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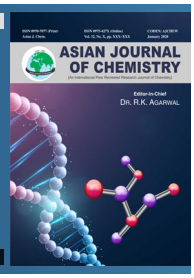

Synthesis, Spectroscopic, Thermal and *in vitro* Antimicrobial Activity of Fe(III) and Mn(III) Metal Complexes of Semicarbazone

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In this work novel pyrazolone based semicarbazone derivatives and their spectroscopic and biological activities were investigated. Pyrazolone based semicarbazone ligands and their Fe(III) and Mn(III) heterochelates were synthesized. The structure of semicarbazone ligands were confirmed by ^{1}H NMR, IR, elemental analysis and their heterochelates were confirmed by thermal studies (TGA/DTG & DSC) and FAB mass spectroscopy. All the ligands and heterochelates were screened for antimicrobial study against Gram positive (*Bacillus megaterium*, *Bacillus subtilis*) and Gram negative (*E. coli*, *Klebsiella*) microorganisms. The results confirmed that semicarbazone based heterochelates have a great potential and significant for further investigation.

Keywords: Pyrazolone, Schiff base, Semicarbazone, Antimicrobial screening, Thermal Studies, Transition metal complexes.

INTRODUCTION

Among pyrazolone, 4-acyl pyrazolone is known for two important characteristics as an important class of β-diketone, which shows a diverse coordination modes as for traditional β-diketones. Coordination chemistry is a fast budding field and the coordination chemistry of 4-acyl pyrazolone is usually reported with transition metals due to several electrons rich contributor sites [1,2] and its variety of applications [3-9]. Acyl pyrazolone and its derivatives are well known for their potential applications in different fields such as DNA binding [10,11], kinetic studies [12,13], catalyst [14,15], dyes and pigments [16] and *in vitro* biological studies [17-20]. Acyl pyrazolone is also known for the effect of tautomerism of keto form and enol form in solid or in solution state [21].

Semicarbazone exhibits tautomeric forms, which have an efficient electron delocalization along the semicarbazone moiety and the aromatic substituents on the semicarbazone skeleton can further enhance the delocalization of electron charge density. These derivative compounds usually react with metallic cations giving complexes in which semicarbazones behave as chelating ligands. In the literature survey, it is also found that semicarbazone possess good pharmacological activities such as antimicrobial [22,23], antioxidant [24], anticonvulsant [25-27], antiepileptic [28], antiproliferative [29], antitubercular [30], antiinflammatory [31] and as intermediates for the preparation of heterocyclic compounds having potent biological activity [32].

Among the transition metals, +3 oxidation state containing metals are less and furthermore coordination of such metals with organic compounds improve its potential to a higher level. In perspective on the significance of transition metal based heterochelates and our curiosity in the science of coordination compounds of pyrazolone based semicarbazone ligands in present work, we illustrate the synthesis, spectroscopic, thermal and antimicrobial screening of some Mn(III) and Fe(III) heterochelates.

EXPERIMENTAL

All the solvents and other compounds *viz*. 1-phenyl-3-methyl-5-pyrazolone (Sigma Ltd. India), semicarbazide hydrochloride (Sigma-Aldrich), acyl chlorides (Spectrochem, Mumbai) were procured and used without further purification.

FT-IR spectra were recorded as KBr pallets on Shimadzu 8201 PC. ^{1}H NMR spectra were recorded on Bruker Advance 400 FT-NMR instrument in DMSO-d_6 solvent. The FAB-mass spectrum of heterochelate was recorded with JEOL SX-102/ 2500 Da/ resolution-10,000 mass spectrometer. Simultaneous TGA/DTG and DSC thermograms were obtained from Model Diamond TG/DTA,Perkin-Elmer, USA. The experiment was performed at heating rate of 10 ºC min^{-1} in N_2 atmosphere.

General procedure for the synthesis of ligands: A 1:1 molar ethanolic solution of semicarbazide hydrochloride (10 mmol) and sodium acetate (10 mmol) was taken in two necked round bottom flask and stirred for several minutes until the solution becomes clear. An ethanolic solution of 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-one (10 mmol) was added dropwise to an above solution in 45-60 min and refluxed for 5 h at 60 ºC with constant stirring and check the reaction completion by TLC.After the reaction completion, a product was allowed to stand overnight at room temperature. Then a solid product was formed, filtered dried and recrystallized using absolute alcohol.

4-Acetylpyrazolone semicarbazone (SL1): Cream colour, yield 74 %, m.p.: 208 ºC, FT-IR (KBr, ν_{max}, cm^{-1}): 3371 (O-H), 3178 (N-H), 1635 (C=O), 1543 (C=N); ^{1}H NMR (400 MHz, DMSO-d_6): δ ppm 2.32 (3H, s, -CH_3); 2.35-2.39 (3H, s, -CH_3); 7.08-7.97 (Ar-H). Elemental analysis of $C_{13}H_{15}N_5O_2$; calcd. found (%): C, 57.13 (57.15); H, 5.53 (5.56); N, 25.63 (25.67); O, 11.71 (11.62).

4-Methoxybenzoylpyrazolone semicabazone (SL2): Purple colour, yield 78 %, m.p.: 213 ºC, FT-IR (KBr, ν_{max}, cm^{-1}): 3487 (O-H), 3371 (N-H), 1689 (C=O), 1558 (C=N); ^{1}H NMR (400 MHz, DMSO-d_6): δ ppm 1.43 (3H, s, -CH_3); 3.80-4.10 (3H, S, -OCH_3); 6.49-7.98 (Ar-H). Elemental analysis of $C_{19}H_{19}N_5O_3$; calcd. found (%): C, 62.46 (62.48); H, 5.24 (5.23); N, 19.17 (19.18); O, 13.14 (13.11).

4-Nitrobenzoylpyrazolone semicabazone (SL3): Greenish yellow colour, yield 69 %, m.p.: 221 ºC, FT-IR (KBr, ν_{max}, cm^{-1}): 3471 (O-H), 3340 (N-H), 1697 (C=O), 1519 (C=N); ^{1}H NMR (400 MHz, DMSO-d_6): δ ppm 1.8 (3H, s, -CH_3); 7.14-8.50 (Ar-H). Elemental analysis of $C_{18}H_{16}N_6O_4$; calcd. found (%): 56.84 (56.82); H, 4.24 (4.27); N, 22.10 (22.11); O, 16.82 (16.80).

4-Furoylpyrazolone semicabazone (SL4): Yellow colour, yield 71 %, m.p.: 256 ºC, FT-IR (KBr, ν_{max}, cm^{-1}): 3471 (O-H), 3140 (N-H), 1681 (C=O), 1527 (C=N); ^{1}H NMR (400 MHz,DMSO-d_6): δ ppm 1.8 (3H, s, -CH_3); 6.3-7.8 (Ar-H). Elemental analysis of $C_{16}H_{15}N_5O_3$; calcd. found (%): C, 59.07 (59.11); H 4.65 (4.64)); N, 21.53 (21.55); O, 14.75 (14.70).

General procedure for the synthesis of heterochelates: A general method has been adopted for the synthesis and isolation of heterochelates. A hot methanolic solution of $FeCl_3$ (10 mmol) and $Mn(CH_3COO)_3{\cdot}2H_2O$ (10 mmol) added dropwise within 30 min. In a solution of respective Schiff bases (20 mmol) in 1:2 molar ratio. The mixture was heated for 4 h at 70 ºC and left overnight at room temperature. The solid product was obtained washed with water, ethanol and then dried it in desiccator.

***in vitro* Antimicrobial activity:** The synthesized ligands **SL1-SL4** and their corresponding Mn(III) and Fe(III) heterochelates were tested for their antimicrobial activity by agar well diffusion method [33]. Two Gram-positive (*Bacillus subtilis* and *Bacillus megaterium*) and two Gram-negative (*Escherichia coli* and *Klebsilla*) bacteria were chosen for the antibacterial screening. The required concentration of compounds was achieved by dissolving compounds in DMSO diluents.

Minimum inhibitory (mg/mL) concentration: On the basis of the results obtained by agar well diffusion method, some of the active ligands and their heterochelates were tested for the MIC was carried out using sequential dilution technique [34]. These ligands and its heterochelates were screened using two Gram-positive (*Bacillus subtilis* and *Bacillus megaterium*) and two Gram-negative (*Escherichia coli* and *Klebsilla*) bacteria. The required concentration of compounds was achieved using DMSO as diluents.

RESULTS AND DISCUSSION

The structural investigation of all the synthesized pyrazolone based semicarbazone ligands and their metal heterochelates were carried out using elemental analysis, IR, ^{1}H NMR, FAB-Mass spectra, TGA/DTG and DSC analysis. The analytical and physical data of synthesized 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.

FTIR analysis: The information acquired from IR spectra of ligands and its corrresponding Fe(III) and Mn(III) heterochelates proposed the coupling method of ligands (**SL1-4**) and its comparision with their heterochelates. A broad band at 3487-3371 cm^{-1} indicates the participation of 5-OH group of Schiff base ligand in intramolecular H-bonding [35-38]. The Schiff base ligand (**SL1-4**) shows a sharp and strong band of a ν(C=N) of acyclic azomethine group at 1558-1519 cm^{-1}. An observed low energy shift of this band in the heterochelates of Fe(III) appeared at 1519-1435 cm^{-1} and in heterochelates of Mn(III) appeared at 1550-1481 cm^{-1} suggested the coordina-

TABLE-1
PHYSICO-ANALYTICAL DATA OF SYNTHESIZED PYRAZOLONE BASED SEMICARBAZONE HETEROCHELATES

Compounds	m.w.	Colour	Yield (%)	Elemental analysis (%): Found (calcd.)				
				C	H	N	O	Fe/Mn
$[Fe(L_1)]{\cdot}H_2O$	619	Brown	73	52.21 (52.19)	4.41 (4.38)	23.44 (23.41)	10.43 (10.39)	9.36 (9.33)
$[Fe(L_2)]4Cl{\cdot}2.5H_2O$	974	Black	71	58.35 (58.32)	4.42 (4.38)	17.92 (17.90)	12.30 (12.27)	7.17 (7.14)
$Fe(L_3)]{\cdot}1.5H_2O$	844	Black	68	53.26 (53.22)	3.48 (3.47)	20.70 (20.69)	15.78 (15.75)	6.89 (6.87)
$[Fe(L_4)]Cl{\cdot}H_2O$	761	Brown	69	55.48 (54.71)	3.75 (3.73)	19.96 (19.94)	13.69 (13.67)	7.96 (7.95)
$Mn(L_1)Ac{\cdot}2.5H_2O$	687	Brown	77	52.29 (52.27)	4.41 (4.39)	23.45 (23.44)	10.73 (10.71)	9.93 (9.91)
$[Mn(L_2)3Ac{\cdot}0.5H_2O$	972	Cream	74	58.42 (58.39)	4.41 (4.38)	17.95 (17.92)	12.29 (12.28)	7.07 (7.03)
$[Mn(L_3)]{\cdot}1.5H_2O$	843	Green	66	53.29 (53.27)	3.50 (3.48)	20.73 (20.71)	15.79 (15.77)	6.78 (6.77)
$[Mn(L_4)]{\cdot}3H_2O$	760	Yellow	76	54.80 (54.79)	3.76 (3.74)	19.99 (19.97)	13.71 (13.68)	7.84 (7.83)

tion of azomethine nitrogen [39,40]. The IR spectra of heterochelates demonstrates an impressive negative move of 10-15 cm^{-1} in ν(C=O) absorption of the coordination through the oxygen atom of ligand. This information confirmed the fact that (**SL1-4**) behave as a dinegative bidentate ligand and forming a conjugate chelate ring with ligand existing in heterochelate in the enolic form.

^{1}H NMR analysis: The ^{1}H NMR spectra of ligand SL1 showed a multiplate of proton signals due to aromatic protons observed in the range of 6.45-7.97 δ ppm and a singlet at 8.77 δ ppm represent a -NH proton of semicarbazide moiety. The proton signal at 2.32 δ ppm represents the signal probably due to -C-CH_3 group. The proton signal at 2.49 δ ppm most probably due to solvent (DMSO-d_6). The appearance of signal at 12.13 δ ppm may be due to enolic proton, however, this signal disappeared when a D_2O exchange experiment was carried out. In some case, signals of -NH protons were merged with aromatic protons and all of these signals were closely spaced in NMR spectrum so it is difficult to assign each signal to a particular aromatic and –NH protons unambiguously [41]. On the basis of ^{1}H NMR spectroscopic data, it is observed that semicarbazones exist in keto-enol form in solution state.

Thermal analysis: Thermogravimetric analysis of heterochelates $[Fe(L_1)_2]\cdot H_2O$ and $[Mn(L_1)_2]Ac\cdot 2.5H_2O$ are shown in Figs. 1-3, respectively.

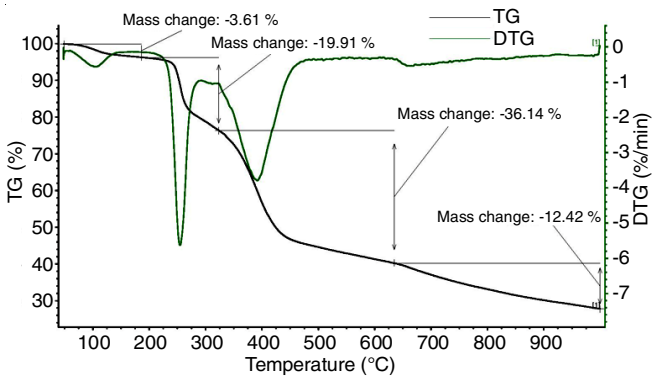


Fig. 1. TGA/DTG curve of $[Fe(L_1)_2]\cdot H_2O$

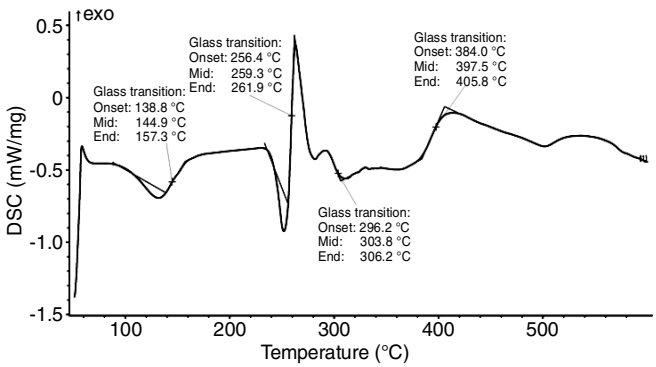


Fig. 2. DSC curve of $[Fe(L_1)_2]\cdot H_2O$

The decomposition of Fe(III) heterochelates $[Fe(L_1)_2]\cdot H_2O$ took place in three stages (Fig. 1). A thermal dehydration of this heterochelate carried out in a single step between 50 to 182 ºC with mass loss of 3.61 % (3.14 %). One mole of crystalline water molecule may remove in this stage. The second step which occurred in the temperature range of 183 to 323 ºC

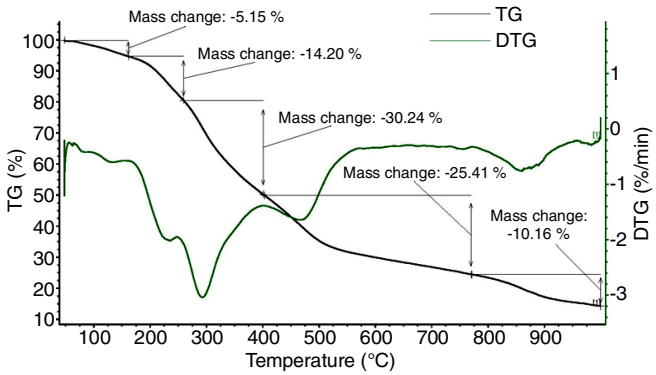


Fig. 3. DSC curve of $[Mn(L_1)_2]Ac\cdot 2.5H_2O$

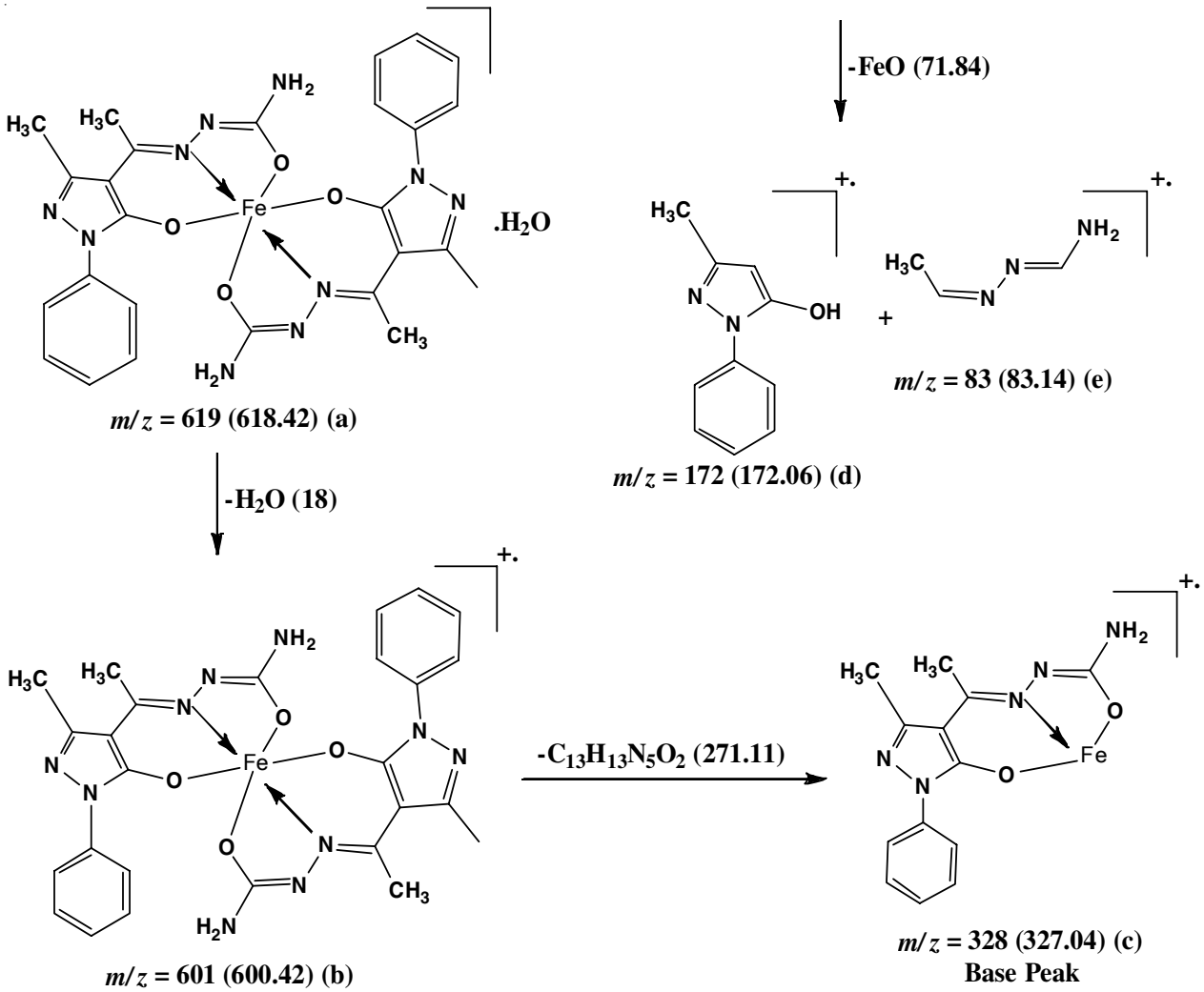
corresponds to decomposition of some part of ligand L_1, which comprises an observed mass loss of 19.91 % (19.55%). The third stage was related to the decomposition of residual part of ligand L_1 and estimated amount of oxide of iron(III) in temperature range of 324 to 999 ºC conducted by mass loss 48.56 % (48.45 %). An overall mass loss observed was 72.08 % as compared to theoretical value 71.14 % and thermodynamic data of heterochelates are reported in Table-2. The process of all three steps was accompanied by endothermic effect at 144.9, 259.3 and 397.5 ºC. These stages are shown by DSC thermogram in Fig. 2.

A decomposition of manganese(III) heterochelates $[Mn(L_1)_2]Ac\cdot 2.5H_2O$ also took place in three stages (Fig. 3). The thermal dehydration and deacetylation of heterochelate carried out in a single step between 50 to 161 ºC with mass loss of 5.15 % (5.14 %). One mole of crystalline H_2O and acetyl molecules may remove in this stage. The second step which occurred in the temperature range of 162 to 401 ºC corresponds to decomposition of some part of ligand L_1, the observed mass loss of 44.44 % (44.10 %). The third stage was related to the decomposition of residual part of ligand L_1 and estimated amount of oxide of Mn(III) in temperature range of 402 to 999 ºC conducted by mass loss 35.57 % (35.55 %). The overall mass loss observed was 85.16 % as compared to theoretical value 84.79 % and thermodynamic data of heterochelates are also shown in Table-2. The process of thermal decomposition is also confirmed by endothermic effect in DSC analysis.

FAB mass analysis: The recorded FAB mass spectrum and the molecular ion peak for heterochelate $[Fe(L_1)_2]\cdot H_2O$ were utilized to confirm the molecular formula. The recommended fragmentation pattern is shown in **Scheme-I**. The first peak at *m/z* 619 represents the molecular ion peak of heterochelates (Fig. 4). **Scheme-I** demonstrates a conceivable fragmentation pathway for the explored heterochelates. The essential discontinuity of heterochelate happened because of the loss of crystalline water molecules from fraction a to give fraction b *m/z* 601. Further, debasement yields fraction c with a loss of $C_{13}H_{13}N_5O_2$. Fraction c *m/z* 328 further degrade to fractions d and e with loss of FeO. A sharp peak (base peak) observed at *m/z* 328 represent the steady fraction c with 99 % abundance. The measured molecular weight for all the suggested degradation steps was with expected value [42]. The FAB mass spectra were also recorded for other metal heterochelates. The peak at *m/z* 688 gives molecular ion peak and used to confirm the molecular formula of heterochelate.

TABLE-2
THERMO ANALYTICAL RESULTS OF HETEROCHELATES

Heterochelates	Temperature range	Mass loss (%): Obs. (Cal.)	Analysis
$[Fe(L_1)]\cdot H_2O$	50-182	3.61 (3.14)	One crystalline H_2O may loss
	183-323	19.91 (19.55)	Some part of ligand may loss
	324-999	48.56 (48.45)	Residual part of ligand may loss by leaving oxide of Fe(III)
$[Fe(L_2)]4Cl\cdot 2.5H_2O$	50-285	19.24 (19.19)	Four crystalline Cl & 2.5 crystalline water may loss
	286-398	25.51 (25.44)	Some part of ligand may loss.
	399-999	35.25 (35.20)	Residual part of ligand may loss by leaving oxide of Fe(III)
$Fe(L_3)]\cdot 1.5H_2O$	50-175	3.23(3.19)	One and half crystalline H_2O may loss.
	176-343	21.28(21.23)	Some part of ligand may loss.
	344-999	51.81 (51.78)	Residual part of ligand removed by leaving oxide as Fe(III)
$[Fe(L_4)]Cl\cdot H_2O$	50-222	7.10(7.03)	One crystalline H_2O and one Cl may loss.
	223-410	27.39(27.31)	Some part of ligand may loss.
	411-999	44.84(44.43)	Residual part of ligand removed by leaving oxide of Fe(III).
$Mn(L_1)Ac\cdot 2.5H_2O$	50-161	5.15(5.14)	2.5 crystalline H_2O may loss.
	162-401	44.44(44.10)	Crystalline Ac and some part of ligand may loss.
	402-999	35.57(35.55)	Residual part of ligand may loss by leaving oxide of Mn(III)
$[Mn(L_2)3Ac\cdot 0.5H_2O$	50-286	19.21(19.13)	Half crystalline H_2O may loss.
	287-358	27.84(27.72)	Three crystalline Ac and some part of ligand may loss.
	359-999	39.83(39.71)	Residual part of ligand may loss by leaving oxide of Mn(III)
$[Mn(L_3)]\cdot 1.5H_2O$	50-210	3.31(3.20)	One and half crystalline H_2O may loss.
	211-412	24.57(24.51)	Some part of ligand may loss.
	413-999	49.89(49.78)	Residual part of ligand may loss by leaving oxide of Mn(III)
$[Mn(L_4)]\cdot 3H_2O$	50-220	7.14(7.10)	Three crystalline H_2O may loss.
	221-417	29.99(29.97)	Some part of ligand may loss.
	418-999	48.81(48.77)	Residual part of ligand may loss by leaving oxide of Mn(III)



Scheme-I: Suggested fragmentation pattern of $[Fe(L_1)]H_2O$

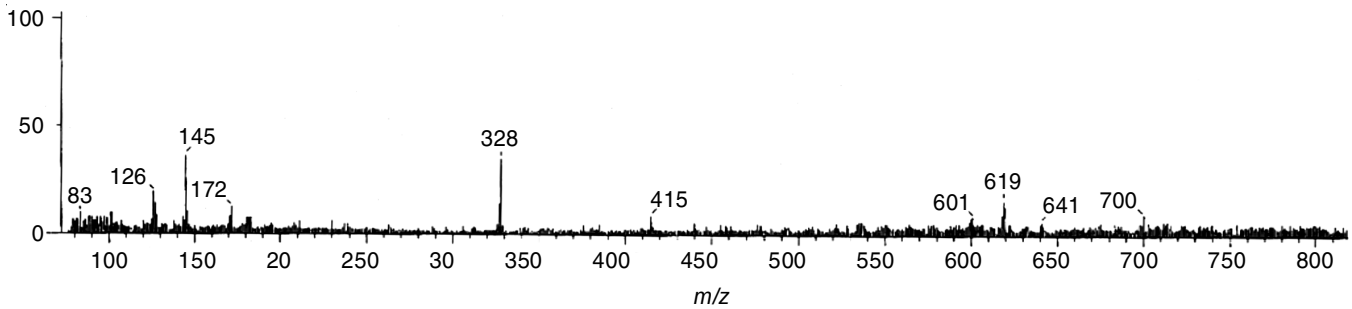


Fig. 4. FAB mass spectrum of $[Fe(L_1)]\cdot H_2O$

***in vitro* antimicrobial screening:** The enhanced in antimicrobial activity of metal heterochelates may be considered with regards to Overtone's concept [43] and Tweedy's chelation theory [44]. In accordance with Overtone's concept of cell permeability, solubility is an important factor controlling the antimicrobial activity. By making complex the polarity of metal ion reduce to greater extent, also increase in delocalization of π-electrons increase lipophilicity of heterochelates and it can easily enter to the cell and control the growth of microorganisms [45]. All the data of antimicrobial susceptibility of the heterochelates are represented in Table-3.

Result obtained from zone of inhibition indicates that the metal heterochelates were found to be progressively powerful against microorganisms contrasted with ligands. The properties of heterochelates rely upon the metal ion, elctron donationg atoms, structure of the ligand and the binding mode of ligand with metal ion. Metal ion plays a significant job in various diverse biological procedures through co-enzymatic frameworks is a subject of excellence. It suggests that some kind of bimolecular binding to the metal ions and electrostatic interactions cause the prevension of biological procedures and inhibit reproduction of organisms. The antimicrobial activities of these compounds which is tested against many bacteria, which is found strongly active for inhibition of bacteria suggest that the requirements of more investigation. The minimum inhibitory data of all the synthesized compounds are shown in Table-3.

Conclusion

In this work, synthesis and characterization of new pyrazolone based semicarbazone ligands and their Fe(III) and Mn(III) complexes were reported. FT-IR, ^{1}H NMR and mass spectral studies revealed that ligand exists in tautomeric enol form both in solid and solution state with intra molecular H-bonding. Based on the spectroscopic and thermal analysis data, a tent-

TABLE-3
ANTIMICROBIAL ACTIVITY OF SYNTHESIZED PYRAZOLONE BASED SEMICARBAZONE METAL(III) COMPLEXES

Compounds	Zone of inhibition (mm)				Minimum inhibitory (mg/mL)			
	B. megaterium	*B. subtilisis*	*E. coli*	*Klebsilla*	*B. megaterium*	*B. subtilisis*	*E. coli*	*Klebsilla*
SL_1	00	00	00	00	0.2	–	–	–
SL_2	10	00	08	00	1.0	–	0.8	–
SL_3	16	18	15	00	0.2	2.0	1.2	1.8
SL_4	20	20	12	18	0.6	1.8	0.1	–
SL_1Fe	14	17	14	00	1.4	0.2	1.4	1.2
SL_2Fe	13	10	08	00	1.3	1.0	0.8	–
SL_3Fe	10	16	11	08	1.0	1.6	1.1	0.1
SL_4Fe	00	10	00	00	–	1.0	–	–
SL_1Mn	18	00	12	00	1.6	–	1.2	–
SL_2Mn	00	00	00	00	–	–	–	–
SL_3Mn	15	00	16	11	1.5	0.1	1.1	0.2
SL_4Mn	00	10	00	09	–	–	0.9	1.0
DMSO	00	00	00	00	–	–	–	–

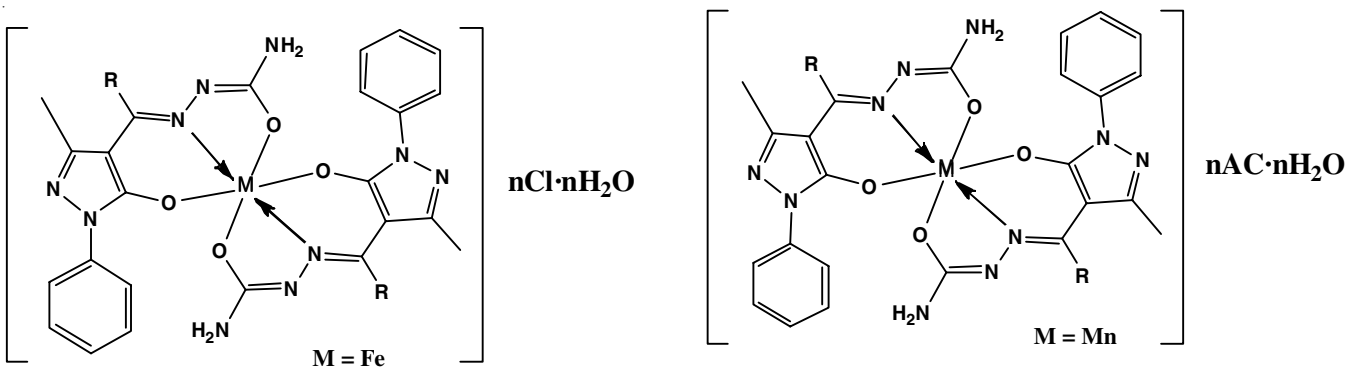


Fig. 5. Proposed structure ofpyrazolone based semicarbazone metal(III) heterochelates

ative structure of metal(III) heterochelates is proposed in Fig. 5. All the synthesized compounds were screened for their bioassay. The heterochelates display strong activities against Gram positive (*Bacillus megaterium* and *Bacillus subtilis*) and Gram negatibve (*E. coli* and *Klebsiella*) microorganisms in comparison to ligands. Some of the ligands and heterochelates were more powerful against one or more bacterial strain presenting a novel class of metal based bactericidal agents.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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