



## *XRD, X-ray absorption spectroscopic study and synthesis of iron complex*

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**Abstract:** In this paper we have discussed preparation of iron complex with ligand [1E,3E,6E,9E] - 4,6,10,12 - tetramethyl-5,11 - bis(E) - p - tolyldiazenyl] - 1,3,7,9 - tetraazacyclodeca - 3,6,9,12 - tetraene ] and its X- ray absorption studies. EXAFS is a spectroscopic method used to find the distances of metal its nearest neighboring atoms. XRD characterization has been done in order to estimate the crystallite size. In present paper nearest neighboring distances have been calculated using various graphical methods like Levy's, Lytle's and LSS method. The distance is also calculated using Fourier Transform method. The values obtained from graphical methods are found to be very close with the distance estimated using Fourier transform method .With the help of XANES spectra the position of principal maxima and k edge is found.

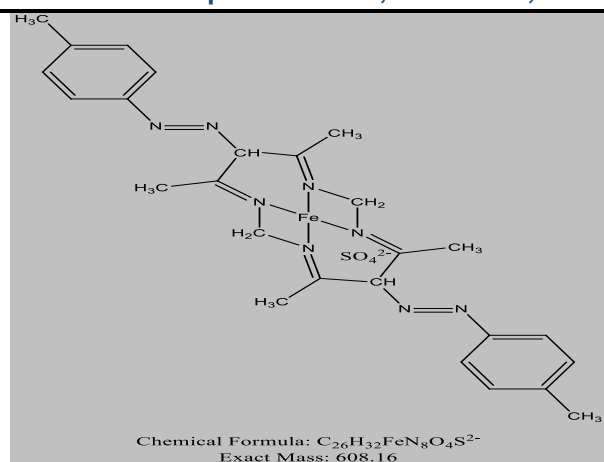
### Introduction

X-ray absorption spectroscopy is used to obtain information about the molecular structure of compounds and complexes. In X-ray absorption spectroscopy, due to absorption of X-ray photons, photo electrons are ejected from the inner core shells of the atoms. Hence, hole is left behind in the inner core shell of the atoms. [1] XAS measures the absorption coefficient  $\mu(E)$  as the function of incident X-ray energy. When an X - ray beam passes through a material, its intensity falls according to the relation,  $I_t = I_0 e^{-\mu x}$ , where  $\mu$  is the absorption coefficient and  $x$  is the thickness of the absorber,  $I_0$  is the intensity of incident X-rays and  $I_t$  is the intensity at distance  $x$  in the material [2].When the incident X-ray energy matches the binding energy of an electron of an atom ,then absorption Edge is formed in the graph. X-ray absorption fine structure is variation of X-ray absorption coefficient near the absorption edge. There are two parts in fine structure, (XANES) X ray absorption near edge structure up to 50 eV above the edge and (EXAFS) extended X-ray absorption fine structure formed between 50 eV to 1000 eV above the edge.[1] The main advantage of using XAS is that ,it is does not require long range

order, hence information can be retrieved from disordered samples. We can get information regarding the nearest neighbours of the central metal ions using the extended X-ray Absorption fine structure. [2] Hence, we have studied X-ray K absorption spectra of iron complex.The extended X-ray absorption fine structure (EXAFS) is used to calculate distances of the neighboring atoms from absorbing elements chemical shift, principal absorption maxima and edge width can be calculated with the help of XANES spectra.

### Experimental Technique:

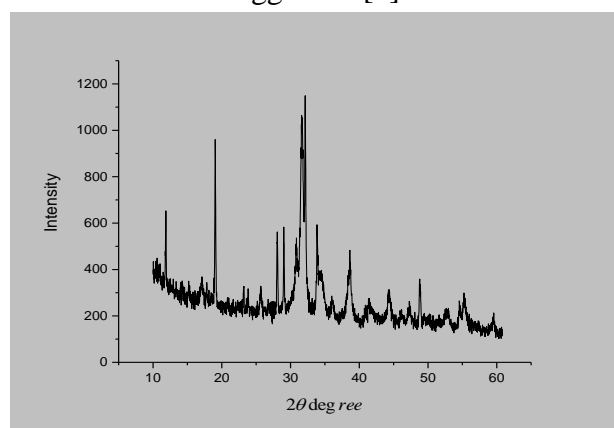
The iron complex has been synthesized by dissolution of metal salt (Ferrous sulphate 0.005mol) with ligand [1E,3E,6E,9E] - 4,6,10,12 -tetramethyl-5,11- bis(E)-p-tolyldiazenyl]-1,3,7,9 -tetraazacyclododeca - 3,6,9,12 - tetraene ] (0.01 mol) in 20 ml of ethanol.. The mixture was then refluxed for 6 hours at 70<sup>0</sup>C on water bath. After reflux colored precipitate was filtered and dried .The crystal structure of iron sample is represented in fig 1.



**Fig 1: Iron complex chemical structure**

### Determination of particle size using XRD:

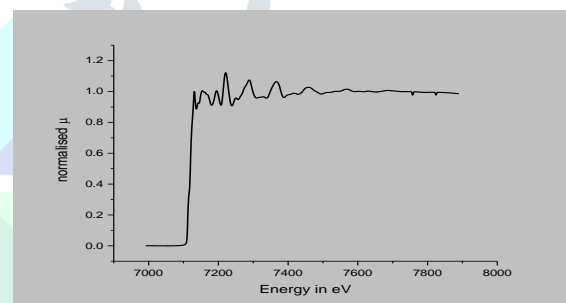
X-ray diffraction studies carried out using Bruker D8 Advance X-ray diffractometer. The X-ray powder diffraction patterns were recorded from powdered sample using monochromatic  $CuK\alpha$  (1.54 Å) radiation. X-ray diffraction technique is used to identify and characterize crystalline materials. When X-ray strikes on a an ordered lattice, elastic scattering of monochromatic photons takes place..When the scattered rays are in phase they produce constructive interference according to Bragg's law  $2d\sin\theta=n\lambda$  Where,  $\lambda$  is the wavelength,  $d$  is the inter planner distance between two lattice planes,  $\theta$  is the angle of reflection, and  $n$  is the spacing of atoms in a plane can be measured by determining the angles that produce maximum intensity .[4] In the powder method, the specimen under investigation is rotated during the irradiation so as to bring as many crystal planes as possible into orientations which satisfies Bragg's law.[5]



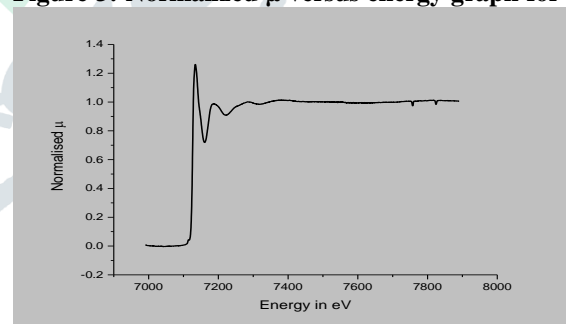
**Figure 2 : XRD graph for iron complex**

### Synchrotron radiation :

In synchrotron the electromagnetic radiation are emitted when charged particles are accelerated. The synchrotron radiation is used in x-ray absorption spectroscopy because of the properties of radiation like brightness, high collimation, high polarization, small spot size. The synchrotron consists of only continuous X-rays. Synchrotron accelerates the electrons up to the speed of light by deflecting them through strong magnetic fields. The synchrotron radiation is channelized into the beam lines towards the experimental work stations where is it used to perform the experiments.[3].The iron k edge spectra were obtained from BL 9 scanning EXAFS beam line at 2.5 GeV INDUS 2 , synchrotron radiation source at Raja Ramanna Center for Advanced Technology (RRCAT) Indore, India . The data recoded has been analysed using the software Athena. From the K-edge absorption spectra ( fig 3 and fig 4) of iron foil and iron complex it is clear that k edge is obtained in both graphs at nearly same energy.



**Figure 3: Normalized  $\mu$  versus energy graph for iron foil**



**Figure 4: Normalized  $\mu$  versus energy graph for iron complex .**

### Information retrieved from XANES spectra:

When the absorption is plotted as a function of energy of incident x ray, the spectrum has three characteristics,1) Decrease in X-ray absorption with increasing energy in pre edge region.2) A sharp increase at certain energy called k absorption edge 3) A series of oscillatory structure in post edge region.[4].The k edge value of iron complex is found to be 7121.2 eV. The chemical shift in iron complex is difference of  $E_k$  and standard value which is found to be 9.2eV.the

standard value of  $E_K$  (iron metal) has been taken as 7112 eV. The principal absorption maximum  $E_A$  for the iron complex has been shifted by 21.9 eV with respect to iron metal. The edge-width ( $E_A - E_K$ ) for the iron complex is 12.7 eV.

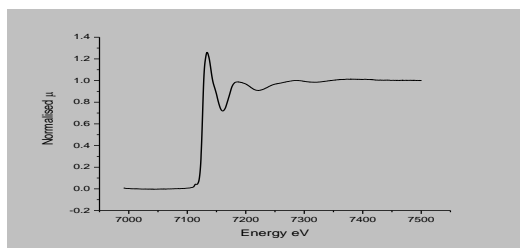


Figure 5 XANES graph for iron complex

### Determination of nearest neighbouring distances from EXAFS spectra:

The nearest neighboring distances have been determined using Levy's, Lytle, Lytle, Sayers and Stern's (LSS) and Fourier transformation.

In Levy's method [11] bond length, are given by  $R_1 = [151/\Delta E]^{1/2}$  Å, where  $\Delta E$  is the difference in eV of the energies of the EXAFS maximum  $B$  and minimum  $\beta$  (fig 6). According to Lytle [12] method the bond length is calculated by the relation  $R_s = [37.60 / M]^{1/2}$ , where  $M$  is slope of  $E$  vs  $Q$  plot Fig (7). In the LSS method [13],  $n$  versus  $k$  graph is plotted (fig 8). The slope of  $n$  versus  $k$  plot gives the value of  $2(R_1 - \alpha_1)/\pi$  where  $R_1$  is the bond length. In Fourier Transform of graph peak is formed at radial distances of the neighboring atoms from the absorbing atom (fig 9). The position of the first peak determines the distance  $R_1 - \alpha_1$  (phase uncorrected)

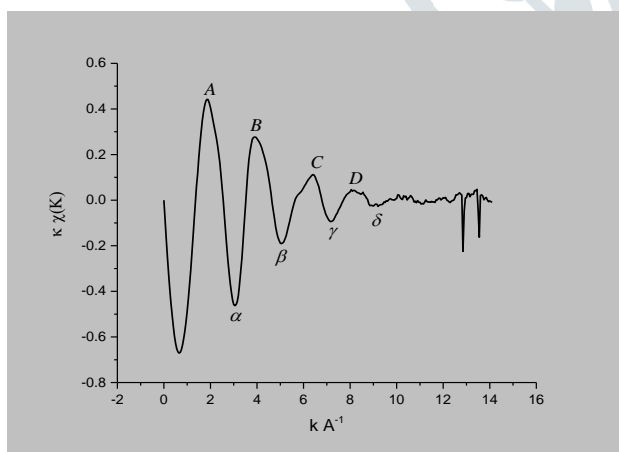


Figure 6 :The  $k\chi(k)$  vs.  $K$  spectra of iron complex

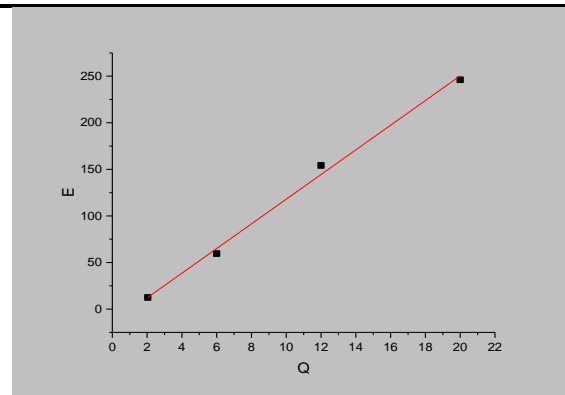


Figure 7 :  $E$  vs  $Q$  plot for iron complex

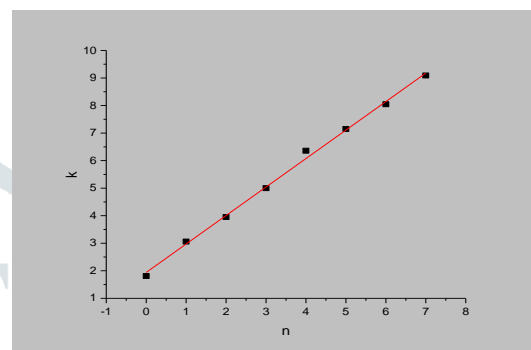


Figure 8:  $n$  vs  $k$  graph for iron complex

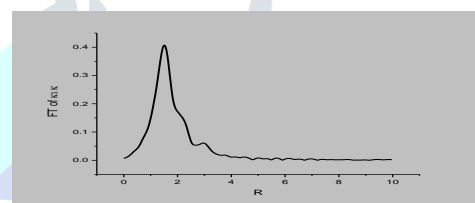


Figure 9: Graph between Fourier transform  $\chi(k)$  and radial distance  $R$ .

### Results and Conclusion:

The K absorption edge and the principal absorption maxima of iron complex has found to be shifted towards the high energy side as compared to the K absorption edge in the metal.

The shift of the K-edge (chemical shift) is found to be 9.2 eV. The values of the chemical shifts suggest that iron is in oxidation state +2 in the complex. According to Scherrer's equation, the average crystallite size is given by  $t = 0.9 \lambda/B \cos\theta$ ,  $B$  is half width full maxima (in radians) of the diffraction peak,  $\theta$  is the Bragg angle and  $\lambda$  is the wavelength [4]. XRD analysis shows that sample is crystalline in nature and particle size is 5.8 nm approximately. The nearest neighbouring distances in the complex determined by Levy's, Lytle's and LSS methods and nearest neighbouring distance obtained from Fourier transformation method are respectively 2.05 Å, 1.68 Å, 1.62 Å, and 1.51 Å which are in good agreement with each other. From EXAFS spectra, it is clear that the LSS method and Fourier transformation methods give phase uncorrected bond length. Due to energy dependence of the phase factors in sine function of expression for

EXAFS, the distances found in Fourier transform are comparatively shorter than the actual distances.

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