EXAFS study of tetrakis(imidazole) dinitratocopper (II) complex

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Abstract. The extended X-ray absorption fine structure (EXAFS) spectra at the K-edge of copper in tetrakis(imidazole)dinitratocopper(II) complex [Cu(im)₄(NO₃)₂] (im = imidazole), has been recorded using the dispersive EXAFS beamline at the 2 GeV Indus-2 synchrotron source at RRCAT, Indore, India. The EXAFS data analysis has been done using the computer programs Athena and Artemis. Theoretical model has been generated using the available crystal structure of the complex and fitted to its experimental EXAFS data. The structural parameters thus obtained, which include bond-lengths, coordination numbers and thermal disorders, have been reported. The results obtained have been found to be in good agreement with crystallographic results. The coordination geometry around the copper site has been determined and depicted. Further, copper has been found to be in +2 oxidation state in this complex.

1. Introduction
The EXAFS (extended X-ray absorption fine structure) in the X-ray absorption spectrum is the normalized oscillatory part of the absorption coefficient above the absorption edge to approximately 1000 eV or higher energy. The EXAFS oscillations are of interest as they contain structural information specific to the scattering atom. In the present work, EXAFS of tetrakis (imidazole)dinitratocopper(II) complex [Cu(im)₄(NO₃)₂] (im = imidazole) at the K-edge of copper has been recorded using synchrotron source. Theoretical model has been generated and fitted to the experimental EXAFS data. The obtained structural parameters, which include bond-lengths, coordination numbers and thermal disorders, have been reported.

2. Experimental details
The complex [Cu(im)₄(NO₃)₂] has been prepared and characterized by standard methods [1]. The K-absorption spectra at the K-edge of copper in the complex has been recorded at the BL-8 dispersive EXAFS beamline at Indus-2 synchrotron, RRCAT, Indore [2-4]. The beamline has 460mm long Si(111) crystal having 2d value equal to 6.2709Å mounted on an elliptical bender, which can bend the crystal to take the shape of an ellipse (the elliptical optics offers minimum aberration). The radiation transmitted through the sample has been detected by a position sensitive CCD detector having 2048
Figure 1.(a). Normalized $\mu(E)$ spectrum of complex at the K-edge of copper.

Figure 1(b). $\chi(k)$ spectrum obtained from (a)

Figure 1.(c). The theoretically calculated contributions to $\chi(R)$ by single scattering paths. The experimental $\chi(R)$ is also given.

Figure 1. (d) Fourier transformed EXAFS data of the complex. Solid line is experimental data and dashed line is modelled fit.

2048 pixels. The whole absorption spectrum can be recorded simultaneously in a short duration of even a few micro seconds in case of a rich sample. The beamline has a resolution of 1eV at the photon energies of 10 KeV. The plot of absorption versus photon energy is obtained by recording the intensities $I_0$ and $I_t$, as the CCD outputs, without and with the sample, respectively and using the relation, $I_t = I_0 e^{-\mu x}$, where $\mu$ is the absorption coefficient and $x$ is the thickness of the absorber. For energy calibration of that particular setting, absorption spectra at Cu K-edge of Cu metal foil and at Lu L$_3$-edge of Lu$_2$O$_3$ 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 L$_3$-edge in Lu$_2$O$_3$ as 8980.5 and 9249 eV, respectively, the CCD channels have been calibrated [5].

3. Data analysis
The EXAFS data has been analyzed by using the computer programs Athena version 0.8.056 and Artemis version 0.8.012 [6]. These programs include FEFF6L for generation of the theoretical EXAFS models and FEFFIT for parameter optimization of the model. The analysis procedure can be divided into two stages: reduction of the measured absorption spectra to EXAFS and analysis of the EXAFS data to obtain the structural parameters.

The spectrum is first normalized by regressing a linear function to the pre-edge region and by regressing a linear or quadratic function to the post-edge region. Normalized $\mu(E)$ spectrum is
produced by subtracting the pre-edge line from the entire data spectrum and then dividing the
spectrum by the step height [7]. Normalized $\mu(E)$ versus E (energy) curve for the complex under
investigation is shown in figure 1(a). Normalized $\mu(E)$ data is then converted into the EXAFS signal
$\chi(k)$ data (figure 1(b)), which is then Fourier transformed (figure 1(c)). The Fourier transformed data is
then fitted with the theoretical model in R-space to obtain the different fitting parameters.

The theoretical model is written as a sum of paths of the contribution from all scattering paths of
photoelectron that travels from the absorbing atom and then scattered from one or more neighbouring
atoms and finally returns to the absorbing atom [7]

$$\chi(k) = \sum \left| N_S^2 F_{\text{eff}}(k) / k R_i^2 \right| \sin[2k R_i + \phi_i(k)] \exp(-2\sigma_i^2 k^2) \exp[-2R_i/\lambda(k)]$$

with $R_i = R_{i0} + \Delta R_i$ and $k^2 = (2m_{e0}E_{e0} + \Delta E_0)/\hbar$

In the above equations, the term $F_{\text{eff}}$, $\phi_i(k)$ and $\lambda(k)$ are the effective scattering amplitude, the
phase shift and the mean free path of the photoelectron respectively, all of which can be calculated by
FEFF program. The term $R_i$ is the half path length of the photoelectron (the distance between the
absorber and the coordinating atom for a single scattering event). The value of $R_{i0}$ is the half path length used in the theoretical calculation which can be modified by $\Delta R_i$. Each path has several adjustable parameters optimized by the computer code FEFFIT to fit the data. These parameters include the passive electron-reduction factor ($S_0^2$), the number of identical paths ($N$), the relative mean square displacement of the atoms included in the path ($\sigma_i^2$), an energy shift for each path ($\Delta E_0$) and a change in the path length ($\Delta R_i$).

The following parameters have been used as input in Artemis for calculating the theoretical model:

Space group: Pna21
Cell constants: $a = 13.85\text{Å}$, $b = 9.83\text{Å}$, $c = 13.39\text{Å}$
Cluster size = 8 Å

The remaining input parameters are listed in table 1. The theoretically calculated contributions to
$\chi(R)$ by the single scattering paths (1) three Cu-N and (2) two Cu-O paths along with experimental
$\chi(R)$ are shown in figure 1(c). One of the Cu-N paths has degeneracy 2. For generating the theoretical
models, we have followed the procedure outlined by Kelly et al. [7]. Accordingly, a single value of $S_0^2$
and $\Delta E_0$ is used for all the paths in the fitting but different values $\Delta R$ and $\sigma_i^2$ can be used for different
paths. Hence for the theoretical model, same $\Delta R$ and $\sigma_i^2$ values have been used for the three Cu-N
paths and another values (i.e., different from the values used for the first three paths) for the remaining
two Cu-O paths. The resulted fitting curve is shown in figure 1(d).

4. Results and discussion
The energy of the K-edge of copper in the given complex is found to be 8986.7 eV. Taking the energy
of copper metal K-edge as 8980.5 eV, the chemical shift is 6.2 which indicates that copper is in $+2$
oxidation state in the complex [8].

![Figure 2. Coordination geometry about the copper metal in the complex $[\text{Cu(im)$_2$(NO$_3$)$_2$}]$, based on reference [1].]
For analysis of the EXAFS data of the given complex, the input parameter, \( R_{\text{bkg}} \), that determines the maximum frequency of the background was set to 1.10 Å. Fourier transform was performed over k-range: \( k_{\text{min}} = 2.553 \text{Å}^{-1}, k_{\text{max}} = 8.860 \text{ Å}^{-1} \). Theoretically modelled data were fitted in the R-space to the experimental data using \( k_R = 1 \). Fitting was performed for coordination shells in the R range of 1.10 - 4.0 Å. In the fitting procedure, we used the first five paths obtained from the FEFF calculations. The results obtained from fitting are given in table 2, which gives the local structural parameters obtained from the analysis. The \( S_0^2 \) value obtained is 0.9, \( \Delta E_0 \) is also reasonable, i.e., 4.19 eV. Our results for the bond lengths, with \( \Delta R \) ranging from 0.02 to 0.15 Å, are given in table 2 and are in good agreement with the crystallographic bond distances reported by McFadden et al. [1].

The distances of the four coplanar imidazole nitrogen atoms which define the basal plane and two bidentate nitrate-oxygen atoms of the tetragonally distorted octahedral at copper (figure 2) i.e., Cu-N(A1), Cu-N(B1), Cu-N(C1), Cu-N(D1), Cu-O(1) and Cu-O(1) are respectively 1.99 Å, 1.99 Å, 2.00 Å, 1.99 Å, 2.45 Å and 2.37 Å. Based on the structure reported in reference [1], the coordinate geometry around copper atom has been depicted in figure 2, showing these distances.

### 5. Conclusion

The aim of the present work was to study the coordinate geometry of the complex \([\text{Cu(im)}_4(\text{NO}_3)_2]\) about the copper metal using the EXAFS spectroscopy. The structural parameters for the complex, obtained by fitting the theoretical model to the experimental EXAFS data, have been found to be in good agreement with the crystallographic data. Further, the copper metal in the complex has been found to be in +2 oxidation state.

### References

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### Table 1. The input positional parameters for the complex \([\text{Cu(im)}_4(\text{NO}_3)_2]\) from reference [1].

| S.No | Element | X   | Y   | Z   |
|------|---------|-----|-----|-----|
| 1    | Cu      | 0.1244 | 0.0064 | 0.2500 |
| 2    | N(A1)   | 0.1251 | 0.1302 | 0.3695 |
| 3    | N(B1)   | 0.2686 | -0.0108 | 0.2601 |
| 4    | N(C1)   | 0.1240 | -0.1196 | 0.1311 |
| 5    | N(D1)   | -0.0202 | 0.0188 | 0.2415 |
| 6    | O(1)    | 0.1016 | -0.2071 | 0.3628 |
| 7    | O(1')   | 0.1501 | 0.2156 | 0.1436 |

### Table 2. The EXAFS fitting results for \([\text{Cu(im)}_4(\text{NO}_3)_2]\) and their comparison with XRD results.

| Atomic pair | EXAFS results | XRD results |
|-------------|---------------|-------------|
| Cu-N(A1)    | 2 1.99 -0.020670 0.0099 2.010 |
| Cu-N(B1)    | 1 1.99 -0.020670 0.0099 2.008 |
| Cu-N(C1)    | 1 2.00 -0.020670 0.0099 2.018 |
| Cu-O(1)     | 1 2.37 -0.153954 0.0001 2.606 |
| Cu-O(1')    | 1 2.45 -0.153954 0.0001 2.526 |