

## Fe (III) complexes with hetero cyclic and cycloketones synthesis by mannich reaction it's Growth, crystal structure, spectral, thermal, antibacterial and antifungal activity studies.

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**Abstract:** A novel single crystal of piperidin-4-ones, pyrimidines, pyrans and cyclohexanones were successfully grown by slow evaporation solution growth technique at constant temperature (303 K) with dimension  $40 \times 5 \times 3 \text{ mm}^3$  in a period of 3 weeks. Powder X rays (XRD) and Fourier transform infrared transmission (FTIR) have confirmed the formation of the new crystal. IR spectra analyses were used to elucidate the functional group present in the compounds. UV-spectral studies indicates that the grown crystals was transparent in the entire visible region with a lower cutoff wavelength of 505 nm. Thermal properties of the crystal have been investigated using thermo gravimetric analysis (TC) and differential thermal analysis (DTA). The mechanical strength of the crystal was estimated by vicker's hardness method. The bacterial activity against the pathogenic microorganisms, *E.coli* (gram positive) and *Staphylococcus aureus* (gram negative) and antifungal activity against *Aspergillus niger*, were carried out for all synthesized compounds.

**Keywords:** Piperidin-4-ones, pyrimidines, XRD, FT-IR, antifungal, antibacterial.

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### I. Introduction

A regular and orderly arrangement was always beautiful. Orderly arranged atoms, ions or molecules in crystalline solids provide the external beauty by their shining appearance and colours. Crystals are still more attractive. The art of growing crystals artificially had always been a fascinating job to human kind from time immemorial. Crystalline solids were widely used in our daily life. Today we are living in an electronic era. In the modern world, crystalline solids find tremendous applications in different fields. Crystals of good quality, suitable size and perfection are required in technological important in industries like electronic industries, computer technology, fiberoptic communications, semiconductors, solid state lasers and ferroelectric materials. Rapid advances in microelectronics, communication technologies and medical instrumentation, energy and space technologies are possible simply because of the remarkable progress in the fabrication of large and rather perfect crystals. High-efficiency light emitting diodes for energy saving illumination and photovoltaic devices for transforming solar and other radiation energy into electric power with high yield depend on significant advances in crystal growth.

Potassium dihydrogen phosphate (KDP), potassium titanyl phosphate (KTP), niobates of lithium and potassium ( $\text{LiNbO}_3$ ,  $\text{KNbO}_3$ ) and L-arginine phosphate (LAP) exhibiting non-linear properties. The main use of Ga As is in the field of microwave devices, high speed digital integrated circuits and as substrate for epitaxial layer growth to fabricate photonic and electronic devices. There is an increasing demand for semi-insulating Ga As in mobile communication and digital telephony. Indium phosphide (InP) is used as the base material for optoelectronic components in long distance fiber optic telecommunications. Oxide single crystals are used as the active component in laser systems, substrates for GaN, silicon epitaxy, optical components and substrates for magnetic bubble devices. The halogenides are the most widely used scintillation materials. The synthesis, structural determination and properties of many new materials would pave the way for various device applications in the modern world. The potential of 'crystal engineering' makes it possible to design new materials for applications in different fields. But in other case iron complexes of biologically important ligands are sometimes less effective than free ligands. Since iron (III) ion is very flexible in adopting various coordination geometries in its complexes. The majority of known iron complexes have a central atom with a tetra, penta, and hexa coordination environment, leading to distorted tetrahedral, square planar, square pyramidal or octahedral geometries. This paper describes the synthesis and results of structural, thermal, spectroscopic studies and biological activity of eight new iron complexes:  $[\text{Fe}(\text{DP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ,  $[\text{Fe}(\text{DMP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ,  $[\text{Fe}(\text{DEP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ,  $[\text{Fe}(\text{MDDP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  and  $[\text{Fe}(\text{MOTTP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ,  $[\text{Fe}(\text{MDTTP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ,  $[\text{Fe}(\text{DPTTP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  and  $[\text{Fe}(\text{DBCH})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  we focused our attention on the studies of the coordinative ability of heterocyclic N, O donor ligands such as (piperidin-4-ones, 2, 6-diphenyl-3-methyl piperidin-3-methyl piperidin-

4-one,2, 6-diphenyl-3-ethyl piperidin-4-one, N-methyl-2,6-diphenyl-3,5-Dimethyl piperidin-4-one, 2-thioxo-6-Methyl-tetrahydro pyrimidin-4(1H)-one, 3-methyl-2,6-diphenyl-tetra hydro thiopyran-4-one, 2, 2<sup>1</sup>-dimethyl-6-phenyl tetrahydro thiopyran-4-one, Dibenzlidencyclohexanone) and to investigate the influence of the obtained iron complexes on their antibacterial and antifungal activity.

## II. Experimental Work

### 2.1 Material and Physical measurements

All chemicals were of reagents grade, purchased from commercial sources and used without further purification (BDH or Merck) was used. Molar conductance of the complexes were measured at room temperature ( $30 \pm 2^\circ\text{C}$ ) in DMF solvent ( $\sim 10^{-3}$  M solution). Magnetic moment of the complexes were recorded using VSM instrument. IR spectra of the complexes were recorded in the region 400-4000  $\text{cm}^{-1}$  using a double beam Perkin Elmer FT-IR spectrometer employing KBr disc technique. The electronic spectra were recorded in DMSO solvent using Hitachi UV-Visible spectrophotometer in the range 200-1200nm. TGA and DTA studies were carried out with a shimadzu STA – 1500 instrument (heating rate  $20^\circ\text{C}$  / minute) in nitrogen atmosphere. Cyclic Voltammetry was carried out with an EG and G instrument model 270/250 research electrochemistry hardware and software using Tetrabutylammonium perchlorate as the supporting electrolyte. XRD measurements were carried out with a Jeol JDX 8030 X-ray diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda=1.54\text{\AA}$ ) instrument.

### 2.2 Preparation of ligands

#### 2.2.1 Preparation of piperidin-4-ones (1)

The compound (1) was prepared by adopting the following procedure<sup>1-2</sup>. A mixture of acetone (14.5g, 0.25mol), benzaldehyde (53g, 0.5 mol), ethanol (20ml) and anhydrous ammonium acetate (19.3g, 0.25 mol) were heated on a waterbath with constant shaking till the content became pale orange in colour. The flask was then cooled; ether (125ml) was added to the cold mixture and filtered. Addition of concentrated hydrochloric acid (13ml) to the clear filtrate afforded the hydrochloride of piperidone (m.pt  $214-216^\circ\text{C}$ ) (lit  $216-217^\circ\text{C}$ ), which was collected after washing several times with ethanol – ether (1:5). The base was liberated by suspending the hydrochloride in acetone and adding ammonia (1:1) till the hydrochloride dissolved and the free base (1) was generated by diluting with water, which was crystallized from ethanol. Yield: 90%, M.pt:  $104-105^\circ\text{C}$  (Lit  $104 - 105^\circ\text{C}$ ). (Anal. calc. %) for ligand: C-81.2, H-6.77, N-4.9 Molecular weight 249.2. Found C-80.9, H-6.77, N-5.88, Molecular weight 251. IR ( $\text{cm}^{-1}$ ) : 3305(s), 3062(s), 2975(s), 1724(s), 1637(s), 1458(sd), 1078(b), 1002(s), 933(b), 821(b), 754(w), 698(b), 663(b), 611(s), 522(l).

#### 2.2.2 Preparation of 2, 6– diphenyl-3-methyl piperidin-3-methyl piperidin-4-one (2)

To a solution of dry ammonium acetate (9.2g, 0.12mol) in glacial acetic acid (12.5g, 0.21 mol), a mixture of benzaldehyde (29g, 0.25mol) and n-butanone (9g, 0.125 mol) was added, then it was heated to boiling and allowed to stand at room temperature to overnight. Concentrated hydrochloric acid (13ml) was added. The precipitated hydrochloride was collected and washed with ethanol-ether mixture (1:5). Crystallization of the pure hydrochloride, 16g (40%) was done in ethanol-ether. M.Pt.  $223-225^\circ\text{C}$  (Lit  $224-226^\circ\text{C}$ ). A suspension of the hydrochloride in acetone was treated with ammonia (1:1) and the free base was obtained by dilution with large quantity of water. The pure form of piperidin-4-one<sup>3-7</sup> was crystallized from ethanol. M.pt  $96^\circ\text{C}$  (Lit  $96-97^\circ\text{C}$ ). (Anal. calc. %) for ligand: C-81.48, H-7.12, N-5.27 Molecular weight 263. Found C-81.51, H-7.17, N-5.28, Molecular weight 265. IR ( $\text{cm}^{-1}$ ) : 3294(s), 3032(s), 2960(s), 1701(s), 1607(s), 1497(sd), 1110(b), 1090(s), 930(b), 822(b), 750(w), 694(b), 663(b), 600(s), 524(l).

#### 2.2.3 Preparation of 2,6-diphenyl-3-ethyl piperidin-4-one (3)

Condensation of 2-pentanone (10.8g, 0.125 mol) with benzaldehyde (29g, 0.25mol) in the presence of dry ammonium acetate (31g, 0.4mol) in ethanol (80ml) was carried out by heating the mixture to boiling and cooled to overnight. The product was separated as a crystalline solid, washed and recrystallised. The free base was converted into hydrochloride by the addition of concentrated hydrochloric acid (50ml) and washed with ethanol-ether mixture (1:5). The crystallized hydrochloride was then generated into free base by addition of (1:1) aqueous ammonia in an alcoholic solution and by dilution with water. The product was allowed to recrystallise from petroleum ether<sup>8-20</sup>. Yield: 88%, M.Pt  $94-95^\circ\text{C}$  (Lit  $92-93^\circ\text{C}$ ). (Anal. calc. %) for ligand: C-80.7, H-7.47, N-4.98 Molecular weight 269.5. Found C-81.7, H-7.53, N-5.02, Molecular weight 279. IR ( $\text{cm}^{-1}$ ) : 3199(s), 3028(s), 2974(s), 1706(s), 1629(s), 1460(sd), 1209(b), 1085(s), 954(b), 825(b), 757(w), 700(b), 638(b), 511(s), 2100(r).

#### **2.2.4 Preparation of N-methyl-2,6-diphenyl-3,5-Dimethyl piperidin-4-one (4)**

To a solution of ammonium acetate (11.5g, 0.15mol) in ethanol (80ml), a mixture of benzaldehyde (20.2g, 0.2mol) and diethyl ketone (8.6g, 0.1mol) were added. The mixture was heated to boiling and allowed to stand at room temperature. The product 3,5-dimethyl-2,6-diphenyl piperidin-4-one was filtered M.Pt: 131-133°C (lit: 131-133°C). The corresponding 3,5-dimethyl-2,6-diphenyl piperidin-4-one (0.04mol) was dissolved in acetone (1.38mol). To this solution, anhydrous potassium carbonate (0.02mol) and methyl iodide (0.08mol) were added. The mixture was refluxed over a water bath for about 3hrs and most of the acetone was removed by distillation. 2,6-diphenyl-3,5,N-trimethyl piperidin-4-one was obtained by dilution with water and followed by treatment with aqueous ammonia (1:1). The product formed was filtered, washed with water, dried and crystallized from ethanol M.pt: 131-133°C.(Anal. calc. %) for ligand: C-80.91, H-7.77, N-4.79 Molecular weight 291. Found C-81.91, H-4.85, N-4.78, Molecular weight 293. IR (cm<sup>-1</sup>) : 3024(s), 2970(s), 1713(s), 1600(s), 1452(s), 1130(s), 1108(sd), 1070(b), 1027(s), 941(b), 836(b), 748(w), 698(b), 642(b), 619(s), 516(l).

#### **2.2.5 General Preparation of 2-thioxo-6-Methyl-tetrahydro pyrimidin-4(1H)-one (5).**

A solution of phenyl ethyl ammine (1.21g), t-Butyl acetoacetate (1.58g) was heated in the presence of O-xylene (5ml) for 1 hr. Then the reaction mixture was poured over crushed ice and separated. The product 3-oxo-N(1)-phenyl butamide was filtered and recrystallized from ethanol. The product (1.025g), Benzaldehyde (0.1g), thiourea (0.38g) dissolved in acetonitrile were refluxed in the presence of CeCl<sub>3</sub>.7H<sub>2</sub>O (0.931g) as catalyzed for 6 hrs. The reaction mixture was poured over crushed ice and separated. The product was filtered and recrystallized from ethanol. Yield 50% melting 144°-147°C. (Anal. calc. %) for ligand: C-41.6, H-5.50, N-19.39 Molecular weight 143. Found C-41.6, H-5.56, N-19.44, Molecular weight 144. IR (cm<sup>-1</sup>) : 3114(s), 3085(s), 2931(s), 1701(s), 1635(s), 1483(sd), 1419(b), 1240(s), 1166(b), 1039(b), 748(w), 696(b), 669(b), 655(s), 511(l).

#### **2.2.6 Preparation of 3-methyl-2,6-diphenyl-tetra hydro thiopyran-4-one (6).**

Gaseous H<sub>2</sub>S was passed into a boiling mixture of 1,4-pentadiene-3-one (40g, 0.29mol) and CH<sub>3</sub>COONa. 3H<sub>2</sub>O (40g, 0.29 mol) in 400ml of ethanol for 15 hrs. The reaction mixture was cooled to room temperature and kept at 0°C for 2hrs. The residue was filtered and the alcoholic solution reformed for three days. The white solid that formed was filtered, recrystallized from petroleum ether (60-80°C). Yield: 11g (25%), M.Pt (123-125°C).(Anal. calc. %) for ligand: C-76.57, H-6.37, S-10.35 Molecular weight 279. Found C-76.69, H-6.38, S-11.35, Molecular weight 282. IR (cm<sup>-1</sup>) : 3158(s), 3052(s), 2925(s), 1701(s), 1629(s), 1492(sd), 1448(b), 1226(s), 1101(s), 1078(s), 1000(s), 933(b), 811(b), 740(w), 586(b), 516(b).

#### **2.2.7 Preparation of 2, 2<sup>1</sup>-dimethyl-6-phenyl tetrahydro thiopyran-4-one (7).**

Into a boiling solution of sodium acetate trihydrate (40g, 0.29mol), 1-phenyl-5-methyl-1,4-hexadien-3-one (1,4- pentadien-3-one-50g, 0.268 mol) and ethanol (300ml) was added. Then H<sub>2</sub>S gas was passed for 8 hrs. The reaction mixture was then poured into water (100ml), extracted with ether (3x200 ml) and dried (Na<sub>2</sub>SO<sub>4</sub>). The solution was filtered and concentrated and the residue was distilled to yield 48.2g (81.5%) of (7)<sup>21-30</sup>. The light yellow viscous oil solidified upon standing was recrystallized from petroleum ether (60-80°C). Yield:81.5% M.Pt: 45-46°C (Lit 42°C).(Anal. calc. %) for ligand: C-70.85, H-7.22, S-14.0 Molecular weight 217. Found C-70.91, H-7.27, S-14.55, Molecular weight 220. IR (cm<sup>-1</sup>) : 3025(s), 2960(s), 1708(s), 1600(s), 1494(sd), 1448(b), 1220(s), 1141(s), 1070(s), 1029(s), 931(b), 808(b), 761(w), 597(b), 533(b).

#### **2.2.8 Preparation of Dibenzlidencyclohexanone (8)**

To the solution of cyclohexane, benzaldehyde (53g, 0.5m) was added. The reaction was catalysed by potassium fluoride supported on alumina. The solution mixture was stirred for 2hrs. the solid formed was collected by filtration and crystallized from ethanol. Yield; 55%, M.Pt: 113-115°C (Lit 114°C).(Anal. calc. %) for ligand: C-88.71, H-6.62, Molecular weight 261. Found C-88.89, H-6.67, Molecular weight 270. IR (cm<sup>-1</sup>) : 3058(s), 2931(s), 1660(s), 1606(s), 1433(sd), 1203(b), 1072(s), 1029(s), 939(b), 838(b), 771(w), 615(b), 518(l).

#### **2.2.9 Preparation of Fe(III) Complexes with compounds (1-8).**

The corresponding compounds (1-8) (0.004 mol) and ferric Nitrate (0.002 mol) was dissolved in ethanol separately, mixed the solutions and refluxed on a water bath for two hours at 35-40°C. A colour change was observed indicating the complex formation; the complexes were separated out by evaporating the solvent, filtered, washed with ethanol, then with ether and dried in vacuum<sup>31</sup>.

### III. Results and Discussion

**Iron (III) complexes with ligands (1-8):** All the Fe (III) complexes of ligands (1-8) were non-hygroscopic in nature and brown in colour. They are insoluble in benzene, carbontetrachloride, chloroform etc., but moderately soluble in methanol, DMF and DMSO. The analytical data and composition of the complexes are presented in Table 1. The molar mass of the complexes were determined by Rast method and are presented in Table 1. The values obtained were in good agreement with those calculated values (given in bracket) from the suggested formula of the complexes.

**Table 1 Analytical Data of Fe (III) complexes with various Ligands (1-8)**

Complex	Carbon % Found (Cal)	Hydrogen % Found (Cal)	Nitrogen % Found (Cal)	Sulphur % Found (Cal)	Metal Ion % Found (Cal)	Nitrate Ion % Found (Cal)	M.Wt Found (Cal)	M.Pt °C
[Fe (DP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	36.12 (35.00)	4.67 (4.63)	9.97 (9.61)	-	10.09 (9.58)	14.80 (15.17)	591.91 (582.84)	200-203
[Fe (DMP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	36.94 (36.19)	5.08 (4.86)	10.11 (9.38)	-	10.01 (9.36)	14.42 (14.73)	597.81 (596.84)	190-192
[Fe (DEP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	37.91 (37.33)	5.86 (5.07)	9.55 (9.17)	-	9.47 (9.14)	13.92 (14.31)	611.84 (610.84)	d 230
[Fe (MDDP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	38.69 (38.41)	5.35 (5.28)	8.99 (8.96)	-	9.19 (8.94)	13.86 (14.31)	624.89 (624.84)	d 230
[Fe (MOTTP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	12.77 (12.61)	3.84 (3.78)	14.91 (14.71)	6.90 (6.72)	11.88 (11.74)	14.20 (14.71)	476.01 (475.84)	304
[Fe (MDTTP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	35.27 (35.19)	4.99 (4.56)	6.93 (6.84)	5.50 (5.2)	9.51 (9.10)	14.12 (14.73)	614.06 (613.84)	251-253
[Fe (DPTTP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	28.31 (28.27)	4.87 (4.71)	7.92 (7.61)	5.99 (5.80)	10.45 (10.12)	14.23 (14.31)	552.07 (551.84)	146-147
[Fe (DBCH) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	39.82 (39.61)	4.75 (4.62)	7.15 (6.93)	-	9.44 (9.22)	13.22 (13.92)	606.01 (605.84)	215-216

#### 3.1 Electrical Conductance

Molar conductance values of different Iron (III) complexes (10<sup>-3</sup>M) in DMF were given in Table 2 and these were in the range of 143-197 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>. The values obtained were compared with standard values.

**Table 2 Molar Conductance of Fe (III) Complexes with Ligands (1-8) (ohm<sup>-1</sup> cm<sup>2</sup>mol<sup>-1</sup>)**

Complex	Molar conductance (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
[Fe (DP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	167
[Fe (DMP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	159
[Fe (DEP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	160
[Fe (MDDP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	192
[Fe (MOTTP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	143
[Fe (MDTTP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	197
[Fe (DPTTP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	181
[Fe (DBCH) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	159

#### 3.2 Magnetic Behaviour

Magnetic moment values of different Iron (III) complexes with various alkyl substituted 2,6-diphenyl piperidin-4-ones, pyrans, pyrimidines and cyclohexanones as ligands were given in the Table 3. These values were very useful in establishing the geometry of the complexes. In high spin complexes, the magnetic moments were always very close to the spin only value of 5.9BM because the ground state has no orbital angular momentum and there was no effective mechanism for introducing any substituents by coupling with excited states<sup>35-50</sup>. The low spin complexes, which usually have considerable orbital contributions to their moment at above room temperature, exhibit the values of ~2.3BM. The magnetic moment values of Fe (III) complexes of the ligands were found to be in the range 5.94 to 6.04BM. These values were in good agreement with values reported for high spin octahedral Fe(III) complexes and they are diamagnetic in nature.

The magnetic moment values of Fe(III) complexes of the ligands were found to be in the range 5.6 – 5.9 BM which corresponds to five unpaired electrons as expected for Fe (III) complexes having no metal –

metal interaction. These values were in good agreement with values reported for high spin octahedral complexes<sup>51-70</sup> and this fact confirms an octahedral geometry for Fe (III) complexes.

**Table 3Magnetic Moment of Fe (III) Complexes with Ligands (1-8)**

Complex	Molar conductance ( $\mu\text{eff}$ )
[Fe (DP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	5.8 BM
[Fe (DMP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	5.9 BM
[Fe (DEP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	5.8 BM
[Fe (MDDP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	5.6 BM
[Fe (MOTTP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	5.7 BM
[Fe (MDTTP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	5.9 BM
[Fe (DPTTP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	5.8 BM
[Fe (DBCH) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	5.7 BM

### 3.3 Electronic Spectra

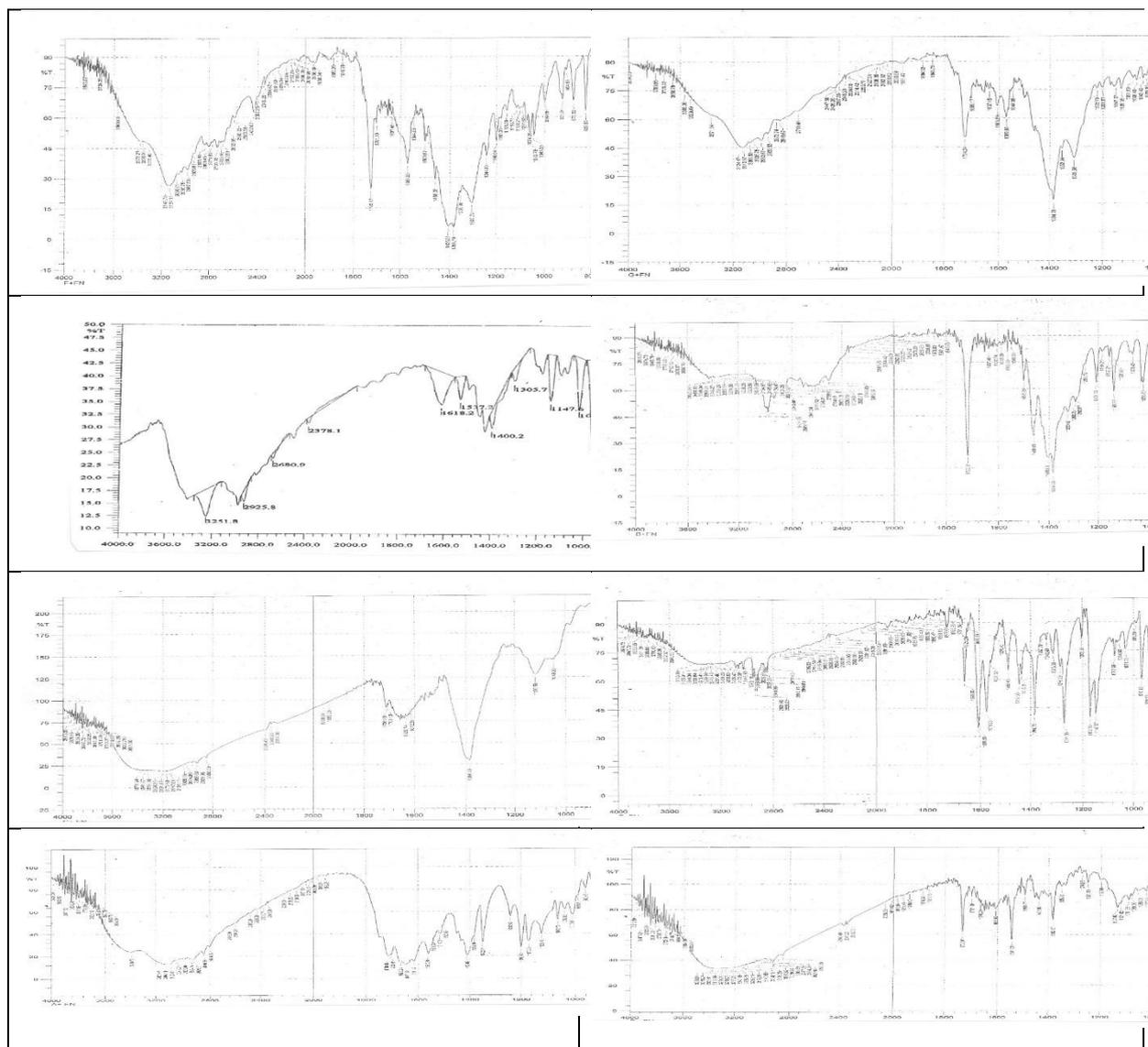
The electronic spectra of all the complexes were recorded in solid state. Since the colour of all the complexes were the same, the spectra of all were found to be the same in nature. The absorption frequencies were presented in Table 4. The electronic spectra of all the complexes exhibit three bands, all in visible region. These absorption frequencies were in accordance with those expected for an octahedral geometry. The absorption bands at the ranges 10141-13333, 16424-22727 and 25641-28571 cm<sup>-1</sup> were assigned to the transitions of <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub> (G), and <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub>(G), <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>A<sub>1g</sub> (G) respectively.

**Table 4 Electronic spectra of Fe (III) complexes with ligands (1-8)**

Complex	<sup>6</sup> A <sub>1g</sub> (S) → <sup>4</sup> T <sub>1g</sub> (cm <sup>-1</sup> )	<sup>6</sup> A <sub>1g</sub> (S) → <sup>4</sup> T <sub>2g</sub> (cm <sup>-1</sup> )	<sup>6</sup> A <sub>1g</sub> (S) → <sup>4</sup> A <sub>1g</sub> (cm <sup>-1</sup> )	C.T (cm <sup>-1</sup> )
[Fe (DP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	10141	16474	26723	37174
[Fe (DMP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	10752	20000	25641	37123
[Fe (DEP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	11037	17829	25764	30769
[Fe (MDDP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	13333	22727	28320	37231
[Fe (MOTTP)(H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	12345	17234	28571	35209
[Fe (MDTTP)(H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	11652	17474	25723	37323
[Fe (DPTTP) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	123323	17434	28571	37241
[Fe (DBCH) (H <sub>2</sub> O) <sub>4</sub> NO <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	12223	16424	27777	37593

### 3.4 Infrared Spectra

IR spectral bands of the ligands and the corresponding Fe (III) complexes with their probable assignments were listed in Table 5 and are shown in Fig1. The moderately strong bands around 3300cm<sup>-1</sup> for free ligands (1-5) were attributed to the stretching mode of N-H vibration<sup>71-100</sup>. But in the complexes (Fig. 2), these bands exhibit a considerable downward shift of 30-50 cm<sup>-1</sup>. This spectral observation suggests that the coordination of the ligands to the metal ion takes place through the lone pair of secondary amine nitrogen atoms and sulphur of the ligands moiety. The observed decreasing trend of C-N and C-S stretching frequencies in accordance with ligands and its complexes confirms the coordination involvement of lone pair of electrons present in the tertiary amine nitrogen atom and sulphur atom of the ligands<sup>101-107</sup>. The existence of slightly increased or decreased absorption bands in the range 860-836 cm<sup>-1</sup> in those complexes confirmed the non-involvement of carbonyl oxygen in coordination. In the case of 2,6-dibenzylidene cyclohexanone ligand, the decrease in carbonyl stretching frequency from the normal frequency of 1720cm<sup>-1</sup> to 1660 cm<sup>-1</sup> confirmed the coordination of carbonyl group along with benzylidene groups moiety which occurs due to conjugation effect. IR has been proved to be a valuable tool in the analysis of the stereochemistry of heterocyclic compounds, pyrimidine, thianones and cycloheranone on the basis of a series of bands in the region 2850-2700cm<sup>-1</sup> called Bohlmann bonds. These bands have also been used in the assessment of conformational equilibria in piperidinesystems. It has been pointed out that the Bohlmann hands arise because of the interaction of 'P' electrons of nitrogen with the antiperiplanar C-H bonds. Piperidin-4-ones, pyrimidine, thianones and cyclohexanones exhibit these bands in the same region indicating that the hydrogen of C-2 and C-6 carbon atoms were antiperiplanar with respect to the lone pair of electrons in nitrogen. The involvement of nitrogen in coordination was further confirmed by presence of new band in region 445-416cm<sup>-1</sup> due to  $\nu$  (M-N). A broad IR band in the region 3452-3398 cm<sup>-1</sup> and medium intensity band in the region 1625-1616 cm<sup>-1</sup> which were attributed to O-H stretching and H-O-H bending vibrations respectively in all complexes of the ligand (1-8) confirmed the coordination of water molecules to the metal ion. The appearance of a new band in the region 546-515 cm<sup>-1</sup> due to M-O bonding<sup>108</sup> can also be considered as a supporting evidence for the coordination of water molecules to the metal ion.



**Fig.1** IR spectrum of Iron complex with ligands (1-8)

**Table 5** Important IR Bands (in  $\text{cm}^{-1}$ ) of Fe (III) complexes with ligands (1-8)

CPD	$\gamma\text{C=O}$ ( $\text{cm}^{-1}$ )	$\gamma^*\text{C=O}$ ( $\text{cm}^{-1}$ )	$\gamma\text{N-}$ H( $\text{cm}^{-1}$ )	$\gamma^*\text{N-}$ H( $\text{cm}^{-1}$ )	$\gamma\text{C-S-}$ C( $\text{cm}^{-1}$ )	$\gamma^*\text{C-S-}$ C( $\text{cm}^{-1}$ )	$\gamma^*\text{M-}$ N( $\text{cm}^{-1}$ )	$\gamma^*\text{M-}$ O( $\text{cm}^{-1}$ )	$\gamma^*\text{O-}$ H( $\text{cm}^{-1}$ )	$\gamma^*\text{N-}$ C( $\text{cm}^{-1}$ )	$\gamma^*\text{H-O-}$ H( $\text{cm}^{-1}$ )
1	1724	1726	3305	3568	-	-	823	503	3143	1199	1637
2	1703	1724	3298	3110	-	-	823	505	3124	1126	1606
3	1706	1713	3287	3189	-	-	824	554	3319	1145	1670
4	1722	1722	3346	3319	-	-	811	518	3145	1141	1637
5	1701	1722	3287	3250	-	-	844	546	3440	1133	1620
6	1701	1736	-	-	669	657	839	567	3384	-	1608
7	1708	1731	-	-	663	663	845	531	3336	-	1649
8	1718	1703	-	-	-	-	831	540	3442	-	1616

$\gamma$  = Ligand Frequency,  $\gamma^*$  - Complexes frequency

### 3.5 Thermal Analysis

TGA & DTA curves of Fe(III) complexes were given in Fig.2-3. TGA and DTA data of  $[\text{Fe}(\text{DP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  and  $[\text{Fe}(\text{DMP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  were presented in the Table 6 and were treated as representative model for all Fe(III) ion complexes of ligands (1-8) to characterize the complexes and to study their thermal stability. The TGA and DTA of Fe(III) – DP complex (Fig. 2) and Fe(III) – DMP complex (Fig. 3) depict four decomposition steps in the range of 125-533°C and 118-531°C respectively with two endothermic and two exothermic changes.

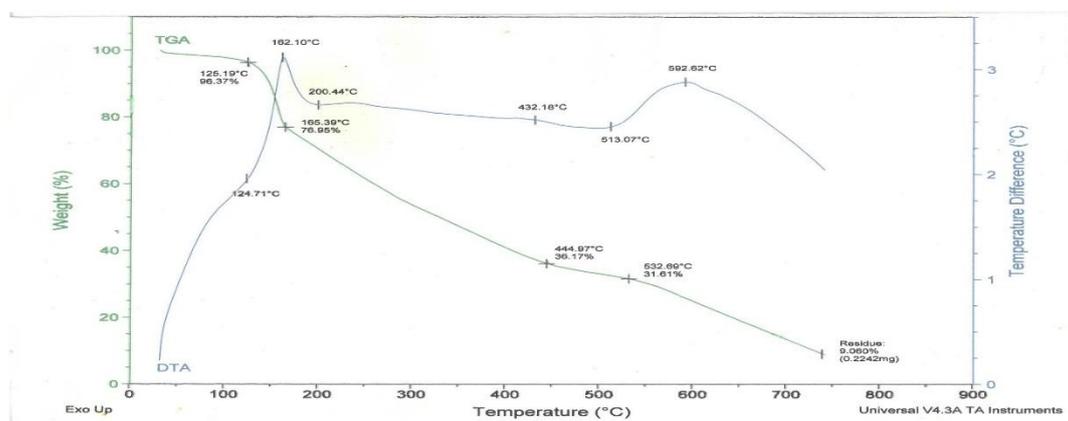


Fig.3 simultaneous TGA & DTA of Iron complex  $[\text{Fe}(\text{DP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$

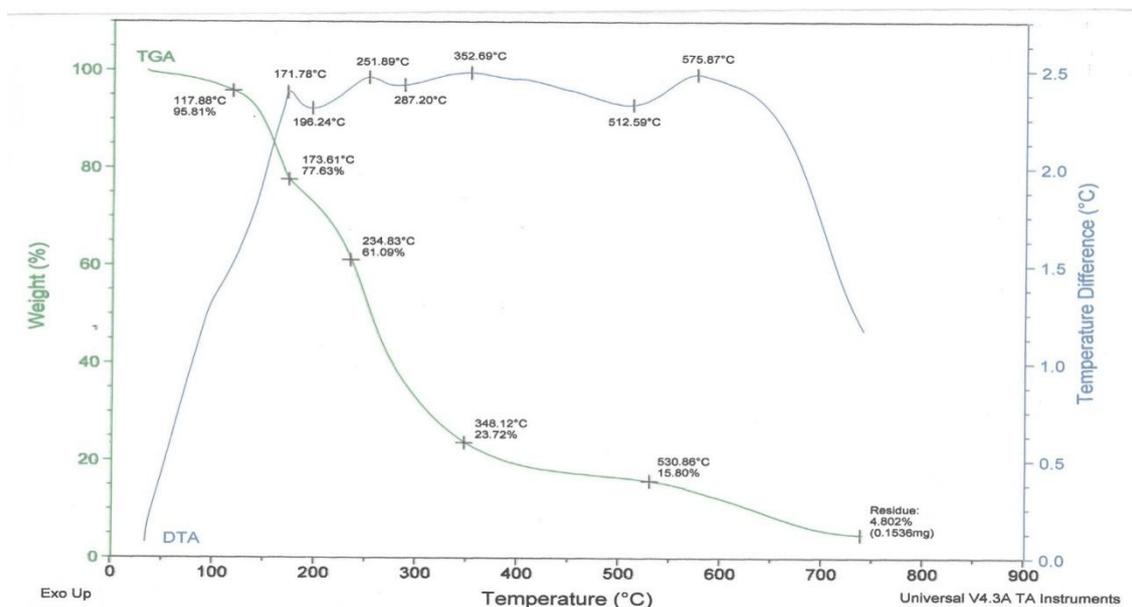
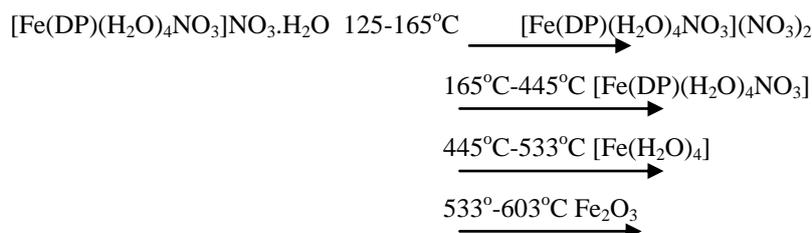


Fig.3 simultaneous TGA & DTA of Iron complex  $[\text{Fe}(\text{DMP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$

#### $[\text{Fe}(\text{DP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$

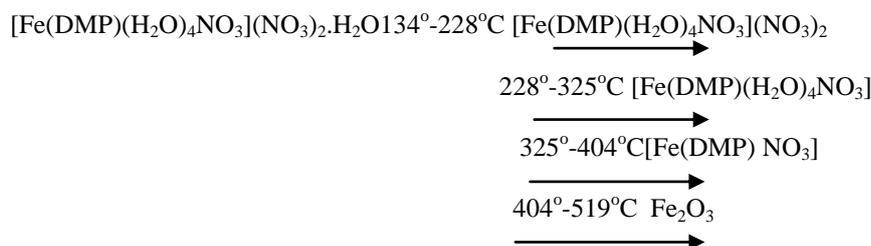
The first decomposition zone attributes to slow decomposition at 125 – 165°C with the corresponding weight loss of 9.06% (theoretical value 9.58) which was due to loss of one coordinated water molecule. The second decomposition with weight loss of 31.61 (theoretical value 32.60) at 165-445°C represents loss of the two nitrate ions. The thermal curve exhibits endothermic DTA peaks at 162°C and 593°C indicating the dehydration of the complex. The loss of mass at the temperature range 120°C – 445°C corresponds to the stepwise loss of water molecules which were in coordination sphere. Since the dehydration takes place at above 100°C, it was assumed that the water molecules were coordinated to the Fe(III) ion. Further decomposition occurs in the range 445°C – 533°C with the elimination of one DP ligand with mass loss of 36.17% (theoretical value 36.40). Thereafter, a continuous mass loss was observed in the range of 533-603°C and the organic part of the complex was completely eliminated leading to the formation of metal oxide ( $\text{Fe}_2\text{O}_3$ ) with a mass loss of 76.95% (theoretical value 76.64). Sharp exothermic peaks were observed at 432°C and 513°C for the third and

the fourth stages of decomposition in DTA curve. The various processes occurring in the thermal changes of  $[\text{Fe}(\text{DP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  were represented in the following sequence of reactions



**$[\text{Fe}(\text{DMP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$**

In this case  $134^\circ - 228^\circ\text{C}$ ,  $228^\circ - 325^\circ\text{C}$ ,  $325 - 404^\circ\text{C}$  and  $404^\circ - 519^\circ\text{C}$ , were the decomposition temperature ranges with four endothermic DTA peaks at  $149^\circ\text{C}$ ,  $228^\circ\text{C}$ ,  $418^\circ\text{C}$  and  $561^\circ\text{C}$  and two exothermic peaks at  $166^\circ\text{C}$  and  $509^\circ\text{C}$ . The various decomposition processes occurring in the thermal changes of  $[\text{Fe}(\text{DMP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  were represented in the following sequence of reactions.



Considering the temperature at which the dehydration processes takes place and the way they proceed, one can determine whether water molecule was coordinated or not.<sup>110</sup> According to Nicolaevet al.<sup>111</sup> two coordinated water molecules were eliminated around the temperature range  $161-197^\circ\text{C}$  while the remaining one water molecule along with three nitrate ions was eliminated above  $254^\circ\text{C}$  for this complex.

The first and the second arrests in TG curves of these complexes show a mass loss corresponding to three water molecules. The DTA curve of Iron (III) complexes shows two sharp endothermic peaks at  $199^\circ\text{C}$  and  $259^\circ\text{C}$ . Thus the thermal studies confirmed the presence of coordinated water molecules in Iron (III) complexes of DP and DMP ligands.

**Table 6 Thermal Analysis of Fe (III) Complexes**

Complex	DTA Peak Temp(°C)	Thermogravimetry		
		Temperature Range (°C)	Mass Loss %	
			Observed	Calculated
$[\text{Fe}(\text{DP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	162 (+)	125-165	9.06	9.58
	593 (+)	165-445	31.61	32.60
	200 (-)	445-533	36.17	36.40
	432 (-)	533-603	76.95	76.64
	513 (-)		96.37	96.91
$[\text{Fe}(\text{DMP})(\text{H}_2\text{O})_4\text{NO}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	172 (+)	118-174	15.80	9.36
	252 (+)		23.72	19.74
	353 (+)	174-235	61.09	64.14
	576 (+)		77.63	76.21
	196 (-)		95.81	96.98
	287 (-)	235-348		
	513 (-)	348-531		

**3.6 Cyclic Voltammeteric Studies**

The cyclic voltammogram of the Iron complex compares two reduction peaks at 0.16 and  $-0.88\text{ V}$ , which were shown in the Table 7. The peak at  $0.16\text{V}$  probably corresponds to the reduction of  $\text{Fe}(\text{III}) - \text{Fe}(\text{II})$ <sup>112</sup>. All the complexes were electro active only with respect to the metal center. In these redox couples, electrons were gained or lost from the  $d\pi$  level orbital of the coordinated metal complexes showed redox couples with peak to peak. Separation values ( $\Delta E_p$ ) ranging from 1.1 to  $1.22\text{V}$  revealing that this process was at best quasi-reversible. This was attributed to slow electron transfer and adsorption of the complexes onto the

electrode surface. The first oxidation and followed by reduction was attributed to the oxidation and reduction of one of the Fe(III) centers to the corresponding mixed valence complex. Hence it was inferred from the electrochemical data that the present ligand system was ideally suitable for stabilizing the higher oxidation state of Fe(III). It has been observed that there was not much variation in the redox potentials due to the replacement of ligands and the nature of bridging ligand present in the complex.

**Table 7 Cyclic voltammetric data of ligands (1-8) and Iron (III) Complex**

Compounds	E <sub>PC</sub> (V)	E <sub>Pa</sub> (V)	ΔE <sub>P</sub> (V)
DP	1.70	-8.27	1.1
DMP	1.66	-8.13	2.7
DEP	1.64	-7.81	2.4
MDDP	1.58	-8.11	1.5
MOTTP	1.62	-8.16	2.9
MDTTP	1.57	-7.85	2.8
DPTTP	2.00	-8.60	3.4
DBCH	1.96	-8.39	2.9
Iron (III) Complex	0.16	-0.88	1.22

### 3.7 X-ray (Powder) Diffraction Study

The X-ray (powder) diffraction photograph was recorded for the iron complex with ligands (1-8). For example [Fe(DP)(H<sub>2</sub>O)<sub>4</sub>NO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O photograph reveals 21 reflexions with maximum reflection at 10.45 (2θ) with the spacing of 4.35 Å. All the lines in the powder photograph were indexed based on Ito's method. The Fe(III) complexes crystallises in a triclinic lattice. The agreement between observed and computed Q<sub>hkl</sub> (within 1%) was displayed in Tables 8-13. The direct cell dimensions calculated from the reciprocal cell dimensions were collected in Table 14 and Fig.4. The molecule is non-centro symmetric and it was a neutral monomer in which Fe(III) was octahedrally coordinated by two each of crystallographically independent N-coordinated and NCS ligands.

The -NH, -NCH<sub>3</sub> groups were quasilinear with 172.1° and 177.7° bonded to the Fe(III) ion through an angle of 168.33° and 167.85° respectively. Interestingly the respective N atoms of ligands were Cis- located whereas the same were trans-positioned in the reported Fe(III) complexes. The complex crystallizes in an orthorhombic type of lattice dimensions as, a = 17.87, b=15.01 and C=13.60. On the basis of above studies, an octahedral geometry for complexes of (1-8) ligands have been proposed.

**Table 8X-ray (Powder) Diffraction data for complex [Fe(DP)(H<sub>2</sub>O)<sub>4</sub>NO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O**

D	2θ	Q <sub>obs</sub> = 1/d <sup>2</sup>	d-spacing [Å]	Rel. Int. [%]	Q <sub>cal</sub>	Index (h k l)
10.4577	4.35	0.8029	8.45934	1.34	0.004275	Q <sub>100</sub>
14.2312	107.61	0.2007	6.22366	33.24	0.005692	Q <sub>010</sub>
15.2115	169.61	0.1338	5.82472	52.39	0.006290	Q <sub>001</sub>
18.7535	92.47	0.2676	4.73183	28.56	0.007271	Q <sub>101</sub>
19.3590	323.66	0.1506	4.58519	99.98	0.010919	Q <sub>111</sub>
20.2240	89.09	0.3346	4.39099	27.52	0.015486	Q <sub>101</sub>
20.5831	53.15	0.1673	4.31517	16.42	0.019662	Q <sub>102</sub>
21.1287	18.91	0.2676	4.20496	5.84	0.031702	Q <sub>301</sub>
22.7838	25.00	0.2676	3.90310	7.72	0.031592	Q <sub>122</sub>
24.2408	234.85	0.1673	3.67171	72.54	0.030193	Q <sub>310</sub>
25.3024	32.06	0.1840	3.52001	9.90	0.034153	Q <sub>122</sub>
25.7276	240.59	0.2175	3.46280	74.32	0.038131	Q <sub>310</sub>
26.4881	323.74	0.3011	3.36507	100.00	0.040385	Q <sub>122</sub>
28.9476	74.06	0.1673	3.08452	22.88	0.052834	Q <sub>130</sub>
31.7033	46.08	0.2676	2.82242	14.23	0.056877	Q <sub>230</sub>
32.5839	31.51	0.2676	2.74813	9.73	0.06248	Q <sub>132</sub>
33.5926	44.70	0.1673	2.66788	13.81	0.07864	Q <sub>112</sub>
34.4296	24.80	0.2007	2.60491	7.66	0.08148	Q <sub>130</sub>
39.2928	36.60	0.1673	2.29299	11.31	0.08123	Q <sub>202</sub>
40.1147	15.70	0.3346	2.24789	4.85	0.08815	Q <sub>240</sub>
41.6153	21.23	0.4015	2.17023	6.56	0.08858	Q <sub>204</sub>
43.9759	45.43	0.2856	2.05736	14.03	0.09574	Q <sub>040</sub>

**Table 9X-ray (Powder) Diffraction data for complex [Fe(DMP)(H<sub>2</sub>O)<sub>4</sub>NO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O**

D	2θ	Q <sub>obs</sub> = 1/d <sup>2</sup>	d-spacing [Å]	Rel. Int. [%]	Q <sub>cal</sub>	Index (h k l)
14.5545	118.37	0.1840	6.08616	84.50	0.004455	Q <sub>100</sub>
15.7005	24.90	0.3346	5.64439	17.77	0.005092	Q <sub>010</sub>
16.0934	60.75	0.1673	5.50746	43.37	0.006230	Q <sub>001</sub>
17.5839	30.56	0.2676	5.04384	21.81	0.007201	Q <sub>101</sub>
18.5014	140.08	0.2007	4.79572	100.00	0.010829	Q <sub>111</sub>
19.7847	61.75	0.2676	4.48747	44.08	0.015436	Q <sub>101</sub>
21.4257	55.23	0.2676	4.14733	39.43	0.019662	Q <sub>102</sub>
22.4537	56.61	0.5353	3.95974	40.41	0.031752	Q <sub>301</sub>
23.6823	39.01	0.2676	3.75702	27.85	0.031542	Q <sub>122</sub>
24.6533	13.81	0.2676	3.61120	9.86	0.033193	Q <sub>310</sub>
25.3129	23.49	0.2676	3.51858	16.77	0.035183	Q <sub>122</sub>
26.6513	41.32	0.2007	3.34484	29.49	0.038171	Q <sub>310</sub>
27.6298	9.88	0.2007	3.22857	7.05	0.039115	Q <sub>122</sub>
28.1870	13.40	0.2007	3.16600	9.57	0.052284	Q <sub>130</sub>
29.3753	18.46	0.2007	3.04058	13.18	0.051577	Q <sub>230</sub>
30.3763	16.03	0.3011	2.94262	11.44	0.062448	Q <sub>132</sub>

**Table 10X-ray (Powder) Diffraction data for complex [Fe(DEP)(H<sub>2</sub>O)<sub>4</sub>NO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O**

D	2θ	Q <sub>obs</sub> = 1/d <sup>2</sup>	d-spacing [Å]	Rel. Int. [%]	Q <sub>cal</sub>	Index (h k l)
16.7965	19.10	0.8160	5.27413	1.67	0.040385	Q <sub>100</sub>
19.4589	207.57	0.1632	4.55809	18.20	0.052834	Q <sub>010</sub>
21.4102	581.44	0.0816	4.14687	50.98	0.056877	Q <sub>001</sub>
22.1630	377.11	0.1632	4.00769	33.07	0.06248	Q <sub>101</sub>
22.7726	1140.49	0.0816	3.90177	100.00	0.07864	Q <sub>111</sub>
23.7371	71.99	0.6528	3.74538	6.31	0.08148	Q <sub>101</sub>
25.8859	11.62	0.9792	3.43913	1.02	0.08123	Q <sub>102</sub>
32.6860	515.89	0.0816	2.73750	45.23	0.08815	Q <sub>301</sub>
58.1748	318.03	0.0816	1.58451	27.89	0.08858	Q <sub>122</sub>
68.4318	179.94	0.1020	1.36988	15.78	0.09574	Q <sub>310</sub>

**Table 11 X-ray Diffraction data for complex [Fe(MDDP)(H<sub>2</sub>O)<sub>4</sub>NO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O**

D	2θ	Q <sub>obs</sub> = 1/d <sup>2</sup>	d-spacing [Å]	Rel. Int. [%]	Q <sub>cal</sub>	Index (h k l)
10.0926	322.09	0.0612	8.75727	100.00	0.004945	Q <sub>100</sub>
10.2337	297.64	0.1632	8.63688	92.41	0.005147	Q <sub>010</sub>
14.1925	96.67	0.1836	6.23541	30.01	0.006010	Q <sub>001</sub>
14.7278	44.67	0.1428	6.00996	13.87	0.007211	Q <sub>101</sub>
20.0838	34.02	0.1428	4.41766	10.56	0.010809	Q <sub>111</sub>
20.5553	20.32	0.2040	4.31737	6.31	0.015486	Q <sub>101</sub>
22.0776	98.86	0.1836	4.02301	30.69	0.019664	Q <sub>102</sub>
22.5911	59.77	0.1428	3.93271	18.56	0.031707	Q <sub>301</sub>
23.2688	62.39	0.2244	3.81968	19.37	0.031591	Q <sub>122</sub>
25.7090	13.55	0.1224	3.46239	4.21	0.033194	Q <sub>310</sub>
26.0507	27.41	0.1224	3.41775	8.51	0.035853	Q <sub>122</sub>
29.6676	22.64	0.1836	3.00879	7.03	0.029131	Q <sub>310</sub>
30.5415	12.43	0.4896	2.92466	3.86	0.039385	Q <sub>122</sub>
36.6541	16.30	0.1224	2.44974	5.06	0.052834	Q <sub>130</sub>
37.2178	47.91	0.1428	2.41393	14.87	0.056877	Q <sub>230</sub>

**Table 12X-ray (Powder) Diffraction data for complex [Fe(MDTTP)(H<sub>2</sub>O)<sub>4</sub>NO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O**

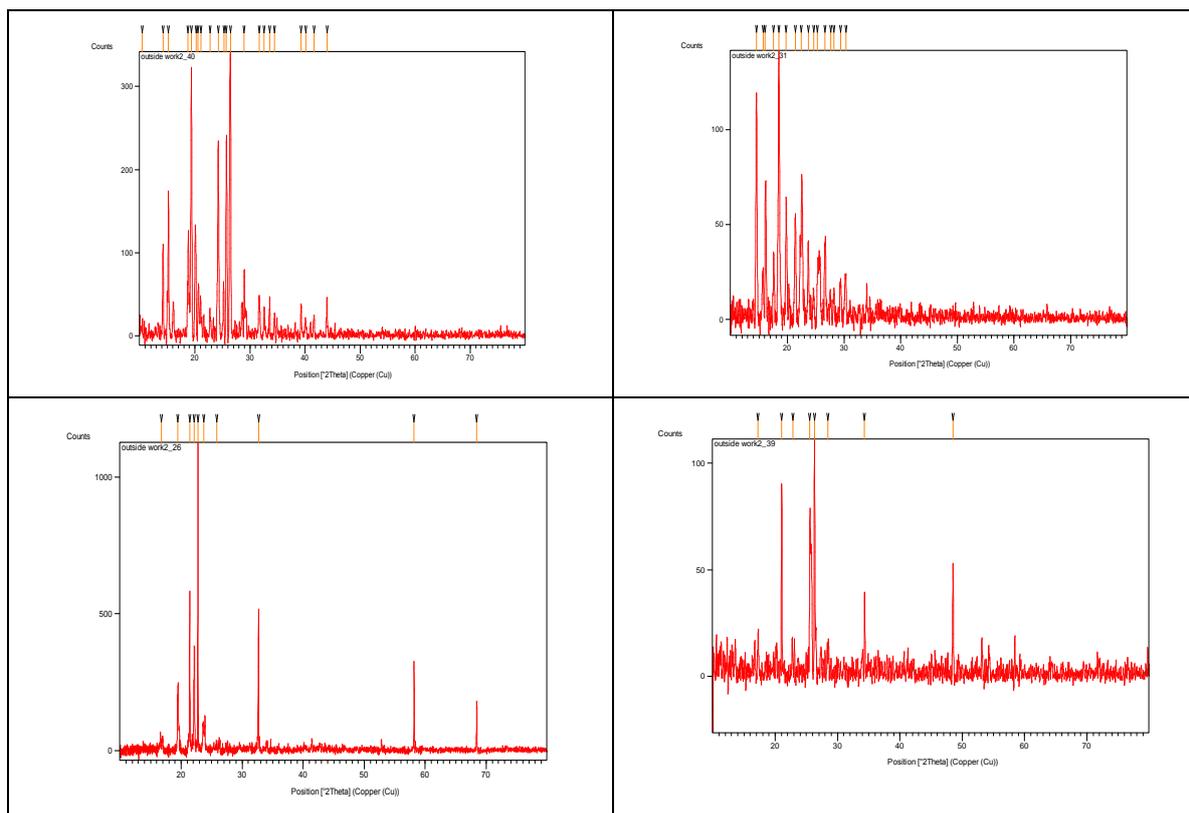
D	2θ	Q <sub>obs</sub> = 1/d <sup>2</sup>	d-spacing [Å]	Rel. Int. [%]	Q <sub>cal</sub>	Index (h k l)
17.2666	18.33	0.2007	5.13581	16.71	0.034475	Q <sub>100</sub>
21.0477	89.97	0.1171	4.22097	81.99	0.015092	Q <sub>010</sub>
22.8303	8.41	0.4015	3.89526	7.67	0.006270	Q <sub>001</sub>
25.5553	70.55	0.1338	3.48575	64.29	0.067211	Q <sub>101</sub>
26.3127	109.74	0.1506	3.38711	100.00	0.010810	Q <sub>111</sub>
28.4717	11.02	0.3346	3.13498	10.05	0.015486	Q <sub>101</sub>
34.3290	37.80	0.1338	2.61232	34.45	0.020662	Q <sub>102</sub>
48.5141	52.10	0.2040	1.87498	47.48	0.031540	Q <sub>301</sub>

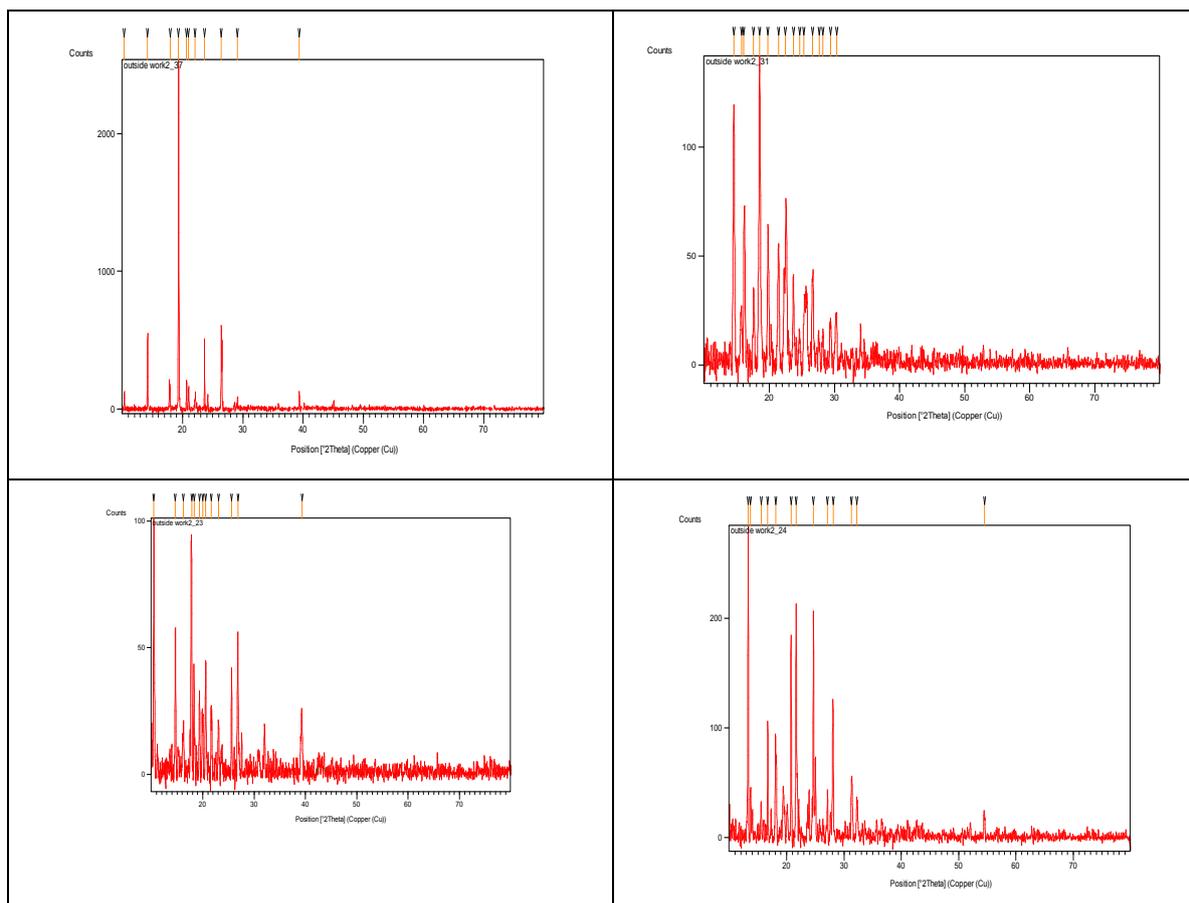
**Table 13 X-ray (P) Diffraction data for complex [Fe(DBCH)(H<sub>2</sub>O)<sub>4</sub>NO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O**

D	2θ	Q <sub>obs</sub> = 1/d <sup>2</sup>	d-spacing [Å]	Rel. Int. [%]	Q <sub>cal</sub>	Index (h k l)
10.3198	94.80	0.2448	8.56499	3.81	0.003474	Q <sub>100</sub>
14.1945	530.90	0.0816	6.23450	21.35	0.005122	Q <sub>010</sub>
17.9111	166.83	0.2448	4.94835	6.71	0.005270	Q <sub>001</sub>
19.3148	2486.19	0.1224	4.59177	100.00	0.007211	Q <sub>101</sub>
20.6503	205.98	0.1632	4.29773	8.29	0.011809	Q <sub>111</sub>
20.9849	139.88	0.1632	4.22995	5.63	0.005486	Q <sub>101</sub>
22.0499	70.94	0.3264	4.02800	2.85	0.019662	Q <sub>102</sub>
23.6491	533.49	0.0816	3.75910	21.46	0.021702	Q <sub>301</sub>
26.4230	605.09	0.0816	3.37043	24.34	0.029582	Q <sub>122</sub>
29.1142	80.02	0.1020	3.06471	3.22	0.033193	Q <sub>310</sub>
39.3588	108.94	0.1632	2.28741	4.38	0.034153	Q <sub>122</sub>

**Table 14 Crystal Parameters of [Fe(DP)(H<sub>2</sub>O)<sub>4</sub>NO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O**

Cell length (Å)	Angular parameters (°)	Cell Volume (Å) <sup>3</sup>
a = 17.87	α = 112.1	2975.57
b = 15.01	β = 147.7	
c = 13.60	γ = 188.0	





**Fig. 5 XRD (Powder) Crystallography with Fe(III) complexes with ligand (1-8)**

### 3.8 Antibacterial and antifungal study

In this work and many previous reports, the coordination of ligands to metal improves Antibacterial and antifungal activity. The overtones concept and tweedys chelation theory were used for explanation of increased activity of the complexes respect to parent ligands. As mentioned earlier, the in-built spiro carbocyclic or heterocyclic systems in a ring increases the biological potency, with the systems having smaller rings. On this basis, the synthesized compounds were evaluated for their in-vitro antibacterial and antifungal activities.

The evaluations were carried out using “paper disc diffusion method” for antibacterial activity and the “Turbidity method” for antifungal activity. All the synthesized compounds (1-8) were evaluated for their in-vitro antibacterial activity against the pathogenic micro-organisms, *Escherichia coli* (gram-positive) and *Staphylococcus aureus* (gram-negative) using paper disc diffusion method. Sterilized 10mm whatman No.1 paper discs were taken, impregnated with 0.1ml of the sample solutions (200µg in DMF) and placed in the petridish containing 25-30ml of nutrient agar inoculated with 18-24hrs test culture. Incubation was carried out at 37°C for 24hrs and the zone of inhibition was measured in mm. All the experiments were done in triplicate. Phenol was taken as standard.

Antifungal activity of the compounds were determined in-vitro against *Aspergillus Niger* adopting the turbidity method. In this method, 0.1ml of the sample solutions (200µg in DMF) in 5ml sterilized fungi medium were treated with 3-4 drops of 48hrs old culture in a test tube. The test tubes were then shaken well and incubated for 48 hrs at 37°C. The extent of inhibition was determined by measuring the decrease in turbidity interms of % transmission at 660µ. Salicyclic acid was taken as standard. Antibacterial and antifungal activities of all the compounds in-vitro against the pathogenic micro-organisms *Escherichia coli* (gram activity) with solvent control: DMF (positive), *staphylococcus aureus* (gram-negative) and *Asperigillus Niger* fungal are given in Table 15.

**Table 15**Result of the Antibacterial and Antifungal activities with various alkyl substituted 2,6-diphenyl piperidin-4-ones, pyrimidine, thianones and cyclohexanone

Compounds	Antibacterial Activity		Antifungal Activity
	E.C	S.A	A.N
1	-	-	+
2	+	+	++
3	+	+	++
4	+	+	++
5	+	+	++
6	+	+	++
7	+	+	++
8	-	-	+

#### IV. Conclusion

The Fe(III) complexes were non-hygroscopic in nature and brown in colour. They were moderately soluble in methanol, DMF and DMSO. The general formula assigned to the complexes were  $[Fe(L)(H_2O)_4NO_3](NO_3)_2.H_2O$ . The conductance values  $143-197\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  indicate that these complexes were 1:2 electrolytes. The molecular mass determined by Rast method also support the 1:2 electrolyte behavior of the complexes. A comparison of IR spectra of the ligands and the corresponding complexes confirm the involvement of lone pair of electrons in ring nitrogen / sulphur atom (1-7) and the benzylidene carbonyl moiety (8) in coordination and monodentate nature of the ligands. The thermal curves (TGA and DTA) of the complexes indicate the presence of four water molecules and one nitrate ion along with a ligand in coordination sphere and one nitrate ion and one water molecule in outersphere of the complexes. The magnetic moment values of the complexes (5.6-5.9BM) indicate that the metal ion contains five unpaired electrons with no metal-metal bonding. The appearance of three strong absorption bands in visible region in electronic spectra reveals that the complexes were in octahedral geometry. Cyclic voltammetric studies show that the metal ion of the complexes were in easy reversibility. XRD shows that all the complexes were in triclinic lattice arrangement.

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