X-ray absorption studies of copper(II) mixed ligand complexes with tetramethylethylenediamine as primary ligands

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Abstract. X-ray absorption near edge structure (XANES) measurements have been made on the K-edge of copper in some of its biologically important complexes involving tetramethylethylenediamine (tmen) as primary ligand. Other inorganic anionic ligands are oxalate anion (ox), acetylacetonate anion(acac), glycinate(gly) anion and ethylenediamine(en). Various X-ray absorption parameters in the near edge region, e.g., chemical shift, i.e., shift of K-edge of copper in complex with respect to K-edge of copper metal, energy position of the principal absorption maximum and edge-width have been determined. The K-edge has been found to split into two components, i.e., $K_1$ and $K_2$ in the complexes. This feature suggests square planar geometry for the complexes. The chemical shift data suggests that in the complexes copper is in oxidation state $+$2 and that the relative ionic character of the complexes is in the following sequence: $\text{Cu(tmen)(ox).4H}_2\text{O} < \text{Cu(tmen)(acac)(ClO}_4\text{) } < \text{Cu(tmen)(gly)ClO}_4 < \text{Cu(tmen)(en)SO}_4\text{.4H}_2\text{O}$. For these four complexes, we observe that the sequence of variation of chemical shifts follows the same trend as obtained in the available spectrochemical series, i.e., oxalate < glycinate < ethylenediamine. The effective nuclear charge has been estimated from the chemical shift data.

1. Introduction

It is well known that the fine structure in the vicinity of an X-ray absorption discontinuity is influenced by the immediate surroundings of the absorbing atom. Studies of the absorption edge and the associated fine structure help in understanding the environment of a metal ion in its complexes and biologically important molecules. Chemical shifts as obtained by X-ray absorption spectroscopic studies have yielded useful information in various kinds of samples having biological relevance and utility in pharmacology. In the present paper, we have studied X-ray absorption near edge structure (XANES) at the K-edge of copper and have also measured various X-ray absorption parameters in some copper complexes involving tetramethylethylenediamine (tmen) as primary ligands and the other ligands being oxalate anion(ox), acetylacetonate anion(acac), glycinate anion(gly) and ethylenediamine(en). The ligands used are common ones (en, gly, ox and acac) with no bulky groups around the donor atoms, little steric hindrance is expected when one of them combines with copper (II) together with a tmen molecule. It was found that all these ligands form quite stable mixed chelates with tmen [1].

2. Experimental

All the complexes were prepared according to the standard methods reported in literature [1] and their purity was checked. All the mixed chelates obtained are fine crystals or apparently crystalline powders. 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 photographically on a bent crystal 0.4 m Cauchois-type transmission spectrograph employing a mica crystal, oriented to reflect from (100) planes, for dispersion. For calibrating the spectra, the tungsten emission lines $W L_{\alpha}, W L_{\beta_4}$ and $W L_{\beta_6}$ were used as reference lines. 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 K$\beta_{1,3}$ 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. Computer programs Origin and Athena [2] were used for data analysis. Derivative spectra were used for obtaining the K-edge position. The error in the measurement of K-edge was ±0.5 eV.

3. Results and Discussion

Figure 1 shows the copper K-absorption edges for all the four complexes studied. The curves in this figure represent the normalized K absorption spectra. The copper K-edges in all of the complexes have been found to split into two components, i.e., $K_1$ and $K_2$. The energies of the copper K-edge ($E_{K_1}$ and $E_{K_2}$) and the principal absorption maximum ($E_A$) along with the values of the edge-width ($E_A - E_{K_1}$) and the chemical shift $\Delta E_{K_1}$ are given in Table 1. It can be readily seen from this table that the K-absorption edge of copper is shifted towards the high energy side in all the complexes studied as compared to the K-absorption edge in the metal.

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

| S. NO. | Complex                  | $E_{K_1}$ (eV) | $E_{K_2}$ (eV) | $E_A$ (eV) | Chemical Shift (eV) | $Z_{eff}$ | Shift in principal absorption maxima (eV) |
|--------|--------------------------|---------------|---------------|------------|---------------------|----------|------------------------------------------|
| 1      | Cu(tmen)(ox).4H$_2$O     | 8980.5        | 8988.2        | 8992.5     | -                   | -        | -                                        |
| 2      | Cu(tmen)(acac) (ClO$_4$) | 8988.3        | 8993.6        | 9002.9     | 5.4                 | 0.67     | 18.5                                     |
| 3      | Cu(tmen)(en)SO$_4$.4H$_2$O | 8988.7    | 8994.0        | 8998.9     | 8.2                 | 0.96     | 22.4                                     |
| 4      | Cu(tmen)(gly)ClO$_4$     | 8988.5        | 8995.0        | 9001.1     | 8.0                 | 0.94     | 18.4                                     |

3.1 Chemical shift

The shift of the X-ray absorption edge $i$ (i = K, L, M,...) of an element in a complex with respect to that of the pure element is written as: $\Delta E_i = E_i(\text{complex}) - E_i(\text{metal})$. It is well known that the position of the K-edge depends on the valence state of the absorbing ion. But the valence state is not the only factor that governs the magnitude of the chemical shift. At least two other factors that must be considered to explain the values of the chemical shifts are stereochemistry and covalent bonding [3]. For the present complexes, the chemical shift values lie in the range 5.4 - 8.2 eV. Earlier workers [4, 5, 6] have reported the chemical shift values of various copper (II) complexes between 5.7-12.9 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 for the four complexes studied in the present work follow the sequence: Cu(tmen)(ox).4H$_2$O<Cu(tmen)(acac)(ClO$_4$)<Cu(tmen)(gly)ClO$_4$<Cu(tmen)(en)SO$_4$.4H$_2$O. For the three complexes, we observe that the sequence of variation of chemical shifts follows the same trend as obtained in the spectrochemical series, i.e., oxalate < glycinate < en. The (acac) complex finds a place between oxalate and glycinate complex. Though we know that the major contribution towards the magnitude of chemical shift depends on the ligands surrounding the central metal ion copper in the first coordination shell, but the effect of distant neighbours in the second coordination shell is not denied. Such a observation of contribution of second and higher shell ligands has been observed earlier by Gupta et al. [7]. As is well known, an ionic bonding enhances the chemical shift, whereas a covalent bonding suppresses it [3]. 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 $Z_{\text{eff}}$

$Z_{\text{eff}}$ (electrons/atom) has been obtained from the measured chemical shift by using the semi-experimental method by employing the procedure suggested by Nigam and Gupta [8]. According to this method the shift in the 1s electron energy under different oxidation state of copper atom is determined from Hartree Fock (HRF) calculations of 1s atomic function. A graph was plotted between the theoretical shift in the binding energy and the oxidation number [9] for copper (Figure 2). The effective nuclear charge $Z_{\text{eff}}$ on the copper atom in the complexes studied was then determined from this plot corresponding to the measured value of the edge shifts. The data given in Table 1 indicate that $Z_{\text{eff}}$ varies between 0.67 – 0.96 electrons/atom in the copper complexes studied.

3.3 Splitting of the main edge

The copper K-edges, as shown in Figure 1, have been found to split into two components, i.e., $K_1$ and $K_2$ in all of the complexes. This feature suggests square planar structure for the complexes investigated. In an extensive XANES study of Cu(I) and Cu(II) compounds Kau et al. [10] have found that a peak about 8984 eV is diagnostic of Cu(I) and has been assigned to the Cu(I) 1s$\rightarrow$4p$_{xy}$ transition. Further, no Cu(II) complex exhibits a significant peak below 8985 eV. Berry et al. [11] 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$\rightarrow$4p$^{*}_{xy}$ 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$\rightarrow$4p transition as well as to the transitions to continuum states. In the spectra of presently studied complexes, the peak like feature at 8984eV, characteristic of Cu (I), is absent. Further, in the absorption edge the shoulder B is present and the feature A at about 9000eV 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 2, we have reported the values of the edge-width ($E_{\text{A}}$-$E_{K1}$). The edge-widths are related to the electronegativity difference between metal atom ($X_M$) and its neighbouring atom ($X_L$) in the coordination sphere in a manner proposed by Nigam and Srivastava [12] as: $[E_{\text{W}}. \sum (X_M - X_L)]^{1/2} = \text{Constant}$, where $X_M$ and $X_L$ are the Pauling’s electronegativities of the central metal atom and the nearest neighbours respectively, and the summation on the right hand side extends over all the atoms in the coordination sphere. In Table 2 we have reported the stoichiometry of the complexes. In general the edge-width values depend not only on stoichiometry but also on the nature of bonding, i.e., ionic/covalent. As seen from Table 2 the constant has a variation from 10.1 to 12.6 the slightly different values for the edge-widths are not unusual as the stoichiometry is different.
Table 2. Values of $X_L$, $\sum (X_M - X_L)$ and constant

| S. No. | Complex                | Stoichiometry Cu: N: O | Donor environment E_W (eV) | $\sum X_L$ | $\sum (X_M - X_L)$ | Constant |
|--------|------------------------|------------------------|-----------------------------|------------|-------------------|----------|
| 1      | Cu(tmen)(ox).4H$_2$O   | 1:2:2                   | 2N, 2O                      | 13.1       | 13.0              | 11.1     | 12.0           |
| 2      | Cu(tmen)(acac) (ClO$_4$) | 1:2:2                  | 2N, 2O                      | 14.6       | 13.0              | 11.1     | 12.6           |
| 3      | Cu(tmen)(en)SO$_4$.4H$_2$O | 1:4:−                 | 4N                          | 10.2       | 12.0              | 10.1     | 10.1           |
| 4      | Cu(tmen)(gly)ClO$_4$   | 1:3:1                   | 3N, O                       | 12.6       | 12.5              | 10.6     | 11.5           |

$\sum X_M$ (for copper) = 1.9

3.5 Principal absorption maximum

For copper metal, the value of the energy of the principal absorption maximum ($E_A$) is 8992.5 eV and for all the complexes it is shifted towards the higher energy side (Table 1). Since, the principal absorption maximum occurs due to the transitions from 1s orbital to the unoccupied antibonding molecular orbitals [1s$\rightarrow$4p (t$_{1u}^*$) in octahedral], the principal absorption maximum, therefore, shifts to the higher energy side. In some cases the strength of the bond has been decided on the basis of the shift values of the principal absorption maximum. In general, the greater the overlap of metal and ligand orbitals, the greater the strength of the bond. Since strengthening of M-L bond would lead to a greater stabilisation of bonding MOs, a shift in the principal absorption maximum towards the high-energy side with increasing M-L bond strength would be expected.

4. Conclusions

The present study on the XANES at the K-edge of copper in all the complexes suggests that copper has valence state +2 in all the complexes. For all the four complexes we observe that the sequence of variation of chemical shifts follows the same trend as obtained in the spectrochemical series. The relative ionic character of the complexes has been found to have the following sequence: Cu(tmen)(ox).4H$_2$O < Cu(tmen)(acac)(ClO$_4$) < Cu(tmen)(gly)ClO$_4$ < Cu(tmen)(en)SO$_4$.4H$_2$O. The estimated effective nuclear charge ($Z_{eff}$) has been found to vary between 0.67 – 0.96 electrons/atom in the copper complexes studied.

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