X-ray diffraction and absorption spectroscopic studies of copper mixed ligand complexes with aminophenol as one of the ligands

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Abstract. X-ray diffraction (XRD) and X-ray absorption spectroscopic (XAS) studies have been conducted on two copper complexes, i.e., copper macrocyclic complex of succinic acid and ortho aminophenol (complex-1) and copper macrocyclic complex of phthalic acid and ortho aminophenol (complex-2). The diffraction pattern of the complexes have been recorded using Rigaku RINT-2000 X-ray diffractometer equipped with rotating anode X-ray tube operated at 40 kV and 100 mA. The X-ray absorption spectra of the complexes have been recorded at the K-edge of copper on Cauchois type bent crystal spectrograph having radius 0.4 m employing a mica crystal, oriented to reflect from (100) planes, for dispersion. The X-ray absorption near edge structure (XANES) parameters, viz., chemical shift, energy position of the principal absorption maximum and edge-width have been determined and discussed. From the extended X-ray absorption fine structure (EXAFS) data, the bond lengths have been calculated using three methods, namely, Levy’s method, Lytle, Sayers and Stern’s (LSS) method and Fourier transformation method. The results obtained have been compared with each other and discussed.

1. Introduction
X-ray absorption spectroscopy (XAS) refers to the details of how X-rays are absorbed by an atom at energies near and above the core-level binding energies of that particular atom. The X-ray absorption spectra is typically divided into two regimes: X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). While XANES refers to the structure on the high energy side of the main edge extending up to ~40 eV from the edge, EXAFS refers to the undulations of the absorption coefficient on the high energy side of the main edge extending from ~40eV to ~1000eV from the edge. XANES is strongly sensitive to formal oxidation state and coordination chemistry of the absorbing atom, while EXAFS is used to determine the distances, coordination number, and species of the neighbors of the absorbing atom. As a result, XAS provides a practical and simple way to determine the chemical state and local atomic structure for a selected atomic species. In the present paper, we have studied X-ray absorption spectra (XAS) at the K-edge of copper in two copper complexes, viz., copper macrocyclic complex of succinic acid and ortho aminophenol (complex-1) and copper macrocyclic complex of phthalic acid and ortho aminophenol (complex-2). XANES parameters, e.g., chemical shift, i.e., shift of K-edge of copper in complex with respect to K-edge of copper metal, energy position of the principal absorption maximum and edge-width have been determined and discussed. The positions of EXAFS maxima and minima have also been determined. Using the EXAFS data, the bond lengths have been calculated using three methods, namely, Levy’s
method, Lytle, Sayers and Stern’s (LSS) method and Fourier transformation method. The X-ray diffraction records of the complexes have been obtained from which the particle size and the lattice parameter have been determined.

2. Experimental

All the complexes have been prepared by chemical root method. The X-ray diffraction patterns of copper complexes have been recorded using Rigaku RINT-2000 X-ray diffractometer with a rotating anode operated at 40 kV and 100 mA. Copper target was used as the source of X-rays at wavelength \( \lambda = 1.54 \text{Å} \).

The X-ray K-absorption spectra of the copper complexes have been recorded using a Rich Seifert X-ray generator with tungsten target operating at 20 kV and 40 mA. A 0.04 m Cauchois type bent crystal transmission spectrograph employing a mica crystal, oriented to reflect from (100) planes for dispersion, has been used to record the spectra. The spectra were recorded on Kodak X-ray photographic films. The exposure time varied from 2 to 4 hours. Digital records of the spectra were obtained on Carl-Zeiss microphotometer coupled to a computer. The computer software Athena version 0.8.056 has been used for analysis of the digital spectral data.

3. Results and discussion

3.1. X-ray diffraction studies:

The X-ray diffraction patterns of the complexes are given in figure 1. Particle size was calculated using Scherer’s formula given by:

\[
t = \frac{0.9\lambda}{B\cos\theta}
\]

where \( t \) is the crystal thickness (in the same units as \( \lambda \)), \( B \) is full width half maxima (in radians) of diffraction line, \( \theta \) is the Bragg angle and \( \lambda \) is the wavelength. The values of particle size and the lattice constant calculated from the diffractometer records are given in table 1.

3.2 X-ray absorption near edge structure:

The X-ray absorption spectra at the K-edge of copper in the complexes are shown in figure 2. The X-ray absorption near edge structure (XANES) parameters, viz., chemical shift, energy position of the principal absorption maximum and edge-width have been determined. The results are given in table 1 and discussed below.

3.2.1. Chemical shift:

The shift of X-ray absorption edge (i.e., K, L, M…) of an element in a complex with respect to that of the pure metal is written as:

\[
\Delta E = E_i (\text{Compound}) - E_i (\text{Element})
\]

The chemical shifts of copper complexes in the present investigation are given in Table 1. The values of shifts are 8.1 and 7.4 eV for complexes 1 and 2 respectively. The compounds studied earlier [1]
CuO, CuCl₂.2H₂O and CuSO₄.5H₂O have been reported to have chemical shifts 4.3, 5.3 and 6.8 eV respectively, which are all +2 oxidation state compounds. Since the chemical shifts in the present work are less than 10 eV, on this basis, the conclusion is that, the two complexes studied are copper (II) complexes. Therefore, copper exists in oxidation state +2 in the complexes studied in the present investigation. The sequence of variation of chemical shifts of the complexes is as follows:

Complex-1 > complex-2

Recalling that the chemical shift value for a compound is largely dependent on the effective nuclear charge on the central metal ion, the decrease in the chemical shift in complex-2 with respect to complex-1 suggested that phthalic acid has lesser field strength than succinic acid.

3.2.2. Shift of principal absorption maxima:

The values for the shifts of the principal absorption maxima with respect to the absorption edge for the complexes are given in Table 1. The shift in the principal absorption maximum in transition metal complexes is known to arise from the transition of an electron from the 1s level to a vacant orbital of appropriate symmetry. This parameter is sensitive to the valency of the metal ion. It is worth comparing the present values for the shift of principal absorption maxima with the values reported by earlier workers for other copper (II) complexes which lie in range of 17.7 - 25.4 eV. [3,4] Hence on the basis of this comparison, we may say that all the samples in the present investigation posses an oxidation state +2. The order of the shifts of the principal absorption maxima is the same as the order of the chemical shifts indicating that the metal ligand bond is stronger in complex 1 as compared to complex 2.

Table 1. Results of X-ray diffraction and absorption spectroscopic studies of complexes

| Complex   | XRD results | XANES results | Bond lengths from EXAFS data |
|-----------|-------------|---------------|------------------------------|
|           | Particle size (nm) | Lattice parameter (nm) | Chemical shift (ev) | Shift of principal absorption maximum (ev) | Edge-width (ev) | R_{Levy's} (Å) | R_{fles} (Å) | RFT (Å) |
| Complex-1 | 38.64       | 0.951         | 8.1                        | 19.40                     | 11.2           | 1.84          | 2.08        | 1.1      |
| Complex-2 | 28.44       | 0.954         | 7.4                        | 15                        | 7.6            | 2.29          | 1.97        | 1.8      |
3.2.3. Edge-width:
The values of the edge width of complexes are given in table 1. Edge-width of the K-absorption edge increases with the increase of covalent character of the bonds [2]. The relative order of the values of edge-width are not supported by the values of the chemical shift or the shift in principal absorption maxima in the present work. The reason may be that the values of edge-width not only depend on the factors responsible for the chemical shift but also on the geometry of the complexes.

3.3 Bond lengths from extended X-ray absorption fine structure data
From the extended X-ray absorption fine structure (EXAFS) data, the bond lengths have been calculated using three methods, namely, Levy’s method, Lytle, Sayers and Stern’s (LSS) method and Fourier transformation method as follows.

3.2.3.1. Levy’s method
In Levy’s method [5], the bond lengths are calculated by using the relation: \( R_1 = (151/\Delta E)^{1/2} \) Å, where \( \Delta E \) is the difference in eV of the EXAFS first maximum and first minimum and \( R_1 \) is the radius of the first coordination sphere. The bond lengths thus determined are given in table 1.

3.2.3.2. LSS method
The values of the wave vector \( k (\text{Å}^{-1}) \) for EXAFS maxima (\( n=0, 2, 4, \ldots \)) and minima (\( n=1, 3, 5, \ldots \)), for all copper complexes have been determined. In the Lytle, Sayers and Stern’s (LSS) method [6] for determination of the nearest neighbour distances, \( n \) versus \( k \) graph is plotted. The plots have been found to be linear for all the complexes. The slope of \( n \) versus \( k \) plot, gives the values of \( 2(R_1 - \alpha_1)/\pi \) where \( R_1 \) is the bond length. The parameters \( \alpha_1 \) depends to a large extent on the central absorbing atom. It is found that for chemically similar system, the values of \( \alpha_1 \) remains more or less the same. The values of \( (R_1 - \alpha_1) \) thus obtained are given in table 1. This is phase uncorrected bond length.

3.2.3.3. Fourier transformation method
The Fourier transform of the oscillatory part of the X-ray absorption spectra are given in figures 3(a) and 3(b) for the two complexes. The Fourier transform peaks at the radial distances of the neighbouring atoms from the absorbing atom. However, the distance found from Fourier transform is about 0.2 Å – 0.5 Å shorter than the actual distance due to energy dependence of the phase factors in the sine function of the EXAFS equation [6]. The peaks in the Fourier transform are shifted towards the origin by an amount \( \alpha_j \) and hence the peaks are at distance \( R_j - \alpha_j \). For the first peak \( j=1 \) and hence the position of the first peak in the Fourier transform determines the distance \( R_1 - \alpha_1 \).

It is important to note here that the distance \( R_1 - \alpha_1 \) should be equal to the distance found from the LSS graphical method outlined above. Hence, both the LSS method and the Fourier transformation method give the value \( R_1 - \alpha_1 \), i.e., both the methods give the value of bond lengths which have not been corrected for the phase shifts. We have called this distance as the phase uncorrected bond length.

It is seen from this table that the values of \( R_1 - \alpha_1 \) as determined from LSS method and those determined from the Fourier transformation method are in good agreement with each other, i.e., both the LSS method and Fourier transformation method give nearly the same value of the phase uncorrected bond length, i.e., \( R_1 - \alpha_1 \).

4. References
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