV, the feature A at ~ 9000eV are present, both of which are characteristics of Cu(II). Thus, copper has been found to have oxidation state +2 in these complexes.

4.2 Chemical shift

The compounds having copper in oxidation state +1 show chemical shifts less than 5 eV while those having copper in oxidation state +2 show chemical shifts more than 5eV [3]. In the presently studied three complexes, the values of chemical shifts are found to be between 5.6 to 7.1eV as shown in table 1. Hence, on the basis of values of the chemical shifts, all the complexes are found to have copper in oxidation state +2. The sequence of the chemical shift is: Cu (en)\(_2\)Br\(_2\)H\(_2\)O < Cu (en)\(_2\)(ClO\(_4\))\(_2\) < Cu (en)\(_2\)SO\(_4\).

4.3 Effective nuclear charge (ENC)

The value of binding energies have been determined as given by Clementi and Roetti[4]. The theoretical shifts are plotted against the oxidation number. Such a graph for copper atom is shown in
figure 3. From this graph, the effective nuclear charges (ENC) on copper in its complexes have been determined and are given in table 1.

![Figure 2. Derivative of the XANES region indicating positions of K and K', shoulder P and A.](image)

![Table 2. Values of first shell bond length (in Å)](table)

| S.No. | Complex           | Phase corrected bond length | Phase uncorrected bond length |
|-------|-------------------|----------------------------|-------------------------------|
|       |                   | Levy’s method | Lytle’s method | LSS method | FT method |
|       |                   | R₁           | Rₛ           | R₁ – α₁   | R          |
| 1.    | Cu(en)$_2$(ClO$_4$)$_2$ | 2.24         | 1.5          | 1.41      | 1.47       |
| 2.    | Cu(en)$_2$Br$_2$.H$_2$.O | 1.80         | 1.6          | 1.60      | 1.81       |
| 3.    | Cu(en)$_2$SO$_4$   | 1.92         | 1.45         | 1.57      | 1.51       |

4.4 Determination of bond length by graphical methods
In Levy’s method[5], the bond lengths are calculated by using the relation $R_1 = [151/\Delta E]^{1/2}$ Å, where $\Delta E$ is the difference in eV of the energies of the EXAFS maximum B and minimum $\beta$, and $R_1$ is the radius of the first coordination sphere.

For Lytle’s method [6], the energy value (E) of the EXAFS maxima are plotted against the Q values for p symmetry, i.e., Q = 2.04, 6.04, 12.0 and 20.0. The (E,Q) plots have been found to be linear (not reproduced here). The slope M of the E versus Q plots have been used to evaluate the radius $R_s$ of equivalent polyhedron, by using the relation, i.e. $R_s = [37.60/M]^{1/2}$.

In the Lytle, Sayers and Stern’s (LSS) method [7], the determination of the nearest neighbor distances, n versus k graph is plotted. The plots have been found to be linear for all the complexes (not reproduced here). The slope of n versus 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 [8]. It is found that for chemically similar system, the value of $\alpha_1$ remains more or less the same.

4.5 Determination of bond length by Fourier transform (FT) method
$\chi(k)$ versus k curves for the copper complexes are given in figure 4. Figure 5 gives the magnitude of the Fourier transform of the $\chi(k)$ versus k curves for the copper complexes. The Fourier transform of the spectra peaks at the radial distance of the neighboring atoms from the absorbing atom. However, the distance found from Fourier transform is about 0.2 Å - 0.5 Å shorter than the actual distance, as a result of energy dependence of the phase factor in the sine function of the EXAFS equation. Hence, the peaks in the Fourier transform are shifted toward the origin by an amount $\alpha_j$. Therefore, the peaks are at distance $(R_j - \alpha_j)$ [9]. For the first peak j=1 and, hence the position of the first peak determines the distance $(R_1-\alpha_1)$. 

3
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 three the complexes. The order of the chemical shift may also be taken as representative of the relative ionic character of the bonding in these complexes. The bond lengths in the complexes have been determined by three different methods viz., Levy’s, Lytle’s and Lytle, Sayers and Stern’s (LSS) methods. From the Fourier transforms of the EXAFS spectra, the bond lengths (uncorrected for phase shift) have been determined. It has been observed that the values of the phase uncorrected bond length, i.e. $R_{1-\alpha}$, as determined from LSS method and that determined from the Fourier transformation method, are in good agreement with each other. This shows that the LSS method also provides reliable results for the bond length of the first co-ordination shell in the complexes.

References
[1] Hinge V K 2010 PhD Thesis, Vikram University, Ujjain
[2] Goodgame M and Haines L I B 1966 J. Chem. Soc. A 174
[3] Kau L S, Spira-Solomon D J, Penner-Hahn J E, Solomon E I and Hodgson K O 1987 J. Am. Chem. Soc. 109 6433
[4] Clementi E and Roetti C 1974 At. Data Nucl. Data Tables 14 177
[5] Levy R M 1965 J. Chem. Phys. 43 1846
[6] Lytle F W 1966 Adv. X-ray Anal. 9 398
[7] Lytle F W, Stern E A and Sayers D E 1975 Phys. Rev. B 11 4825
[8] Nigam A K and Gupta M K 1974 J. Phys. Metal Phys. F 4 1084
[9] Stern E A, Sayers D E and Lytle F W 1975 Phys. Rev. B 11 4836