

Ni(II) Heterochelates: Synthesis, spectroscopic and thermal characterization

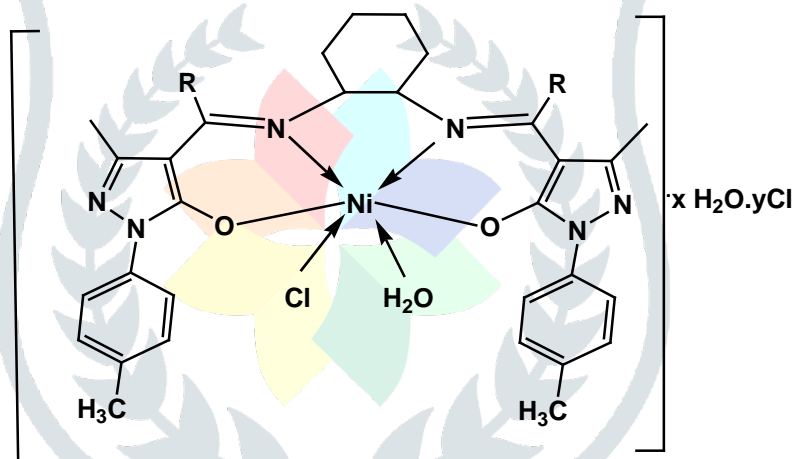
M.N. Raja*, D.H. Jani

*Research Scholar, R.K. University, Rajkot, 360020, Gujarat, India
Department of Chemistry, OM College of Science, Junagadh, 362001, Gujarat, India

Abstract

In present work organic base bispyrazolone derivatives and their thermal activities were investigated. A novel series of Bis-pyrazolone based ligand and their Ni(II) heterochelate were synthesis by various acyl chlorides of pyrazolone derivatives. The structure of bis-pyrazolone ligands were confirmed by ^1H NMR, IR, Elemental analysis and their heterochelates were confirmed by thermal studies (TG/DTG & DSC) and FAB Mass spectroscopy. The results confirm that novel bis pyrazolone based Ni(II) complex have a higher stability and important for further investigation.

Graphical Abstract:



Sr.no	Ligand	R	x	y
1	LX ₁	-CH ₃	1	-
2	LX ₂	-CH ₂ CH ₃	1.5	-
3	LX ₃	-CH ₂ CH ₂ CH ₃	1	1
4	LX ₄	-C ₆ H ₅	1.5	1
5	LX ₅	-C ₆ H ₅ NO ₂	3	1

Keywords: Ni (II) Heterochelates, Schiff Base, Spectral Studies, TG/DTG and DSC studies

Introduction

The co-ordination chemistry in recent decades, the construction of heterochelates has witnessed tremendous growth due to their interesting structure and potential properties [1-3]. During recent years there has been intense investigation of different bis pyrazolone derivatives. Many of which have demonstrated a broad spectrum of in-vitro antibacterial [4], as a catalyst [5], co-ordination polymer [6], anti-tumor [7] and solid-acid catalyst [8]. Accordingly, we have synthesized a series of bis-pyrazolone based ligands. This new type of chelating ligand has two donor sites centered at 5,5'-OH

group. Because of two active donor site they can form various types of heterochelates. In continuous to our earlier work on bis-pyrazolone base compounds [9]. Here, we describe synthesis, spectroscopic and thermal studies of some newly synthesized Ni(II) heterochelates. The general structure of ligand is shown in (Fig. 1).

Experimental

Materials

1(4-Tolyl) Phenyl 3-Methyl 5-Pyrazolone was obtained from Nutan Dye chem Pvt Ltd, Sachin Surat and were used after recrystallization. Acyl chlorides and dioxane were purchased from sigma Ltd. (India). Alcohol of HPLC grade was Purchased from FINAR. Calcium Hydroxide and Cupric Chloride were purchased from LOBA chem. Pvt. Ltd.

Techniques

Elemental analysis (C, H, N) were performed on a model 2400 Perkin-Elmer elemental analyzer. Infrared (IR) spectra were recorded on a model RX 1 FTIR Perkin Elmer as KBr pellets. ¹H NMR spectra was recorded with Bruker AV 400MHz using DMSO-d₆ as a solvent and TMS as internal reference. Mass Spectra (FAB) of the compounds were recorded at SAIF CDRI Lucknow. A TG/DTG was recorded on EX STAR 6000 TG/DTG 6300 model. DSC was carried out on universal V3.0G TA instrument in the range 0-1000°C at CSMCRI-Bhavnagar. The experiment was performed in N₂ atmosphere at heating rate of 10°Cmin⁻¹.

Synthesis of Schiff base (LX_n) (Where n=1-5)

The Schiff base were synthesized by refluxing methanolic solution of Cyclohexyl diamine (0.01 mol) with 1(4-Tolyl) Phenyl 3-methyl 5-pyrazolone (0.02 mol) in 25 ml methanolic solution heated for 3-4 hours by adding catalytic amount of glacial acetic acid and check the reaction completion by TLC. A solid mass separated was collected and washed by ether. Crystallization Was done with ethanol and then dried over CaCl₂.

4-Acylated bis-pyrazolone: M.F-C₃₂H₃₈N₆O₂ Yield 74%; M.P. 219°C; Light Yellow; FT-IR (KBr,cm⁻¹): 3520.09 ν(O-H), 3103.46 ν(N-H), 1608 ν(C=O), 1533.41 ν(C=N); ¹H NMR (400 MHz,DMSO-d₆): δ (ppm) = 2.17-2.21 (6H, s, -2CH₃); 1.48-2.0 (10H, m, -4CH₂, 2-CH); 2.24-2.28 (6H,s,-2CH₃); 2.33-2.36 (6H,s, 2CH₃) 7.16-7.85 (Ar-H); (8H,d,Py-H) 11.45-11.47(2H;s 2-OH). Elemental analysis found (%) C, 72.06; H, 7.47; N, 14.83; Cl, O, 5.94 N, Calculated for C₃₂H₃₈N₆O₂: C, 71.93%; H, 7.35%; N, 14.68%, O, 5.63%.

4-propionyl bis-pyrazolone :M.F-C₃₄H₄₂N₆O₂ Yield 73%; M.P. 238°C; Dark Yellow; FT-IR (KBr,cm⁻¹): 3221.12 ν(O-H), 3030.17 ν(N-H), 1624.06 ν(C=O), 1533.41 ν(C=N); ¹H NMR (400 MHz,DMSO-d₆): δ (ppm) = 32H (1.18-3.39) Aliphatic Protons, 8H(7.15-7.87) (Ar-H ,d, Py-H), 11.51-11.53 (2H, s; -2OH) Elemental analysis found (%) C, 72.06; H, 7.47; N, 14.83; O, 5.65 Calculated for C₃₄H₄₂N₆O₂: C, 71.93%; H, 7.26%; N, 14.02 %; O, 5.36%.

4-Butyryl bis-pyrazolone : M.F-C₃₆H₄₆N₆O₂ Yield 74%; M.P. 256°C; Yellow Powder; FT-IR (KBr,cm⁻¹): 3221.12 ν(O-H), 3084.18 ν(N-H), 1625.99 ν(C=O), 1533.41 ν(C=N); ¹H NMR (400 MHz,DMSO-d₆): δ (ppm) = 36H (0.91-4.0) Aliphatic Protons, 8H (7.07-7.92) (Ar-H ,d, Py-H), 11.56-11.58 (2H, s, -2 OH) Elemental analysis found (%) C, 72.70; H, 7.80; N, 14.13; O, 5.39 Calculated for C₃₆H₄₆N₆O₂: C, 71.85%; H, 7.26%; N, 14.01%; O, 5.01%.

4-Benzoyl bis-pyrazolone : M.F-C₄₂H₄₂N₆O₂ Yield 78%; M.P. 296°C; Reddish Brown; FT-IR (KBr,cm⁻¹): 3223.05ν(O-H), 3059.1 ν(N-H), 1627.92 ν(C=O), 1533.41 ν(C=N); ¹H NMR (400 MHz,DMSO-d₆): δ (ppm) = 26H (1.20-3.37) Aliphatic Protons, 16H(7.17-7.88) Aromatic Protons, 11.18 (1H, s; -OH). Elemental analysis found (%) C, 76.11; H, 6.39; N, 12.68; O, 4.84 Calculated for C₄₂H₄₂N₆O₂: C, 75.83%; H, 5.84%; N, 12.51% O, 4.44%.

4-Nitrobenzoyl bis-pyrazolone :M.F-C₄₂H₄₀N₈O₆ Yield 61%; M.P. 303°C;Reddish brown powder; FT-IR(KBr,cm⁻¹): 3070.68 ν(O-H), 2945.3 ν(N-H), 1622.13 ν(C=O), 1600.92 ν(C=N); ¹H NMR (400 MHz,DMSO-d₆): δ (ppm) = 24H (1.29-2.50) Aliphatic Protons, 18H(7.04-8.43) Aromatic Protons, 11.12-11.15 (1H, s; -OH).. Elemental analysis found (%) C, 67.01; H, 5.36; N, 14.98; O, 12.78; Calculated for C₄₂H₄₀N₈O₆: C, 66.98 %; H, 5.24 %; N, 14.46 %; O, 12.32%.

Synthesis of Schiff base complexes of Nickel (II)

All the Nickel (II) complexes of the Schiff base were prepared by the following general method. NiCl₂.6H₂O (0.01 mol) solution in methanol (20 mL) was added to a warm (~68°C), stirred solution of the corresponding Schiff base LX₁ (0.01 mol) or LX₂ (0.01 mol) or LX₃ (0.01 mol) or LX₄ (0.01 mol) LX₅ (0.01 mol) in 25mL methanol. After the complete addition, the reaction mixture refluxed for 6-7 h and then concentrated to half of its volume. The resulting precipitate was filtered by suction and dried in vacuum over anhydrous CaCl₂.

n	x(H ₂ O)	y(Cl)
1	1	-
2	1.5	-
3	1	1
4	1.5	1
5	3	1

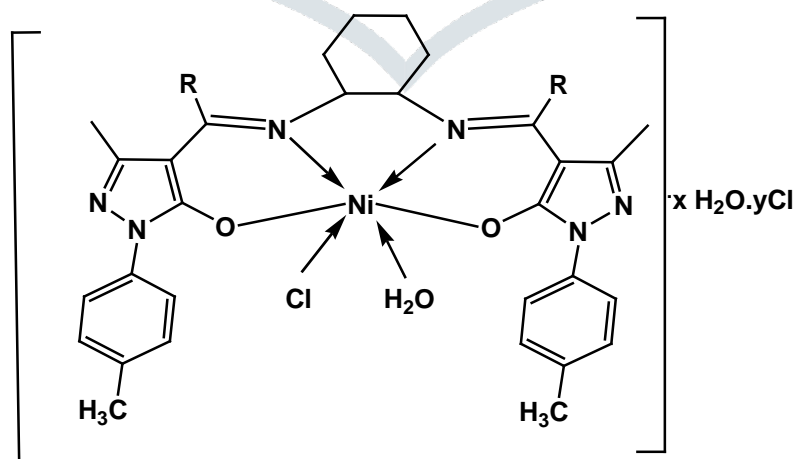
TG curve of heterochelate $[\text{Ni}(\text{LX}_1)\text{Cl}\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$ are represented in (Fig.3) and DSC curve of heterochelate are represented in (Fig.4). The decomposition of heterochelates $[\text{Ni}(\text{LX}_1)\text{Cl}\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$ takes place in three stage. The thermal dehydration and dehalogenation of this heterochelates take place in a single step between 50 to 301°C with mass loss of 5.28% (5.19%). 2 mol of coordinated H₂O and Cl molecule may remove in this stage. This process is accompanied by endothermic effect at 264.8°C and 278.9°C respectively. The second step which occurs in the temperature range of 302 to 688°C corresponds to decomposition of some part of the LX₁ ligand. The observed mass loss 44.67% (44.56%). The endothermic peak at 335°C corresponds to this stage is given by DSC curve. The third stage is related to the decomposition of related part of LX₁ Ligand and estimated amount of NiO in temperature range of 689 to 987°C accompanied by mass loss 46.02% (45.92%). The overall mass loss observed is 98.49% as compare to theoretical value 95.67%. From the above discussion proposed octahedral structure of heterochelate can be assumed as shown in (Fig.1) and thermodynamic data of heterochelate are reported in (Table 2).

FAB Study

The recorded FAB mass spectrum (Fig. 5) and the molecular ion peak for the heterochelate $[\text{Ni}(\text{LX}_1)\text{Cl}\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$ have been used to confirm the molecular formula. The mass spectrum of $[\text{Ni}(\text{LX}_1)\text{Cl}\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$ shows a large number of peaks corresponding to the successive degradation of the molecule as shown in (Fig.5) and its fragmentation pattern is given in (Scheme 1). The first peak at the m/e 708 represents the molecular ion peak of the heterochelates. The primary fragmentation of the heterochelate take place due to the loss of 2.5 H₂O & 1 Cl molecule from the species (a) to give species (b) with peak at m/e 628 (base peak) with 97% abundance. Further degradation yields species (c) with loss of C₁₃H₁₃N₃O. Species (c) further degrade to species (d) with leaving residue of NiO [21].

Conclusion

The design and synthesis of new bis pyrazolone ligand have been successfully demonstrated FT-IR and ¹H NMR Spectral studies and reveal that ligand exist in tautomeric enol form both in solid and solution state with intramolecular H-bonding. TG/DTG, DSC and FAB studies support the final structure of Ni (II) complex. On the basis of above studies, the general proposed structure of the Ni(II) complex shown in (Fig.1).



Sr.no	Ligand	R	x	y
1	LX ₁	-CH ₃	1	-
2	LX ₂	-CH ₂ CH ₃	1.5	-
3	LX ₃	-CH ₂ CH ₂ CH ₃	1	1
4	LX ₄	-C ₆ H ₅	1.5	1
5	LX ₅	-C ₆ H ₅ NO ₂	3	1

Figure 1: The proposed structure of Heterochelate

Table 1: Analytical and physical data of Heterochelates

Sample No.	Compounds	Formula Weight	Color (% Yield)	Analysis (%) Found (Cal)					
				C	H	Cl	N	O	Ni
NiLX ₁	[Ni(LX ₁)Cl.H ₂ O].H ₂ O C ₃₂ H ₄₀ ClN ₆ NiO ₄	666.8	Greenish Yellow (71)	57.64 (57.58)	6.05 (6.01)	5.32 (5.12)	12.60 (12.39)	9.60 (9.42)	8.80 (8.59)
NiLX ₂	[Ni(LX ₂)Cl.H ₂ O].1.5 H ₂ O C ₃₄ H ₄₂ ClN ₆ NiO _{4.5}	703.19	Brown (73)	60.33 (60.24)	6.25 (6.11)	5.24 (5.14)	12.42 (12.19)	7.09 (7.01)	8.67 (8.58)
NiLX ₃	[Ni(LX ₃)Cl.H ₂ O].Cl.H ₂ O C ₃₆ H ₄₈ Cl ₂ N ₆ NiO ₄	760.09	Light Green (69)	57.01 (56.95)	6.38 (6.23)	9.35 (9.19)	11.08 (11.01)	8.44 (8.24)	7.74 (7.56)
NiLX ₄	[Ni(LX ₄)Cl.H ₂ O].Cl.1.5H ₂ O C ₄₂ H ₄₂ Cl ₂ N ₆ NiO ₃	833.55	Green (74)	65.26 (65.13)	5.48 (5.34)	4.59 (4.46)	10.87 (10.67)	6.21 (6.10)	7.59 (7.43)
NiLX ₅	[Ni(LX ₅)Cl.H ₂ O].Cl.3H ₂ O C ₄₂ H ₄₆ Cl ₂ N ₈ NiO ₁₀	954.49	Dark Green (63)	52.96 (52.78)	4.87 (4.68)	7.44 (7.22)	11.76 (11.63)	16.80 (16.53)	6.16 (6.07)

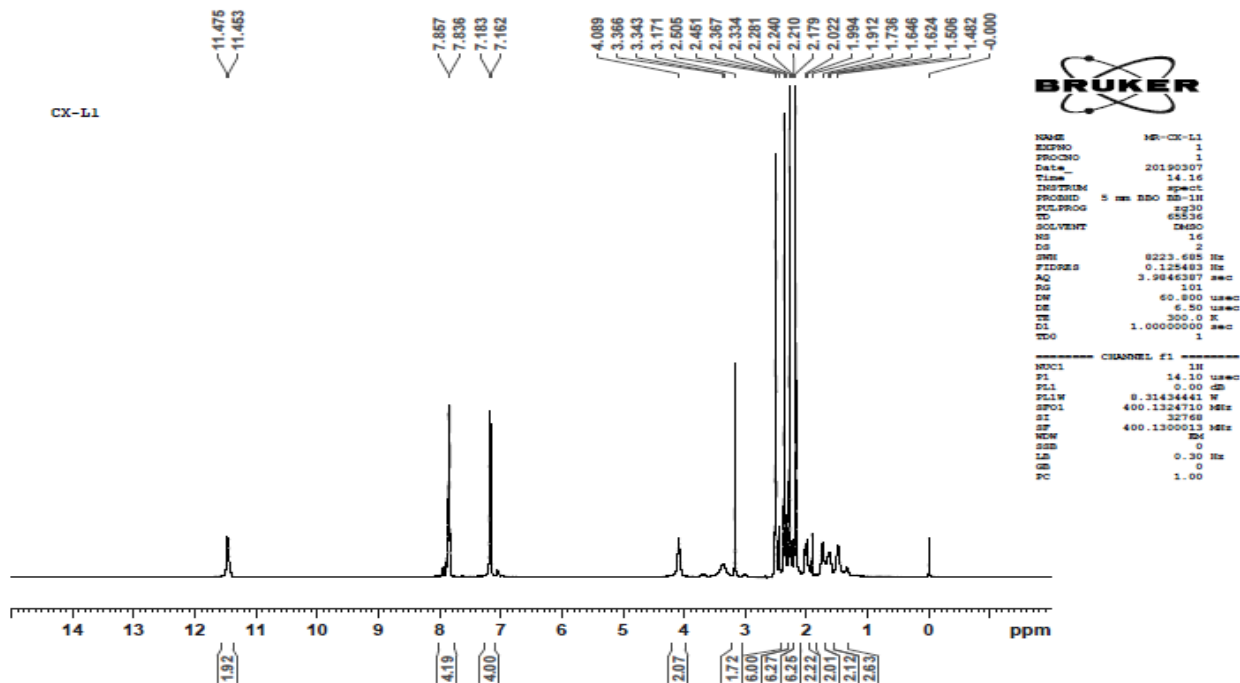


Figure 2: NMR spectrum of LX₁

Table 2: Thermo Analytical Results of Heterochelates

Sr. no.	Heterochelates	Temp. Range	Mass Loss (%) Obs. (Cal.)	Analysis
1	[Ni(LX ₁) Cl.H ₂ O].H ₂ O	50-301	5.28 (5.19)	H ₂ O crystalline molecule may loss
		302-688	44.67 (44.56)	Cl.H ₂ O Co-Ordinated molecule and some part of ligand may loss
		689-987	46.02 (45.92)	Remaining Ni may present as NiO
2	[Ni(LX ₂)Cl.H ₂ O].1.5H ₂ O	50-272	6.42 (6.39)	1.5H ₂ O crystalline molecule may loss
		273-576	39.18 (39.03)	Cl.H ₂ O Co-Ordinated molecule and some part of ligand may loss
		577-989	52.18 (52.01)	Leaving NiO residue
3	[Ni(LX ₃)Cl.H ₂ O].Cl.H ₂ O	50-275	17.97 (17.77)	Cl.H ₂ O crystalline molecule may loss
		276-603	34.33 (34.03)	Cl.H ₂ O Co-Ordinated molecule and some part of ligand may loss
		604-985	42.19 (42.06)	Leaving NiO residue
4	[Ni(LX ₄)Cl.H ₂ O].Cl.1.5H ₂ O	50-303	7.59 (7.49)	Crystalline -Cl and 1.5 H ₂ O molecule may loss
		304-606	58.19 (58.09)	Cl.H ₂ O Co-Ordinated molecule and some part of ligand may loss
		606-991	32.19 (32.03)	Leaving NiO residue
5	[Ni(LX ₅)Cl.H ₂ O].Cl.3H ₂ O	50-306	9.45 (9.37)	Crystalline -Cl and -3H ₂ O molecule may loss
		307-608	37.08 (36.99)	Cl.H ₂ O Co-Ordinated molecule and some part of ligand may loss
		609-980	49.23 (49.05)	Leaving NiO residue

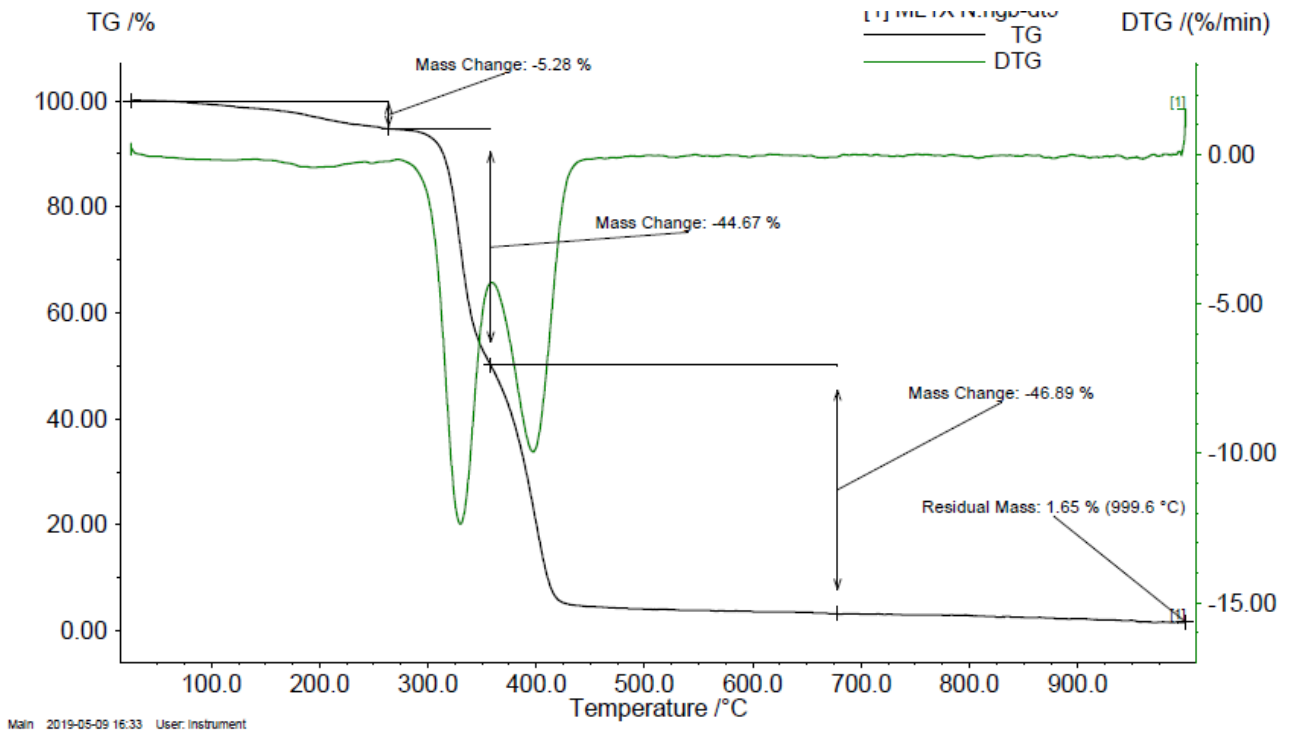


Figure 3. TG/DTG Analysis of $[\text{Ni}(\text{LX}_1)\text{Cl}\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$

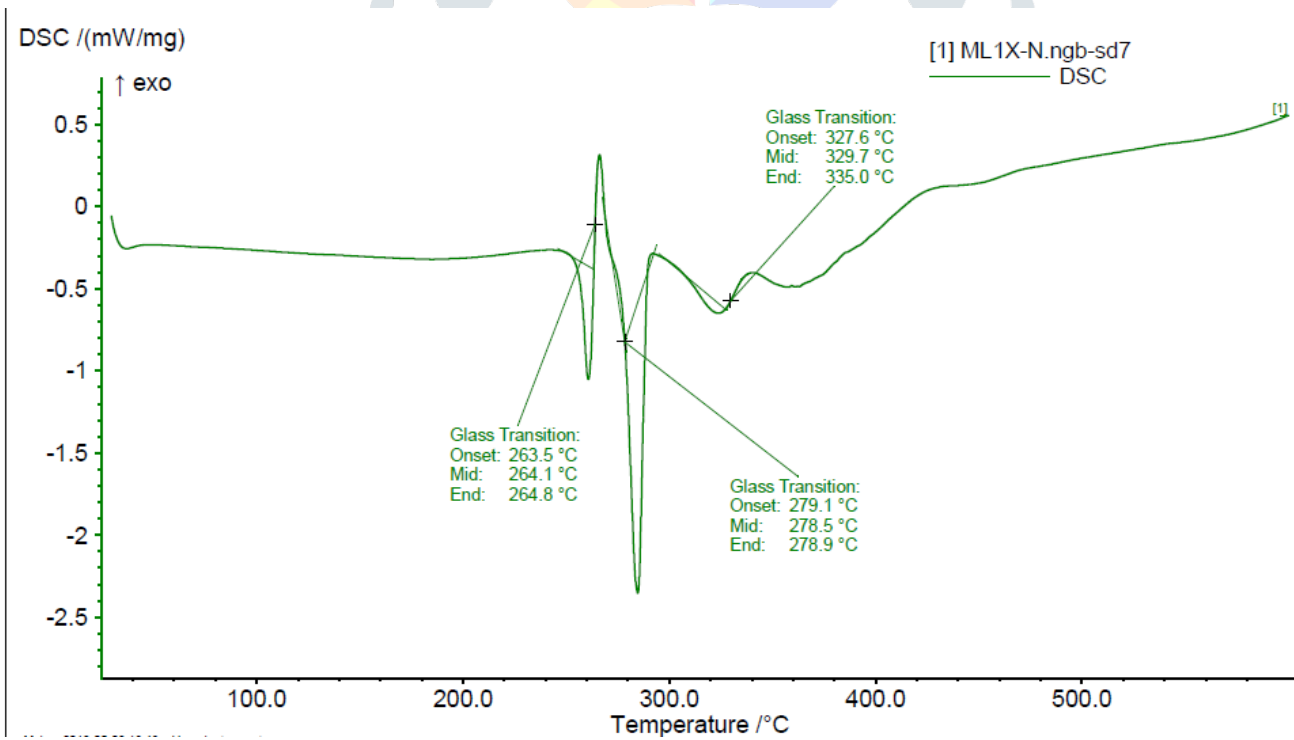


Figure 4. DSC Analysis of $[\text{Ni}(\text{LX}_1)\text{Cl}\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$

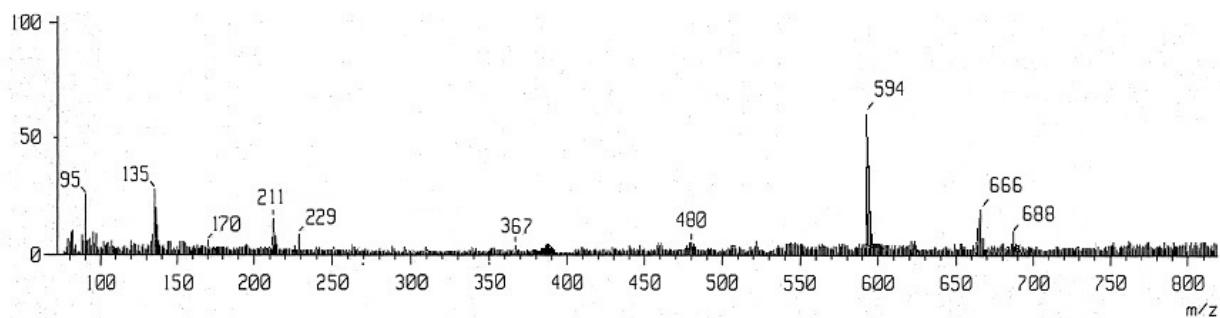
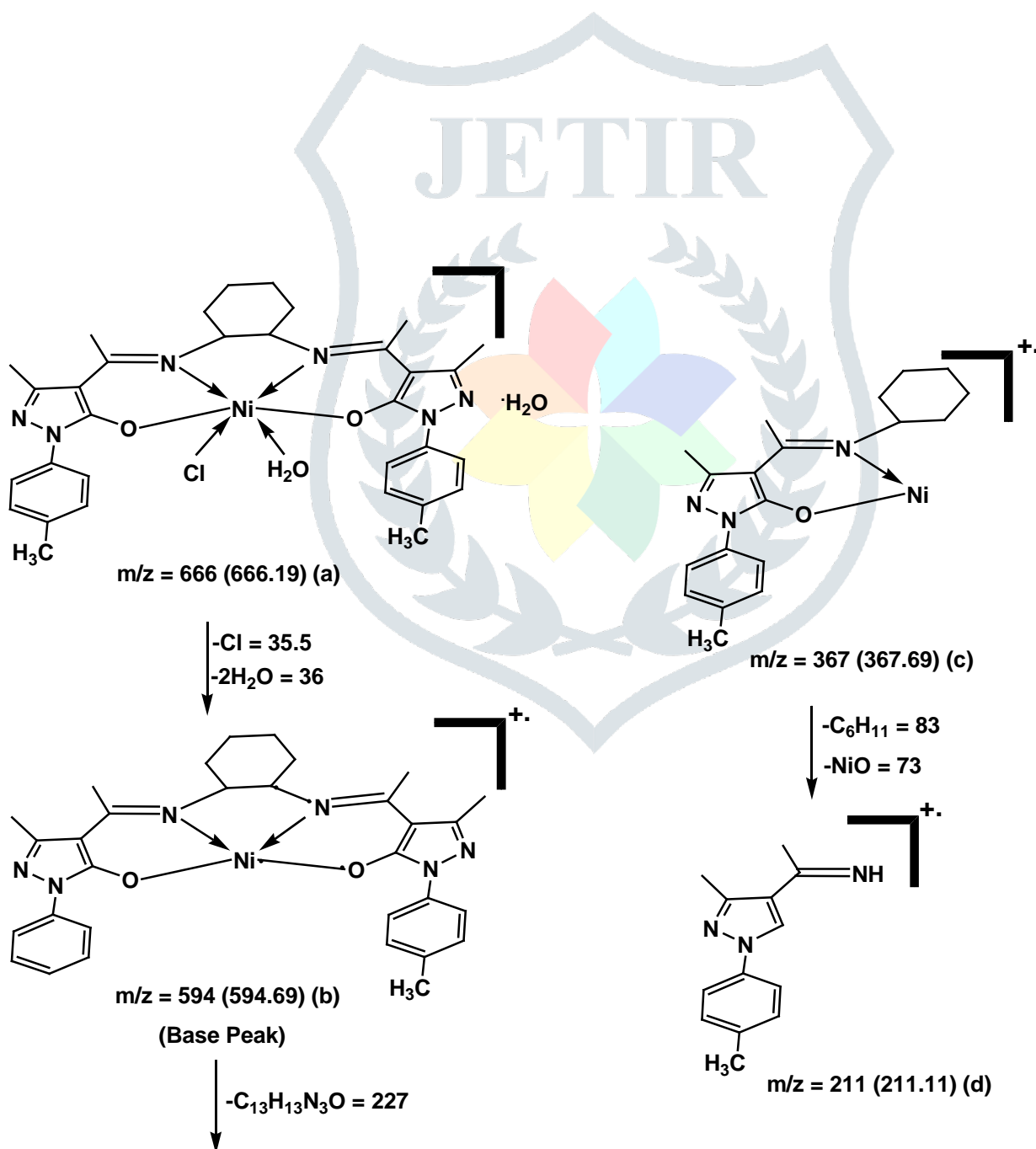


Figure 5. FAB Mass Spectrum of $[\text{Ni}(\text{LX}_1)\text{Cl}\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$



Scheme 1: The Suggested Fragmentation pattern of $[\text{Ni}(\text{LX}_1)\text{Cl}\cdot\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$

References

1. C.K Modi, D.H Jani, *Journal of Thermal Analysis and Calorimetry*, 102(3), **2010**, 1001-1010.
2. D.H Jani, C.K Modi, *Applied Organometallic Chemistry*, 25(6), **2011**, 429-436.
3. Nilesh S. Pawar, Sanjay R. Chaudhari, *Journal of Emerging Technology and innovative Research*, 6(3), **2019**, 561-569.
4. D.H Jani, H. S Patel, H.Keharia and C.K Modi, *Applied Organometallic Chemistry*, 24, **2010**, 99-111.
5. Tadatsugu Yoshikuni, *Journal of molecular catalysis A: Chemical.*, 187, **2002**, 143-147.
6. Sergey N. Semenov, Andrey Yu. Rogachev, Svetlana V. Eliseeva, Claudio Pettinari and Sergey, *Chem.Comm.*, **2008**, 1992-1994.
7. Lauin Yang, Jinguang Wu, *Transition Met. Chem*, 24, **1994**, 340-345.
8. Khodabakhsh Niknam, Dariush Saberi, Mohsen Sadegheya and Abdollah Deris, *Tetrahedron Letters*, 51, **2010**, 692-694.
9. M. N Raja, D.H Jani and S. Koradiya., *Journal of Applicable Chemistry*, 8(3), **2019**, 1241-1251.
10. Y. Akama, A. Tong, N. Matsumoto, T. Ikeda, S. Tanaka, *Vibr. Spectrosc.*, 13, **1996**, 113.
11. Y. Akama, A. Tong, *Microchem.J.*, 53, **1996**, 34.
12. J.M. Kauffmann, M. Alafandy, R. Willem, B. Mahieu, M. Alturky, M. Biesemans, F. Legros, F. Camu, M. Gielen, *Inorg. Chim. Acta.*, 255, **1997**, 175.
13. J. Kidri, D. Hadi, D. Kocjan, V. Rutar, *Org. Magnet. Reson.*, 15, **2004**, 280.
14. R.N. Jadeja, J.R. Shah, *Polyhedron.*, 26, **2007**, 1677-1685.
15. C.K Modi, B.T Thaker, *J. Theram Anal Calorim.*, 94(2), **2008**, 567-77.
16. K.R. Surati B.T Thaker, *J. coord chem.*, 59, **2006**, 1191-2002.
17. F. Marchetti, C. Pettinari, R. Pettinari, A. Cingolani, A. Rossi, M. Caruso, *J. organomet Chem.*, 645, **2002**, 134-45.
18. F. Marchetti, C. Pettinari, R. Pettinari, A. Cingolani, D. Leonesi and A. Lorenzotti, *Polyhydron*, 18, **1999**, 3041-50.
19. G.Xu , L. Liu, L. Zhang, G. Liu, D. Jia, J. Lang. *Struct Chem.*, 16, **2005**, 431-38.
20. C.K Modi, B.T Thaker, *Indian J.Chem.*, 41A, **2002**, 2544-7.
21. S.H. Patel, P.B. Pansuriya, M.R. Chhasatia, H.M. Parekh, M.N. Patel, *J. Therm. Anal. Calorim.*, 91, **2008**, 413.