

# Supramolecular Assembly of Fe Metal Based on Azide and Nicotinamide as Co-ligand: Synthesis, Characterization and Magnetic Studies

Deepanjali Pandey<sup>a\*</sup>, Shahid S. Narvi<sup>a</sup>, Shiva Arun<sup>a</sup> & Jaromir Marek<sup>b</sup>

Department of Chemistry, Motilal Nehru National Institute of Technology Allahabad-211004, India<sup>a</sup>.  
Masarykova univerzita - CEITEC MU<sup>b</sup>

## 1. Introduction

The synthesis and study of mono or polynuclear coordination polymers and their characterization has been a hot topic in the field of molecular magnetism, because it acts as building blocks with applicability in molecular-based materials. In order to achieve molecular based magnets linkers such oxo, chlorido, hydroxido, alkoxo, carboxylato, or azido are often used to react with metal ions. These small bridges are very good candidate for the magnetic exchange phenomenon. The azide anion is an excellent ligand to build low dimensional coordination polymer. It is so versatile that  $\mu$ -1, 1(end-on, EO),  $\mu$ -1,3 (end-to-end, EE),  $\mu$ -1,1,3 and other modes are allowed. The most important aspects of these azido-bridged complexes are the exchange of magnetic interactions [1].

To study the magneto-structural correlation of azido-bridged complexes, various suitable co-ligands were used and magnetic properties of the complexes have systematically been investigated. Many azido- complexes including dinuclear, trinuclear, and tetranuclear species, together with 1D, 2D and 3D coordination polymers have been reported [2]. For example, metal organic frameworks based on 4,4bipyridine or polycarboxylic ligands have been extensively studied.

The investigation reports show that introduction of nicotinic acid derivatives as coligand to the metal based azido complex may produce some interesting structures and magnetic properties due to the coordination flexibility of the various nitrogen donor atoms of the co-ligand. Nicotinamide ligand has much biological importance such as it is the component of the vitamin B-complex as well as component of the coenzyme, (NAD). It plays important role in the metabolism of living cells and some of its compounds are biologically active e.g. insulin-mimetic agents [3]. Thus the structure of nicotinamide attracted the attention of many researchers. Another most important reason for using nicotinamide as ligand is that these ligands with aromatic rings such as pyridine, 2,2-bipyridine, 4,4-bipyridine, 1,10-phenanthroline and nicotinic acid derivatives act as an antenna for the energy absorption in photoluminescent materials [4]. If distance of aromatic ring in the complex is appropriate then pi-pi interaction may exist. These pi-pi interactions stabilise the MOFs structure further.

In Metal organic framework compounds, supramolecular networks are usually built through strong covalent bond and extensive lateral weak intermolecular interactions like hydrogen bonding, pi-pi stacking, C-H...pi interactions etc. Among these interactions, hydrogen bonding and pi-pi stacking interactions generally play an important role in the synthesis of coordination supramolecular architecture because of their relative strength and directional properties. As a result, many 1D,2D and 3D metal organic frameworks have been reported with weak interactions. Thus these non-covalent interactions are very important in the stabilization of self-assembly of supramolecular architectures [5].

Here we have selected metal for synthesis of metal organic frameworks i.e.  $\text{Fe}^{2+}$  because  $\text{Fe}^{2+}$  ( $d^6$ ) exhibit various structural topologies which may vary its magnetic property [6]. Many  $d^{10}$  metal coordination polymers namely  $[\text{Cd}(\text{SCN})_2(\text{isonicotinamide})_2]\cdot\text{H}_2\text{O}$ ,  $[\text{Cd}(\text{SCN})_2(\text{nicotinic acid})_2]\cdot\text{H}_2\text{O}$ ,  $[\text{Cd}(\text{SCN})(\text{nicotinic acid})(\text{H}_2\text{O})]$  and  $[\text{Cd}(\text{SCN})_2(\text{nicotinamide})_2]_3$  are reported in literature with thiocyanate and nicotinamide as mixed ligands.

In this complex,  $\text{N}_3^-$  and nicotinamide ligand is used. To the best of our knowledge, no framework has been reported in the literature using this combination of mixed ligands. Both complexes characterized through IR spectroscopy, TGA and X-ray single crystal analysis techniques.

## 2. Experimental

### 2.1. Materials and Physical Measurements

Iron (II) chloride hexa-hydrate (Sigma Aldrich), Cadmium (II) chloride (Sigma Aldrich), Sodium azide (Sigma Aldrich), Nicotinamide (Aldrich), were purchased and used without further purification. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the  $4000\text{--}400\text{ cm}^{-1}$  region. In order to reveal the thermal stability of compound TGA measurement has been carried out on Perkin-Elmer Diamond TGA/DTA instrument with a flow of Dry nitrogen at a heating rate of  $5^\circ\text{C}/\text{min}$  from room temperature to  $1000^\circ\text{C}$  (for compound-1). Compound-2 was analysed under inert atmosphere, while ramping the temperature at a rate of  $10^\circ\text{C min}^{-1}$  from 0 to  $1200^\circ\text{C}$  Variable-temperature magnetic susceptibility data were collected using a Quantum Design MPMS SQUID magnetometer. Magnetic susceptibility of complex was corrected for diamagnetism of the constituent atoms, which was calculated using Pascal's constant. The fluorescent spectra were performed for compound 1 on HITACHI F-2500 fluorescence spectrometer in solid state at room temperature.

### 2.2. Crystallographic Details of complex

The crystal structure was solved by direct methods using the program SHELXS of the SHELX-97 program package [7]. Single crystal X-ray data were collected at  $293(2)\text{ K}$  on a Bruker SMART APEX diffractometer using graphite monochromatic  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). The diffraction radiation source of 'fine focused sealed tube'. The linear absorption coefficients, scattering factors for the atoms, and the anomalous

dispersion corrections were taken from International Tables for X-Ray Crystallography [8]. The data integration and reduction were processed with SAINT software. An empirical absorption correction was applied to the collected reflections with SADABS using XPREP. The structure was refined on F<sup>2</sup> by full-matrix least-squares technique using non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically fixed and treated as riding atoms using SHELXL default parameters. Crystal data and structure refinement parameters are listed in Table 1. The final  $R = 0.0121$ ,  $wR = 0.0568$  calc [ $w = 1/[\sigma^2(F_o^2) + (0.0290P)^2 + 7.0000P]$  where  $P = (F_o^2 + 2F_c^2)/3$ ]  $S = 1.062$ ,  $(\Delta\rho)_{\max} = 273 \text{ e}/\text{\AA}^3$ ,  $(\Delta\rho)_{\min} = -0.652 \text{ e}/\text{\AA}^3$  and  $(\Delta/\sigma)_{\max} = 0.090$ .

### 2.3. Geometric Special Detail

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

### 2.4. Refinement Special Details

Refinement of F<sup>2</sup> against all reflections. The weighted R-factor wR and goodness of fit S are based on F<sup>2</sup>, conventional R-factors R are based on F, with F set to zero for negative F<sup>2</sup>. The threshold expression of F<sup>2</sup> > 2sigma (F<sup>2</sup>) is used only for calculating R-factors (gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F<sup>2</sup> are statistically about twice as large as those based on F, and R-factors based on all data will be even larger.

### 2.5. Synthesis of complex

A solution (10 ml) of Ferrous chloride (in 1:1 ethanol/wt) (0.126g, 1mmol) and Sodium azide (0.196g, 2mmol) was slowly added drop wise to hot aqueous solution (10ml) of Nicotinamide (0.244g, 2mmol) with stirring. Yellow colour solution was obtained. After filtration the final clear solution left undisturbed at room temperature for slow evaporation. After one week, small needle shaped light yellowish crystals were collected and dried in vacuum over silica gel. The crystal for X-ray study was selected manually and immersed in silicon oil.

## 3. Results and Discussion

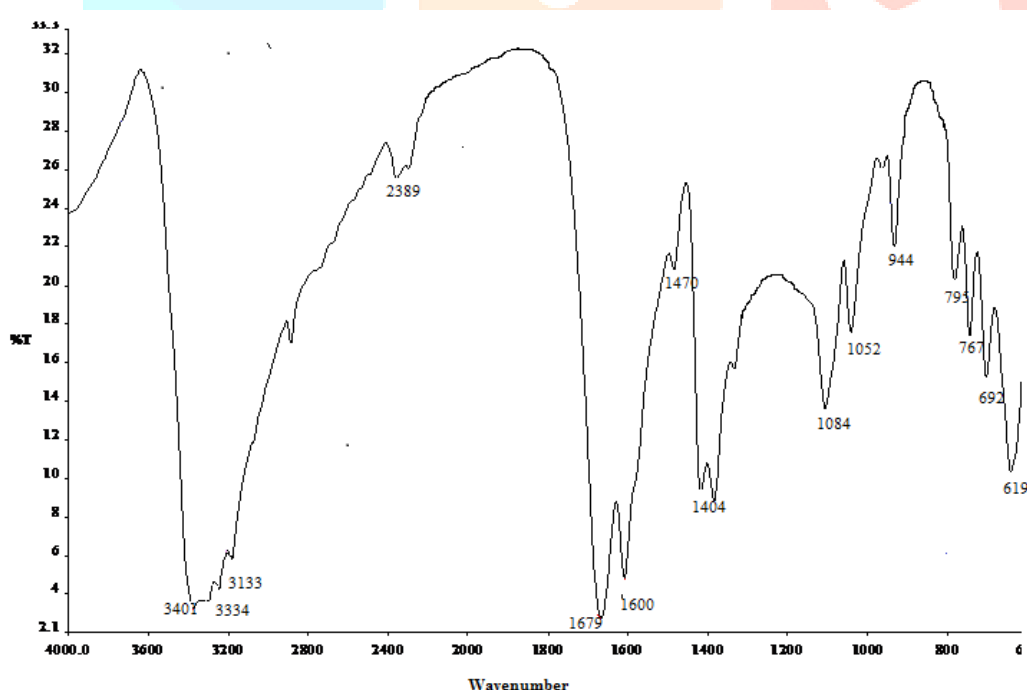
Metal estimation for Cd (II) and Fe (II) were done by standard procedures. The metal ion and C, H, N and S were found in relevant percentage and are listed in Table 3.1

**Table 1: Elemental Analysis of both compounds**

S.N.	Compound	Physical state	Colour	Elemental Analysis	
				Calculated (%)	Found (%)
1.	C12 H16 N12 Fe N8 O4	Crystalline	yellowish	C 36.9, H 3.5, N 18.4, , Fe 26.1	C 36.7, H 3.4, N18.2, Fe 26.3

### 3.2. IR Spectral Analysis for complex

In the IR spectrum, the peak over  $3100\text{ cm}^{-1}$  indicated the presence of coordinated water molecules. The broad peak near  $3300\text{ cm}^{-1}$  shows presence of hydrogen bonding through water molecules. The broad and very low intensity peak observed near  $2187\text{ cm}^{-1}$  may be assigned to N-N stretching of  $\text{N}_3^-$  ligand. It observed the two bands near  $3334$  and  $3133\text{ cm}^{-1}$  assigned to symmetric and asymmetric stretching vibrations. The free pyridine ring of nicotinamide shows peak at  $1592\text{ cm}^{-1}$  which is shifted towards lower frequency  $1470\text{ cm}^{-1}$  indicating coordination of pyridine ring. The IR spectrum shows two bands near  $1979$  and  $1600\text{ cm}^{-1}$ , due to stretching vibration of C=O group of nicotinamide moiety. Other skeletal ring vibrations observed at  $1084\text{ cm}^{-1}$ ,  $1052\text{ cm}^{-1}$ ,  $944\text{ cm}^{-1}$ ,  $692\text{ cm}^{-1}$ . (Figure 1)

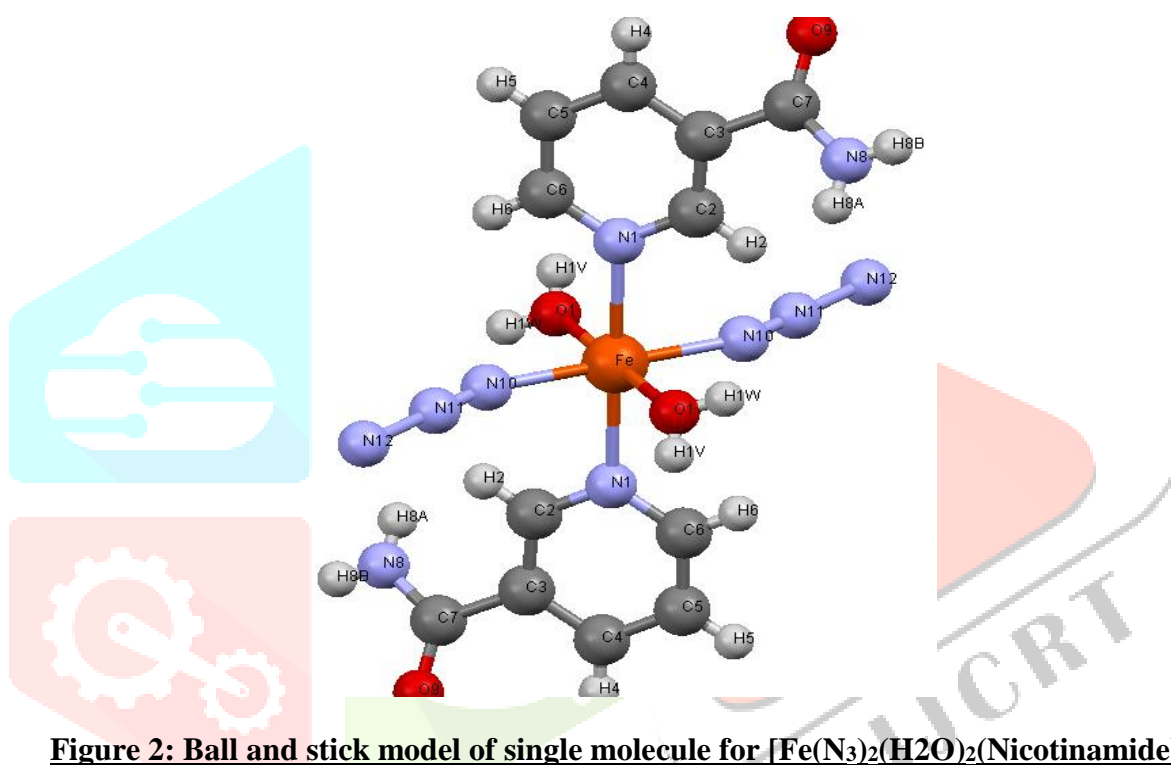


**Figure 1: IR Spectrum of  $[\text{Fe}(\text{N}_3)_2(\text{Nicotinamide})_2(\text{H}_2\text{O})_2]$**

### 3.3. Single Crystal X-ray Analysis for complex

The compound crystallizes in triclinic systems belonging to P-1 space group. The crystal structure reveals that central metal atom has an octahedral geometry. Its coordination environment is completed with two nitrogen

atoms from nicotinamide molecule at axial position, two oxygen from water molecule and two nitrogen from  $N_3^-$  anion ligand at equatorial position. The metal atom is present at inversion centre. The octahedral geometry is distorted with small axial elongation (bond length Fe-N(1)=2.21 Å). The bond distance between metal centre Fe ion and nitrogen atom N(10) of  $N_3^-$  anion ligand is 2.128(2) Å and bond angle of N(10)FeN(10) is  $180.00(8)^\circ$ . The metal centre Fe(II) ion is attached with nitrogen atom N(1) from nicotinamide ligand and oxygen atom O1W from water molecule with a distance of 2.220(2) Å and 2.101 Å respectively. The equatorial plane of distorted octahedral geometry is defined by two nitrogen (N10, N10) from  $N_3^-$  ligand and two oxygen (O1, O1) from water molecules respectively. While axial position is occupied by (N1, N1) nitrogen atom from nicotinamide molecules. (Figure 4.13)



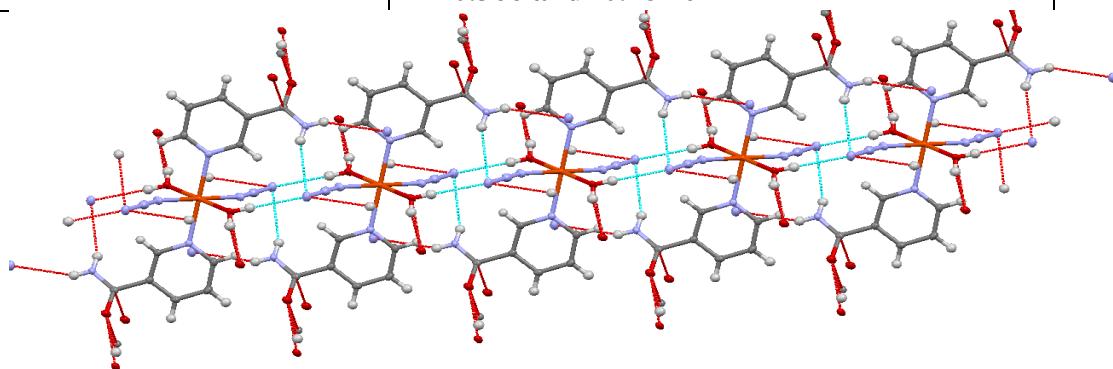
**Figure 2: Ball and stick model of single molecule for  $[Fe(N_3)_2(H_2O)_2(Nicotinamide)_2]$**

The bond angle between O1W-Fe-O1W and N(1)-Fe-N(1) is  $180.0^\circ$ . This ligand can also bridge two metal centres in  $\mu_{1,3}$  fashions. The azido anion is excellent ligand, may adopt  $\mu_{1,1}$  (end on, EO),  $\mu_{1,3}$  (end to end),  $\mu_{1,1,3}$  and other mode. However, in this case no bridging by azide ligand was observed.

Pseudohalides are polyatomic analogues of halogens and possess property similar to halogens. Most popular pseudohalides are azide, thiocyanate, cyanate etc. and are known for their versatile ligational modes.  $N_3^-$  is also a pseudohalide. It is coordinated to metal centre in bent fashion with bond angle of N(11)N(10)Fe is  $157.7^\circ$ . The bond angle of  $N_3^-$  is  $178.15(2)^\circ$  which deviates from  $180^\circ$  that found in other azide complexes. The complex is air sensitive and soluble in common organic solvents.

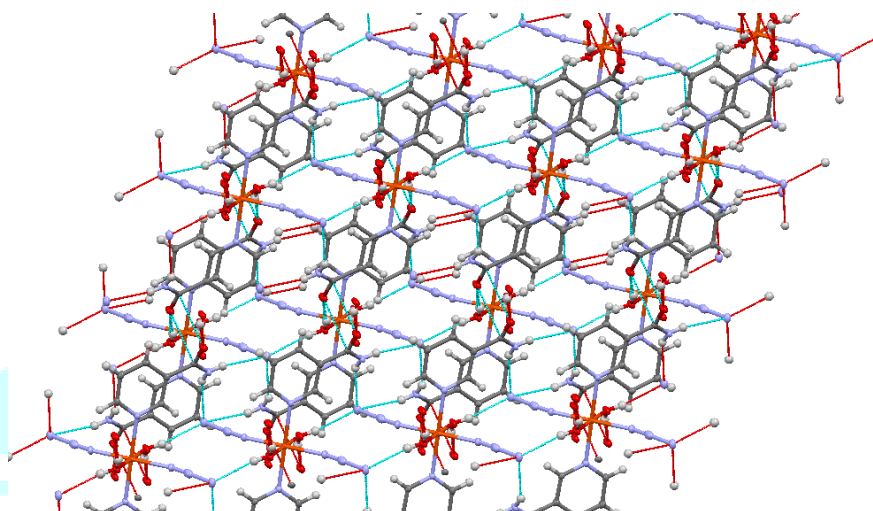
Table 2: Crystal Data for complex

(CCDC-1412379)	
Empirical formula	C <sub>12</sub> H <sub>16</sub> Fe N <sub>8</sub> O <sub>4</sub>
Formula weight	459.08
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 7.5182(2) Å
	b = 8.1615(3) Å
	c = 9.0259(3) Å
Alpha	73.036(3)
Beta	69.504(3)°
Gamma	66.431(3)°
Volume	468.004 Å <sup>3</sup>
Z	1
Density (calculated)	1.643 mg/m <sup>3</sup>
Absorption coefficient	1.128 mm <sup>-1</sup>
F(000)	236
Theta range for data collection	3.0 to 25.24°
Index ranges	-7<=h<=9, -9<=k<=9, -10<=l<=10
Reflections collected	1644
Independent reflections	1689 [R(int) = 0.0317]
Completeness to theta =	25.24° 99.1 %
Absorption correction	empirical
Max. and min. transmission	0.6806 and 0.7090
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1689 / 0 / 136
Goodness-of-fit on F <sup>2</sup>	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0297, wR2 = 0.0801
R indices (all data)	R1 = 0.0292, wR2 = 0.0798
Largest diff. peak and hole	0.366 and -0.482 e Å <sup>-3</sup>



**Figure 3: 1D chain along the b-axis (showing hydrogen bonding between N12 atom and H1W atom) for  $[\text{Fe}(\text{N}_3)_2(\text{Nicotinamide})_2(\text{H}_2\text{O})_2]$  complex**

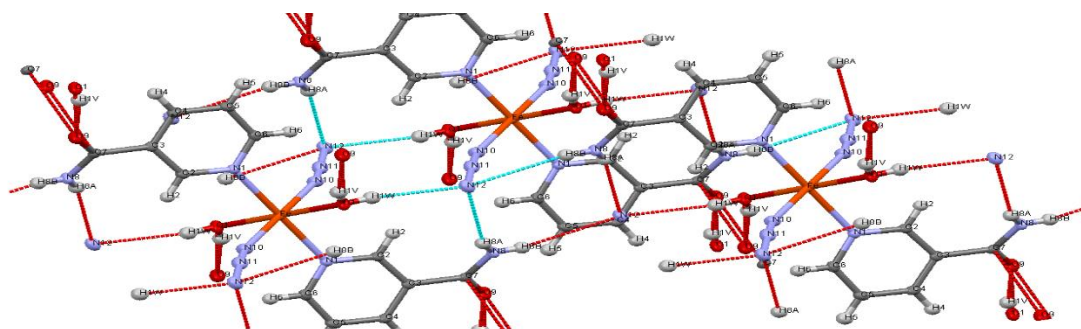
The nitrogen atom of  $\text{N}_3^-$  ligand participate in hydrogen bonding with hydrogen atom of water molecules and form N (11)-N12- -H1W interlayer (bond length N12- -H1W=2.417Å). This hydrogen bonding gives 1D (Figure 4.14) chain to the complex. The distance between two metal atoms is Fe-Fe = 7.518Å.



**Figure 4: Perspective view of 2D chain along the b-axis for complex**

Further the 2D (Figure 4) structure is formed by hydrogen bonding between oxygen atom O(9) of carbonyl group of nicotinamide molecule and hydrogen atom H1W of water on adjacent molecule, forming O(9)- -H1W-O1 interlayer [O(9)---H1W=1.97(3)Å]. Nitrogen atom from  $\text{N}_3^-$  anion ligand exhibit trifurcated intermolecular hydrogen bonding with hydrogen atom of water molecules (H1W), hydrogen atom (H8A) of amide group of nicotinamide molecule and hydrogen atom (H8B) of amide group from another nicotinamide molecule. While the bond distances between H1W- -N12-N11, O9- -H8B-N8 and N12- -H8B-N8 are 2.44(2) Å, 2.69(2) Å and 2.746(2)Å respectively. These intermolecular hydrogen bondings give extra stability to crystal structure.

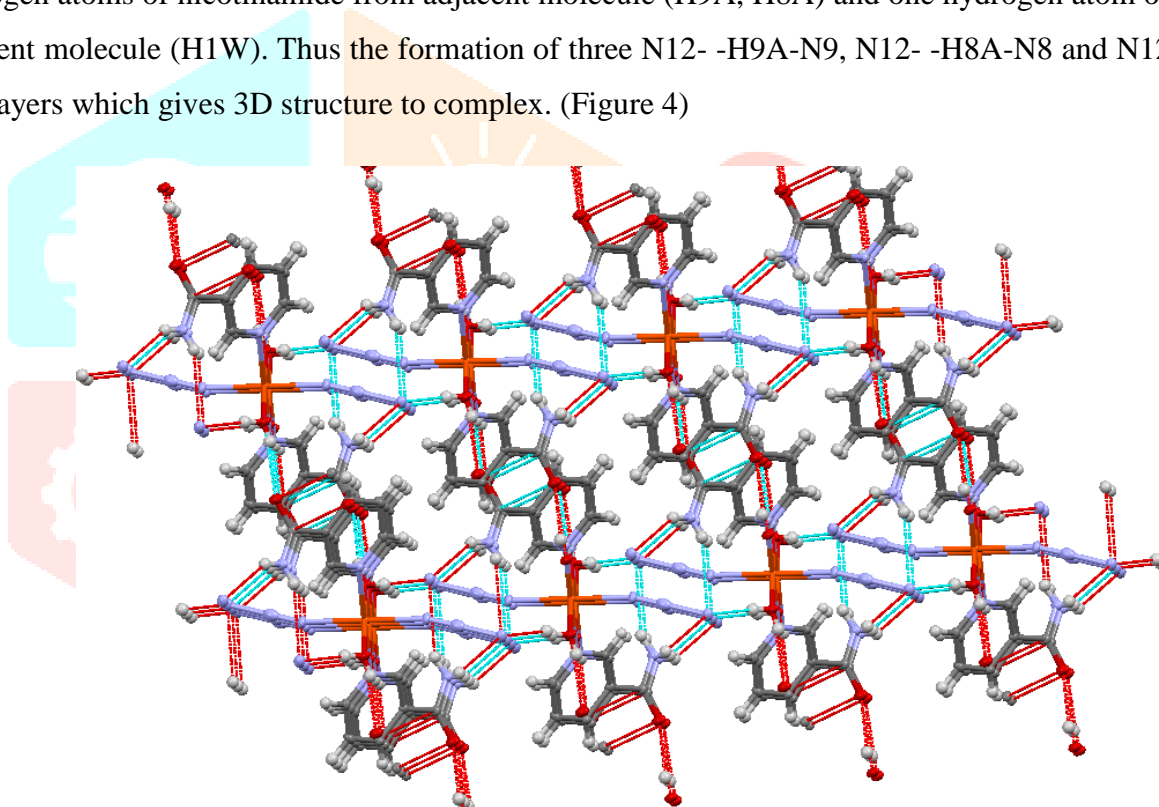
The nicotinamides molecules are trans to each other with angle N(10)-Fe-N(10) is  $180^\circ$ . The nicotinamide ligand generally acts as a bidentate chelating ligand, coordinating to the metal ion through the carbonyl O and pyridine N atoms, but in this structure it again acts as a unidentate ligand in which the pyridine N is coordinated to the Fe ion while the carbonyl O is involved in hydrogen bonding with another water molecule and hydrogen atom of amide group make hydrogen bond with nitrogen atom of azide. Water was used as solvent but it involved in coordination with metal ions and act as ligand.



**Figure 5: showing trifurcated hydrogen bonding through nitrogen atom along the a axis for complex**

The short contacts formed between Oxygen atom O9 from nicotinamide molecule and carbon atom C7 of benzene ring and further stabilise the crystal structure. The oxygen atom from amide group also involves in stabilising 3D structure; through short contacts C(7)-O(1)---C(7), C(7)-O(9A)-H(9)WA interlayer interaction.

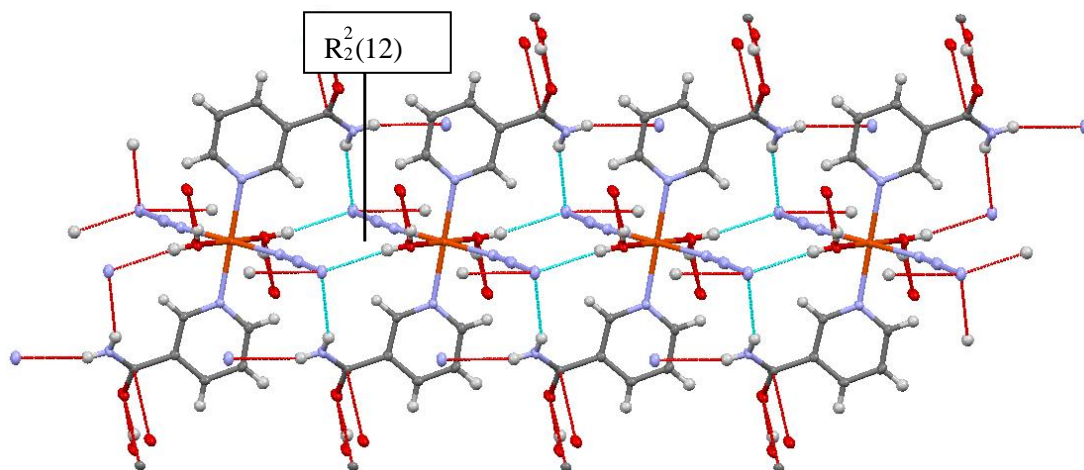
The most appealing point of this structure is nitrogen atom involves in trifurcated hydrogen bonding with two hydrogen atoms of nicotinamide from adjacent molecule (H9A, H8A) and one hydrogen atom of water from adjacent molecule (H1W). Thus the formation of three N12- -H9A-N9, N12- -H8A-N8 and N12- -H1W-O1 interlayers which gives 3D structure to complex. (Figure 4)



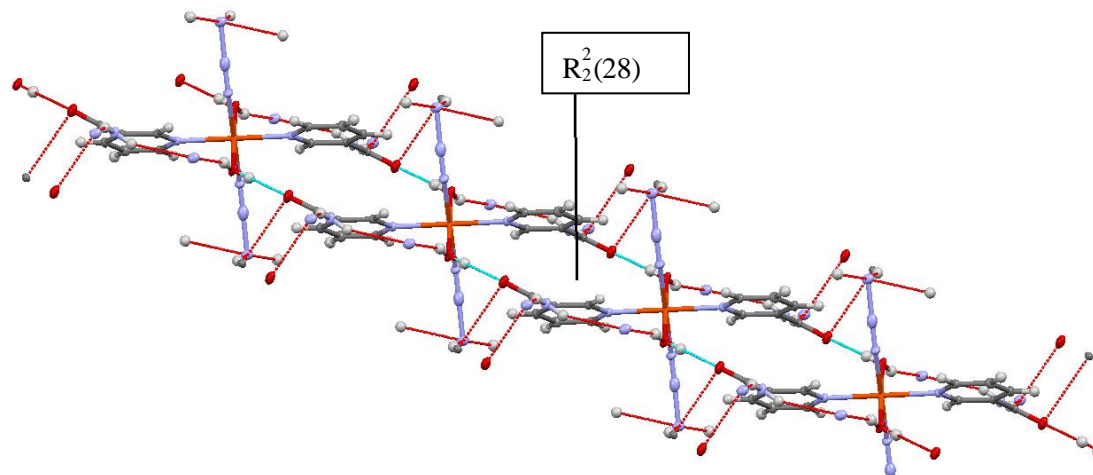
**Figure 6: Perspective view of 3D structure along the a axis for complex**

(a)



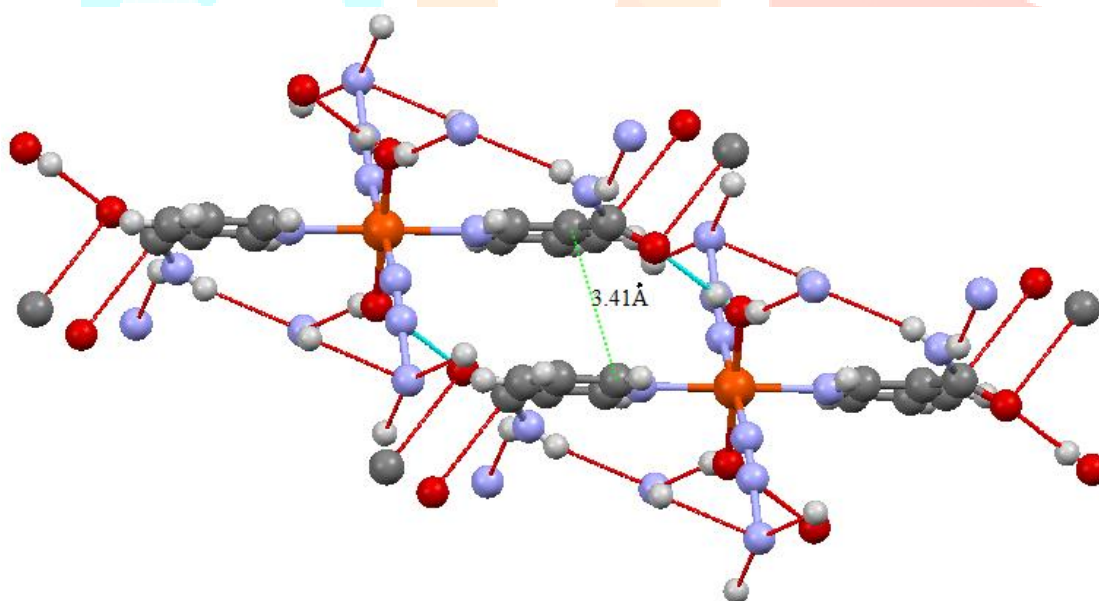


(b)



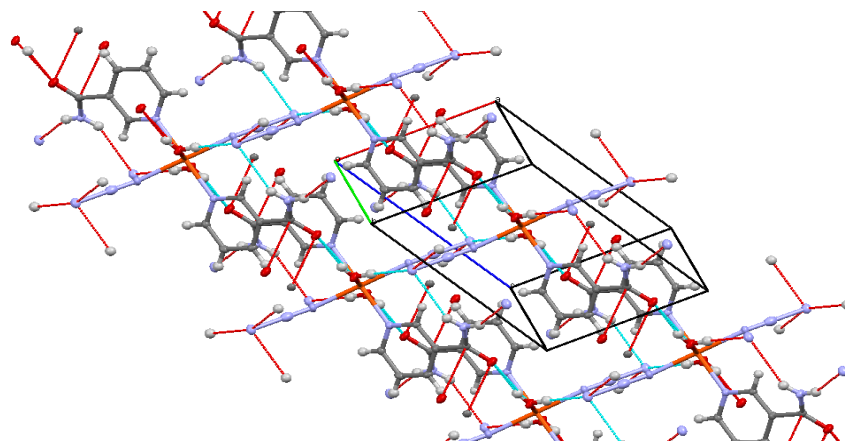
**Figure 7: Intermolecular hydrogen bonding &  $R_2^2(12)$  and  $R_2^2(28)$  motifs (View of the 1D single polymeric chain along the b axis) (a) nicotinamide positioned axial.(b) nicotinamide positioned equatorial).light blue dotted line shows intermolecular hydrogen bonding for complex.**

As can be seen in (Figure 7) that the intermolecular hydrogen bonding gives the molecular units  $R_2^2(12)$  and  $R_2^2(28)$  appears to have reliable utility for construction of high dimensions of molecular assembly.



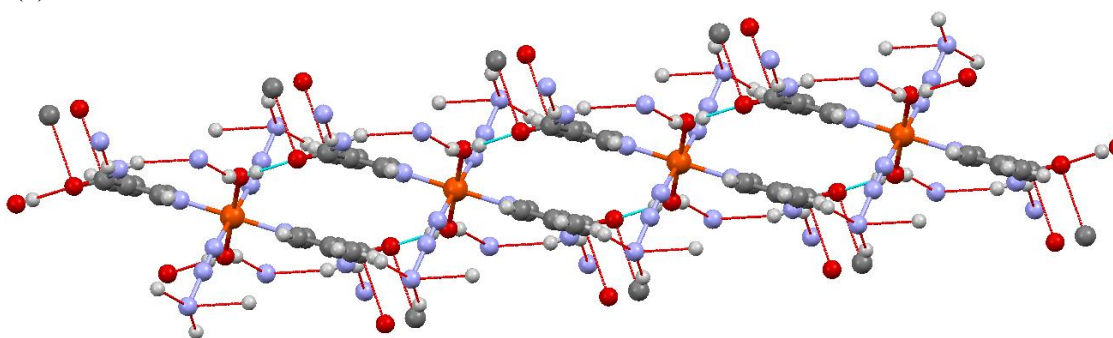
**Figure 8: Stacking of two pyridine rings of the neighbouring ligands through  $\pi$ - $\pi$  interactions running along the c axis for complex**

Further the structure stabilized through pi-pi interaction between pyridine rings on two different molecules. The shortest distance between two parallel benzene rings from the parallel nicotinamide ligands of the ladder structure is 3.41 Å, as shown in (Figure 9). This is in good agreement with the literature data, indicating a significant pi-pi interaction [12]. The space fill diagram of hydrogen bonded complex shows small rectangular cavity.

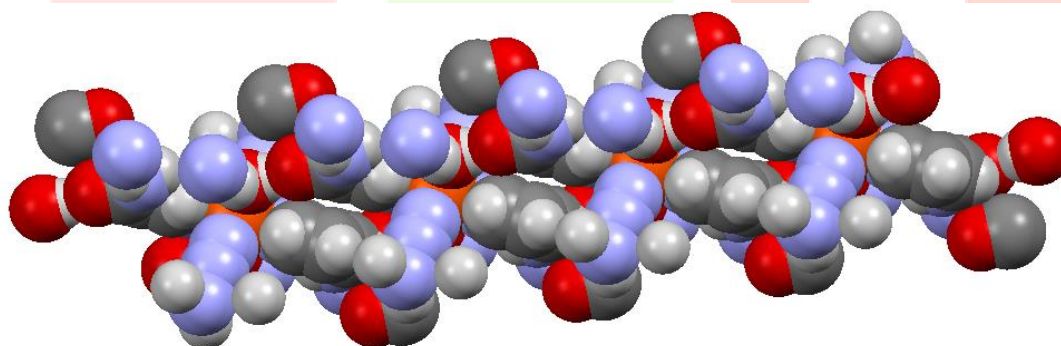


**Figure 9: Unit Cell packing diagram of the along the b axis (2). Hydrogen bonds are shown as dashed lines.**

(a)



(b)



**Figure 10 (a) Fragment of the complex  $[\text{Fe}(\text{Azide})_2(\text{Nicotinamide})_2(\text{H}_2\text{O})_2]$  (b) Space fill diagram of 1D chain showing narrow rectangular cavity**

As can be seen from the packing diagram (Figure10), the Fe atoms are located at the centre of the axis of the unit cell and the molecules of complex are connected through intermolecular hydrogen bonds, O—H---O, O—H---N12 and N—H---N12 hydrogen bonds, forming a supramolecular structure. Dipole–dipole and van der Waals interactions are also effective in the molecular packing. The space fill diagram of hydrogen bonded structure shows small rectangular cavities.

**Table 3: Bond Angles (Å) for complex**

Atom1	Atom2	Atom3	Angle
O1	Fe	N1	90.64(7)
O1	Fe	N10	91.20(8)
O1	Fe	O1	180.00(7)
O1	Fe	N1	89.36(7)

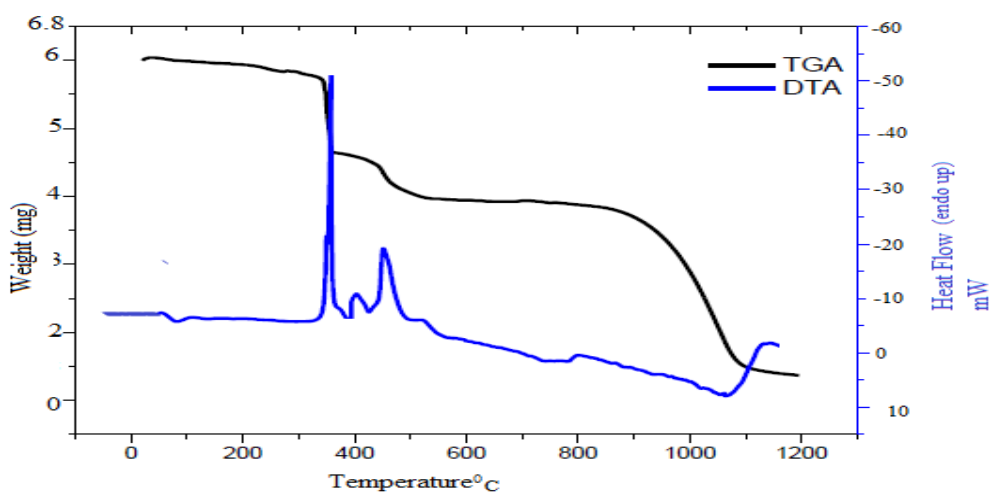
O1	Fe	N10	88.80(8)
N1	Fe	N10	88.07(8)
N1	Fe	O1	89.36(7)
N1	Fe	N1	180.00(7)
N1	Fe	N10	91.93(8)
N10	Fe	O1	88.80(8)
N10	Fe	N1	91.93(8)
N10	Fe	N10	180.00(8)
O1	Fe	N1	90.64(7)
O1	Fe	N10	91.20(8)
N1	Fe	N10	88.07(8)
Fe	O1	H1W	119(2)
Fe	N1	C2	120.1(2)
Fe	N1	C6	122.3(2)
C2	N1	C6	117.6(2)
N1	C2	H2	118.3(2)
N1	C2	C3	123.2(2)
H2	C2	C3	118.4(2)
C2	C3	C4	118.3(2)
C2	C3	C7	121.4(2)
C4	C3	C7	120.3(2)
C3	C4	H4	120.6(2)
C3	C4	C5	118.8(2)
H4	C4	C5	120.6(2)
C4	C5	H5	120.5(2)
C4	C5	C6	118.9(2)
H5	C5	C6	120.6(2)
N1	C6	C5	123.1(2)
N1	C6	H6	118.5(2)
C5	C6	H6	118.4(2)
C3	C7	N8	116.5(2)
C3	C7	O9	121.0(2)
N8	C7	O9	122.4(2)
C7	N8	H8A	124(2)
C7	N8	H8B	119(2)
H8A	N8	H8B	117(3)
Fe	N10	N11	157.7(2)
N12	N11	N10	178.1(2)
Fe	O1	H1W	119(2)
Fe	N1	C2	120.1(2)
Fe	N1	C6	122.3(2)
C2	N1	C6	117.6(2)
N1	C2	H2	118.3(2)
N1	C2	C3	123.2(2)
H2	C2	C3	118.4(2)

**Table 4: Bond length (Å) for complex**

Atom1	Atom2	Length
Fe	O1	2.101(2)
Fe	N1	2.220(2)
Fe	N10	2.128(2)
Fe	O1	2.101(2)
Fe	N1	2.220(2)
Fe	N10	2.128(2)
N12	N11	1.652(2)
O1	H1W	0.80(4)
N1	C2	1.340(4)
N1	C6	1.342(3)
C2	H2	0.930(2)
C2	C3	1.389(4)
C3	C4	1.391(3)

C3	C7	1.502(4)
C4	H4	0.930(3)
C4	C5	1.382(4)
C5	H5	0.930(2)
C5	C6	1.382(4)
C6	H6	0.929(3)
C7	N8	1.324(3)
C7	O9	1.233(4)
N8	H8A	0.79(4)
N8	H8B	0.77(4)
N10	N11	1.158(3)
N12	N11	1.652(2)
O1	H1W	0.80(4)
N1	C2	1.340(4)
N1	C6	1.342(3)
C2	H2	0.930(2)
C2	C3	1.389(4)
C3	C4	1.391(3)
C3	C7	1.502(4)
C4	H4	0.930(3)
C4	C5	1.382(4)
C5	H5	0.930(2)
C5	C6	1.382(4)
C6	H6	0.929(3)
C7	N8	1.324(3)
C7	O9	1.233(4)
N8	H8A	0.79(4)
N8	H8B	0.77(4)
N10	N11	1.158(3)
Fe	O1	2.101(2)
Fe	N1	2.220(2)
Fe	N10	2.128(2)
Fe	O1	2.101(2)
Fe	N1	2.220(2)
Fe	N10	2.128(2)
N12	N11	1.652(2)
O1	H1W	0.71(4)

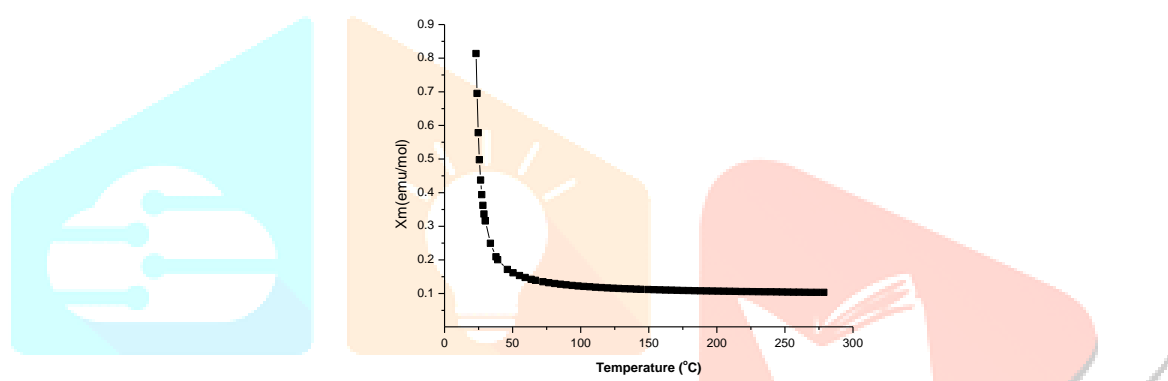
#### 4. Thermal Analysis for $[\text{Fe}(\text{Azido})_2(\text{Nicotinamide})_2(\text{H}_2\text{O})_2]$



**Figure 11: Thermo-gram of  $[\text{Fe}(\text{Azido})_2(\text{Nicotinamide})_2(\text{H}_2\text{O})_2]$**

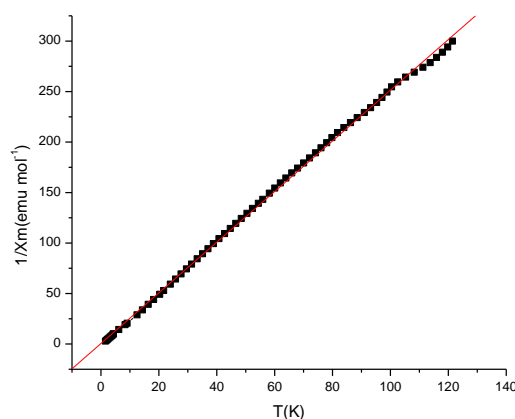
TGA curve show small weight loss (8.2%) occurred immediately upon heating (between 180<sup>0</sup>C -240<sup>0</sup>C) and was completed before the temperature reached 260<sup>0</sup>C and this weight loss is indicative of the loss of two coordinated water molecules which is supported by endo-thermic peak. In addition, a continuous, gradual weight loss is observed, which ceased at about 1050<sup>0</sup>C and is followed by framework decomposition as indicated by an abrupt weight loss which is due to liberation of N<sub>3</sub><sup>-</sup> ligand followed by removal of two nicotinamide molecules in the wide range of temperature (380<sup>0</sup>C-1050<sup>0</sup>C).The second and third weight loss are 8.2 (8.3%) and 53.4 (53.6%) respectively. End product was iron oxide as confirmed by powder x-ray of the residue (Figure 11).

### 5. Magnetism for [Fe(Azide)<sub>2</sub>(Nicotinamide)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]



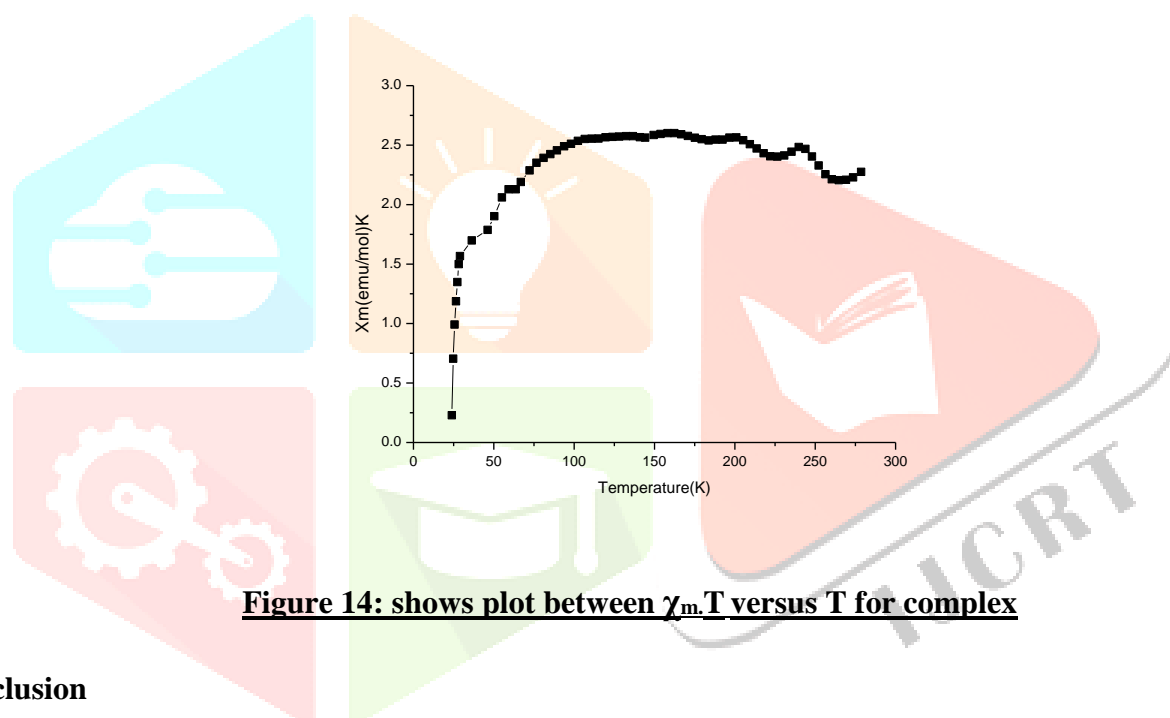
**Figure 12: shows plot between  $\chi_m$  versus T for complex**

To investigate the magnetic properties of compound their temperature dependence of the susceptibility was measured applying a magnetic field of  $H = 10000\text{Oe}$  in the temperature range of 300-2K. Magnetic data of compound fitted according to the Curie Weiss law yields Weiss constant  $\Theta = -23.8$  and curie constant = 1.91 emu/mol K.



**Figure 13: shows plot between  $1/\chi_m$  versus T for complex**

The plot between  $\chi_m$  vs T,  $1/\chi_m$  vs T and  $\chi_m T$  vs T shown in Figure 4.25, 4.26 and 4.27 respectively. The values of  $\chi_m T$  are dependent on the temperature. At 300K, the value of  $\chi_m T$  is 2.47 emu/mol-K which is slightly less than the value reported in literature for two magnetically isolated Iron (II) ions. The value of  $\chi_m T$  decrease from 2.47 to 1.82 at 2K which indicates antiferromagnetic intermolecular interactions (Figure 4.27) through intermolecular forces, such as  $\pi$ - $\pi$  stacking and hydrogen bonds. The weak  $\pi$ - $\pi$  stacking interaction seems to be the minor and hydrogen bonding interaction being the major contributor of magnetic interactions as found in other system [14]. It can be seen from (Figure-4.25) that the  $\chi_m$  value increases gradually upon cooling and the  $\mu_{\text{eff}}$  value at 300 K is 4.48, which is less than that expected for the spin only value for unpaired spins in high spin Fe(II) complexes ( $\mu_{\text{eff}}=4.80$ ). These values also indicate the presence of magnetic interaction.



**Figure 14: shows plot between  $\chi_m T$  versus T for complex**

## Conclusion

This paper is mainly based on azido complexes with nicotinamide as coligand.  $\text{Fe}^{2+}$   $[\text{Fe}(\text{Azido})_2(\text{Nicotinamide})_2(\text{H}_2\text{O})_2]$  (2). The compounds are characterized with X-ray Single Crystal Analysis, IR spectroscopy thermal analysis and variable temperature magnetic susceptibility. In compound  $[\text{Fe}(\text{Azido})_2(\text{Nicotinamide})_2(\text{H}_2\text{O})_2]$ ,  $\text{Fe}^{2+}$  ion adopts octahedral geometry. The octahedral geometry is distorted with small axial elongation (bond length  $\text{Fe}-\text{N}(1)=2.21\text{\AA}$ ). The nitrogen atom of azido ligand involves in hydrogen bonding with hydrogen atom of water moiety and produced 1D chain. Most interesting point in this crystal structure is nitrogen atom shows trifurcated hydrogen bonding. Nicotinamide ligand acts as unidentate ligand and coordinated through nitrogen atom of pyridine ring. A variable temperature magnetic susceptibility measurement of compound (2) shows antiferromagnetic character with negative value of  $\Theta$ .

## References

- [1] Viau, G.; Lombardi, M.G.; Munno, G.D.; Julve, M.; Floret, F.; Faus, J.; Caneschi, A.; Clemente-Juan, M. J. J. Chem. Soc. Chem. Comm. (1997)1195.
- [2] Cortes, R.; Lezana, L.; Pizarro, J. L.; Arriortua, M. I.; Solans, X.; Rojo, T. Angew. Chem. Int. Ed. Engl. 33 (1994) 2488.
- [3] Kose, D.A.; Icbudak, H.; Hacettepe, N.H. J. Biol. & Chem. 35 (2007)123.
- [4] Yu, J.B.; Zhou, L. H.; Zhang, J.; Zheng, Y.X.; Li, H.R.; Deng, R.P.; Peng, Z.P.; Li, Z.F. Inorg. Chem. 44 (2005) 1611.
- [5] Lin, W.; Wang, Z.; Ma, L.; J Am Chem Soc, 121 (1999) 11249.
- [6] Zang, S. Q.; Su, Y.; Li, Y. Z.; Zhu, H. Z.; Meng, Q. J. Inorg. Chem45 (2006) 2972.
- [7] G.M. Sheldrick, SHLEX 93, University of Gottigen, Germany, 1993
- [8] Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112–122
- [9] Ribas, J.; Monfort, M.; Diaz, C.; Bastos, C.; Solans, X. Inorg. Chem. 33 (1994) 484.
- [10] Ding, B.; Yi, L.; Wang, Y.; Cheng, P.; Liao, D.-Z.; Yan, S.-P.; Jiang, Z.-H.; Song, H.-B.; Wang, H. G. Dalton Trans. (2002) 665.
- [11] Guang Yang, Huai-Gang Zhu, Bing-Hua Liang and Xiao-Ming Chen J. Chem. Soc., Dalton Trans. (2001) 580–585