

XAFS Study of Mixed Ligand Copper (II) Complex of Salicylic Acid

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Abstract

X-ray K-absorption spectroscopic studies have been carried out on the copper (II) mixed-ligand complex [Cu(SA)₂(Py)₂] where ligands SA= Salicylic acid and Py= Pyridine. XAFS spectra have been recorded at the K-edge of copper using the dispersive beam line at 2.5GeV Indus-2 synchrotron radiation source RRCAT(Raja Ramanna Center for Advance Technology), Indore, India. XAFS data analysis program Athena and the computer software Origin 6.0 professional have been used to process the obtained data. Various X-ray absorption parameters e.g., chemical shift, edge-width and shift of the principal absorption maximum have been obtained in the present study. The chemical shift data have been utilized to estimate effective nuclear charge on the absorbing atom. The XAFS data obtained has also been used to determine the bond length by using four different methods, i.e., Levy's, Lytle, Lytle, Sayers and Stern's (LSS) and Fourier transformation methods. The results of the study have been reported in this paper.

Keywords: XAFS, Athena, Copper complex, LSS, Origin 6.0 professional,

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1. Introduction

Salicylic acid (SA) is a phenolic phytohormone and is found in plants with roles in plant growth and development [1]. Salicylic acid is biosynthesized from the amino acid phenylalanine and can be produced by sodium salicylate [2, 3]. In modern medicine, salicylic acid and its derivatives are used as constituents of some rubefacient products, for example, methyl salicylate is used as a liniment to soothe the joint and muscle pain, choline salicylate is used typically to relieve the pain of aphthous ulcers [4].

Pyridine(Py) is a simple aromatic heterocyclic organic compound with chemical formula (C₅H₅N). Pyridine was industrially produced by extraction of coal tar, it is currently synthesized from formaldehyde, ammonia and acetaldehyde. It is harmful if inhaled, swallowed or absorbed through the skin [5]. Effect of pyridine in toxication includes dizziness, headache, nausea and loss of appetite [6,7]. Pyridine is readily degraded by bacteria to ammonia and carbon dioxide.[8] The nitrogen atom on pyridine features a basic lone pair of electrons because this lone pair is not delocalized into the aromatic pi-system. Pyridine is widely used as a ligand in coordination chemistry [9,10]. In this work, pyridine and salicylic acid were used as ligands with CuCl₂.

X-ray absorption fine structure (XAFS) 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 atom. Specifically, XAFS is the modulation of an atom's x-ray absorption probability due to the chemical and physical state of the atom. The x-ray absorption spectrum is typically divided into two regimes: X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine-structure spectroscopy (EXAFS).

XANES has been extensively used to obtain information about the molecular structure viz. the oxidation state and the effective nuclear charge of the absorbing atom in compounds and complexes.

The Extended X-ray Absorption Fine Structure (EXAFS) yields information regarding the nearest neighbors of the central metal ions, i.e. bond length. The Fourier transform of an EXAFS spectrum provides information on the distribution of atomic shells as a function of distance from the target absorber. The bond lengths have also been determined by three graphical methods, namely, Levy's [11], Lytle's [12], and Lytle, Sayers and Stern's (LSS) [13, 14] methods.

A search through literature reveals that no work has been done on XAFS study of the transition metal complex of Salicylic acid with Pyridine. This gave us the motive to synthesis and characterization of Cu (II) complex of mixed ligand, Salicylic acid with Pyridine.

2. Experimental Details

The X-ray absorption spectra at the K-edge of copper of this complex have been recorded at BL-8 Dispersive EXAFS beamline at the 2.5-GeV INDUS-2 Synchrotron Source, Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India [15], [16], [17]. The experimental data have been analyzed using the available computer software packages Origin 6.0 professional and Athena [18].

The complex studied in the present investigations is $[\text{Cu}(\text{SA})_2(\text{Py})_2]$ where ligands SA= Salicylic acid and Py= Pyridine. The complex was prepared according to the standard method reported in literature and its purity was checked [19].

Material

All chemicals were of analytical grade purity. Metal salt $\text{Cu}(\text{CL})_2 \cdot 2\text{H}_2\text{O}$ was obtained from E-Merck company while Salicylic acid and Pyridine from System. Ethanol absolute 99% (Fluka), KOH (Merck) and diethyl ether (Merck) were used as received from the suppliers.

General Method for Synthesis:

Salicylic acid (SA) was deprotonated at room temperature. For that KOH is added to Salicylic acid in presence of ethanol. Then water is added to the product in order to obtain deprotonated Salicylic acid (SA^-) separating potassium (K^+) from it.

Synthesis of Complexes:

Ethanol solution of the metal salt was added to the solution of the ligand (SA^-) in ethanol using stoichiometric amounts (1:2) (Metal: Ligand). The mixture was stirred for two hours at room temperature, product was separated by adding excess of pyridine (4.5-1ml). By treating the solution with diethyl ether until complete precipitation takes place. The precipitates were crystallized from ethanol and dried at 50°C .

3. Results and Discussion

The curve in Figure 1 represents the normalized K absorption spectra. The energies of the copper K-edge (E_K) and the principal absorption maximum (E_A) along with the value of the edge-width ($E_A - E_K$), the chemical shift (ΔE_K) and effective nuclear charge Z_{eff} are given in Table 1.

The Fourier transformation technique along with the three graphical methods i.e. Levy's, Lytle and Lytle, Sayers and Stern's (LSS) have been used for the determination of the bond lengths. The results are given in Table 3.

The EXAFS spectra converted into k space has been given in Figure 3. The values of energy E and wave vector k corresponding to these maxima and minima have been shown in Table 2. The slope of energy level Q Vs energy E curve, shown in Figure 4, has been used to evaluate the bond length by Lytle method. The slope of channel number n Vs wave vector k curve, shown in Figure 5, has been used to evaluate the bond length by LSS method. The magnitude of Fourier transform of Figure 3 is shown in Figure 6.

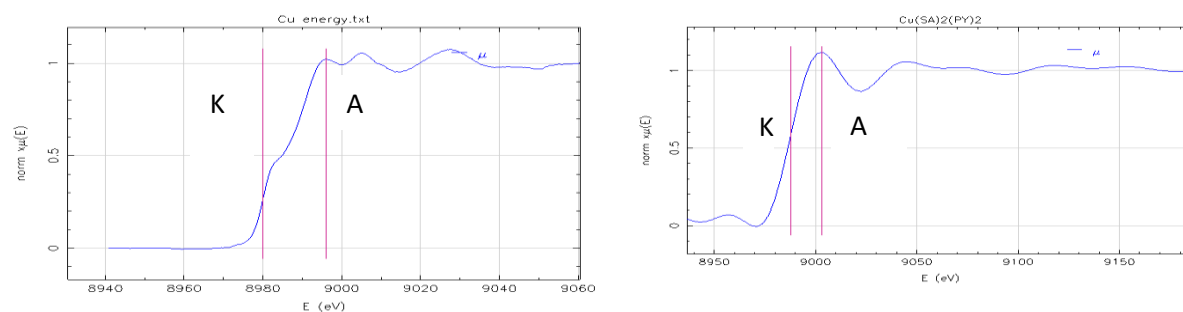


Fig 1. The XANES region of the absorption spectrum at the K-edge of copper metal and in the complex indicating positions of the absorption edge K and the principal absorption maxima A.

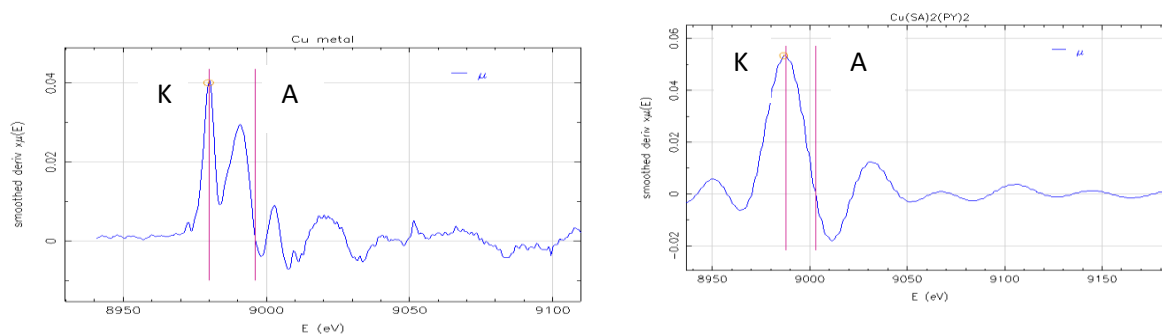


Fig. 2. Derivative of the XANES region of the absorption spectrum at the K-edge of copper metal and in the complex indicating positions of the absorption edge K and the principal absorption maxima A.

Table 1. XANES data for the K absorption edge of copper in the complex.

Complexes	E _K (eV)	E _A (eV)	Chemical shift (eV)	Shift of the principal absorption maximum (eV)	Edge-width (E _A - E _K) (eV)	ENC Electron/atom	% Covalency
Copper metal	8980.12	8996.21	-	-	16.088	-	-
Cu(SA)2(Py)2	8988.67	8998.9	8.54	2.68	10.23	0.84	52.62

3.1 Chemical Shift:

For computing the chemical shift, the value of E_K (Cu metal) has been taken as 8980.12 eV. The shift of the X-ray absorption edge of copper in a complex with respect to that of the copper metal is written as:

$$\Delta E_K = E_{K(\text{complex})} - E_{K(\text{metal})}$$

In Table 1, the complex has the value of chemical shift as 8.54 eV. Hence, on the basis of value of the chemical shift, the complex is found to have copper in oxidation state +2 [20].

As compared to the K-absorption edge in the metal, the K-absorption edge of copper has been found to be shifted towards the high-energy side in the complex studied [21].

3.3 Principal absorption maximum:

The data for the principal absorption maximum E_A for the complex is also included in Table 1.

The shift of the principal absorption maximum at the K-absorption edge of copper in the complex with respect to that of copper metal has been determined according to the eqn.

$$\Delta E_A = E_A(\text{complex}) - E_A(\text{metal})$$

For computing the principal absorption maximum, the value of E_A(Cu metal) has been taken as 8996.21 eV. It has been observed that the value of E_A is shifted towards the higher energy side with respect to copper metal [21].

3.4 Edge-width:

In Table 2, we have reported the value of the edge-width (E_A-E_K). The edge-width value is 10.23 eV.

3.5 Effective nuclear charge Z_{eff}:

For the estimation of effective nuclear charge, various methods have been proposed [22], [23]. In the present work, Z_{eff} has been obtained from the measured chemical shift by using the semi-experimental method by employing the procedure suggested by Nigam and Gupta [24]. The effective nuclear charge on the copper in the complex under present study is 0.84 electrons/atom.

3.6 Percentage Covalency

To calculate the percentage covalency of the bonds, a theoretical graph is plotted between the calculated value of binding energy of 1s electron using Clementi's results of atomic function and percentage covalency for copper [25]. The percentage covalency for the copper complex under present study is 52.62 % .

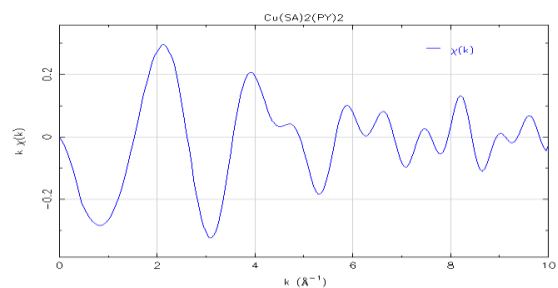


Fig 3. $\chi(k)$ versus k curve for the copper complex

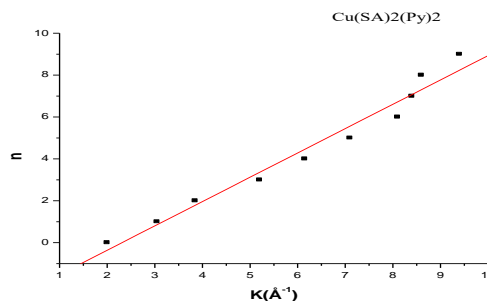


Fig 4. n versus k curve for the copper complex

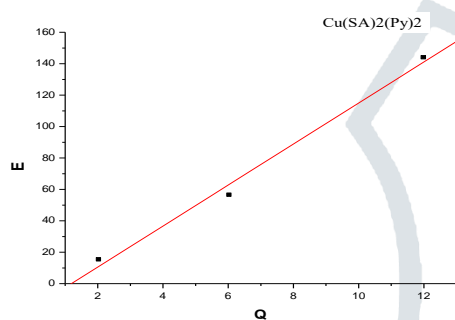


Fig 5. Q versus E curve for the copper complex

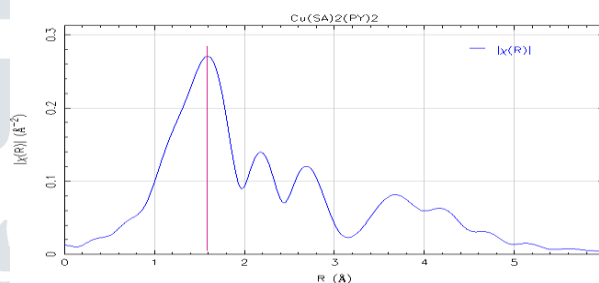


Fig 6. Magnitude of Fourier transform of the $\chi(k)$ versus k curve for the copper complex

Table 2. Energy E (eV) and wave vector k (\AA^{-1}) for EXAFS maxima and minima at the K absorption edge of copper in the complex and their corresponding values of n and energy level Q

Structure	n	Q	[Cu(SA)2(Py)2] E (eV)	k (\AA^{-1})
A	0	2.04	15.209	2.00
α	1	-	35.370	3.05
B	2	6.04	56.359	3.85
β	3	-	102.813	5.2
C	4	12.0	143.811	6.15
γ	5	-	191.673	7.1

Table 3. Values of first shell bond lengths (in \AA) calculated from Levy's, Lytle's, LSS and Fourier transform methods for the copper complex

Complex	Levy's method	Lytle's method	LSS method	Fourier transform
[Cu(SA)2(Py)2]	1.93	1.67	1.57	1.6

4. Conclusions

X-ray absorption spectra of mixed ligand copper complex at the K-edge of copper have been recorded at the recently developed EXAFS beamline setup at the Indus-2 synchrotron source at RRCAT, Indore. The energy of K-edge (E_K), and principal absorption maxima (E_A) have been reported. From these, the shift of the K-edge (chemical shift), shift of the principal absorption maximum and edge-width has been obtained. The chemical shift has been used to determine the effective nuclear charge on the absorbing atom and percentage covalency. The value of the chemical shift suggest that copper is in oxidation state +2 in the complex.

From the positions of the EXAFS maxima and minima, the bond length in the complex has been determined by three different methods viz. Levy's, Lytle's and LSS methods. From the Fourier transforms of the EXAFS spectra, the bond length (uncorrected for phase shift) has been determined. It has been observed that the value of the phase-uncorrected bond length, i.e. $R1-\alpha1$, as determined from LSS method and that determined from the Fourier transformation method, agree with each other within the limits of experimental error.

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