Coordination geometry around copper in a Schiff-base trinuclear copper complex using EXAFS spectroscopy

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Abstract. In the present investigation, we have studied extended X-ray absorption fine structure (EXAFS) spectra of a trinuclear Schiff-base copper complex tetraaqua-di-µ3-(N-salicylidene-DL-glutamato)-tricopper(II)heptahydrate, $[\text{Cu}_3(C_12H_{10}NO_5)_2(H_2O)_4].7H_2O$, in which three metal sites are present. One metal site is square-pyramidal (4+1) and other two similar metal sites are tetragonally distorted octahedral (4+2). EXAFS has been recorded at the K-edge of copper in the complex at the dispersive EXAFS beamline at 2 GeV Indus-2 synchrotron source at RRCAT, Indore, India. The analysis of EXAFS spectra of multinuclear metal complexes pose some problems due to the presence of many absorbing atoms, even when the absorbing atoms may be of the same element. Hence, using the available crystal structure of the complex, theoretical models have been generated for the different copper sites separately, which are then fitted to the experimental EXAFS data. The two coordination geometries around the copper sites have been determined. The contributions of the different copper sites to the experimental spectrum have been estimated. The structural parameters, which include bond-lengths, coordination numbers and thermal disorders, for the two types of copper sites have been reported. Further, copper has been found to be in +2 oxidation state at these metal sites.

1. Introduction

The extended X-ray absorption fine structure (EXAFS) spectroscopy is an effective technique for selectively investigating the local coordination environment around the metal active site of complexes. However, the analysis of EXAFS spectra of multinuclear metal complexes pose some problems due to the presence of many absorbing atoms, even when the absorbing atoms may be of the same element [1]. In the present work, EXAFS spectra of a Schiff-base copper complex catena-tetraaqua-di-µ1-(N-salicylidene-DL-glutamato)-tricopper(II)heptahydrate, $[\text{Cu}_3(C_12H_{10}NO_5)_2(H_2O)_4].7H_2O$, formed from amino acid and salicylaldehyde have been investigated. In this complex, each Schiff-base ligand is hexadentate, coordinated through one N and four O atoms to two Cu atoms in the trimeric unit and through one carboxyl O atom to Cu in the adjacent trimeric unit, thus forming a polymeric structure [2]. This trinuclear Schiff-base copper complex in which there are three metal sites, one site being
square-pyramidal (4+1) and other two similar sites being tetragonally distorted octahedral (4+2) is an interesting sample from the point of view of analysis of its EXAFS spectral data.

Table 1. The EXAFS fitting results for square-pyramidal structure

| Atomic pair | EXAFS results | XRD results |
|-------------|---------------|-------------|
|             | R(Å) | delr(Å) | σ(Å²) | σ²(Å²) | R |
| Cu1-O3 1    | 1.90 | -0.008 | 0.0045 ± 0.0040 | 1.91 |
| Cu1-N1 1    | 1.92 | -0.008 | 0.0045 ± 0.0040 | 1.93 |
| Cu1-O1 1    | 1.95 | -0.008 | 0.0045 ± 0.0040 | 1.96 |
| Cu1-O4 1    | 1.97 | -0.008 | 0.0045 ± 0.0040 | 1.98 |
| Cu1-O5 2    | 2.26 | -0.221 | 0.0081 ± 0.0045 | 2.48 |

Table 2. The EXAFS fitting results for tetragonally distorted octahedral structure

| Atomic pair | EXAFS results | XRD results |
|-------------|---------------|-------------|
|             | R(Å) | delr(Å) | σ(Å²) | σ²(Å²) | R |
| Cu1-O6 2    | 1.89 | -0.052 | 0.0061 ± 0.0017 | 1.94 |
| Cu1-O2 2    | 1.90 | -0.052 | 0.0061 ± 0.0017 | 1.95 |
| Cu1-O7 2    | 2.70 | -0.004 | 0.0174 ± 0.00167 | 2.71 |

2. Experimental

Copper complex has been prepared by following the standard methods. The prepared complexes were characterized by standard chemical methods [2]. The complex was finely powdered and then absorption screens were prepared by carefully spreading calculated amount of the powder on 1 cm² area of kapton tape. The copper K-edge EXAFS spectra of these absorption screens have been recorded at the BL-8 dispersive EXAFS beamline at 2 GeV Indus-2 synchrotron source at Raja Ramanna Center for Advanced Technology (RRCAT), Indore, India. The details of this beamline and the procedure for recording the spectra have already been described [3].

3. Data analysis

The EXAFS data of the complex has been analyzed using the available computer software packages Athena version 0.8.061 and Artemis version 0.8.013 [4]. The spectrum is first normalized and the normalized μ(E) vs. E (energy) curve for the complex is shown in figure 1. Normalized μ(E) data is converted to the EXAFS signal χ(k) data, which is then Fourier transformed. χ(k) vs. k spectrum for complex is shown in figure 2. The Fourier transformed data is then fitted with theoretical model in R-space to obtain the different fitting parameters. As the complex has three copper sites, one site having square-pyramidal structure and other two sites having distorted octahedral structure, two theoretical models have been generated, one for square-pyramidal structure and another for distorted octahedral structure. In the present work we have used the following parameters as input in Artemis for generating the two theoretical models: Space group: P -1, Cell constants: a = 7.874 Å, b = 8.702 Å, c = 13.278 Å, α = 97.32°, β = 104.06°, γ = 97.83°. Cluster size = 10 Å. The remaining input positional parameters are taken from ref [2].

For square-pyramidal structure, the theoretically calculated contribution to |γ(R)| by the single scattering three axial Cu-O paths, one axial Cu-N path and one apical Cu-O path are shown in figure 3. Similarly, for distorted octahedral structure of the complex, the theoretically calculated contribution to |γ(R)| by the single scattering four Cu-O axial paths and two longer apical Cu-O paths are shown in figure 4. This figure shows only three paths as each path has a degeneracy of 2.

Table 3. The EXAFS fitting in complex with 30% square-pyramidal site and 70% octahedral site contributions.

| Atomic pair | EXAFS results | XRD results |
|-------------|---------------|-------------|
| Cu1-O3 1    | 1.83 | -0.080 | 0.0054 ± 0.0017 | 1.91 |
| Cu1-N1 1    | 1.85 | -0.080 | 0.0054 ± 0.0017 | 1.93 |
| Cu1-O1 1    | 1.90 | -0.080 | 0.0054 ± 0.0017 | 1.98 |
| Cu1-O4 1    | 2.40 | -0.080 | 0.0054 ± 0.0017 | 2.48 |
For generating the two theoretical models we have followed the procedure outlined by Kelly et al. [5]. Accordingly, a single value of $S_0^2$ and $\Delta E_0$ is used for all the paths in the fitting but different values of $\Delta R$ can be defined for different paths. Unique Debye-Waller factor ($\sigma^2$) values are given to each of the scattering paths in the model. As multiple scattering paths also have important contribution, they have also been included in modeling the data. The resulting fitted curves are shown in figure 5 for square-pyramidal structure of complex and in figure 6 for distorted octahedral structure of the complex. After doing the above mentioned two types of fittings, a third type of fitting has also been done (not shown here). This fitting has been done using the theoretical models of complex for both the square-pyramidal and octahedral structure, simultaneously. Using this type of fitting we have tried to estimate the contributions of the different copper sites to the experimental EXAFS spectra.

For this third type of fitting we have set a new parameter $x_1$ which can be varied from 0.1 to 0.9. Using this parameter, $S_0^2$ for paths of octahedral structure have been defined as $\text{amp} \times x_1$ and for paths of square pyramidal structure as $\text{amp} \times (1-x_1)$. Same value of $E_0$ has been defined for all the paths of both structures. One value of $\Delta R$ has been defined for paths of octahedral structure and another value of $\Delta R$ has been defined for paths of square pyramidal structure. Unique Debye-Waller factor ($\sigma^2$) values are given to each of the scattering paths in the model. The value of parameter $x_1$ has been varied during different fittings and the values of statistical factor reduced $\chi^2$ have been noted each time. The value of parameter $x_1$ for which minimum value of reduced $\chi^2$ is obtained has been taken as contribution of octahedral copper site to the experimental EXAFS spectrum. 

4. Results

For the complex, the energy of the K-edge of copper is found to be 8988.03 eV which suggests that copper is in +2 oxidation state in this complex [6, 7].

The EXAFS data of complex has been fitted in three different ways: firstly, by its own octahedral structure, secondly, by its own square pyramidal structure and lastly, by both of its structures simultaneously. These three fittings are discussed below. In all these fittings, Fourier transform was performed over k-range: $k_{\text{min}} = 2.67 \text{ Å}^{-1}$, $k_{\text{max}} = 7.97 \text{ Å}^{-1}$. Theoretically modeled data was fitted in the R-space to the experimental data using $k_o = 2$ and in the R ranges of 1.0 - 5.0 Å.

4.1 Octahedral structure fit

For the analysis of the EXAFS data of complex, the first type of fitting has been done using the theoretical model for its own octahedral structure. In the fitting procedure, we have used first eleven scattering paths obtained from Feff calculations. The value of goodness-of-fit parameter, i.e., reduced chi-square ($\chi^2$) obtained is 676.12. The results obtained from fitting are given in table 2, which are in agreement with the crystallographic bond distances (also given in table). The four axial Cu-O
distances are found to be 1.89 Å, 1.89 Å, 1.90 Å and 1.90 Å. Two apical Cu-O distances are found to be 2.70 Å. Hence, this theoretical model generated by us appears to be quite reasonable.

**Figure 4.** Contribution to $|\chi(R)|$ by single scattering paths for octahedral structure.

**Figure 5.** Fourier transformed experimental data and the theoretical fit for square pyramidal structure.

**Figure 6.** Fourier transformed experimental data and the theoretical fit for octahedral structure.

### 4.2 Square pyramidal structure fit

For the analysis of the EXAFS data of complex, the second type of fitting has been done using the theoretical model for its own square pyramidal structure. In the fitting procedure, we have used ten scattering paths obtained from Feff calculations. The value of goodness-of-fit parameter, i.e., reduced chi-square ($\chi^2$) obtained is 326.06. The results obtained from fitting are given in table 1, which are in agreement with the crystallographic bond distances (also given in table). The three axial Cu-O distances are found to be 1.90 Å, 1.95 Å and 1.97 Å and one axial Cu-N distance is found to be 1.92 Å. Hence, this theoretical model generated by us appears to be quite reasonable.

### 4.3 Fitting both the structures simultaneously

Third type of fitting has been done by using the theoretical models for both of its own octahedral and the square pyramidal structures simultaneously. In the fitting procedure, we have used first three scattering paths of octahedral structure and first five scattering paths of square pyramidal structure, obtained from Feff calculations.

As already explained in data analysis a new variable $x_1$ has been defined for this fitting procedure, which gives the contribution of octahedral Cu site to the experimental EXAFS data. By varying $x_1$ from 0.1 to 0.9 during consecutive fittings, the values of reduced $\chi^2$ have been determined for each fitting. The value of $x_1$ for which minimum value of reduced $\chi^2$ is obtained has been taken as contribution of octahedral copper site to the experimental EXAFS spectrum. In the present case, the minimum value of $\chi^2$ has been obtained at $x_1 = 0.7$. Thus, it can be said that octahedral Cu site has 70% and square pyramidal Cu site has 30% contributions to the experimental EXAFS spectrum. The results obtained from fitting are given in table 3, which are in agreement with the crystallographic bond distances (also given in table). These results are nearly the same as obtained from fitting the two structures separately (as mentioned above).

### 5. Conclusions

The aim of the present work is to show how EXAFS spectra of the complexes, having different types of coordination environment, can be analyzed to yield the geometry around the central metal ion. In the present case, the EXAFS data of complex has been fitted in three different ways: firstly, by theoretical model of its own octahedral structure, secondly, by theoretical model of its own square pyramidal structure and lastly, by theoretical models of both of its structures simultaneously. The results obtained by fitting two structures simultaneously are nearly the same as obtained from fitting the two structures separately as well as those obtained from the crystallography. Using this kind of fitting, the contributions of the different copper sites to the experimental spectrum have been found to be 70% from the two octahedral copper sites and 30% from the one square pyramidal copper site. The obtained value of the chemical shift suggest that copper is in +2 oxidation state in this complex.
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7. References
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