Synthesis, Spectroscopic, Thermal and In-Vitro Biological Studies of Some Transition Metal Based Heterochelates

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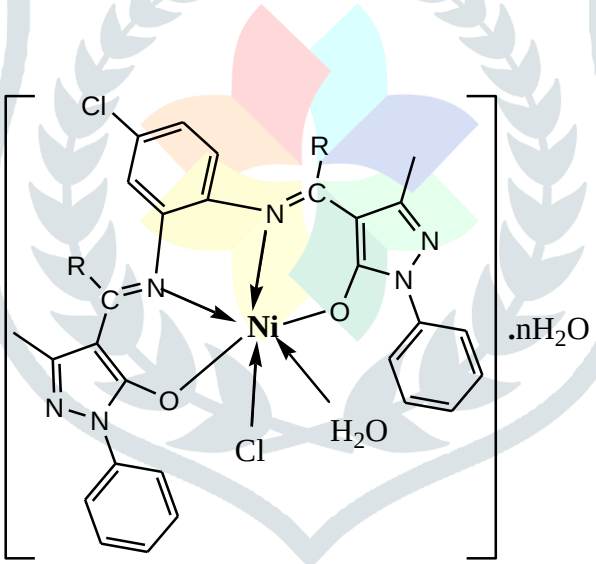
Abstract

4-acyl pyrazolone derivatives and their heterochelates are well known for their thermal fluorescence and biological activity. However, here we represent the biological and thermal studies of some 4-acyl bis pyrazolone Schiff bases as ligand and their transition metal heterochelates. Structural and spectroscopic properties have been studied on the basis of elemental analysis, FT-IR, ^{1}H-NMR spectral studies. The ligand and their heterochelate were screened for their in vitro antibacterial activity against range of Gram^{+ve} (*Bacillus cerus, Bacillus Magaterium*) and Gram^{-ve} *(E.coli, E.aerogens*) organisms.

Graphical Abstract



Keywords: Heterochelate, Biological Activity, Bis-pyrazolone, Novel Schiff base

Introduction

The Chemistry of pyrazolone and its derivatives are particularly interesting because of their potential application in thermal[1], fluorescence[2], analytical[3] and biological studies[4,5]. Further, more 4-Acyl pyrazolone derivatives have potential to form different type of coordination compounds due to the several electron rich donor centers[6,7] and the tautomeric effect of enol form and keto form[8]. Complexes containing these ligands are known for almost every transition and main group metal[9]. They are also known to show extensive solid state tautomerism and in the section of substituents with special conjugated system leads to them formation of compounds with intense stable colour[10]. Meanwhile the design of new bis pyrazolone based chelating ligand in coordination chemistry has been extensively investigated[11-20].

Accordingly, in continuous to our earlier work we have synthesized a series of bis pyrazolone based ligands, these new types of chelating ligands have two donor sites centered at 5,5'-OH groups. 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 Ni(II) heterochelates and the general structure is shown in **Figure (1).**

Experimental

Materials

All the chemicals used were of analytical grade and used without further purification. The compounds l-phenyl-3-methyl-5-pyrazolone were purchased from Sigma Ltd (India). Acyl chlorides were purchased from eualigens Fine Chemicals, India and used-without further purification.

Detection Methods

FT-IR spectra were recorded as KBr pallets on Nicolet-400D spectrophotometer. ^{1}H 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 were obtained by a model 5000/2960 SDT. The experiment was performed in N_2 atmosphere at heating rate of 10^oCmin^{-1}.

General Procedure for Ligand

A 2:1 Molar ratio of above prepared intermediates with 4-Cl-OPDA 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 crystalized by 50 ml of methanol and washed with diethyl ether so primrose yellow solid was obtained. Final ligands are confirmed with ^{1}H NMR, IR and mass spectroscopic technique.

4-Acylated bis-pyrazolone M.F-$C_{30}H_{27}ClN_6O_2$ Yield 76%; M.P. 218°C; Green powder; FT-IR (KBr,cm^{-1}): 3437.15 ν(O–H), 3226.91 ν(N–H), 1624 ν(C=O), 1593 ν(C=N); ^{1}H NMR (400 MHz,DMSO-d_6): δ (ppm) = 2.2-2.5 (3H, s, -CH_3); 2.2-2.5 (3H, s, -CH_3); 6.6-8.0 (Ar-H); (4H,m,Py-H). Elemental analysis found (%) C, 67.01; H, 5.12; N, 15.64; Cl, 6.63 O, 5.94 N, 15.59 calculated for $C_{30}H_{27}ClN_6O_2$: C, 66.85%; H, 5.05%; N, 15.59% Cl, 6.58% O, 5.94%.

4-Propiyonal bis-pyrazolone M.F-$C_{32}H_{31}ClN_6O_2$ Yield 76%; M.P. 223°C; Green powder; FT-IR (KBr,cm^{-1}): 3408.22 ν(O–H), 3224.98 ν(N–H), 1624.06 ν(C=O), 1593.2 ν(C=N); ^{1}H NMR (400 MHz,DMSO-d_6): δ (ppm) = 1.03-1.08 (3H,s,-CH_3); 2.51-2.53 (3H,t,-CH_3); 2.54-2.58 (2H,q,-CH_2) 7.1-8.0 (Ar-H); (4H,m,Py-H). Elemental analysis found (%) C, 67.78; H, 5.51; N, 14.82; Cl, 6.25 O, 5.64 N, 15.59 calculated for $C_{32}H_{31}ClN_6O_2$: C, 67.02%; H, 5.21%; N, 14.02 % Cl, 6.01% O, 5.21%.

4-Butyryl bis-pyrazolone M.F-$C_{34}H_{35}ClN_6O_2$ Yield 74%; M.P. 228°C; Green powder; FT-IR (KBr,cm^{-1}): 3423.65 ν(O–H), 3224.98 ν(N–H), 1627.92 ν(C=O), 1589.34 ν(C=N); ^{1}H NMR (400 MHz,DMSO-d_6): δ (ppm) = 1.42-1.48 (3H,s,-CH_3); 1.54-1.58 (2H,m,-CH_2); 2.38-2.41(3H,t,-CH_3); 2.53-2.55 (2H,t,-CH_2); 7.1-8.04 (Ar-H); (4H,m,Py-H). Elemental analysis found (%) C, 68.62; H, 5.93; N, 14.12; Cl, 5.96 O, 5.38 N, 15.59 calculated for $C_{34}H_{35}ClN_6O_2$: C, 68.02%; H, 5.43%; N, 14.01% Cl, 5.27% O, 5.03%.

4-Benzoyal bis-pyrazolone M.F-$C_{40}H_{31}ClN_6O_2$ Yield 79%; M.P. 249°C; Red powder; FT-IR (KBr,cm^{-1}): 3408.22 ν(O–H), 3223.05 ν(N–H), 1627.92 ν(C=O), 1589.34 ν(C=N); ^{1}H NMR (400 MHz,DMSO-d_6): δ (ppm) = 1.41-1.43 (3H,s,-CH_3); 6.71-7.38 (Ar-H) (5H,s); 7.46-8.27 (Ar-H); (4H,m,Py-H). Elemental analysis found (%) C, 72.44; H, 4.71; N, 12.67; Cl, 5.35 O, 4.83 N, 12.67 calculated for $C_{40}H_{31}ClN_6O_2$: C, 71.93%; H, 4.41%; N, 12.61% Cl, 5.01% O, 4.34%.

4-Nitrobenzoyal bis-pyrazolone M.F-$C_{40}H_{29}ClN_8O_6$ Yield 63%; M.P. 263°C; Reddish brown powder; FT-IR (KBr,cm^{-1}): 3441.01 ν(O–H), 3116.97 ν(N–H), 1620.21 ν(C=O), 1577.77 ν(C=N); ^{1}H NMR (400 MHz,DMSO-d_6): δ (ppm) = 1.41-1.43 (3H,s,-CH_3); 6.75-7.42(Ar-H) (4H,s) 7.46-8.27 (Ar-H); (4H,m,Py-H). Elemental analysis found (%) C, 63.79; H, 3.88; N, 14.88; Cl, 4.71; O, 12.75; calculated for $C_{40}H_{29}ClN_8O_6$: C, 63.08 %; H, 3.31 %; N, 14.26 % Cl, 4.23% O, 12.02%.

General Procedure for Heterochelate

A general method has been adopted for the preparation and isolation of heterochelate. Hot methanolic solution of $NiCl_2.6H_2O$(10mmol) and solution of respective Schiff bases(10mmol) were mixed in1:1 molar ratio. The pH of the solution was adjusted by drop wise addition of 25% NaOH solution in water. The mixture was heated for 4-hour at 70^0c 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. The physical and analytical data of heterochelates are shown in **Table (1).**

Result and Discussion

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

^{1}H NMR spectra of ligands

The tautomerism of pyrazolone is a subject of considerable number of studies[21,22]. The ^{1}H NMR studies of studies of Schiff base ligands were carried out in DMSO-d_6 at room temperature. The data are represented in experimental section in case of ^{1}H NMR spectra of ligand one broad singlet equivalent to one proton observed in the range of 9-10 δ ppm corresponding to -OH group[23,24]. This Signal disappeared when a D_2O exchange experiment was carried out. Aromatic protons are observed in the range of 6.5-8.5 δ ppm and singlet for methyl group in Schiff base ligands are observed in the range of 1.5 to 3.0 δ ppm. In some case signals of methyl group are overlapped with either solvent or moisture peak and all of these signals are closely spaced show it is difficult to assigned each signal to a particular methyl group unambiguously[25]. On the basis of ^{1}H NMR spectroscopic data it is observed that Schiff base ligand exists in Keto-Enol form in Solution State.

Infrared Spectra

In order to study the binding mode of Schiff base (L_1 to L_5) to the Ni(II) 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 3408 to 3441 cm^{-1} this indicates the involvement of the 5-OH group in intramolecular H-bonding [26-29]. With the lone pair of azo methine it also suggests that the ligand exist in enol form of solid state. The Schiff base ligand (L_1 to L_5) shows a sharp and strong band of a υ(C=N) of the acyclic azomethine group at 1577 to 1593 cm^{-1}. The observed low energy shift of this band in the heterochelates and appearing at 1535 to 1562 cm^{-1} suggest the co-ordination of azomethine nitrogen[30,31]. The IR spectra of heterochelates shows a considerable negative shift of 15-20 cm^{-1} in υ(C=O) absorption of the pyrazolone group indicating a decrease in the stretching force constant of υ(C=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.

TGA study

The thermal behavior of heterochelates was determine using 5000/2960 SDTA, TA instrument differential thermal analysis apparatus operating at heating rate of 10^0C per minute in the range of 50-800^0C in N_2 atmosphere. In first decomposition step the weight loss during 50 to 148^0C correspond to two crystalline water molecules. A loss in weight observed in 2nd step correspond to loss of coordinated Cl and H_2O molecules in the range of 126-405^0C. Finally, liberation of the remaining part of the ligand molecule in the temperature range 370-725^0C was observed and the remaining weight consist with metal oxide[32]. Thermodynamic data of heterochelates are reported in **Table (2)** and TGA curves of Ni(II) heterochelates are shown in **Graph (1).**

FAB Study

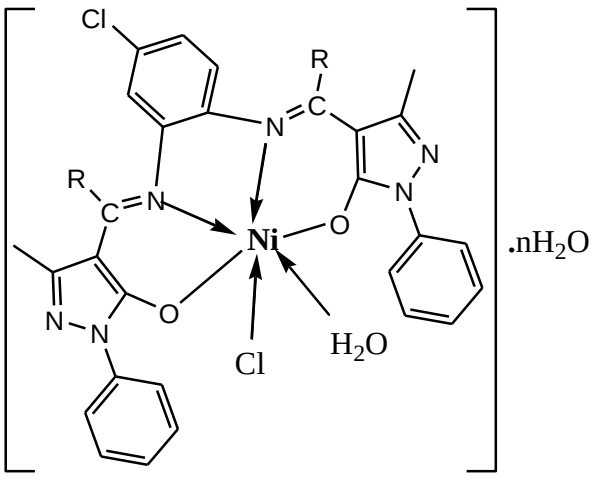
The recorded FAB mass spectrum **Figure (2)** and the molecular ion peak for the heterochelate $[Ni(L_1)Cl.H_2O].H_2O$ were used to confirm the molecular formula. The proposed fragmentation pattern is shown in **Scheme (1).** The first peak at m/z=665 represents the molecular ion peak of heterochelates. **Scheme (1)** demonstrate the possible degradation path way for the investigated heterochelates. The primary fragmentation of the heterochelate take place due to the loss of one crystalline H_2O and two coordinated Cl and H_2O molecule from the species **(a)** to give species **(b)** with peak at m/z=594. Further degradation yields species **(c)** and **(d)** with loss of $C_{12}H_{11}N_3O$. Species **(c)** and **(d)** further degrade to species **(e)** and **(f)** with loss of NiO. The sharp peak (base peak) observed at m/z=594 represent the stable species **(b)** with 99.0% abundance. The measured molecular weight for all the suggested degradation steps were with expected value[33].

Zone of Inhibition

A stock solution of 10 mg ml^{-1} was made by dissolving compound in minimum amount of DMSO and making it up to the mark with double distilled water. The medium was made up by dissolving bacteriological agar (20g) and Luria broth (20g;SRL,India) in 1-liter distilled water. The mixture was autoclave for 15 min at 120^0C 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 µl of activated strain was placed onto 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 (10mgml^{-1}) were used for the application in the well of earlier inoculated agar plates. When the disks were applied, they were incubated at 30^0C ($Gram^{+ve}$) and 37^0C ($Gram^{-ve}$) for 24 hours. The zone of inhibition was then measured (in mm) around the disk shown in **figure (3)** 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)** [34].

Conclusion

The design and synthesis of new bis pyrazolone ligand have been successfully demonstrated FT-IR and ^{1}H NMR Spectral studies revel that ligand exists in tautomeric enol form both in solid and solution state with intramolecular H-bonding. We have synthesized a series of some novel Ni(II) heterochelates with bis-pyrazolone derivative and characterize their properties. All the synthesized compounds were screened for their bioassay. The heterochelates exhibit strong activities against $Gram^{+ve}$ (*Bacillus cerus, Bacillus Magaterium*) and $Gram^{-ve}$ *(E.coli, E.Aerogen*) organisms in comparison with ligand. The heterochelates were more active against one or more bacterial strain introducing a novel class of metal based bactericidal agents.



Ligand	R	n.H2O
L_1	$-CH_3$	1 H_2O
L_2	$-CH_2CH_3$	1.5 H_2O
L_3	$-CH_2CH_2CH_3$	3 H_2O
L_4	$-C_6H_5$	2 H_2O
L_5	$-C_6H_5NO_2$	2.5 H_2O

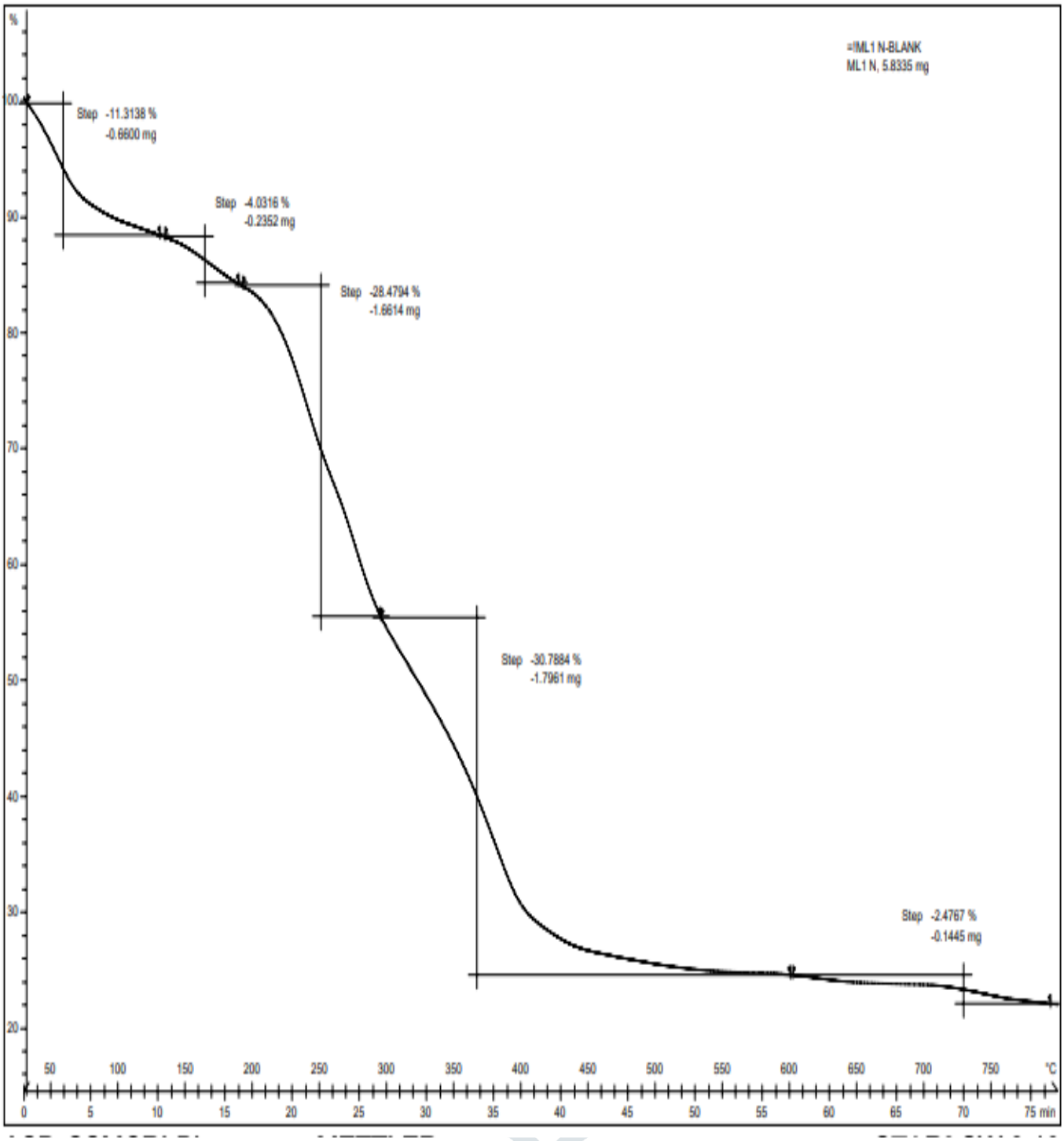
Figure 1: The suggested structure of Heterochelate

Table 1: Analytical and physical data of Heterochelates

Sample No.	Compounds	Formula Weight	Colour (%Yield)	Analysis (%) Found(Cal)					
				C	H	Cl	N	O	M
ML_1	$[Ni(L_1)Cl.H_2O].H_2O$ $C_{30}H_{29}Cl_2N_6NiO_4$	665.01	Yellow (76)	57.04 (56.96)	4.63 (4.41)	5.61 (5.43)	13.30 (13.01)	10.13 (10.02)	9.29 (9.18)
ML_2	$[Ni(L_2)Cl.H_2O].1.5\ H_2O$ $C_{32}H_{34}Cl_2N_6NiO_{4.1/2}$	702.5	Pale yellow (73)	59.89 (59.63)	4.87 (4.63)	5.52 (5.43)	13.09 (12.97)	7.48 (7.38)	9.15 (9.04)
ML_3	$[Ni(L_3)Cl.H_2O].3H_2O$ $C_{34}H_{41}Cl_2N_6NiO_6$	757.7	Dark Yellow (71)	60.97 (60.67)	5.27 (5.18)	5.29 (5.17)	12.55 (12.39)	7.17 (7.02)	8.76 (8.57)
ML_4	$[Ni(L_4)Cl.H_2O].2H_2O$ $C_{40}H_{35}Cl_2N_6NiO_5$	807.6	Reddish Yellow (69)	65.11 (65.02)	4.23 (4.12)	4.80 (4.63)	11.39 (11.21)	6.51 (6.39)	7.95 (7.68)
ML_5	$[Ni(L_5)Cl.H_2O].2.5\ H_2O$ $C_{40}H_{34}Cl_2N_8NiO_{9.1/2}$	906.6	Reddish Yellow (62)	27.11 (27.01)	1.65 (1.48)	2.00 (1.94)	4.74 (4.59)	6.21 (6.14)	3.31 (3.21)

Table 2: Thermo Analytical Results of Heterochelates

Sr. no.	Heterochelates	Temp. Range	Mass Loss (%) Obs. (Cal.)	Analysis
1	$[Ni(L_1)Cl.H_2O].H_2O$	0-138	11.31 (11.18)	One crystalline, one co-ordinated H_2O& Cl may loss.
		139-370	63.28 (63.01)	Ligand molecule may loss and remaining Ni.
		370-550	2.47 (2.39)	Remaining Ni may present as NiO
2	$[Ni(L_2)Cl.H_2O].1.5\ H_2O$	0-125	4.21 (4.0)	1.5 H_2O crystalline molecule may loss
		126-385	7.99 (7.92)	$Cl.H_2O$ Co-Ordinated molecule may loss
		386-650	83.92(83.85)	Leaving NiO residue
3	$[Ni(L_3)Cl.H_2O].3\ H_2O$	0-131	7.78(7.13)	3 H_2O crystalline molecule may loss
		132-388	7.88(7.10)	$Cl.H_2O$ Co-Ordinated molecule may loss
		388-630	78.69(78.46)	Leaving NiO residue
4	$[Ni(L_4)Cl.H_2O].2\ H_2O$	0-140	4.51(4.46)	2 H_2O crystalline molecule may loss
		141-398	6.75(6.62)	$Cl.H_2O$ Co-Ordinated molecule may loss
		399-650	83.10(82.88)	Leaving NiO residue
5	$[Ni(L_5)Cl.H_2O].2.5\ H_2O$	0-148	5.01(4.96)	2.5 H_2O crystalline molecule may loss
		148-405	6.01(5.90)	$Cl.H_2O$ Co-Ordinated molecule may loss
		406-725	87.45(87.34)	Leaving NiO residue



Graph 1: TGA Analysis of $[Ni(L_1)Cl.H_2O].H_2O$

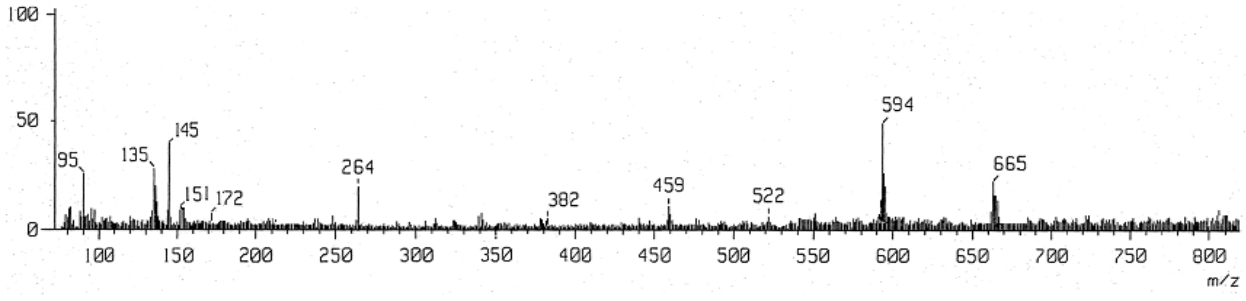


Figure 2: FAB Mass Spectrum of $[Ni(L_1)Cl.H_2O].H_2O$

Scheme 1: The Suggested Fragmentation pattern of $[Ni(L_1)Cl.H_2O].H_2O$

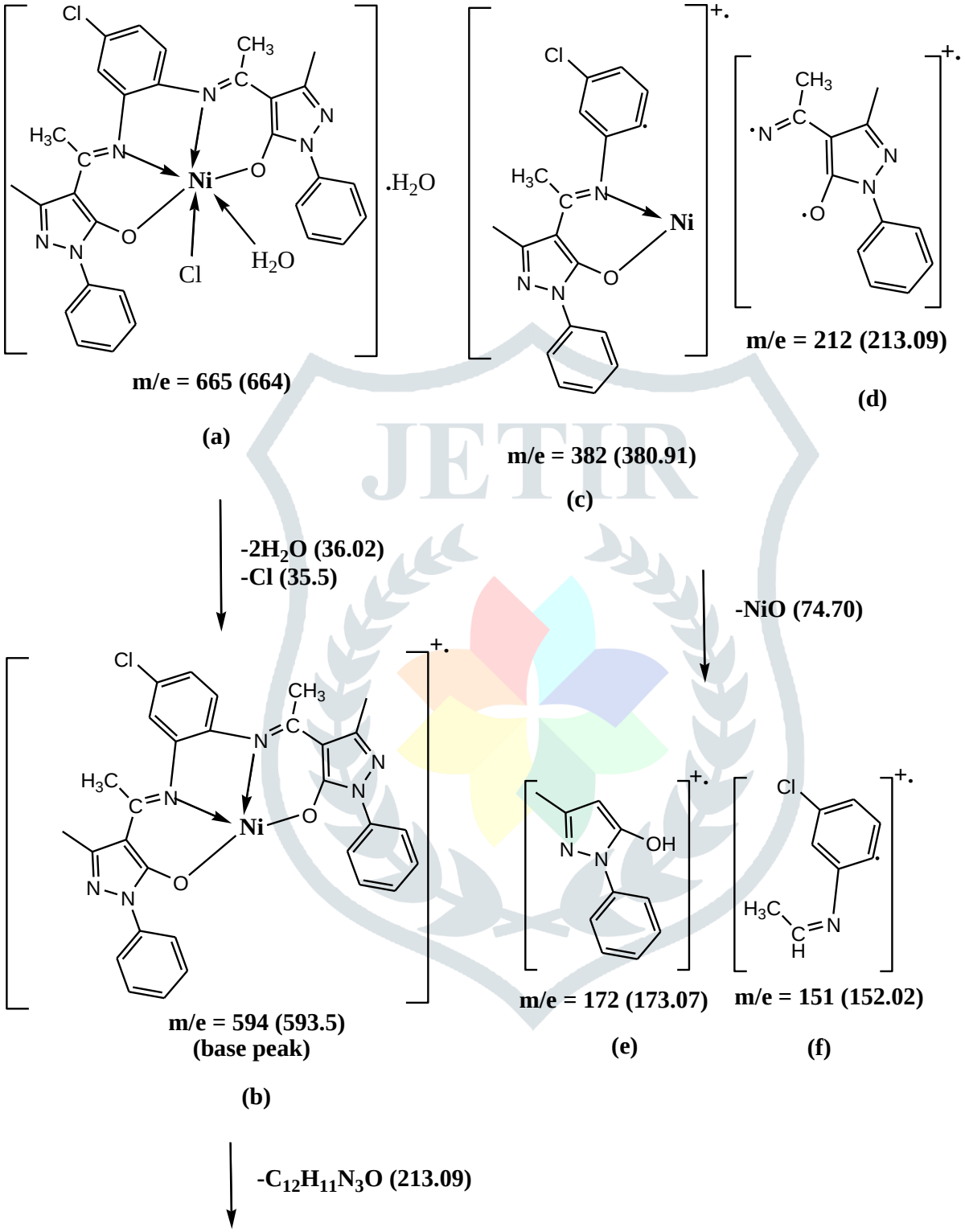


Table 3: Antimicrobial Effects of the Ligands and Their Heterochelate

Sr.No.	Compound	Gram^{+ve}		Gram^{-ve}	
		Bacillus Cerus	*Bacillus Megaterium*	*E.coli*	*E.Aerogen*
1	L_1	5	4	7	5
2	L_2	7	5	10	6
3	L_3	4	6	10	6
4	L_4	8	8	8	7
5	L_5	8	8	6	6
6	NiL_1	12	19	13	13
7	NiL_2	13	16	14	11
8	NiL_3	15	19	16	10
9	NiL_4	14	14	10	14
10	NiL_5	17	17	12	11

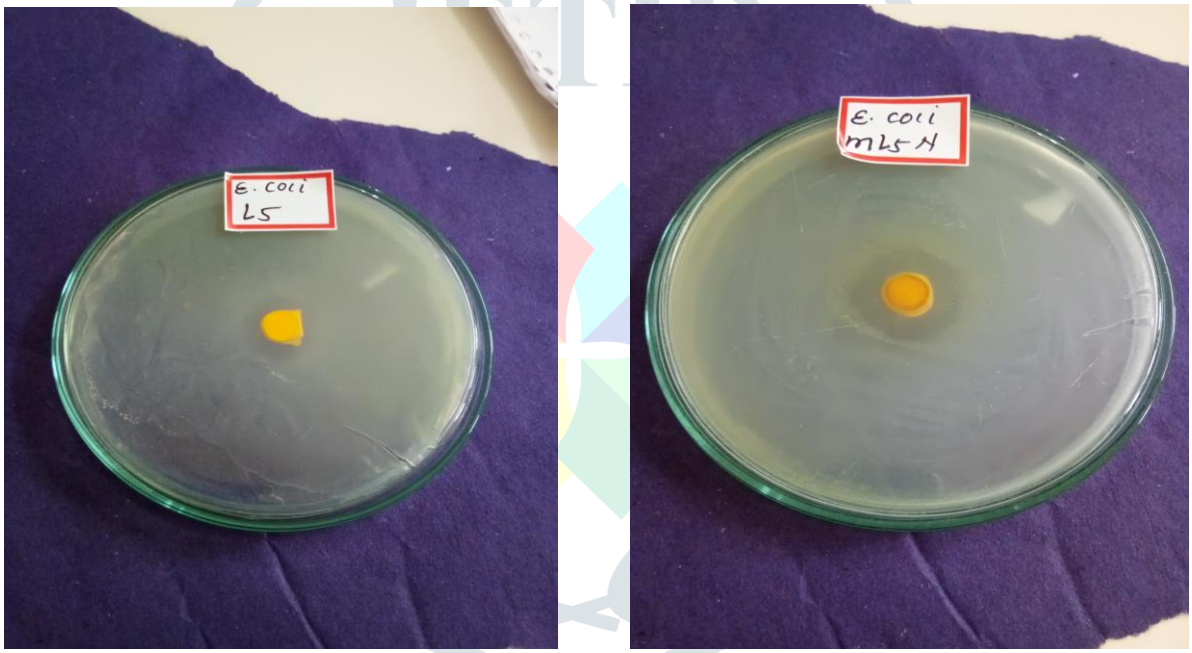


Figure 3: Zone of inhibition (mm) of Ligand and its Hetrochelates

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