



Synthesis, Spectroscopic, Thermal and *in-vitro* Biological studies of some pyrazolone based Fe(III) heterochelates

Chintan P. Somaiya^{1*}, Dinesh S. Patel¹ and Darshan H. Jani²

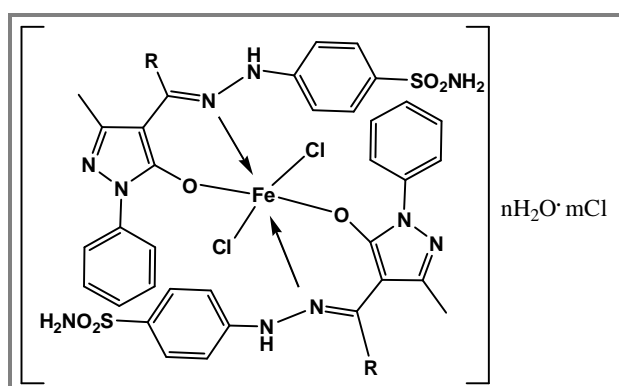
1. Shree P.M Patel Institute of Post Graduate Studies and Research in Science, Anand-388001, Gujarat, **INDIA**
Recognized Research Center of Sardar Patel University, V.V. Nagar-388 120, Gujarat for
Ph. D (Applied Chemistry), Ph. D (Forensic Science) and M. Phil (Chemistry)
2. Department of Chemistry, OM College of Science, BKNM University, Junagadh -362001, Gujarat, **INDIA**
Email: somaiyachintan11@gmail.com

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ABSTRACT

In this work novel organic based compound sulphonamide phenyl hydrazone derivatives and their thermal and biological activities were investigated. A new series of sulphonamide phenyl hydrazone containing ligand and their Fe(III) based heterochelate were synthesized by various acyl chloride. The structure of sulphonamide phenyl hydrazone ligands were confirmed by ¹H NMR, IR, Elemental analysis and their heterochelates were confirmed by thermal studies (TGA/DTG & DSC) and FAB Mass spectroscopy. All the synthesized compounds were screened for their In-Vitro biological study against Gram+ve (*Bacillus megaterium*) and Gram-ve (*E.coli*) microorganism. The results confirmed that sulphonamide phenyl hydrazone based heterochelates have a great potential and significant for further investigation.

Graphical Abstract



TGA/DTG Analysis of $[Fe(L_4)Cl_2] \cdot 2H_2O$.

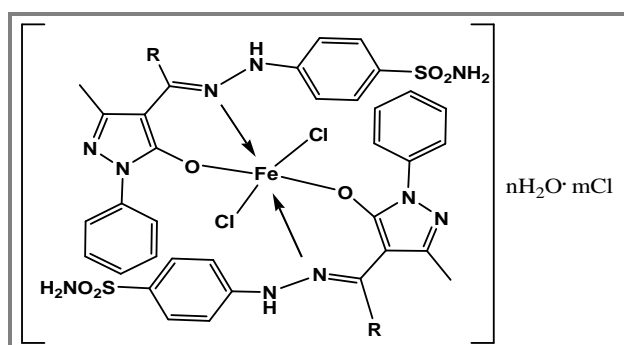
Keywords: Heterochelate, Biological Activity, Sulphonamide phenyl hydrazone, Acyl pyrazolone, Schiff base, Thermal Studies.

INTRODUCTION

Schiff bases can be said to be one of the most researched group of chemical molecules by scientists, the reasons being their versatility, selectivity, sensitivity, stability and ease of synthesis, just to mention but a few, which have resulted in their wide applications [1–3]. In the midst of their well-researched bioactive medicinal and pharmacological applications [4–6], azomethines, as they are also called, either alone or by some sort of modification, have attracted uses as analytical reagents [7], catalysts [8, 9] and as azo compounds for use as dyes and pigments [10]. The lone pair electron in the sp^2 hybridized orbital of the azomethine nitrogen is another reason for their chemical reactivity. To a great extent the properties of the Schiff base metal complexes depend on the nature of the ligand and that of the metal ion; usually the Schiff base exhibits a certain electronic environment around a metal ion for their unique characteristics.

Pyrazolone and its derivatives form an important class of compounds and have attracted considerable scientific and applied interest. Pyrazolones especially, Acylpyrazolones are an interesting class of b-diketone compounds which are widely used for their potential application in thermal [11], fluorescence [12], analytical [13] and biological studies [14, 15]. Further, more 4-Acyl pyrazolone derivatives have potential to form different type of coordination compounds due to the several electron rich donor centers [16, 17] and the tautomeric effect of enol form and keto form [18]. Complexes containing these ligands are known for almost every transition and main group metal [19]. They are also known to show extensive solid state tautomerism and in the section of substituent with special conjugated system leads to them formation of compounds with intense stable color [20].

Accordingly, in continuous to our earlier work we have synthesized a series of sulphonamide phenyl hydrazone based ligands, these new types of chelating ligands have two donor sites. Because of the presence of two active donor site they confirm various types of heterochelates with transition metal. Here, in present work we describe synthetic, spectroscopic, thermal and in-vitro bacterial studies of some novel Fe(III) heterochelates and the general structure is shown in figure 1.



S. No.	Ligand	R	nH ₂ O	mCl
1	L ₁	-CH ₃	-	-
2	L ₂	-CH ₂ CH ₃	2 H ₂ O	2Cl
3	L ₃	-CH ₂ CH ₂ CH ₃	2 H ₂ O	1Cl
4	L ₄	-C ₆ H ₅	2 H ₂ O	-
5	L ₅	-C ₆ H ₅ NO ₂	-	-

Figure 1. The suggested structure of Heterochelate.

MATERIALS AND METHODS

Materials: All the chemicals used were of analytical grade and used without further purification. The compounds 1-phenyl-3-methyl-5-pyrazolone was purchased from Sigma Ltd (India). Acylchlorides were purchased from spectrochem, Mumbai used-without further purification.

Detection Methods: FT-IR spectra were recorded as KBr pallets on Nicolet-400D spectrophotometer. ^1H NMR spectra were recorded on Advance 400 Bruker FT-NMR instrument in DMSO-d_6 solvent. The FAB-mass spectrum of heterochelate was recorded with JEOL SX-102/DA-6000 mass spectrometer. Simultaneous TGA/DTG and DSC were obtained by a model 5000/2960 SDT. The experiment was performed in N_2 atmosphere at heating rate of $10^\circ\text{C min}^{-1}$.

General Procedure for Ligands: A 1:1 Molar ratio of 4-acyl-3-methyl-1-phenyl-2-pyrazo-5-one (amphp) with 4-sulfonamide phenyl hydrazine in 50 ml of methanol heated for 3-4 hours by adding catalytic amount of acetic acid and check reaction completion by TLC. Obtained product crystallized by 50 mL of methanol and washed with diethyl ether so primrose cream solid was obtained. Final ligands are confirmed with ^1H NMR, Mass and IR spectroscopic technique.

4-Acylated hydrazine-pyrazolone: M.F- $\text{C}_{18}\text{H}_{19}\text{N}_5\text{O}_3\text{S}$ Yield 78%; M.P. 218°C ; light pink; FT-IR (KBr, cm^{-1}): 3340 $\nu(\text{O-H})$, 3240 $\nu(\text{N-H})$, 1625 $\nu(\text{C=O})$, 1543 $\nu(\text{C=N})$; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm)=2.3 (3H, s, $-\text{CH}_3$); 2.48-2.49 (3H, s, $-\text{CH}_3$); 6.86-7.98 (Ar-H). Elemental analysis found (%) C, 56.12; H, 4.99; N, 18.09; O, 12.47 S, 8.33 calculated for $\text{C}_{18}\text{H}_{19}\text{N}_5\text{O}_3\text{S}$: C, 56.09%; H, 4.97%; N, 18.17% O, 12.45% S, 8.32%.

4-Propiylonal hydrazine-pyrazolone: M.F- $\text{C}_{19}\text{H}_{21}\text{N}_5\text{O}_3\text{S}$ Yield 76%; M.P. 215°C Cream powder; FT-IR (KBr, cm^{-1}): 3348 $\nu(\text{O-H})$, 3251 $\nu(\text{N-H})$, 1600 $\nu(\text{C=O})$, 1539 $\nu(\text{C=N})$; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm)=2.5 (3H,s, $-\text{CH}_3$); 1.20-1.24 (3H,t, $-\text{CH}_3$);2.76-2.78(2H,q, $-\text{CH}_2$) 6.89-7.99 (Ar-H). Elemental analysis found (%) C, 57.15; H, 5.32; N, 17.55 S, 8.05 O, 12.08 calculated for $\text{C}_{19}\text{H}_{21}\text{N}_5\text{O}_3\text{S}$: C, 57.13%; H, 5.30%; N, 17.53 % S, 8.03% O, 12.02%.

4-Butyryl hydrazine-pyrazolone: M.F- $\text{C}_{20}\text{H}_{23}\text{N}_5\text{O}_3\text{S}$ Yield 76%; M.P. 218°C ; White powder; FT-IR (KBr, cm^{-1}): 3358 $\nu(\text{O-H})$, 3226 $\nu(\text{N-H})$, 1618 $\nu(\text{C=O})$, 1531 $\nu(\text{C=N})$; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm)=2.5 (3H,s, $-\text{CH}_3$); 1.60-1.64 (2H,q, $-\text{CH}_2$);2.71-2.75(2H,m, $-\text{CH}_2$);0.97-1.60(3H,t, $-\text{CH}_3$); 6.89-7.99 (Ar-H). Elemental analysis found (%) C, 58.12; H, 5.64; N, 16.96; S, 7.77 O, 11.63 S, 7.77 calculated for $\text{C}_{20}\text{H}_{23}\text{N}_5\text{O}_3\text{S}$: C, 58.09%; H, 5.61%; N, 16.94% S, 7.75% O, 11.61%.

4-Benzoyal hydrazine-pyrazolone: M.F- $\text{C}_{23}\text{H}_{21}\text{N}_5\text{O}_3\text{S}$ Yield 71%; M.P. 256°C Light pink powder; FT-IR (KBr, cm^{-1}): 3342 $\nu(\text{O-H})$, 3182 $\nu(\text{N-H})$, 1595 $\nu(\text{C=O})$, 1516-3 $\nu(\text{C=N})$; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm)=1.88 (3H,s, $-\text{CH}_3$); 6.86-7.98(Ar-H) . Elemental analysis found (%) C, 61.75; H, 4.71; N, 15.67; O, 10.75; S, 7.16; calculated for $\text{C}_{23}\text{H}_{21}\text{N}_5\text{O}_3\text{S}$: C, 61.73%; H 4.73%; N, 15.65% S, 7.16% O, 10.73%.

4-Nitrobenzoyal hydrazine-pyrazolone: M.F- $\text{C}_{23}\text{H}_{20}\text{N}_6\text{O}_5\text{S}$ Yield 62%; M.P. 261°C ; yellow powder; FT-IR (KBr, cm^{-1}): 3200 $\nu(\text{O-H})$, 3076 $\nu(\text{N-H})$, 1597 $\nu(\text{C=O})$, 1558 $\nu(\text{C=N})$; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm)=1.92 (3H,s, $-\text{CH}_3$); 7.14 -8.26(Ar-H). Elemental analysis found (%) C, 56.11; H, 4.12; N, 17.09; S, 6.53; O, 16.27; calculated for $\text{C}_{23}\text{H}_{20}\text{N}_6\text{O}_5\text{S}$: C, 56.09%; H, 4.09%; N, 17.06 % S, 6.51% O, 16.24%.

General Procedure for Heterochelate: A general method has been adopted for the preparation and isolation of heterochelate. Hot methanolic solution of anhydrous FeCl_3 (10 mmol) and solution of respective Schiff bases (10 mmol) was mixed in 1:1 molar ratio. The mixture was heated for 4-h at 70°C and kept it overnight at room temperature. The obtained colored crystals were washed with water, methanol and finally with diethyl ether and dried in air.

RESULTS AND DISCUSSION

The structural investigation of all the prepared Schiff base ligands and heterochelates were carried out using elemental analysis, IR, ^1H NMR, FAB-Mass spectra, TGA/DTG and DSC analysis. The ^1H

NMR data of Schiff base ligands are given in experimental section. The analytical and physical data of heterochelates are given in table 1. Heterochelates were sparingly soluble in methanol and completely soluble in DMF and DMSO. All the heterochelates were stable in air for extended period of time.

Table 1. Analytical and physical data of Heterochelates

Compounds	Formula Weight	Color (% Yield)	Analysis (%) Found(Cal)						
			C	H	Cl	S	N	O	Fe
[Fe(L ₁)Cl ₂]	957.68	Brown (73)	54.25 (54.18)	3.98 (3.95)	6.98 (6.95)	6.75 (6.29)	13.05 (13.74)	9.48 (9.41)	5.51 (5.48)
[Fe(L ₂)Cl ₂]·2Cl·2H ₂ O	1078.71	Black (74)	51.44 (51.42)	4.12 (4.0)	7.48 (7.40)	6.27 (6.70)	14.69 (14.63)	10.13 (10.02)	5.87 (5.83)
[Fe(L ₃)Cl ₂]·Cl·2H ₂ O	1057.24	Dark Brown (67)	52.11 (52.39)	4.33 (4.29)	7.25 (7.19)	6.67 (6.50)	14.32 (14.21)	9.70 (9.74)	5.62 (5.67)
[Fe(L ₄)Cl ₂]·2H ₂ O	1056	Dark Brown (69)	54.22 (54.18)	3.98 (3.95)	6.90 (6.66)	6.09 (6.02)	13.81 (13.74)	9.46 (9.41)	5.54 (5.48)
[Fe(L ₅)Cl ₂]	1135.75	Green (71)	51.60 (51.89)	3.72 (3.69)	6.69 (6.66)	6.08 (6.02)	14.52 (14.47)	12.10 (12.02)	5.29 (5.24)

¹H NMR spectra of ligands: The tautomerism of pyrazolone is a subject of considerable number of studies [21, 22]. The ¹H NMR studies of Schiff base ligands were carried out in DMSO-d₆ at room temperature. The data are represented in experimental section in case of ¹H NMR spectra of ligand two sharp singlet equivalent to one and two protons observed in the range of 12-13 δ ppm corresponding to -OH group [23, 24]. This signal disappeared when a D₂O exchange experiment was carried out. Aromatic protons are observed in the range of 6.8-9.0 δ ppm and singlet's for methyl group in Schiff base ligands are observed in the range of 1.5 to 3.0 δ ppm. The NMR spectrum of L₁H is shown in figure 2. In some case signals of -NH protons are merged with aromatic protons and all of these signals are closely spaced in NMR spectrum so it is difficult to assign each signal to a particular aromatic and -NH protons unambiguously [25]. On the basis of ¹H NMR spectroscopic data it is observed that Schiff base ligand exists in Keto-Enol form in solution state.

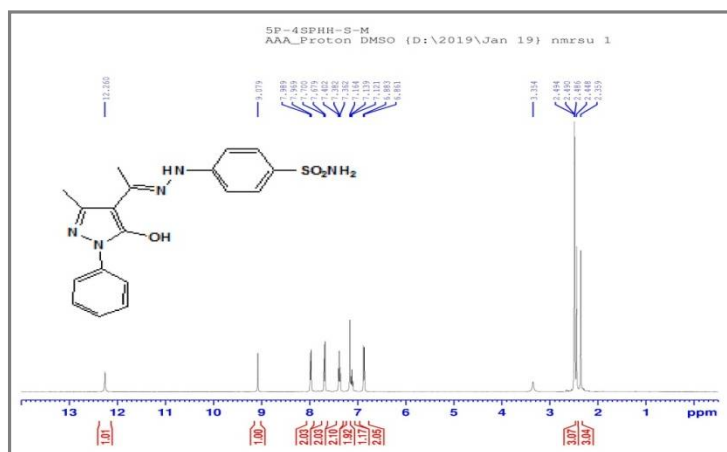
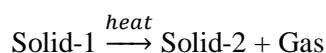


Figure 2. NMR spectrum of L₁.

Infrared Spectra: In order to study the binding mode of Schiff base (L₁ to L₅) to the Fe(III) ion in the heterochelates the IR spectra of Schiff base were compare with spectra of corresponding heterochelates. The Schiff base ligand in this investigation exhibits a broad band centered at 3199 to 3348 cm⁻¹ this indicates the involvement of the 5-OH group in intramolecular H-bonding [26-29]. With the lone pair of azomethine it also suggests that the ligand exist in enol form of solid state. The Schiff base ligand (L₁ to L₅) shows a sharp and strong band of a ν(C=N) of the acyclic azomethine group at 1539 to 1595 cm⁻¹. The observed low energy shift of this band in the heterochelates and

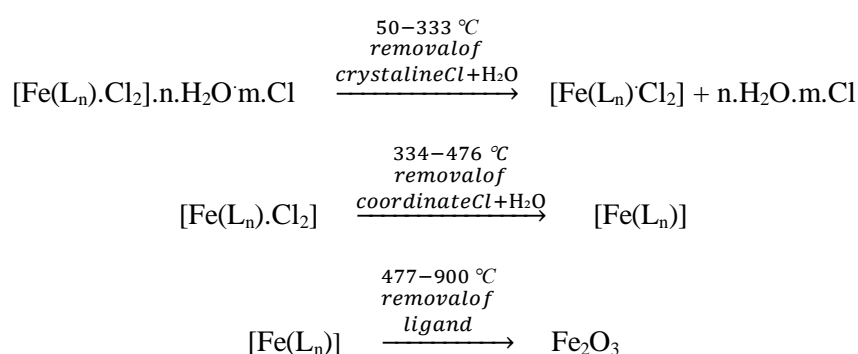
appearing at 1560 to 1571 cm^{-1} suggest the co-ordination of azomethine nitrogen [30, 31]. The IR spectra of heterochelates shows a considerable negative shift of 25-30 cm^{-1} in $\nu(\text{C}=\text{O})$ absorption of the pyrazolone group indicating a decrease in the stretching force constant of $\nu(\text{C}=\text{O})$ as a consequence of co-ordination through the oxygen atom of the ligand. All of this data confirms the fact that (L_1 to L_5) behave as a dinegative bidentate ligand and forming a conjugate chelate ring with the ligand existing in the heterochelate in the enolic form.

Thermal Studies: Each decomposition process follows the trend



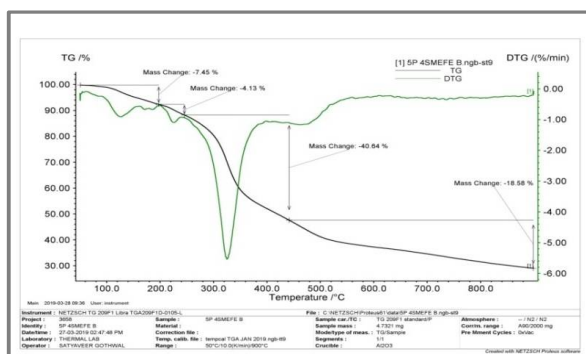
This process comprises of several stages.

The thermal fragmentation scheme for heterochelates $[\text{Fe}(\text{L}_n)\cdot\text{Cl}_2]\cdot n\cdot\text{H}_2\text{O}\cdot m\cdot\text{Cl}$ is as shown below



L_n	$n(\text{H}_2\text{O})$	$m(\text{Cl})$
1.	-	-
2.	2	2
3.	2	1
4.	2	-
5.	-	-

TG/DTG curves of heterochelates $[\text{Fe}(\text{L}_4)\cdot\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ are represented in Graph 1. The decomposition of heterochelates $[\text{Fe}(\text{L}_4)\cdot\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ takes place in three stage. The thermal dehydration and dehalogenation of this heterochelates take place in a single step between 50 to 250 $^\circ\text{C}$ with mass loss of 11.58% (10.12%). Two mol of crystalline H_2O molecule may remove in this stage. This process is accompanied by endothermic effect at 153.8 $^\circ\text{C}$. The second step which occurs in the temperature range of 251 to 400 $^\circ\text{C}$ corresponds to decomposition of some part of the L_4 ligand, the observed mass loss of 40.64% (40.48%). The endothermic peak at 219.3 $^\circ\text{C}$ corresponds to this stage is given by DSC curve.

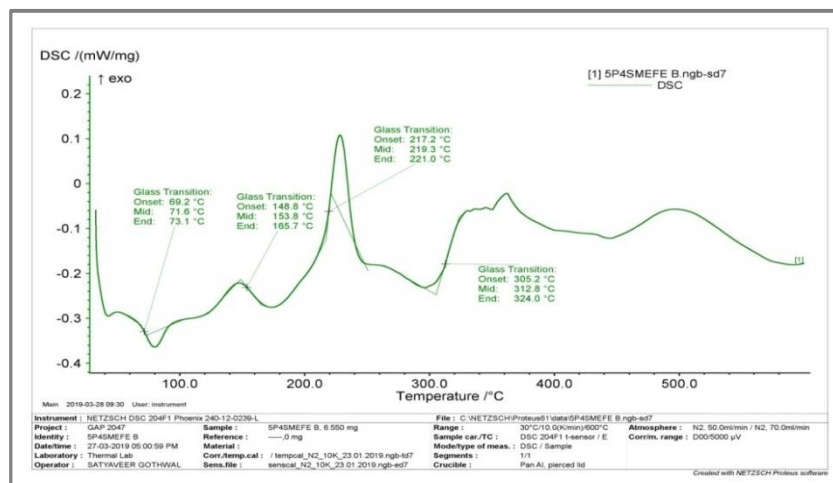


Graph 1. TGA/DTG Analysis of $[\text{Fe}(\text{L}_4)\text{Cl}_2]\cdot 2\text{H}_2\text{O}$.

The third stage is related to the decomposition of remaining part of L₄ Ligand and estimated amount of Fe₂O₃ in temperature range of 400 to 900°C accompanied by mass loss 18.58% (17.56%). The overall mass loss observed is 70.8% as compare to theoretical value 68.16% and thermodynamic data of heterochelate are reported in table 2 and DSC curves of Fe(III) heterochelates are shown in Graph 2.

Table 2. Thermo analytical results of Heterochelates

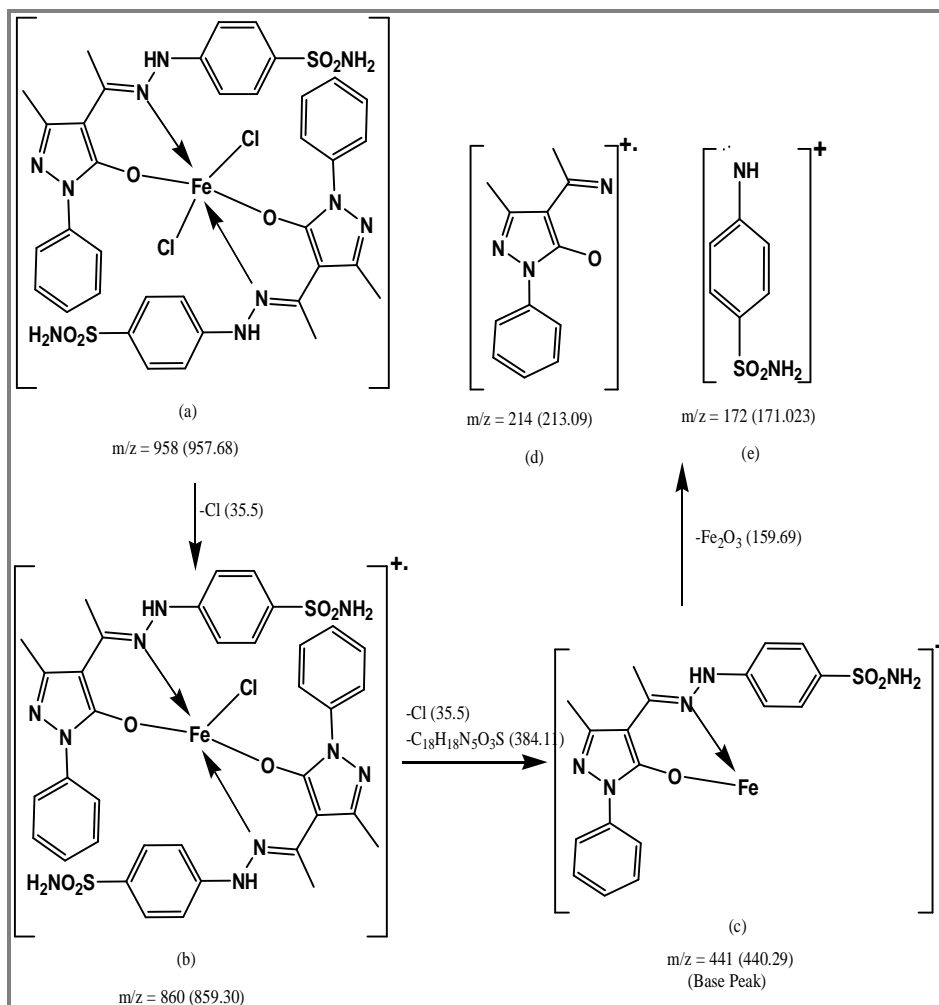
S. No.	Heterochelates	Temp. Range	Mass Loss (%) Obs. (Cal.)	Analysis
1	[Fe(L ₁)Cl ₂]	50-325 326-418 419-900	7.96 (7.91) 57.12 (57.07) 17.23 (17.19)	Two co-ordinated -Cl may loss. Some part of the ligand may loss. Remaining part of ligand removed by leaving oxide of Fe(III).
2	[Fe(L ₂)Cl ₂]·2Cl·2H ₂ O	50-228 229-437 438-900	10.38 (10.35) 45.52 (45.49) 28.72(28.68)	Two crystalline Cl and H ₂ O may loss. Two coordinated Cl & some part of ligand. Remaining part of ligand removed by leaving oxide of Fe(III).
3	[Fe(L ₃)Cl ₂]·Cl·2H ₂ O	50-213 214-433 434-900	6.97 (6.92) 47.32(47.27) 30.24(30.21)	One crystalline Cl & two H ₂ O may loss. Two coordinated Cl & some part of ligand. Remaining part of ligand removed by leaving oxide of Fe(III).
4	[Fe(L ₄)Cl ₂]·2H ₂ O	50-250 251-400 400-900	10.15(10.12) 40.52(40.48) 17.59(17.56)	Two crystalline H ₂ O & two co-ordinated Cl may loss. Some part of ligand may loss. Remaining part of ligand removed by leaving oxide of Fe ₂ O ₃
5	[Fe(L ₅)Cl ₂]	50-333 333-476 477-900	6.54(6.50) 45.22(45.18) 44.89(44.86)	Two coordinated Cl may loss. Some part of ligand may loss. Remaining part of ligand removed by leaving oxide of Fe(III)



Graph 2. DSC curve of [Fe(L₄)Cl₂].2H₂O.

FAB Study: The recorded FAB mass spectrum figure 3 and the molecular ion peak for the heterochelate [Fe(L₁)Cl₂] were used to confirm the molecular formula. The proposed fragmentation pattern is shown in scheme (1). The first peak at m/z=958 represents the molecular ion peak of heterochelates. Scheme (1) demonstrates the possible degradation path way for the investigated heterochelates. The primary fragmentation of the heterochelate take place due to the loss of coordinated Cl molecule from the species (a) to give species (b) with peak at m/z=860. Further degradation yields species (c) with loss of C₁₈H₁₈N₅O₃S and Cl. Species (c) further degrade to species (d) and (e) with loss of Fe₂O₃. The sharp peak (base peak) observed at m/z=441 represent the stable

species (c) with 99% abundance. The measured molecular weight for all the suggested degradation steps was with expected value [32].



Scheme 1. The Suggested Fragmentation pattern of $[Fe(L_1)Cl_2]$.

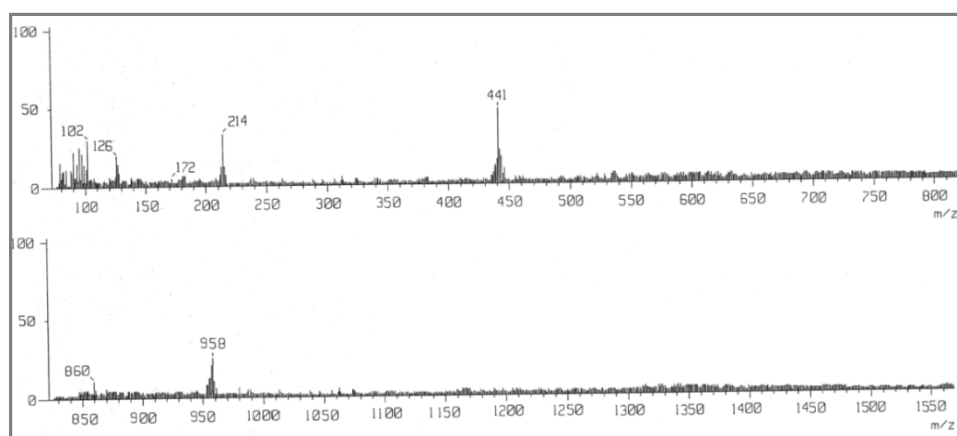


Figure 3. FAB Mass Spectrum of $[Fe(L_1)Cl_2]$.

Zone of Inhibition: A stock solution of 10 mg mL^{-1} was made by dissolving compound in minimum amount of DMF and making it up to the mark with double distilled water. The medium was made up by dissolving bacteriological agar (20 g) and Luria broth (20 g; SRL, India) in 1-liter distilled water.

The mixture was autoclave for 15 min at 120°C and then dispensed into sterilized Petri dishes, allowed to solidify and then used for inoculation. The target microorganism cultures were prepared separately in 15 mL of liquid Luria broth medium for activation. Inoculation was done with the help of micropipette with sterilized tips; 100 μ L of activated strain was placed on to the surface of an agar plate and spread evenly over the surface by means of a sterile, bent glass rod. Then two wells having diameter of 10 mm were made using a sterilized borer in each plate. Application of disks Sterilized stock solutions (10 mg mL⁻¹) were used for the application in the well of earlier inoculated agar plates. When the disks were applied, they were incubated at 30°C (Gram+ve) and 37°C (Gram-ve) for 24 h. The zone of inhibition was then measured (in mm) around the disk shown in figure 4 The control experiments were performed with only the equivalent volume of solvents without added test compounds and the zone of inhibitions was measured (in mm) shown in table 3[33].

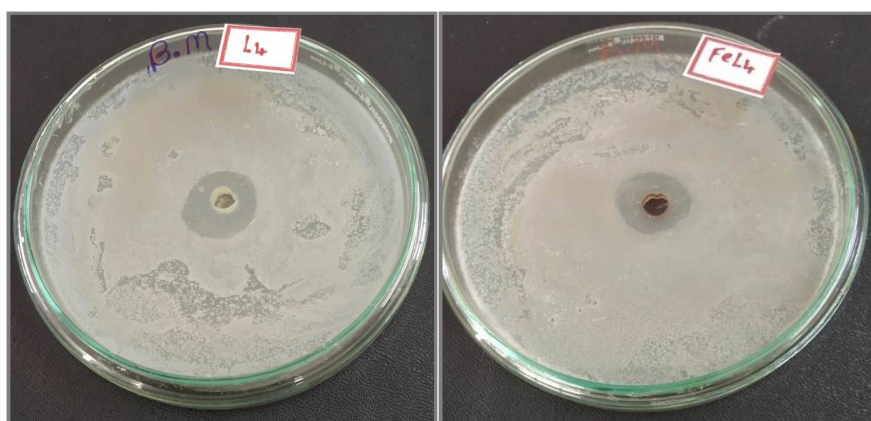


Figure 4. Zone of inhibition (mm) of Ligand and its Heterochelates

APPLICATION

All the synthesized ligands namely L1-L5 and their heterochelates ML1-ML5 (where M = Fe) were screened against the bacterial strains. The antimicrobial screening data (Table 3) shows that heterochelate exhibit more inhibitory effects towards both Gram +ve and Gram -ve bacteria than the parent ligand. The ligands (L₄) and heterochelates (FeL₃) are much powerful bactericides against *E. coli*. The increased activities of the heterochelates as compared to ligands can be explained on the basis of overtone concept [34] and chelation theory [35].

Table 3. Antimicrobial Effects of the Ligands and their Heterochelates

S. No.	Compounds	Gram+ve	Gram-ve
		<i>Bacillus megaterium</i>	<i>E. coli</i>
Ref. Drug	Penicillin	35	20
1	L ₁	17	10
2	L ₂	10	06
3	L ₃	06	07
4	L ₄	20	30
5	L ₅	15	20
6	FeL ₁	12	15
7	FeL ₂	18	21
8	FeL ₃	25	25
9	FeL ₄	17	15
10	FeL ₅	12	15

CONCLUSION

The design and synthesis of new sulphonamide phenyl hydrazone ligand have been successfully demonstrated FT-IR and ¹H NMR and Mass Spectral studies reveal that ligand exists in tautomeric enol form both in solid and solution state with intra molecular H-bonding. We have synthesized a series of some novel Fe(III) heterochelates with sulphonamide phenyl hydrazone derivative and characterize their properties. All the synthesized compounds were screened for their bioassay. The heterochelates exhibit strong activities against Gram+ve (*Bacillus magaterium*) and Gram-ve (*E. coli*) organisms in comparison with ligand and drug penicillin. Some of the ligands and heterochelates were more active against one or more bacterial strain introducing a novel class of metal based bactericidal agents.

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