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XAFS study of copper(II) diethylenetriamine complexes having different coordination geometries

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Abstract. XAFS of three Cu(II) diethylenetriamine complexes (in crystalline form) having different coordination geometries have been investigated. First complex has distorted tetragonal pyramidal, second has distorted square planar and third has distorted square pyramidal geometry. The difference in coordination geometries has been inferred from the differences in pre-edge peak, rising part of edge and in shape of white line, which are seen clearly in the derivative XANES spectra. The distortion in geometry has been correlated with the intensity of peaks in derivative spectra. These inferences have been corroborated from EXAFS analysis where the different paths have been used in the theoretical fits in R space to show contributions of different scatterers at different distances.

1. Introduction

The properties of copper (II) sites, catalytic, redox and so forth, generally depend upon the particular copper(II) geometrical arrangement [1]. It is well known that copper(II) exhibits plasticity, i.e., it is able to adapt itself to the ligand coordination constraints, thus assuming different coordination geometries in its complexes [1]. For the present study we have chosen three copper (II) mixed ligand complexes with diethylenetriamine (dien) as one of the ligands. Diethylenetriamine (dien) has varied applications, e.g., in removal of transition metal ions in waste waters and in measuring capacities of clays to exchange cation. It easily forms complexes with metals in aqueous solution. These complexes are stable in air and moisture and hence it is easy to obtain information about the coordination geometries using their spectroscopic signatures. The study of these complexes is interesting since they are stereochemically flexible and can have wide range of coordination geometries [2].

In the present work, X-ray absorption fine structure (XAFS) at the Cu K-edge of the copper (II) diethylenetriamine complexes, $\text{Cu}_2(\text{dien})_2\text{Br}_2(\text{ClO}_4)_2$ (**1**), $\text{Cu}_2(\text{dien})_2(\text{na})_2(\text{ClO}_4)_3\text{MeOH}$ (**2**), $\text{Cu}_2(\text{dien})_2(\text{na})_4$ (**3**) (where na = nicotinate), has been investigated. Complex **1** has distorted tetragonal pyramidal geometry [3], complex **2** has distorted square planar geometry [4] and Complex **3** has distorted square pyramidal geometry [4]. The aim of the present work is to study variation in the



XANES features with the change in coordination environment and to study the contribution of different scatterers present at different distances to the EXAFS data of these complexes.

2. Experimental

The copper complexes have been prepared and characterized by following standard methods [3,4]. The complexes were in powder form (solid state) and the absorption screens were in the form of pellets. XANES and EXAFS spectra have been recorded (in transmission mode at RT) at beamline BL-8 of the Synchrotron Light Research Institute, Thailand [5]. For calibration, K-edge XANES spectra of pure copper foil were collected simultaneously. The K-edge energy of copper metal was taken as 8,979 eV. The XAFS data have been analyzed by using *Athena* and *Artemis* [6].

3. Results and discussions

3.1 XANES

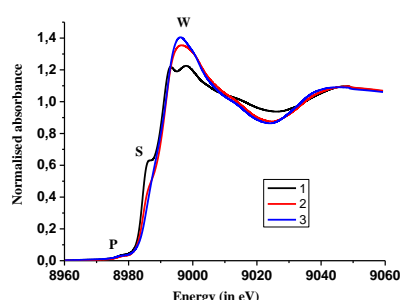


Fig 1. $\mu(E)$ vs. E spectrum

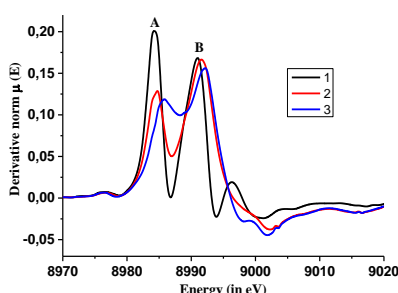


Fig 2. Derivative $\mu(E)$ vs. E

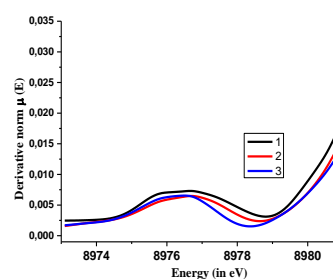


Fig 3. Peak P in the pre-edge

Fig. 1 shows XANES spectra of the studied complexes. The values of chemical shifts are found to be 5.1, 5.8 and 6.8 eV for complexes **1**, **2** and **3**, respectively, showing presence of copper(II). There are three features observed in the absorption edge region of the complexes which reflect coordination geometry of the complexes [7]. First is the pre-edge feature marked P at ~ 8976 eV due to the $1s \rightarrow 3d$ quadrupole transition. Second is the shoulder S on the rising part of the edge attributed to a $1s \rightarrow 4p$ transition and the third is the white line W due to the $1s \rightarrow$ continuum transitions [8]. The edge portions below S and above S appear as two peaks A and B in the derivative spectra (fig. 2) because of the arctangent nature of the edge portions. The intensity of peak A is found to vary with change in coordination geometry. It has been shown earlier that this peak is characteristic of tetragonal distortion [7]. In the present study, the intensity of this peak is larger for **1** than for **2** and **3** showing higher distortion in **1**. The intensity is comparatively high in **2** than **3**. Thus, it can be inferred that the order of distortion is **1** (tetragonal pyramidal) > **2** (square planar) > **3** (square pyramidal).

The pre-edge peak P has been shown separately in the derivative spectra in fig. 3. It has been observed that the pre-edge intensity of one structural type is distinct from other structural types [9]. Earlier workers have quantified the intensity of the pre-edge peak by the area under the peak and correlated it with 4p mixing. A linear relationship between the 4p character in the ground state and the total pre-edge intensity has been observed which led to a general rule: $I_{\text{OCTAHEDRAL}} < I_{\text{5-COORDINATE}} < I_{\text{TETRAHEDRAL}}$ (I = intensity), which has been applied to different systems containing Mn, Cu, Ni and Co [8]. In the present work, we have determined the intensity of this feature by calculating the area under the peak by Gaussian fitting. The order of peak intensity as determined from Gaussian fitting is **1** (0.0210 ± 0.0043) > **2** (0.0122 ± 0.0008) \approx **3** (0.0119 ± 0.0010). In case of complex **1**, the high intensity may be attributed to stronger interaction of Cu orbitals with bromo orbitals in such distorted geometry. Thus, complex **1** having tetragonal pyramidal geometry has maximum contribution from 4p in ground state. However, in case of **2** and **3**, little difference is observed between their peak intensity showing similar amount of 3d-4p mixing in these two complexes.

In fig. 1, the white line peak W is found to have lower intensity in **1** and also the rising edge is shifted to lower energy in **1** with respect to **2** and **3**. In case of Fe, Ni, Mn and Cu complexes, it has

been observed that the rising-edge shifts to lower energy for the ligands having higher metal–ligand covalency than with ligands containing lighter atoms such as O and N [8]. This higher covalency decreases the effective nuclear charge and leads to delocalization of metal 4p orbitals. Thus, the rising-edge shifts to lower energies and also the intensity of the main edge transition also decreases. Therefore, in case of complex **1**, the less intense peak W and shifting of the rising edge to lower energy points out towards the presence of ligand with higher covalency, i.e., Br. Presence of Br can thus be inferred from the intensity and position of white line W.

3.2 EXAFS

The inferences obtained from XANES analysis have been further investigated by EXAFS analysis. The procedure for EXAFS analysis was similar to that described earlier by the authors [7]. The fitting of the theoretical model to the experimental data of the complexes are described below:

3.2.1 Complex 1

The crystal structure of this complex is available [3] and it has been used to generate the theoretical model by putting input parameters from ref. [3] in *Artemis*. The theoretical model so generated has been fitted to the experimental data of the complex in R-space. A single value of ΔE_0 has been defined for all the paths in the fitting but different values of ΔR have been defined for different paths. Hence, for complex **1**, one ΔR has been defined for the three Cu-N paths and two different ΔR values have been defined for the two Cu-Br paths. Another ΔR has been defined for the Cu-C paths. Different Debye-Waller factor (σ^2) values have been defined for each of the scattering path.

For the analysis of the EXAFS data, the input parameter R_{bkg} , was set to 1.05 Å. Fourier transform was performed over k-range: $k_{\text{min}} = 2.69 \text{ \AA}^{-1}$, $k_{\text{max}} = 8.37 \text{ \AA}^{-1}$. Theoretically modeled data was fitted in the R-space to the experimental data using $k_w = 3$. Fitting was performed for the coordination shells in the R range of 1.0-4.0 Å. Fig. 4(a) shows the fitting in R-space along with the contributions of different paths. The local structure parameters obtained from the analysis are given in table 1. Amplitude reduction factor S_0^2 as determined from fitting is 1.03 ± 0.14 . The value of goodness-of-fit parameter, i.e., reduced chi-square (χ^2) obtained is 42. ΔE_0 value is also reasonable, i.e., $5.00 \text{ eV} \pm 1.40$. The three Cu-N distances have been found to be 2.00 Å along with the Br atom at 2.39 Å, forming the basal plane. The apical Br atom has been found at 2.84 Å. Also, there are C atoms at 2.74, 2.75 and 2.79 Å.

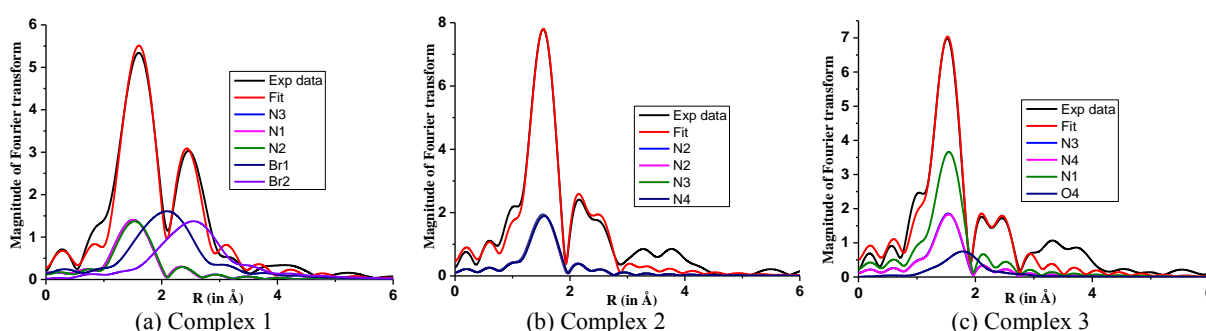


Fig. 4. EXAFS fittings of the complexes in R-space. The experimental curve (black line) and the theoretical fit (red line) along with contributions of different paths are shown in the figure.

3.2.2 Complex 2 and 3

Theoretical models for these complexes have been generated using their own crystal structures [4]. The input parameters used as input in *Artemis* are taken from ref. [4]. For the analysis of the EXAFS data, the input parameter R_{bkg} was set to 1.0 Å. Fourier transform was performed over k-range: $k_{\text{min}} = 2.69 \text{ \AA}^{-1}$, $k_{\text{max}} = 10.71 \text{ \AA}^{-1}$. Theoretically modeled data was fitted in the R-space to the experimental data using $k_w = 3$. Fitting was performed for the coordination shells in the R range of 1.0 - 4.0 Å.

In case of **2**, one ΔR has been defined for the four Cu-N paths and another ΔR has been defined for the Cu-C paths. Fig. 4(b) shows the fitting in R-space along with the contributions of different paths. The results obtained from fitting are given in table 1. The value of χ^2 obtained is 73 and ΔE_0 value, $5.29 \text{ eV} \pm 1.22$, is also reasonable. The value of S_0^2 is 1.03 ± 0.15 . The four N atoms have been found at a distance of 1.98 Å. Further, there are C atoms at 2.81, 2.82, 2.85 and 2.89 Å.

In case of **3**, One ΔR has been defined for the four Cu-N paths, another for the Cu-O path and separate ΔR has been defined for the Cu-C paths. The fitting in R-space is shown in fig. 4(c) and the results are given in table 1. χ^2 obtained is 135, ΔE_0 value is $4.41 \text{ eV} \pm 2.35$, and S_0^2 is 1.09 ± 0.30 . The four N atoms have been found at a distance of 1.99 Å and the Cu-O distance has been found to be 2.24 Å. Further, there are two C atoms at 2.90 Å.

Table 1. The EXAFS fitting results for the complexes

Path	Complex 1			Complex 2			Complex 3		
	N	R(Å)	$\sigma^2(\text{Å}^2)$	N	R(Å)	$\sigma^2(\text{Å}^2)$	N	R(Å)	$\sigma^2(\text{Å}^2)$
Cu-N	3	2.00 ± 0.01	0.0068 ± 0.0027	4	1.98 ± 0.02	0.0051 ± 0.0015	4	1.99 ± 0.02	0.0062 \pm 0.0025
Cu-Br /O	1	2.39* ± 0.03	0.0069 ± 0.0020	-	-	-	1	2.24** ± 0.02	0.0170 \pm 0.0085
Cu-Br	1	2.84 ± 0.05	0.0041 ± 0.0029	-	-	-	-	-	-

*For Cu-Br

** For Cu-O

4. Conclusion

In the present study, XAFS analysis of three copper(II) diethylenetriamine complexes having different coordination geometries, i.e., tetragonal pyramidal, square planar and square pyramidal have been performed. The intensity of peak A is larger in **1** than **2** and **3** showing that distortion is maximum in tetragonal pyramidal geometry. Also, the pre-edge peak P intensity as determined from Gaussian fitting has the order $1 > 2 \approx 3$, which shows that complex **1** has maximum 3d-4p mixing in the ground state. Further, the less intense peak W and shifting of the rising edge to lower energy in **1** indicate the presence of a ligand having higher covalency, i.e., Br.

These inferences have been corroborated from EXAFS analysis where the different paths have been used in the theoretical fits in R space to show contributions of different scatterers at different distances. The contributions of different paths to the experimental data are also shown in the figures. In case of **1**, three N atoms are present at 2.00 Å, one Br atom at 2.39 Å and another Br at 2.84 Å. In **2**, Cu is bound to four N atoms with bond lengths 1.98 Å. In **3**, there are four N atoms at 1.99 Å and one O atom at 2.24 Å. Thus, EXAFS analysis also confirms the presence of different scatterers at different distances in these complexes which corresponds to different coordination geometries.

Thus, the pre-edge and XANES features have been used to infer the presence of different coordination geometries and then inferences were confirmed by EXAFS analysis. Using similar analysis, these edge features can be useful to investigate the local geometry around a metal ion in complicated systems such as metal-enzyme systems and catalysts.

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