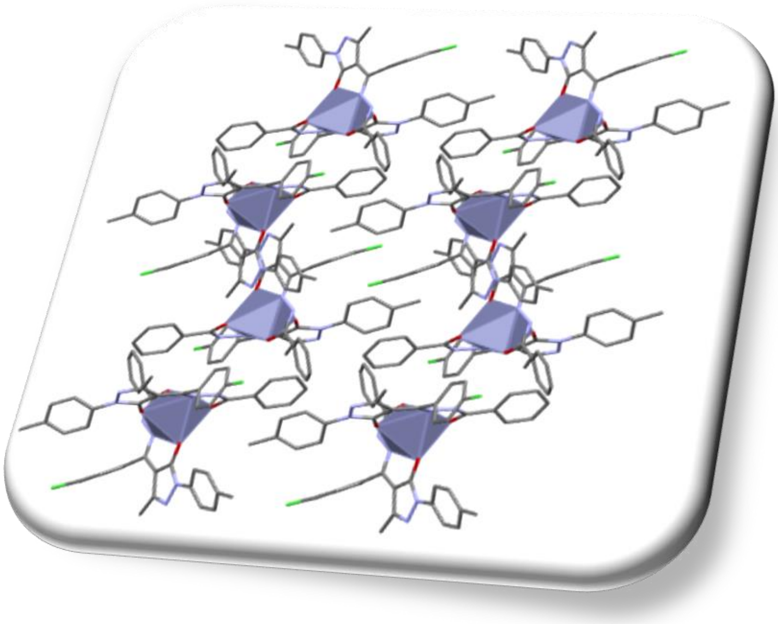
Chapter 3

4-Acylhydrazone-5-Pyrazolones and their Zinc(II) Metal Complexes: Synthesis, Characterization and Crystal Study



Chapter 3 (Part-a):

Synthesis, Characterization and Crystal Study of Zinc(II) Complexes of 4-Acylhydrazone-5-Pyrazolones

3.1.1. Introduction

Pyrazolone and its derivatives have gripped more attention in recent years due to wide applications in chemical industries, dyes and pharma sector. Especially interest in derivatives of 4-acyl pyrazolone because of the chelating arm with β-diketone in the structure.[1,2]

Formica *et. al.* (2018) reported the synthesis from N-aryl hydrazone and 1,2- diaza-1,3-diene through a base indorsed Michael addition reaction.[3,4] Komal *et al.* (2011) has been reported two bidentate Schiff base, 5-methyl-2-*p*-tolyl-4-(1-*p*-tolylimino-propyl)-2H-pyrazol-3-ol and 2-(3-chloro-phenyl)-5-methyl-4-(1-*p*-tolylimino-propyl)-2H-pyrazol-3-ol, were synthesized by condensation of 4-acyl pyrazolones with *p*-toluidine in ethanol (see Fig. 3.1.1).[5] Based on this concept asymmetrical bis-Schiff-base from o-vanillin and the half-unit Schiff-based ligand has been synthesized from 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and o-phenylenediamine.[6]

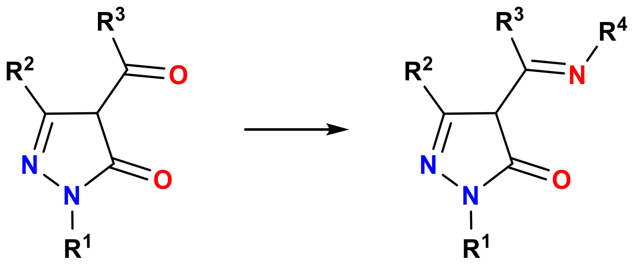


Fig. 3.1.1. Synthesis route of Schiff base derivatives of acyl pyrazolone, where **R¹**=-Ph; Me-Ph; Cl-Ph, **R²**=Me, **R³**=aryl or alkyl group.

4-acylhydrazone-5-pyrazolones have been prepared through the reaction between 4-acylpyrazolones and acyl hydrazones (*see* Fig. 3.1.2).[7,8] Li *et. al.* (2007) and Wang *et al. (*2019) have been reported 4-acylhydrazone-5-pyrazolone (N-(1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone)-2-salicylidene hydrazide) through the reaction of 1-phenyl-3-methyl-4(4-fluorobenzoyl)-5-pyrazolone and 2-salicylidene hydrazide.[8,9]

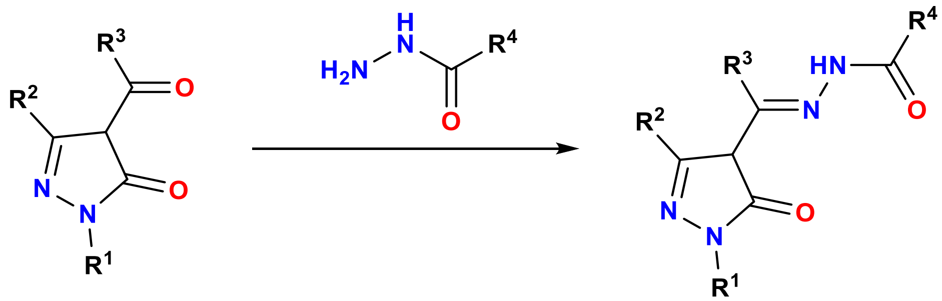


Fig. 3.1.2. Synthesis route of 4-acylhyrazone-5-pyrazolones, where **R¹**=-Ph; Me-Ph; Cl-Ph, **R²**=Me, **R³** & **R⁴**=aryl or an alkyl group.

The reaction between 4-acylpyrazolone and 2-thiophene carboxylic acid hydrazide to produced two 4-acylhydrazone-5-pyrazolones (N-(1-phenyl-3-methyl-4-benzoyl-5-pyrazolone)-2-thiophene carboxylic acid hydrazide and N-(1-phenyl-3-methyl-4-propenylidene-5-pyrazolone)-2-thiophene carboxylic acid hydrazide) was reported in Li *et al.*, 2015 article.[10] Pyrazolones and 4- acyl pyrazolones have been studied for many biological activities like anticancer[11], antimalarial[12], antimicrobial[13], DNA cleavage[14] etc. 4-acylhydrazone-5-pyrazolones are derivatives of 4-acyl-5-pyrazolones. N-(1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone)-2-salicylidene hydrazide and its Cu(II) complexes, which have been mononuclear structure and the Cu(II) ions are located in a five-coordinated distorted square pyramidal geometry and studied on DNA binding and antitumor activity.[8] The isonicotinoyl hydrazone derived from isoniazid with l-phenyl-3-methyl-4-benzoyl-5-pyrazolone was synthesized and used for the 3d metal complexes of Cr, Mn, Fe, Co, Ni and Cu, which general formula is ML nH_2O (where n = 0, 1) (*see* Fig. 3.1.3). It was discovered that the complexes possess certain scavenger effects on O_2^-radicals.[15]

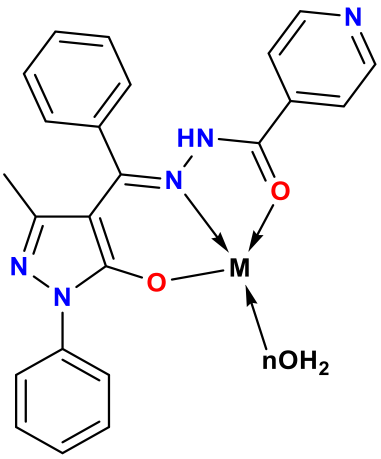


Fig. 3.1.3. 3d complexes of isonicotinoyl hydrazone. M= Cr, Mn, Fe, Co, Ni and Cu where n = 0, 1.

The Sm(III), Eu(III), and Gd(III) complexes of 4-acylhydrazone-5-pyrazolone displayed promising fluorescence spectra.[9] Zinc(II) complexes of 4-acylhydrazone-5-pyrazolones possess good fluorescence properties.[16] The DNA-binding properties of Mn(II) complexes of –Acylhydrazone-5-pyrazolone have been examined by absorption spectroscopy, fluorescence spectroscopy and cyclic voltammetry, which suggested that the complexes could interact with DNA via weak intercalation.[10]

Objectives of this work

Derivatives of acyl pyrazolone can be made easily and mostly are stable at room temperature.[17,18] The interest in the coordination chemistry of 4-acylhydrazone-5-pyrazolone has increased greatly in the last decade.[18] Many 4-acylhydrazone-5-pyrazolone based metal complexes have been confirmed owning biological and pharmaceutical activities.[18]

Following our interest in the design and development of novel zinc(II) complexes with good biological activity, we have synthesized three 4-acylhydrazone-5-pyrazolones and their three homoleptic zinc(II) complexes. To obtain single crystal of zinc(II) complexes is always difficult task. We have discussed crystal structures of Zn(II) complexes of 4-acylhydrazones-5-pyrazolones.

3.1.2. Experimental

3.1.2.1. Materials and methods

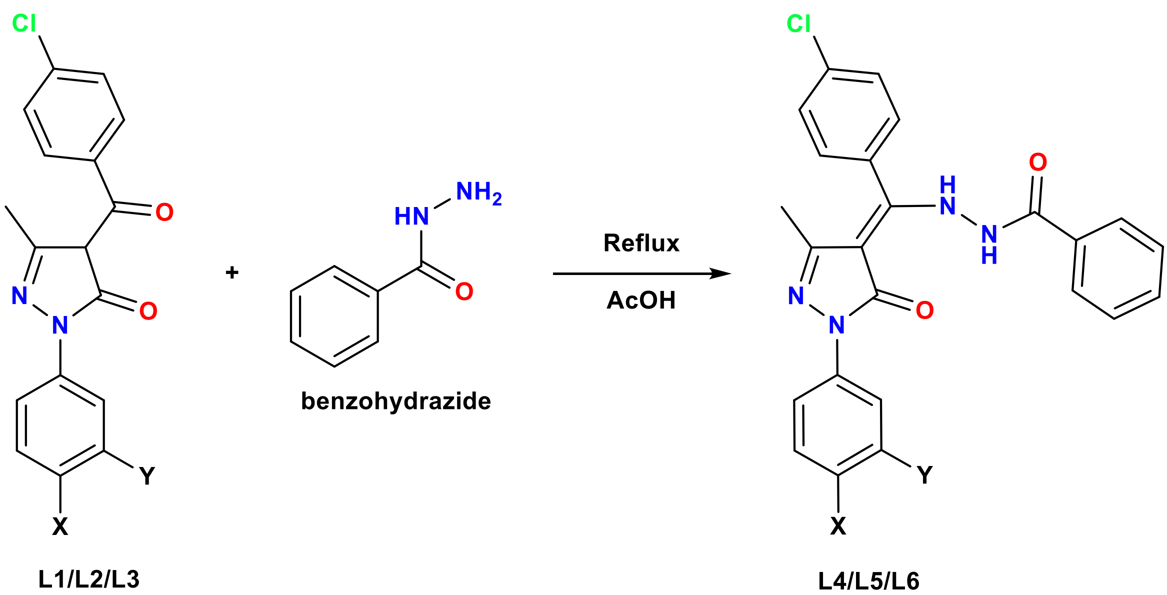
Pyrazolones were obtained from Sidhdhanath industries, Sachin (Surat), India as gift samples. All necessary reagents and solvents were obtained from commercial sources. Zinc acetate and glacial acetic acid and Benzhydrazide were purchased from spectrochem PVT. LTD., Mumbai. Infrared (IR) spectra were recorded on Bruker Alpha Fourier transform IR (FT-IR) spectrometer as KBr pellets. ^{1}H and ^{13}C NMR spectra of the ligand were recorded with an AV 400 MHz Bruker FT-NMR instrument. Single crystal data were collected on an Xcalibur, EOS, Gemini diffractometer. The electronic spectra were recorded on a Perkin Elmer Lambda 35 UV-Vis spectrometer. Elemental analyses were performed with a Thermo Finnigan (FLASH EA 1112) microanalyzer. Conductometer model-EQ664A was used for conductance measurement for 10^{-3}M solutions of complexes and ligands. Gravimetric and volumetric analysis were performed for the determination of zinc after decomposition of the complex in nitric acid. A simultaneous TG/DTA was carried out on an SII EXSTAR6000 TG/DTA 6300 instrument. The experiments were performed in N_2 at a heating rate of 10 ºC min^{-1} in the temperature range 30–550 ºC using an aluminium pan.

3.1.2.2. Synthesis of Ligands

Primary 4-acylpyrazolones (**L1**, **L2** and **L3**) were carried out by following the reported method.[12,19]

Synthesis of Ligand L4 ((Z)-N'-((4-chlorophenyl)(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)benzohydrazide)

Recrystallized **L2** (1.563 g, 0.005 mol) was dissolved in a minimum amount of absolute ethanol (~25mL) in a single necked round bottom flask. In this, ethanolic solution of benzohydrazide (0.680 g, 0.005 mol) was added drop wise. A few drops of glacial acetic acid was added as a catalyst in the reaction mixture. The reaction mixture was then refluxed for four hours. After cooling the solution to room temperature, the reaction mixture was placed for overnight at room temperature to get the yellowish crystalline product. The yellowish crystalline product was filtered, washed with water and dried in oven. Yield: 65%, M.P.: 190 °C, M.F.: $C_{24}H_{19}ClN_4O_2$, F.w.: 430.89, Ele. Ana. Calcd. (Found): C, 66.90 (66.88); H, 4.44(4.56); N, 13.00(13.45) %. **FTIR (KBr) cm^{-1}:** 1640 (C=O, pyz), 1593 (C=O, bhz), 1569 (C=N, imine), 1455(C=C, pyz), 1349 (C-N, pyz), 903(C-Cl, *p*-chloro benzoyl pyz). **^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm:** 1.8 (s, 3H, Me-pyz), 7.25 (t, 1H, ph-pyz), 7.45-7.54 (m, ar-H), 7.60 (t, 1H, bhz), 7.96 (s, 1H, -NH, bhz), 8.01(d, *J*=8 Hz, ar-H). **^{13}C NMR ($CDCl_3$, 100MHz)δ :** 16.4 (CH_3-pyz), 99.1, 100.7, 119.6, 120.2, 125.3, 127.2, 127.4, 128.0, 128.7, 128.9, 129.6, 130.5, 131.4, 132.5, 132.8, 137.1, 138.0, 138.7, 139.0, 147.9, 148.8, 153.6 (C-O), 163.3 (C=N), 163.7 (C=O). Synthesis route of ligands (L4-L6) displays in Scheme 3.1.1.



Scheme 3.1.1. Synthesis route of ligands **L4-L6**, where **(i) L1** and **L4: X=Y=-H, (ii) L2** and **L5: X=-H; Y=-Cl**, and **(iii) L3** and **L6: X=-CH_3; Y=-H.**

Synthesis of Ligand L5 ((Z)-N'-((4-chlorophenyl) (1-(3-chlorophenyl)-3-methyl-5-oxo-4, 5-dihydro-1H-pyrazol-4-yl) methylene) benzohydrazide)

Recrystallized **L2**(0.005 mol, 1.736 g) was dissolved in a minimum amount of absolute ethanol (~25mL) in a single necked round bottom flask. In this, ethanolic solution of benzohydrazide (0.005 mol, 0.6805 g) was added drop wise. A few drops of glacial acetic acid was added as a catalyst in the reaction mixture. The reaction mixture was then refluxed for four hours. After cooling the solution to room temperature, the reaction mixture was placed for overnight to get the yellowish crystalline product. The yellowish crystalline product was filtered, washed with water and dried in the oven. M.P.: 195 °C, M.F.: $C_{24}H_{18}Cl_2N_4O_2$, F.w.: 465.33, EA Calcd (Found): C, 61.95(61.88); H, 3.90(3.99); N, 12.04(12.55) %. **FTIR (KBr plates) cm^{-1}:** 1641 (C=O, pyz), 1592 (C=O, bhz), 1571 (C=N, imine), 1455(C=C, pyz), 1351 (C-N, pyz), 900(C-Cl, *p*-chloro benzoyl pyz). **^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm:** 1.8 (s, 3H, CH_3-pyz), 7.21(d, 1H, m-Cl-ph, *J*=8Hz), 7.38(t, 1H, bhz), 7.51-7.64(m, 6H), 7.98(s, 1H,-NH), 8.11(d, 1H, *J*=8Hz), 15.4 (s, 1H, OH-pyz). **^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm:** 16.4 (CH_3-pyz), 98.9, 103.7, 117.8, 119.9, 120.6, 125.0, 126.6, 129.1, 130.2, 131.3, 133.0, 135.5, 138.1, 139.4, 148.0, 149.2, 153.3, 161.9 (C=N), 163.7(C=O, bhz), 190.2 (C=O, pyz).

Synthesis of L6 ((Z)-N'-((4-chlorophenyl) (3-methyl-5-oxo-1-(*p*-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)methylene)benzohydrazide)

Recrystallized **L3** (0.005 mol, 1.633 g) was dissolved in a minimum amount of absolute ethanol (~25ml) in a single necked round bottom flask. The ethanolic solution of benzohydrazide (0.005 mol, 0.680 g) was added drop wise to the solution of ligand L3. A few drops of glacial acetic acid was added as a catalyst in the reaction mixture. The reaction mixture was then refluxed for four hours. After cooling the solution to room temperature, the reaction mixture was placed for overnight at room temperature to get the yellowish crystalline product. The yellowish crystalline product was filtered, washed with water and dried in the oven. Yield: 72%, M.P.: 195 °C, M.F.: $C_{25}H_{21}ClN_4O_2$, F.w.: 444.92, Ele. Ana. Calcd (Found): C, 67.49(67.55); H, 4.76(4.88); N, 12.59 (12.67) %, **FTIR (KBr plates) cm^{-1}:** 1641 (C=O, pyz), 1595 (C=O, bhz), 1571 (C=N, imine), 1487(C=C, pyz), 1348 (C-N, pyz), 897 (C-Cl, *p*-chloro benzoyl pyz). **^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm:** 1.6 (s, 3H, Me-pyz), 2.40 (s, 3H, *p*-tolyl), 7.25 (d, 2H, *p*-tolyl pyz, *J*=8Hz), 7.50 (t, 2H, phenyl bhz), 7.60 (t, 2H, bhz), 7.77 (d, 2H, *p*-tolyl bhz, *J*=8Hz), 7.99 (d, 2H, phenyl, *J*=8Hz), 15.8 (s, 1H, pyz-OH) . **^{13}C NMR (DMSO-d6, 100 MHz) δ ppm:** 16.0(CH3-pyz), 21.0(p-tolyl-pyz), 118.9, 120.5, 121.1, 121.7, 128.3, 128.8, 129.0, 129.2, 129.5, 129.7, 129.9, 130.3, 131.2, 135.8, 136.7, 137.0(C-O), 147.5(C=N), 165.1(C=O, pyz).

3.1.2.3. Synthesis of complex 10-12

Synthesis of complex 10 [Zn (L4)$_2$]

The ligand L4 (0.860 g, 0.002 mol) was dissolved in a minimum amount of anhydrous ethanol (~25 mL) in a two necked round bottom flask. An ethanolic solution of zinc acetate dihydrate (0.219 g, 0.001 mol) was added drop wise to the solution of ligand **L4**. The reaction mixture was then refluxed for 4 h. After reflux, the compound obtained was crystallized from DMF'
Yield: 75%, M.P. >200 C, Molecular formula: 925.15, $C_{48}H_{36}Cl_2N_8O_4Zn$, Ele. Ana. Calcd (found): C, 62.32 (62.33); H, 3.92 (3.88); N, 12.11 (12.22) %, Metal est. Calcd (found): Zn, 7.07(7.11) %. **FTIR (KBr Plates, cm^{-1}):** 3378 (N-H, bhz), 1601(C=O, bhz), 1583 (C=N, pyz), 1565 (C=N, imine of bhz), 1286 (C-O, pyz), 917 (C=C, pyz), 440(M-O, pyz-Zn). **^{1}H NMR ($CDCl_3$, 400MHz) δ ppm:** 1.64 (s, 3H, Me-pyz), 7.01-7.90 (m, 8H, bhz-pyz), 8.09-8.11 (d, 2H, bhz-pyz), 8.95(s, 1H, N-H).

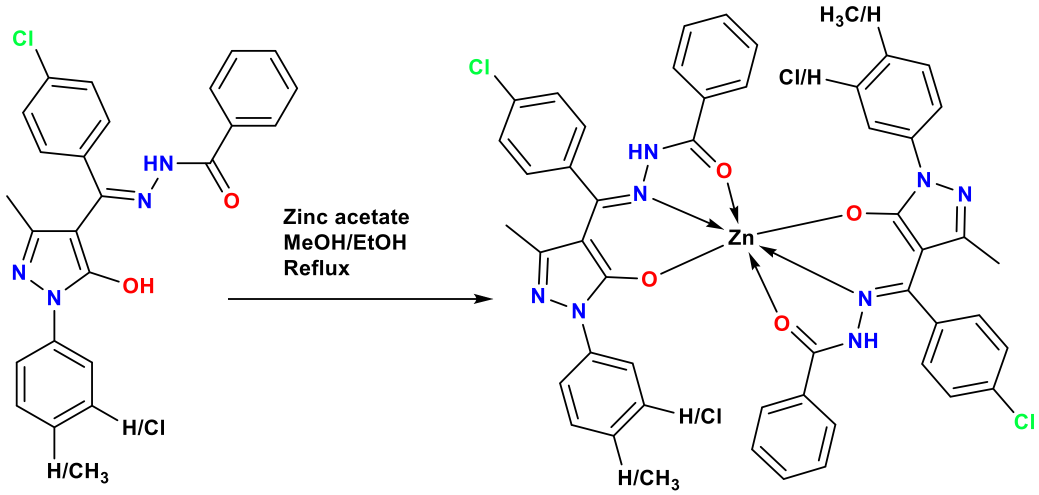
Synthesis of complex 11 [Zn (L5)$_2$].

The complex **11** was synthesized by following the same procedure as that of complex **10** except ligand **L5** was used instead of ligand **L4**.
Yield: 72%, M.P.: >200 C, Molecular formula: $C_{48}H_{34}Cl_4N_8O_4Zn$, Elem. anal. Calcd (found): C, 58.00(57.88); H, 3.45(3.77); N, 11.27(11.45), Formula weight: 994.03, Metal estimation theoretical (found): Zn, 6.58(6.75) %. **FTIR selected bands (KBr Plates, cm^{-1}):** 3378 (N-H, bhz), 1601(C=O, bhz), 1583 (C=N, pyz), 1541 (C=N, imine of bhz), 1286 (C-O, pyz), 917 (C=C, pyz), 440(M-O, pyz-Zn). **^{1}H NMR ($CDCl_3$, 400MHz) δ ppm:** 1.62 (s, 3H, Me-pyz), 7.00-8.09(m, 8H, ligand L5), 8.95 (rs, 1H, N-H, bhz). **^{13}C NMR ($CDCl_3$, 100 MHz)δ:** (16.2, 117.9, 119.8, 123.6, 126.8, 139.1, 139.6, 130.0, 130.3, 130.5, 133.0, 133.6, 137.0, 140.5, 157.9, 162.3 (C-O), 163.1 (C=N), 164.0 (C=O).

Synthesis of complex 12 [Zn (L6)$_2$]

The compound was synthesized by following the same procedure as that of complex **10** except **L6** was used instead of **L4.**

Yield: 70%, M.P.: >200 C, M.F.: $C_{50}H_{40}Cl_2N_8O_4Zn$, Elem. anal. Calcd. (Found): C, 63.00(63.34); H, 4.23(4.48); N, 11.76(12.00), F.w.: 953.20 Metal estimation theoretical (found): Zn, 6.86(7.01) %. **FTIR selected bands (KBr, cm^{-1}):** 3378 (N-H, bhz), 1616(C=O, bhz), 1567 (C=N, pyz), 1539 (C=N, imine of bhz), 1283 (C-O, pyz), 944 (C=C, pyz), 439(M-O,pyz-Zn). **^{1}H NMR ($CDCl_3$, 400MHz) ppm:** 1.62 (s, 3H, Me-pyz), 2.29(s, 3H, *p*-tolyl,-pyz), 7.01 (d, 2H, *p*-tolyl), 7.36-7.52 (m, 4H, bhz-pyz), 8.88(rs, 1H, N-H, bhz). **^{13}C NMR ($CDCl_3$, 100 MHz) δ :** 15.8 (CH_3-pyz), 21.0 (CH_3, *p*-tolyl), 97.1, 121.0, 126.7, 128.9, 129.0, 129.4, 129.6, 130.3, 130.4, 130.5, 132.7, 134.0, 136.8, 147.6, 157.9 (C-O), 162.7 (C=N), 163.6 (C=O). Synthesis route is depicted in scheme 3.1.2.



Scheme 3.1.2. Synthesis route of complex **10-12**.

3.1.2.4. X-ray single crystal structure analysis

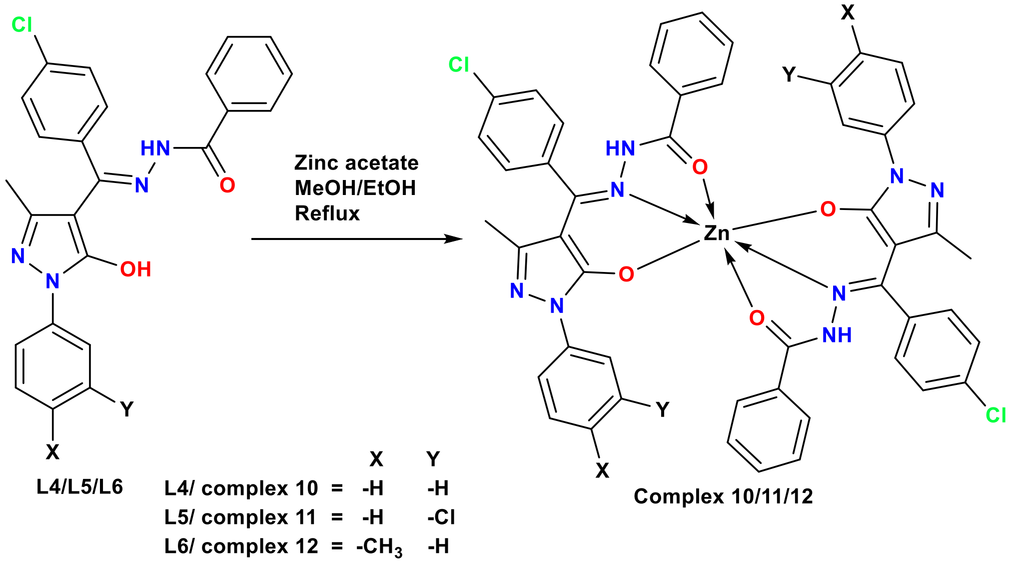
The X-ray single crystal data of ligand L4 and a complex **12** were collected on an Xcalibur, EOS, Gemini diffractometer with graphite monochromatic MoKα radiation (λ= 0.71073Å). All structures were solved and refined using the Olex2 and SHELXL-97 refine package.[20,21] All structures were solved by direct methods and refined by the full-matrix least-square method based on F^2 technique using SHELXL-97 program package.[22] The geometries of the molecules were determined using the software PLATON[23] and PARST[24]. Graphics of **L4** and complex **12** were generated using MERCURY (version 4.1.0) software.[25] In all the cases, non-hydrogen atoms were treated anisotropically. The hydrogen atoms (except hydrogen atoms bonded to O or N) were geometrically fixed. The H atoms of the NH/OH group were identified in difference syntheses and both the positional and displacement parameters were refined. The crystallographic parameters for ligand and complexes are given in Table 3.1.1. ORTEP diagram, H-bond and crystal packing diagram of ligand and complexes are shown in Fig. 3.1.5-3.1.17.

Table 3.1.1. Structure refinement parameters for **L4** and **L6** and complex **12**.

Identification code	**L4**	**L6**	**Complex12 [Zn(L6)$_2$] DMF**
Empirical formula	$C_{24}H_{20}ClN_4O_2$	$C_{25}H_{21}ClN_4O_2$	$C_{53}H_{47}Cl_2N_9O_5Zn$
Formula weight	431.89	444.92	1026.26
Temperature/K	293	293	293
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	7.2587(6)	7.2219(11)	14.5172(7)
b/Å	10.4100(12)	10.5815(15)	14.7328(6)
c/Å	14.7840(14)	14.1870(18)	14.9096(6)
α/°	102.895(9)	82.987(11)	62.875(4)
β/°	100.929(7)	87.617(11)	61.219(5)
γ/°	94.377(8)	89.285(12)	82.703(4)
Volume/Å^3	1060.96(19)	1075.1(3)	2470.0(2)
Z	2	5	2
μ/mm^{-1}	0.209	0.209	0.663
F(000)	450.0	462.0	1064.0
Crystal size/mm^3	0.3 × 0.1 × 0.1	0.3 × 0.1 × 0.1	0.3 × 0.3 × 0.2
Radiation	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.976 to 58.354	6.24 to 58.382	6.142 to 57.896
Index ranges	-9 ≤ h ≤ 9, -13 ≤ k ≤ 14, -20 ≤ l ≤ 20	-9 ≤ h ≤ 9, -14 ≤ k ≤ 14, -18 ≤ l ≤ 19	-19 ≤ h ≤ 19, -19 ≤ k ≤ 20, -20 ≤ l ≤ 20
Reflections collected	23334	23620	54010
Independent reflections	5193 [R_{int} = 0.0691, R_{sigma} = 0.0754]	5205 [R_{int} = 0.1424, R_{sigma} = 0.1806]	11770 [R_{int} = 0.0658, R_{sigma} = 0.0645]
Data/restraints/parameters	5193/0/281	5205/0/292	11770/0/638
Goodness-of-fit on F^2	1.086	1.006	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0956, wR_2 = 0.2755	R_1 = 0.0797, wR_2 = 0.1309	R_1 = 0.0670, wR_2 = 0.1360
Final R indexes [all data]	R_1 = 0.1707, wR_2 = 0.3157	R_1 = 0.2400, wR_2 = 0.1859	R_1 = 0.1128, wR_2 = 0.1564
CCDC	2048410	2024094	2024095

3.1.3. Results and discussion

In this chapter, three zinc(II) complexes have been prepared by following the scheme 3.1.3 described below;



Scheme 3.1.3. Synthesis route of complexes **10-12**.

All these complexes are light yellow solid, stable at room temperature and soluble in DMF and DMSO.

The detailed characterization of these complexes is described in succeeding sections.

3.1.3.1. Single crystal X-ray diffraction Study

Crystal features of ligand L4

The single crystal was obtained and the study was carried out which is a perfect agreement of ligand formation of structure. The atom numbering scheme is depicted in Fig. 3.1.4 and structure refinement data are given in Table 3.1.1. In the single crystal structure, C7-O1 of pyrazolone bond length 1.250(6) Å and C18-O2 of benzohydrazide 1.234(5) Å were found. Which are indicates O1-C7 double bond and also having C18-O2 double bond of benzhydrazone.[26] Distance of N1-N2 and N3-N4 were found 1.394(5) Å and 1.378(5) Å respectively. The bond length of C7-C8 is 1.433(6) Å and C8-C9 is 1.446(7) Å both are near to typical C-C single bonds. Furthermore the C11- N1 bond (1.310 Å) is longer than a C-N double bond and since an H atom is attached to N reveals that the ligand is present in the NH amine form.[26,27] Crystal packing of ligand L4 is shown in Fig. 3.1.5. Ligand L4 having an intermolecular H-bond between O2···H3a-N2 and also created intramolecular H-bond between O1-H4···N4. H-bonds parameters are given in Table 3.1.2. Nominated bond length and bond angles are given in Table 3.1.3.

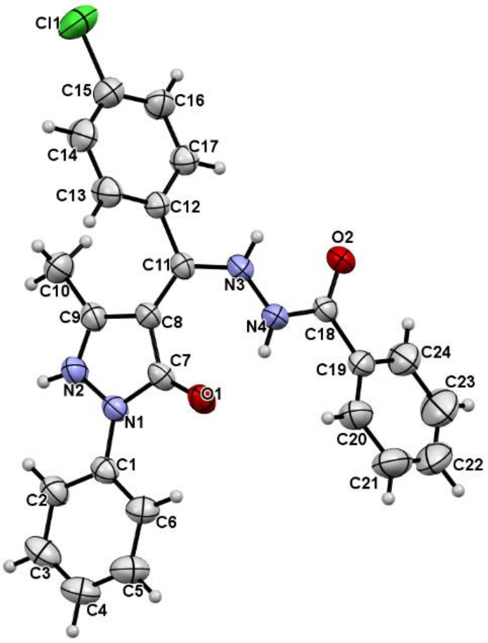


Fig. 3.1.4. ORTEP diagram with ellipsoid 50% probability of ligand **L4**. H-atoms are denoted as white small spherical.

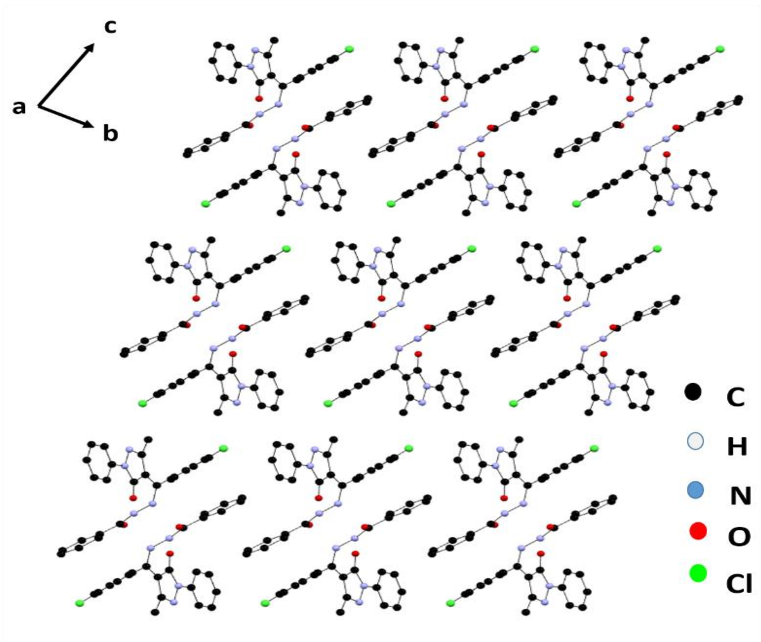


Fig. 3.1.5. Crystal packing of ligand **L4** showed down the 'a' axis.

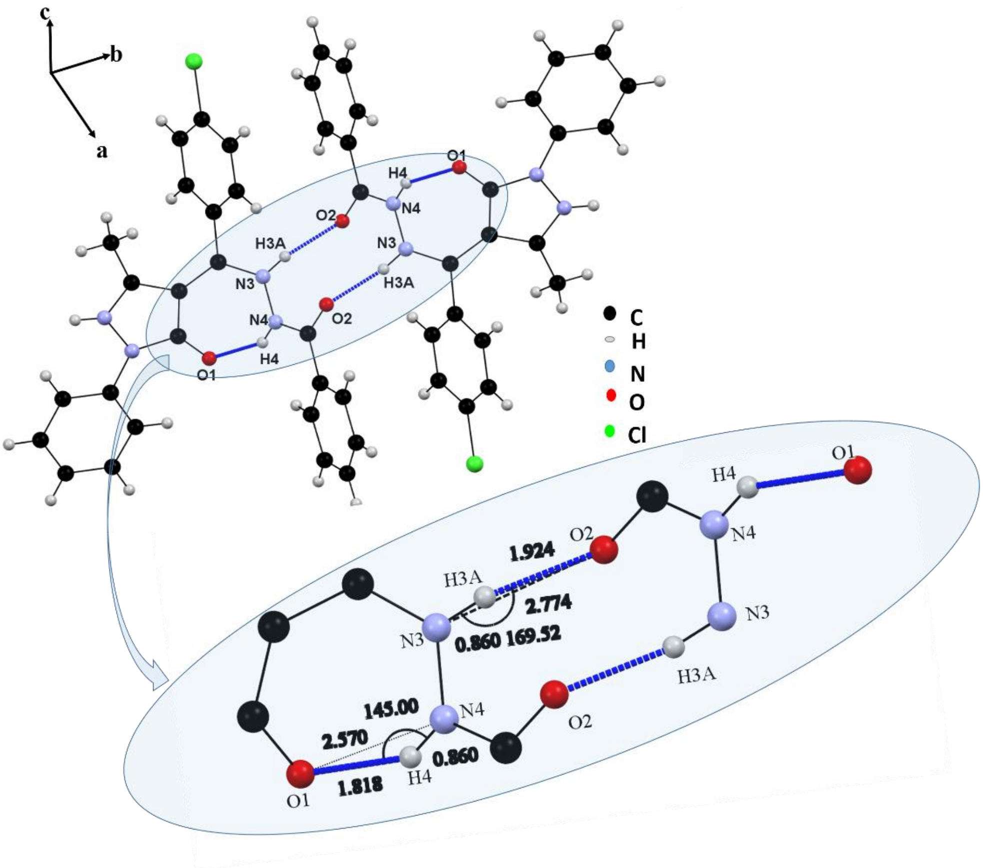


Fig. 3.1.6. Intermolecular and intramolecular H-bond in ligand **L4**.

Table 3.1.2. H-bond parameters of ligands and complexes **10-12**.

	D-H…A	**(D-H) / Å**	**(D-A)/ Å**	**(H…A)/ Å**	**(D-H-A)/º**
L4	N3-H3a…O2	0.860	2.774	1.924	169.52
	O1-H4…N4	0.860	2.570	1.818	145.00
L6	N21-H21…O23 ^{i}	1.04(4)	2.77(4)	1.77(4)	163.0(3)
	N22-H22…O5 ^{ii}	0.97(0)	2.52(4)	1.62(4)	157.8(5)
Complex 12	N4-H4…O5 ^{iii}	0.81(4)	2.90(5)	2.16(4)	153.0(3)
Symmetry (i) –x+2, -y, -z+2 (ii) ^{1}2-x,-y,2-z (iii) –x+2, -y+1, -z.					

Crystal features of ligand L6

In the single crystal of ligand **L6**, atom numbering scheme is shown in Fig. 3.1.7 and bond lengths and bond angles are given in Table 3.1.3. In the ligand, the C5-O5 (1.257(4)Å) of pyrazolone and C23-O23 (1.221(4)Å) of benzhydrazone are similar to a typical C=O double bond.[26,27] The bond length of C4-C5 (1.447(5) Å) and C3-C4 (1.438(5)Å) are near to aromatic C-C single bonds. Furthermore, the C3- N2 (1.302(4)Å) and C14-N21(1.318(4)Å) are very close to the C=N double bond. There is intramolecular hydrogen bonding between the –NH group of benzhydrazone and the carbonyl (C=O) group of the pyrazolone. The stability of the NH amino diketone form may be due to the presence of intramolecular hydrogen bonding. Furthermore, intermolecular H-bond found in the ligand structure (Fig. 3.1.8). Furthermore, in the crystal packing system, molecules arrangement design depicted in Fig.3.1.9. H-bond parameters of ligand L6 are given in Table 3.1.2.

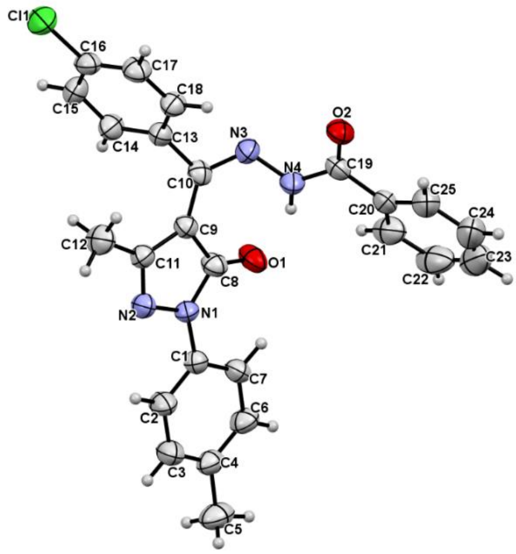


Fig. 3.1.7. ORTEP diagram with ellipsoid 50% probability of ligand L6. H-atoms denotes as white small spherical balls.

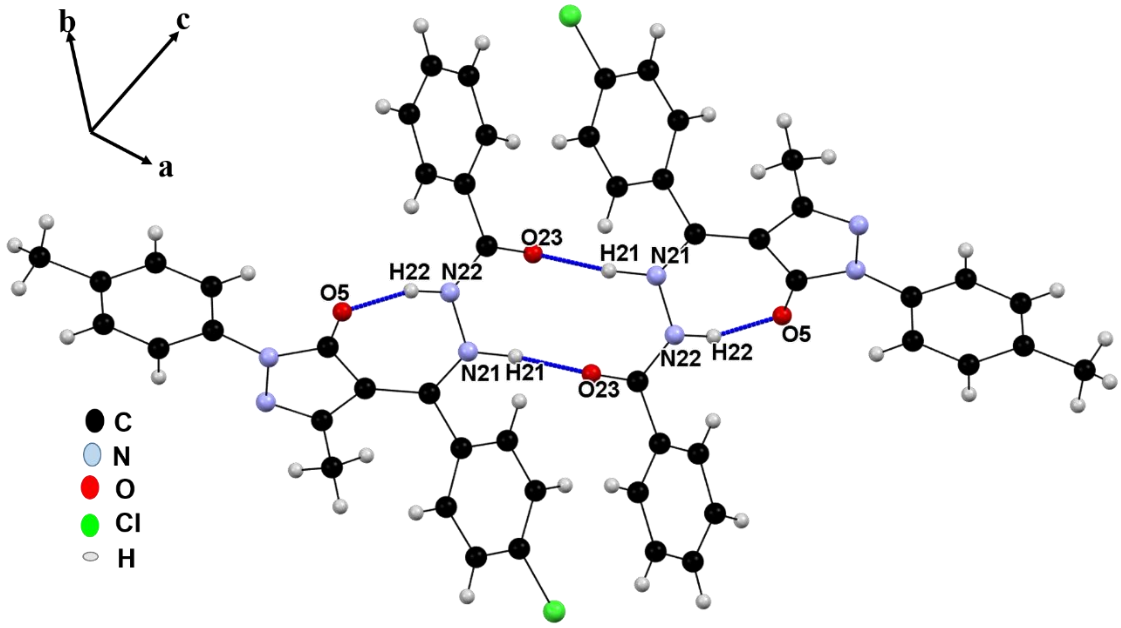


Fig. 3.1.8. Intramolecular H-Bond in ligand L6.

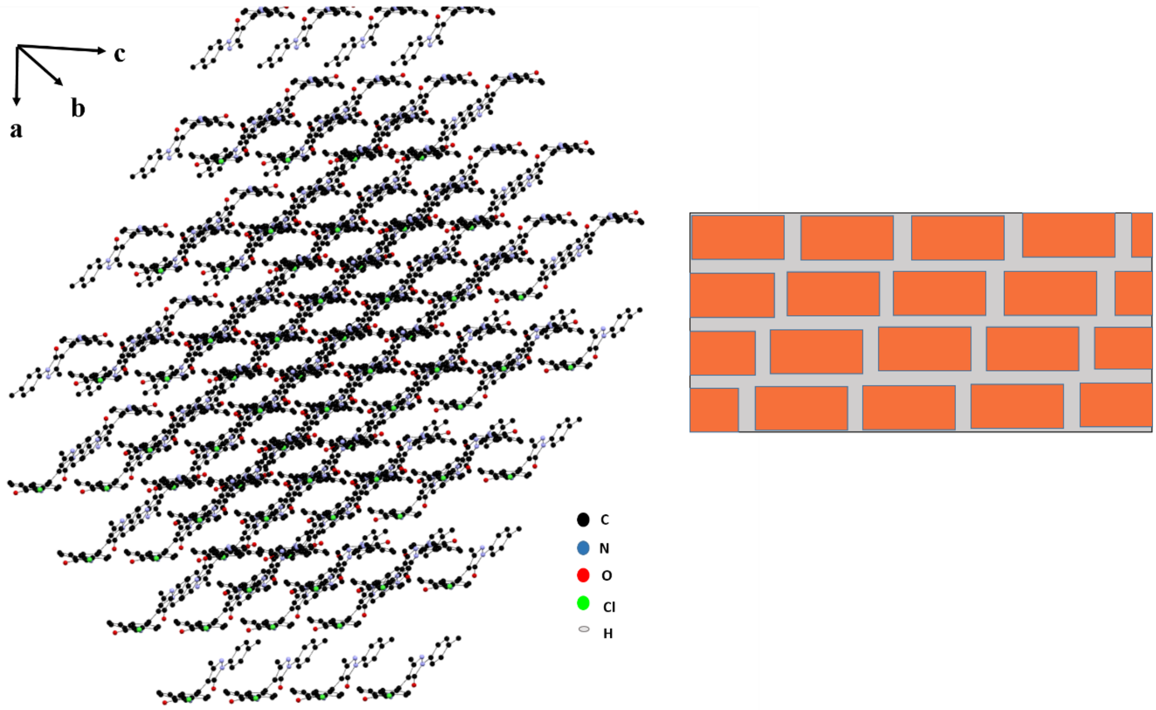


Fig. 3.1.9. Brick-wall motif in the Crystal packing system of ligand **L6.**

Single crystal features of complex 12

The atom numbering scheme of complex **12** depicted in Fig. 3.1.10. Single crystal of complex **12** was obtained from the solution of DMF. Selected bond length and bond angles are given in Table 3.1.3. As shown in Fig. 3.1.10, the Zn(II) is Hexa coordinated with two tridentate 4-acylhydrazone-5-pyrazolone ligands, which coordinate in a meridional ONO fashion. Two oxygen (O1 & O2) donors of first 4-acylhydrazone-5-pyrazolone molecules and two oxygen atoms (O3 & O4) of second 4-acylhydrazone-5-pyrazolone occupy the basal sites of the octahedral structure, whereas the two nitrogen atoms (N3 & N7) of each 4-acylhydrazone-5-pyrazolone coordinated the zinc at the apical site. In this complex, the incorporation of two **L6** ligands occupied the distorted octahedral geometry around the zinc(II) metal. In the complex, the zinc atom occupies a distorted octahedral environment, formed by four oxygen atoms [O1, O2, O3 and O4] supplied by **L6** ligands (Fig. 3.1.10). The fifth and sixth coordination sites are occupied by nitrogen atoms of each ligand molecule. The Zn–O distances of the basal plan Zn1-O1, Z1-O2, Zn1-O3 and Zn1-O4 are 2.023(2) Å, 2.177(2) Å, 2.014(2) Å and 2.140(2) Å respectively, whereas the axial distance of Zn1-N3 and Zn1-N7 are 2.153(3) Å and 2.180(2) Å respectively [21]. The angles of O2–Zn1–O1, O3–Zn1–O4 and N3–Zn1–N7 are 160.47(9) °, 158.81(9) ° and 175.94(10) ° respectively, which deviate from the theoretical value of 180° of a proper octahedron.

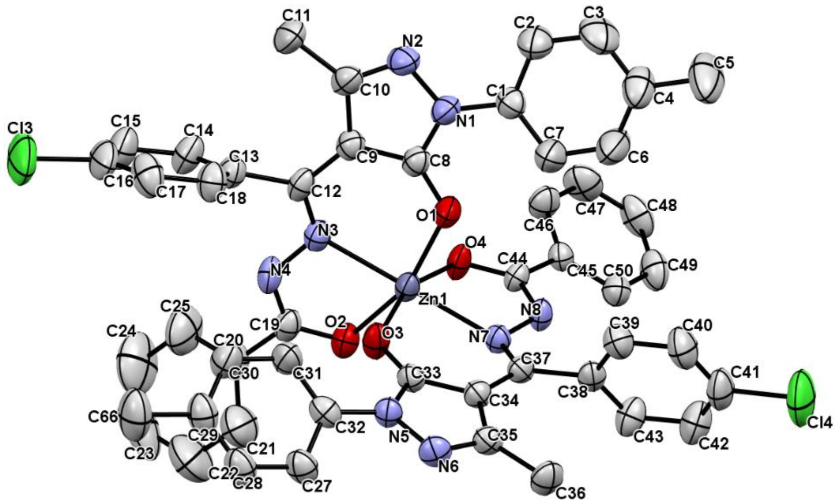


Fig. 3.1.10. ORTEP diagram with ellipsoid 50% probability of complex **12**.

The angles of complex **12** for O3–Zn1–O1(100.35(10)º), O1–Zn1–O4(91.21(9)º), O3–Zn1–N3(89.39(9)º), O1–Zn1–N3(88.30(9)º), O4–Zn1–N3(108.81(9)º), O3–Zn1–O2(89.91(9)º), O4–Zn1–O2(84.63(9)º), N3-Zn1-O2(75.07(9)º), O3-Zn1-N7(87.36(9)º), O1-Zn1-N7(89.90(9)º), O4-Zn1-N7(74.86(8)º) and O2–Zn1–N7(107.33(9)º), which are deviated from 90º angle between the axial line and equatorial plane. Therefore, the local coordination geometry around the Zn(II) centre can be described as a distorted octahedron (Fig.3.1.11).

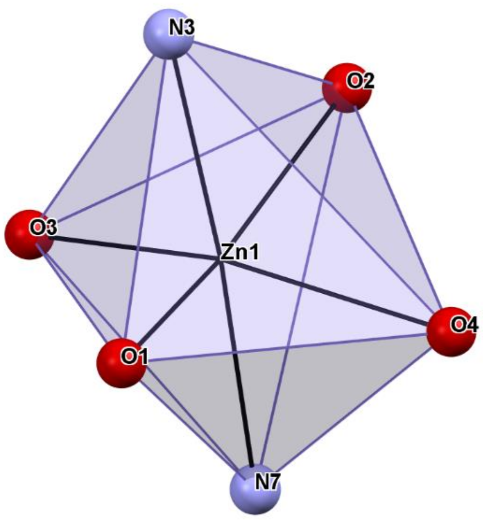


Fig. 3.1.11. Distorted octahedral geometry of binary zinc(II) complex **12**.

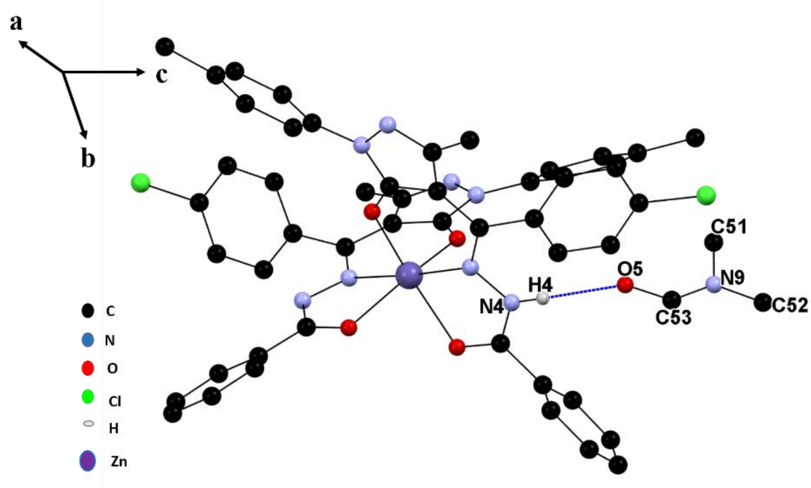


Fig. 3.1.12. Intermolecular H-bond between O(5) of DMF and H(4)-N(4) of complex **12**. Blue dotted line indicating H-bond.

Intermolecular H-bond showed in the complex **12** packing system between Oxygen atom (O5) of DMF and a hydrogen atom (H4) of 4-acylhydrazone-5-pyrazolone (Fig. 3.1.12), where H-bond dimensions are given in Table 3.1.2 and crystal packing system presented in the Fig. 3.1.13.[12].

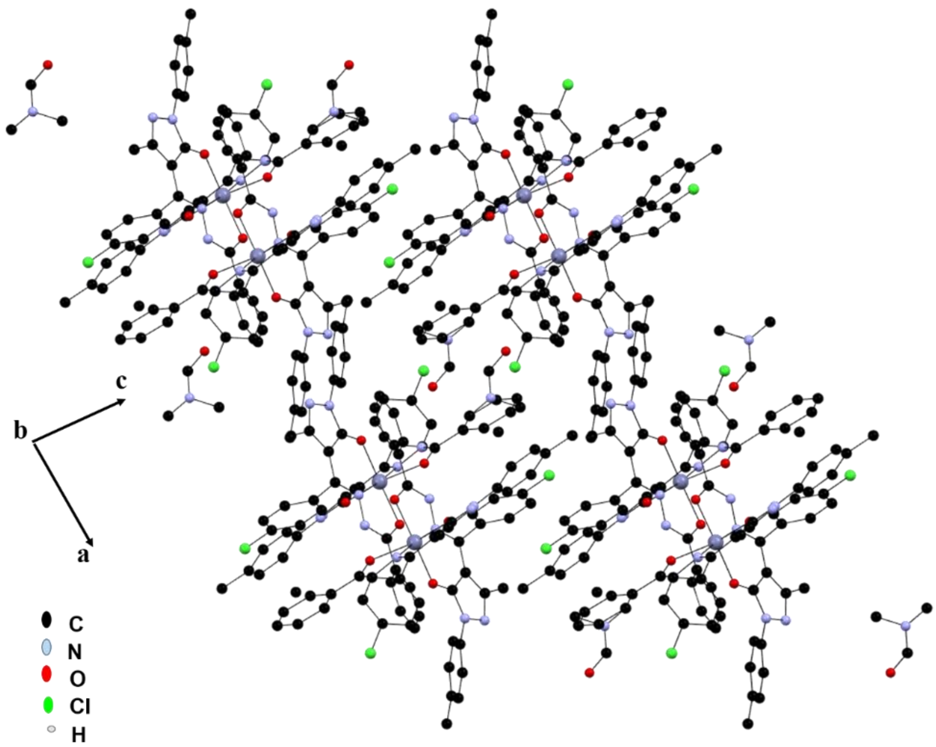


Fig. 3.1.13. Crystal packing of complex **12**. Viewed down from the b-axis.

Table 3.1.3. Bond length and Bond angles of ligands (**L4** & **L6**) and complex **12**.

Ligand L4.

Atom	Length/Å	Atom	Angle/°
Cl1-C15	1.736(6)	N2-N1-C1	119.0(4)
O2-C18	1.234(5)	C7-N1-N2	111.2(4)
O1-C7	1.250(6)	C7-N1-C1	129.8(4)
N1-N2	1.394(5)	C18-N4-N3	117.9(4)
N1-C7	1.385(6)	C9-N2-N1	107.4(4)
N1-C1	1.415(6)	O2-C18-N4	121.7(4)
N4-C18	1.336(6)	O2-C18-C19	121.8(4)
N4-N3	1.378(5)	N4-C18-C19	116.5(4)
N2-C9	1.301(6)	C11-C8-C7	127.6(4)
C18-C19	1.493(7)	C11-C8-C9	127.3(4)
C8-C11	1.398(6)	C7-C8-C9	105.0(4)
C8-C7	1.433(6)	C8-C11-C12	122.7(4)
C8-C9	1.446(7)	N3-C11-C8	123.9(4)
C11-C12	1.487(6)	N3-C11-C12	113.4(4)
C11-N3	1.331(6)	O1-C7-N1	123.8(4)
C9-C10	1.498(7)	O1-C7-C8	130.8(4)
C1-C6	1.383(7)	N1-C7-C8	105.2(4)

Ligand L6

Atom	Length/Å	Atom	Angle/°
Cl1-C18	1.727(4)	C5-N1-N2	111.9(3)
N1-C5	1.368(4)	C5-N1-C6	130.2(3)
N1-N2	1.400(4)	N2-N1-C6	117.9(3)
N1-C6	1.415(4)	C3-N2-N1	106.8(3)
N2-C3	1.302(4)	N2-C3-C4	111.4(3)
C3-C4	1.438(5)	N2-C3-C13	117.7(3)
C3-C13	1.498(4)	C4-C3-C13	130.9(3)
C4-C14	1.404(5)	C14-C4-C3	128.1(3)
C4-C5	1.447(5)	C14-C4-C5	126.9(3)
C5-O5	1.257(4)	C3-C4-C5	104.9(3)
C6-C11	1.368(5)	O5-C5-N1	124.1(3)
C6-C7	1.390(4)	O5-C5-C4	130.8(4)
C7-C8	1.387(5)	N1-C5-C4	104.9(3)

Complex 12 [Zn(L6)$_2$] DMF

Atom	Length/Å	Atom	Angle/°
Zn1-O3	2.014(2)	O3-Zn1-O1	100.35(10)

Zn1-O1	2.023(2)	O3-Zn1-O4	158.81(9)
Zn1-O4	2.140(2)	O1-Zn1-O4	91.21(9)
Zn1-N3	2.153(3)	O3-Zn1-N3	89.39(9)
Zn1-O2	2.177(2)	O1-Zn1-N3	88.30(9)
Zn1-N7	2.180(2)	O4-Zn1-N3	108.81(9)
Cl1-C16	1.744(4)	O3-Zn1-O2	89.91(9)
Cl2-C41	1.740(4)	O1-Zn1-O2	160.42(9)
O1-C8	1.274(4)	O4-Zn1-O2	84.63(9)
O2-C19	1.243(4)	N3-Zn1-O2	75.07(9)
O3-C33	1.272(4)	O3-Zn1-N7	87.36(9)
O4-C44	1.237(3)	O1-Zn1-N7	89.90(9)
N1-C8	1.371(4)	O4-Zn1-N7	74.86(8)
N1-N2	1.400(4)	N3-Zn1-N7	175.94(10)

3.1.3.2. FTIR spectroscopic study

The ligand used in the present study can exhibit different tautomerism like keto, enol etc. From the FTIR studies, it is possible to assign the correct tautomeric form of the ligand. In the FTIR spectrum of ligand L4**,** The spectrum shows a broad peak at 3136 cm^{-1} due to the υ(N-H) stretching of benzhydrazone in the ligand. Two stretching frequency of amidic ketone υ(C=O) of pyrazolone ring and benzhydrazone indicate at 1640 cm^{-1} and 1593 cm^{-1}, respectively. The spectrum shows a band at 1090 cm^{-1} is due to N-N bond stretching. In the FTIR spectrum of ligand L5, the spectrum shows a broad peak at 3138 cm^{-1}, which can be assigned to *v*(NH)(amine) of the neutral ligand. Two sharp bands at 1641 and 1592 cm^{-1} are also observed, which can be assigned to *v*(C=O) of pyrazolone and *v*(C=O) of benzhydrazone, respectively. The band at 1091 cm^{-1} is due to υ(N-N) bond in the neutral ligand molecule. In the FTIR spectrum of ligand L6, the spectrum shows a broad peak at 3137 cm^{-1}, which can be assigned to NH (amine). Two sharp peaks are observed at 1641 and 1595 cm^{-1} and can be assigned to *v*(C=O) of pyrazolone and *v*(C=O) of benzhydrazone, respectively. A sharp band at 1013 cm^{-1} is due to the *v*(N-N) stretching frequency. The FTIR data suggest that all three ligands are in the keto form in the solid state [29].

In the FTIR spectrum of complex **10**, the spectrum shows a sharp peak at 1601 cm^{-1}, which can be assigned C=O of pyrazolone ring of ligand L6. The spectrum shows a sharp peak at 1583 cm^{-1} is due to the υ(C=N)(imine) of ligand L6. Two small peaks exhibit at 440 cm^{-1} and 564cm⁻

^{1} are due to υM-O and υM-N, respectively.[12,28,30,31] In the FTIR spectrum of complex **11**, strong band at 1601 cm^{-1} is due to the υ(C-O) stretching. Pyrazolone υ(C=N) stretching frequency exhibits at 1571cm^{-1} in the spectrum. Two bands at 440 and 565 cm^{-1} are due to the metal-ligand bond of M-N and M-O, respectively. The FTIR spectrum of complex **12** displays a sharp peak at 1616 cm^{-1}, which can be assigned to υ(C=O) of benzhydrazone. The spectrum shows a broad peak at 3378 cm^{-1} is due to *v*(NH) of benzhydrazone moiety. The spectrum shows sharp bands at 1567 and 1539 cm$^{-1,}$ which can be assigned to stretching frequency of *v*(C=N)(pyrazolone) and *v*(C=N)(benzhydrazone), respectively. New sharp band detects at 1283 cm^{-1} is due to *v*(C-O)$_{(}$pyrazolone) in the complex spectrum. Two sharp bands at 439 and 511 cm^{-1} are due to stretching frequencies of metal-ligand bonds of M-N and M-O, respectively. FTIR spectra are presented in Fig. 3.1.14-Fig. 3.1.19. Important frequencies of FTIR are given in Table 3.1.4.

Table 3.1.4. FTIR spectral data for 4-acylhyrazone-5-pyrazolones and its zinc complexes (cm^{-1}).

Code	***v* (N-H)**	***v*(C=O)^{A}**	***v*(C=O)^{B}**	***v*(C=N)**	***v*(N-N)**	***v*(C-O)^{B}**	***v*(M-N)**	***v*(M-O)**
L4	3136	1640	1593	-	1090	-	-	-
L5	3138	1641	1592	-	1091	-	-	-
L6	3137	1641	1595	-	1090	-	-	-
[Zn(L4)$_2$] **10**	3378	1601	-	1583	1286	1091	440	565
[Zn(L5)$_2$] **11**	3378	1601	-	1571	1278	1091	440	565
[Zn(L6)$_2$] **12**	3377	1616	-	1568	1284	1091	439	548

^{A} Benzhydrazide moiety, ^{B} Pyrazolone ring

FTIR spectra of ligands and complexes

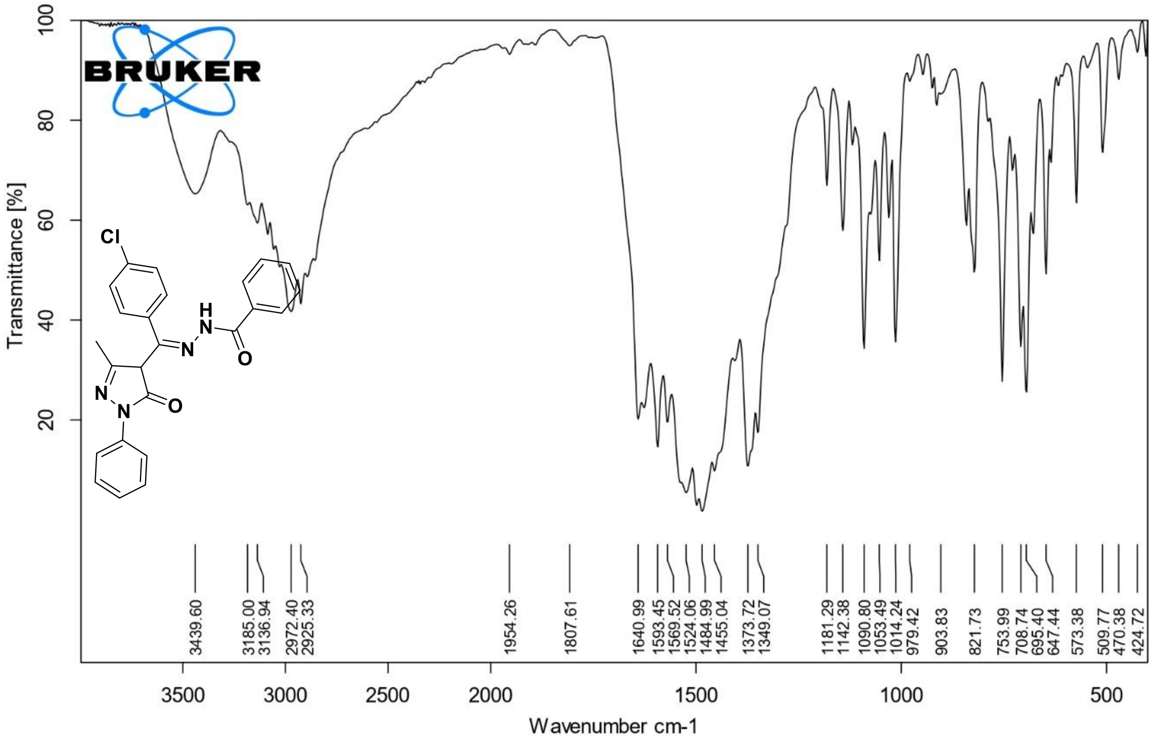


Fig. 3.1.14. FTIR spectrum of ligand **L4**.

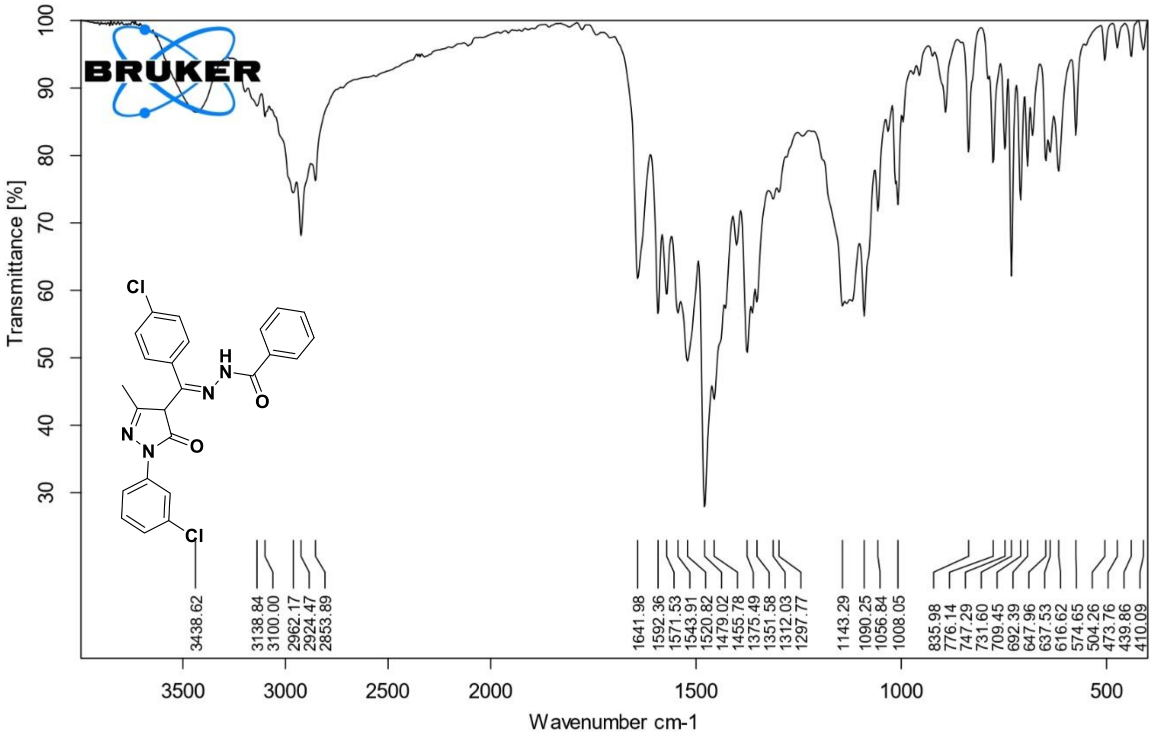


Fig. 3.1.15. FTIR spectrum of ligand **L5**.

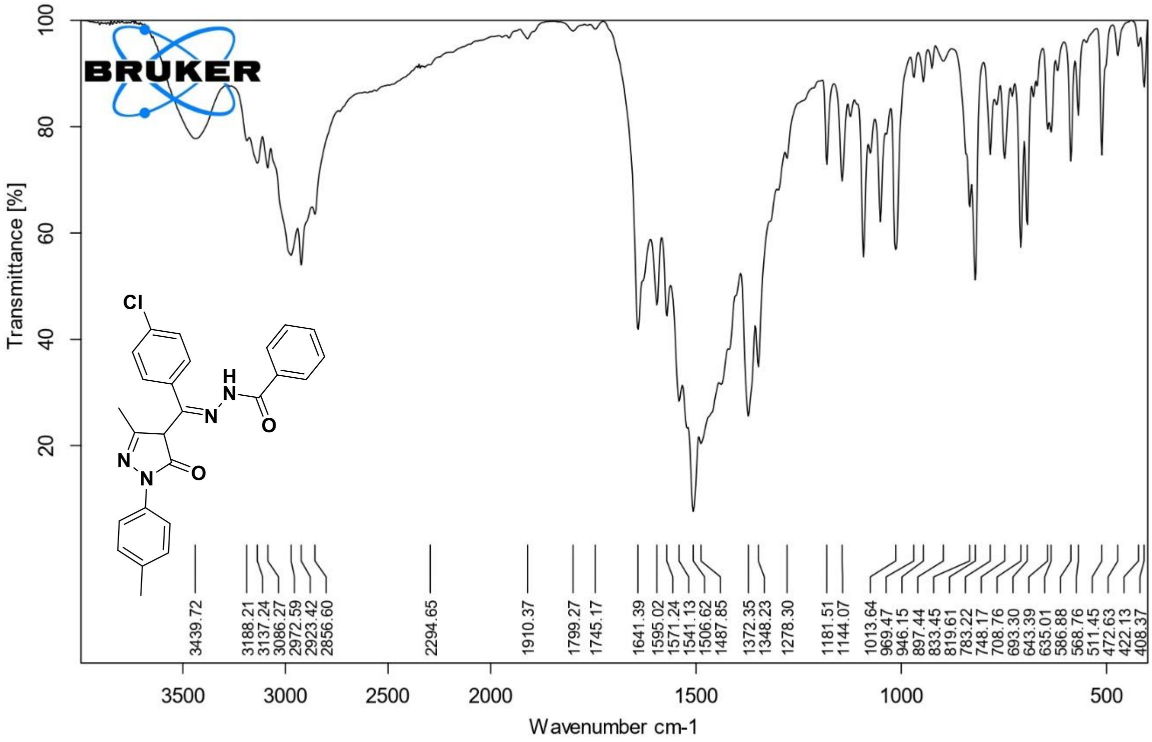


Fig. 3.1.16. FTIR spectrum of ligand L6.

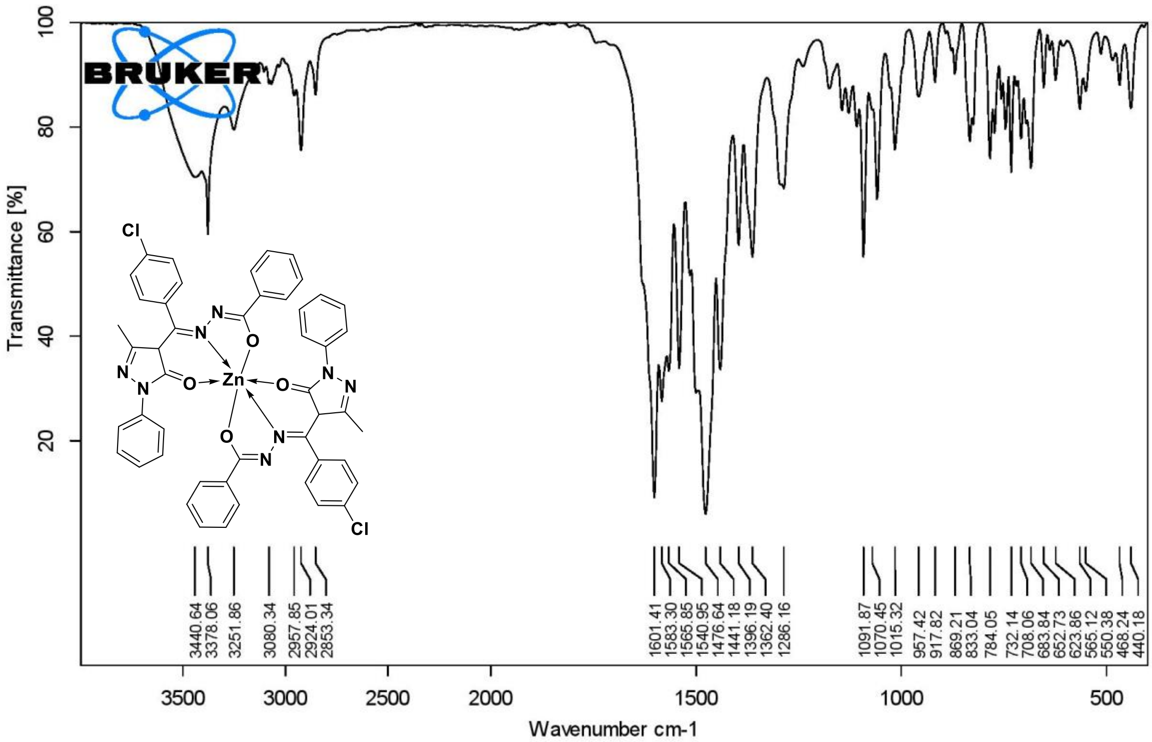


Fig. 3.1.17. FTIR spectrum of complex **10 [Zn(L4)$_2$].**

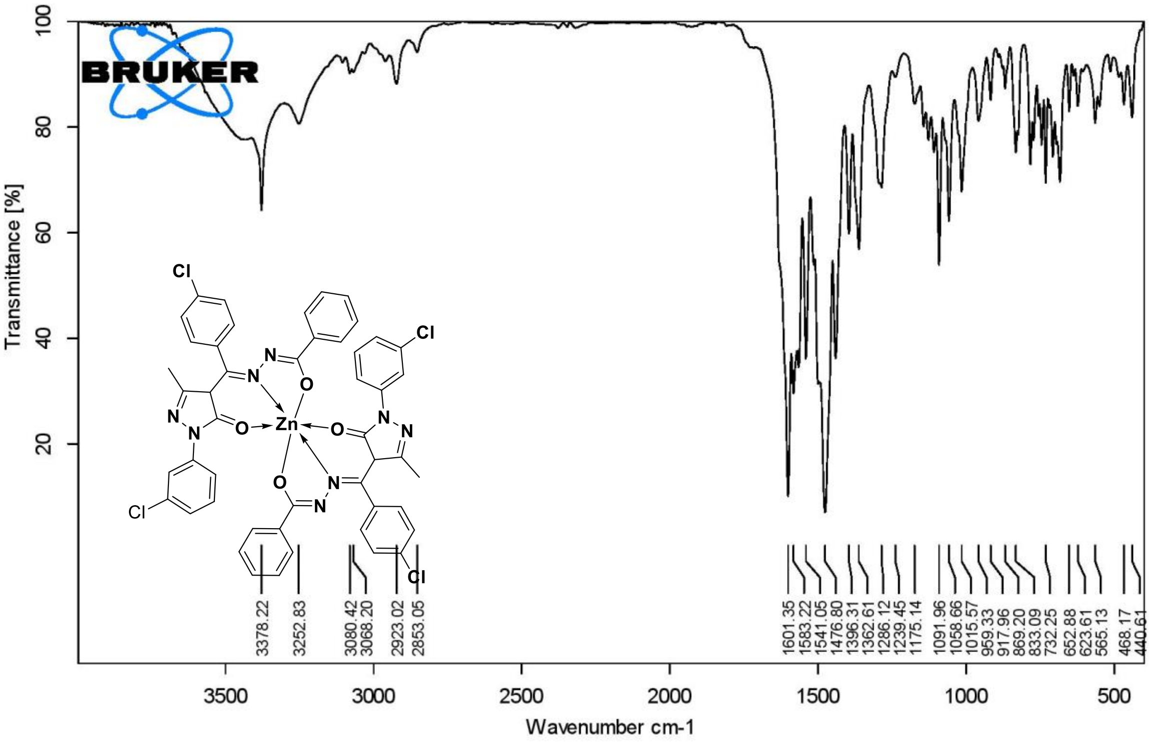


Fig. 3.1.18. FTIR spectrum of complex **11 [Zn(L5)2].**

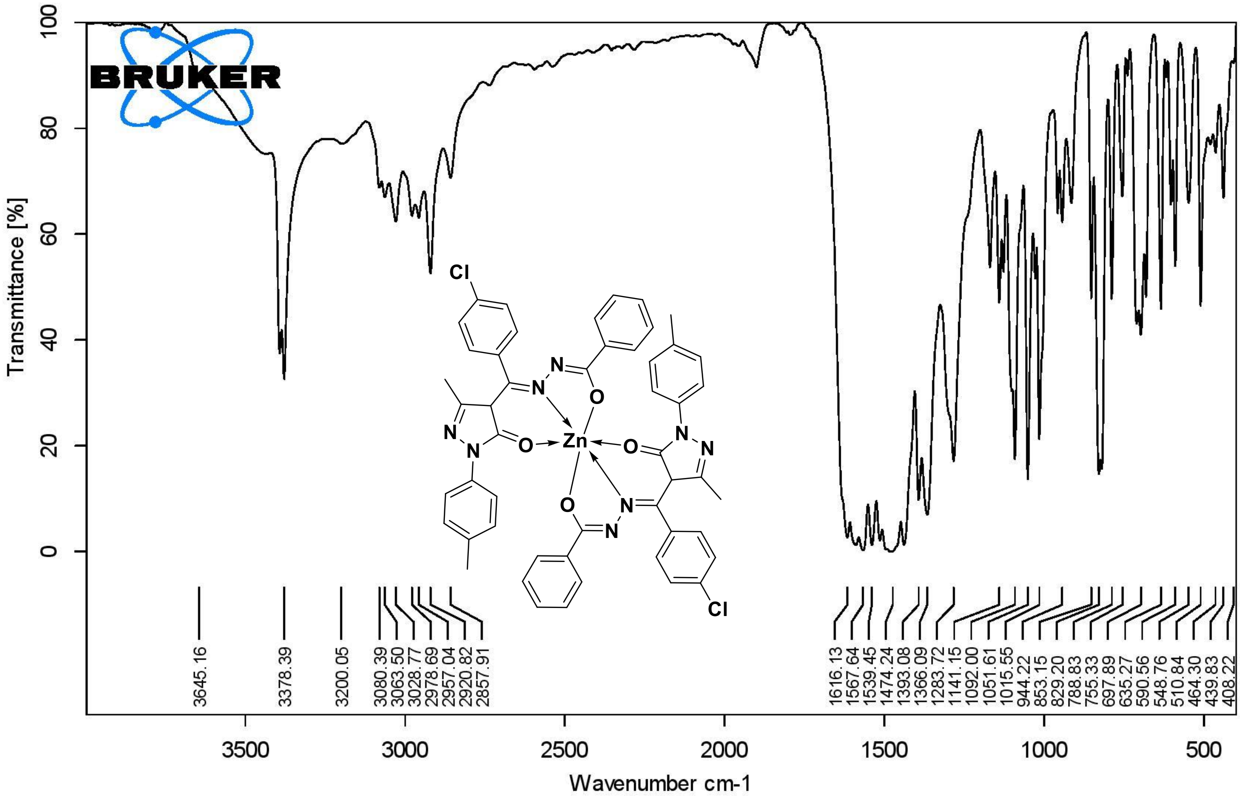


Fig. 3.1.19. FTIR spectrum of complex **12 [Zn(L6)2].**

3.1.3.2. ^{1}H & ^{13}C NMR spectroscopic study

^{1}H & ^{13}C NMR spectra of ligands and complexes presented in Fig. 3.1.20 to Fig 3.1.30. The ^{1}H NMR spectrum of ligand **L4,** the spectrum shows a singlet at 1.6 (3H) δ ppm which confirmed the methyl group at the C3 position of the pyrazolone ring. A triplet at 7.25 (1H) δ ppm is due to phenyl proton of benzhydrazone. Doublets and triplets are an aromatic ring indicated aromatic protons of the ligand. One small signal at 15.7 δ ppm indicated the hydroxyl group (pyz-OH) proton of benzhydrazone.^{13}C NMR spectrum of **L4** shows a signal at 16.4 δ ppm which also confirmed the methyl group at the C3 position of pyrazolone. The spectrum shows signals at 153.6, 163.3 and 163.7 δ ppm due to carbon of C-O, C=N and C=O, respectively. In the ^{1}H NMR spectrum of ligand L5, a singlet at 1.6 (3H) δ ppm confirm methyl at the C3 position of pyrazolone. ^{13}C NMR spectrum also confirms the presence of the methyl group by exhibiting the peak at 16.4 δ ppm. The spectrum shows a doublet at 7.21 (1H) δ ppm, which can be assigned to two aromatic protons of *m*-chlorophenyl. The presence of a triplet at 7.38 (2H) δ ppm, which can be assigned to two aromatic protons of benzhydrazone. A doublet of doublets and quartet show at the region of 7.57 (7H) δ ppm confirm the presence of aromatic protons of the ligand. A small peak observes at 15.4 (1H) δ ppm is due to enolic proton (pyz-OH) of the neutral ligand. In the ^{13}C NMR spectrum of **L5** peaks at 163.7 and 196.2 δ ppm appeared, which can be assigned to two C=O of the ligand. All carbon signals have appeared at their expected region. In the ^{1}H NMR spectrum of ligand **L6**, spectrum exhibits two singlets in the aliphatic region at 1.6 (3H) and 2.3 (3H) δ ppm, which confirm methyl and tolyl groups of pyrazolone, respectively. A doublet at 7.27 (2H) δ ppm assigned to two aromatic protons of a *p*-tolyl group. Multiplet exhibits at 7.55 (2H) δ ppm due to aromatic protons of phenyl. Doublets at 7.87 (1H) δ ppm and 7.99 (1H) δ ppm can be assigned to aromatic protons of benzhydrazone moiety. A small peak observes at 15.8 (1H) δ ppm is due to enolic proton (pyz-OH) of the neutral ligand. The ^{13}C NMR spectrum of ligand (**L6**) shows two carbon signals at 16.0 and 21.0 δ, which confirm methyl and a *p*-tolyl group of pyrazolone, respectively. Signals appeared at 137.0, 147.5 and 165.1 δ ppm are due to the presence of C-O, C=N and C=O, respectively.

In the ^{1}H NMR spectrum of complex **10**, the spectrum shows 1.62 (3H) δ ppm which confirm methyl group at the C3 position of pyrazolone. Multiplet at 7.50 (8H) is due to aromatic protons of a ligand. Rough singlet appears at 8.95 (1H) of amine (NH) proton of benzhydrazone. In the ^{1}H NMR spectrum of complex **11**, the spectrum shows a singlet at 1.62 δ ppm due to the methyl group of pyrazolone. Many doublets and triplets appeared due to aromatic protons of ligands.

The rough signal is shown at 8.95 δ ppm which can be assigned amine proton of benzhydrazone. ^{13}C NMR of complex **11** also confirmed the methyl group at the C3 position of pyz by the peak at 16.2 δ. Signals obtain at 162.3 (C-O), 163.1 (C=N) and 164.0 (C=O) are also confirmed the formation of the complex.

In the ^{1}H NMR spectrum of complex **12**, the spectrum shows two singlets at 1.6 (3H) and 2.9 (3H) δ ppm, which confirm the presence of methyl at C3 position and tolyl group at the N1 position of pyrazolone ring. The spectrum shows a doublet at 7.02 (2H) δ ppm due to aromatic protons of *p*-tolyl. A triplet at 7.18 (2H) δ ppm was observed, which confirm the presence of phenyl group of benzhydrazone. Multiplets exhibit in the region of 7.77 (10H) δ ppm, which assigned aromatic protons of 4-acylhydrazone-5-pyrazolone. A new peak observed at 8.85 (1H) δ ppm due to NH (amine) proton of benzhydrazone. ^{13}C NMR spectrum also confirms the presence of two methyl groups by the appearance of the peaks at 15.9 and 21.0 δ ppm. The spectrum shows peaks at 163, 157 and 147 δ ppm due to the presence of C=O, C=N and C-O respectively.

^{1}H NMR spectra of ligands and complexes

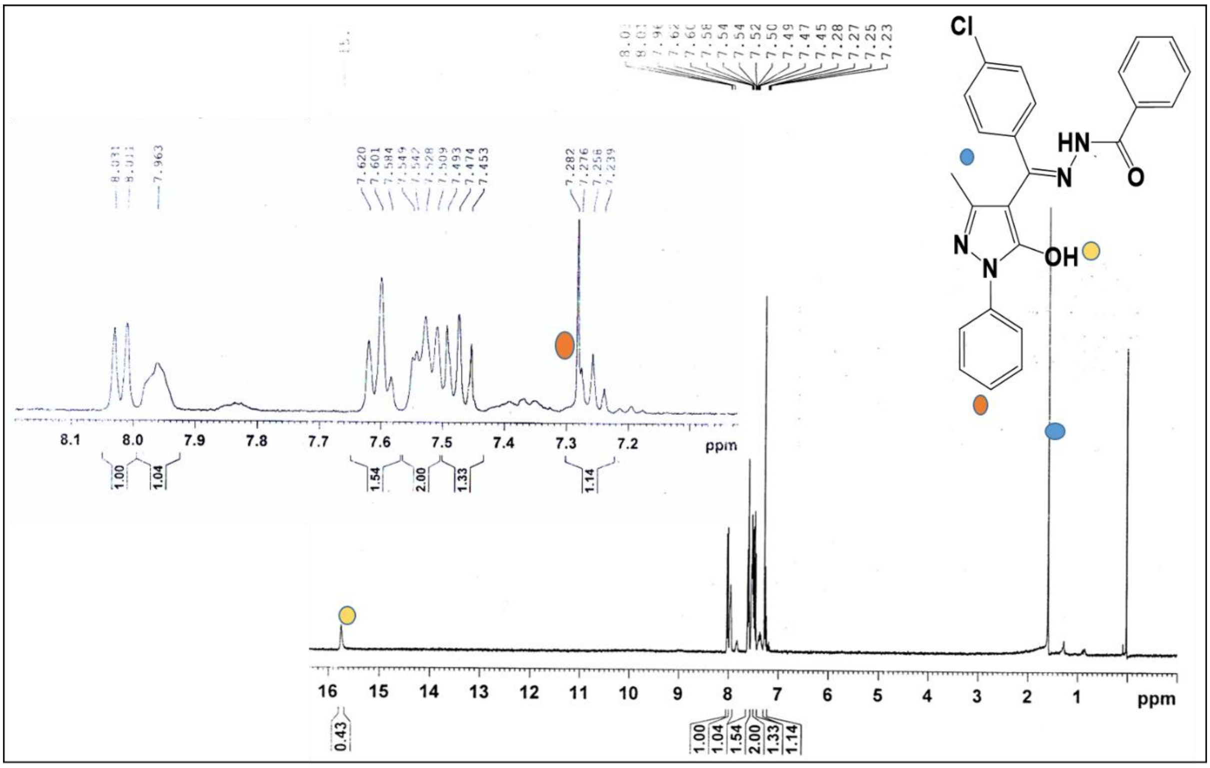


Fig. 3.1.20. ^{1}H NMR spectrum of ligand **L4.**

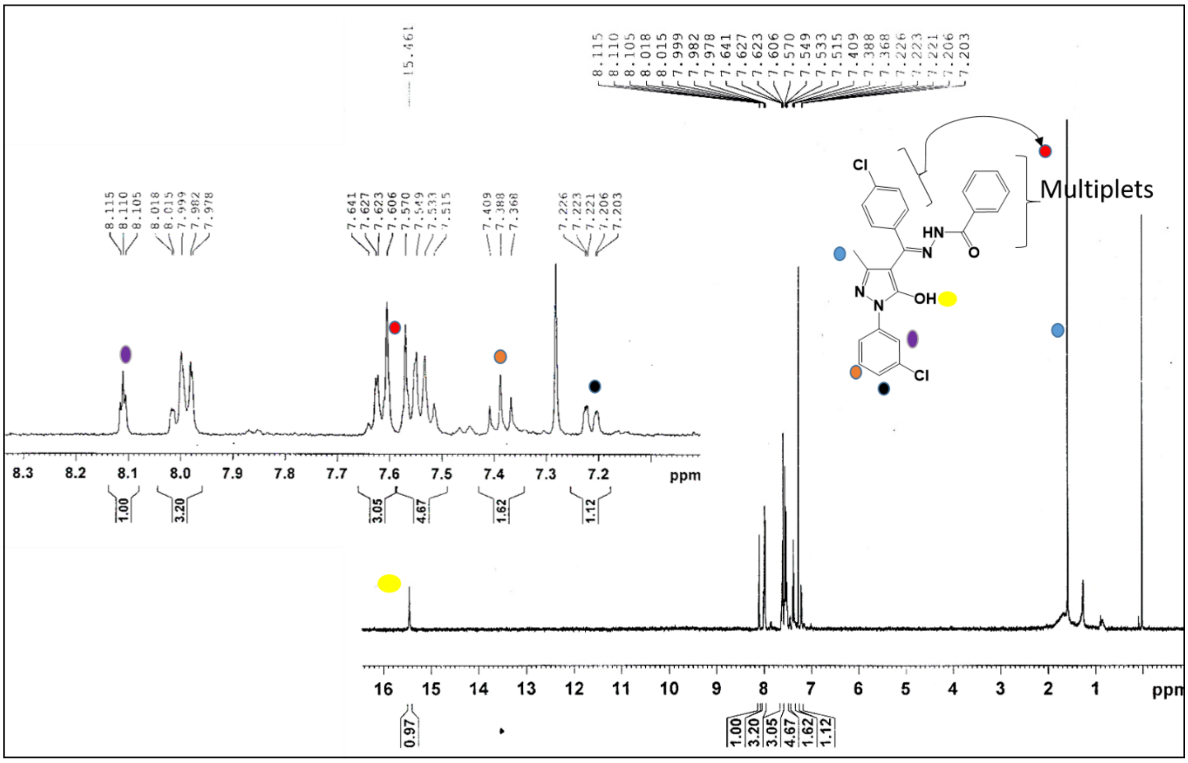


Fig. 3.1.21. ^{1}H NMR spectrum of ligand **L5.**

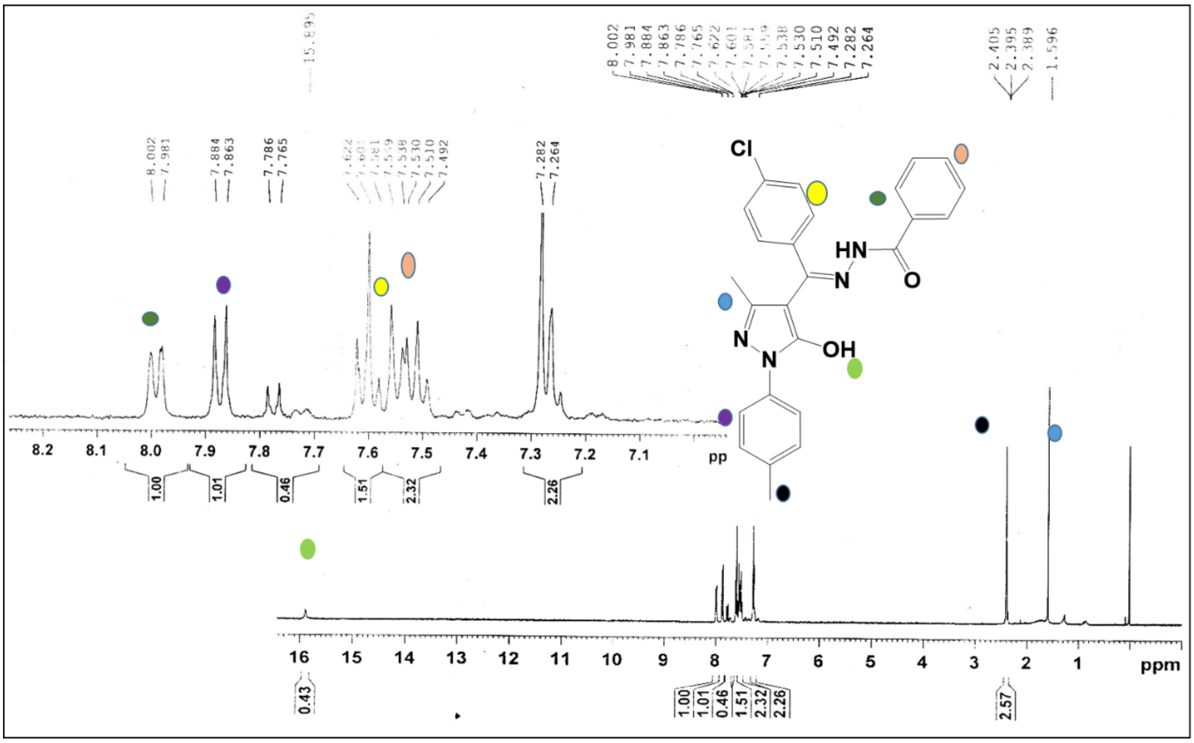


Fig. 3.1.22. ^{1}H NMR of ligand **L6**.

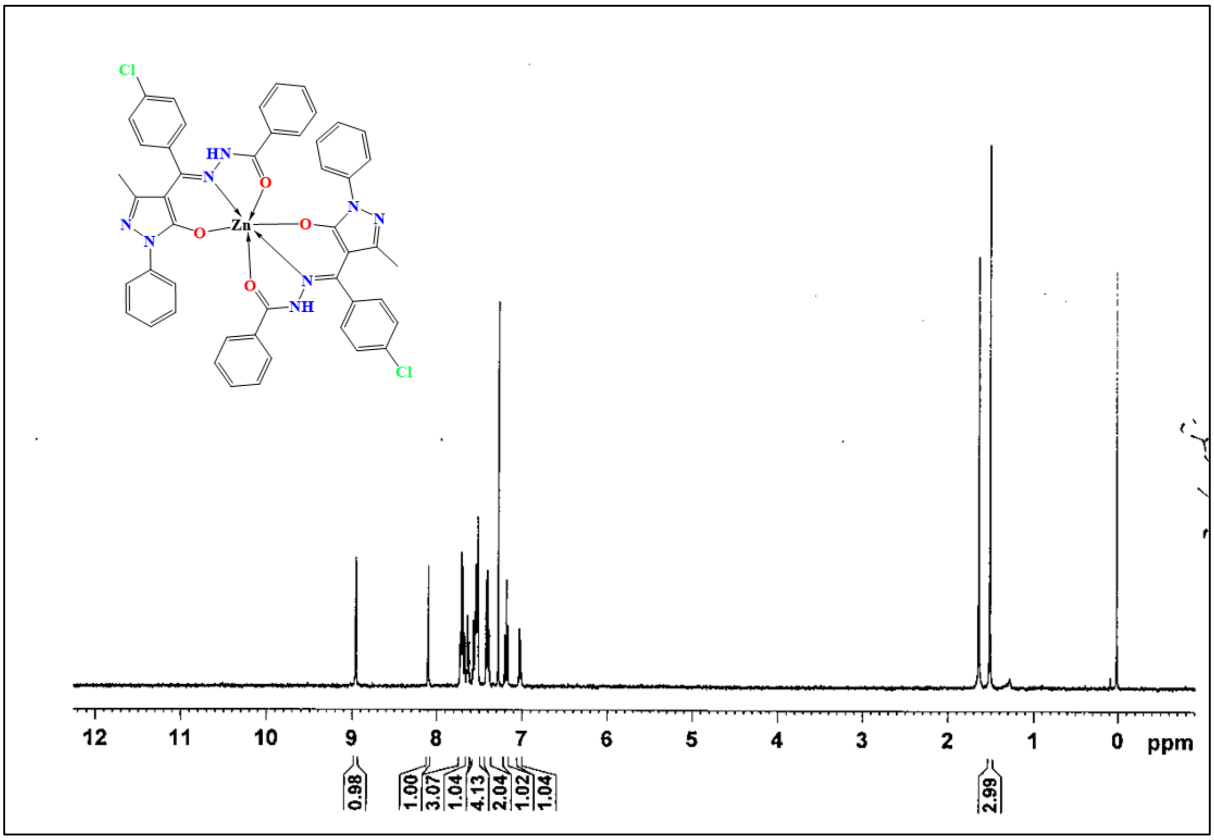


Fig. 3.1.23. [1]H NMR of complex **10 [Zn(L4)2].**

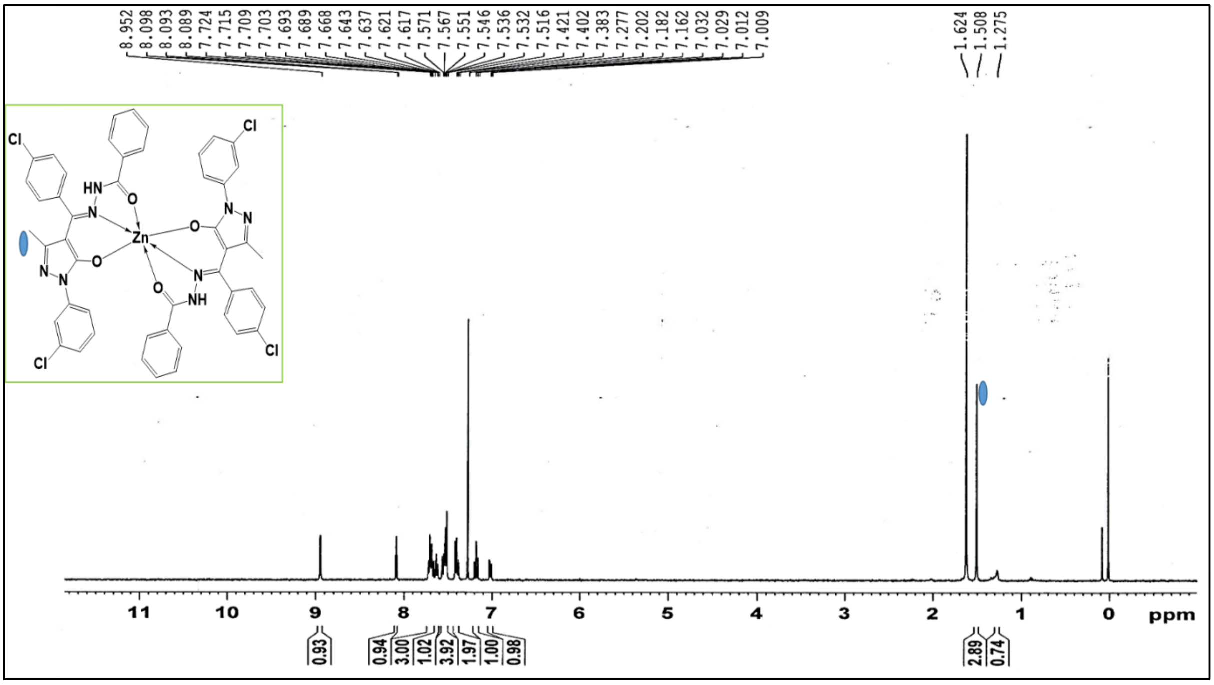


Fig. 3.1.24. [1]H NMR of complex **11 [Zn(L5)2].**

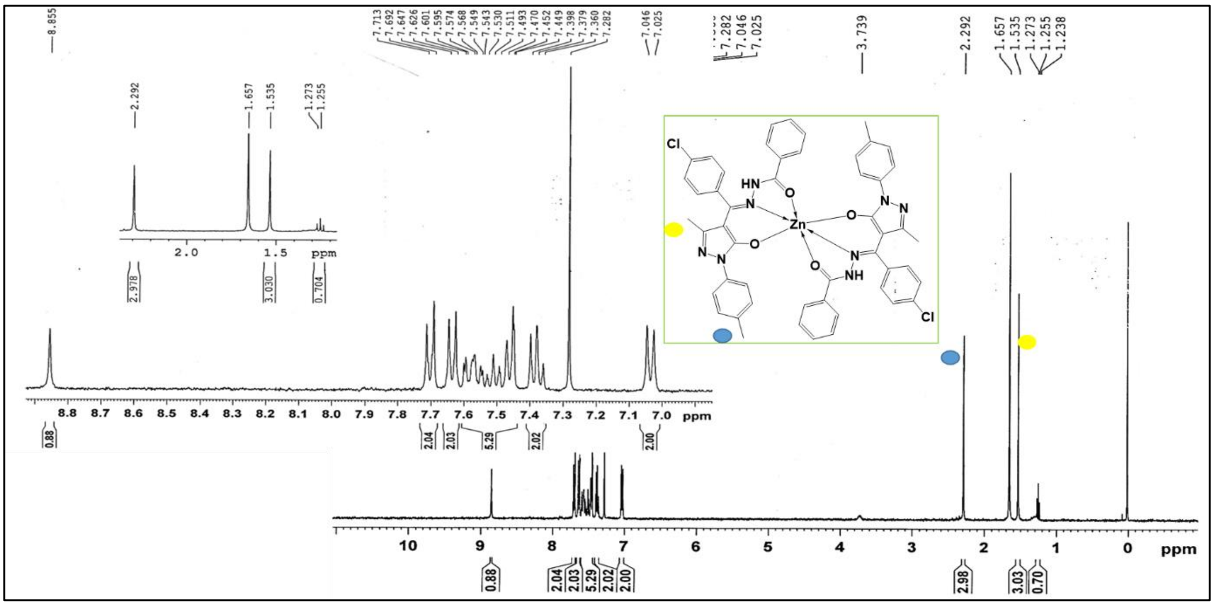


Fig. 3.1.25. ^{1}H NMR spectrum of complex **12 [Zn(L6)$_3$].**

^{13}C NMR spectra of ligands and complexes

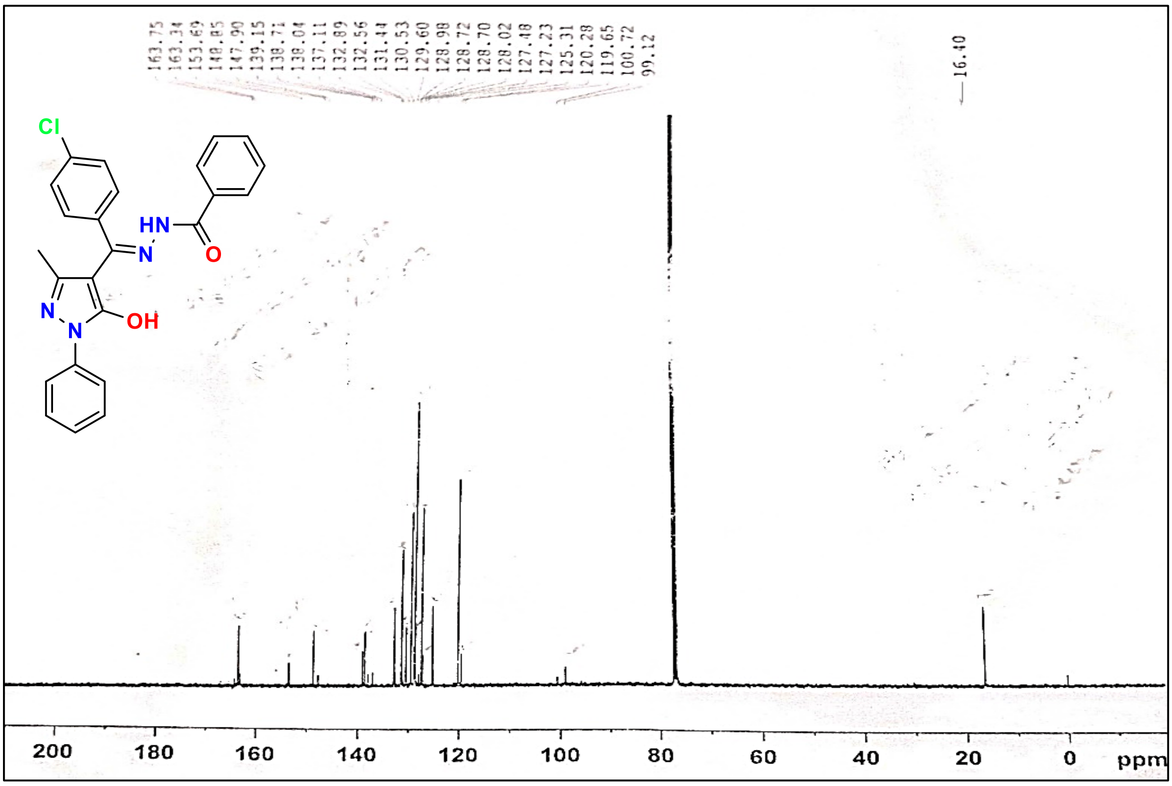


Fig. 3.1.26. ^{13}C NMR spectrum of ligand **L4**.

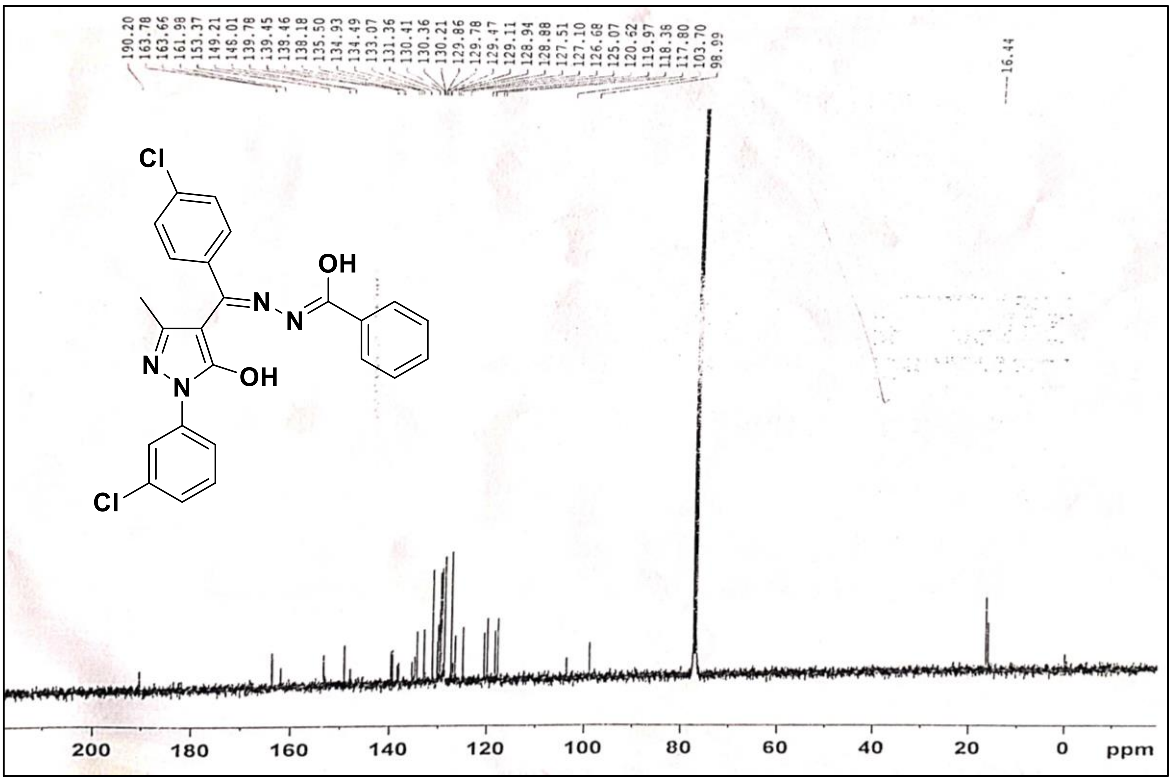


Fig. 3.1.27. ^{13}C NMR spectrum of ligand **L5**.

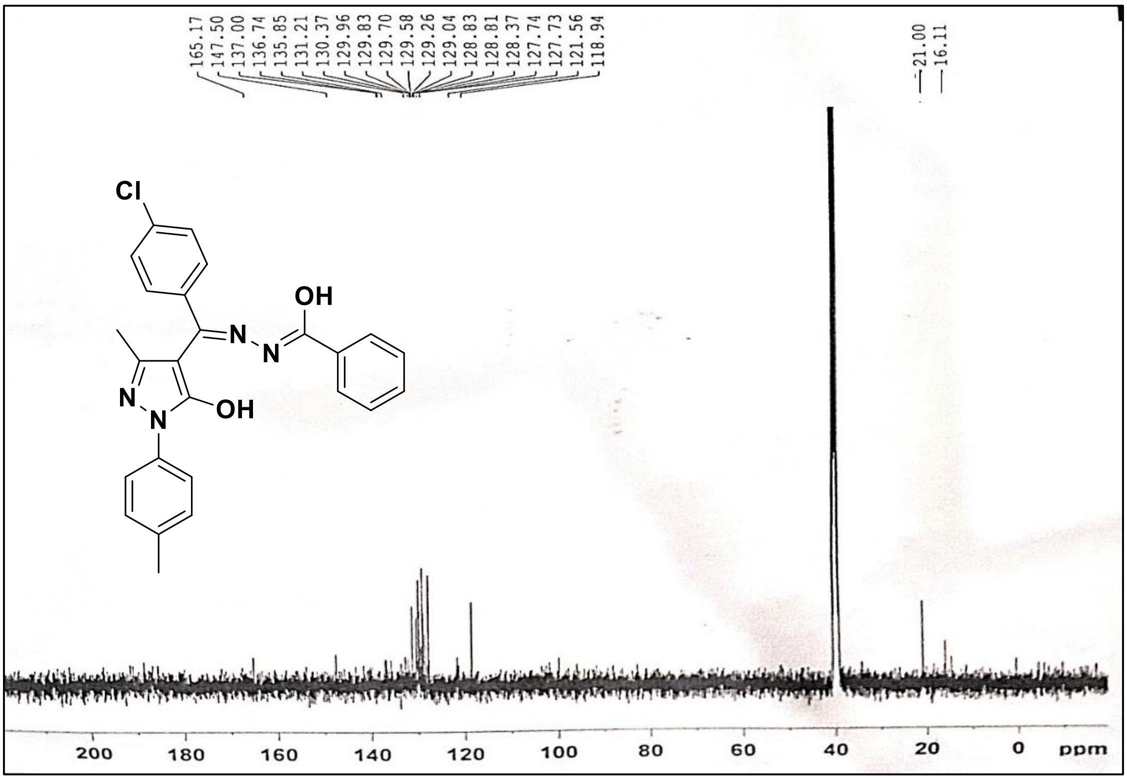


Fig. 3.1.28. ^{13}C NMR spectrum of ligand **L6**.

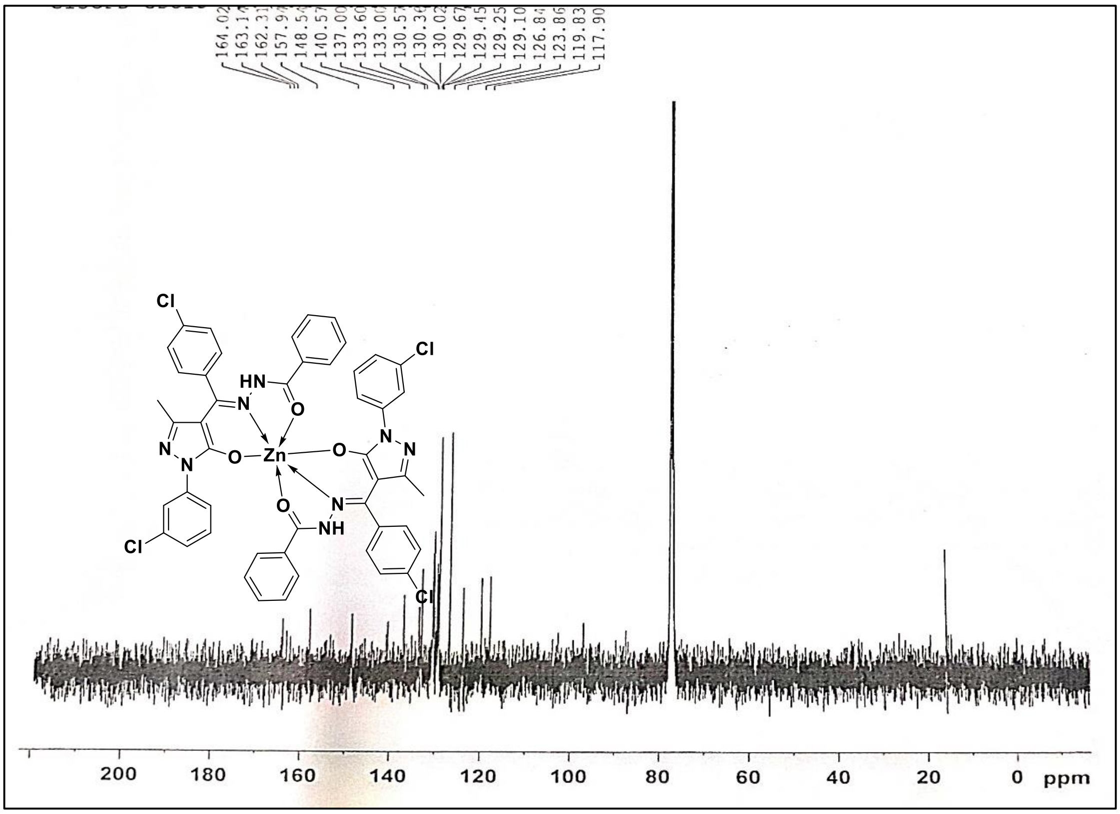


Fig. 3.1.29. ^{13}C NMR of complex **11**.

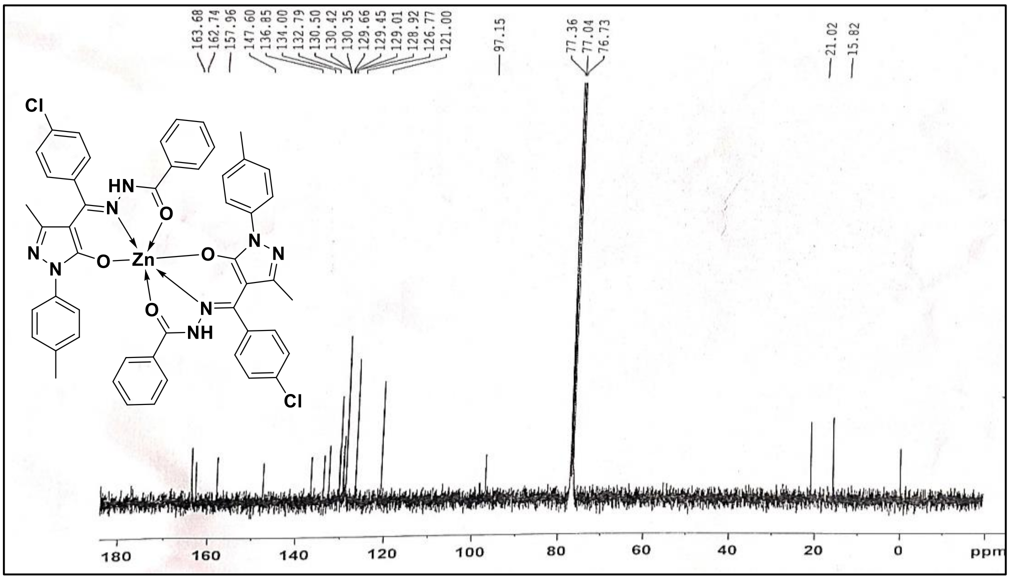


Fig. 3.1.30. ^{13}C NMR spectrum of complex **12**.

3.1.3.4. Thermogravimetric analysis

Thermogravimetric analysis observed of complexes **10-12**. TGA plots of all complexes showed the same degradation after 320 °C due to pyrolysis of 4-acylhydrazone-5-pyrazolones (**L4-L6**) of all three complexes. There was no degradation observe up to 300 °C (*see* Fig. 3.1.31). Hence, there were coordinated or lattice molecules solvent not present in complexes **10-12**. All complexes showed air and heat stable up to 320 °C temperature. TGA graph reviled that all complexes showed the same configuration ML_2 (L=**L4/L5/L6**) in their structure geometry.

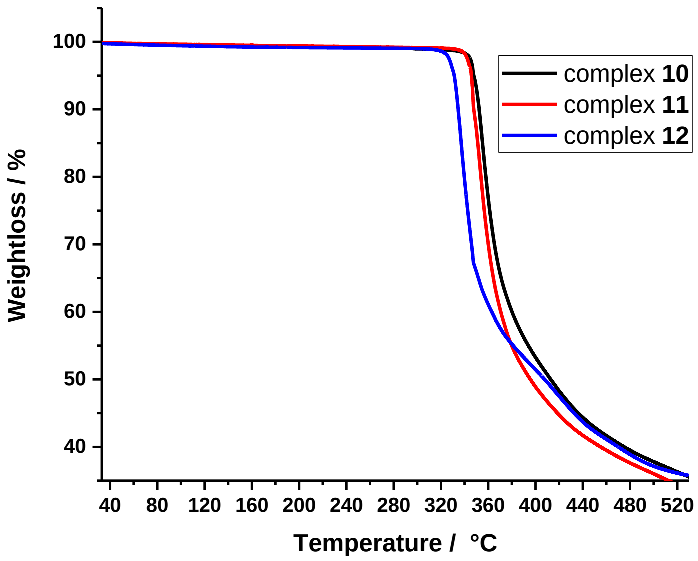


Fig. 3.1.31. TGA plot of complexes **(10-12)**.

3.1.3.5. Electronic spectra of ligands (L4-L6) and complexes 10-12.

All ligands and complexes were completely soluble in DMSO. 10^{-5} M prepared solution of ligands and complexes. UV/Visible spectra were recorded in the range of 250–800 nm. In the complexes Uv/Vis spectra, the first intense band at 270-280 nm attributed to a ligand-centered (LC) π–π* transition localized on the aromatic rings of the ligand, while the shoulder is due to its metal coordination (Fig. 3.1.32). LMCT bands observed at around 340-350 nm. There is no d-d transition in all complexes due to d^{10} metal.

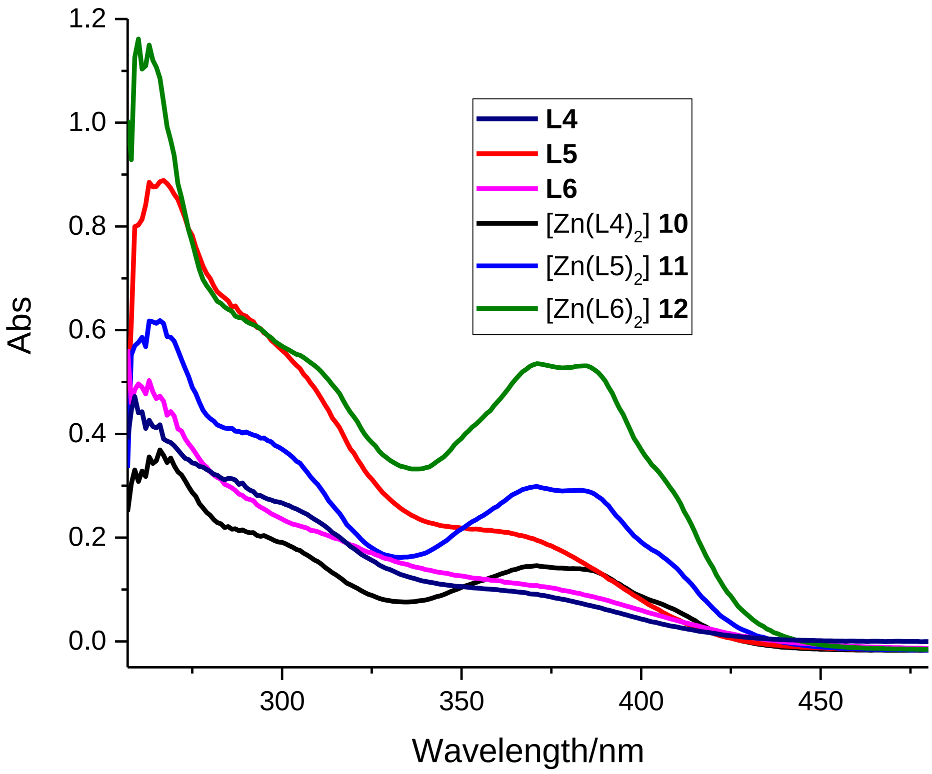


Fig. 3.1.32. Electronic spectra of ligands and complexes **10-12.**

3.1.3.6. Molar conductance of ligands and complexes.

Molar conductivity of ligands and complexes measured in 10^{-3} M solution. Compounds are soluble in DMSO solvent. All ligands and complexes molar conductance observed to be below 14 ohm^{-1} cm^{2} mol^{-1}. Thus the conductance measurements suggest that they are non-electrolytes. The conductivity values are given in Table .3.1.5.[12,32]

Table 3.1.5. Molar conductance of ligands and complexes.

Compound code	Λ_m (s cm^2 mol^{-1})
L4	10.7
L5	11.1
L6	11.1
10	12.7
11	12.2

12	13.4

Conclusion

In summary, three new 4-acylpyrazolone derivatives (**L4-L6**) were synthesized and **characterized by various spectroscopic techniques.** The structures of the synthesized 4-acyl hydrazone-5-pyrazolones were determined by **single-crystal X-ray diffraction** and found to exist in the **keto** form in the solid-state. Synthesized three new mononuclear binary **zinc(II) complexes of 4-acylhydrazone-5-pyrazolones**. Complexes **10-12** were characterized by **^{1}H and ^{13}C NMR, FT-IR, TGAs, Single crystal X-ray diffraction, elemental analysis and UV-Vis spectroscopy.** Study on **SXRD** has been suggested a distorted octahedral environment around the zinc through coordination of many of **trident O,*N*,O-chelating 4-acylhydrazone-5-pyrazolone ligands.**

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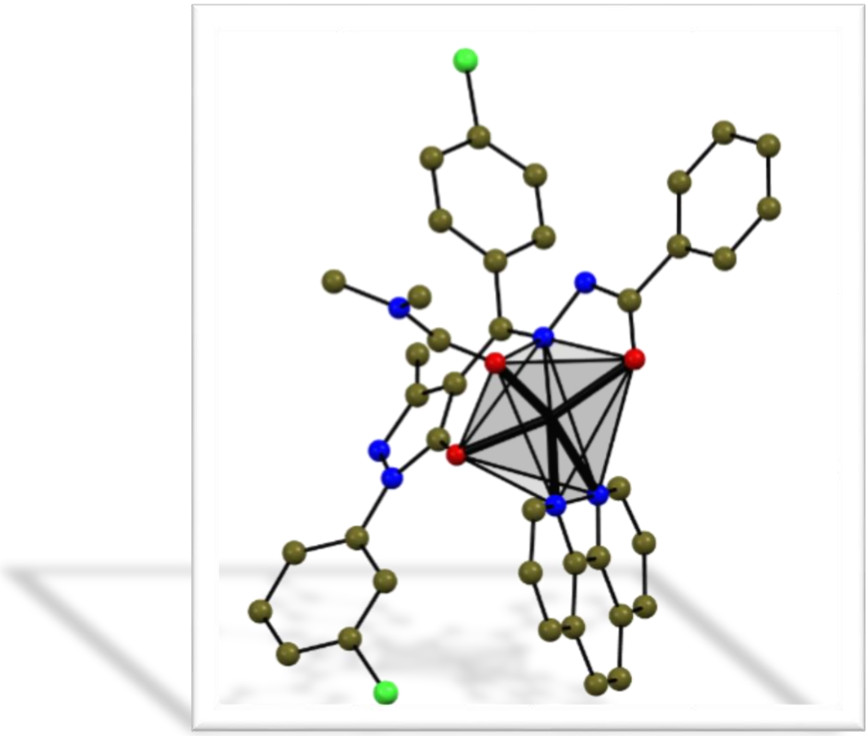
Chapter 3(b)



Chapter 3(part-b)

Synthesis, Characterization and Crystal Study of Mixed Ligand Zinc(II) Complexes of 4-Acylhydrazone-5-Pyrazolone with 2,2′-Bipyridine and 1,10-Phenanthroline

Introduction

In recent years, derivatives of pyrazolones have acquired much interest because of their many applications in coordination, medicinal chemistry and functional materials.[1–9] In the 4-acyl pyrazolone derivatives, 4-acylhydrazolone-5-pyrazolones are of significant interest due to their structure features, coordination sites and importance in fluorescence properties, biological activity, DNA binding, antitumor activity etc.[10–13]

Mixed ligand complexes of 4-acylhyrazone-5-pyrazolone

The zinc(II) mixed ligand complex contains an ONO-tridentate 4-acylhydrazone-5-pyrazolone ligand and 2,2′-bipyridine, with an additional methanol molecule completing the octahedral geometry on zinc.[14,15] 4-acylhydrazone-5-pyrazolones, the great efficient binding ability to metal due to tautomerism in structure moiety.[16] Furthermore, 4-acylhydrazone-5pyrazolones have been reported good biological active compound in recent year.[10] AHP and its Cu and Mn complexes have examined DNA-binding properties and the cytotoxic activity against HeLa and Eca-109 cells displayed better results, where Cu(II) complexes showed good results than the commercial antitumor drug cisplatin.[10,13]

Objectives of this work

The zinc(II) complex of AHP well-coordinated through one imine nitrogen atoms and one benzoyl oxygen atom and bind with the oxygen atom of pyrazolone and treated as ONO tridentate ligand in complexation. zinc(II) complexes showed good biological activity in recent years.[14] Here we have prepared mixed ligands zinc(II) complexes with secondary ligands bpy and phen. AHP reacted as tridentate or bidentate ligands in complex formation. Single crystal of AHPs and their zinc(II) complexes look unique and novel in pyrazolone based complexes.

3.2.2. Experimental

3.2.2.1. Materials and methods

Pyrazolones were obtained from Sidhdhanath industries, Sachin (Surat), India as gift samples. All necessary reagents and solvents were obtained from commercial sources. Zinc acetate, 2,2′-bipyridine and 1,10-phenanthroline were purchased from spectrochem PVT. LTD., Mumbai. Infrared (IR) spectra were recorded on Bruker Alpha Fourier transform IR (FT-IR) spectrometer as KBr pellets. ^{1}H and ^{13}C NMR spectra of the ligand were recorded with an AV 400 MHz Bruker FT-NMR instrument. Single crystal data were collected on an Xcalibur, EOS, Gemini diffractometer. The electronic spectra were recorded on a Perkin Elmer Lambda 35

UV-Vis spectrometer. Elemental analyses were performed with a Thermo Finnigan (FLASH EA 1112) microanalyzer. Conductometer model-EQ664A was used for conductance measurement for 10^{-3}M solutions of complexes and ligands. Gravimetric and volumetric analysis were performed for the determination of zinc after decomposition of the complex in nitric acid.

3.2.2.2. Synthesis of Ligands

Primary 4-acylpyrazolones (**L1-L3**) were carried out following the reported method.[17,18] Ligands **(L4-L6**) have been prepared as the following method of chapter **3 (part-a)**.

3.2.2.3. Synthesis of complexes 13-18

Synthesis of complex 13 [Zn(L4)(bpy)(H_2O)]

The ligand **L4** (0.001 mol, 0.460 g) was dissolved in a minimum amount of anhydrous ethanol (~25 mL) in a two necked round bottom flask. Drop wise added an ethanolic solution of zinc acetate dihydrate (0.001 mol, 0.219 g) to the solution of ligand **L4**. After half an hour added an ethanolic solution of 2,2′-bipyridine (0.001 mol, 0.156 g). After 4 h of reflux, a clear reaction mixture was obtained and placed for two days at room temperature. Product was recrystallized from DMF. Yield: 78%, M.P. >200 C, M.F.: $C_{34}H_{27}ClN_6O_3Zn$, F.w.: 668.46 g mol^{-1}, EA Calcd. (Found): C, 61.09(61.33); H, 4.07(4.18); N, 12.57(12.25) %, metal est. Calcd. (Found): Zn, 9.78 (9.11) %. **FTIR (KBr, cm^{-1}):** 3375 (N-H, bhz), 1601(C=O, bhz), 1567 (C=N, pyz), 1540 (C=N, imine of bhz), 1052 (C-O, pyz), 913 (C=C, pyz), 440(M-N, bhz-Zn). **^{1}H NMR ($CDCl_3$, 400MHz) δ ppm:** 1.53 (s, 3H, Me-pyz), 7.07 (t, 1H, *J*=7.2; 14.8 Hz, ar-H), 7.24 (t, 2H, *J*=8; 15.6 Hz,),7.38 (t, 2H, *J*=8; 15.2 Hz, bhz) 7.48-7.60 (m, 5H, bhz-pyz), 7.71(d, 2H, *J*=8Hz, ar-H), 7.79 (d, 2H, *J*=8Hz, ar-H), 8.71(N-H, bhz). **^{13}C NMR ($CDCl_3$, 100MHz) δ:** 16.2(CH_3-pyz), 97.3, 120.1, 124.4, 127.6, 128.2, 128.7, 128.9, 129.0, 129.6, 130.8, 131.4, 132.2, 135.2, 139.7, 160.9 (C-O), 163.2 (C=N), 166.7 (C=O). Synthesis route of complexes shown in scheme 3.2.1.

Synthesis of complex 14 [Zn(L4)(phen)(H_2O)]

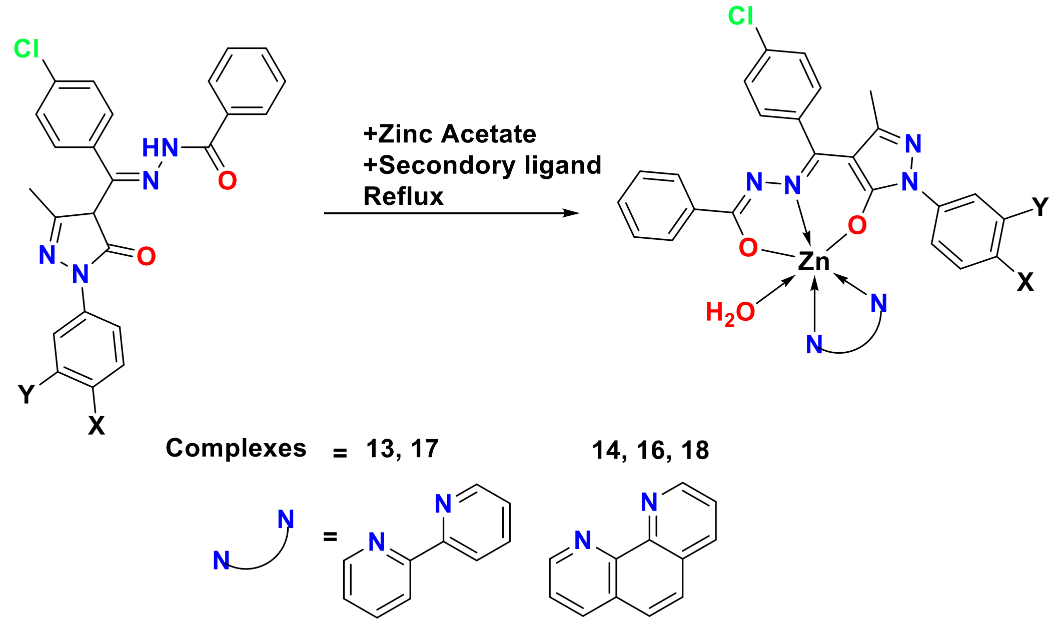
The ligand **L4** (0.001 mol, 0.460 g) was dissolved in a minimum amount of anhydrous ethanol (~25 mL) in a two necked round bottom flask. Drop wise added an ethanolic solution of zinc acetate dihydrate (0.001 mol, 0.219 g) to the solution of ligand **L4**. After half an hour added an ethanolic solution of 1,10-phenanthroline (0.001 mol, 0.186 g). After refluxed, the yellowish compound obtained and DMF was used for crystallisation. Yield: 76 %, M.P.: >200 °C, M.F.: $C_{36}H_{27}Cl_1N_6O_3Zn$, F.w.:692.48 g mol^{-1}, EA Calcd (found): C, 62.44(62.88); H, 3.93(3.78); N, 12.14(12.45), metal estimation Calcd (found): Zn, 9.44(9.75) %. **FTIR (KBr Plates, cm^{-1}):** 3376 (N-H, bhz), 1600(C=O, bhz), 1566 (C=N, pyz), 1493 (C=N, bhz), 917 (C=C, pyz), 510(M-O, AHP-Zn), 440(M-O, pyz-Zn). **^{1}H NMR ($CDCl_3$, 400MHz) δ ppm:** 1.35 (s, 3H, Me-pyz), 7.04 (t, 1H, *J*=8; 14.4 Hz, Ar-H), 7.18 (t, 2H, *J*=5.2; 14.8 Hz), 7.38-7.74 (m, 10H, ar-H), 8.87 (N-H, bhz). **^{13}C NMR ($CDCl_3$, 100MHz) δ:** 16.2(CH_3-pyz), 97.3, 120.1, 124.4, 127.7, 128.2, 128.4, 128.7, 128.9, 129.6, 130.9, 131.5, 132.3, 135.2, 139.7, 147.4, 160.9 (C-O), 163.2 (C=N), 166.7 (C=O).

Synthesis of complex 15 [Zn(L5)(bpy)(AcO)]

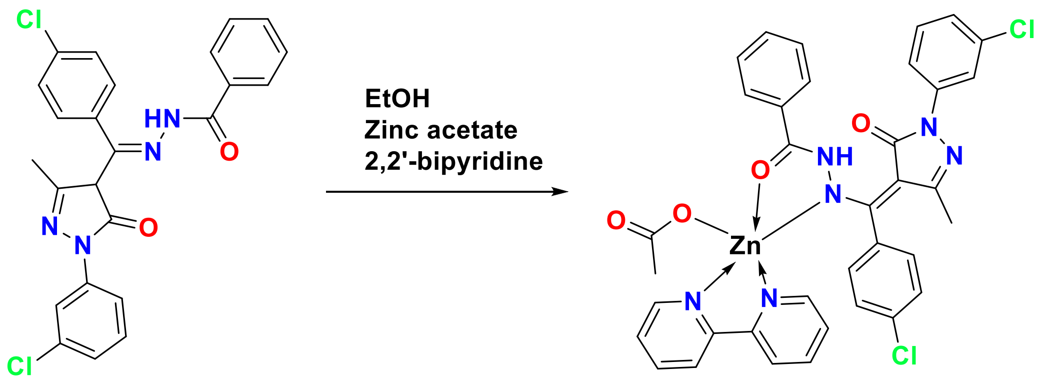
Ligand **L5** (0.001 mol, 0.435 g) was dissolved in anhydrous ethanol (~25 mL) in a two necked round bottom flask. An ethanolic solution of zinc acetate dihydrate (0.001 mol. 0.219 g) was added drop wise to the solution of ligand **L5**. The resultant solution was refluxed for half an hour, followed by drop wise addition of an ethanolic solution of 2,2′-bipyridine (0.001 mol, 0.156 g) and continued reflux. After 4 h of reflux, a clear reaction mixture was obtained and placed for two days at room temperature. Filtered the resultant light yellow crystalline complex was filtered and dried. It was then recrystallized from ethanol. Yield: 72%, M.P.: >200 °C, M.F.: $C_{38}H_{36}Cl2N_6O_5Zn$, F.w.: 793.02 g mol^{-1}, EA Calcd (found): C, 57.55(57.34); H, 4.58(4.57); N, 10.60(10.66) %, metal estimation Calcd (found): Zn, 8.24 (8.21) %. **FTIR (KBr Plates, cm^{-1}):** 3377 (N-H, bhz), 1603(C=O, bhz), 1540 (C=N, bhz), 1285 (C-O, pyz), 954 (C=C, pyz), 513(M-O, pyz-Zn), 440(M-N, bpy). **^{1}H NMR ($CDCl_3$, 400MHz) δ ppm:** 1.51 (s, 3H, Me-pyz), 7.02(d, 2H, J=7.6 Hz, ar-H), 7.18 (t, 1H, J=5.6; 16 Hz), 7.40(t, J= 7.6; 15.2 Hz), 7.64 (m, 8H), 8.09 (t, J=2; 4 Hz), 8.88(s, 1H, N-H, bhz). **^{13}C NMR ($CDCl_3$, 100 MHz) δ:** 15.8 (CH_3-pyz), 97.0, 117.9, 119.8, 123.8, 126.8, 129.0, 129.2, 129.4, 129.6, 130.0, 130.3, 130.3, 130.5, 132.9, 133.6, 137.0, 140.5, 148.5 (C-O), 157.9 (C=N), 164.02 (C=O, bhz). Synthesis route is displayed in scheme 3.2.2.

Synthesis of complex 16 [Zn(L5)(phen)(H_2O)].

The complex **3** was synthesized by following the same procedure as that of complex **2** except secondary ligand **1,10-phenanthroline** was used instead of 2,2′-bipyridine. After refluxed, the yellowish compound obtained and DMF used for crystallisation. Yield: 72%, M.P.: >200 °C, M.F.: $C_{36}H_{26}Cl_2N_6O_3Zn$, F.w.:726.92 g mol^{-1}, Ele. Ana. Cald (found): C, 59.48 (59.88); H, 3.61 (3.73); N, 11.56 (12.00) %, metal estimation Cald (found): Zn, 9.00(9.35) %. **FTIR (KBr, cm^{-1}):** 3378 (N-H, bhz), 1601(C=O, bhz), 1583 (C=N, pyz), 1541 (C=N, imine of bhz), 1285 (C-O, pyz), 918 (C=C, pyz), 513(M-O, pyz-Zn), 440(M-N). **^{1}H NMR ($CDCl_3$, 400MHz) δ ppm:** 1.51 (s, 3H, Me-pyz), 7.02 (d, 1H, J=7.6 Hz), 7.18 (t, 1H, 8; 16 Hz), 7.62 (m, 8H), 8.09(s, 1H), 8.95 (s, 1H, N-H-bhz). **^{13}C NMR ($CDCl_3$, 100 MHz) δ:** 15.8(CH_3-pyz), 97.0, 117.9, 119.8, 123.8, 126.8, 129.0, 129.2, 129.4, 130.0, 130.3, 130.3, 130.5, 132.9, 133.6, 137.0, 140.5, 148.5(C-O), 157.6(C=N), 164.0(C=O).



Scheme 3.2.1. Synthesis route of complexes **13, 14, 16-18.** Where for complexes **13** & **14: X=Y=** -H, **16: X=-H, Y= -Cl, 17**&**18: X=** -CH_3**, Y=** -H.



Scheme 3.2.2. Synthesis route of complex **15**.

Synthesis of complex 17 [Zn (L6) (bpy) (H_2O)]

The compound was synthesized by following the same procedure as that of complex **13** except **L6** was used instead of **L4.** Yield: 82%, M.P.: >200 C, M.F.: $C_{35}H_{29}ClN_6O_3Zn$, F.w.:682.49 g mol^{-1}, EA Calcd (found): C, 61.60(59.88); H, 4.28(4.27); N, 12.31(12.45), metal estimation Calcd (found): Zn, 9.58(9.75) %. **FTIR (KBr, cm^{-1}):** 3378 (N-H, bhz), 1616(C=O, bhz), 1567 (C=N, pyz), 1539 (C=N, imine of bhz), 1284 (C-O, pyz), 944 (C=C, pyz), 511(M-O, pyz-Zn), 440(M-N). **^{1}H NMR ($CDCl_3$, 400MHz) δ:** 1.53 (s, 3H , Me-pyz), 2.29(s, 3H, *p*-tolyl-pyz), 7.03(d, 2H, *J*=8.4), 7.37 (t, 2H, *J*=7.6; 15.6), 7.51 (m, 5H, bhz-pyz), 7.63 (d, 2H, *J*=8) 7.70 (d, 2H, *J*=8Hz), 8.85(N-H, bhz).

Synthesis of complex 18 [Zn (L6) (phen) (H_2O)].

The complex **16** was synthesized by following the same procedure as that of complex **14** except ligand **L6** was used instead of ligand **L4**. Complexes **13-18** syntheses route displayed in scheme 3.2.1.

Yield: 75%, M.P.: >200 C, Molecular formula: $C_{37}H_{29}ClN_6O_3Zn$, F.w.:706.51g mol^{-1}, EA Calcd (found): C, 62.90(62.78); H, 4.14(4.27); N, 11.90(11.45), metal estimation Calcd (found): Zn, 9.25 (9.75) %. **FTIR (KBr, cm^{-1}):** 3378 (N-H, bhz), 1616 (C=O, bhz), 1589 (C=N, pyz), 1539 (C=N, imine of bhz), 1284 (C-O, pyz), 915 (C=C, pyz), 511(M-O), 440(M-N, pyz-Zn). **^{1}H NMR ($CDCl_3$, 400MHz) δ ppm:** 1.53 (s, 3H, Me-pyz), 2.29 (s, 3H, tolyl), 7.03 (d, 2H, J=8Hz), 7.38 (t, 2H, J=8; 15.6 Hz), 7.53 (m, 7H, ar-H, AHP), 7.70 (d, 2H, J=8.4 Hz), 8.85 (N-H, bhz).

3.2.2.4. X-ray Single Crystal Structure Analysis

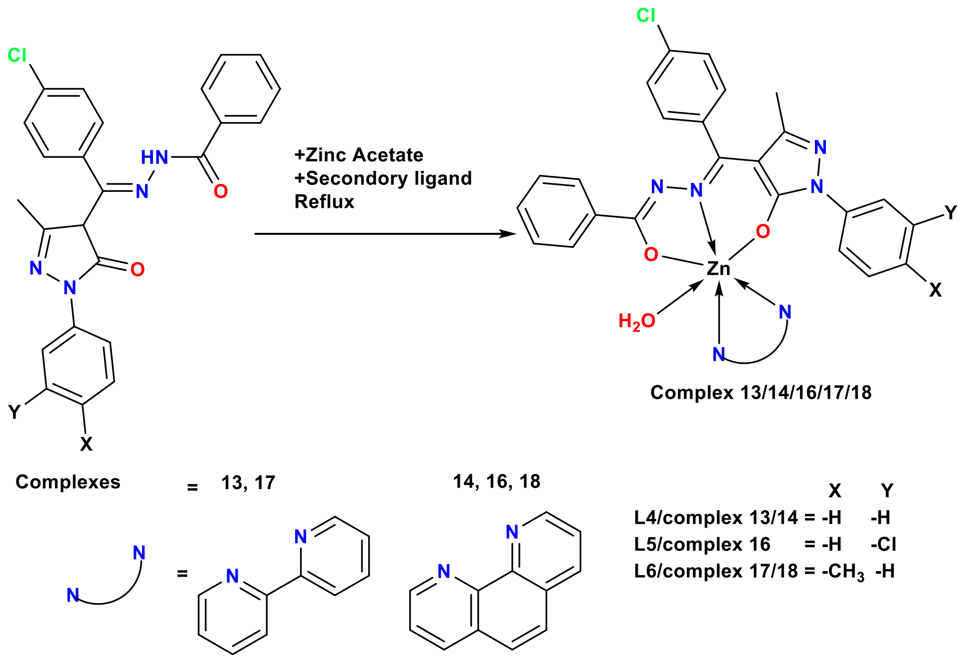
The X-ray single crystal data of complexes **15** and **16** were collected on an Xcalibur, EOS, Gemini diffractometer with graphite monochromatic MoKα radiation (λ= 0.71073Å). All structures were solved by direct methods using SHELXS-97[19] and refined by the full-matrix least-square method based on F2 using the SHELXL-2018 program.[20] All crystallographic calculations were done with the Olex2 GUI.[21] The geometries of the molecules were determined using the software PLATON [22] and PARST.[23] Graphics of complexes **15** and **16** were generated using MERCURY (version 4.1.0) software.[24] In all the cases, non-hydrogen atoms were treated anisotropically. The hydrogen atoms (except hydrogen atoms bonded to O or N) were geometrically fixed. The H atoms of the NH/OH group were identified in difference syntheses and both the positional and displacement parameters were refined. The crystallographic parameters for complexes are given in Table 3.2.1.

Table 3.2.1. Crystal structure refinement data for complexes **15** and **16**.

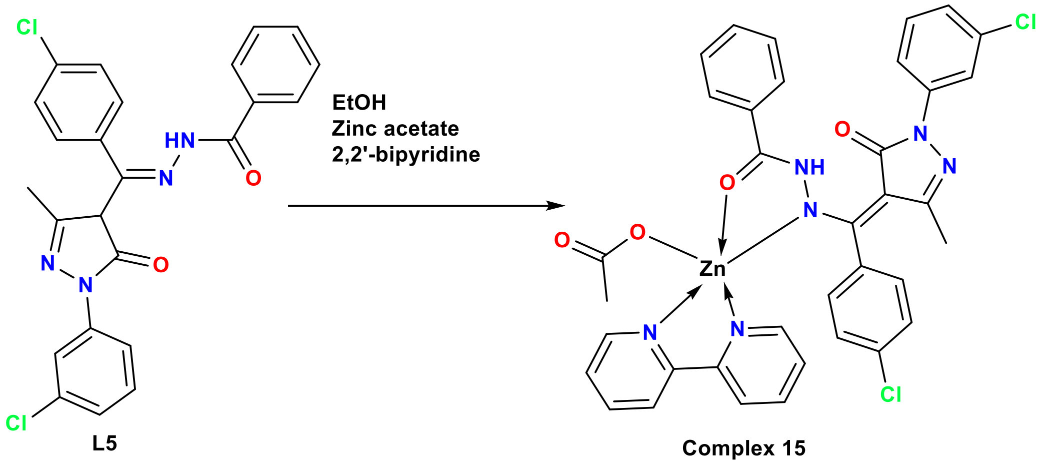
Identification code	**Complex 15 [Zn(L5)(bpy)(OAc)]EtOH**	**Complex 16 [Zn(L5)(phen)(DMF)]**
Empirical formula	$C_{38}H_{34}Cl_2N_6O_5Zn$	$C_{39}H_{31}Cl_2N_7O_3Zn$
Formula weight	790.98	781.98
Temperature/K	293	293
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/n$
a/Å	10.4160(6)	16.5116(9)
b/Å	11.2176(5)	10.1796(6)
c/Å	15.8354(7)	21.6806(12)
α/°	94.303(4)	90
β/°	95.451(4)	93.963(5)
γ/°	93.971(4)	90
Volume/Å^3	1831.24(16)	3635.4(4)
Z	2	4
ρ_{calc}g/cm^3	1.434	1.429
μ/mm^{-1}	0.869	0.871
F(000)	816	1608
Crystal size/mm^3	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2
2Θ range for data collection/°	6.094 to 58.072	6.732 to 58.048
Reflections collected	36350	36941
Independent reflections	7194	7095
Data/restraints/parameters	7194/4/507	7095/0/472
Goodness-of-fit on F^2	1.027	1.078
R_{int}	0.0465	0.1306
R_{sigma}	0.0331	0.1248
R_1	0.0405	0.0521
wR_2	0.1046	0.1046
Largest diff. peak/hole / e Å^{-3}	0.457/-0.513	0.318/-0.287
CCDC	2024096	2024097

3.2.3. Results and Characterization

In this chapter, six heteroleptic zinc(II) complexes have been prepared by following the scheme 3.2.3-3.2.4 described below;



Scheme 3.2.3. Synthesis route of complex **13/14/16/17/18.**



Scheme 3.2.4. Synthesis route of complex **15.**

All these complexes are light yellow solid , stable at room temperature and soluble in DMF and DMSO.

The detailed characterization of these complexes is described in succeeding sections.

3.2.3.1. Single Crystal X-ray diffraction Study

Structure features of Complex 15 [Zn(L5)(bpy)(AcO)]EtOH

Crystallographic data of complex **15** are given in Table. 3.2.1. Atom numbering scheme of complex **15** is presented in Fig. 3.2.1. As shown in Fig. 3.2.2, the Zn(II) binds with two oxygen atoms of **L5** and AcO^-. Two nitrogen atoms (N5 & N6) of 2,2′-bipyridine and two oxygen atoms (O2 and O3) of ligand **L5** and AcO^- ion occupied basal sites of geometry. A nitrogen atom (N3) of ligand **L5** occupied the apical site of square pyramidal structure. In this complex, the incorporation of the acetate ion binds with zinc metal to neutralize the charge.

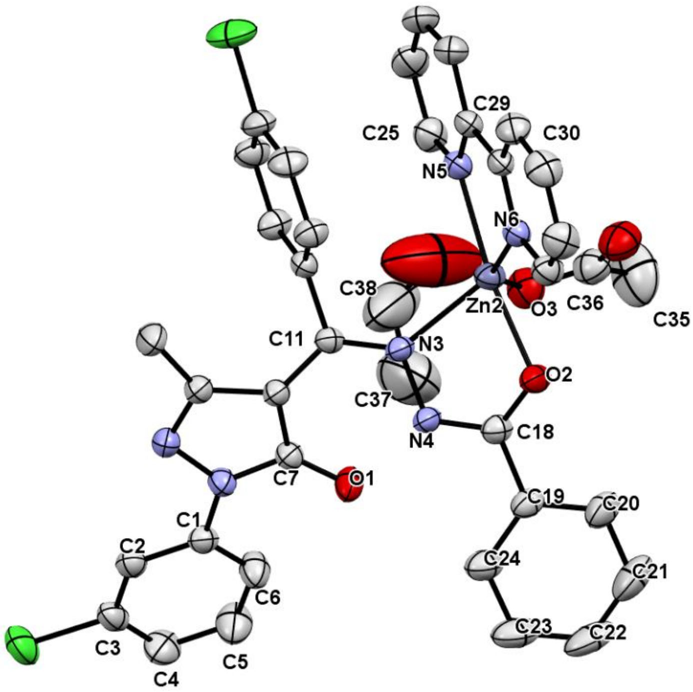


Fig. 3.2.1. ORTEP ellipsoid with 50% probability diagram of complex **15** [Zn(L5)(bpy)(AcO)]EtOH. H-atoms are omitted for clarity.

Ligand **L5** treated as a mono-ionic N, O bidentate ligand in this complex. The complex **15** shows distorted square pyramidal geometry around zinc(II) ion. The distance between basal sites and metal ion Zn1-O3. Zn1-N6, Zn1-N5 and Zn1-O2 are 2.013(2) Å, 2.077(19) Å, 2.130(19) Å and 2.131(16) Å respectively. Distance between apical site atom (N3) and zinc(II) (Zn1) is 2.121(19) Å. Basal of geometry showed bond angles O3-Zn1-N6 and O2-Zn1-N5 are 143.25(8)˚ and 168.03(7)˚ respectively, which are deviated from the theoretical value 180˚. The angles O3-Zn1-N3 (97.11(8)˚), N6-Zn1-N3 (119.00(8)˚), O3-Zn1-N5 (95.75(8)˚), N6-

Zn1-N5(77.73(7)˚), N3-Zn1-N5(112.19(7)˚), O3-Zn1-O2(91.10(8)˚), N6-Zn1-O2(90.91(7)˚) and N3-Zn1-O2(76.52(7)˚), which are deviated from the theoretical value 90˚of the geometry.

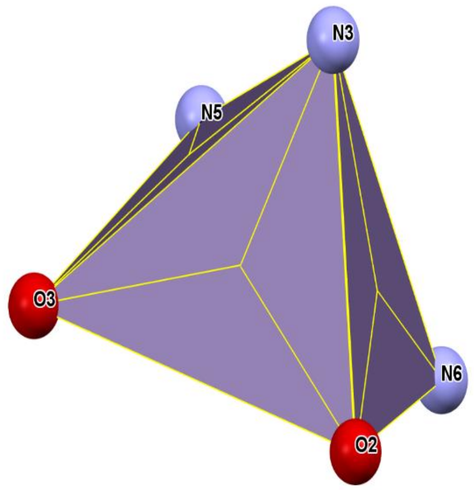


Fig. 3.2.2. Distorted square pyramidal geometry around zinc (II) ion in complex **15.**

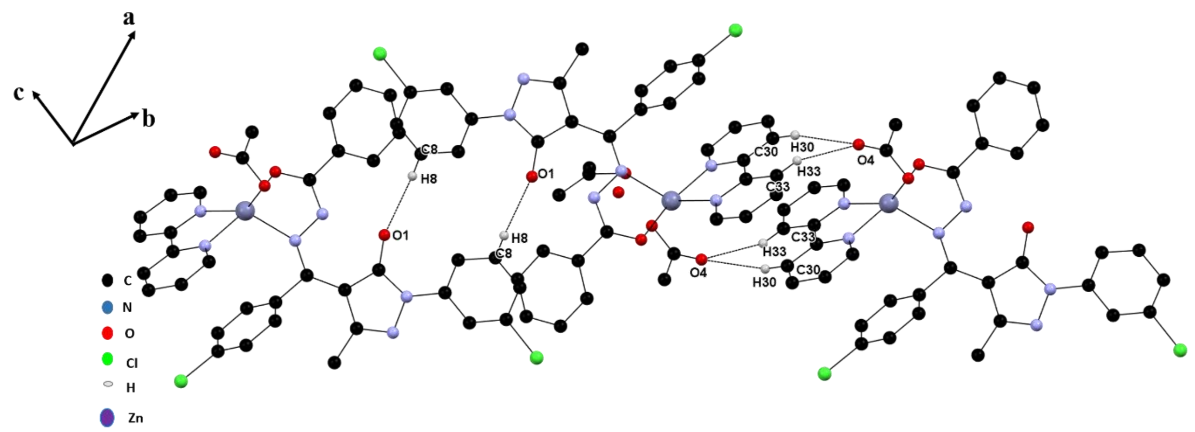


Fig. 3.2.3. Intermolecular H-bonds in the complex **15.**

The value of trigonality index τ is 0.411[τ = (β - α)/60), β > α], where α = O3-Zn1-N6 = 143.25(8)˚ and β = N5-Zn1–O2 =168.03(7)˚ and τ=1 for perfect trigonal bipyramidal and τ=0 square pyramidal geometries. Thus, the coordination geometry of the Zn(II) center is best described as a strictly distorted square pyramid (Fig.3.2.2).[25] Structure packing of complex **15** exhibits H-bonds (i) C8-H8…O1 and (ii) C30-H30…O4 and (iii) C33-H33…O4 (Fig. 3.2.3). H-bond dimensions are given in Table 3.2.2. The main bond distances and angles are given in

Table 3.2.3. Crystal packing viewed from the a-axis of the complex **15**. Crystal packing system depicted in Fig.3.2.4.

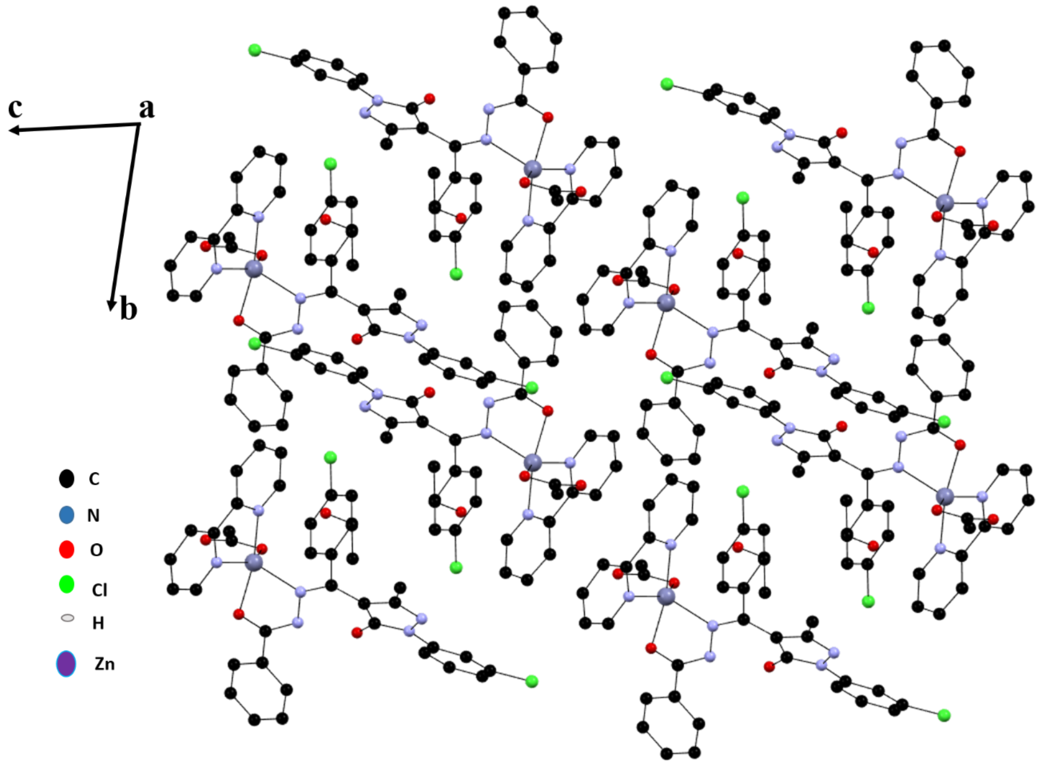


Fig. 3.2.4. Crystal packing of complex **15** [Zn(L5)(bpy)(OAc)]EtOH. Viewed down from the a-axis. H-atoms are omitted for clarity.

Structure feature of complex 16 [Zn(L5)(phen)(DMF)]

The structure of complex **16** is depicted in Fig. 3.2.5. Selected bond lengths and bond angles are listed in Table 3.2.3. Crystallization of complex **16,** single crystal was obtained from the solution of DMF, As the water molecule has weak coordination ability than DMF, coordinated water molecule was replaced by DMF molecules during the crystallization of complex.[17] Complex **16** is six-coordinate Zn(II) with three oxygens and three nitrogens, two oxygen atoms (O1 and O2) and a nitrogen atom (N3) of tridentate acylhydrazone pyrazolones(**L5**). An oxygen atom (O3) of DMF coordinated to metal and two nitrogen atoms (N5 and N6) of 1,10-phenanthroline have coordinated to Zn(II) metal ion in the complex. The coordination geometry around Zn(II) metal ion was described as distorted octahedral. Nitrogen atoms (N5 and N6) of 1, 10-phenanthroline and a nitrogen atom (N3) of ligand **L5** and an oxygen atom

(O3) of DMF occupied basal plan of octahedral geometry. Oxygen atoms O1 and O2 were shown on the axial position of structure geometry.

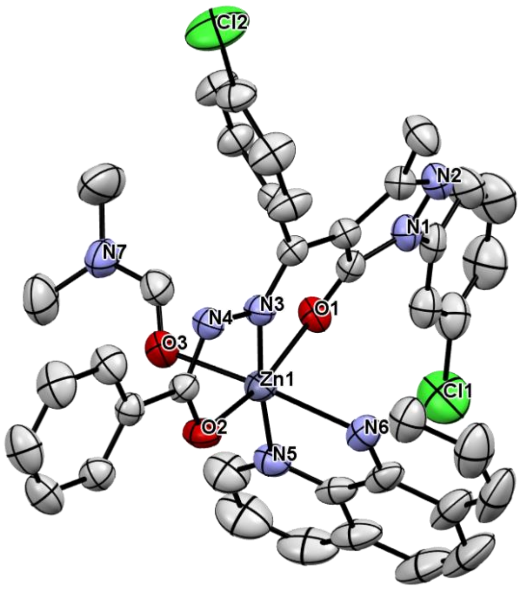


Fig. 3.2.5. ORTEP ellipsoid with 50% probability diagram of complex **16**. H-atoms are omitted for clarity.

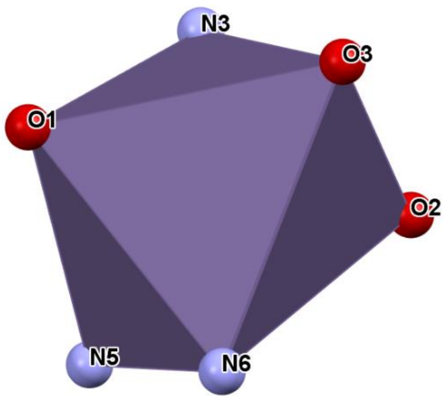


Fig. 3.2.6. Distorted octahedral geometry of complex **16** [Zn(L5)(phen)(DMF)]. Where N3, N5, N6 and O3 occupied basal plan and Oxygen atoms O1 and O2 occupied an axial position in the octahedral geometry.

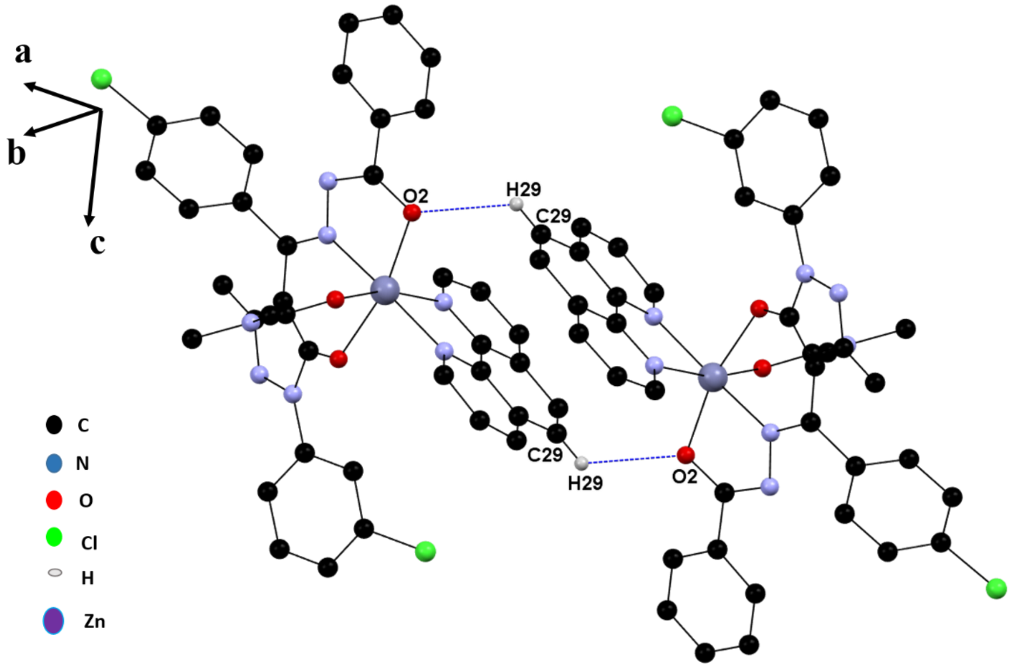


Fig. 3.2.7. Intermolecular H-bond in the complex **16**.

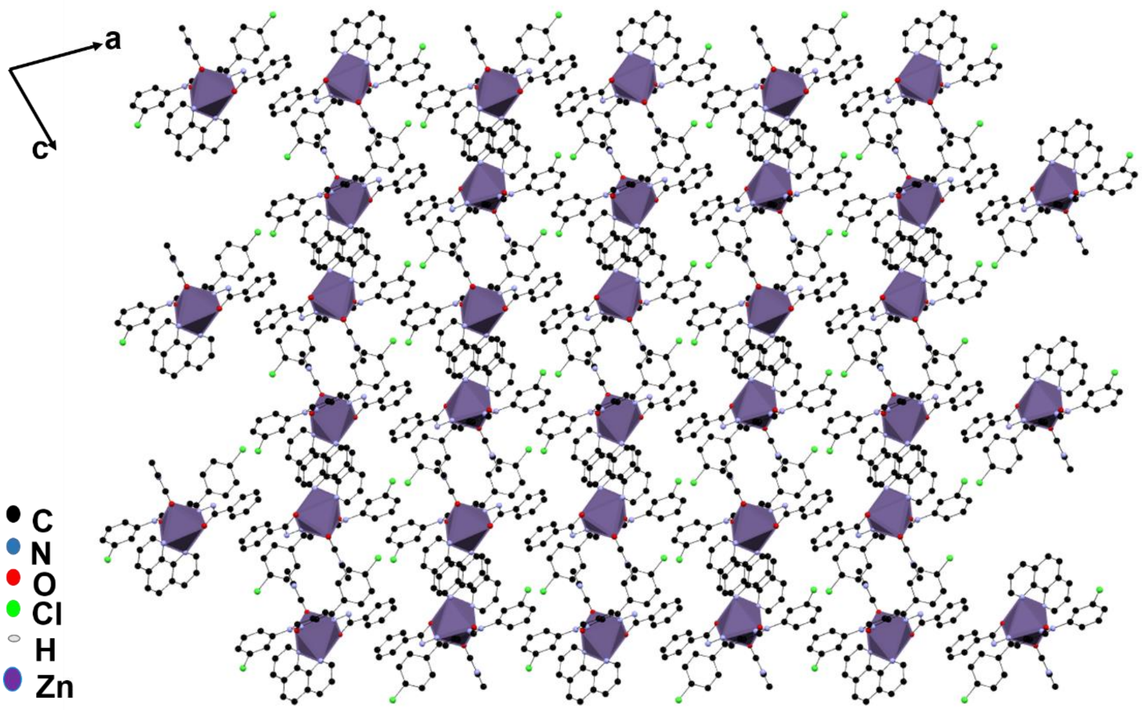


Fig. 3.2.8. Crystal packing of complex **16.**

The bond distance observed between Zn1-O2, Zn1-N3, Zn1-O1, Zn1-N6, Zn1-N5 and Zn1-O3 are 2.045(19) Å, 2.083(2) Å, 2.099(19) Å, 2.129(2) Å, 2.199(3) Å and 2.210(2) Å respectively. The angles O1-Zn1-O2, N5-Zn1-O3 and N6-Zn1-N3 are 165.75(7)˚, 165.31(9)˚ and 174.30(9)˚ respectively, which are deviated from theoretical value 180˚ of the geometry. The angles O2-Zn1-N3(77.19(8)°), N3-Zn1-O1(89.24(8)°), O2-Zn1-N6(107.00(8)°), O1-Zn1-N6(86.83(8)°), O2-Zn1-N5(99.59(9)°), N3-Zn1-N5(98.55(9)°), O1-Zn1-N5(86.61(8)°), N6-Zn1-N5(77.10(10)°), O2-Zn1-O3(88.90(8)°), N3-Zn1-O3(95.00(9)°), O1-Zn1-O3(87.93(8)°) and N6-Zn1-O3(88.99(10)°), which are deviated from theoretical value 90°.[26] Therefore geometry around the zinc (II) ion in the complex is distorted octahedral. Crystal packing of complex **16** is shown in Fig.3.2.8. Intermolecular H-bond found in the complex **16** (Fig. 3.2.7) (Table 3.2.2).[27]

Table 3.2.2. H-bond refinement data of ligand and complexes **15** and **16**.

	D-H…A	(D-H) / Å	(D-A)/ Å	(H…A)/ Å	(D-H-A)/º
Complex 15	C8-H8…O1 ^{i}	0.93(0)	3.42(3)	2.49(0)	175.1(0)
	C30-H30…O4 ^{ii}	0.93(0)	3.39(4)	2.49(0)	163.7(0)
	C33-H33…O4 ^{ii}	0.93(0)	3.34(3)	2.46(0)	158.4(0)
Complex 16	C29-H29…O2 ^{iii}	0.93(0	3.09(4)	2.47(0)	125.2(0)

Symmetry (i) -x+1, -y, -z+1 (ii) –x+2, -y+1, -z (iii) ^{1}-x,-y,1-z

Table 3.2.3. Selected bond length and bond angles of complex **15** and complex **16**.

Complex 15 [Zn(L5)(bpy)(AcO)]EtOH

Atom	Length/Å	Atom	Angle/˚
Zn1-O2	2.1313(16)	N5-Zn1-O2	167.95(7)
Zn1-N5	2.1311(19)	N6-Zn1-O2	90.79(7)
Zn1-N6	2.0758(19)	N6-Zn1-N5	77.78(8)
Zn1-N3	2.1220(19)	N6-Zn1-N3	118.97(7)
Zn1-O3	2.012(2)	N3-Zn1-O2	76.51(7)
Cl1-C3	1.750(3)	N3-Zn1-N5	112.26(7)
Cl2-C15	1.737(2)	O3-Zn1-O2	91.14(8)
O2-C18	1.259(3)	O3-Zn1-N5	95.77(8)

O1-C7	1.273(3)	O3-Zn1-N6	143.29(8)
N5-C25	1.331(3)	O3-Zn1-N3	97.08(8)
N5-C29	1.342(3)	C18-O2-Zn1	109.58(14)
N6-C30	1.343(3)	C25-N5-Zn1	126.14(18)
N6-C34	1.340(3)	C25-N5-C29	118.9(2)
N3-N4	1.403(2)	C29-N5-Zn1	114.93(15)
N3-C11	1.314(3)	C30-N6-Zn1	116.66(15)
N1-N2	1.392(3)	C34-N6-Zn1	124.77(16)
N1-C1	1.421(3)	C34-N6-C30	118.6(2)
N1-C7	1.364(3)	N4-N3-Zn1	108.34(13)
N4-C18	1.338(3)	C11-N3-Zn1	134.23(15)
O3-C36	1.276(4)	C11-N3-N4	116.31(18)
N2-C9	1.316(3)	N2-N1-C1	118.39(19)
O4-C36	1.224(4)	C7-N1-N2	112.31(18)

Complex 16 [Zn(L5)(phen)(DMF)]

Atom	Length/Å	Atom	Angle/°
Zn1-O2	2.047(2)	O2-Zn1-O1	165.92(9)
Zn1-O1	2.095(2)	O2-Zn1-O3	88.91(10)
Zn1-O3	2.213(3)	O2-Zn1-N3	77.22(9)
Zn1-N3	2.083(3)	O2-Zn1-N6	107.06(10)
Zn1-N6	2.129(3)	O2-Zn1-N5	99.57(11)
Zn1-N5	2.200(3)	O1-Zn1-O3	87.84(9)
Cl2-C17	1.742(4)	O1-Zn1-N6	86.58(10)
Cl1-C5	1.738(5)	O1-Zn1-N5	86.67(10)
O2-C18	1.282(4)	N3-Zn1-O1	89.42(9)
O1-N2	1.274(4)	N3-Zn1-O3	94.96(11)
O3-C37	1.223(5)	N3-Zn1-N6	174.28(11)
N3-N4	1.395(3)	N3-Zn1-N5	98.62(11)
N3-C11	1.297(4)	N6-Zn1-O3	88.97(12)
N6-C32	1.349(5)	N6-Zn1-N5	77.09(12)
N6-C25	1.331(5)	N5-Zn1-O3	165.29(11)
N4-C18	1.309(4)	C18-O2-Zn1	109.86(19)
N5-C33	1.353(4)	N2-O1-Zn1	117.72(19)

N5-C34	1.321(5)	C37-O3-Zn1	118.4(2)
C7-N1	1.388(4)	N4-N3-Zn1	112.72(18)
C7-C8	1.305(4)	C11-N3-Zn1	129.6(2)
N1-N2	1.390(4)	C11-N3-N4	117.0(3)
N1-C1	1.418(4)	C32-N6-Zn1	114.0(3)
N7-C37	1.319(5)	C25-N6-Zn1	126.5(3)
N7-C39	1.442(6)	C25-N6-C32	119.0(3)
N7-C38	1.453(5)	C18-N4-N3	110.0(2)
C11-C12	1.508(4)	C33-N5-Zn1	112.1(3)
C11-C9	1.441(4)	C34-N5-Zn1	128.7(3)
C12-C13	1.366(5)	C34-N5-C33	119.0(3)
C12-C15	1.380(5)	C8-C7-N1	104.6(3)
C18-C19	1.495(4)	C7-N1-N2	112.7(3)
C24-C19	1.385(5)	C7-N1-C1	119.0(3)

3.2.3.2. ^{1}H and ^{13}C NMR spectroscopy of complexes 13-18.

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$/DMSO-d6 solvent at room temperature. ^{1}H NMR spectra of all complexes are presented in Fig. 3.2.9 - Fig. 3.2.18.

Complex 13:

In the ^{1}H NMR spectrum of complex **13,** the spectrum shows a singlet in the aliphatic region at 1.51 (3H) δ due to a methyl group of pyrazolone. The spectrum exhibits three triplets at 7.07 (1H), 7.24 (2H) and 7.38 (2H) which can be assigned to ph-ring, bpy and bhz protons, respectively. Multiplets in the aromatic region in the range of 7.48-7.60 (5H) δ, which can be assigned aromatic protons of ligand. Two doublets at 7.71 (2H) and 7.79(2H) δ indicate protons of p-chloro benzoyl. A singlet at 8.87 δ ppm in proton NMR indicates amine (NH) proton of the ligand. ^{13}C NMR spectrum also confirmed the methyl group at C3 position by the signal at 16.2 δ. The ^{13}C NMR spectrum displays signals at 160.9, 163.2 and 166.7 δ ppm are due to C-O, C=N and C=O, respectively.

Complex 14:

In the ^{1}H NMR spectrum of complex **14**, the spectrum exhibits a singlet at 1.35 δ ppm is confirm a methyl group of pyrazolone of ligand **L4**. The spectrum shows two triplets at 7.04 and 7.18 δ, which can be assigned to aromatic proton of phenyl ring and benzhydrazone respectively. Multiplet at in the range of 7.38-7.74 δ ppm due to aromatic protons of the phenyl ring and 1,10-phenanthroline. The amine (NH) proton indicates a singlet at 8.87 δ ppm in proton NMR. In the ^{13}C NMR spectrum, the spectrum shows a signal at 16.2 δ ppm due to the methyl group at the C3 position of pyrazolone ring. The spectrum indicates signals at 160.9, 163.2 and 166.7 δ ppm are due to C-O, C=N and C=O, respectively.

Complex 15:

1.51 (s, 3H, Me-pyz), 7.02(d, 2H, J=7.6 Hz, tolyl-ph), 7.18 (t, 1H, J=5.6; 16 Hz), 7.40(t, J= 7.6; 15.2 Hz), 7.64 (m, 8H), 8.09 (t, J=2; 4 Hz), 8.88(s, 1H, N-H, bhz).

In the ^{1}H NMR spectrum of complex **15**, a singlet at 1.51 δ ppm confirm a methyl group of pyrazolone of ligand **L5**. The spectrum shows doublet at 7.02 (2H), which attributes to m-chloro phenyl, the spectrum shows two triplets at 7.18(1H) and 7.40(2H) which can be assigned to m-chloro phenyl and bhz. The spectrum shows multiplet at the region of 7.52-7.80 δ ppm due to the aromatic protons of the phenyl ring and 2,2′-bipyridine. A singlet at 8.10 δ of m-chloro phenyl. NH (amine) proton exhibits a singlet at 8.87 δ ppm. In the ^{13}C NMR spectrum, the spectrum shows a signal at 15.8 δ ppm in the aliphatic region which confirms methyl at the C3 position of pyrazolone ring. ^{13}C NMR signals exhibit at 148.5, 157.9 and 164.0 δ ppm are due to C-O, C=N and C=O, respectively.

Complex 16:

In the ^{1}H NMR spectrum of complex **16**, a singlet at 1.51 δ ppm confirm a methyl group at C3 position of pyrazolone. The spectrum shows a doublet at 7.02(1H) for m-chloro phenyl and a triplet at 7.18 (1H) for bhz. The spectrum shows multiplet at the region of 7.62-7.73 δ due to aromatic protons. NH proton observed a singlet at 8.95 δ ppm in proton NMR. The ^{13}C NMR spectrum shows a signal at 15.8 δ ppm which also confirmed a methyl group at the C3 position of pyrazolone ring. The spectrum shows signals at 148.5, 157.6 and 164.0 δ ppm are due to C-O, C=N, and C=O, respectively.

Complex 17:

In the ^{1}H NMR spectrum of complex **17,** two singlets at 1.64 δ ppm and 2.24 δ ppm, which confirm methyl group of pyrazolone at C3 position and tolyl at the N1 position of ligand **L6**. NH proton observed a singlet at 8.85 δ ppm in proton NMR. In the aromatic region, doublets, triplets overlapped doublet show the aromatic protons of primary ligand (**L6**) and secondary ligand (**bpy**).

Complex 18:

In the ^{1}H NMR spectrum of complex **18,** two singlets at 1.65 δ ppm and 2.29 δ ppm, which confirm a methyl group of pyrazolone at C3 position and *p*-tolyl at the N1 position of ligand **L6**. NH proton observed a singlet at 8.85 δ ppm in proton NMR. In the aromatic region, doublets, triplets overlapping doublet show the aromatic protons of primary ligand (**L6**) and secondary ligand (**phen**).

^{1}H NMR spectra of complexes:

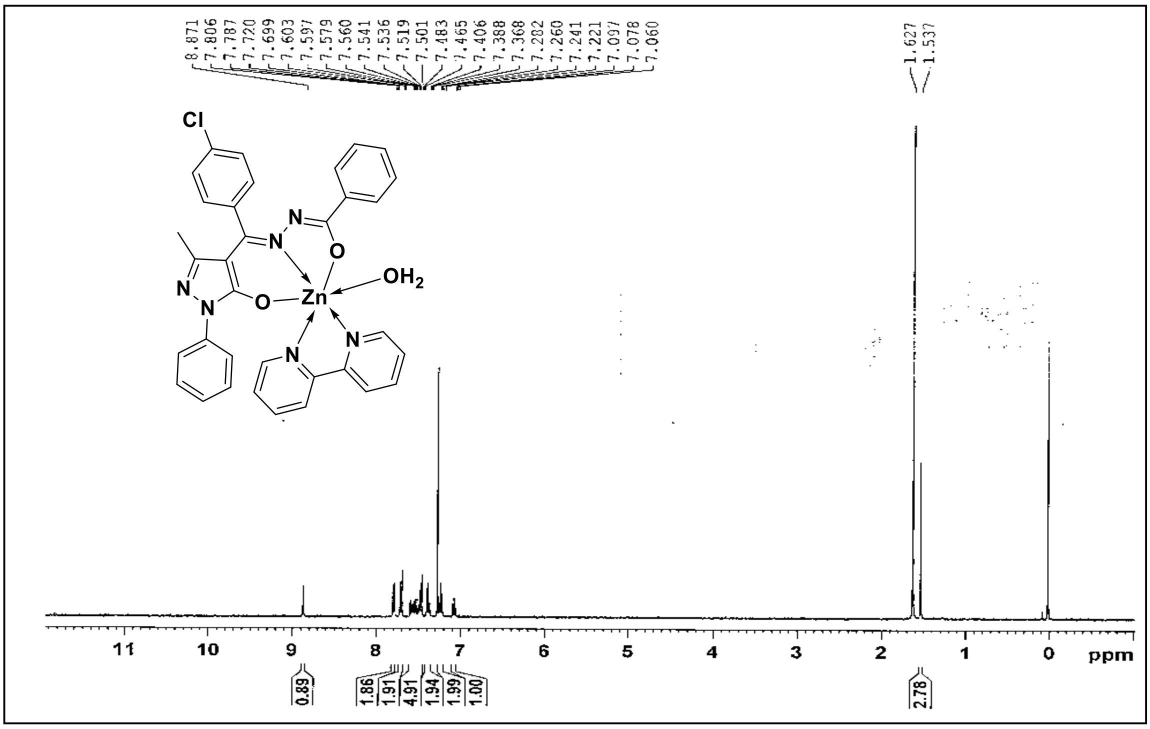


Fig. 3.2.9. ^{1}H NMR spectrum of complex **13.**

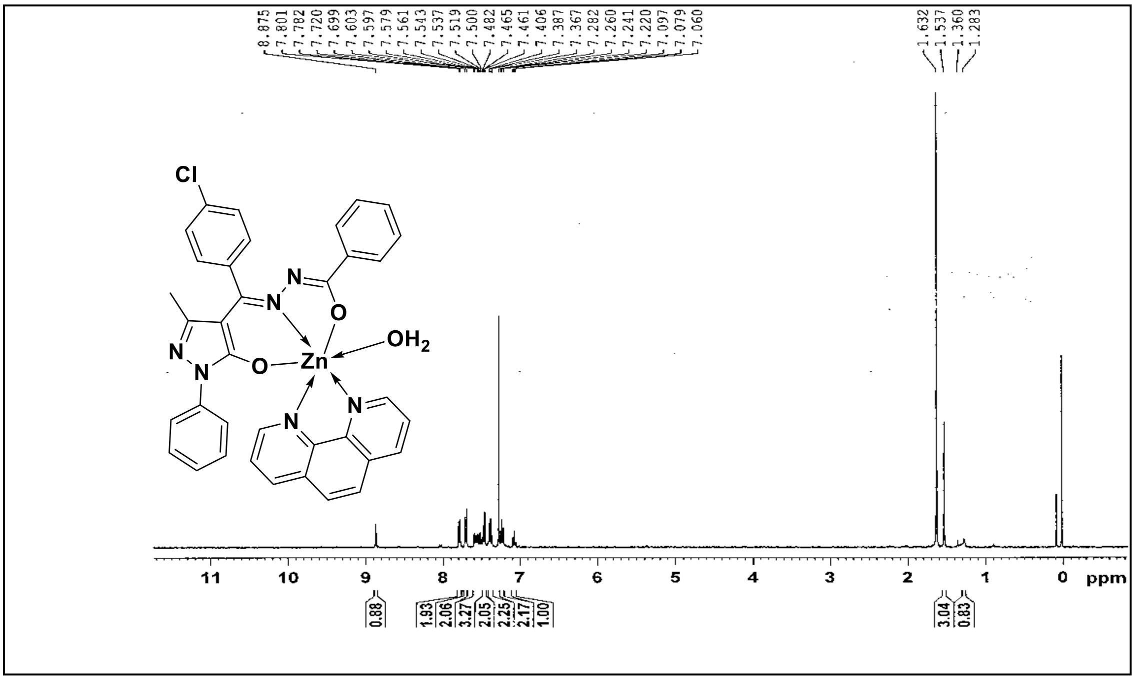


Fig. 3.2.10. ^{1}H NMR spectrum of complex **14.**

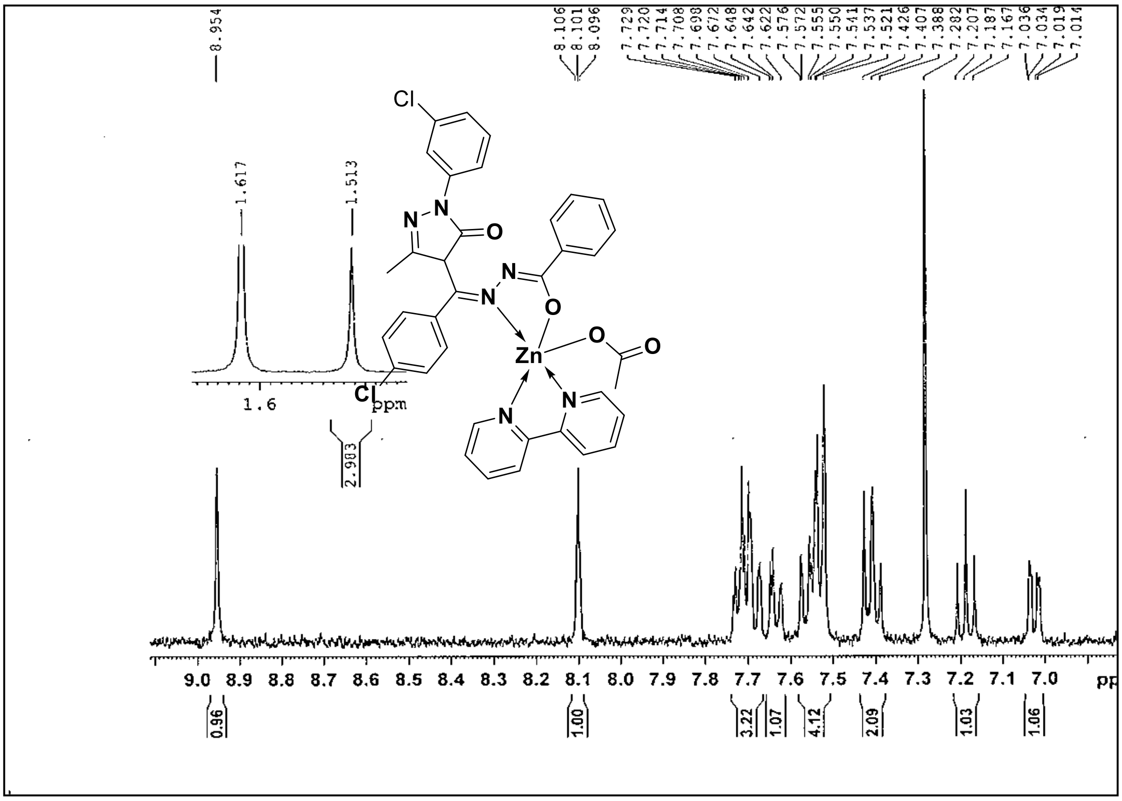


Fig. 3.2.11. ^{1}H NMR spectrum of complex **15.**

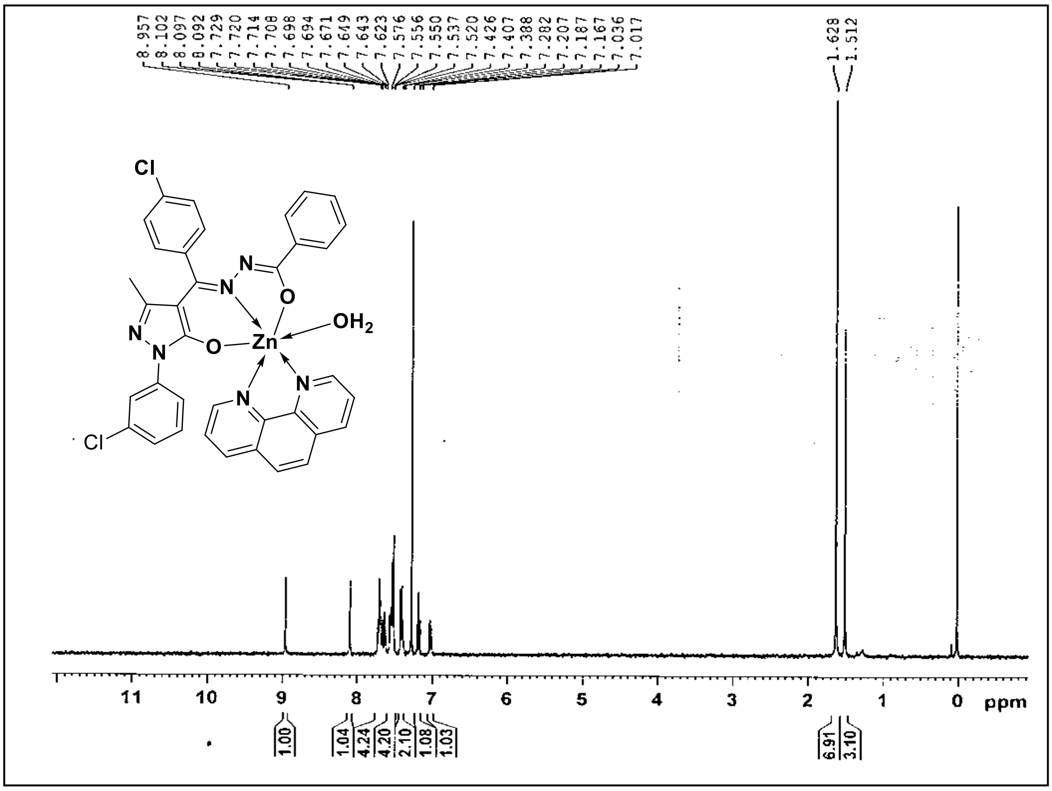


Fig. 3.2.12. ^{1}H NMR spectrum of complex **16.**

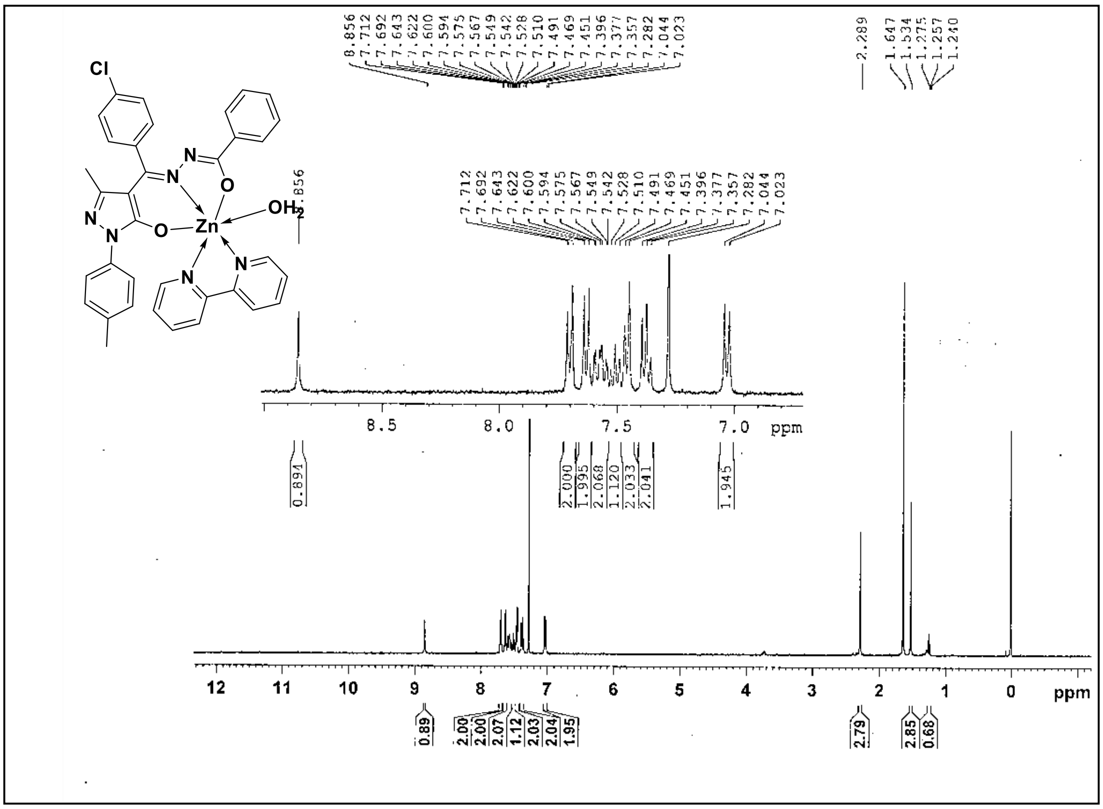


Fig. 3.2.13. ^{1}H NMR spectrum of complex **17.**

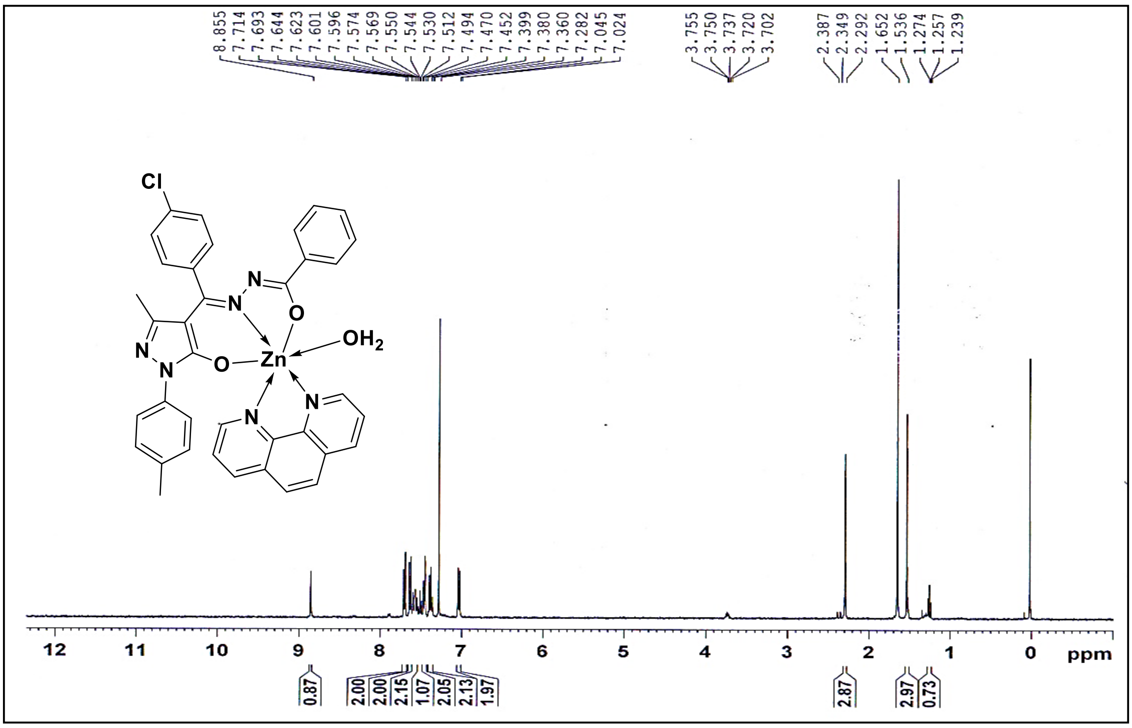


Fig. 3.2.14. ^{1}H NMR spectrum of complex **18.**

^{13}C NMR spectrum of complexes

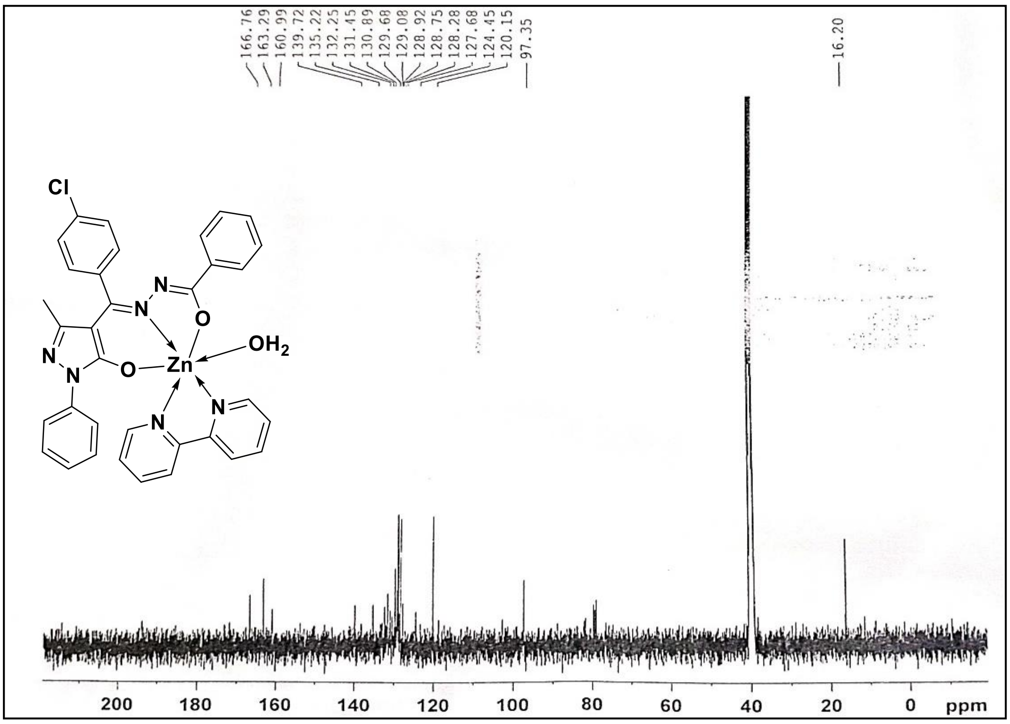


Fig. 3.2.15. ^{13}C NMR spectrum of complex **13** [Zn(L4)(byp)(H_2O)].

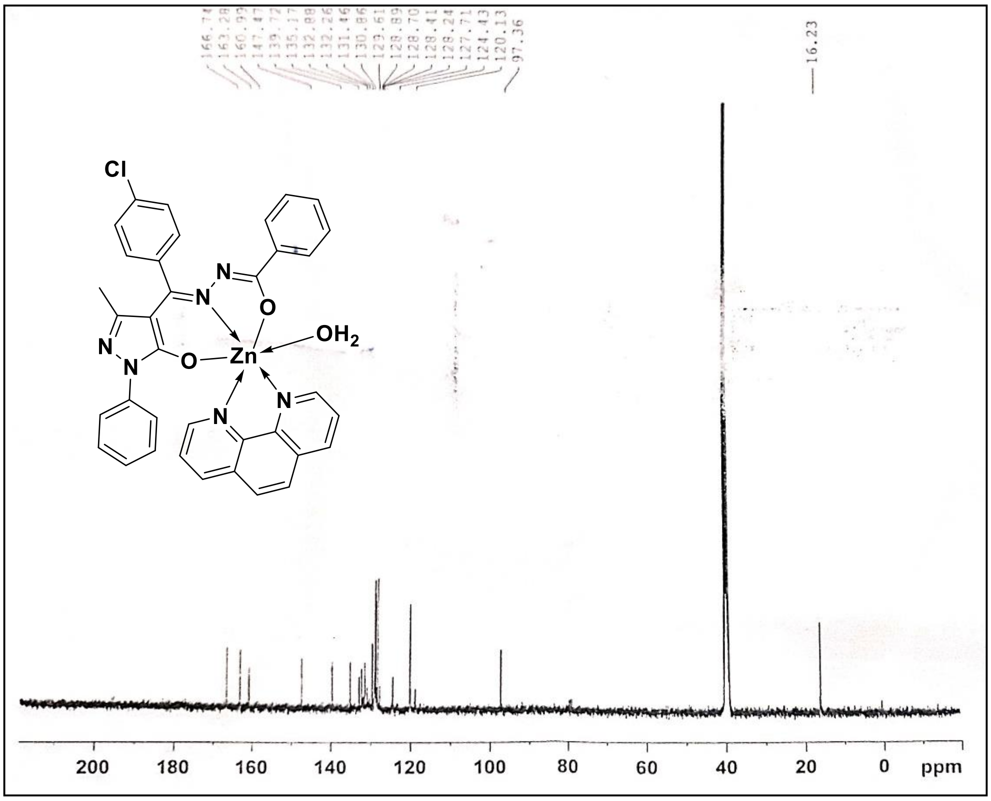


Fig. 3.2.16. ^{13}C NMR spectrum of complex **14** [Zn(L4)(phen)(H_2O)].

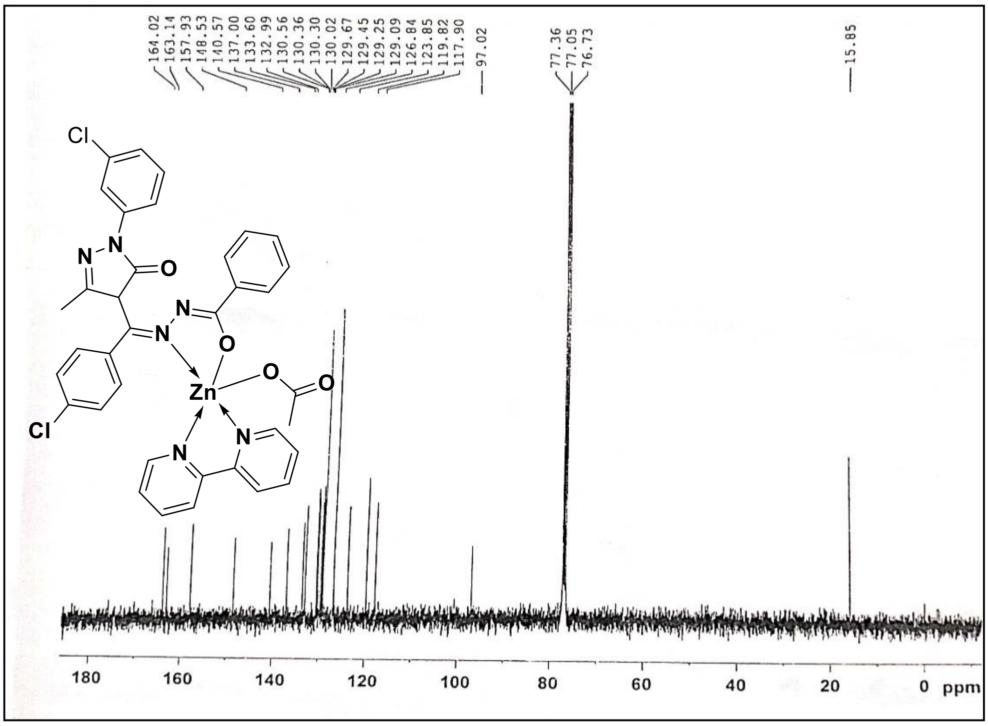


Fig. 3.2.17. ^{13}C NMR spectrum of complex **15** [Zn(**L5**)(bpy)(OAc)]EtOH.

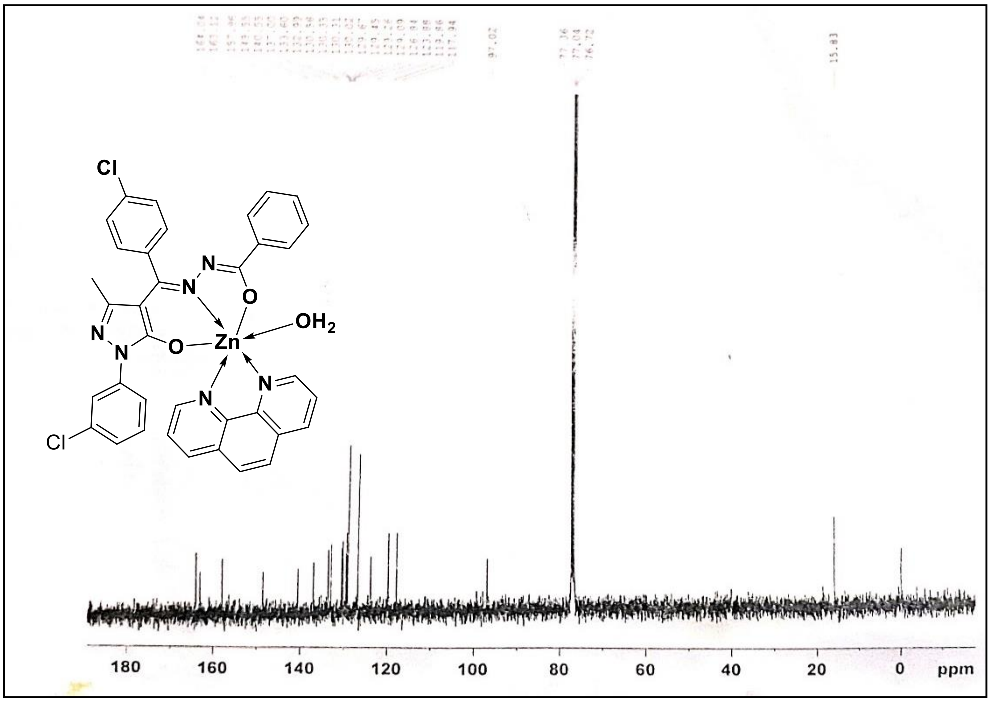


Fig. 3.2.18. ^{13}C NMR spectrum of complex **16** [Zn(**L5**)(phen)(H_2O)].

3.2.3.3. FTIR spectroscopic study

We have discussed FTIR spectral results of ligands in chapter 3(a). The ligand used in the present study can exhibit different tautomerism like keto, enol etc. The FTIR spectra provide valuable information in coordination chemistry about their coordination-binding sites of the ligand. As shown in Table 3.2.4 of the values of FTIR spectra of complexes **13-18**, all complexes show absorption in the range 3377-3378 cm^{-1}, which is due to the coordination water molecule stretching. The amidic carbonyl ν(C=O) stretching frequency absorption at 1640 cm^{-1} for the ligand which shifted to 1601-1615 cm^{-1} in complexes, which is due to the interaction with the metal ion. The IR spectra of complexes **13-18** show the absorption within 439-440 cm^{-1} which can be assigned to the ν(M-N) metal-ligand bond. The complexes show bands 511- 565 cm^{-1} due to the ν(M-O) of Zn(II) complexes. FTIR spectra of the Zn(II) complexes **13-18** are displayed in Fig. 3.2.19-3.2.24. Imported bond frequencies of FTIR spectra are given in Table 3.2.4.

Table 3.2.4. Selected stretching frequencies of FTIR spectra.

Code	**H_2O**	**N-H**	**C=O^A**	**C=O^B**	**C=N**	**N-N**	**C-O^B**	**M-N**	**M-O**
L4	-	3136	1640	1593	-	1090	-	-	-
L5	-	3138	1641	1592	-	1091	-	-	-
L6	-	3137	1641	1595	-	1090	-	-	-
[Zn(L4)(byp)(H_2O)] **13**	3378	-	1601	-	1585	1285	1091	440	565
[Zn(L4)(phen)(H_2o)] **14**	3377	-	1601	-	1565	1285	1090	438	565
[Zn(L5)(byp)(AcO)]EtOH **15**	3375	-	1603	-	1567	1283	1090	440	565
[Zn(L5)(phen)(H_2O)] **16**	3378	-	1604	-	1567	1283	1091	439	565
Zn(L6)(byp)(H_2O)] **17**	3378	-	1615	-	1567	1284	1092	439	548
Zn(L6)(phen)(H_2O)] **18**	3378	-	1615	-	1568	1284	1091	439	549

^{A} Benzhydrazide moiety, ^{B} Pyrazolone ring

FTIR Spectra:

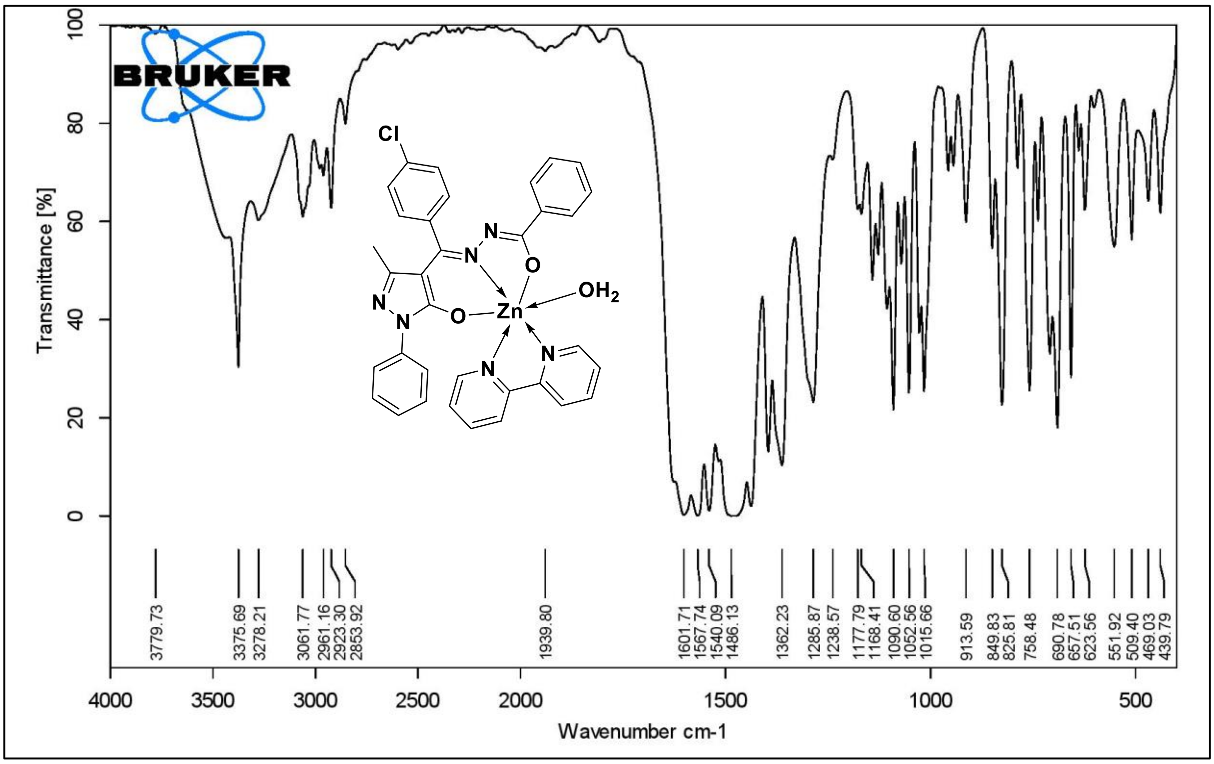


Fig. 3.2.19. FTIR spectrum of complex **13**.

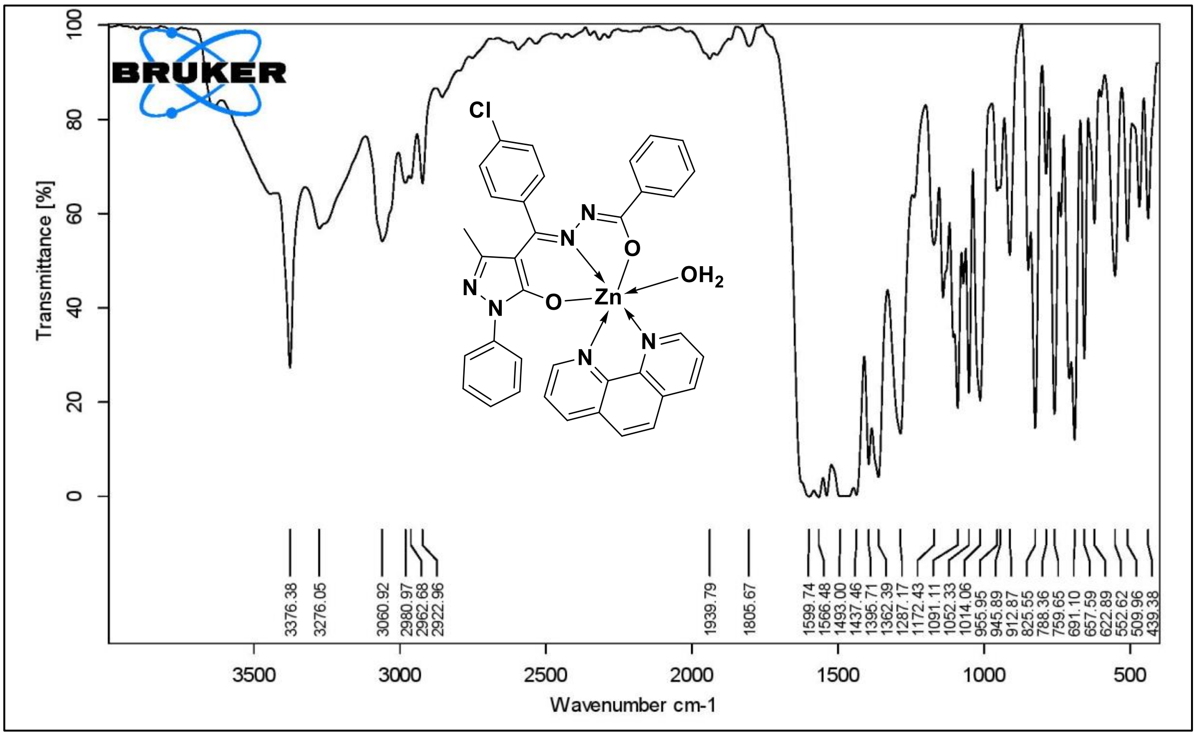


Fig. 3.2.20. FTIR spectrum of complex **14.**

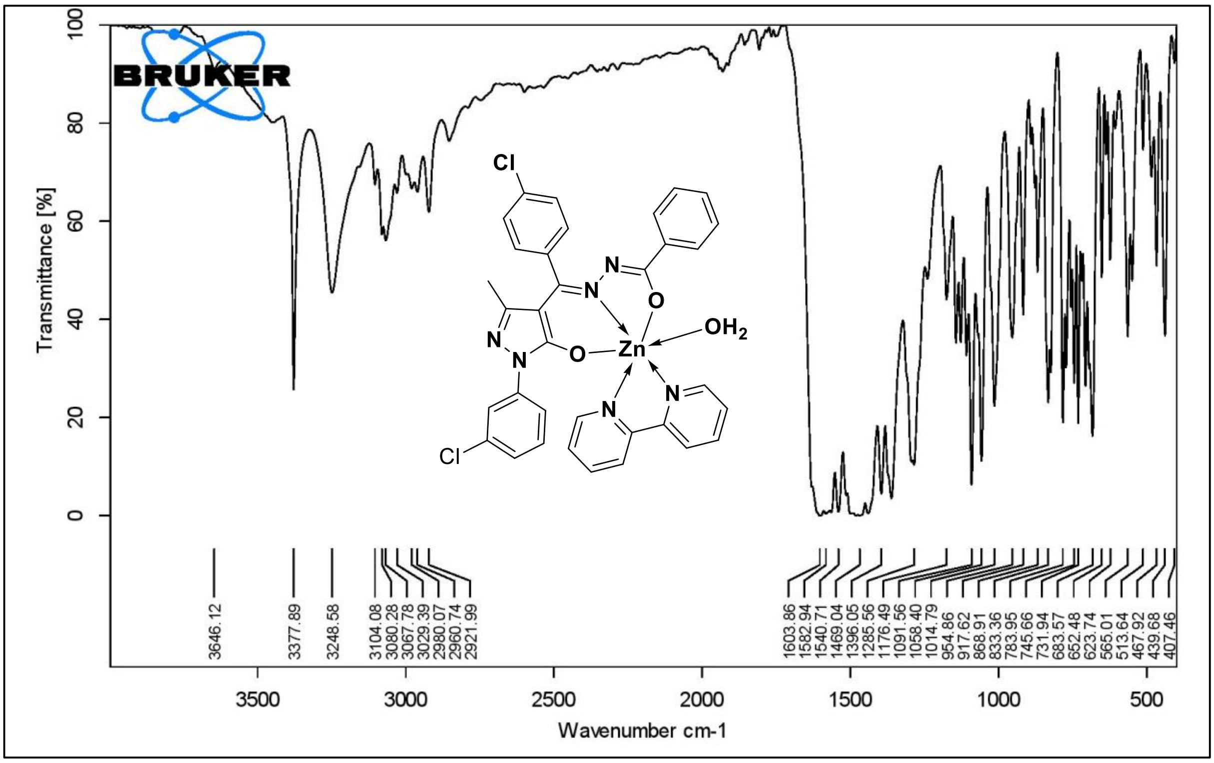


Fig. 3.2.21. FTIR spectrum of complex **15.**

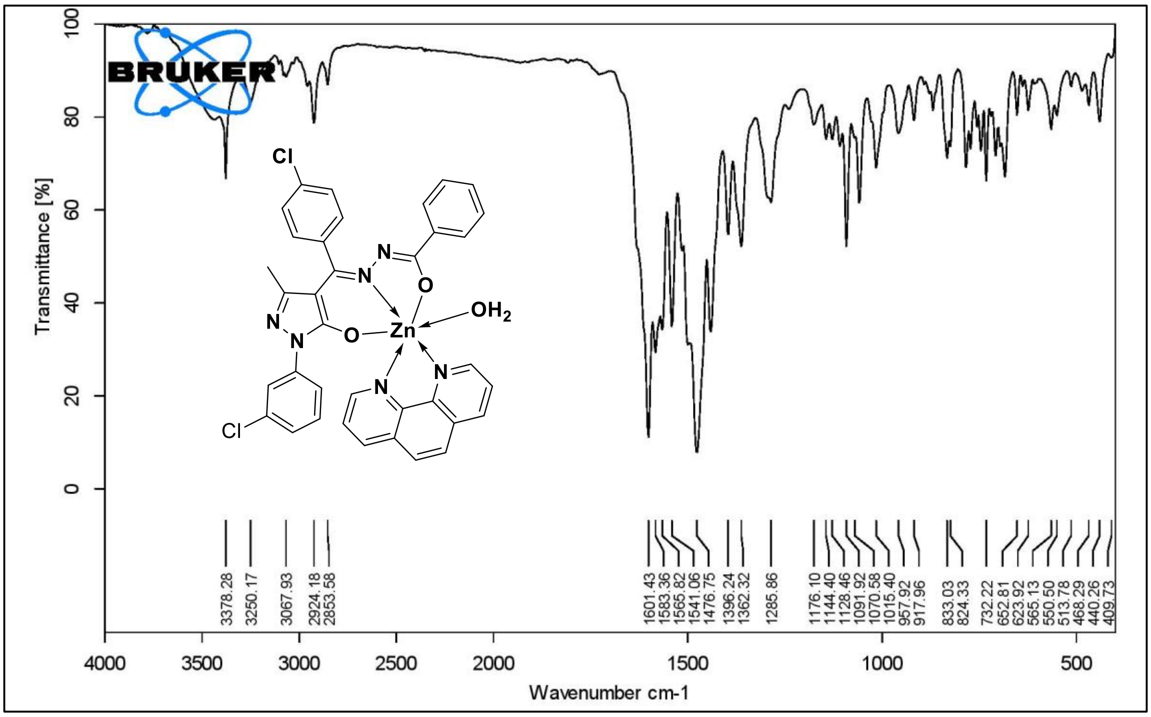


Fig. 3.2.22. FTIR spectrum of complex **16.**

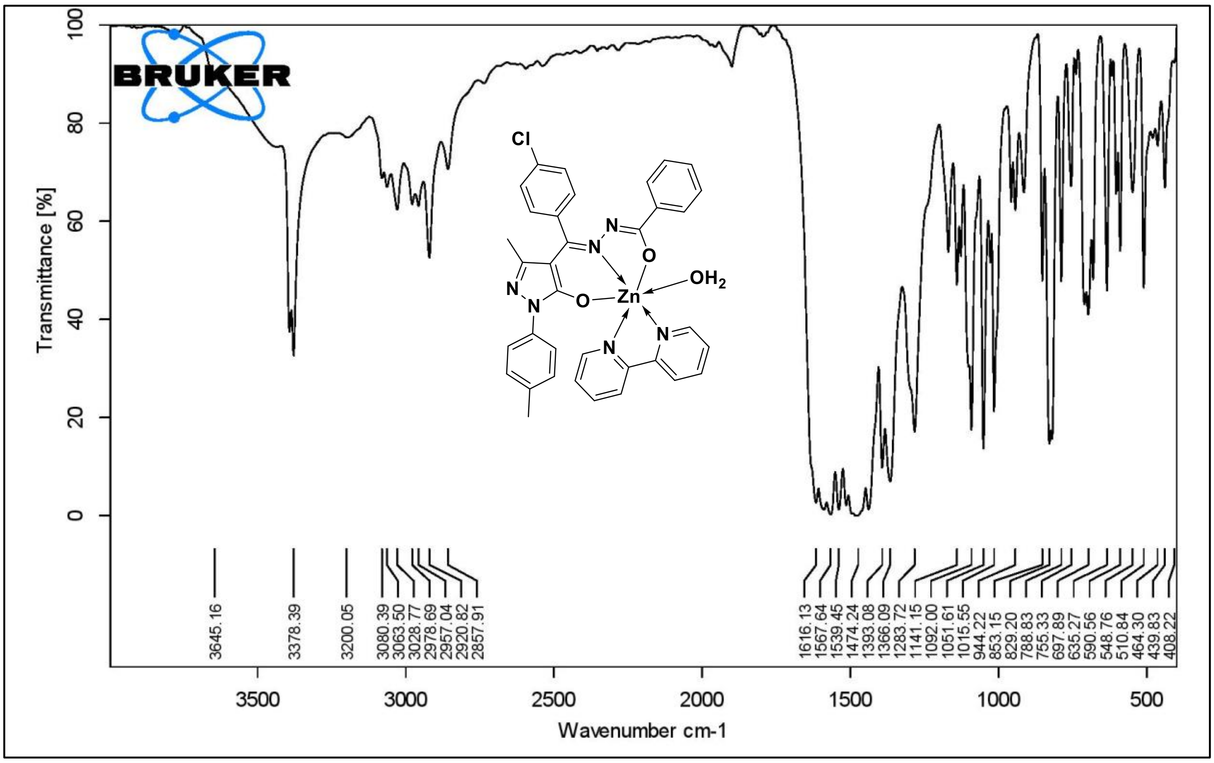


Fig. 3.2.23. FTIR spectrum of complex **17.**

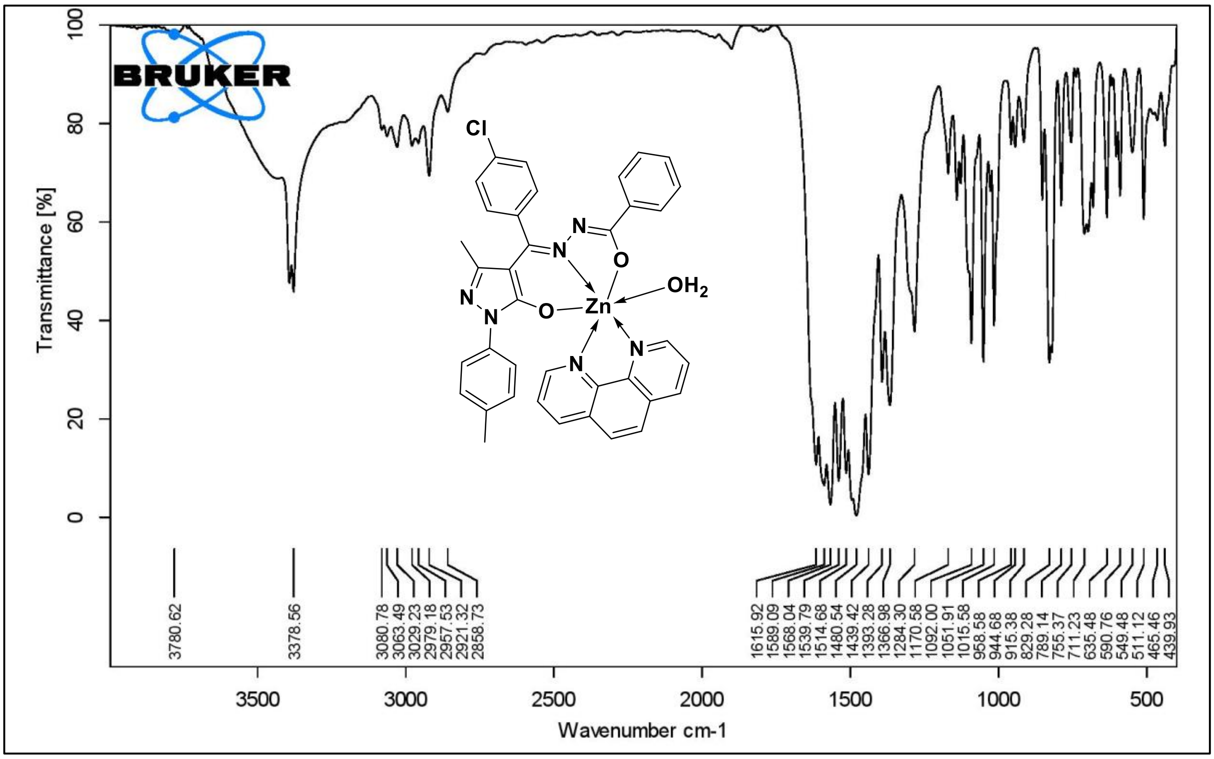


Fig. 3.2.24. FTIR spectrum of complex **18.**

3.2.3.4. Electronic spectra of 4-acylhydrazone-5-pyrazolones and zinc(II) complexes

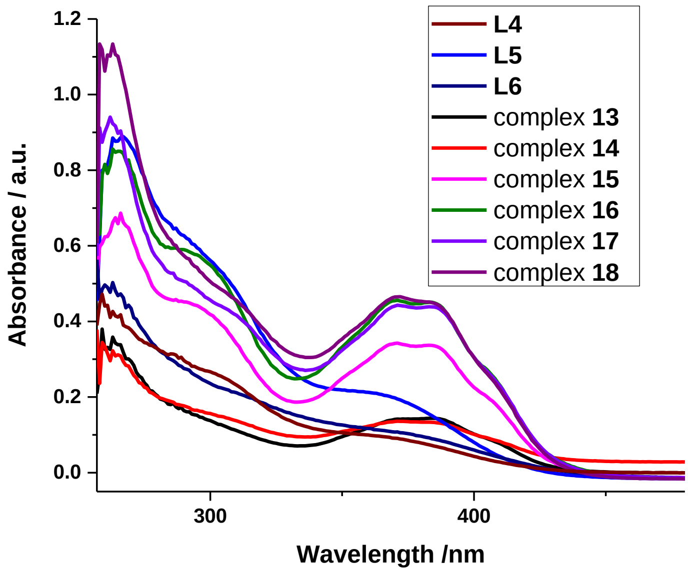


Fig. 3.2.25. Electronic spectra of ligands and complexes.

All complexes were completely soluble in DMSO and prepared out 10^{-5} M solution of ligands and complexes for UV/Vis spectroscopy (Fig. 3.2.25). UV-Vis spectra were recorded in the range of 250–700 nm. In the UV/Vis spectra of complexes, the first intense band is attributed to a ligand-centred (LC) π–π* transition localized on the aromatic rings of the ligand. In the spectra showed the shoulder is due to its metal coordination in complexes. There is no d-d transition in all complexes due to d^{10} metal. Compounds bearing the coordinated N, N-aromatic ligands, showed an intense band at 260 nm, and a moderately intense band at 300 nm, all due to the 2,2′-bipyridine and 1,10-phenanthroline ligand. In the spectra, complexes observed LMCT band at around 380 nm.[18]

3.2.3.5. Molar conductivity of complexes

Molar conductivity of ligands and complexes measured in 10^{-3} M solution. Compounds are soluble in DMSO. Complexes **13-18** molar conductance observed to be below 14 ohm^{-1} cm^{2} mol^{-1}. So the conductance measurements suggest that they are non-electrolytes. The conductivity values are tabulated in Table 3.2.5.[18,28,29]

Table 3.2.5. Molar conductivity of complexes and ligands.

Compound code	**Λ_m (s $cm^2 \cdot mol^{-1}$)**
13 [Zn(L4)(byp)(H_2O)]	11.2
14 [Zn(L4)(phen)(H_2O)]	11.6
15 [Zn(L5)(byp)(AcO)]EtOH	10.4
16 [Zn(L5)(phen)(H_2O)]	12.5
17 [Zn(L6)(byp)(H_2O)]	12.4
18 [Zn(L6)(phen)(H_2O)]	12.6
byp= 2,2′-bipyridine, phen= 1, 10-phenanthroline	

Conclusion

In summary, three new 4-acylpyrazolone derivatives (**L4-L6**) were synthesized and **characterized by various spectroscopic and analytical techniques (**Chapter 3(a))**.** Synthesized six mixed ligand zinc (II) complexes **13-18 of 4-acylhydrazone-5-pyrazolones and 2,2′-bipyridine/1,10-phenanthroline.** All complexes have been characterized by **FTIR, ^{1}H and ^{13}C NMR, single crystal X-ray diffraction, elemental analysis, Uv-Vis spectroscopy**, **TGA and conductance.** The evidence from single crystal X-ray diffraction spectroscopy has been suggested a distorted octahedral environment around the zinc through coordination of many of O, *N*, O-chelating 4-acylhydrazone-5-pyrazolone ligand for complex **16.** The single crystal X-ray analysis of complex **15** showed distorted square pyramidal geometry. In complex **16**, DMF replacing coordinated water molecule during crystallization.

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