Extended X-ray absorption fine structure data analysis of copper (II) hydroxamic acid mixed ligand complexes

N Parsai¹, A Mishra¹ and B D Shrivastava²

¹School of Physics, Devi Ahilya University, Indore 452001, India
²School of Studies in Physics, Vikram University, Ujjain 456010, India

* E-mail: parsai.neetu@gmail.com

Abstract. The X-ray absorption spectra of copper mixed ligand complexes, having hydroxamic acid as one of the ligands, have been recorded at the K-edge of copper at BL-8 Dispersive EXAFS beamline at the 2.5 GeV INDUS-2 Synchrotron, RRCAT, Indore, India. For the analysis of EXAFS data, crystallographic data of the complex or of its analog is required, which is not available. Hence, for the analysis of EXAFS data, theoretical EXAFS data of the studied complexes have been generated using the EXAFS equation employing computer software program Mathcad. Firstly, the experimental data has been processed using the computer program Athena to obtain the normalized absorption versus energy data. From the experimental EXAFS data, the phase shift parameter (an energy independent constant δ) has been computed using Lytle, Sayers and Stern’s (LSS) method. The backscattering amplitude has been taken from the available theoretical tabulations and other parameters have been taken from crystallographic data of the copper metal. Fourier transforms of both the experimental and theoretical data have been computed, and the two Fourier transforms are found to agree with each other for all the complexes. The position of the first peak in the Fourier transform gives the value of the first shell bond length, which is shorter than the actual bond length as a result of energy dependence of the phase factor (δ(k)) in the sine function of the EXAFS equation. Since, the Fourier transform method and LSS method both are uncorrected for phase and other parameters of the EXAFS equation, the present method gives phase uncorrected bond length of the first coordination shell.

1. Introduction
For the analysis of extended X-ray absorption fine structure (EXAFS) data, the crystal structure of either the complex studied or of its analogous complex is required. The crystallographic information is used to generate theoretical model by using software programs like Artemis. In the present work some copper complexes have been studied of which the crystallographic data is not available. Hence, for the analysis of their EXAFS data, the method outlined by us in our earlier communications has been used [1, 2]. The method is simple as it generates theoretical EXAFS data employing computer software program Mathcad. The copper complexes studied have been listed in table 1. The experimental EXAFS data of the copper complexes have been recorded at the K-edge of copper at BL-8 Dispersive EXAFS beamline at the 2.5 GeV INDUS-2 Synchrotron, RRCAT, Indore, India.
2. Analysis of experimental EXAFS data
Firstly, the experimental data has been processed using the computer program Athena to obtain the normalized absorption (μx) vs. energy (E) data and then the EXAFS oscillations χ(k) vs. wave vector (k) data is obtained, which are shown in fig. 1. Fourier transforms of the experimental EXAFS data, given fig. 1, have been computed, which are given in fig. 2.

3. Computation of theoretical EXAFS data
The theoretical EXAFS data has been computed for the complexes using the standard form of EXAFS equation [3].

\[ \chi(k) = \sum_j N_j S^2_j F_j(k) \times \exp(-2\sigma^2_j k^2) \times \exp\left(-2R_j / \lambda(k)\right) \times \sin[2kR_j + \delta_j(k)] \] … (1)

The subscript \( j \) denotes the various scattering paths, \( N_j \) is the number of atoms in the \( j \)th coordination shell, \( R_j \) is the average radial distance to the \( j \)th atom and \( \sigma^2_j \) is mean square deviation about the bond length. \( S^2_j \) is the passive electron reduction factor and accounts for the slight relaxation of the remaining electrons in the presence of the core-hole vacated by the photoelectron. \( S^2_j \) usually has a value between 0.7 and 1.0 and is different for different elements. The function \( F_j(k) \) is the photoelectron backscattering amplitude and \( \delta_j(k) \) is the scattering phase shift for each scattering path. \( \lambda(k) \) is the photoelectron mean free path which is dominated by lifetime of the excited state.

In our earlier works [1, 2], we have developed a simple analysis procedure for extracting bond length for the first coordination shell from the experimental EXAFS data. The method is simple and novel because calculations are done using the computer software Mathcad. The theoretical model is generated through the EXAFS equation given in eqn. (1) for the first shell. The values of \( N_j, \sigma^2_j \) and \( \lambda \) have been taken from the crystallographic data of copper metal [4, 5]. The backscattering amplitude \( F_j(k) \) has been taken from the table of Mckale [6]. The phase shift \( \delta_1 \) has been extracted from the experimental data in the following manner.

The analysis depends on the argument of the sine term in eqn. (1), i.e., \( \sin[2kR_1 + 2\delta(k)] \) where \( \delta_1 \) is assumed as linear in \( k \), i.e., \( \delta_1 = -\alpha k + \beta_1 \). Substituting into the argument of sine and rearranging for the first coordination shell \( j = 1 \), it is convenient to define \( n \) by [7]:

\[ (n + \frac{1}{2})\pi = 2k(R_1 - a_i) + 2\beta_1 \] … (2)

where \( n = 0, 2, 4… \) for maxima and \( n = 1, 3, 5… \) for minima. Using the graphical method outlined by Lytle, Sayers and Stern (LSS method) [4, 5], a plot of \( n \) versus \( k \) for the maxima and minima of the measured EXAFS data determines \( (R_1 - a_i) \) from slope and \( \beta_1 \) from intercept.

4. Results and Discussion
From the experimental \( \chi(k) \) versus \( k \) plots, given in fig. 1, the values of \( k \) corresponding to maxima and minima of \( \chi(k) \) have been obtained and are given in table 3. The \( n \) versus \( k \) curves are given in fig. 3 for the complexes. The values of \( (R_1 - a_i) \) and \( \beta_i \) determined respectively from the slope and the intercept of these plots. Taking \( a_i \) to be 0.31 Å, \( R_1 \) and \( \delta_1 \) have been calculated and used in eqn. (1) and the theoretical EXAFS \( \chi(k) \) data have been obtained for all the complexes and are given in fig 4. This theoretical EXAFS data has been Fourier transformed which are given in fig. 5. Fourier transforms of both the experimental and theoretical data, given in figs. 2 and 5 respectively, have been found to agree with each other for all the complexes. The position of the first peak in this Fourier transform gives the value of the bond length, i.e., the average distance between the absorbing atom and the neighboring atoms. However, the position of the first peak in these Fourier transforms gives the value of the first shell bond length, which is shorter than the actual bond length as a result of energy dependence of the phase factor \( \delta(k) \) in the sine function of the EXAFS equation [8]. The phase uncorrected bond lengths thus determined from the theoretical EXAFS data are given in table 2.

Thus the present method gives phase uncorrected bond length of the first coordination shell. It can be seen from Figs. 2 to 5 that the theoretical \( \chi(k) \) curves as well as their Fourier transforms are in good agreement with their experimental counterparts, showing that the simplified method presented in this
work is quite satisfactory. The values of bond length for the first shell in all copper complexes obtained from the present analysis of the experimental and theoretical EXAFS data, given in table 2 are in good agreement with each other.

### Table 1 Copper (II) hydroxamic mixed ligand complexes with their abbreviations and molecular formulae.

| S.No. | Complex                                | Abbreviation | Molecular formula   |
|-------|----------------------------------------|--------------|--------------------|
| 1.    | Cu(II) 5 chloro-benzohydroxamic acid   | Cu 5CBHA     | CuC₅H₇O₂NCl       |
| 2.    | Cu(II) malanohydroxamic acid           | Cu MHA       | CuC₂H₇O₃          |
| 3.    | Cu(II) succenohydroxamic acid          | Cu SuHA      | CuC₅H₉O₂N₂       |

### Table 2 Values of the first shell bond lengths R(Å) obtained from the Fourier transforms of the experimental EXAFS data and from the theoretical data.

| S.No. | Complex | R (from FT of experimental data) | R (from FT of theoretical data) |
|-------|---------|---------------------------------|---------------------------------|
| 1     | Cu 5CBHA| 1.81                            | 1.87                            |
| 2     | Cu MHA  | 1.38                            | 1.44                            |
| 3     | Cu SuHA | 2.07                            | 2.11                            |

### Table 3 Wave vector k (Å⁻¹) for EXAFS maxima and minima at the K-absorption edge of copper in the complexes and their corresponding values of n for LSS plots.

| n   | Wave vector k (Å⁻¹) | Cu 5CBHA | Cu MHA | Cu SuHA |
|-----|--------------------|----------|--------|---------|
| 0   | 1.94               | 1.90     | 1.85   |
| 1   | 3.45               | 3.40     | 4.05   |
| 2   | 5.00               | 4.80     | 4.95   |
| 3   | 5.75               | 5.60     | 5.55   |
| 4   | 6.45               | 6.95     | 6.45   |
| 5   | 7.80               |          | 7.15   |

5. Conclusions

A simplified technique has been presented for the analysis of extended X-ray absorption fine structure (EXAFS) data and determining the first shell bond length. The method employed here is simple and straightforward, thereby providing a physical picture of the X-ray absorption fine structure. The analysis uses easily available computer program Mathcad. The method can be applied for any pure metal and is quite suitable for complex systems also. In the present case, analysis has been carried out only for the first shell, but it can be extended to other shells also.

### References

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Figure 1 - Experimental $\chi(k)$ versus $k$ curves for copper complexes.

Figure 2 - Magnitude of Fourier transform of $\chi(k)$ versus $k$ curves of the experimental EXAFS data, given in figure 2, for copper complexes.

Figure 3 - $n$ versus $k$ curves for the copper complexes.

Figure 4 - Theoretical $\chi(k)$ versus $k$ curves for copper complexes. For calculations, backscattering amplitude has been taken from Mckale [6] (values for $R = 2.5 \, \text{Å}$)

Figure 5 - Magnitude of Fourier transform of $\chi(k)$ versus $k$ curves of the theoretical EXAFS data, given in figure 3, for copper complexes.