

# Synthesis, Spectral, Thermal Stability and Antimicrobial Assay of Six Co-Ordinate Complexes of Fe (III) Derived from N (4) Thiosemicarbazone

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## ABSTRACT

Fe (III) complexes have been synthesized by the reaction of FeCl<sub>3</sub> with 5-chloro-2-hydroxy acetophenone methyl thiosemicarbazone in presence of heterocyclic bases like pyridine (py),  $\alpha/\beta/\gamma$ -picoline. Thiosemicarbazone has been characterized by <sup>13</sup>C, <sup>1</sup>H NMR, ESI-MS as well as IR, electronic spectra. Spectral and magnetic measurements indicated Octahedral geometry for the six coordinate complexes. The thiosemicarbazone and its Fe (III) complexes have been found. The metal complexes and their corresponding ligands were tested against bacterial parasites. It was found that the iron complexes synthesized are more biologically active than their corresponding thiosemicarbazone.

**Keywords :** Metal Salts, Bioactive metal complexes, Antimicrobial activity. MIC.

## I. INTRODUCTION

Schiff bases are ligands in coordination chemistry and have applications in different fields [1,2]. Metal complexes of Schiff bases derived from aminophenols have been synthesized and reported [3,4]. Fe(III) complexes of tridentate Schiff bases derived from simple or substituted salicylaldehyde and 2-aminophenol have been characterized [5]. The complexes of transition metals have been prepared and characterized, rare earth metals and main group metals with Schiff base salicylidene-2-aminophenol and salicylidene-2-hydroxy-1-naphthyl amine [6]. Cu(II) and Ni(II) complexes of some dibasic tridentate Schiff bases prepared by condensation of 2-aminophenol with 5-X-salicylaldehyde and 2-hydroxy-1-naphthaldehyde [7].

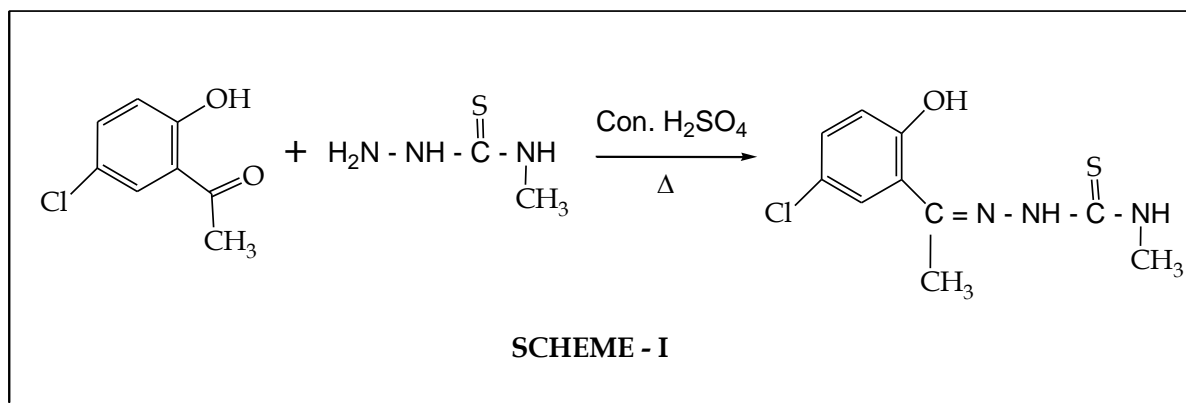
The synthesis and characterization of Cu(II), Ni(II), Fe(III), Zn(II) and Cd(II) complexes of polystyrene supported resin containing Schiff base derived from 3-

formyl salicylic acid and 2-aminophenol prepared [8]. Complexes of some metal ions with Schiff base ligands derived from isatin and 2-amino-phenol were synthesized and characterized by elemental analysis, IR, electronic spectral data, <sup>1</sup>H NMR spectra, conductance and magnetic measurements [9]. The synthesis of new high spin Co(II) chelates with tetradentate Schiff base ligand obtained by condensing 2-aminophenol or 4-nitro-2-aminophenol with glyoxal or glutaraldehyde have been reported [10]. The synthesis and characterization of Schiff bases from 2-aminophenol and crotonaldehyde, 2, 7-dimethyloctatrienal or terephthalaldehyde were carried out by [11]. New transition metal complexes of Schiff base quinoxaline-2-carboxaldehyde-2-aminophenol synthesized [12]. Fe(III) complex, an octahedral dimeric structure was reported. Schiff bases derived from salicylaldehyde and 2-aminophenol were synthesized and characterized [13].

In the present work the synthesis, spectral characterisation and biological assay of six coordinate complexes of Fe (III) with 5-chloro 2-hydroxy acetophenone and N (4) methyl thiosemicarbazide have been reported.

## II. EXPERIMENTAL

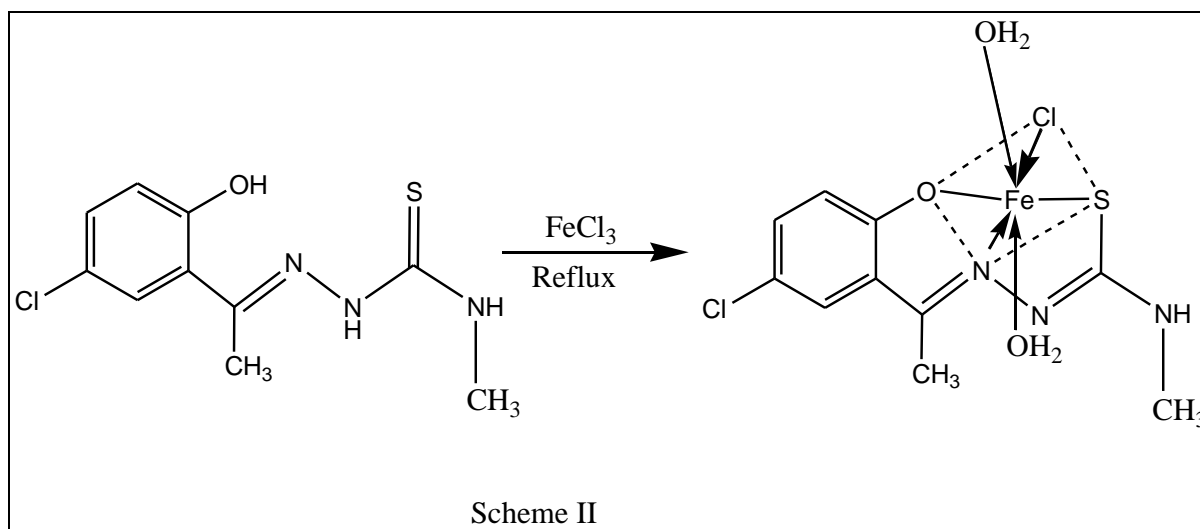
### Materials and instrumentation



### Preparation of complex

FeCl<sub>3</sub> salt was dissolved in absolute ethanol. The ethanolic solution of thiosemicarbazone in slight excess over the metal:ligand ratio of 1:1 was added to it dropwise and with constant

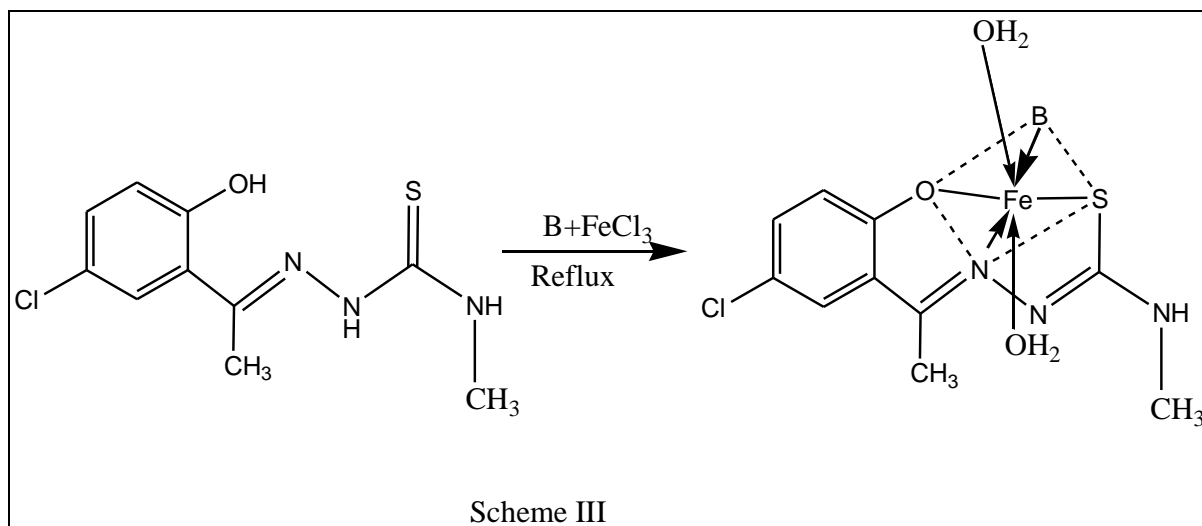
stirring. The reaction mixture was refluxed for three hours. The dark brown product thus obtained was filtered and washed well with absolute ethanol and then diethyl ether and dried over P<sub>2</sub>O<sub>5</sub> in vacuum.



### Preparation of complexes with heterocyclic bases

The complex Fe.L.B (B is heterocyclic base like pyridine,  $\alpha$ -picoline,  $\beta$ -picoline,  $\gamma$ -picoline) was synthesized by adding slowly ethanolic solution of FeCl<sub>3</sub> heterocyclic base to the hot ethanolic solution

of ligand in the ratio 1:1:1 and refluxing reaction mixture for three hours. The brown adduct obtained was filtered and washed with hot water, cold ethanol and diethyl ether and dried over P<sub>2</sub>O<sub>5</sub> in vacuum.



(B= pyridine,  $\alpha$ -picoline,  $\beta$ -picoline,  $\gamma$ -picoline)

### Physical measurements-

Magnetic susceptibility measurements were measured by Faraday method. IR spectra were recorded in the range 4000-200  $\text{cm}^{-1}$  range. NMR spectra were recorded in the mixture of  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  (1:1 v/v) with a Bruker AC-300F 300MHz spectrometer. Conductivity measurements were carried out on conductivity Bridge, Systonics conductivity meter-

304. Thermo gravimetric analysis was carried out in the temp rnge 30-800 $^{\circ}\text{C}$ . UV-Visible spectra were measured on Jasco UV-visible double beam spectrophotometer. Metal in the complex and adducts was estimated by standerizedxylenol orange as an indicator. Chloride in the complex was estimated by Mohr's method.

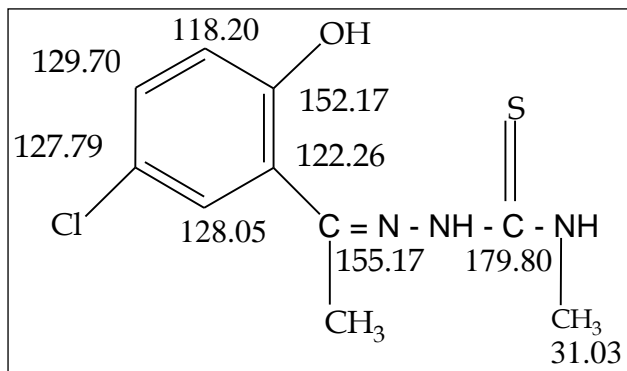
**Table 1.** Physical properties:

Compounds	Colour	Empirical Formula	Molar conductance $\text{Ohm}^{-1}\text{cm}^2\text{mole}^{-1}$	Magnetic Moment B.M.
L	Yellow	$\text{C}_{10}\text{H}_{12}\text{ClN}_3\text{OS}$	-	-
$\text{Fe-L.Cl.}(\text{H}_2\text{O})_2$	Brown	$\text{C}_{10}\text{H}_{14}\text{N}_3\text{O}_3\text{Cl}_2\text{SFe}$	45.2	5.26
$\text{Fe.L.Py.}(\text{H}_2\text{O})_2$	Brown	$\text{C}_{15}\text{H}_{19}\text{N}_4\text{O}_3\text{ClSFe}$	48.6	5.40
$\text{Fe.}\alpha\text{-Pico.}(\text{H}_2\text{O})_2$	Brown	$\text{C}_{16}\text{H}_{21}\text{N}_4\text{O}_3\text{ClSFe}$	45.7	5.50
$\text{Fe.L.}\beta\text{-Pico.}(\text{H}_2\text{O})_2$	Brown	$\text{C}_{16}\text{H}_{21}\text{N}_4\text{O}_3\text{ClSFe}$	40.4	5.45
$\text{Fe.L.}\gamma\text{-Pico.}(\text{H}_2\text{O})_2$	Brown	$\text{C}_{16}\text{H}_{21}\text{N}_4\text{O}_3\text{ClSFe}$	43.3	5.32

### $^1\text{H-NMR}$

NMR signals at 13.00 and 2.2 ppm are assigned to -OH and -CH<sub>3</sub> protons respectively. The signals at 2.40, 3.00 correspond to  $^4\text{NH}$  and  $\text{H}^4\text{N-CH}_3$  respectively. Signal at 10.3 ppm corresponds to  $^2\text{NH}$ . Aromatic protons show multiplets at 6.9, 7.25, 7.45, ppm.

$^{13}\text{C-NMR}$  (DMSO-D<sub>6</sub>):  $\delta_{\text{ppm}}$  118.20 (C = C), 129.70 (C = C), 127.79 (C = C - Cl), 128.05 (C = C), 122.26 (C = C), 152.17 (C = C - OH), 155.39 (C = N), 179.80 (C = S), 31.03 (NH - CH<sub>3</sub>)



(Calcd) found ESI-MS  $m/z$ , ion  $M^+$ :  $C_9H_{10}ClN_3OS$  (243.70) 243.20,  $C_{10}H_{14}N_3O_3Cl_2SFe$  (383.19) 383.90,  $C_{15}H_{19}N_4O_3ClSFe$  (426.84) 426.06,  $C_{16}H_{21}N_4O_3ClSFe$  (440.87) 440.11,  $C_{16}H_{21}N_4O_3ClSFe$  (440.87) 440.14,  $C_{16}H_{21}N_4O_3ClSFe$  (440.87) 440.11.

#### Analytical data

1. **L**: % C 46.07 (46.80), % H 4.87 (4.69), % N 16.72 (16.30), % S 12.89 (12.44)

2. **Fe-L.Cl.(H<sub>2</sub>O)<sub>2</sub>**: % Fe 14.12 (14.61), % Cl 9.07 (9.25), % C 31.03 (31.34), % H 3.81 (3.68), % N 10.13 (10.97), % S 8.72 (8.37), % O 12.08 (12.53)

3. **Fe.L.Py.(H<sub>2</sub>O)<sub>2</sub>**: % Fe 13.87 (13.12), % C 42.96 (42.21), % H 4.84 (4.48), % N 13.72 (13.13), % S 7.77 (7.51), % O 11.96 (11.25)

4. **Fe.α-Pico.(H<sub>2</sub>O)<sub>2</sub>**: % Fe 12.17 (12.70), % C 43.02 (43.59), % H 4.03 (4.80), % N 12.08 (12.71), % S 7.71 (7.27), % O 10.10 (10.89)

5. **Fe.L β-Pico.(H<sub>2</sub>O)<sub>2</sub>**: % Fe 12.10 (12.70), % C 43.11 (43.59), % H 4.18 (4.80), % N 12.18 (12.71), % S 7.75 (7.27), % O 10.19 (10.89)

6. **Fe.L.γ-Pico.(H<sub>2</sub>O)<sub>2</sub>**: % Fe 12.22 (12.70), % C 43.11 (43.59), % H 4.23 (4.80), % N 12.25 (12.71), % S 7.81 (7.27), % O 10.14 (10.89)

**Table 2.** Electronic spectral data (cm<sup>-1</sup>)

Compound	Mode	MLCT	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
L	DMF	-	30965	35850
Fe-L.Cl.(H <sub>2</sub> O) <sub>2</sub>	DMF	25800	32500	34600
Fe.L.Py.(H <sub>2</sub> O) <sub>2</sub>	DMF	25820	32530	34630
Fe.α-Pico.(H <sub>2</sub> O) <sub>2</sub>	DMF	25850	32550	34650
Fe.L β-Pico.(H <sub>2</sub> O) <sub>2</sub>	DMF	25886	32580	34670
Fe.L.γ-Pico.(H <sub>2</sub> O) <sub>2</sub>	DMF	25825	32565	34690

#### Infrared Spectroscopic data (cm<sup>-1</sup>)

1. **L**:  $\nu$  (- OH) 3325;  $\nu$  (C = N) 1635;  $\nu$  (- C = S) 785, 1360;  $\nu$  (N - N) 1060;  $\nu$  (N-H) 3245;  $\nu$  (C - O) 1290.

2. **[Fe-L.Cl.(H<sub>2</sub>O)<sub>2</sub>]**:  $\nu$  (C = N) 1590;  $\nu$  (C = N-N=C) 1550,  $\nu$  (C-S) 715, 1304,  $\nu$  (N-N) 1130,  $\nu$  (M - N) 410,  $\nu$  (M-O) 530,  $\nu$  (M-S) 340,  $\nu$  (C - O) 1230,  $\nu$  (Fe-Cl) 388.  $\nu$  (H<sub>2</sub>O) 3550, 3585.

3. **[Fe.L.Py.(H<sub>2</sub>O)<sub>2</sub>]**:  $\nu$  (C = N) 1580;  $\nu$  (C = N-N=C) 1545,  $\nu$  (C-S) 716, 1310;  $\nu$  (N-N) 1125,  $\nu$  (M - N) Base 260,  $\nu$

(M - N) 420,  $\nu$  (M - O) 520,  $\nu$  (M-S) 345,  $\nu$  (C - O) 1235, Band due to HB 1455,  $\nu$  (H<sub>2</sub>O) 3565, 3570.

4. **[Fe.α-Pico.(H<sub>2</sub>O)<sub>2</sub>]**:  $\nu$  (C = N) 1585;  $\nu$  (C = N-N=C) 1550,  $\nu$  (C-S) 718, 1315,  $\nu$  (N-N) 1130,  $\nu$  (M - N) Base 265,  $\nu$  (M - N) 430,  $\nu$  (M - O) 525,  $\nu$  (M-S) 350,  $\nu$  (C - O) 1240, Band due to HB 1460,  $\nu$  (H<sub>2</sub>O) 3540, 3550.

5. **[Fe.L β-Pico.(H<sub>2</sub>O)<sub>2</sub>]**:  $\nu$  (C = N) 1588;  $\nu$  (C = N-N=C) 1555,  $\nu$  (C-S) 720, 1320,  $\nu$  (N-N) 1140,  $\nu$  (M - N) Base

270,  $\nu$  (M - N) 435,  $\nu$  (M - O) 530,  $\nu$  (M-S) 355,  $\nu$  (C - O) 1245, Band due to HB 1475,  $\nu$ (H<sub>2</sub>O) 3550,3575.

6.[Fe.L. $\gamma$ -Pico.(H<sub>2</sub>O)<sub>2</sub>]: $\nu$  (C = N) 1590;  $\nu$  (C = N-N=C) 1560,  $\nu$  (C-S) 728, 1330, $\nu$  (N-N) 1145,  $\nu$  (M - N) Base 275,  $\nu$  (M - N) 440,  $\nu$  (M - O) 535,  $\nu$  (M-S) 360,  $\nu$  (C - O) 1250, Bands due to HB 1480,  $\nu$ (H<sub>2</sub>O) 3555,3585.

#### TGA analysis data:

The TGA curves of complexes were recorded between the temperatures 30 °C to 800 °C

- 1.[Fe-L.Cl.(H<sub>2</sub>O)<sub>2</sub>]: First step, 114.0 °C, Mass loss 4.05 % second step, 135.0 °C, Mass loss, 9.50 % Third Step 245.0 °C, Mass loss, 32.0 % Fourth Step, 370.0 °C, Mass loss 62.0 %, Residue 800 °C, % of Fe<sub>2</sub>O<sub>3</sub>, 67.12 (67.85).
- 2.[Fe.L.Py.(H<sub>2</sub>O)<sub>2</sub>]:First step, 115 °C, Mass loss 4.20 % second step,131.40 °C, Mass loss, 8.10 % Third Step 250 °C, Mass loss, 35.02 %Fourth Step,

369.0°C, Mass loss, 60.0 %, Residue, 792.34 °C, % of Fe<sub>2</sub>O<sub>3</sub>, 60.14 (60.91).

- 3.[Fe. $\alpha$ -Pico.(H<sub>2</sub>O)<sub>2</sub>]:First step, 115.35 °C, Mass loss 4.15 % second step, 130.50 °C, Mass loss, 8.26 % Third Step 249 °C, Mass loss, 30.47 % Fourth Step, 365.15°C, Mass loss 62.5 %, Residue 800 °C, % of Fe<sub>2</sub>O<sub>3</sub>, 58.21 (58.97).
- 4.[Fe.L  $\beta$ -Pico.(H<sub>2</sub>O)<sub>2</sub>]:First step, 115.26 °C, Mass loss 4.17 % second step, 132.14 °C, Mass loss, 8.27 % Third Step 250 °C, Mass loss, 29.02 % Fourth Step, 366.35°C, Mass loss, 65.27 %, Residue, 779.50 °C, % of Fe<sub>2</sub>O<sub>3</sub>, 58.33 (58.97).
- 5.[Fe.L. $\gamma$ -Pico.(H<sub>2</sub>O)<sub>2</sub>]:First step, 114.92 °C, Mass loss 4.16 % second step, 131.20 °C, Mass loss, 8.25 % Third Step 245 °C, Mass loss, 33.28 % Fourth Step, 370.28 °C, Mass loss 60.78 %, Residue 800 °C, % of Fe<sub>2</sub>O<sub>3</sub>, 58.27 (58.97).

### BIOLOGICAL ACTIVITY(AGAR PLATE DIFFUSION METHOD)

Table 3. Minimum Inhibitory concentration L , Fe (III) complexes and standered

Compound	Staphylococcus aureus		Bacillus subtilis		Escherichia Coli		Pseudomonas aeruginosa	
	Gram positive				Gram negative			
	2 $\mu$ g/ml	2.5 $\mu$ g/ml	2 $\mu$ g/ml	2.5 $\mu$ g/ml	2 $\mu$ g/ml	2.5 $\mu$ g/ml	2 $\mu$ g/ml	2.5 $\mu$ g/ml
L	0.71	0.40	0.73	0.43	0.74	0.42	0.75	0.44
Fe-L.Cl.(H <sub>2</sub> O) <sub>2</sub>	0.62	0.33	0.64	0.22	0.64	0.23	0.67	0.24
4Fe.L.Py.(H <sub>2</sub> O) <sub>2</sub>	0.62	0.32	0.64	0.26	0.65	0.22	0.64	0.25
Fe. $\alpha$ -Pico.(H <sub>2</sub> O) <sub>2</sub>	0.67	0.33	0.66	0.23	0.67	0.25	0.69	0.27
Fe.L $\beta$ -ico.(H <sub>2</sub> O) <sub>2</sub>	0.68	0.35	0.68	0.24	0.70	0.24	0.68	0.26
Fe.L. $\gamma$ -co.(H <sub>2</sub> O) <sub>2</sub>	0.61	0.32	0.62	0.24	0.63	0.22	0.66	0.23
Fe-L.Cl.(H <sub>2</sub> O) <sub>2</sub>	0.22	0.16	0.23	0.18	0.15	0.24	0.13	0.26
Standard	0.15	0.13	0.14	0.14	0.25	0.14	0.16	0.13

(Std-Amphiciline)

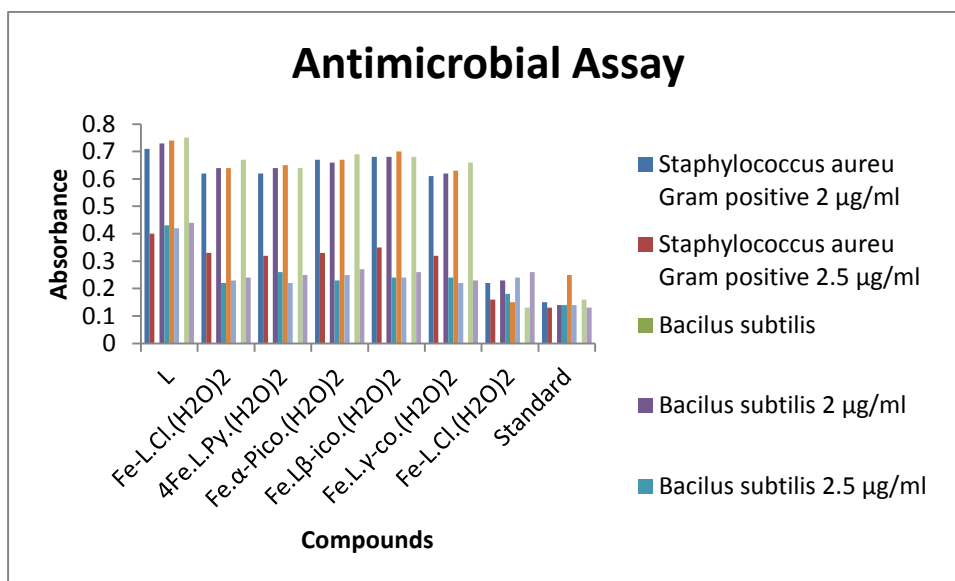


Figure 1. Antimicrobial Assay

### III. RESULTS AND DISCUSSION

Physical data of thiosemicarbazone and its complexes are presented in Table 1. Elemental analysis confirmed with 1:1 ratio of metal ion, thiosemicarbazone for complex and 1:1:1 ratio for metal, thiosemicarbazone and heterocyclic base for all adducts. The complex and all adducts are soluble in DMF in which conductivity measurements were made (30°C), showing all complexes to be non electrolyte [14]. The magnetic moments were measured at room temperature (30°C). The magnetic moments are in between 5.22-5.54 B.M. Mass spectral data confirmed the structure of the thiosemicarbazone as indicated by molecular ion peak (M + 1) corresponding to their molecular weights. UV-visible spectra of metal complexes in DMF solution are presented in Table no.2 The thiosemicarbazone showed band  $\pi$ - $\pi^*$  band at 35,850  $\text{cm}^{-1}$  and  $n$ - $\pi^*$  [18,19] at 30,965  $\text{cm}^{-1}$  [15-17]. The  $\pi$ - $\pi^*$  absorption bands are shifted to longer wavelength in complexes due to the weakening of the C=S bond conjugation system gets enhanced on complexation [20,21]. The reduction in intensity of  $n$ - $\pi^*$  bands in the complexes is due to transfer of lone pair of electrons to the metal and coordination of azomethine nitrogen. MLCT bands

are broad and observed in the region 25000-26000  $\text{cm}^{-1}$  which are assignable to Fe→S transitions.

Coordination through azomethine nitrogen  $^7\text{C}=\text{N}^1$  shifts the frequency to the lower side [22]. New bands in the range 410-440  $\text{cm}^{-1}$  confirms the participation of azomethine nitrogen in coordination [23,24]. There is increase in frequency of  $^1\text{N}-^2\text{N}$ . This confirms the coordination of thiosemicarbazone to metal through the azomethine nitrogen atom. The band  $^2\text{N}-\text{H}$  of thiosemicarbazone disappears in the complexes indicating the deprotonation of the  $^2\text{N}-\text{H}$  proton. A thioamide band partly due to C=S found at 1365 and 788  $\text{cm}^{-1}$  in thiosemicarbazone shifted to lower side in complexes. This indicates coordination through thiolate sulfur [25]. New bands in 340-360 range due to Zn-S confirms involvement of sulfur coordination. The phenolic oxygen indicates the third coordination on loss of OH protons. This causes shifting of  $\nu(\text{C}-\text{O})$  1290  $\text{cm}^{-1}$  in thiosemicarbazone to lower side in the complexes. New bands due to Fe-O in complexes in the range 520-535  $\text{cm}^{-1}$  confirms coordination through oxygen. The heterocyclic base nitrogen atom occupies fourth coordination site. The band is assigned for  $\nu(\text{Fe}-\text{N})$  due to heterocyclic base in 260-275  $\text{cm}^{-1}$  range in the spectra of all complexes. The characteristics

bands due to coordinated heterocyclic bases are also observed in IR spectra of all complexes[26-28].

Thermogravimetric curves of Fe (III) complex and adducts were recorded within a temperature range 30-800°C. The decomposition of complex proceeded in steps. Hydrated molecules of water were lost in between 30-110°C. Then two coordinated water molecules were lost in the temperature range 114-116°C. Mass lost at this stage is about 4-5 %. No change observed ~ 130°C after that break observed in the curves due to evaporation of molecule of thiosemicarbazone. The remaining part of thiosemicarbazone removed from the coordination sphere at ~ 600°C. Finally the metal oxides were formed above 600°C. The decomposition was complete at ~ 800°C.

Fe (III) complex and adducts are thermally stable up to 114°C and decomposition started at this temperature. The second step temperature is in the range of 131-135°C. The third step temperature is in the range of 245-250°C. The solid residue is Fe<sub>2</sub>O<sub>3</sub>. The complexes prepared with metal decompose in steps. It is concluded that the thermal stability of the complexes is due to the coordination of metal ion to thiosemicarbazone [29].

The bacterial assay was carried out by the agar plate diffusion method. Activity was measured by measuring the absorbance. As compared to complex and thiosemicarbazone, adducts showed good activity against bacterial species than free ligand. The minimum inhibitory concentration was determined by liquid dilution method [30]. The solutions of thiosemicarbazone and complexes with 2 µg/ml, 2.5 µg/ml and 3 µg/ml concentrations were prepared in the solvent DMF. The solutions of standard drug ampicillin and metal salt were also prepared in the same concentration. Inoculums of the overnight culture were prepared. 0.2 ml of the inoculums was added to the test tubes containing the solutions of the compounds of different concentrations. After the addition of sterile water to each of the test tubes,

these were incubated for 24 hours and observed for turbidity. The absorbance of the turbid solutions was measured at 520 nm. The same method was used for standard [31]. It was observed that at 2 µg/ml the absorbance is more. Less absorbance at 2.5 µg/ml and no absorbance observed at 3 µg/ml. The inhibition is more at 2.5 µg/ml. The inhibitory concentration is 2.5 µg/ml. Thus increase in coordination number in coordination and coordination of metal ion to ligand enhances microbial activity. The free metal ion was found more effective than thiosemicarbazone and complexes.

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