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Synthesis and Characterization of Six Co-Ordinate Complexes of Fe (III) Derived from N (4) Phenyl Thiosemicarbazone

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ABSTRACT

Fe (III) complexes have been synthesized by the reaction of $FeCl_3$with 5-chloro-2-hydroxy acetophenone phenyl thiosemicarbazone in presence of heterocyclic bases like pyridine (py), α/β/γ-picoline. Thiosemcarbazone has been characterized by ^{13}C, ^{1}H NMR,ESI-MS as well as IR, electronic spectra.Spectral and magnetic measurements indicated Octahedral geometry for the six coordinate complexes. The metal complexes and their corresponding thiosemicarbazone were tested against bacterial parasites. It was found that the iron complexes synthesized are more biologically active then their corresponding thioemicarbazone.

Keywords : Metal Salts, Bioactivemetalcomplexes, Antimicrobialactivity, MIC.

I. INTRODUCTION

The complexes derived from salicylaldehyde and 2–aminophenol were synthesised and characterised [1]. Magnetic electronic spectral studies provide the evidence of the existence of octahedral geometry for the complexes.Schiff base ligands by the reaction of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with 2-amino phenol and 2-amino-p-cresol respectively have been prepared [2]. Co(II) complexes were studied by elemental analysis, 1H NMR, IR, UV-Visible spectra and TGA. The molar ratio of ligand to the metal of complexes is 1:1. Co (II) complexes have a hexa coordinated octahedral configuration. The redox process of ligands and complexes in DMSO solution were studied.Schiff bases derived from condensation of 2- hydroxy-1-naphthaldehyde and 2-amino phenol have been studied [3]. The copper complexes were characterised by elemental analysis, molar conductance, electronic absorption spectra, IR and ESR spectral data and magnetic susceptibility data. The copper complexes as antibacterial agents were also studied.

The synthesis of new coordination compounds of Cu(II), Ni(II), Co(II),Sn(II), Hg(II) etc. with Schiff bases derived from 7-formyl-8-hydroxy quinoline(oxine) and 2-aminophenol have been reported by Sonbati and Bindary[4]. The ligands and the complexes were characterised by elemental analysis, IR, UV, EPR and NMR spectra together with magnetic susceptibility measurements. Infrared and NMR studies show that Schiff bases behave as monobasic and tridendate ligand, coordinating through the oxygen atom of the deprotonated phenolic group, the nitrogen atom of the azomethine group and pyridine.

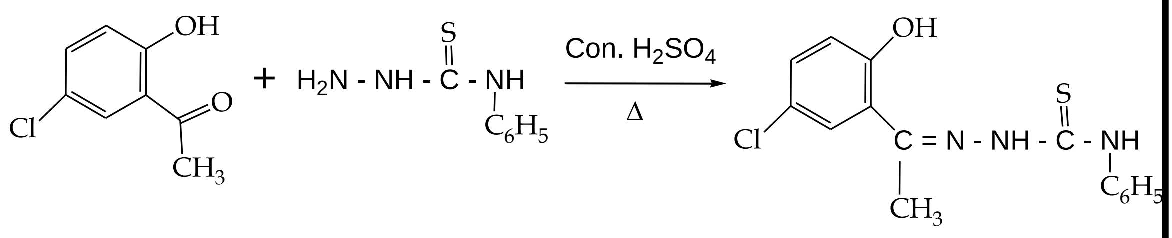
The synthesis of mixed ligand transition metalcomplexes of Cu, Ni and Co ions with Schiff base ligands derived from the condensation of o-hydroxy benzaldehyde with amino phenols and nitrogen donor amine bases, like ethylenediamine, 2-aminopyridine, and o-phenylene diamine or thiocyanate have been synthesised [5]. These complexes were characterised and their antibacterial,anti-fungal and toxicological activity have been evaluated.

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

II. EXPERIMENTAL

Materials and instrumentation

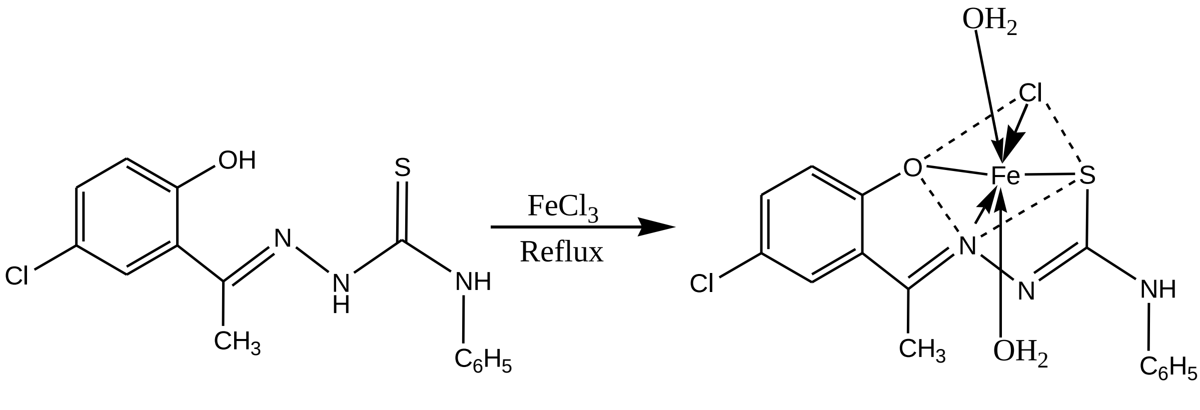
The thiosemicarbazone was synthesized by refluxing 5-chloro 2-hydroxy acetophenoneand N (4) phenyl thiosemicarbazide in ethanol in the mole ratio 1:1 for 3 hours. The pale yellow product obtained was filtered and washed with cold ethanol and then diethyl ether. It was recrystalised by hot ethanol and dried over P_2O_5 in vacuum.



SCHEME - I

Preparation of complex

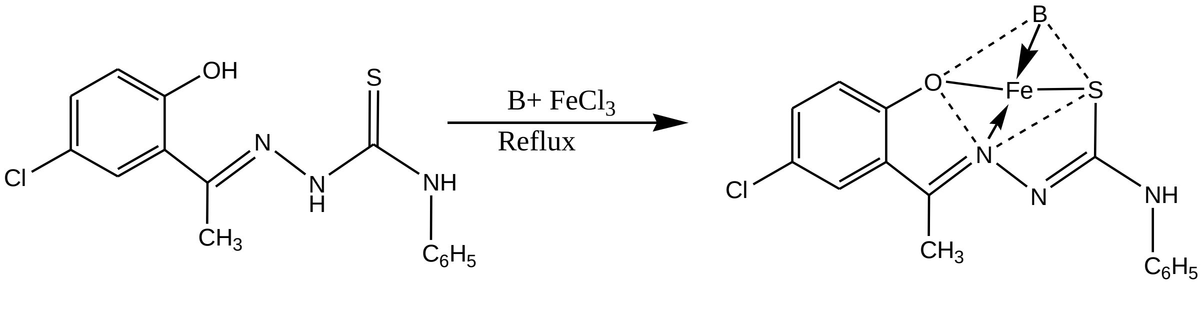
$FeCl_3$salt was dissolved in absolute ethanol.Theethanolic solution of thiosemicarbazone in slight excess over the metal:ligand ratio of 1:1 was added to it dropwise and with constant stirring.Therection mixture was refluxed for three hours.Thedarkbrownproduct thus obtained was fitered and washed well with absolute ethanol and then diethyl ether and dried over P_2O_5 in vacuum.



Scheme II

Preparation of complexes with heterocyclic bases

The complex Fe.L.B (B is heterocyclic base like pyridine, α-picoline, β-picoline,γ-picoline) was synthesized byadding slowly ehanolic solution of $FeCl_3$,heterocyclic baseto the hot ehanolic solution of ligandin the ratio 1:1:1and refluxingreaction mixtureforthree hours. The brownadduct obtained was filtered and washed with hot water, cold ethanol and diethyl ether and dried over P_2O_5 in vacuum.



Scheme III

(B= pyridine,α-picoline,β-picoline,γ-picoline)

Physical measurements-

Magnetic susceptibility measurements were carried out by by Faraday method. IR spectra were recorded in the range 4000-200 cm^{-1} range. NMR spectra were recorded in the mixture of $CDCl_3$ and 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°C.UV-Visible spectra were measured on Jasco UV-visible double beam spectrophotometer.Metal in the complex and adducts was estimated by standerdizedxylenol orange as an indicator.Chloride in the complex was estimated by Mohr's method.

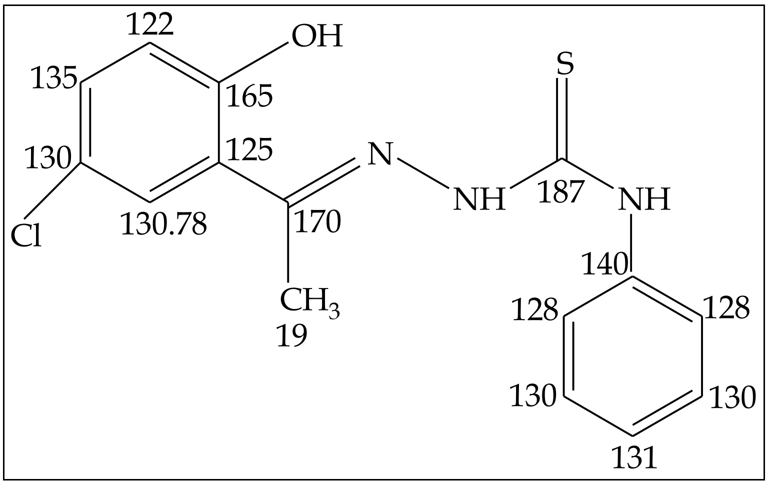
Table 1. Physical properties:

Compounds	Colour	Empirical Formula	Molar conductance $Ohm^{-1}cm^2mole^{-1}$	Magnetic Moment B.M.
L	Yellow	$C_{15}H_{14}ClN_3OS$	-	-
Fe-L.Cl.$(H_2O)_2$	Brown	$C_{15}H_{16}N_3O_3Cl_2SFe$	40.0	5.20
Fe.L.Py.$(H_2O)_2$	Brown	$C_{20}H_{21}N_4O_3ClSFe$	43.0	5.25
Fe.α-Pico.$(H_2O)_2$	Brown	$C_{21}H_{23}N_4O_3ClSFe$	48.0	5.30
Fe.L β-Pico.$(H_2O)_2$	Brown	$C_{21}H_{23}N_4O_3ClSFe$	46.0	5.32
Fe.L.γ-Pico.$(H_2O)_2$	Brown	$C_{21}H_{23}N_4O_3ClSFe$	48.0	5.27

^{1}H-NMR

NMR signals at 13.00 and 3.1 ppm are assigned to –OH and – CH_3 protons respectively. Absence of ^{2}NH proton signal suggests enolisation of ^{2}NH – C = S group to ^{2}N=C-SH. Signal at 3.9 ppm cooresponds to ^{4}NH Aromatic protons show multiples at 6.9, 7.20 , 7.60,7.65,7.77,7.30,6.20,7.29 ppm range.

^{13}C-NMR (DMSO-D_6): δppm 122 (C=C), 135 (C=C), 130 (C=C-Cl), 130.78 (C=C), 125(C=C),165 (C=C-OH),170 (C=N),19 (=C-CH_3),187 (C=S),140 (NH-C=C),128 (C=C),130 (C=C),131 (C=C),130 (C=C),128 (C=C).



(Calcd) found ESI-MS m/z, ion M+:$C_{15}H_{14}ClN_3OS$ (319.79) 319.18,$C_{15}H_{16}N_3O_3Cl_2SFe$ (445.26) 445.92,$C_{20}H_{21}N_4O_3ClSFe$ (488.91) 488.03,$C_{21}H_{23}N_4O_3ClSFe$ (502.93) 502.10,$C_{21}H_{23}N_4O_3ClSFe$ (502.93) 502.14,$C_{21}H_{23}N_4O_3ClSFe$ (502.93) 502.11.

Analytical data

1. **L:** % C 56.07 (56.33),% H 4.87 (4.41),% N 13.80 (13.14),% S 10.89 (10.03)

2.**Fe-L.Cl.(H_2O)$_2$:** % Fe 13.01 (12.58),%Cl 7.09 (7.96),%C 40.02 (40.45),%H 3.07 (3.62),%N 9.97 (9.44),%S 7.80 (7.20).% O 10.78 (10.16)

3. **Fe.L.Py.(H_2O)$_2$** :% Fe 11.90 (11.45),%C 49.78 (49.13),%H 4.91 (4.33),%N 11.97 (11.46),%S 6.01 (6.56).,% O 9.09 (9.82)

4.**Fe.α-Pico.(H_2O)$_2$**: % Fe 11.73 (11.13),%C 50.72 (50.15),%H 4.04 (4.61),%N 11.75 (11.14),%S 6.93 (6.37).% O 9.10 (9.54)

5.**Fe.L β-Pico.(H_2O)$_2$**: % Fe 11.70 (11.13),%C 50.70 (50.15),%H 4.10 (4.61),%N 11.70 (11.14),%S 6.90 (6.37).% O 9.12 (9.54)

6.**Fe.L.γ-Pico.(H_2O)$_2$**: % Fe 11.77 (11.13),%C 50.78 (50.15),%H 4.12 (4.61),%N 11.78 (11.14),%S 6.90 (6.37).% O 9.14 (9.54)

Table 2.Electronic spectral data (cm^{-1})

Compound	Mode	MLCT	n→π*	π→π*
L	DMF	-	30800	35806
Fe-L.Cl.(H_2O)$_2$	DMF	25700	32400	34700
Fe.L.Py.(H_2O)$_2$	DMF	25720	32430	34730
Fe.α-Pico.(H_2O)$_2$	DMF	25750	32450	34750
Fe.L β-Pico.(H_2O)$_2$	DMF	25786	32480	34770
Fe.L.γ-Pico.(H_2O)$_2$	DMF	25725	32465	34790

Infrared Spectroscopic data (cm^{-1})

1.**L:** ν (- OH) 3340; ν (C = N) 1678; ν (- C = S) 790, 1375 ; ν (N – N) 1075; ν (^{2}N-H) 3240; ν (C – O) 1285.

2 [Fe-L.Cl.(H_2O)$_2$]**:**ν (C = N) 1570; ν (C = N-N=C) 1560, ν (C-S) 710, 1301,ν (N-N) 1125, ν(M - N) 415, ν (M-O) 525, ν (M-S) 325, ν (C - O) 1210,ν(Fe-Cl) 370. ν(H_2O) 3530,3550.

3.[Fe.L.Py.$(H_2O)_2$]**:**ν (C = N) 1575; ν (C = N-N=C) 1565, ν (C-S) 715, 1305; ν (N-N) 1130, ν (M - N) Base 250, ν (M - N) 420, ν (M - O) 530, ν (M-S) 330, ν (C - O) 1215, Band due to HB 1450, ν(H_2O) 3540,3560.

4.[Fe.α-Pico.$(H_2O)_2$]**:**ν (C = N) 1580; ν (C = N-N=C) 1570, ν (C-S) 718, 1310,ν (N-N) 1135, ν (M - N) Base 255, ν (M - N) 425, ν (M - O) 535, ν (M-S) 335, ν (C - O) 1220, Band due to HB 1455, ν(H_2O) 3545,3565.

5.[Fe.L β-Pico.$(H_2O)_2$]**:**ν (C = N) 1585; ν (C = N-N=C) 1575, ν (C-S) 720, 1315,ν (N-N) 1140, ν (M - N) Base 260, ν (M - N) 430, ν (M - O) 540, ν (M-S) 340, ν (C - O) 1230, Band due to HB 1460, ν(H_2O) 3550,3570.

6.[Fe.L.γ-Pico.$(H_2O)_2$]**:**ν (C = N) 1590; ν (C = N-N=C) 1580, ν (C-S) 725, 1320,ν (N-N) 1145, ν (M - N) Base 270, ν (M - N) 435, ν (M - O) 545, ν (M-S) 345, ν (C - O) 1240, Bands due to HB 1465, ν(H_2O) 3555,3575.

TGA analysis data:

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

1. [Fe-L.Cl.$(H_2O)_2$]: First step, 114.0 °C, Mass loss 4.05 % second step, 134.0 °C, Mass loss, 8.50 % Third Step 240.0 °C, Mass loss, 32.0 % Fourth Step, 375.0 °C, Mass loss 63.0 %, Residue 800 °C, % of Fe_2O_3, 58.12 (58.39).
2. [Fe.L.Py.$(H_2O)_2$]**:**First step, 115 °C, Mass loss 3.20 % second step,130.0 °C, Mass loss, 7.10 % Third Step 250 °C, Mass loss, 35.0 %Fourth Step, 370.0°C, Mass loss, 65.0 %, Residue, 790.0 °C, % of Fe_2O_3, 53.90 (53.18).
3. [Fe.α-Pico.$(H_2O)_2$]**:**First step, 115.0 °C, Mass loss 3.15 % second step, 130.0 °C, Mass loss, 7.76 % Third Step 249.0 °C, Mass loss, 30.0 % Fourth Step, 365.0°C, Mass loss 62.0 %, Residue 800 °C, % of Fe_2O_3, 51.21 (51.70).
4. [Fe.L β-Pico.$(H_2O)_2$]**:**First step, 115.0 °C, Mass loss 3.17 % second step, 132.0 °C, Mass loss, 7.70 % Third Step 250 °C, Mass loss, 29.0 % Fourth Step, 366.0°C, Mass loss, 65.0 %, Residue, 779.0 °C, % of Fe_2O_3, 51.21 (51.70)..
5. [Fe.L.γ-Pico.$(H_2O)_2$]**:**First step, 114.0 °C, Mass loss 3.16 % second step, 131.0 °C, Mass loss, 7.77 % Third Step 245.0 °C, Mass loss, 33.0 % Fourth Step, 370.0 °C, Mass loss 60.0 %, Residue 800 °C, % of Fe_2O_3, 51.21 (51.70).

BIOLOGICAL ACTIVITY(AGAR PLATE DIFFUSION METHOD)

Table 3. Absorbances of solutions of L , Fe (III) complexes and standered

Compound	Staphylococcus aureu		Bacilus subtilis		Escherichia Coli		Peudomonas aeruginosa	
	Gram positive				Gram negative			
	2 μg/ml	2.5 μg/ml	2 μg/ml	2.5 μg/ml	2 μg/ml	2.5 μg/ml	2 μg/ml	2.5 μg/ml
L	0.70	0.41	0.72	0.42	0.73	0.41	0.74	0.43
Fe-L.Cl.$(H_2O)_2$	0.63	0.34	0.65	0.23	0.65	0.24	0.68	0.25
4Fe.L.Py.$(H_2O)_2$	0.63	0.33	0.65	0.27	0.66	0.23	0.65	0.26
Fe.α-Pico.$(H_2O)_2$	0.68	0.34	0.67	0.24	0.68	0.26	0.70	0.28
Fe.Lβ-ico.$(H_2O)_2$	0.69	0.36	0.69	0.25	0.71	0.25	0.69	0.27
Fe.L.γ-co.$(H_2O)_2$	0.62	0.33	0.63	0.25	0.64	0.23	0.69	0.24
Fe-L.Cl.$(H_2O)_2$	0.23	0.17	0.24	0.19	0.16	0.25	0.14	0.27
Standard	0.16	0.14	0.14	0.14	0.26	0.15	0.17	0.14

(Std-Amphiciline)

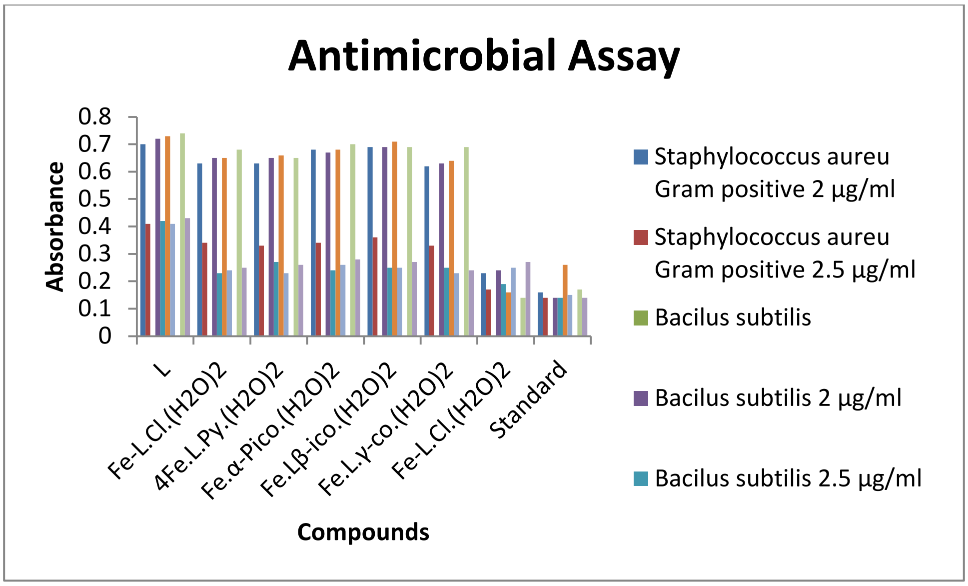


Figure 1. Antimicrobial Assay

III. RESULTS AND DISCUSSION

Physical data of thiosemicarbazone and its complexes are presented in Table 1. 1:1 ratio of metal ion, thiosemicarbazone for complex and 1:1:1 ratio for metal,thiosemicarbazone and heterocyclic base for all adducts was confirmed from elemental analysis. The solutions for conductivity measurement was made in DMF and measurements were made 30^{0}C.All complexes were found non electrolyte [6].The magnetic moments were measured at room temperature 30^{0}C .The magnetic moments are in between 5.20-5.32 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 spectral data are presented in Table no.2 The thiosemicarbazone showed band π- π*band at 35,806 cm-1 and n-π*[10,11] at 30,800 cm^{-1}[7-9]. The π- π*absorption bands are shifted to longer wavelength in complexes due to the weakening of the C=S bond conjugation system gets enhanced on complexation [12,13].The reduction in intensity of n- π*bands in the complexes is due to transfer of lone pair of electrons to the metal and coordination of azomethinenitrogen.MLCT bands are broad and observed in the region 25000-26000 cm^{-1} which are assignable to Fe→S transitions.

Coordination through azomethine nitrogen shifts^{7}C=N^1 frequency to the lower side [14].New bands in the range 415-435 cm^{-1}were observed confirms the participation of azomethine nitrogen in coordination [15,16]. There is increase in frequency of ^{1}N-^{2}N. This confirms the coordination of thiosemicarbazone to metal through the azomethine nitrogen atom. The band ^{2}N-H of thiosemicarbazone disappears in the complexes indicates the deprotonation of the ^{2}N-H proton. A thioamide band partly due to C=S found at 1375 and 790 cm^{-1} in thiosemicarbazone.It is shifted to lower side in complexes.This indicates coordination through thiolate sulfur [17]. New bands in 325-340 range were oberved due to Fe-S confirms involvement of sulfur coordination. The phenolic oxygen indicates the third coordination on loss of OH protons. This shifts ν(C-O) 1285 cm^{-1}in thiosemicarbazone to lower side in the complexes. New bands observed due to Fe-O in complexes in the range 525-540 cm^{-1} confirms coordination through oxygen.The heterocyclic base nitrogen atom occupies fourth coordination site. The band is assigned for ν (Fe-N) due to heterocyclic base in 250-270 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[18-20].

Themogravimetric analysis was carried out within a temperature range 30-800^{0}C. The decomposition of complex proceeded in steps. Hydrated molecules of water in complexes were lost in between 30-110^{0}C.

Then two coordinated water molecules were lost in the temperature range 114-116^{0}C. Mass lost at this stage is about 4-5 % for one H_2O and upto 9 % for two H_2O molecules. No change observed ~ 130^{0}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^{0}C. Finally the metal oxides were formed above 600^{0}C. The complexes decomposed at ~ 800^{0}C.

Fe (III) complex and adducts are thermally stable up to 114^{0}C and decomposition started at this temperature. The temperature range for second step is 131-135^{0}C. The third step temperature range is 245-250^{0}C. The solid residue is Fe_2O_3.The complexes prepared with metal decomposed at higher temperature.. It is concluded that the thermal stability of the complexes is due to the coordination of metal ion to thiosemicarbazone [21].

The antibacterial assay was carried out by the agar plate diffusion method. Activity was measured by measuring the absorbance. Adducts prepared with heterocycic bases showed good activity against bacterial species than free thiosemicarbazone.The minimum inhibitory concentration was determined by liquid dilution method [22].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 ampicilin 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 [23].It was observed that at 2µg/ml the absorbance is more. Less absorbance at 2.5 µg/ml and no absorbance observed at 3µg/ml.The inhibition is more at 2.5 µg/ml. The inhibitory concentration is 2.5 µg/ml. Thus increase in coordination number and coordination of metal ion to ligand enhance microbial activity.

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