Synthesis, Characterization, XRD And EXAFS Studies Of Fe(III) Complexes

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Abstract: Present work reviews the synthesis of Fe(III) complexes of Schiff base ligand which derived from benzoin and two different amino acids. The synthesized ligand and its metal complexes were characterized by X-ray diffraction, and EXAFS. X-ray diffraction pattern analyzed that both Fe(III) complexes have Hexagonal structure and crystalline in nature, using BRUKER D8 Advance instrument. EXAFS technique extracts the local structure of complexes. The nearest neighboring atom distance commonly known as 'bond length' were calculated using Fourier transform method. The bond lengths determined from these methods were also compared with the bond length obtained from several others.

INTRODUCTION

Metal complexes of O, S, and N containing Schiff bases have been the subject of current and growing interest because it has wide range of pharmacological activities [1]. In particular Schiff bases with 2-amino thiophenol, 2-amino phenol, 2- amino benzoic acid, and 2-amino 3-hydroxy pyridine exhibit various biological activities such as antimicrobial activity, protein tyrosine phosphates inhibition, and nuclease activity [2, 3]. Several aromatic amine Schiff bases have been investigated but few works deal with chromone skeleton derivatives. Chromones are a group of naturally occurring compounds that are ubiquitous in nature especially in plants. Molecules containing the chromone skeleton have extensive biological applications including antimycobacterial, antifungal, anticancer, antioxidant, antihypertensive, and antiinflammatory applications.[4–5]. The most common technique for characterizing abundant soil minerals is X-ray diffraction (XRD), which relies on long range ordering of atomic planes to probe crystalline structure at a length scale of approximately 50 Å or more [6].

Although most of the absorption spectrum is quite smooth, oscillatory features called fine structure is found directly above an edge. This fine structure is intrinsically quantum mechanical phenomenon that is based on the X-ray photoelectric effect, in which an X-ray photon incident on an atom within a sample is absorbed and liberates an electron from an inner atomic orbital (e.g., 1s). The "photoelectron" wave scatters from the atoms around the X-ray absorbing atom, creating interferences between the outgoing and scattered parts of the photoelectron wave function. These quantum interference effects cause an energy dependent variation in the X-ray absorption probability, which is proportional to the X-ray absorption coefficient, a measurable quantity. This fine structure contains a wealth of local structural information. When properly decoded these modulations provide information about the structure, atomic number, structural disorder, and thermal motions of neighboring atoms. X-ray absorption fine structure (XAFS) spectroscopy is a unique tool for studying, at the atomic and molecular scale, the local structure around selected elements that are contained within a material. For this reason, XAFS is a very important probe of materials, since knowledge of local atomic structure, i.e., the species of atoms present and their locations, is essential to progress in many scientific fields: physics, chemistry, biology, biophysics, medicine, engineering, environmental science, materials science, and geology.[7-8]

EXPERIMENTAL PROCEDURE

To prepared the complexes, Chemical root method is used. For synthesized the Iron (II) complexes, first we prepared the Schiff base ligands using benzoin and both different amino acids (H2N-R). With the help of these Schiff base ligands, we prepared both Iron (II) complexes which is in the ratio of 2:1 Presently the synthetic macrocyclic complexes are most important from the biological point of view as they are structurally comparable to some naturally occurring macrocyclic complexes.[9]

The X-ray diffraction pattern (XRD) using Bruker D-8 advance, X-ray powder diffractometer was obtained with Ni-filtered Cu-Kα radiation (λ=1.54Å) having voltage 40kV and current 100mA. The diffraction pattern of complexes recorded between 2θ ranging from 10 to 80 and step size is 0.02.

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 absorption of X-rays on the high energy side of absorption edges does not vary monotonically in condensed matter but has a complicated behavior which extends past the edge up to about ~1 keV. This non-monotonic variation has received the name of X-ray absorption fine structure (XAFS). Spectra have been recorded using synchrotron radiation. The X-ray spectroscopy setup is available at Raj Ramanna Center for Advanced Technology (RRCAT) and is called beam line. This beam line BL-8 has been recently commissioned at the 2.5 GeV Indus-2 synchrotron radiation sources. In Fourier Transform method has been determined by the Fourier transformation method for the iron complexes studied however, determined only the phase uncorrected bond lengths by this method. No attempt has been made to employ the fitting procedures by which phase corrected bond length can be determined, because the required crystallographic data is not available for any of the complexes studied. From EXAFS bond length data shown in table 2 and Figure 2.

1. 2-{[(1*E*)-2-hydroxy-1,2-diphenylethylidene]amino}pentanedioic acid- Complex 1
2. 2-{[(1*E*)-2-hydroxy-1,2-diphenylethylidene]amino}-4-(methylsulfanyl)butanoic acid- Complex 2

RESULT AND DISCUSSION

The X-ray diffraction pattern of prepared samples was obtained by varying the scattering angle 2θ from 10° to 80° in step size of 0.02°.The pattern has been indexed using JCPDF software and lattice parameters have been using the Braggs law. The XRD analysis shows that chromium complexes have hexagonal structure and crystalline, in nature which is shown in Figure 1 and Table 1.
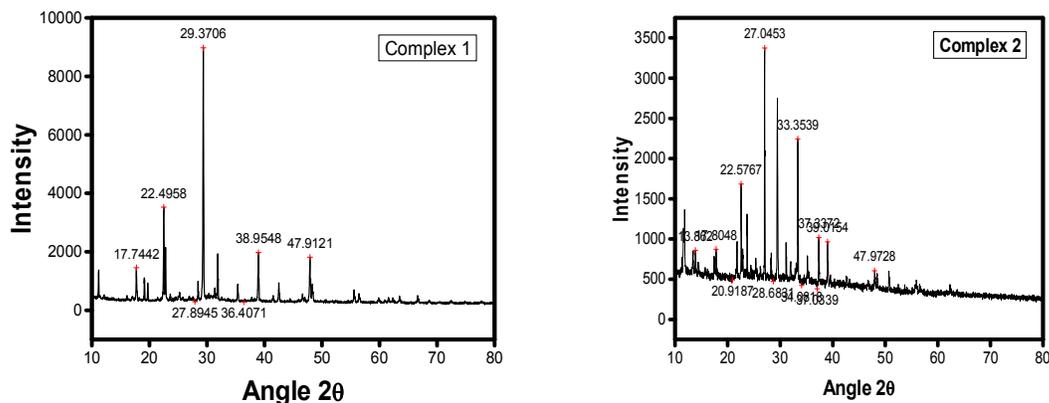

Fig1 XRD pattern of Fe (III) complexes.

Table 1 Lattice parameter and particle size

Complex	Particle Size (nm)	Lattice Parameter(Å)	
		a	c
Complex 1	12.38	4.77	7.89
Complex 2	15.32	6.02	3.93

EXAFS have been used extensively in the investigation of local atomic structures such as the number and type of neighboring atoms, inter-atomic distances and disorder. Since the application of EXAFS does not require the materials to have long-range order. It is well suited for determining the local structures of both non-crystalline materials. The well marked EXAFS feature on the high energy side of the K-absorption edge up to several hundred eV, have been observed in the cobalt complexes. From the knowledge of EXAFS, we have calculated the bond length for the Iron(III) complexes with the help of Levy's, LSS, Lytle and F.T. methods. The Values of bond length R is tabulated in table 2. The bond lengths obtained in Fe(III) Complexes by LSS, Levy's, and Lytle method with F.T. Method are comparable each other. From F.T.magnitude curve for Fe(III) shown in figure 2.
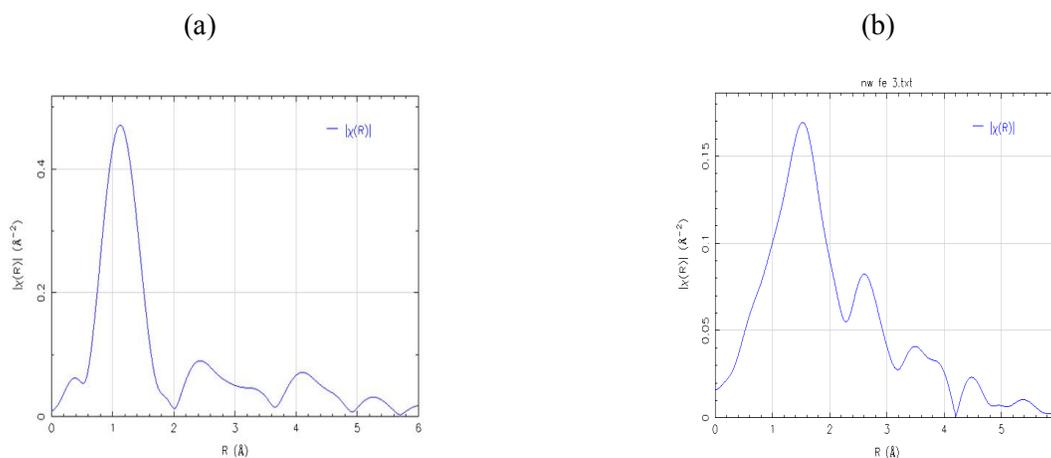
(a)   (b)

Figure:2 From F.T.magnitude curve for Fe(III) complexs.(a) complex 1 (b) complex 2

Table:2: Average values of bond length in (Å) and phase parameters for both Fe (III) Complexes.

Complexes	R_{LSS}	$R_{Levy's}$	R_{Lytle}	$R_{F.T.}$
Complex 1	1.21	1.37	1.33	1.52
Complex 2	1.61	1.49	2.35	1.35

CONCLUSION

On the basis of the above discussion, table 1 Figure 2 shows the suggested structure for Iron (III) complexes are hexagonal and crystalline in nature. The particle size and lattice parameter were found to be within in the range 8.20 to 15.32nm and 4.76 to 6.02 Å (for a and b) and 7.87 to 3.93 Å (for c).

It has been observed that the value of the phase corrected bond length, i.e., R_1 as determined from Levy's method and Rs as determined from the Lytle's method are in good agreement with each other, i.e., both method give nearly the same value of the phase corrected bond length. From the Fourier transforms of the EXAFS spectra the bond lengths have been determined which have then been Fourier transformed using the software Athena.

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