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

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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 benzimidazole (BzImH) and other inorganic anionic ligands (X), viz; [Cu(BzImH)₄X₂] and [Cu(BzIm)₂], where X = Cl, Br, ¹/₂SO₄, ClO₄, NO₃, and BzIm = benzimidazolato anion. Various X-ray absorption parameters in the near edge region, such as, 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 estimated. All the complexes have been found to have copper in oxidation state +2. The shape of the K-edge has been found to show splitting of the K-edge into two components, i.e., K₁ and K₂ in all of these complexes. This feature suggests elongated octahedral and distorted tetrahedral geometries for the complexes which have also been proposed from the earlier studies. Further, the values of the chemical shift suggest the relative ionic character of the complexes in the following sequence: Cu(BzImH)₂Br₂ < Cu(BzImH)₂Cl₂ < Cu(BzImH)₂SO₄ < Cu(BzImH)₂(ClO₄)₂ < Cu(BzImH)₂(NO₃)₂. The edge-widths of the K-edge also support this relative ionic character.

Keywords: Cu K-edge XANES, Cu(II)-benzimidazole complexes

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 K-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. The imidazole ring, as a histidine moiety, and benzimidazole ring, particularly as its 5,6-dimethyl derivative, function as ligands towards transition metal ion in a variety of biologically important molecules including iron-heme systems, vitamin B₁₂ and its derivatives and several metallo-proteins. The effectiveness of the imidazole group to act as a metal binding site has been attributed to its great flexibility, availability at physiological pH (pKa ca. 7.0) and capacity to form both σ- and π-bonds with metal ions. Moreover, benzimidazole is extensively used in industrial processes as corrosion inhibitor for metal and alloy surfaces particularly that of copper. 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 benzimidazole (BzImH) and other inorganic anionic ligands (X), viz; [Cu(BzImH)₄X₂] and [Cu(BzImH)₂], where X = Cl, Br, ¹/₂SO₄, ClO₄, NO₃; and BzIm = Benzimidazolato anion. The structures of the complexes studied have been shown in Fig. 1. It should be mentioned that [Cu(BzIm₃)] has polymeric structure in which each copper involves distorted tetrahedral coordination through four N-atoms and the deprotonated benzimidazole acts as a bidentate monoanionic ligand coordinating through both of its nitrogen atoms. In Cu(BzImH)₄(ClO₄)₂ and Cu(BzImH)₄(NO₃)₂ complexes, perchlorate and nitrate groups are weakly coordinated unidentately with the Cu(II) ion through one of their oxygen atoms. All of the tetrakis-(benzimidazole) Cu(II) complexes [Cu(BzImH)₄X₂], have tetragonally distorted octahedral geometry, where neutral benzimidazole functions as a monodentate ligand coordinating through its N(3) atom.
2 Experimental Details

All the complexes were prepared according to the standard methods and their purity was checked. 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 1 cm$^2$ 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$_\alpha^2$, WL$_\beta^4$, and WL$_\beta^6$ were used as reference lines and their energies were taken from the tables of Deslattes et al. 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. For recording the K-absorption edge and the associated fine structures, it was found that accurate results were obtained when the photographic film was advanced through 10$^{-2}$ mm and the photo-detector readings were recorded. The digital records were fed into the computer. Computer programs Origin and Athena were used for data analysis. Derivative spectra were used for obtaining the K-edge position. For each sample several microphotometer records were taken and each film was scanned at three heights. Thus, the values of the K-edge features reported herein are the average of at least 9 measurements. The accuracy in the measurement of K-edge was ±0.05 eV.

3 Results and Discussion

The shapes of the copper K-edge and the associated near edge structure (XANES) for all the complexes are shown in Fig. 2. The curves in this figure represent the normalized X-ray 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 $\Delta E_{K1}$ are given in Table 1.

![Diagram](https://example.com/diagram.png)

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{K1}$ (eV)</th>
<th>$E_{K2}$ (eV)</th>
<th>$E_A$ (eV)</th>
<th>Chemical shift (eV)</th>
<th>Edge-width $E_A - E_{K1}$ (eV)</th>
<th>$Z_{eff}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper metal</td>
<td>8980.0</td>
<td>8992.5</td>
<td></td>
<td>-</td>
<td>12.5</td>
<td>-</td>
</tr>
<tr>
<td>Cu (BzIm)$_2$Cl$_2$</td>
<td>8985.8</td>
<td>8992.0</td>
<td>9003.0</td>
<td>5.8</td>
<td>17.2</td>
<td>0.71</td>
</tr>
<tr>
<td>Cu (BzIm)$_2$Br$_2$</td>
<td>8986.7</td>
<td>8993.7</td>
<td>8999.7</td>
<td>6.7</td>
<td>13.0</td>
<td>0.81</td>
</tr>
<tr>
<td>Cu (BzIm)$_2$Cl$_2$</td>
<td>8987.0</td>
<td>8995.9</td>
<td>8999.0</td>
<td>7.0</td>
<td>12.0</td>
<td>0.84</td>
</tr>
<tr>
<td>Cu (BzIm)$_2$SO$_4$</td>
<td>8987.5</td>
<td>8996.0</td>
<td>9001.2</td>
<td>7.5</td>
<td>13.7</td>
<td>0.89</td>
</tr>
<tr>
<td>Cu (BzIm)$_2$(ClO$_4$)$_2$</td>
<td>8988.3</td>
<td>8996.9</td>
<td>9004.1</td>
<td>8.3</td>
<td>15.8</td>
<td>0.97</td>
</tr>
<tr>
<td>Cu (BzIm)$_2$(NO$_3$)$_2$</td>
<td>8988.5</td>
<td>8996.1</td>
<td>9000.9</td>
<td>8.5</td>
<td>12.4</td>
<td>0.99</td>
</tr>
</tbody>
</table>

**Fig. 1** — The structure of Cu(BzIm)$_4$X$_2$ complexes where X= Cl$^-$, Br$^-$, ClO$_4^-$, NO$_3^-$

**Fig. 2** — Copper K-edge XANES spectra for the copper complexes. The different spectra have been shifted vertically for better presentation.
3.1 Chemical shift
The shift of the X-ray absorption edge $i$ ($i = K, L, M, \ldots$) of an element in a compound/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. For the present complexes, the chemical shift values lie in the range 5.8-8.5 eV. Earlier researchers have reported the chemical shifts of Co(bipy)Cl as 5.93 and 8.15 eV, respectively. In these reports, such decreases in the chemical shift from chloro to bromo derivatives have been attributed to the large polarizability of the bromide ion.

In the present case, the chemical shifts observed for Cu(BzImH)$_3$(NO$_3$)$_2$ and Cu(BzImH)$_4$(ClO$_4$)$_2$ are nearly the same, i.e., 8.5 and 8.3 eV, respectively. Nearly similar values of the chemical shifts in these complexes suggest that NO$_3$ and ClO$_4$ anions have almost similar effect on the chemical shift in these complexes. The chemical shift of 7.5 eV for Cu(BzImH)$_2$SO$_4$, though less than those for nitro and perchlorato analogues, is slightly greater than those for chloro and bromo analogues. It should be noted that the sulphato group is coordinated through two of its oxygen atoms in the complex, Cu(BzImH)$_2$SO$_4$.

For the complexes under study, the order in which the ligands contribute to the chemical shift is: Br < Cl < SO$_4$ < 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 $Z_{\text{eff}}$
Various methods have been proposed for the estimation of effective nuclear charge. Suchet’s method and other methods based on the work of Ovsyannikova et al. and Gianturco and Coulson have been applied by a large number of researchers to estimate $Z_{\text{eff}}$ (electrons/atom) on the metal atom. 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. According to this method, the chemical shift in the 1s electron energy under different oxidation state of copper atom is determined from Hartree Fock (HRF) calculations of 1s atomic orbitals. 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.

3.3 Splitting of main edge
The copper K-edges, as shown in Fig. 2, have been found to split into two components, i.e., $K_1$ and $K_2$ in all of the complexes. This feature suggests tetragonally elongated octahedral structure for the complexes Cu(BzImH)$_3$Cl$_2$, Cu(BzImH)$_3$Br$_2$, Cu(BzImH)$_4$(NO$_3$)$_2$, Cu(BzImH)$_4$(ClO$_4$)$_2$ and Cu(BzImH)$_2$SO$_4$ and distorted tetrahedral structure for Cu(BzIm)$_2$. 
Because X-ray absorption spectra are taken over a range of increasing X-ray energies, single and multiple scattering events dominate in different portions of the spectrum. The higher energy portions, i.e., extended X-ray absorption fine structure spectra are dominated by single-scattering events within only some tenths of nm (500-600 pm) from the absorber, and contain information specific to the local structure surrounding the absorber. On the other hand, XANES spectra, being centred close to the absorption jump, are dominated by multiple scattering events extending a few nm from the absorber. The shape of the absorption edge is related to the density of states available for the excitation of the photoelectron. Therefore, the binding geometry and the oxidation state of the atom affect the XANES part of the absorption spectra.

In an extensive XANES study of Cu(I) and Cu(II) compounds Kau et al. have found that a peak about 8984 eV is diagnostic of Cu(I) and has been assigned to the Cu(I) $1s \rightarrow 4p_{x,y}$ transition. Further, no Cu(II) complex exhibits a significant peak below 8985 eV.

Berry et al. 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) $1s \rightarrow 4p_{x,y}$ 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 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

Table 1 presents the values of the edge-width ($E_A - E_{K1}$). In general, edge-width of the K-absorption edge increases with the increase of covalent character of the bonds provided other factors like molecular symmetry remain the same. The values of the edge-width are 12.0 and 13.0 eV for chloro and bromo complexes, respectively. This order is just opposite to that of the chemical shift values. The reverse trend for these two complexes is justified on the basis of the above-mentioned criterion. In chloro, nitro, bromo, sulphato and perchlorato complexes, the edge-widths are 12.0, 12.4, 13.0, 13.7 and 15.8 eV, respectively, whereas for Cu(BzIm)$_2$ complex, the edge-width is 17.2 eV. All the complexes have tetragonally elongated octahedral geometry except Cu(BzIm)$_2$ which has distorted tetrahedral geometry. Previous studies support this observation because complexes with tetrahedral and square planar geometries show larger edge-widths than the octahedral ones.

### 3.5 Principal absorption maximum

Table 1 also presents 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 ($1s - 5t_{1u}$ in octahedral), the principal absorption maximum, therefore, shifts to the higher energy side.

### 4 Conclusions

The present study on the XANES at the K-edge of copper in Cu(BzIm)$_2$ and Cu(BzImH)$_2$X$_2$, where X= Cl, Br, 1/2SO$_4$$_2$, ClO$_4$, NO$_3$; and BzIm = Benzimidazolato anion suggests that copper has valence state +2 in all the complexes. The estimated X-ray absorption parameters suggest that the relative
ionic character of the complexes has the following sequence: \( \text{Cu(BzImH)}_4\text{Br}_2 < \text{Cu(BzImH)}_4\text{Cl}_2 < \text{Cu(BzImH)}_4\text{SO}_4 < \text{Cu(BzImH)}_4\text{ClO}_4 < \text{Cu(BzImH)}_4(\text{NO}_3)_2 \). The study supports tetragonally elongated octahedral geometry for the mixed ligand complexes.

References