

XAFS Study of Benzimidazole Mixed Ligand Complexes of Copper

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Abstract. X-ray absorption fine structure has been studied at the Cu K-edge in copper complexes having benzimidazole as primary ligand and chloride, bromide, nitrate, sulphate as secondary ligands. The spectra have been recorded on beamline BL-8 of Indus-2 synchrotron at RRCAT, Indore. From the X-ray absorption near edge structure (XANES) data, various X-ray absorption parameters, viz., shift of the edge, shift of the principal absorption maximum and edge-width have been obtained. The experimentally observed values of chemical shifts indicate that copper is in oxidation state +2 in the samples. The chemical shifts have also been used to determine effective nuclear charge on the central metal ion in the complexes. The first shell bond distances have been determined from the extended X-ray absorption fine structure (EXAFS) data by three different graphical methods, namely, Levy's, Lytle's and LSS methods. Fourier transforms of the normalized spectra have also been used to obtain bond lengths. The bond lengths determined from LSS method and that determined from the Fourier transformation method are in good agreement with each other. The present results obtained using synchrotron have been compared with those reported earlier using laboratory X-ray spectroscopic set-up employing X-ray tube.

INTRODUCTION

Benzimidazole is a bicyclic compound which consists of fusion of benzene and imidazole. Benzimidazole moieties are important class of heterocyclic compounds which possess many pharmacological properties. Benzimidazole derivatives were synthesized by derivatization at N-H of benzimidazole by electron donating group and substitution with long chain of different ligands. Based on their broad biological functions, they are used in clinical medicine as anti-ulcer, antitumor and anti-viral agents [1]. 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 [2]. The effectiveness of the imidazole group to act as a metal binding site has been attributed to its great flexibility, its availability at physiological pH (pK_a ca. 7.0) and its 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 [3].

In the present investigation, we have studied X-ray K-absorption spectra of copper in the copper complexes with benzimidazole (BzImH) as primary ligand. The secondary ligands are: chloride, bromide, nitrate and sulphate. Also the parent complex Cu(BzIm)₂ has been included in the present studies. The formulae of the complexes investigated are: Cu(BzImH)₄(NO₃)₂ (**I**), Cu(BzImH)₄SO₄ (**II**), Cu(BzImH)₄Cl₂ (**III**), Cu(BzImH)₄Br₂ (**IV**) and Cu(BzIm)₂ (**V**). [Cu(BzIm)₂] 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. 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.

EXPERIMENTAL

The samples were prepared by methods reported in literature [4]. Dispersive extended X-ray absorption fine structure (DEXAFS) beamline BL-8 at the 2.5 GeV synchrotron Indus-2 at RRCAT, Indore [5] have been utilized for recording the X-ray absorption fine structure (XAFS) spectra according to the procedure outlined in ref. [5]. For data analysis, computer program *Athena* [5] was used.

RESULTS

Fig.1 displays the normalized absorption spectra at the K-edge of copper in the five complexes. Fig.2(a) shows the first derivative of the XAFS spectra of one of the complex, namely, $\text{Cu}(\text{BzImH})_4\text{Cl}_2$ (as an example spectra) indicating positions of the absorption edges K_1 and K_2 and principal absorption maximum (PAM) A. Fig.2(b) represents the extended X-ray absorption fine structure (EXAFS) spectra in k space. Conventional Latin and Greek alphabets have been used to represent EXAFS maxima and minima in Fig.2(b). The magnitude of Fourier transform of Fig.2(b) is shown in Fig.2(c). Table 1 gives the X-ray absorption near edge structure (XANES) data. The values of energies of K-edges E_{K1} and E_{K2} , principal absorption maximum (A) E_A , chemical shift ΔE , edge-width ($E_A - E_{K1}$), shift of A with respect to that of metal. The values from ref. [6,8] (Laboratory experiment) are also given in parenthesis below the present values for comparison. All energy values are in eV (± 0.5). The estimated effective nuclear charge on copper ion is also given in Table1.

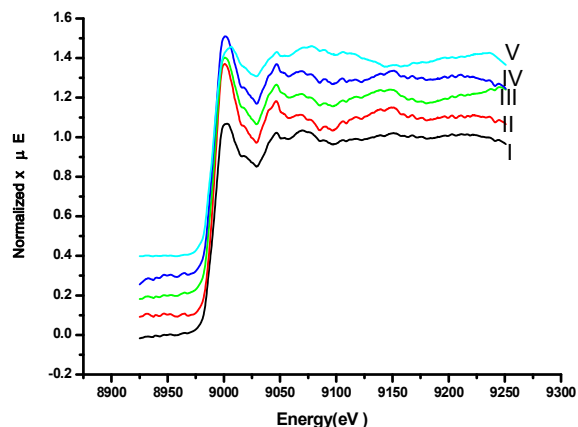


FIGURE 1 X-ray absorption fine structure (XAFS) at Cu K-edge in the five copper mixed ligand complexes I to V. The different spectra have been shifted vertically for better presentation.

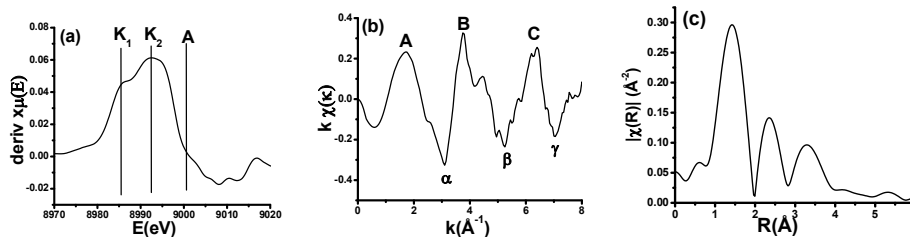


FIGURE 2 (a) Derivative of XAFS spectrum indicating position of absorption edges K_1 and K_2 and principal absorption maxima A (b) $\chi(k)$ versus k curve showing maxima A, B and C and minima α , β and γ and (c) Magnitude of Fourier transform of the $\chi(k)$ versus k curve for copper complex $\text{Cu}(\text{BzImH})_4\text{Cl}_2$ (as a representative example).

TABLE 1. Values of energies of K-edges E_{K1} and E_{K2} , principal absorption maximum (A), E_A , chemical shift ΔE , edge-width ($E_A - E_{K1}$) and shift of A w.r.t. metal. The values from ref. [6] (Laboratory experiment) are also given in parenthesis below the present values for comparison. All energy values are in eV (± 0.5). The estimated effective nuclear charge on copper ion is also given.

Complex Code	Energy E_{K1}	Energy E_{K2}	Energy E_A	Chemical Shift ΔE	Edge-Width ($E_A - E_{K1}$)	Effective Nuclear Charge	Shift of A w.r. t. Metal
Metal	8980.5 (8980.0)	8988.2 (8988.2)	8992.5 (8992.5)	-	12.0 (12.5)	-	-
I	8987.5 (8988.5)	8995.2 (8996.1)	9002.2 (9000.9)	7.0 (8.5)	14.7 (12.4)	0.81 (0.99)	9.7 (8.4)
II	8987.1 (8987.5)	8994.0 (8996.0)	9002.7 (9001.2)	6.6 (7.5)	15.6 (13.7)	0.69 (0.87)	10.2 (10.2)
III	8986.8 (8987.0)	8992.4 (8995.9)	9001.0 (8999.0)	6.3 (7.0)	14.2 (12.0)	0.65 (0.84)	8.5 (8.5)
IV	8986.4 (8986.7)	8992.8 (8993.7)	9001.6 (8999.7)	5.9 (6.7)	15.2 (13.0)	0.62 (0.81)	9.1 (7.2)
V	8985.6 (8985.8)	8991.6 (8992.0)	9005.9 (9003.0)	5.1 (5.8)	20.3 (17.2)	0.55 (0.71)	13.4 (10.5)

TABLE 2. Values of bond lengths R_1 calculated from Levy's method, R_s calculated from Lytle's method and $R_1 - \alpha_1$ calculated from LSS and FT methods. The values from ref. [8] (Laboratory experiment) are also given in parenthesis below the present values for comparison. All values are in Å (± 0.1).

Code	Complex	Levy's method R_1	Lytle's method R_s	LSS method $R_1 - \alpha_1$	FT method $R_1 - \alpha_1$
I	Cu(BzImH) ₄ (NO ₃) ₂	1.80 (1.85)	1.60 (1.61)	1.53 (1.42)	1.40 (1.48)
II	Cu(BzImH) ₄ SO ₄	1.75 (1.83)	1.59 (1.67)	1.52 (1.46)	1.46 (1.42)
III	Cu(BzImH) ₄ Cl ₂	1.73 (1.81)	1.57 (1.56)	1.51 (1.35)	1.44 (1.25)
IV	Cu(BzImH) ₄ Br ₂	1.76 (1.85)	1.60 (1.60)	1.54 (1.36)	1.51 (1.23)
V	Cu(BzIm) ₂	1.52 (1.89)	1.40 (1.60)	1.17 (1.41)	1.15 (1.39)

DISCUSSION

X-ray absorption near edge structure (XANES)

Chemical shift (ΔE): A perusal of Table 1 indicates that the chemical shift values obtained in the present studies lie in the range 5.1 to 7.0 eV, whereas for earlier reported values [6] the range is 5.8 to 8.5 eV. Earlier workers have reported the shift ΔE values of various copper (II) complexes between 5.7 to 12.9 eV. Considering this range of shift ΔE values, it may be safely concluded that our samples possess oxidation state +2. The magnitude of chemical shift for the distorted tetrahedral complex, Cu(BzIm)₂ is 5.1 eV. In the parent compound Cu(BzIm)₂, when other ligands are introduced in the environment around the central metal ion, the shift values ΔE has been found to increase. The chemical shifts for the two complexes, Cu(BzImH)₄Cl₂ and Cu(BzImH)₄Br₂ are 6.3 eV and 5.9 eV, respectively. Similar trend of variation, i.e., a slightly smaller value of shift ΔE for bromo complex in comparison to chloro complex has also been observed in previous studies. A decrease in shift value ΔE from chloro to bromo derivatives in the presently studied complexes may be attributed to the large polarizability of the bromide ion and also to less electro negativity of bromine as compared to chlorine. It also reveals the fact that chloro bonding is more ionic as compared to bromo bonding. To understand the order of chemical shifts in the three complexes, viz., Cu(BzImH)₄Br₂, Cu(BzImH)₄Cl₂ and Cu(BzImH)₄(NO₃)₂ a look on the spectrochemical series is useful. For the ligands involved in the above complexes, the order in the spectrochemical series is: $Br^- < Cl^- < NO_3^-$. A perusal of chemical shift values also exhibits the same sequence of variation. The order in which the ligands contribute to the

chemical shift is: $\text{Br} < \text{Cl} < \text{SO}_4 < \text{NO}_3$. Thus, the above sequence represents the relative ionic character of the bonding in these samples.

Effective nuclear charge (ENC): ENC has been estimated from the measured chemical shift values by employing the procedure suggested by Nigam and Gupta [7]. The data given in Table 1 indicate that ENC varies between 0.55 to 0.81 electrons/atom in the copper complexes studied.

Splitting of the main edge: Fig. 2(a) shows that the K-edges have been found to split into two components, i.e., K_1 and K_2 in all the samples. This type of splitting is suggestive of tetragonally elongated octahedral structure for the complexes whereas the parent complex $\text{Cu}(\text{BzIm})_2$ is having distorted tetrahedral structure.

Edge-width (E_w): In chloro, nitro, bromo and sulphato complexes, the edge-widths are 14.2, 14.7eV, 15.2eV, and 15.6eV, respectively, whereas for $\text{Cu}(\text{BzIm})_2$ complex, the edge-width is 20.3eV. This observation supports the proposed structure of complexes because tetrahedral and square planar geometries show larger edge-widths than the octahedral ones.

Shift of the principal absorption maximum: The shift of the principal absorption maxima values may also be used for defining the oxidation state of central metal ion copper. In the present case the variation of the values for the shift of principal absorption maxima is in a narrow range, therefore the studied samples possess oxidation state +2.

Determination of bond lengths from extended X-ray absorption fine structure (EXAFS)

By graphical methods from EXAFS spectra: On the high energy side of the K-absorption edge, EXAFS have been observed in all the complexes. In the present work, the bond lengths have been determined for the copper complexes with the help of three methods: (a) Levy's method, (b) Lytle's method and (c) LSS method [8]. The results are given in Table 2.

By Fourier transform (FT) of EXAFS spectra: The position of the first peak in the Fourier transform gives the value of $(R_1 - \alpha_1)$ and the values are collected in Table 2 for all the complexes. The parameter α_1 depends to a large extent on the central absorbing atom. It is found that for chemically similar system, the values of α_1 remain more or less the same. It is seen from this table that the values of $(R_1 - \alpha_1)$ obtained from LSS method and that determined from the FT method are in good agreement.

CONCLUSIONS

The XANES data for the complexes studied have provided the evidence that all the samples possess oxidation state +2. From the EXAFS data, bond distances have been determined by three different graphical methods. The normalized spectra, i.e., $\mu(E)$ versus E curves have been obtained. From these curves, $\chi(k)$ versus k curves have been obtained, which have then been Fourier transformed using the software *Athena*. From the Fourier transforms of the EXAFS spectra the bond lengths have also been determined. The bond lengths determined from LSS method and that determined from the Fourier transformation method are in good agreement with each other. A comparison of the present values with those reported earlier [6,8] shows that the results obtained in the present work using synchrotron are highly reliable and more accurate than those obtained using laboratory X-ray spectroscopic set up employing X-ray tube.

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