X-ray absorption near edge structure (XANES) study of some hydroxamic mixed ligand copper complexes

A Mishra†, N Parsai†, N.Soni and B D Shrivastava*
†School of Physics, Devi Ahilya University, Indore, 452 001
†School of Studies in Physics, Vikram University, Ujjain, 456 010

E-mail: parsai.neetu@gmail.com

Abstract. With the advent of modern bright synchrotron radiation sources, X-ray absorption spectra has emerged as a powerful technique for local structure determination, which can be applied to any type of material. The X-ray absorption measurements of four hydroxamic mixed ligand copper complexes have been performed at the recently developed BL-8 Dispersive EXAFS beamline at 2.5 GeV Indus-2 synchrotron at RRCAT, Indore, India. The X-ray absorption near edge structure (XANES) data obtained has been processed using data analysis program Athena. The energies of the K absorption edge, chemical shifts, edge-widths, shifts of the principal absorption maximum in the complexes have been determined. The values of the chemical shift suggest that copper is in oxidation state +2 in all of the complexes. The chemical shift data has been utilized to estimate effective nuclear charge on copper atom. The order of the chemical shifts has been correlated to the relative ionic character of the bonding in these complexes.

1. Introduction
Hydroxamic acids have been used as therapeutic agents in chelation theraphy and as metalloenzyme inhibitors [1]. Other medicinal applications of hydroxamates which utilize their affinity for high charge density metal ions include the possible use of their complexes as imaging agent [2]. With regards to the strong ability of hydroxamic acids to form chelates, clarification of their interaction with metal ions is of particular importance in terms of biological effects. In the present work, X-ray K-absorption spectra of copper in the four mixed ligand copper complexes having hydroxamic acid as primary ligand have been studied. The details of the four complexes are given in table 1.

2. Experimental
In the present investigation, the X-ray absorption spectra have been recorded using synchrotron radiation. The X-ray spectroscopic setup is available at Raja Ramanna Center for Advanced Technology (RRCAT), Indore, India and is called dispersive EXAFS beamline BL-8. This beamline has been recently commissioned at the 2.5 GeV Indus-2 synchrotron radiation source [3]. In this beamline a bent crystal (Si 111) polychromator is used to select a band of energy from the white synchrotron beam which is horizontally dispersed and focused on the sample. The crystal is bent in the shape of an ellipse in such a way that source and sample positions are at two focii of the ellipse. The transmitted beam intensity from the sample is recorded on a position sensitive CCD detector, thus enabling recording of the whole EXAFS spectrum around an absorption edge in a single shot (typical acquisition time of one spectrum is ~300 msec). The intensities I0 and It, are obtained as the CCD outputs without and with the sample respectively. Using the relation, It = I0e-µx, where µ is the absorption coefficient and x is the thickness of the absorber, the absorption µ(E) corresponding to the photon energy (E) are obtained. The experimental data has been analyzed using the available computer software package Athena.
Table 1. Copper (II) hydroxamic mixed ligand complexes. Abbreviation and molecular formula.

| S. No. | Complex                      | Abbreviation | Molecular formula |
|--------|------------------------------|--------------|-------------------|
| 1      | Cu(II) 5 chloro-benzo hydroxamic acid | Cu 5CBHA     | CuC₂H₈O₄NCl      |
| 2      | Cu(II) malanohydroxamic acid | Cu MHA       | CuC₂H₄O₂         |
| 3      | Cu(II) succenohydroxamic acid | Cu SuHA      | CuC₂H₆O₂N₂       |
| 4      | Cu(II) acetylohydroxamic acid | Cu ActHA     | CuC₂H₁₀O₃N       |

Table 2. XANES data for the copper K-absorption edge in copper (II) hydroxamic mixed ligand complexes.

| Complex  | Eₖ₁  | Eₖ₂  | Eₐ  | Chemical shift (eV) | ENC | Shift of the principal ab.max. (eV) | Edge-width (Eₐ-Eₖ) (eV) |
|----------|------|------|-----|---------------------|-----|------------------------------------|-------------------------|
| Cu 5CBHA | 8986.7 | 8992.7 | 9001.0 | 6.2               | 0.67 | 6                                 | 14.3                    |
| Cu MHA   | 8987.1 | 8992.4 | 9000.9 | 6.6               | 0.70 | 5.9                                | 13.8                    |
| Cu SuHA  | 8987.8 | 8992.9 | 9000.8 | 7.3               | 0.75 | 5.8                                | 13.0                    |
| Cu ActHA | 8988.4 | 8993.4 | 8999.5 | 7.9               | 0.80 | 4.5                                | 11.1                    |

3. Results
The normalized XANES spectra in the region -30 < E < 50 eV, indicating positions of the absorption edges K1 and K2 and principal absorption maximum A are shown in figure 1. The first derivatives of the spectra in this region, indicating positions of the absorption edges K1 and K2 and principal absorption maximum A are shown in figure 2. First peak in the derivative spectra gives the position of first inflection point, i.e., the K1-absorption edge (Ek1) and second peak gives the second inflection point, i.e., the K2-absorption edge (Ek2). The position where the derivative is zero, gives the position of principal absorption maxima (EA). The results of the energies of the K-absorption edges (Ek1 and Ek2) and the energies of principal absorption maximum A (EA) of copper in its four complexes are presented in table 2. The chemical shifts (in eV) of the K-absorption edge of copper in the complexes are also given in table 2. For all the complexes the distance (in eV) of the principal absorption maximum A with respect to the respective K-absorption edge have also been computed and are collected in the same table. It can be readily seen from table that copper K-edge is found to be shifted towards the high energy side in all the four complexes, as compared to the copper metal K-absorption edge.

4. Discussions

4.1 Chemical shift
The shifts of the K-absorption edge of copper in the complexes with respect to that of copper metal have been determined according to the eqn.

\[ \Delta E_k = E_k \text{(complex)} - E_k \text{(metal)} \]

The results are given in table 2. For computing the chemical shift the value of Ek (Cu metal) has been taken as 8980.5 eV. The compounds having copper in oxidation state +1 show chemical shifts less than 5 eV while those having copper in oxidation state +2 show chemical shifts more than 5 eV [4]. In table 2, all the four
complexes have the values of chemical shifts between 6.2 to 7.9 eV. Hence, on the basis of values of the chemical shifts, all the complexes are found to have copper in oxidation state +2.

The chemical shift is largest for CuActHA complex and the order for other complexes is as follows: 

- Cu ActHA > Cu SuHA > Cu MHA > Cu 5CBHA.

As is well known, an ionic bonding enhances the chemical shift, whereas a covalent bonding suppresses it. Hence, the above order may also be taken as representative of the relative ionic character of the bonding in these complexes.

4.2 Effective nuclear charge (ENC)

If the binding energies of K electron of copper in different oxidation states are determined, one can find from the difference in binding energies of the neutral atom and the ionized atom, the so-called theoretical shifts in the X-ray absorption edge. In the present work, the values of binding energies have

**Figure 1.** XANES spectrum for copper (II) hydroxamic mixed ligand complexes indicating position of absorption edges K1 and K2 and principal absorption maxima A.

**Figure 2.** Derivative of the XANES spectrum for copper (II) hydroxamic mixed ligand complexes indicating position of absorption edges K1 and K2 and principal absorption maxima A.
been determined from the tables of Clementi and Roetti [5] using Koopman’s theorem[6]. The theoretical shifts are plotted against the oxidation number. From the graph (not shown here), the effective nuclear charge on copper in its complexes has been determined and the results have been presented in table 2.

4.3 Principal absorption maximum
In table 2, the data for the principal absorption maximum $E_{A}$ for the complexes have also been included. It has been observed that with respect to copper metal, the value of $E_{A}$ is shifted towards the higher energy side. For the complexes mentioned in table 2, the energy range of chemical shift in these complexes is between 6.2 – 7.9 eV while the range for shift of principal absorption maximum is between 4.5 - 6.0 eV. Hence, on the basis of the shift of the principal absorption maximum also, it can be inferred that copper is in +2 oxidation state in these complexes. The shift of the principal absorption maximum for Cu (II) complexes are in the order

Cu ActHA < Cu SuHA < Cu MHA < Cu 5CBHA

The order of the shift of the principal absorption maximum is in the reverse order of the chemical shift of the complexes.

4.4 Edge-width
In table 2, the values of the edge-width ($E_{A}$-EK1) have been reported. The experimental data of edge-width of Cu (II) complexes show that the edge-width decreases as follows:

Cu ActHA < Cu SuHA < Cu MHA < Cu 5CBHA

The order of the edge-width is in the reverse order of chemical shift of the same complexes. This represents that the edge-width is inversely proportional to ionic character for this series. The reverse trend for these complexes is justified on the basis of the criterion that, in general, edge-width of the K-absorption edge increases with the increase of covalent character of the bonds provided other factors like molecular symmetry etc., remain the same [7].

5. Conclusions
The copper K-edge has been found to split into two components, i.e., K1 and K2 in all of these complexes. The energies of K1 edge (EK1), K2 edge (EK2) and principal absorption maxima (EA) have been reported. From these, the shift of the K1-edge (chemical shift), shift of the principal absorption maximum and edge-width has been obtained. The values of the chemical shifts suggest that copper is in oxidation state +2 in all of the complexes. The chemical shift has been used to determine the effective nuclear charge on the absorbing atom. The order of the chemical shifts is representative of the relative ionic character of the bonding in these complexes.

Acknowledgement
Thanks are due to Drs. S. N. Jha, D. Bhattacharya, A. Poswal, Applied Spectroscopy Division, BARC, Mumbai and S. K. Deb, RRCAT, Indore for their help in recording the spectra.

References
[1] Rockwell M, Melden R A, Copeland K, Hardman C P, Decicco W W and Degrado 1996 J. Am. Chem. Soc. 18 10337
[2] Miller M J and Lin Y M 1999 J. Org. Chem. 64 7451
[3] Bhattacharya D, Poswal A K, Jha S N, Sangeeta and Sabharwal S C 2009 Bull. Mater. Sci. 32(1) 103
[4] Kau L S, Spira-Solomon D J, Penner-Hahn J E, Hodgson K O, and Solomon E I 1987 J. Am. Chem. Soc. 109 6433
[5] Clementi E and Roetti C 1974 Atomic data and Nuclear data tables 14 177
[6] Koopmans T 1934 Physica 1 104
[7] Kumar A, Nigam A N and Shrivastava B D 1981 X-ray Spectrom. 10 25