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Structural studies of Hexanitroferrate of Lead K$_2$Pb[Fe(NO$_2$)$_6$]

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A detailed structural analysis of the title compound was performed using Extended X-ray absorption spectroscopy in order to understand the electronic structure of the ground state with a view to explain the magnetic and the related spectroscopic features. The structural details reported here were found to be deviating from the earlier results proposed based on the powder X-ray diffraction method.

1. Introduction

Dipositive iron in its low spin state is described by a non-degenerate orbital and spin ground state where the symmetry at the Iron site is close to octahedral in character. This will not give any net electron density at the site of the nucleus resulting in single narrow Mossbauer spectrum. If there are distortions from the perfect octahedral symmetry it results in the quadrupolar splitting of the Mossbauer spectral line at low temperature [1]. Temperature dependent quadrupolar splitting in Mossbauer spectroscopy resulting from the spin crossover behaviour with high spin at high temperature and low spin at low temperature is an entirely different behaviour. However the observation of the hyperfine splitting in the Mossbauer spectrum of high spin Fe^{2+} is rather unusual due to the rapid spin lattice relaxation at these temperatures where one might expect it to be observed. In an earlier report Padmakumar K *et al*. [2] it was established that the compound with a formula K$_2$Ba[Fe(NO$_2$)$_6$] (dipotasium barium hexanitroferrate) was found to be exhibiting unusual magnetic and electronic relaxation properties This was attributed to the ^{5}E ground state of the ferrous ion in the high spin state originated from the Jahn-Teller distortion of the ^{5}T$_2$ ground state. This doubly degenerate ground state is responsible for the temperature dependent Mossbauer spectral properties of these series of compounds K$_2$M[Fe(NO$_2$)$_6$] where M is Pb, Ba, Sr, Ca, Zn,. The details of the structure reported earlier Caulton KG *et al*. [3] were found to be not agreeing with the Mossbauer spectral data that we have recorded. So a detailed EXAFS data analysis was carried out at room temperature as well as at low temperature for K$_2$Pb[Fe(NO$_2$)$_6$] to get an explanation for the Mossbauer spectral pattern and the associated magnetic behaviour, which can be further extended to other systems.

2. Experimental

The compound was prepared according to the earlier reported procedure [4]. The purity of the compound was checked by the elemental analysis and IR spectroscopy which concur with the earlier reported results [4]. It should be noted here that the compounds are unstable in presence of water even though it is prepared in aqueous medium, but by quick filtration followed by drying.

EXAFS (Extended X-ray absorption fine structure spectroscopy) measurements
X-ray absorption data on K-edge and L$_{III}$ edge were collected at the Stanford Synchrotron radiation laboratory(SSRL) on beam line II-3 under dedicated ring conditions (3.0 GeV 50-100 mA) using a Si (220) double crystal monochromator. Harmonic rejection was accomplished by detuning the monochromator by 50%. The samples were ground to

a fine powder, diluted with boron nitride and sealed with Kapton in Al sample holders. Spectra were measured both at 10K, using an Oxford instrument helium cryostat and at room temperature. Absorption data were collected in the transmission mode using ionizing chambers filled with Nitrogen gas. The samples were calibrated using an Iron foil internal standard with the first reflection point of the Iron foil defined as 7111.2 eV. The Pb edge was calibrated by setting the first inflection point to 13055 eV. EXAFS spectra were measured by using 10eV, with 1sec. integration time on pre edge region, 0.5 steps in the edge region, 0.05 $Á^{-1}$ steps in the K-max 2-17 $Á^{-1}$ using integration times up to 8sec at k=T/ $Á^{-1}$. The total integration time per scan was 35- 40 minutes. Two spectra were averaged for each sample.

Data analysis
The first order polynomial was subtracted from the pre edge region and a multiple region spline was subtracted from the EXAFS region. The threshold energy (k=0) was set to 713.0 eV. from the Iron and

13055 eV for the Lead. The EXAFS data were analysed using EXAFS PAK data analysis programs [5]. All the data were k^3 weighted and the average spectra were fit between a k range of 2.0 to 11.0 $Á^{-1}$ for the Fe and 2.0 to 17 $Á^{-1}$ for Pb.

3. Results and Discussion
EXAFS data analysis
The spectra have been recorded for different samples and were found to have excellent reproducibility. The EXAFS spectra were recorded at room temperature and at 10K. All the features of the spectra were identical at both temperatures except for the broadening at room temperature. For the room temperature EXAFS the high R features are all strongly damped. This could be due to the contributions from the thermal and static damping factors which are high at high temperature. But the very immediate co-ordination environment, (such as Fe-N and Fe-O) appear identical at both the temperatures.
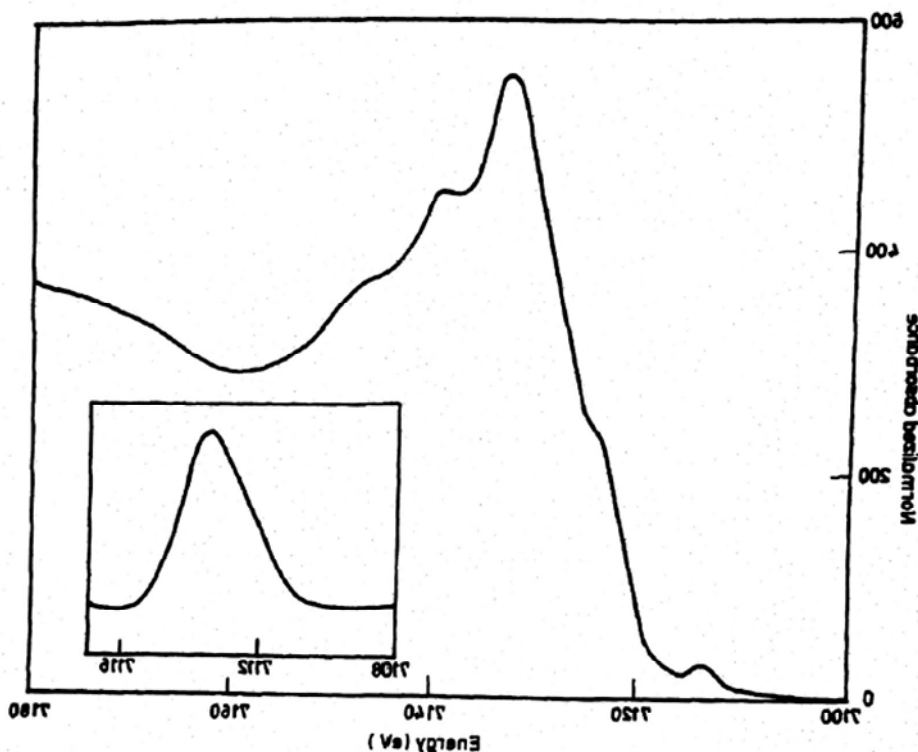

Fig 1: XANES spectrum of the Fe-edge region with 1s→3d intensity expanded in the inset.

XANES (X-ray absorption near edge spectroscopy) spectrum
Fe XANES spectrum was compared with few other Fe spectra. There are several resolved transitions and

a couple of shoulders in this region. This could be used as finger print of the local structure. The absence of any change with temperature suggests that the average environment remains the same as the

temperature is raised. The spectra of the Fe-edge is shown in Fig 1. The well resolved transition at ca 7111.3 eV is the 1s→3d transition. The isolated background subtracted 1s→3d transition is shown in inset. This transition which is forbidden by dipole selection rule is quadrupole allowed and is always seen for Fe (II) spectra even in centrosymmetric systems, but with a small intensity. In model studies the intensity of the 1s→3d transition has been found to increase as the Fe site distorts perfectly from octahedral symmetry. The pre-edge intensity gradually increases with a decrease in co-ordination number and the departure from a centrosymmetric co-ordination environment. This general principle has been adopted for probing the site symmetry of the metal centre in biologically important proteins [6]. This is a consequence of the 3d and 4p mixing which is allowed in distorted geometry. The intensity of the 1s→3d transition for $K_2Pb[Fe(NO_2)_6]$ is surprisingly large, for an earlier proposed octahedral Fe(II) site. This anomalous behaviour could be explained on the basis of the disorder in the material which mainly arises due to the distorted nature of the NO_2 groups. It was reported that the opposite NO_2 groups are lying in a plane [3]. Thus the three sets of NO_2 groups make three mutually perpendicular planes. These explanations are based on the crystal structure data available for the hexanitroferrate compound of Cu which are easily crystalisable. The Cu compound was found to undergo Jahn-Teller distortion [4]. But the hexanitro could be entirely different due to difference in electronic structure. Thus the overall distortion is manifested as a peak in the pre-edge region even though the appearance of this peak is attributed to lower co-ordination environment of the central metal atom. All the NO_2 groups are distorted from the normal plane giving an overall distortion from the perfect octahedral symmetry. This distortion is also confirmed by the presence of nearly four to five peaks in the asymmetric stretch of the NO_2 group, in the infrared spectrum of this compound (to be communicated). The isolated 1s→3d transition (see inset) shows a shoulder at ca 7112 eV in addition to the principle transition at ca 7113.5 eV. These most likely represent transition into different $(1s^1)$ $(3d^7)$ final states and are thus measure of 3d orbital splitting. Several more partially resolved transitions are observed in the XANES. There is a shoulder on the edge at about 7124 eV. It is impossible to say what it is due to. However, numerous studies of

Cu(II) and Fe(II) complexes have shown, empirically that the transition at about this place on the edge is often correlated with the presence of a square planar or square pyramidal metal site. This transition was variously assigned as the 1s – 4p or 1s-4p +shake down. Normally we should not expect to see a transition at this energy for pseudo octahedral Fe. However in this case it is very difficult to interpret this transition in terms of a 5 co-ordination or lower than that for the central metal atom. Thus the unusual high intensity of 1s→3d transition suggests that the Fe site is distorted from the cubic crystallographic symmetry. Such distortions are not expected for a low spin Fe(II), but are quite reasonable for the high spin case. Further evidence for the high spin character comes from the resolution of the two transitions within 1s→3d region. Low spin Fe(II) is expected to show only one 1s→3d transition.

Edge Region
The observed edge energy for this compound is slightly higher than what is expected for a normal Fe(II) complex. Comparative plots of the edge region for the various oxidation states of Fe are given Fig 2. Here again the normal interpretation is that the edge energy is a measure of the oxidation state. The energy at hlf height is typical of that found for Fe(III) complexes and is substantially (ca 2-3 eV) higher than the six co-ordinate Fe(II) complexes, which typically have edge energies between 7118-7122 eV [6]. As the oxidation state increase the edge energy will also be shifted to higher side. Penner-Hahn and co-workers suggest that the bond length information is the principle determinant of the edge energy rather than the simple oxidation state of the element of interest. The bond length is inversely related to the edge energy. Hence we have a first co-ordination sphere of six nitrogen atoms with a very short Fe-N bond. This information has been obtained from the Fe EXAFS region. Thus it is not necessarily surprising that the edge energy is usually high.

EXAFS spectrum
The 10K EXAFS spectra for the Fe K-edge and Pb L_{III} edge are shown is Fig 3 and the corresponding Fourier transforms are shown in Fig.4. The presence of strong outer shell scattering is apparent in the high frequencies of EXAFS and the presence of large high-R peaks in FT's. The nearest neighbour interactions are nearly identical in the room temperature spectra,

however the outer shell scattering is strongly damped at room temperature. In general the FT's are consistent with the structure expected from powder XRD pattern. According to the powder XRD pattern the Fe atom is surrounded by six nitrite N at 2 Å 12 nitrite O at 2.8 Å 8 Potassium at 4.5 Å and six Pb at 5.16 Å. In the FT all of the peaks are shifted by $\alpha = -0.4$ Å, thus leading to the assignments indicated on Fig 4. Similarly the Pb atom is surrounded by 12 nitrite O at 2.8 Å, 6 nitrite N at 3.2 Å, 8 Potassium at 4.5 Å, and 6 Fe at 5.16 Å.

Quantitative curve fitting analysis is consistent with the structure picture. In particular there is a striking agreement between the Fe-Pb and Pb-Fe distances obtained by EXAFS (5.18 Å and 5.16 Å) as expected crystallographically (5.16 Å), (Table 1).
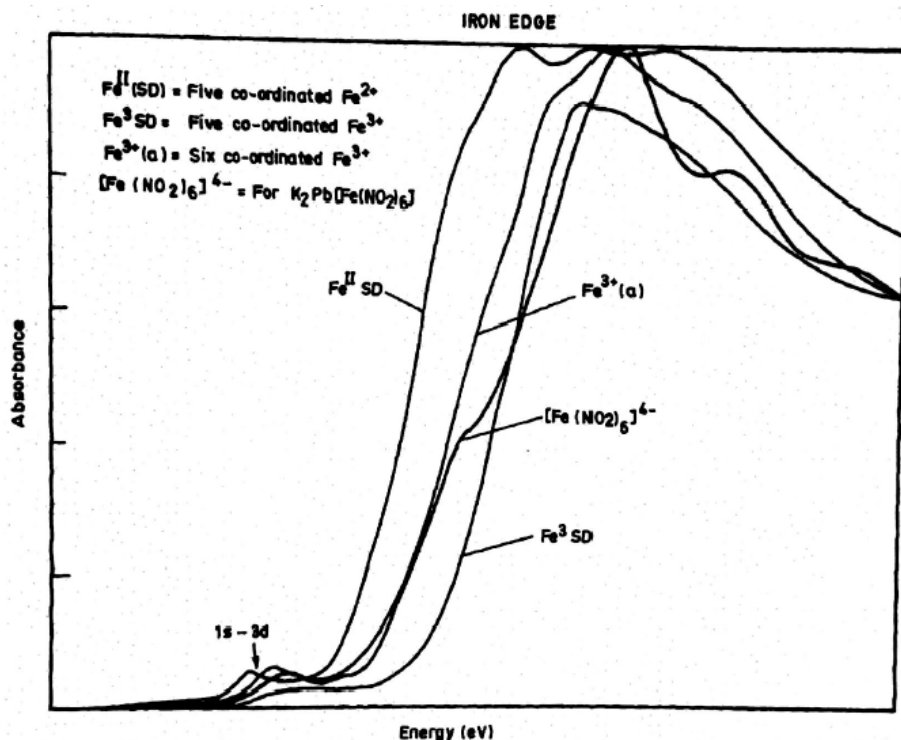

Fig 2: Comparative plots of the edge region of the Iron in various oxidation states.

Table 1: Various bond lengths for the title compound at room temperature. (Similar values are obtained at 10K also)

Type Fe EXAFS	Distance Å	Type Pb EXAFS	Distance Å
Fe-N	1.97	Pb-O	2.77
Fe-O	2.80	Pb-N	3.22
Fe-K	4.50	Pb-K	4.33
Fe-Pb	5.26	Pb-Fe	5.24

Fits to the first FT peak (Fig 5) gave a reasonable Fe-N co-ordination number of 5-6 but an unusually short apparent bond length of 1.93 Å. (Table 2)

Table 2: Best fit to Iron EXAFS:

Shell	Scatterer	R Å	$\sigma^2(Å^2*10^3)$
1	N	1.97	0.5
2	O	2.82	0.7
3	K	4.45	2.7
4	Pb	5.22	2.1

This distance is too short for a six co-ordinated Fe (II), particularly for the high spin Iron case. More typically the distances for such systems are 2.11 to 2.15 Å. A short bond length could produce a low spin Fe(II) which will be diamagnetic at all temperatures due to the presence of $^1A_{1g}$ ground state which is nonmagnetic at all temperatures. But here is an Fe atom in the high spin ground state with +2 oxidation state, as proved by magnetic data (to be communicated), having a short bond length of the

order of 1.97 Å. This bond length is about 0.2 Å lesser than what is calculated from crystallographic data. The apparent first shell co-ordination is about 4 which is rather puzzling. This anomaly could be due to the disorder in the Fe site which is random from one to the other. Since the overall lattice is cubic, there could be some tetragonal distortions of Fe giving 4 equitorial Fe-N at 1.95 Å and two longer axial Fe-N distances. In such a case when 1/3 distortions are long "a" 1/3 of them long "b" and 1/3

of them along "c" in different Fe centers. Such distortions are acceptable and understandable since the high spin octahedral Fe^{2+} with $^5T_2$ ground state is expected to undergo Jahn-Teller distortion. This could lead to axial compression or elongation along the X, Y, Z co-ordinates. But the overall lattice would still look like a perfect cube. These distortions are not evident from EXAFS because of the wide distribution of Fe-N bond distances at random direction.
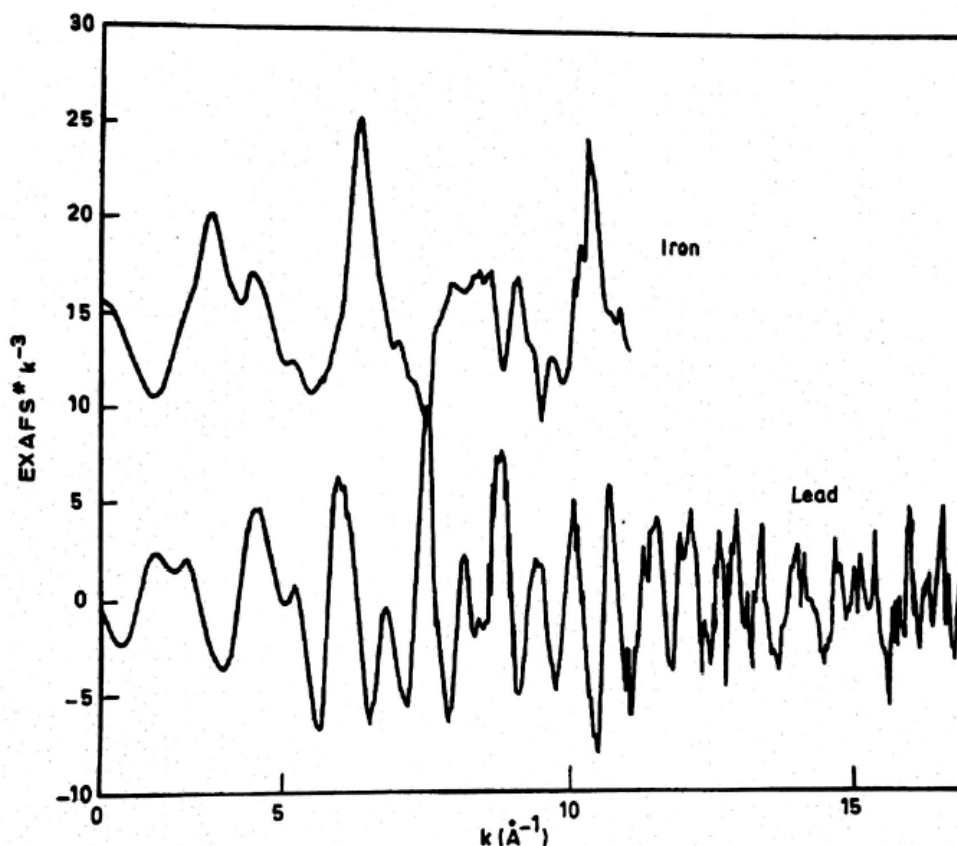

Fig 3: The k^3 weighted EXAFS spectra of the Iron edge and the Lead edge.

We could see the outer shell oxygen very clearly. These at about 2.8 Å which are completely consistent with the known structure of the metal co-ordination nitrites, ie the Fe-N and Fe-O distances are mutually consistent, which shows most of the Fe atom co-ordinated by nitrites as required by the crystal structure. The apparent co-ordination number for the

Fe-O is little low but it is approximately double the Fe-N co-ordination number. It is interesting to note here that the crystallographic parameters based on powder XRD correctly predict the Fe-O but not the Fe-N distance. But the EXAFS distances Fe-N and Fe-O are consistent which again points to some inaccuracies in the crystal structure.
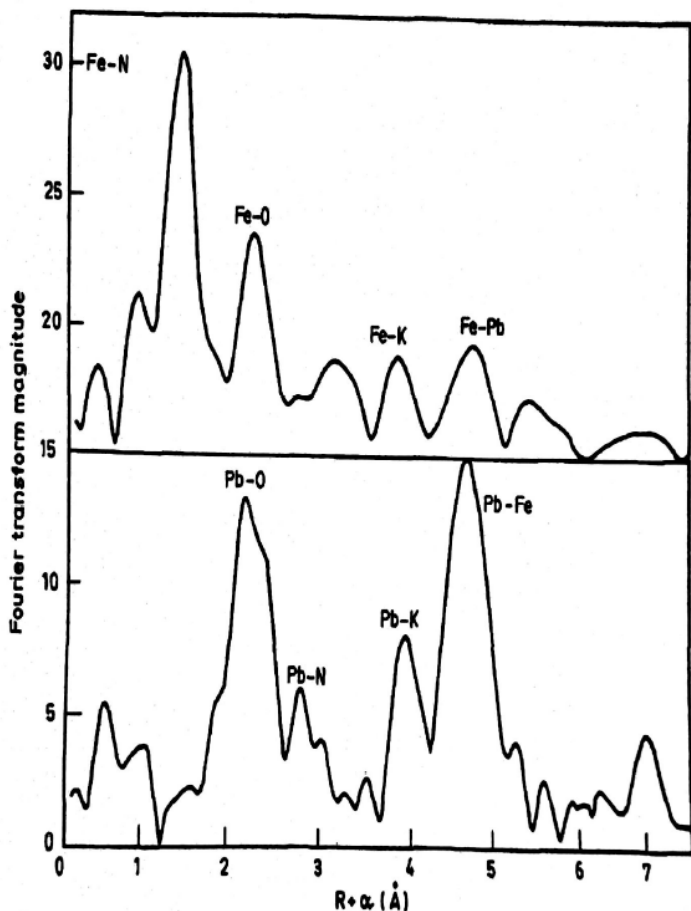
Fig 4: The fourier Transform of the k^3 weighed EXAFS producing the pseudo radial distribution function for the Iron and Lead edge.

Fig 5: Fits to the first shell co-ordination of nitrogen and oxygen

Outer shell

We could see three highly reproducible peaks in the FT of the outer shell. Two of these could be fit by a potassium at a ca of 4.45 Å and shell of Lead at 5.22 Å. Both of these are in good agreement with the radial distribution that is predicted from crystal structure. The apparent Fe-K and Fe-Pb co-ordination numbers are rather low which is due to the low amplitude resulting from a long distance weak interaction. The Fe-Pb distance turns out to be half of the unit cell distance which is in good agreement with the powder XRD data. This also indicates a long range order in the structure.

Pb EXAFS

The Pb EXAFS data are consistent with the Fe EXAFS data and the crystal structure. The Pb is in a very unusual 12 co-ordinate site with nearest neighbours being 12 oxygens from nitrite at 2.78 Å and six nitrite nitrogen atoms at 2.99 Å. This is pretty
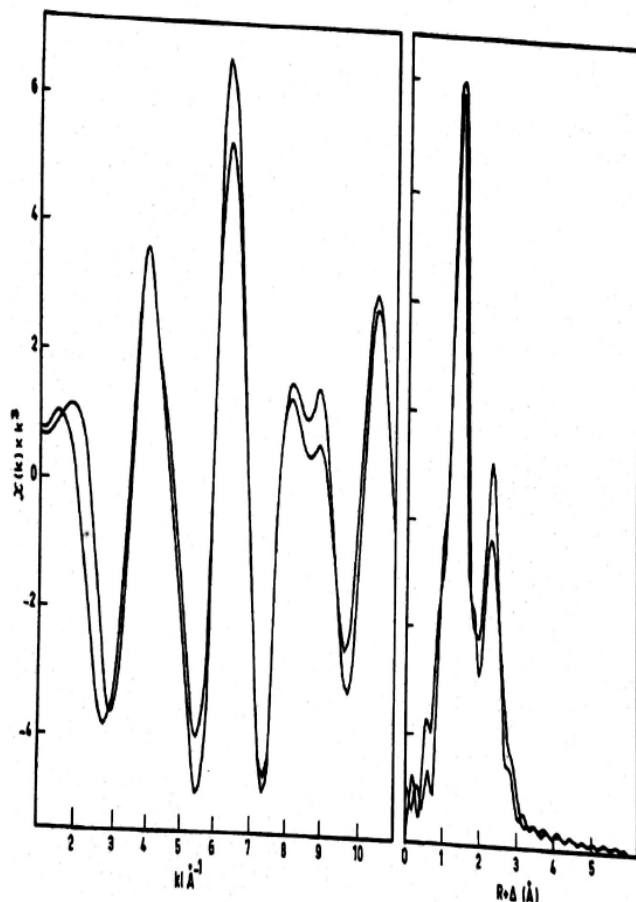
much what we see in EXAFS. We do not see any effect of distortion of the Fe site on the Pb EXAFS. This probably suggests that there is not any significant distortion of nitrites in the direction of the Pb ions, it is very surprising to see that Pb-Fe peak is 5 times higher in amplitude than the Fe-Pb peak. This is due to the destructive interference Fe EXAFS whereas it is constructive in the case of Pb. All bond distance calculated on the basis of EXAFS are shown in Table 1.

4. Conclusions

In conclusion we could say that the EXAFS give the Fe-N distance as 1.95 Å. There is a possibility for long range order which is again predicted by the EXAFS results. It could also be concluded that the overall co-ordination number in the first co-ordination sphere is six. In addition to this the X-ray photoelectron spectroscopy was also used to confirm the presence and oxidation state of Lead and Iron.

6. Reference

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