EXAFS study of mixed ligand copper complexes having nicotinic acid as one of the ligands

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Abstract. Copper K-edge EXAFS spectra of the copper (II) complexes [Cu₃(NA)₄(dca)₂(H₂O)₈]·2H₂O (1) and [Cu₂(2,2'-bipy)(NA)₂](ClO₄)₂·H₂O (2) (where NA = Nicotinic acid; dca = dicyanamide anion; 2,2'-bipy = 2-2’ bipyridine) having different coordination environments and geometries have been investigated. The complex 1 is supposed to have six coordinated geometry and complex 2 five coordinated geometry. 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. Theoretical models have been generated for both the complexes separately using their reported crystal structures. These theoretical models have been fitted to the respective experimental EXAFS data and the structural parameters, which include bond lengths, coordination numbers and thermal disorders, have been determined. The results obtained have been found to be comparable with those reported using crystallography. The coordination geometry about the copper (II) ion has been depicted for both the complexes. Further, copper has been found to be in +2 oxidation state in both the complexes. The study shows that the dispersive EXAFS beamline can be used to obtain information about the coordination geometry of a sample, though the beamline provides limited range of EXAFS data.

1. Introduction

The nicotinate ion, NA’, is a quite interesting ligand: first of all, its exodentate nature makes it a valuable tecton for designing high-dimensional coordination polymers. The nicotinato ligand combines the coordination ability of the pyridyl moiety with the various coordination modes of the carboxylato group. The nicotinic acid itself, acting as a ligand, can generate extended structures: it coordinates with the nitrogen atom to the metal ion, the structure being further expanded on the base of the classical synthon [1, 2].

In the present work, the extended X-ray absorption fine structure (EXAFS) has been studied in the two coordination complexes involving nicotinate ion: Cu₃(NA)₄(dca)₂(H₂O)₈·2H₂O (1) and [Cu₂(2,2'-bipy)(NA)₂](ClO₄)₂·H₂O (2) (where NA = Nicotinic acid; dca = dicyanamide anion; 2,2'-bipy = 2-2’ bipyridine). Complex 1 is supposed to have six coordinated geometry and the complex 2 five...
coordinated geometry. The aim of the present work is to investigate the copper K-edge EXAFS spectra of the copper (II) complexes having different coordination environments and geometries and to show that the dispersive EXAFS beamline can be used to obtain information about the coordination geometry of a sample, though the beamline provides limited range of EXAFS data. To our knowledge, the EXAFS study of these mixed ligand complexes have not been made earlier. Madalan et al. [3] have only reported the crystal structure (from XRD studies) and magnetic properties of the complexes.

2. Experimental
The complexes have been prepared and characterized by following the standard methods [3]. The complexes were finely powdered and then absorption screens were prepared by carefully spreading calculated amount of the powder on 1sq.cm. square 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 described earlier [4-6]. It is worth mentioning here that for the setting of the bent crystal to record the XAFS spectra at the K-edge of copper, the spectra can be recorded only upto ~ 300 eV (i.e., \( k = 9 \text{ Å}^{-1} \)) above the edge.

3. Data analysis
In the present work, EXAFS data of the complexes have been analyzed using the available computer software packages Athena and Artemis [7]. Figures 1(a, b) shows the normalized EXAFS spectra at the K-edge of copper in the complexes. \( \chi(k) \) vs. \( k \) spectra have been shown in fig. 2(a, b). Using the available crystallographic data [3], the theoretical models for these complexes have been generated which are then fitted to the experimental EXAFS data to obtain the structural parameters. Two theoretical models have been generated, one for each complex by using its own crystal structure. The theoretically calculated contribution to \( \vert \chi(R) \vert \) by the different scattering paths in the complexes 1 and 2 are shown in figures 3(a) and 3(b) respectively. The experimental \( \vert \chi(R) \vert \) is also shown in these figures. For generating the theoretical models the procedure outlined by Kelly et al. [8] has been followed. 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

![Fig 1 (a) \( \mu(E) \) vs. E of 1](image1)

![Fig 1 (b) \( \mu(E) \) vs. E of 2](image2)

![Fig 3(a) Paths used in theoretical model in 1](image3)

![Fig 2(a) \( \chi(k) \) vs. k of 1](image4)

![Fig 2(b) \( \chi(k) \) vs. k of 2](image5)

![Fig 3(b) Path used in theoretical model in 2](image6)
each of the scattering paths in the models. One $\Delta R$ has been defined for the axial O and N paths and another $\Delta R$ has been defined for the apical O and N path. In case of both the complexes, there is a N apical path, while in case of 1 there is additional O apical path. The resulting fitted curves for 1 and 2 are shown in figures 4(a) and 4(b), respectively. The parameters so obtained for 1 and 2 are given in tables 1(a) and 1(b), respectively.

Table 1(a-b) The EXAFS fitting results for complexes 1 and 2. The XRD results for the complexes (from Madalan et al. 2005) are also given.

### 4. Results and discussions

The energies of the K-edge of copper are found to be 8988.42 eV and 8987.68 eV for complexes 1 and 2, respectively. Taking the energy of copper metal K-edge as 8980.5 eV, the chemical shifts are found to be 7.92 eV and 7.18 eV for complexes 1 and 2 which suggest that copper is in +2 oxidation state in these complexes. [9, 10]. The results of the EXAFS analysis and the discussions are as follows:

#### 4.1. Complex 1:

For the analysis of the EXAFS data of 1, the input parameters are $R_{bg}=1.02 \, \text{Å}$, k-range: $k_{min}=2.64 \, \text{Å}^{-1}$, $k_{max}=7.06 \, \text{Å}^{-1}$, $k_o=3$ and R range is 1.0 - 5.0 Å. In the fitting procedure, 12 paths obtained from Feff calculations have been used. The results obtained from fitting are given in table 1(a), which gives the local structure parameters for complex 1. The value of reduced chi-square ($\chi^2$) is 188.34, $S_0^2$ value obtained is 0.75 with an error of ± 0.13 and $\Delta E_0$ value is 1.25 eV with an error of ± 1.11. From the present EXAFS analysis, the axial Cu-O bond distance is found to be 1.94 Å. Three axial Cu-N distances are observed in the range of 1.95 - 2.00 Å.

The equatorial distance Cu-O bond, has a value of 2.32 Å and the equatorial distance Cu-N bond, has a value of 2.64 Å.

#### 4.2. Complex 2:

For the analysis of the EXAFS data of 2, the input parameters are $R_{bg}=1.0 \, \text{Å}$, k-range: $k_{min}=2.46 \, \text{Å}^{-1}$, $k_{max}=7.89 \, \text{Å}^{-1}$, $k_o=1$ and R ranges of 1.2 - 5.0 Å. In the fitting procedure, the 8 paths obtained from Feff calculations have been used. The results obtained from fitting are given in table 1(b), which gives the local structure parameters for complex 2. The value of reduced chi-square ($\chi^2$) is 146.49, $S_0^2$ value obtained is 0.80 with an error of ± 0.13 and $\Delta E_0$ value is 1.87 eV with an error of ± 0.92. From the present EXAFS analysis, two nitrogen atoms have been found at a distance of 1.99 and 2.00 Å and two oxygen atoms have been found at a distance of 2.02 and 1.98 Å. The apical nitrogen atom has been found at a distance of 2.33 Å.

As can be seen from table 1(a) and (b), the results obtained for the bond distances are in agreement with the crystallographic bond distances. Thus, the theoretical models generated by us appear to be
quite reasonable. Using the present results, the inner coordination sphere around the copper (II) centers in 1 and 2 has been depicted in fig. 5(a) and (b), respectively. These figures are based on the figures given by Madalan et al. [3] but show the distances obtained by us in the present study.

![Fig 5(a) Coordination geometry in 1](image)

![Fig 5(b) Coordination geometry in 2](image)

5. Conclusions
The EXAFS spectra have been recorded at the Cu K-edge in copper(II) complexes [Cu_3(NA)_4(dca)_2(H_2O)]_2H_2O 1 and [Cu_2(2,2'-bipy)(NA)_2] (ClO_4)_2H_2O 2 using the dispersive EXAFS beamline at 2.5 GeV Indus-2 synchrotron source at RRCAT, Indore, India. Theoretical models have been generated for the complexes using their available crystallographic data and then fitted to the respective experimental data to obtain the structural parameters, which include bond-lengths, coordination numbers and thermal disorders. The results obtained have been found to be comparable with the crystallographic results. Based on the present EXAFS data analysis the coordination geometry around the Cu(II) atom in the complexes has been depicted.

As already mentioned, the aim of the present work was to investigate the copper K-edge EXAFS spectra of the copper (II) complexes having different coordination environments and geometries. From the EXAFS analysis, it has been shown that complex 1 has six coordinated geometry and complex 2 five coordinated geometry. The study shows that the dispersive EXAFS beamline available at Indus-2 synchrotron source can be used satisfactorily to obtain information about the samples having different coordination geometries, though the EXAFS data is obtained over a limited range on this beamline.

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