IJBPAS, August, 2023, 12(8): 3590-3603

ISSN: 2277–4998

International Journal of Biology, Pharmacy and Allied Sciences (IJBPAS)

'A Bridge Between Laboratory and Reader'

www.ijbpas.com

DESIGN OF CU(II) BASED COORDINATION COMPOUNDS: SYNTHESIS, SPECTROSCOPIC AND THERMAL ASPECTS

RAJA M[1], JANI D[2,*] AND KORADIYA S[1]

1: Asst. Prof. Chemistry, Atmiya University, Rajkot, 360020, Gujarat, India

2: Associate Prof. & Head, School of Science, Dr. Subhash University, Junagadh, 362001, Gujarat, India

[*]Corresponding Author: Dr. Darshan Jani: E Mail: darshanjani09@gmail.com

Received 14th Sept. 2022; Revised 20th Oct. 2022; Accepted 7th Nov. 2022; Available online 1st Aug. 2023

https://doi.org/10.31032/IJBPAS/2023/12.8.7337

ABSTRACT

In present work we synthesized some novel bispyrazolone Schiff base ligands and their Cu(II) based coordination compounds. Newly synthesized ligands were confirmed with Elemental analysis, ^{1}H NMR, IR analysis and their coordination compounds were confirmed by FAB Mass spectroscopy and Thermal analysis like TG/DTG and DSC. The results reveals that the Cu(II) based coordination compounds having higher stability compare to Novel bispyrazolone Schiff base ligands and extremely significant for further investigations.

Keywords: Bis-pyrazolone, Coordination compounds, Cu (II) Complexes, Schiff Bases, Spectral Studies, TG/DTG and DSC studies

INTRODUCTION

The coordination chemistry play vital role in recent era, the synthesis of coordination compounds has witnessed tremendous growth due to their interesting structure and latent properties **[1-3]**. In current phase there has been influential exploration of various bis pyrazolone derived compounds. Several out of which have established a broad range of antibacterial **[4]**, catalytic **[5]**, co-ordination polymer **[6]**, anti-tumor **[7]** and solid-acid catalyst **[8]** activity. Consequently, we have prepared a sequence of bis pyrazolone based ligands. This novel type of bis pyrazolone ligand has two donor sites. Due to couple of active donor site they can form a variety of coordination compounds. In continuance to our previous work on bis-pyrazolone base compounds **[9]** here, we describe synthesis, spectroscopic and thermal aspects of some newly synthesized Cu(II) coordination compounds. The general structure of coordination compound is shown in (**Figure 1**).

Experimental

Materials

1(4-Tolyl) Phenyl 3-Methyl 5-Pyrazolone was obtained from Nutan Dye chem Pvt Ltd, Sachin Surat and was 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.^{1}H NMR spectra was recorded with Bruker AV 400MHz using DMSO-$d_6$as a solvent and TMS as internal reference. Mass Spectra (FAB) of the compounds was 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 N_2 atmosphere at heating rate of 10°C min^{-1}.

Synthesis of Schiff base (LXn) (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 $CaCl_2$.

4-Acylated bis-pyrazolone: M.F- $C_{32}H_{38}N_6O_2$ Yield 74%; M.P. 219°C; Light Yellow; FT-IR (KBr,cm^{-1}): 3520 ν(O–H), 3103 ν(N–H), 1608 ν(C=O), 1533 ν(C=N); ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.17-2.21 (6H, s, -2CH_3); 1.48-2.0 (10H, m, -4CH_2 , 2-CH); 2.24-2.28 (6H, s, -2CH_3); 2.33-2.36 (6H, s, 2CH_3) 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; O, 5.94, Calculated for $C_{32}H_{38}N_6O_2$: C, 71.93%; H, 7.35%; N, 14.68%, O, 5.63%.

4-propiyonal bis-pyrazolone: M.F- $C_{34}H_{42}N_6O_2$ Yield 73%; M.P. 238°C; Dark Yellow; FT-IR (KBr,cm^{-1}): 3221 ν(O–H), 3030 ν(N–H), 1624 ν(C=O), 1533 ν(C=N); ^{1}H NMR (400 MHz, DMSO-d_6): 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 $C_{34}H_{42}N_6O_2$: C, 71.93%; H, 7.26%; N, 14.02 %; O, 5.36%.

4-Butyryl bis-pyrazolone: M.F- $C_{36}H_{46}N_6O_2$ Yield 74%; M.P. 256°C; Yellow Powder; FT-IR (KBr,cm^{-1}): 3221 ν(O–H), 3084 ν(N–H), 1625 ν(C=O), 1533 ν(C=N); ^{1}H NMR (400 MHz, DMSO-d_6): 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, -2OH) Elemental analysis found (%) C, 72.70; H, 7.80; N, 14.13; O, 5.39, Calculated for $C_{36}H_{46}N_6O_2$: C, 71.85%; H, 7.26%; N, 14.01%; O, 5.01%.

4-Benzoyal bis-pyrazolone: M.F- $C_{42}H_{42}N_6O_2$ Yield 78%; M.P. 296°C; Reddish Brown; FT-IR (KBr,cm^{-1}): 3223 ν(O–H), 3059 ν(N–H), 1627 ν(C=O), 1533 ν(C=N); ^{1}H NMR (400 MHz, DMSO-d_6): 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 $C_{42}H_{42}N_6O_2$: C, 75.83%; H, 5.84%; N, 12.51% O, 4.44%.

4-Nitrobenzoyl bis-pyrazolone: M.F- $C_{42}H_{40}N_8O_6$ Yield 61%; M.P. 303°C; Reddish brown powder; FT-IR (KBr,cm^{-1}): 3070 ν(O–H), 2945 ν(N–H), 1622 ν(C=O), 1600 ν(C=N); ^{1}H NMR (400 MHz, DMSO-d_6): 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 $C_{42}H_{40}N_8O_6$: C, 66.98 %; H, 5.24 %; N, 14.46%; O, 12.32%.

Synthesis of Schiff base complexes of Copper (II)

All the Metal complexes of the Schiff base were prepared by the following general method. $CuCl_2.2H_2O$ (0.01 mol) solution in methanol (20 ml) was added to a warm (~68°C), stirred solution of the corresponding Schiff base DPL_1 (0.01 mol) or DPL_2 (0.01 mol) or DPL_3 (0.01 mol) or DPL_4 (0.01 mol) or DPL_5 (0.01 mol) in 25mL methanol. After the complete addition, the reaction mixture refluxed for 6–7 hr and then concentrated to half of its volume. The resulting precipitate was filtered by suction and dried in vacuum over anhydrous $CaCl_2$.

RESULTS AND DISCUSSION

The recently prepared Schiff base ligands and its coordination compounds are very stable at room temperature. The Schiff base ligands are soluble in ordinary organic solvents. The coordination compounds are soluble in Co-coordinating solvents like DMF and DMSO. The structural analysis of all the prepared Schiff base ligands and coordination compounds were carried out using elemental analysis, IR, ^1H NMR, FAB-Mass spectra and TGA/DTG and DSC analysis. The ^1H NMR data of Schiff base ligands are given in experimental section. The investigative data are in good harmony with the projected structure of the Cu (II) coordination compound (**Table 1**).

^{1}H NMR spectra of ligands

Number of studies can be carried out for pyrazolone due to the presence of tautomerism properties **[10]**. The ^1H NMR studies for all the Schiff base ligands were carried out by taking DMSO-d_6 as a solvent at room temperature. The results obtain for the same are represented in experimental section. Each of the spectra for Schiff base ligands having two sharp singlet equivalents to one and two protons observed in the range of 11-12 δppm represent the presence of –OH group **[11]**. Confirmation of the signal was carried out D_2O exchange experiment. Aromatic & Aliphatic protons are observed in the range of 7.5-8.5 δppm & 1.5 to 3.0 δppm respectively. The NMR spectrum for both the ligands LX_1 and LX_2 are shown in (**Figure 2 & Figure 3**). All the signals of -CH_3, aromatic protons and -OH group in NMR are respectively in repetitive manner may indicate the presence of both **keto and enol** form. Also from the intensity of the signal we may define the approximate percentage ratio of each form throughout the analysis. In some case peaks of aliphatic protons are merged with either solvent or moisture peak and also all of these peaks are closely spaced so it is complicated to define each peak of aliphatic portion clearly **[12]**. On the basis of ^1H NMR spectroscopic data it is observed that schiff base ligand exists in both **Keto & Enol** form.

Infrared Spectra

The comparison of IR spectral data of the Schiff base ligands and its Cu(II) coordination compounds are listed in **Table 2**. The IR spectra of all Schiff base ligands having broad band centered in the range of 3070 to 3520 cm^{-1} indicates the involvement of the 5-OH group in intramolecular H-bonding **[13-16]**. The schiff base ligand (LX_1 to LX_5) shows a sharp and strong band of a υ(C=N) of the acyclic azomethine group at 1516 to 1600 cm^{-1}. The band for same functional group in coordination compounds obtains at 1508 to 1575 cm^{-1}. The observed low energy shift of this band in the coordination compound suggest the co-ordination of azomethine nitrogen **[17, 18]**. Co-ordination through the oxygen atom of the ligand confirmed by considerable negative shift of 15-20 cm^{-1} in υ(C=O) absorption of the pyrazolone group due to the decrease in the stretching force constant. All IR results indicate that (LX_1 to LX_5) behave as a dinegative bidentate ligand and forming a conjugate coordination compound with the ligand existing in the enolic form.

Thermal Studies

Each disintegration method follows the trend

$$\text{Solid-1} \xrightarrow{heat} \text{Solid-2} + \text{Gas}$$

This route includes of some phases:

The thermal destruction method for coordination compound $[Cu(LX_n).Cl.H_2O].x.H_2O.y.Cl$ is as shown below:

$$[Cu(LX_n).Cl.H_2O].x.H_2O.y.Cl \xrightarrow{\substack{50-277^\circ C \\ removal\ of \\ crystaline\ Cl+H_2O}} [Cu(LX_n).Cl.H_2O] + x.H_2O.y.Cl$$

$$[Cu(LX_n).Cl.H_2O] \xrightarrow{\substack{278-477\ ^\circ C \\ removal\ of \\ coordinate\ Cl+H_2O}} [Cu(LX_n)]$$

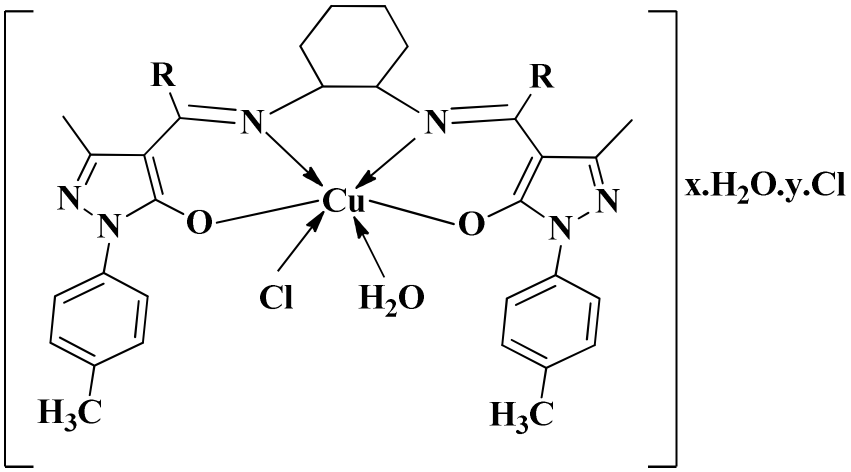
$$[Cu(LX_n)] \xrightarrow{\substack{478-9\quad ^\circ C \\ removal\ of \\ ligand}} CuO$$

n	x(H_2O)	y(Cl)
1	1	-
2	1.5	-
3	4	3
4	1	1
5	1	2

TGA plot of coordination compound $[Cu(Lx_1)Cl.H_2O].H_2O$ is signified in (**Figure 6**) The disintegration of coordination compound $[Cu(Lx_1)Cl.H_2O].H_2O$ takes place in following three stage. In the first step coordination compound undergoes thermal dehydration and dehalogenation between 50 to 277℃ with mass loss of 5.40% (5.28%). 1 mol of coordinated H_2O may eliminate in this phase. This process is followed by endothermic effect at 259.6℃ and 263.3℃ correspondingly. The second step which occurs in the temperature range of 278 to 477℃ correspond to decay of Cl & H_2O molecule with several part of the LX_1 ligand. The observed mass loss 48.11% (48.03%). The endothermic peak at 544.7℃ corresponds to this stage is given by DSC curve in (**Figure 7**). The third step is related to the estimated amount of CuO in temperature range of 478 to 988℃ accompanied by mass loss 42.06% (41.98%). The general mass loss observed is 95.57% as match up to the theoretical value 95.73%. On the basis of above conversation proposed octahedral structure of coordination compound can be assumed as shown in (**Figure 1**) and thermodynamic results of coordination compounds are reported in **Table 3**.

FAB Study

The coordination compound $[Cu(LX_1)Cl.H_2O].1.5\ H_2O$ were confirmed with molecular ion peak found in the FAB mass spectrum (**Figure 8**). The projected disintegration pattern is shown in **Scheme 1**. The first peak at m/z=708 signifies the molecular ion peak of coordination compound. **Scheme 1** reveals the possible disintegration path way for the explored coordination compound. The main division of the coordination compound take place due to the removal of coordinated H_2O and Cl molecule from the species **(a)** to give species **(b)** with peak at m/z=628. Advance disintegration yields species **(c)** with removal of $C_{20}H_{25}N_3O$. Species **(c)** further disintegrate to species **(d)** with removal of CuO. The pointed peak (base peak) observed at m/z=628 represent the steady species **(b)** with 97.0% abundance. The calculated molecular weights for all the recommended disintegration steps were accurately match with the expected value.



Sr. No.	Ligand	R	x	y
1	LX_1	$-CH_3$	1	-
2	LX_2	$-CH_2CH_3$	1.5	-
3	LX_3	$-\ CH_2CH_2CH_3$	1	1
4	LX_4	$-C_6H_5$	1.5	1
5	LX_5	$-C_6H_5NO_2$	3	1

Figure 1: The proposed structure of Heterochelate

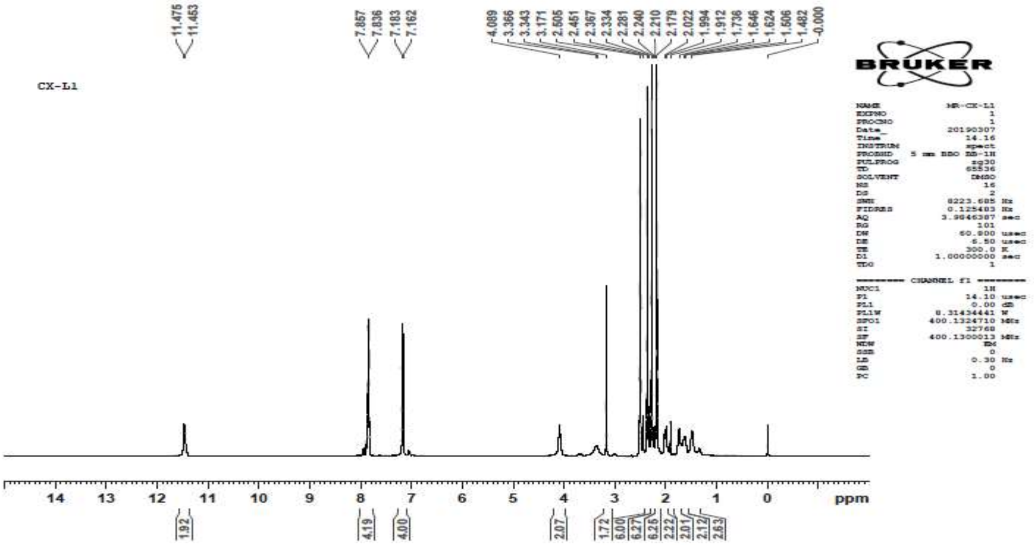


Figure 2: NMR spectrum of LX_1

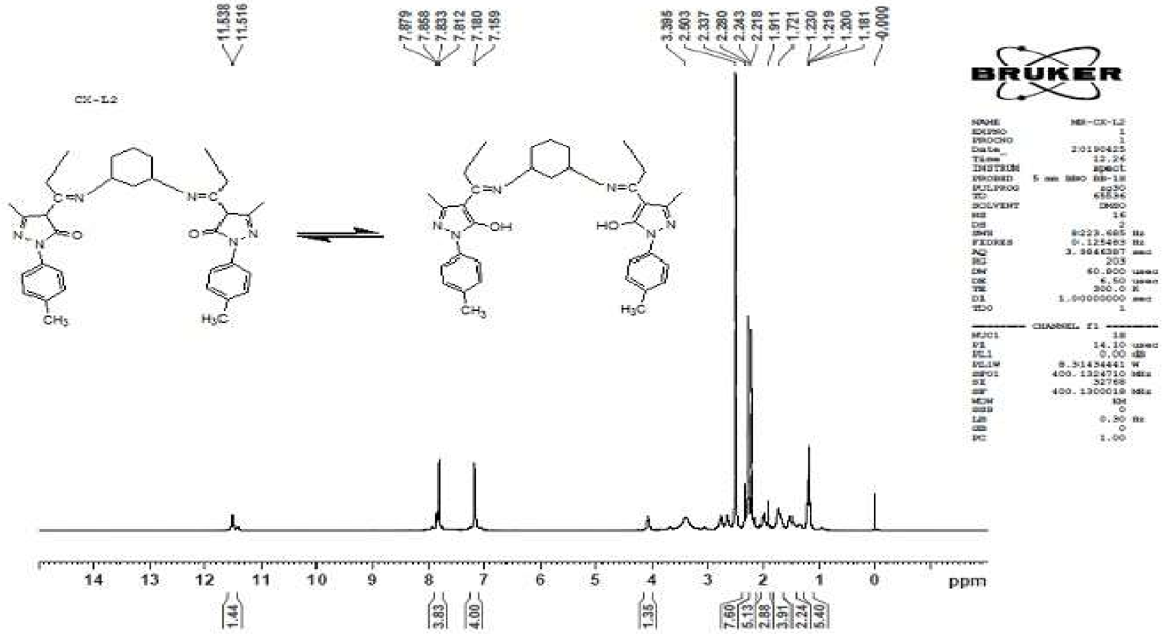


Figure 3: ^{1}H NMR Spectra of Ligand LX_2

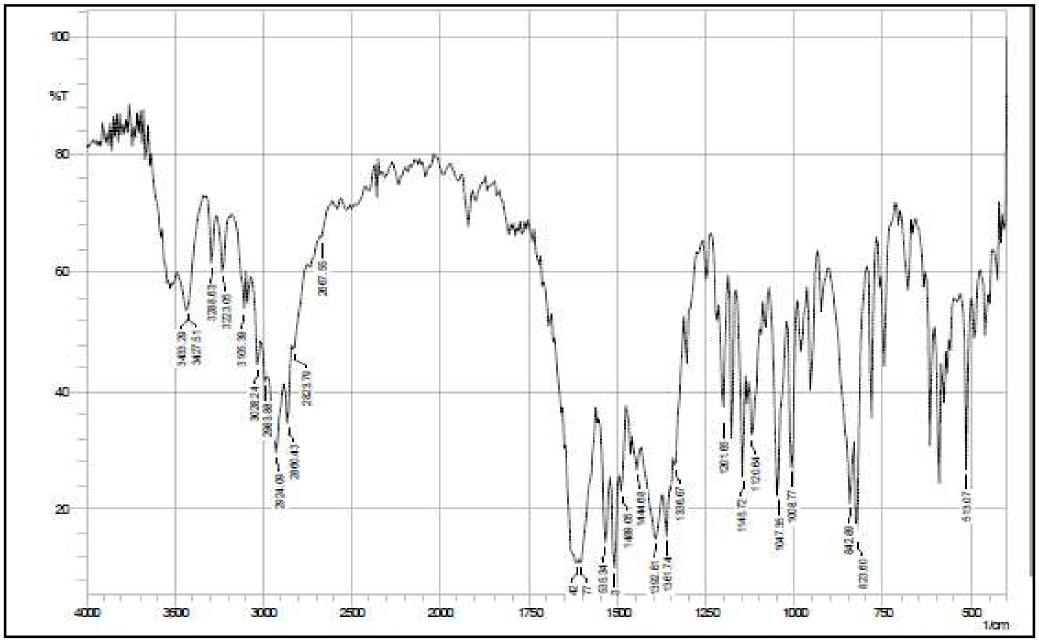


Figure 4: IR Spectra of [Cu(Lx$_1$)Cl.H$_2$O].H$_2$O

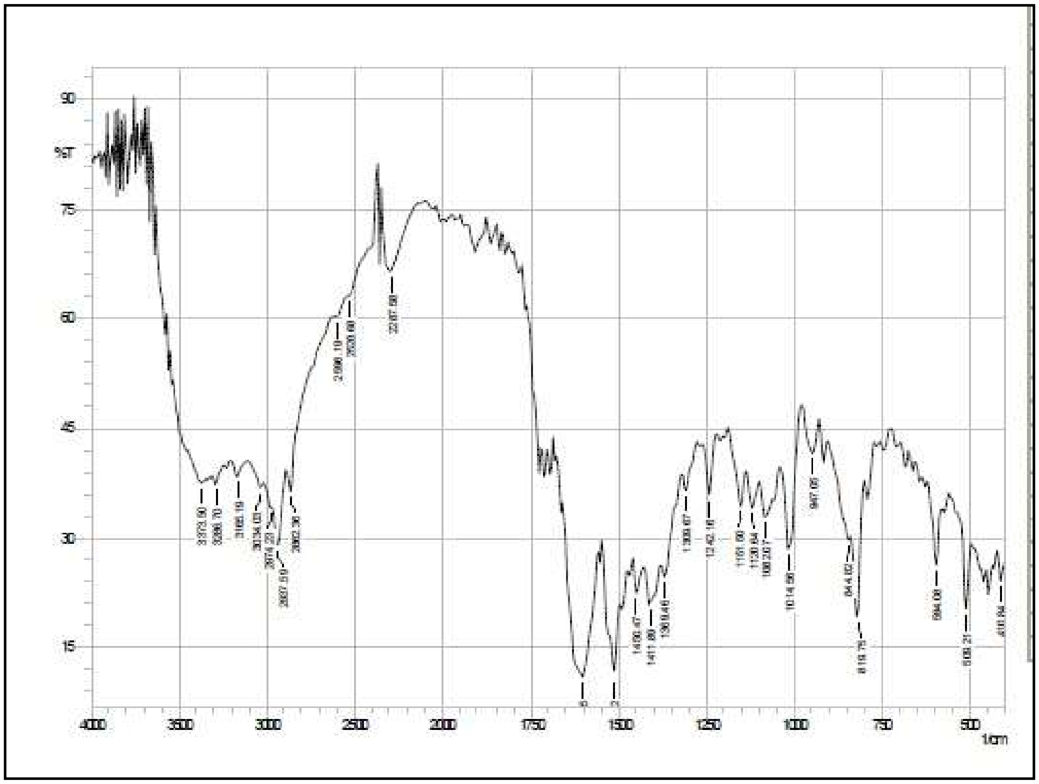


Figure 5: IR Spectra of [Cu(LX$_2$)Cl.H$_2$O].1.5 H$_2$O

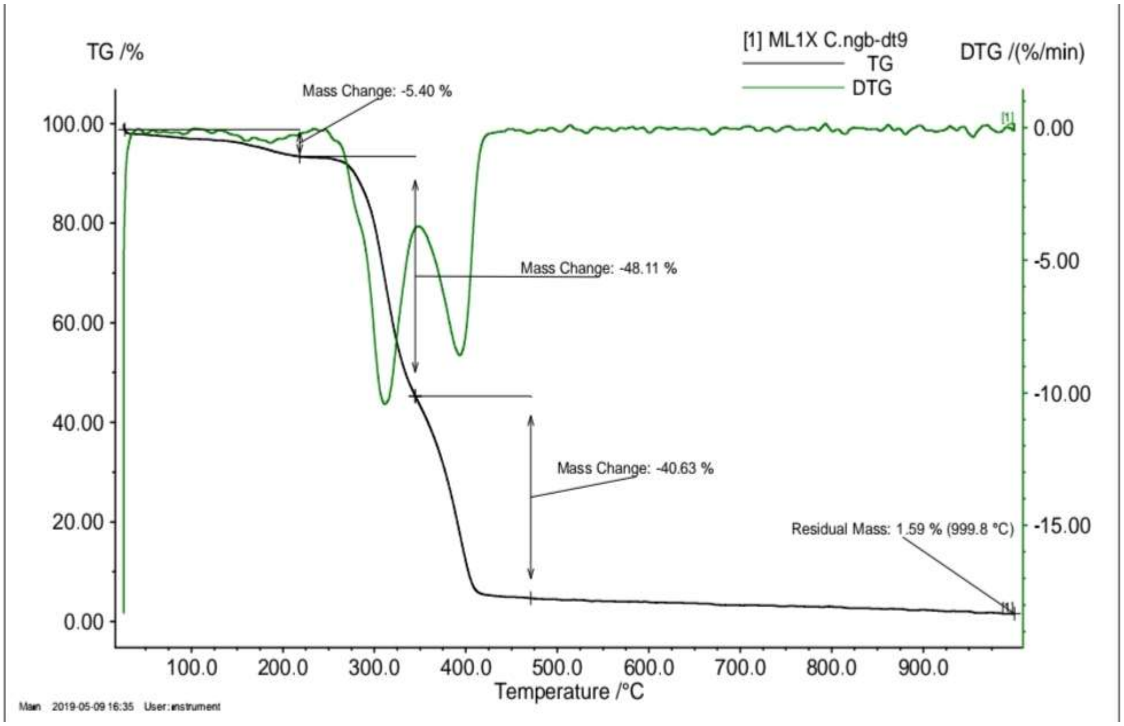


Figure 6: TGA Analysis of $[Cu(LX_1)Cl.H_2O].H_2O$

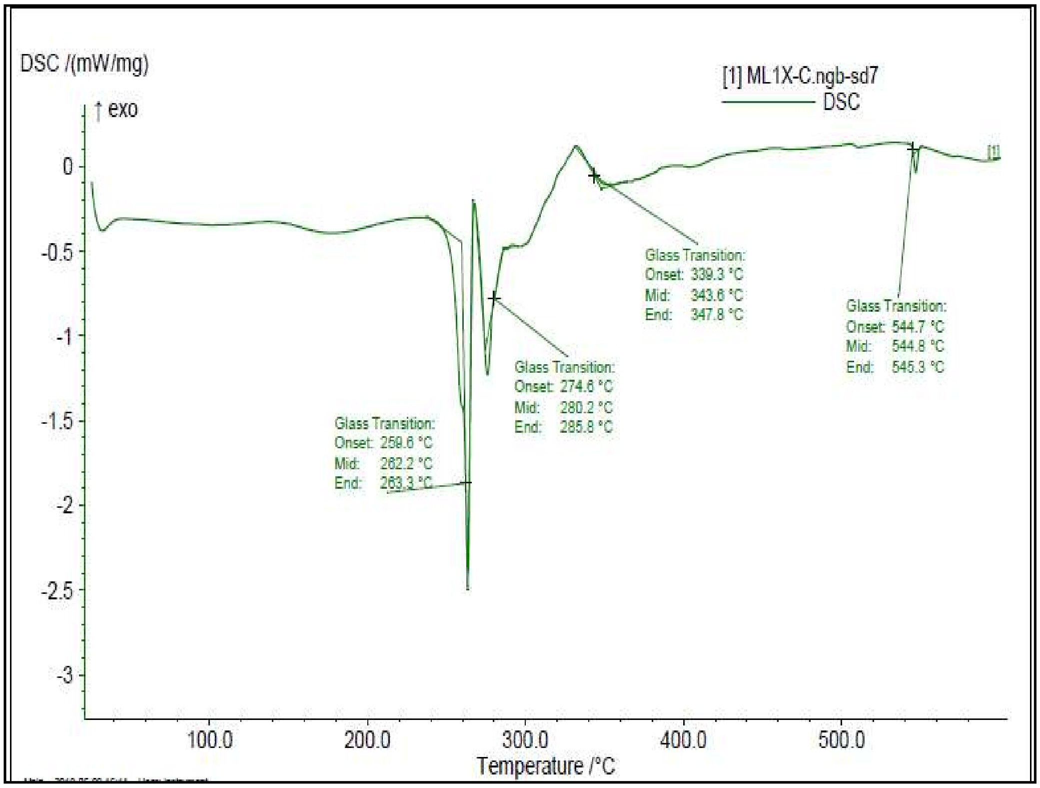


Figure 7: DSC Analysis of $[Cu(Lx_1)Cl.H_2O].H_2O$

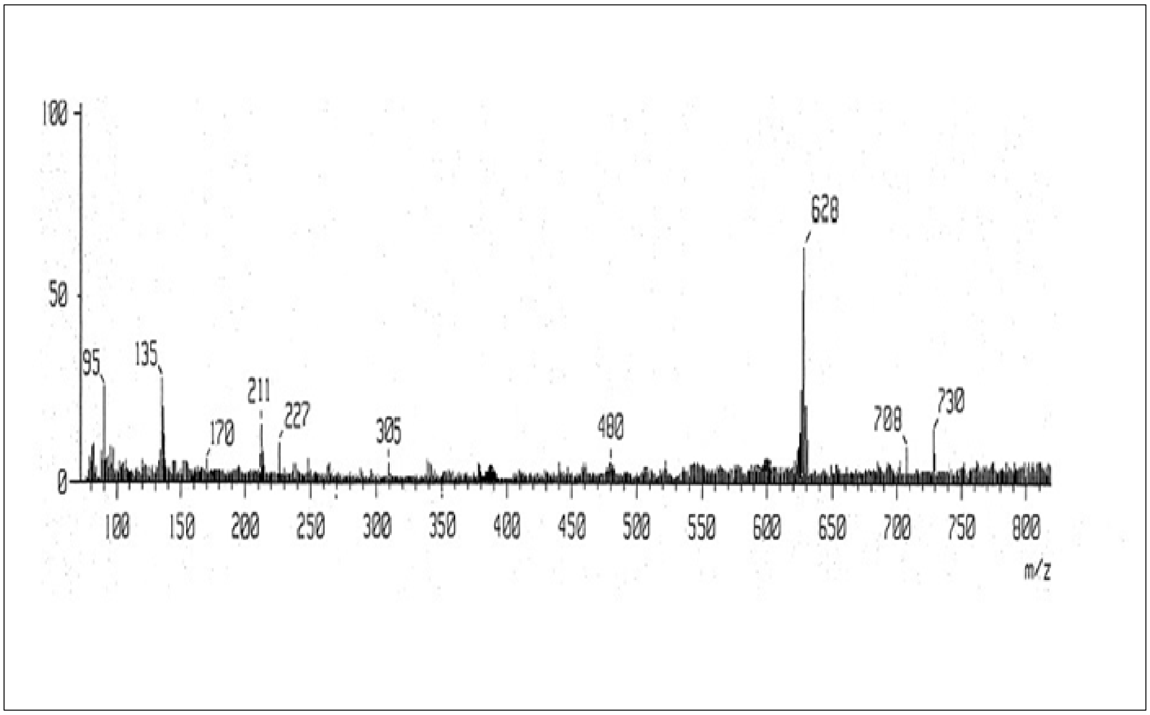


Figure 8: FAB Mass Spectrum of $[Cu(Lx_1)Cl.H_2O]1.5\ H_2O$

Table 1: Analytical and physical data of Heterochelates

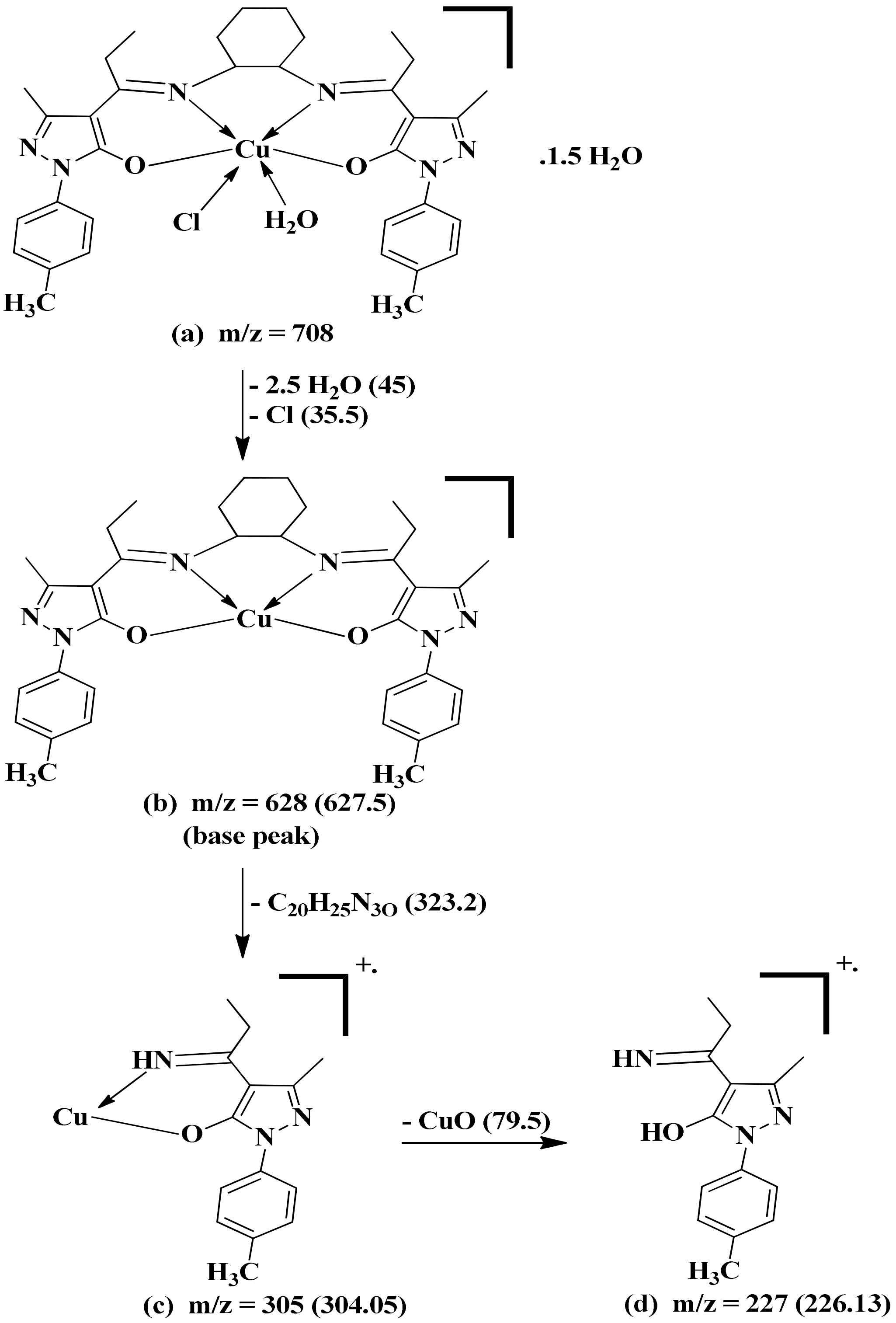
Sample No.	Compounds	Formula Weight	Colour (%Yield)	Analysis (%) Found(Cal)					
				C	H	Cl	N	O	Cu
$CuLx_1$	$[Cu(Lx_1)Cl.H_2O].H_2O$ $C_{34}H_{42}ClN_4CuO_4$	669.7	Dark Yellow (76)	60.98 (60.69)	6.32 (6.08)	5.29 (5.02)	8.37 (8.10)	9.56 (9.35)	9.49 (9.35)
CuL	$[Cu(Lx_2)Cl.H_2O].1.5\ H_2O$ $C_{36}H_{47}ClN_4CuO_{4.5}$	706.8	Brown (74)	61.18 (61.03)	6.70 (6.45)	5.07 (4.97)	7.93 (7.46)	10.19 (10.01)	8.99 (8.3)
$CuLx_3$	$[Cu(Lx_3)Cl.H_2O].3Cl.4H_2O$ $C_{38}H_{56}Cl_4N_4CuO_7$	886.2	Yellow (71)	51.50 (51.35)	6.37 (6.12)	16.00 (15.4)	6.32 (6.08)	12.64 (12.35)	7.17 (7.0)
$CuLx_4$	$[Cu(Lx_4)Cl.H_2O].H_2O.Cl$ $C_{44}H_{46}Cl_2N_4CuO_4$	829.3	Greenish Yellow (69)	63.72 (63.53)	5.59 (5.32)	8.55 (8.23)	6.76 (6.43)	7.72 (7.46)	7.66 (7.2)
$CuLx_5$	$[Cu(Lx_5)Cl.H_2O].H_2O.2Cl$ $C_{44}H_{44}Cl_3N_6CuO_8$	954.8	Reddish Yellow (62)	55.35 (55.12)	4.65 (4.36)	11.14 (11.0)	8.80 (8.56)	13.41 (13.12)	6.66 (6.4)

Table 2: Comparison of IR data of ligands with Heterochelates

Compounds	ν(O-H)	ν(N-H)	ν(C=O)	ν(C=N)
LX_1	3520	3226	1624	1593
LX_2	3221	3224	1624	1593
LX_3	3221	3224	1627	1589
LX_4	3223	3223	1627	1589
LX_5	3070	3116	1620	1577
$[Cu(LX_1)Cl.H_2O]. H_2O$	3433	3069	1601	1539
$[Cu(LX_2)Cl.H_2O].1.5 H_2O$	3373	3045	1591	1535
$[Cu(LX_3)Cl.H_2O].3Cl.4H_2O$	3286	3043	1591	1541
$[Cu(LX_4)Cl.H_2O].H_2O.Cl$	3251	2926	1556	1523
$[Cu(LX_5)Cl.H_2O].H_2O.2Cl$	3157	2932	1598	1519

Table 3: Thermo Analytical Results of Heterochelates

Sr.no.	Heterochelates	Temp. Range	Mass Loss (%) Obs. (Cal.)	Analysis
1	$[Cu(LX_1)Cl.H_2O].H_2O$	50-277	5.40 (5.28)	H_2O crystalline molecule may loss
		278-477	48.11 (48.03)	$Cl.H_2O$ Coordinated molecule and some part of ligand may loss
		478-988	42.06 (41.98)	Remaining Cu may present as CuO
2	$[Cu(LX_2)Cl.H_2O].1.5 H_2O$	50-257	6.42 (6.31)	$1.5H_2O$ crystalline molecule may loss
		258-483	48.70 (48.59)	$Cl.H_2O$ Coordinated molecule and some part of ligand may loss
		484-991	42.77 (42.47)	Leaving CuO residue
3	$[Cu(LX_3)Cl.H_2O].3Cl.4 H_2O$	50-268	17.97 (17.77)	$3Cl.4H_2O$ crystalline molecule may loss
		269-494	34.33 (34.03)	$Cl.H_2O$ Coordinated molecule and some part of ligand may loss
		495-946	42.19 (42.06)	Leaving CuO residue
4	$[Cu(LX_4)Cl.H_2O].H_2O.Cl$	50-269	13.93 (13.82)	Crystalline -Cl and $–H_2O$ molecule may loss
		270-498	44.32 (44.10)	$Cl.H_2O$ Coordinated molecule and some part of ligand may loss
		499-989	39.02 (38.80)	Leaving CuO residue
5	$[Cu(LX_5)Cl.H_2O].H_2O.2Cl$	50-284	9.43 (9.31)	Crystalline 2Cl and H_2O molecule may loss.
		285-501	45.16 (45.1)	$Cl.H_2O$ Coordinated molecule and some part of ligand may loss
		502-994	40.24 (40.04)	Leaving CuO residue



Scheme 1: The Suggested Fragmentation pattern of $[Cu(Lx_1)Cl.H_2O].1.5\ H_2O$

CONCLUSION

The plan and synthesis of new bis pyrazolone schiff base ligand have been effectively confirmed by FT-IR and ^{1}H NMR Spectral studies. From the data for Schiff base ligand it is confirm that the Schiff base 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 Cu(II) coordination compound. From the source of above studies, the common projected configuration of the Cu(II) coordination compound shown in (**Figure 1**).

REFERENCES

[1] Modi, C.K., Jani, D.H., *Journal of Thermal Analysis and Calorimetry,* 2010, vol. 102(3), p. 1001. https://doi.org/10.1007/s10973-010-0890-x

[2] Jani, D.H., Modi, C.K., *Applied Organometalic Chemistry,* 2011, vol. 25(6), p. 429. https://doi.org/10.1002/aoc.1782

[3] Pawar, N.S., Chaudhari, S.R., *Journal of Emerging Technology and innovative Research,* 2019, vol. 6(3), p. 561. https://www.jetir.org/download1.php

[4] Jani, D.H., Patel, H.S., Keharia H. and Modi, C.K., *Applied Organometalic Chemistry,* 2010, vol. 24, p. 99. https://doi.org/10.1002/aoc.1581

[5] Yoshikuni, T., *Journal of molecular catalysis A: Chemical.,* 2002, vol. 187, p. 143. https://doi.org/10.1016/S1381-1169(02)00053-5

[6] Semenov, S.N., Rogachev, A.Y., Eliseeva, S.V., Pattinari, C., *Chem.Comm.,* 2008, vol. 17, p. 1992. https://doi.org/10.1039/B719171E

[7] Yang, L., Wu, J., *Transition Met. Chem,* 1999, vol. 24, p. 340. https://doi.org/10.1023/A:1006952117118

[8] Niknam, K., Saberi, D., Sadegheya, M. and Deris, A., *Tetrahedron Letters,* 2010, vol. 51, p. 692. https://doi.org/10.1016/j.tetlet.2009.11.114

[9] Raja, M., Jani D. and Koradiya, S., *Journal* of *Appicable Chemistry*, 2019, vol. 8(3), p. 1241. http://www.joac.info › 2019 › 40-8-3-38-29

[11] Akama, Y., Tong, A., *Microchem. J*, 1996, vol. 53, p. 34. https://doi.org/10.1006/mchj.1996.0006

[12] Kauffmann, J., Alafandy, M., Willem, R., Mahieu, B., Alturky, M., Biesemans, M., Legros, F., Camu, F., Gielen, M., *Inorg. Chim. Acta.,* 1997, vol. 255, p. 175. https://doi.org/10.1016/S0020-1693(96)05337-6

[13] Jadeja, R., Shah, J., *Polyhedron,* 2007, vol. 26, p. 1677. https://doi.org/10.1016/j.poly.2006.12.016

[14] Modi, C., Thaker, B., *J. Theram Anal Calorim.,* 2008, vol. 94(2), p. 567. https://doi.org/10.1007/s10973-007-8645-z

[15] Surati, K., Thaker, B., *J. coordchem.,* 2006., vol. 59, p. 1191. https://doi.org/10.1080/00958970500468513

[16] Marchetti, F., Pettinari, C., Pettinari, R., Cingolani, A., Rossi, A., Caruso, M., *J. organomet Chem.,* 2002, vol. 645, p. 134. https://doi.org/10.1016/S0022-328X(01)01333-X

[17] Marchetti, F., Pettinari, C., Pettinari, R., Cingolani, A., Leonesi, D. and Lorenzotti, A., *Polyhydron*, 1999, vol. 18, p. 3041. https://doi.org/10.1016/S0277-5387(99)00230-2

[18] Xu, G., Liu, L., Zhang, L., Liu, G., Jia, D., Lang, J., *Struct Chem.,* 2005, vol. 16, p. 431. https://doi.org/10.1007/s11224-005-6352-6

[19] Modi, C., Thaker, B., *Indian J.Chem.,* 2002, vol. 41A, p. 2544.

http://nopr.niscair.res.in