Abstract. Extended X-ray absorption fine structure (EXAFS) spectra have been studied at the K-edge of copper in some of its biologically important complexes, viz., [Cu(BzImH)\textsubscript{4}X\textsubscript{2}] and [Cu(BzIm)\textsubscript{2}], where X = Cl, Br, 1/2SO\textsubscript{4}\textsuperscript{2-}, ClO\textsubscript{4}\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, and BzIm = Benzimidazolato anion. The spectra have been recorded using a bent crystal 0.4 m Cauchois-type transmission spectrograph. The positions of EXAFS maxima and minima have been used to determine the bond lengths in the complexes with the help of three different methods, namely, Levy’s, Lytle’s and Lytle, Sayers and Stern’s (L.S.S.) methods. The phase uncorrected bond lengths have also been determined from Fourier transforms of the experimental spectra. The results obtained from these methods have been discussed and it has been found that the results obtained by L.S.S. method are comparable with the results obtained by Fourier transformation method and that these two methods give phase uncorrected bond lengths.

1. Introduction
The X-ray absorption spectra at the K-edge of copper have been studied in some of its biologically important complexes, viz., [Cu(BzImH)\textsubscript{4}X\textsubscript{2}] and [Cu(BzIm)\textsubscript{2}], where X = Cl, Br, 1/2SO\textsubscript{4}\textsuperscript{2-}, ClO\textsubscript{4}\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, and BzIm = Benzimidazolato anion. All the complexes studied have benzimidazole as primary ligand. Benzimidazole is extensively used in industrial processes as corrosion inhibitor [1] for metal and alloy surfaces particularly that of copper. Earlier [2] we have reported the measurements on X-ray absorption near edge structure (XANES), e.g., chemical shift, energy of the principal absorption maximum and edge-width in all the complexes. The present paper reports the results of the studies of extended X-ray absorption fine structure (EXAFS) of these complexes.

2. Experimental
All the complexes were prepared according to the standard methods reported in literature [3] and their purity was checked. A sealed Machlett X-ray tube with 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 digital records of the K absorption spectra were obtained using a Carl-Zeiss GII microphotometer. Computer programs Origin and Athena [4] have been used for data analysis. The normalized spectra for all the copper complexes

Extended X- ray absorption fine structure study at the K-edge of copper in mixed ligand complexes having benzimidazole as one of the ligands

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under consideration are given in Fig. 1. EXAFS have been observed on the high energy side of the K-absorption edge in all the copper complexes studied. In Fig. 1 the maxima have been labeled as A, B, C, …, while minima by Greek letters α, β, γ, ….. The values of energy (E) of maxima and minima and the corresponding k values (where \( k = 0.263(E - E_0)^{1/2} \)) are given in Table 1. Other experimental details are the same as the reported earlier [2].

Table 1. EXAFS parameters for Cu(II) complexes

| Structure | Q | n | Cu(BzImH)\(_4\) \(\text{(NO}_3\text{)}_2\) | Cu(BzImH)\(_4\) \(\text{(ClO}_4\text{)}_2\) | Cu(BzImH)\(_4\) \(\text{SO}_4\) | Cu(BzImH)\(_4\) \(\text{Cl}_2\) | Cu(BzImH)\(_4\) \(\text{Br}_2\) | Cu(BzIm)\(_2\) |
|-----------|---|---|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| A         | 2.04 | 0 | 12 | 1.80 | 15.8 | 2.03 | 13. | 1.89 | 12. | 1.77 | 13.0 | 1.84 | 17. | 2.1 |
| α         | - | 1 | 40 | 3.24 | 40 | 3.24 | 40 | 3.24 | 40 | 3.24 | 35 | 3.03 | 42 | 3.3 |
| B         | 6.04 | 2 | 71 | 4.32 | 68 | 4.22 | 63 | 4.07 | 78 | 4.52 | 65 | 4.13 | 78 | 4.5 |
| β         | - | 3 | 115 | 5.49 | 124 | 5.71 | 10 | 5.32 | 12 | 5.71 | 109 | 5.35 | 120 | 5.6 |
| C         | 12.0 | 4 | 157 | 6.42 | 163 | 6.54 | 14 | 6.21 | 16 | 6.58 | 158 | 6.44 | 163 | 6.5 |
| γ         | - | 5 | 201 | 7.27 | 232 | 7.81 | 20 | 7.36 | 21 | 7.55 | 217 | 7.55 | 226 | 7.7 |

3. Results and Discussion

Bond lengths have been determined from EXAFS by four different methods as given below.

3.1 Levy’s method:
Levy [5] has given a method for obtaining the bond lengths from the analysis of EXAFS. According to Levy, the maximum, labeled A should correspond to a transition from the 1s to a vacant 4p level, and the maximum, labeled B, to a kind of ionization or escape energy for the 1s electron. Furthermore, the distance \( \Delta E \), from the maximum at B to the minimum at \( \alpha \) should be a measure of the radius \( R_1 \) of the first coordination sphere through Bragg relation \( R_1 = (151 /\Delta E)^{1/2} \) Å. The values of \( R_1 \) determined by this method are given in Table 2. \( R_1 \) calculated in this way represents the average bond length.

3.2 Lytle’s method:
Lytle [6] has proposed a theory in which a nearly spherical polyhedron is constructed in the lattice and approximated by a sphere of equivalent volume with radius \( R_s \). In this method photoelectron ejected as a result of absorption of X-rays are thought of as if they are in a particle in a box. Solving the Schrodinger equation, Lytle has found that an absorption maximum will occur whenever \( E \) satisfies the equation \( E = (h^2 / m R_s^2) Q \), where \( h \) is Planck’s constant, \( m \) is the electron mass, and \( Q \) represents the zero roots of the half-order Bessel function which appear in the radial part of the solution of the wave equation. The \( Q \) values for the K-edge are 2.04, 6.04, 12.00 and 20.00. A simple data analysis scheme is obtained, when \( E \) is plotted against \( Q \), where the slope of the straight line contains \( R_s \). If \( M \) is the slope, the following relation holds \( R_s = (37.60/M)^{1/2} \) Å. The plot of \( E \) vs \( Q \) for the complexes studied are found to be linear and are shown in Fig 2. The values of \( R_s \) determined from these plots are given in Table 2. It may be remarked here that the interatomic distance obtained by this method has to be multiplied by a factor greater than unity and appropriate to the geometry of the system to obtain the correct bond length.

3.3 Lytle, Sayers and Stern’s (L.S.S.) method:
In Lytle, Sayers and Stern’s (L.S.S.) method [7], plot of \( n \) vs \( k \) for the different maxima (\( n = 0, 2, 4, ... \)) and minima (\( n = 1, 3, 5, ... \)) should results in a straight line. \( n \) vs \( k \) graph for the complexes studied are linear as shown in Fig. 3. The slope (\( M' \)) of this line is given by \( M' = 2(R_1 - \alpha_1)/\pi \). The value of \( (R_1 - \alpha_1) \) can be obtained from the slope of the \( n \) vs \( k \) plot. Once \( \alpha_1 \) is evaluated for a standard,
R₁ for unknown materials can be determined. It is found that for chemically similar systems, the value of α₁ remains more or less the same. In the present work, the value of α₁ has been taken as 0.43 [8]. The values of R₁ thus obtained by this method are given in Table 2. The distance R₁ obtained from this method is phase uncorrected bond length.

3.4 Fourier transform method:
The fine structure amplitude function, χ(E), of an EXAFS spectrum has been determined using the relation χ(E)=[μ(E)−μ₀(E)]/Δμ₀(E), where μ(E) is the experimental absorption coefficient, μ₀(E) is the atomic contribution to the absorption coefficient and Δμ₀(E) is the measured absorption jump. This χ(E) has been first converted to χ(k), and then χ(k) has been Fourier transformed (Fig. 4). The position of the first peak in the Fourier transform corresponds to the distance between the absorbing atom and its nearest neighboring atoms, i.e., the radius of first coordination sphere. However, the bond length thus obtained is less than the actual bond length, because it is phase uncorrected. The values for the phase uncorrected bond lengths for all the complexes are given in Table 2.

Table 2. Values of bond lengths (in Å ± 0.1)

| Complex No. | Complex | Levy’s method R₁ | Lytle’s method Rₙ | LSS method R₁-α₁ | Fourier Transform method (R₁ phase uncorrected) R₁-α₁ |
|-------------|---------|------------------|-------------------|-----------------|----------------------------------|
| 1           | Cu(BzImH)₄(NO₃)₂ | 1.85             | 1.61              | 1.42            | 1.85                             | 1.48                             |
| 2           | Cu(BzImH)₄(ClO₄)₂ | 1.64             | 1.59              | 1.35            | 1.78                             | 1.28                             |
| 3           | Cu(BzImH)₄SO₄      | 1.83             | 1.67              | 1.46            | 1.89                             | 1.42                             |
| 4           | Cu(BzImH)₂Cl₂      | 1.81             | 1.56              | 1.35            | 1.78                             | 1.25                             |
| 5           | Cu(BzImH)₂Br₂      | 1.85             | 1.60              | 1.36            | 1.79                             | 1.23                             |
| 6           | Cu(BzIm)₂           | 1.89             | 1.60              | 1.41            | 1.84                             | 1.39                             |

Figure 1. The K-absorption edge of copper along with the fine structure for the copper complexes. The different spectra have been shifted vertically for better presentation.

Figure 2. E vs Q plot (Lytle plot) for the copper complexes. The different spectra have been shifted vertically for better presentation.

Figure 3. n vs k (in Å⁻¹) plot (LSS plot) for the copper complexes. The different spectra have been shifted horizontally for better presentation.
Figure 4. Fourier transformed EXAFS spectra for the complexes

4. Conclusions
A comparison of the values of $R_s$ are found to be slightly lesser than the corresponding bond lengths obtained by Levy’s method. This may be ascribed to the fact that Levy’s method gives the radius of coordination sphere directly where as Lytle’s method does not. In the later method, the interatomic spacing is obtained by multiplying $R_s$ with a factor appropriate to the geometry of the system. The values of the phase uncorrected bond length obtained from LSS method are comparable with the values of phase uncorrected bond length obtained from Fourier transformation method with an error of ±0.05 Å.

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