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

V K Hinge\(^a\), S K Joshi\(^b\), B D Shrivastava\(^c\), J Prasad\(^d\) and K Srivastava\(^d\)

\(^a\)Physics Department, Ujjain Engineering College, Ujjain 456010, M.P.

\(^b\)Government Arts and Science College, Ratlam 457001, M.P.

\(^c\)School of Studies in Physics, Vikram University, Ujjain 456010, M.P.

\(^d\)Chemistry Department, University of Allahabad, Allahabad 211002, U.P.

E-mail: vjayhinge1@rediffmail.com

Abstract. X-ray K-absorption spectra of six biologically important copper (II) complexes having ethylenediamine (en) as primary ligand and nitrate, thio-cyanate, perchlorate, bromide, chloride and sulphate as secondary ligands have been studied using a bent crystal 0.4 m Cauchois-type transmission spectrograph. Various parameters, e.g., chemical shift, energy position of the principal absorption maximum, effective nuclear charge and edge-width have been determined. The K-absorption edges have been found to split into two components, i.e., K\(_1\) and K\(_2\) in all of these complexes. All the complexes have been found to have copper in oxidation state \(+2\). The relative ionic character of the complexes has also been determined and correlated with spectrochemical series.

1. Introduction
The X-ray absorption fine structure analysis can give details about the electronic structure and the local arrangement of atoms around the absorbing atom. X-ray absorption near edge structure (XANES) is a powerful and promising tool for determination of the local structure of samples. Ethylenediamine is a well-known chelating agent. A chelating agent is a substance whose molecules can form several bonds to a single metal ion. In other words, a chelating agent is a multidentate ligand. A single molecule of ethylenediamine can form two bonds to a transition-metal ion such as Cu\(^{2+}\). The bonds are formed between the metal ion and the nitrogen atoms of ethylenediamine. In the present work XANES spectra of six mixed ligands complexes of Cu(II) having ethylenediamine (en) as one of the ligand, has been studied.

2. Experimental
The six complexes studied in the present investigations are Cu(en)\(_2\)(ClO\(_4\))\(_2\), Cu(en)\(_2\)(ONO\(_2\))\(_2\), Cu(en)\(_2\)(SCN)\(_2\), Cu(en)\(_2\)Cl\(_2\)H\(_2\)O, Cu(en)\(_2\)Br\(_2\)H\(_2\)O, Cu(en)\(_2\)SO\(_4\) where en = ethylenediamine. All the complexes were prepared according to the standard methods reported in literature and their purity was checked [1]. A sealed Machlett tube with a tungsten target was employed as X-ray radiation source and was operated at 17 kV and 15 mA. The X-ray absorption spectra at the K-edge of copper were recorded on a bent crystal 0.4 m Cauchois-type transmission spectrograph employing a mica crystal, oriented to reflect from (100) planes, for dispersion. The absorption screens were prepared by spreading about 30 mg of substance on 1cm\(^2\) area of cellophane tape and covering it by another piece of cellophane tape. The exposure time was 2-3 hrs on Kodak X-ray films. For calibrating the spectra, the tungsten emission lines WL\(\alpha\), WL\(\beta\)\(_1\) and WL\(\beta\)\(_2\) were used as reference lines and their energies.
Figure 1. Copper K-edge XANES spectra for the copper complexes. The different spectra have been shifted vertically for better presentation

were taken from the tables of Deslattes et al [2]. The dispersion of the spectrograph was about 0.8 eV/10^{-2} mm of the X-ray film. The resolution of the spectrograph was tested by recording the Mo Kβ1,3 doublet as two separate lines, which was adequate for this study. The measurements at the K absorption edge were made on digital records obtained using a Carl-Zeiss G II microphotometer. The digital records were analyzed using computer programs Origin and Athena [3] were used for data analysis. Derivative spectra were used for obtaining the K-edge position.

3. Results and Discussion
The shapes of the copper K-absorption discontinuity and the associated near edge structure (XANES) for all the complexes are shown in Fig 1. The curves in this figure represent the normalized K absorption spectra. The energies of the copper K-edge (E_{K1} and E_{K2}) and the principal absorption maximum (E_A) along with the values of the edge-width (E_A-E_{K1}) and the chemical shift ΔE_{K1} are given in Table 1.

3.1 Chemical shift
The shift of the X-ray absorption edge i (i = K, L, M, . . .) of an element in a compound/complex with respect to that of the pure element is written as:

ΔE_i = E_i(complex) - E_i(metal)

It is well known that the position of the K-edge depends on the valence state of the absorbing ion. In general, the chemical shift is towards high energy side of the metal edge, it increases progressively with increase of the valency of the cation, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of the metal-metal bonding [4]. In the present work, the K-absorption edge for copper is found to be shifted towards the high energy side in all the six complexes studied. It is well established that on compound formation, usually the interatomic distance increases and dehybridization sets in. Consequently, the 4p band becomes narrower and no more admixes with 3d and 4s bands before it finds an empty 4p state. Transition from 1s to 4p levels thus, gives rise to the shift of K-edge in the complexes under present study towards the high energy side. The values of chemical shifts obtained for all the complexes are tabulated in Table 1. For the present complexes, the chemical shift values lie in the range 4.1 to 9.7 eV. Hence on the basis of values of the chemical shifts, all our complexes are found to have copper in oxidation state +2.

The chemical shift values of the Cu(en)2Cl2.H2O and Cu(en)2Br2.H2O complexes of the present work are 8.5 and 7.8 eV respectively. Shift for the chloro complex is greater than the shift for the
bromo complex. This has been attributed to the large polarizability of bromine as compared to the chlorine. Further on the Pauling’s electronegative scale, the values for chlorine and bromine are 3.0 and 2.8 respectively and hence the metal-chlorine bond is more ionic as compared to metal-bromine bond. Thus, the contribution due to such a bonding towards chemical shift in the chloro complex is more than that of bromo complex.

The chemical shift values of the Cu(en)$_2$(ONO)$_2$ and Cu(en)$_2$(ClO$_4$)$_2$ complexes of the present work are 9.7 and 8.6 eV respectively. Earlier workers have reported the chemical shift values of Cu(O$_2$PO)$_2$ (ONO)$_2$ and Cu(O$_2$PO)$_2$ (ClO$_4$)$_2$ copper(II) complexes as 12.6 and 9.7 eV respectively. Similarly for the complexes Co(oatsc)$_2$ (NO$_3$)$_2$ to Co(oatsc)$_2$ (ClO$_4$)$_2$ the shift values are 7.1 and 6.5 eV respectively. From above discussion, it is obvious that (ONO)$_2$ and (ClO$_4$)$_2$ ligands follow the same trend for chemical shift variation irrespective of the fact that the other ligand in the mixed ligand complexes may be (O$_2$PO)$_2$, (oatsc)$_2$ or even (en)$_2$ ligand. The sequence of variation of the chemical shift remains the same for both the transition metals, i.e., copper and cobalt.

The chemical shift in the three complexes Cu(en)$_2$Cl$_2$H$_2$O ,Cu(en)$_2$Br$_2$.H$_2$O and Cu(en)$_2$(ONOs)$_2$ follows the order Br $<$ Cl $<$ ONO$^-$ . This order can be explained on the basis of the order of these ligands in the spectrochemical series, which is also the same, i.e. Br$^-$ $<$ Cl$^-$ $<$ ONO$_2^-$ . Thus, the variation of the chemical shifts follows the same sequence as in the spectrochemical series for the three ligands Br$^-$, Cl$^-$ and ONO$_2^-$.

The chemical shift of 8.1 eV for Cu(en)$_2$SO$_4$ and 4.1 eV for Cu(en)$_2$(SCN)$_2$ are less than those for nitro and perchlorato complexes. It should be noted that the sulphato group is coordinated through two of its oxygen atoms in the complex Cu(en)$_2$SO$_4$ and in the complex Cu(en)$_2$(SCN)$_2$ the copper atom has four short bonds and two long bonds frequently encountered with Cu$^{2+}$ ions. The sulfur atom of the thiocyanate group completes a distorted octahedron, which suppresses the value of chemical shift.

The chemical shift values for all the complexes studied in the present investigation are lower than those of the corresponding simple salt. The lowering of the chemical shift values occurs due to the covalent character of the metal-ligand bond, as also expected for the N and S donor atoms of the ligand. The linkage to Cu(II) in ON$_2$O and ClO$_4$ is with one oxygen, in SO$_4$ it is with two oxygen, where as for Cl$_2$ and Br$_2$ complexes it is through chlorine and bromine respectively. For the SCN complex the linkage with Cu(II) is through S.

For the complexes under study, the order in which the ligands contribute to the chemical shift is: SCN $<$ Br $<$ SO$_4$ $<$ Cl $<$ ClO$_4$ $<$ NO$_3$. As is well known, an ionic bonding enhances the chemical shift, whereas a covalent bonding suppresses it. Hence, the above order may also be taken as representative of the relative ionic character of the bonding in these complexes.

### 3.2 Effective nuclear charge $Z_{eff}$

One can define effective nuclear charge as a total charge within a certain molecular volume around the nucleus [5]. Various theoretical and phenomenological methods have been proposed for the estimation

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**Table 1. Copper K-edge XANES data for the copper complexes**

| S.NO. | Complex          | $E_{K1}$ (eV) | $E_{K2}$ (eV) | $E_{A}$ (eV) | Chemical Shift ($E_{K1}$-8980.5) (eV) | Edge width ($E_{A}$-$E_{K1}$) (eV) | $Z_{eff}$ |
|------|-----------------|--------------|--------------|-------------|-------------------------------------|-------------------------------|----------|
| 1    | Cu(en)$_2$(ClO$_4$)$_2$ | 8989.1       | 8994.7       | 9000.3      | 8.6                                  | 11.2                          | 1.00     |
| 2    | Cu(en)$_2$(ONO)$_2$ | 8990.6       | 8994.9       | 9000.6      | 9.7                                  | 10.4                          | 1.10     |
| 3    | Cu(en)$_2$(SCN)$_2$ | 8984.6       | 8988.4       | 9002.3      | 4.1                                  | 17.7                          | 0.52     |
| 4    | Cu(en)$_2$Cl$_2$.H$_2$O   | 8989.0       | 8994.4       | 9003.0      | 8.5                                  | 14.0                          | 0.99     |
| 5    | Cu(en)$_2$Br$_2$.H$_2$O   | 8988.3       | 8993.9       | 9002.5      | 7.8                                  | 14.2                          | 0.92     |
| 6    | Cu(en)$_2$SO$_4$       | 8988.6       | 8992.3       | 8998.4      | 8.1                                  | 9.8                           | 0.95     |
of the effective nuclear charge. In the present work, \( Z_{\text{eff}} \) has been obtained from the measured chemical shift by using the semi-experimental method by employing the procedure suggested by Nigam and Gupta [5]. The effective nuclear charge on the copper in the complexes under present study varies between 0.52 – 1.10 electrons/atom.

3.3 Splitting of the main edge

The K-edges, as shown in Fig. 1, have been found to split into two components, i.e., K\(_1\) and K\(_2\) in all of the complexes. In an extensive XANES study of Cu(I) and Cu(II) compounds Kau et al. [6] have found that a peak about 8984 eV is diagnostic of Cu(I) and has been assigned to the Cu(I) 1s→4p transition. Further, no Cu(II) complex exhibits a significant peak below 8985 eV. Berry et al. [7] have reported that in Cu(II) compounds a shoulder B in the absorption edge has been observed which is strongly \( z \)-polarized and has been assigned Cu(II) 1s→4p transition simultaneous with ligand to metal charge transfer. Another characteristic feature of Cu(II) is the maximum A at about 9000 eV which also corresponds to 1s→4p transition as well as to the transitions to continuum states. In the spectra of presently studied complexes, the peak like feature at 8984 eV, characteristic of Cu(I), is absent. Further, in the absorption edge the shoulder B is present and the feature A at about 9000 eV is also present, which are characteristic of Cu(II). Thus, copper has been found to have oxidation state +2 in the complexes, on this basis also.

3.4 Edge-width

In Table 1, we have reported the values of the edge-width (\( E_A-E_{K_1} \)). In general, edge-width of the K-absorption edge increases with the increase of covalent character of the bands provided other factors like molecular symmetry etc., remain the same [8]. In chloro, nitro, bromo, sulphato, perchlorato and thio-cyanate complexes, the edge-widths values are 14.0, 10.4, 14.2, 9.8, 11.2 and 17.7 eV, respectively.

3.5 Principal absorption maximum

In Table 1, we have also included the data for the principal absorption maximum \( E_A \) in the complexes and in the metal. It has been observed that for copper metal, the value of \( E_A \) is 8992.5 eV and for all the complexes it is shifted towards the higher energy side. The shift of principal absorption maximum depends on the type of overlap between metal and ligand orbitals. The greater the overlap of the metal and the ligand orbitals, more stable are the bonding molecular orbitals and hence the corresponding antibonding molecular orbitals are more unstable. Since, the principal absorption maximum occurs due to the transitions from 1s orbital to the unoccupied antibonding molecular orbitals (1s-5\( t_{1u} \), in octahedral), the principal absorption maximum, therefore, shifts to the higher energy side [9].

4 Conclusions

XANES study at the K-edge of copper in the six complexes studied in the present work, suggests that copper has valence state +2 in all the complexes. The effective nuclear charge on the copper in the complexes under present study varies between 0.52 – 1.10 electrons/atom. The relative ionic character has been found to follow the sequence:

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\text{Cu(en)}_2(\text{SCN})_2 < \text{Cu(en)}_2\text{Br}_2\text{H}_2\text{O} < \text{Cu(en)}_2\text{SO}_4 < \text{Cu(en)}_2\text{Cl}_2\text{H}_2\text{O} < \text{Cu(en)}_2(\text{ClO}_4)_2 < \text{Cu(en)}_2(\text{ONO}_2)_2
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