EXAFS study of tetramethylethylenediamine copper(II) complexes with Cl and Br as secondary ligands

V K Hinge1, A Gaur2, Davood Ah. Dar3, S K Joshi3, B. D. Shrivastava2*
J. Prasad4, K. Srivastava4, S. N. Jha5, D. Bhattacharyya5 and A. Poswal5

1Physics Department, Ujjain Engineering College, Ujjain-456010, India.
2School of Studies in Physics, Vikram University, Ujjain-452001, India
3Physics Department, Government P G Arts and Science College, Ratlam-457001, India
4Department of Chemistry, University of Allahabad, Allahabad 211002, India.
5Applied Spectroscopy Division, Bhabha Atomic Research Centre, Mumbai-400085, India.
email: rashmibasant@gmail.com

Abstract. Extended X-ray absorption fine structure (EXAFS) have been recorded at the K-edge of copper in binuclear copper(II) complex [Cu(tmen)Cl2] (1) and its analogous complex [Cu(tmen)Br2] (2) (where tmen = tetramethylethylenediamine), using the dispersive EXAFS beamline at 2 GeV Indus-2 synchrotron source at RRCAT, Indore, India. Theoretical model has been generated for 1 using its available crystallographic data [1] and then fitted to the experimental EXAFS data of 1 to obtain its structural parameters, which include bond-lengths, coordination numbers and thermal disorders. The results obtained have been found to be comparable with the crystallographic results. As complex 2 is analogous to complex 1, the same theoretical model, which was generated for 1, has been fitted to the experimental EXAFS data of 2. The structural parameters, thus determined for 2 have been reported. The coordination geometry around the copper center in both the complexes has been depicted showing the bond-lengths obtained in the present study. It has been demonstrated that if crystal structure is available for a complex from X-ray crystallographic studies, the structural parameters can be determined for an analogous complex from EXAFS studies. Further, the values of the chemical shifts suggest that copper is in +2 oxidation state in these complexes.

1. Introduction
In the present work EXAFS of the two copper complexes, [Cu(tmen)Cl2] (1) and [Cu(tmen)Br2] (2), (tmen = tetramethylethylenediamine), at the K–edge of copper has been recorded using the dispersive EXAFS beamline at the synchrotron source. The theoretical model for the complex 1 has been generated from the available crystallographic data [1] and then fitted to its experimental EXAFS data to obtain the structural parameters, which include bond-lengths, coordination numbers and thermal disorders. The structural parameters thus obtained are found to be in good agreement with XRD results. As complex 2 is analogous to the complex 1, the same theoretical model which was generated for complex 1, is fitted to the EXAFS data of complex 2. The structural parameters thus obtained for 2 have been reported and the coordination geometry around the copper site has been depicted.
2. Experimental details
The complexes have been prepared and characterized by standard methods [1]. The K- absorption spectra at the K-edge of copper in the complexes have been recorded at the BL-8 dispersive EXAFS beamline at 2 GeV Indus-2 synchrotron source at RRCAT, Indore, India [2-4]. The beamline has 460mm long Si(111) crystal having 2d value equal to 6.2709Å mounted on an elliptical bender. The radiation transmitted through the sample is detected by a position sensitive CCD detector having 2048×2048 pixels. For energy calibration of that particular setting, absorption spectra at Cu K-edge of Cu metal foil and at Lu L3-edge of Lu2O3 powder have been recorded under the same setting of crystal bender and the goniometer. Taking the values of the energies of Cu K-edge in metal and Lu L3-edge in Lu2O3 as 8980.50 and 9249.00 eV, respectively, the CCD channels have been calibrated [5].

3. Data analysis
The EXAFS data have been analyzed by using the computer programs Athena and Artemis [6]. The analysis procedure has two stages: reduction of the measured absorption spectra to EXAFS and analysis of the EXAFS data to obtain the structural parameters. Normalized μ(E) versus E (energy) curve for the two complexes under investigation are shown in figure 1, χ(k) versus k curves are shown in figure 2 and the Fourier transformed curves are shown in figure 3 and figure 4. The Fourier transformed data is then fitted with the theoretical model in R-space to obtain the fitting parameters.

![Graph 1](image1.png)

Fig. 1. Normalized μ(E) versus Energy (eV)

![Graph 2](image2.png)

Fig. 2. χ(k) spectrum obtained from Fig. 1.

The crystallographic data is available for 1, from which the theoretical model for this complex has been generated using the following parameters as input in Artemis: Space group: P -1, Cell constants: a = 7.713Å, b = 8.560Å, c = 9.249Å; α = 98.44, β = 94.39, γ = 118.63 and Cluster size = 8 Å. The remaining input positional parameters have been taken from reference [1]. For generating the theoretical model, we have followed the procedure outlined by Kelly et al. [7]. Accordingly, a single value of S0² and ΔE0 is used for all the paths in the fitting but different values of ΔR and σi² can be used for different paths. The resulted fitting curve for complex 1 is shown in figure 3. The structural parameters thus obtained for 1 are given in table 1 and are comparable with the crystallographic results.

The crystallographic data for 2 is not available in the literature. As the theoretical model generated by us for 1 fits well to its experimental EXAFS data and because the complex 2 is analogous to 1, we have fitted the same theoretical model, which has been generated for 1, to the experimental EXAFS data of 2, to determine the structural parameters of 2. The resulting fitted curve is shown in figure 4 and the structural parameters so obtained are given in table 1.

4. Results and discussion
The energies of the K-edge of copper are found to be 8986.73 and 8988.97eV for complex 1 and complex 2 respectively. The chemical shifts are thus found to be 6.23 and 8.47 eV for 1 and 2 respectively, which indicates that copper is in +2 oxidation state in the two complexes [8]. The
EXAFS analysis procedure and the structural parameters obtained by fitting the theoretical model to the two complexes are given in table 1 and are discussed below:

Table 1. The EXAFS fitting results for complex 1 and 2.

| Atomic pair | N | R(Å) | ΔR(Å) | σ²(Å⁻²) | R(Å) |
|-------------|---|------|-------|---------|------|
| Cu-N(1)     | 1 | 2.05 | 0.001 | 0.016 ± 0.003 | 2.05 |
| Cu-N(2)     | 1 | 2.08 | 0.001 | 0.016 ± 0.003 | 2.08 |
| Cu-Cl(1)    | 1 | 2.10 | 0.160 | 0.004 ± 0.009 | 2.26 |
| Cu-Cl(2)    | 1 | 2.10 | 0.160 | 0.004 ± 0.009 | 2.26 |
| Cu-Cl(1')   | 1 | 2.89 | 0.255 | 0.005 ± 0.009 | 3.15 |


4.1. Complex 1: For the analysis of EXAFS data of complex 1, the input parameter, $R_{bgk}$, was set to 1.05 Å and the Fourier transform was performed over the k-range: $k_{min}=2.31\,Å^{-1}$, $k_{max}=7.38\,Å^{-1}$. Theoretically modeled data were fitted in the R-space to the experimental data using $k_w=1$. Fitting was performed for coordination shells in the R range of 1-5 Å using seven single scattering and five multiple scattering paths obtained from the FEFF calculations and the results obtained are given in table 1. The $S_0^2$ value obtained is 0.80, $\Delta E_0$ is also reasonable, i.e., 3.81 eV. Our results for the bond lengths, given in table 1, are in good agreement with the crystallographic bond distances reported by Estes et al. [1]. In complex 1, the coordination about copper is a distorted tetragonal pyramid, with two chlorine (Cl(1) and Cl(2)) and two nitrogen (N(1) and N(2)) atoms in the base and the out of plane chlorine (Cl(1')) atom at the apex [1]. The distances of the four basal atoms Cu-N(1), Cu-N(2), Cu-Cl(1) and Cu-Cl(2), and the apical chlorine Cl(1') atom have been found from the present EXAFS data analysis as 2.05, 2.08, 2.10, 2.10 and 2.89 Å, respectively. Based on the structure reported in reference [1], the coordinate geometry around copper atom has been depicted in figure 5. The distances shown in this figure are those which have been obtained by us in the present study.

4.2. Complex 2: For analyzing the EXAFS data of complex 2, the input parameter, $R_{bgk}$, was set to 1.0 Å and the Fourier transform was performed over the k-range: $k_{min}=2.45\,Å^{-1}$, $k_{max}=7.82\,Å^{-1}$. As already pointed out above, because complex 2 is analogous to 1, we have fitted the same theoretical model, which has been generated for 1, to the experimental EXAFS data of 2 using $k_w=1$. Fitting was performed in the R range of 1-5 Å using six single scattering and seven multiple scattering paths. The results obtained are given in table 1. The obtained values of $S_0^2$ and $\Delta E_0$ are 0.80 and -1.35 eV, which are reasonable. As complex 2 is analogous to complex 1, the coordination about copper is expected to be distorted tetragonal pyramid, with two bromine (Br(1) and Br(2)) and two nitrogen (N(1) and N(2))...
atoms in the base and the out of plane bromine (Br(1')) atom at the apex. From the present EXAFS data analysis, the distances of the four basal atoms Cu-N(1), Cu-N(2), Cu-Br(1) and Cu-Br(2), and the apical bromine Br(1') atom have been found to be 1.91, 1.94, 2.17, 2.17 and 3.19 Å respectively. Based on these results, the coordinate geometry around the copper atom has been shown in figure 6.

5. Conclusions
The EXAFS spectra at the K-edge of copper have been recorded for two copper complexes: [Cu(tmen)Cl$_2$] (1) and [Cu(tmen)Br$_2$] (2), (tmen = tetramethylethylenediamine). Using the available crystallographic data of complex 1, theoretical model has been generated which is then fitted to the experimental EXAFS data of 1 to obtain the bond-lengths, coordination numbers and thermal disorders of complex 1. The structural parameters, thus obtained, are found to be comparable with the crystallographic results. The crystal structure of complex 2 is not available. As the two complexes are analogous to each other, the theoretical model generated for 1 was fitted to the experimental EXAFS data of 2 to determine the structural parameters of 2. The coordination geometry around the copper atom in the complexes has been depicted showing the present results. Thus, the present study has demonstrated that, if crystallographic data is available for a complex, structural parameters can be determined for an analogous complex from EXAFS studies. Further, from the values of chemical shifts, the copper metal in both the complexes has been found to be in +2 oxidation state.

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