

# Synthesis and spectroscopic studies of mixed-ligand and metal (II) complexes with 1,4-diformylpiprazine bis (2-hydroxy-2, 2-diphenylacetohydrazone) and 1,10-Phenanthroline

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## ABSTRACT

Three types of cobalt(II), nickel(II), copper(II) and zinc(II) complexes derived from 1,4-diformyl piprazine bis (2-hydroxy-2, 2-diphenylacetohydrazone (LH<sub>4</sub>) and bidentate heterocyclic base [1,10-phenanthroline (phen)] with metal(II) chlorides of the general formulas [M(LH<sub>2</sub>)Cl<sub>2</sub>], [M<sub>2</sub>(LH<sub>2</sub>)Cl<sub>4</sub>] and [M<sub>2</sub>(LH<sub>2</sub>)(phen)<sub>2</sub>]Cl<sub>2</sub> where [M=Co(II),Ni(II),Cu(II) and Zn(II)] have been synthesized and characterized by elemental analysis (CHN), molar conductance, infrared spectra IR, <sup>1</sup>H- NMR and <sup>13</sup>C-NMR spectra, UV-vis electronic absorption spectra and magnetic susceptibility measurements. According to the IR spectra, the ligand act as dianionic tetradentate and coordination takes place in the enol tautomeric form with the enolic oxygen and azomethine nitrogen atoms while the alcoholic hydroxyl group ν(O-H) of benzilic moiety do not participate in coordination. On the basis of electronic spectral data and magnetic susceptibility measurements of the complexes indicate a six-coordinated octahedral geometry for, [M(LH<sub>2</sub>)Cl<sub>2</sub>] complexes, and a four-coordinated tetrahedral geometry for [M<sub>2</sub>(LH<sub>2</sub>)Cl<sub>4</sub>] and [M<sub>2</sub>(LH<sub>2</sub>)(phen)<sub>2</sub>]Cl<sub>2</sub> complexes may be assigned.

**Keywords:** Schiff base; Mixed-ligand; dimeric complexes; binuclear; 1, 10-phenanthroline.

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## Introduction

The interest in studying the hydrazides of organic acids and their derivatives arises from the fact that most of these compounds have relevant biological properties such as virus inhibitors (Vasudevachari and Antony, 1985), antitumor agents (Awaluddin *et al.*, 1987), antiradiation drugs (Atkinson *et al.*, 1965), and other pharmacological activities. The biological activity of hydrazides was ascribed to their ability to form chelates with transition metal ions (Fox and Gibas, 1956). Transition metal ion complexes with aroylhydrazones have found many applications as catalysts in various chemical and photochemical reactions as well as in some biological systems (Rollas *et al.*, 1988). The use of aroylhydrazone complexes in a given reaction depends to a great extent on their molecular structure.

Aroylhydrazones are potential ligands due to having a number of bonding sites. They can act a neutral or monoanionic bidentate or tridentate ligand depending on the substituents and the reaction conditions. Furthermore, 1,10-Phenanthroline (phen) is widely used as a classical *N,N*-bidentate ligand to prepare mixed ligand complexes in coordination chemistry. The presence of mixed-ligand can infer differences in bonding, spectral properties, geometry in coordination compounds (Al-Shemary *et al.*, 2016).

Intensive investigations of the coordination chemistry of dinuclear metal complexes with chelating ligands continue to be stimulated by interest for Metallo biomolecules (Karlin and Zubieta, 1983), the search for appropriate systems for binding and activating simple molecules (Vigato *et al.*, 1990), catalysis (Eisenberg and Hendrikson, 1979) and magnetic interactions (Gatteschi *et al.*, 1991). In spite of the greatest effort and success in the study of dinuclear copper(II) complexes, such complexes have still attracted much attention due to their interesting properties and the relative simplicity of their synthesis.

In our previous work, we reported the synthesis and spectroscopic studies of mononuclear copper and nickel complexes of Schiff base prepared by condensing aroyl ketones with anthranilhydrazide and salicylohydrazide (Gup and Kirkan, 2005).

In this paper, we report the synthesis and spectroscopic studies of mononuclear and dinuclear Co(II), Ni(II), Cu(II), Zn(II) complexes containing 1,4-diformyl-piprazine bis(2-hydroxy-2,2-diphenylacetohydrazone) as well as mixed-ligand complexes with 1,10-phenanthroline.

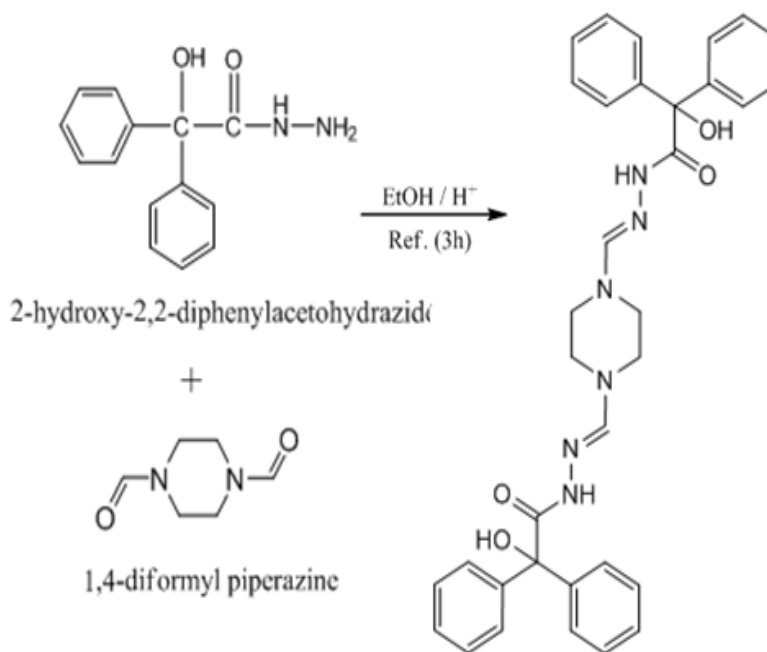
## MATERIALS AND METHODS

**Chemicals.** All the chemicals have been used as supplied (Fluka, BDH or Aldrich) Chemicals without further purification.

**Analytical and physical measurements.** FT-IR spectra were recorded as KBr pellets in the region 4000-400  $\text{cm}^{-1}$  using Bruker-ALPHA FTIR-4100. CHN analyzer was measured on Euro-vector-AC-3000 (Italy).  $^1\text{H}$ -NMR spectra were recorded on a Bruker 400MHz spectrometer in  $\text{DMSO}-d_6$  with TMS as the internal standard. Magnetic susceptibility measurements were performed at room temperature by Faraday method (Bruker B.M6). Molar conductivities of the complexes have been measured on a digital conductivity meter (Jenway - model 4070 meter) using  $10^{-3}$  M of the complexes in dimethylformamide (DMF) solution at  $25^\circ\text{C}$  conductivity bridge at room temperature. The electronic spectra of the ligands and complexes were recorded on a Jasco V-350 Spectrophotometer (Japan) in the regions (50000-9090  $\text{cm}^{-1}$ ) for  $10^{-2}$  M solution of the complexes in DMF at room temperature using 1cm cells. The metal contents of the complexes were determined Spectrophotometry using AAS Phoenix-986 (UK), after decomposition with conc.  $\text{HNO}_3$ .

**Synthesis of 1,4-diformylpiprazine bis(2-hydroxy-2,2-diphenylacetohydrazone) ( $\text{LH}_4$ ).** 2-hydroxy-2,2-diphenylacetohydrazone was prepared by refluxing methyl 2-hydroxy-2,2-diphenylacetate (10 mmol, 2.42 g) in 50ml methyl alcohol with hydrazine hydrate 2.5 ml (80%,  $d=1.03$ ) for 4 h. The compounds precipitated on standing over night, filtered and washed with distilled water. The pure hydrazone was obtained by recrystallization from hot ethanol (Al-Neaimi and Al-Khuder, 2013). (colour; pale yellow, yield 90%, m.p.=170-171  $^\circ\text{C}$ ).

The ligand synthesized in this work are shown in (Scheme 1) and their syntheses are described as follows. A solution of 2-hydroxy-2,2-diphenylaceto-hydrazone (10 mmol, 2.42 g) in 30 ml of hot ethanol was added to solution 1,4-diformyl piprazine (5 mmol, 0.71 g) with (3-5) drops of glacial acetic acid in 20 ml of ethanol. The reaction mixture was stirred while refluxing for 3 h. after left the resultant to cold at room temp. added (100 ml) of cold water distillation resulting yellow precipitate were filtered off and washed with ethanol ( $3 \times 5\text{ml}$ ), and recrystallization of precipitate from *n*-hexane and filtered and dried under reduced pressure (Scheme 1). Some properties of the synthesized ligand and complexes are given in Table1.



Scheme 1: Synthesis of ligand  $\text{LH}_4$

Table 1: Color, melting points, yields and elemental analytical results of the ligand and their metal complexes

Comp.	Formulas (MW)	Color	m.p. <sup>a</sup> (°C)	$\mu_{\text{eff}}$ B. M.	$\Lambda_m$ $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Yield (%)	Calculated (Found) %				
							C	H	N	Cl	M
LH <sub>4</sub>	C <sub>34</sub> H <sub>34</sub> N <sub>6</sub> O <sub>4</sub> (590.67 g.mol <sup>-1</sup> )	Yellow	212-214	---	---	86	69.14 (69.44)	5.80 (5.70)	14.23 (14.38)	----	----
[Co(LH <sub>2</sub> )Cl <sub>2</sub> ] (1)	C <sub>34</sub> H <sub>32</sub> Cl <sub>2</sub> CoN <sub>6</sub> O <sub>4</sub> (718.49 g.mol <sup>-1</sup> )	Dark brown	289 <sup>a</sup>	4.92	7.7	77	56.84 (56.27)	4.49 (4.03)	11.70 (11.82)	9.87 (9.22)	8.20 (8.27)
[Ni(LH <sub>2</sub> )Cl <sub>2</sub> ] (2)	C <sub>34</sub> H <sub>32</sub> Cl <sub>2</sub> NiN <sub>6</sub> O <sub>4</sub> (718.26 g.mol <sup>-1</sup> )	Green	278	3.10	8.4	78	56.85 (56.19)	4.49 (4.22)	11.70 (11.91)	9.87 (9.74)	8.17 (8.23)
[Cu(LH <sub>2</sub> )Cl <sub>2</sub> ] (3)	C <sub>34</sub> H <sub>32</sub> Cl <sub>2</sub> CuN <sub>6</sub> O <sub>4</sub> (723.11 g.mol <sup>-1</sup> )	Light Green	269-271	1.92	11.2	81	56.47 (56.08)	4.46 (4.16)	11.62 (11.97)	9.81 (9.57)	8.79 (8.81)
[Zn(LH <sub>2</sub> )Cl <sub>2</sub> ] (4)	C <sub>34</sub> H <sub>32</sub> Cl <sub>2</sub> ZnN <sub>6</sub> O <sub>4</sub> (724.97 g.mol <sup>-1</sup> )	White	302 <sup>a</sup>	Dia	9.2	75	56.33 (55.89)	4.45 (3.99)	11.59 (11.20)	9.78 (9.83)	9.02 (9.12)
[Co <sub>2</sub> (LH <sub>2</sub> )Cl <sub>4</sub> ] (5)	C <sub>34</sub> H <sub>32</sub> Cl <sub>4</sub> Co <sub>2</sub> N <sub>6</sub> O <sub>4</sub> (848.33 g.mol <sup>-1</sup> )	Dark Olive	234 <sup>a</sup>	4.39	15.6	83	48.14 (48.21)	3.80 (3.87)	9.91 (9.38)	16.72 (16.52)	13.89 (13.78)
[Ni <sub>2</sub> (LH <sub>2</sub> )Cl <sub>4</sub> ] (6)	C <sub>34</sub> H <sub>32</sub> Cl <sub>4</sub> Ni <sub>2</sub> N <sub>6</sub> O <sub>4</sub> (847.85 g.mol <sup>-1</sup> )	Green	238	3.59	23.1	73	48.16 (47.89)	3.80 (3.33)	9.91 (9.22)	16.73 (16.81)	13.85 (13.92)
[Cu <sub>2</sub> (LH <sub>2</sub> )Cl <sub>4</sub> ] (7)	C <sub>34</sub> H <sub>32</sub> Cl <sub>4</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>4</sub> (857.56 g.mol <sup>-1</sup> )	Brown	278 <sup>a</sup>	2.28	13.4	78	47.62 (47.72)	3.76 (3.51)	9.80 (9.23)	16.54 (16.72)	14.82 (14.91)
[Zn <sub>2</sub> (LH <sub>2</sub> )Cl <sub>4</sub> ] (8)	C <sub>34</sub> H <sub>32</sub> Cl <sub>4</sub> Zn <sub>2</sub> N <sub>6</sub> O <sub>4</sub> (861.29 g.mol <sup>-1</sup> )	Pale yellow	319-321	Dia	4.5	72	47.41 (47.57)	3.74 (3.85)	9.76 (9.61)	16.47 (16.56)	15.19 (15.34)
[Co <sub>2</sub> (LH <sub>2</sub> )(phen) <sub>2</sub> ]Cl <sub>2</sub> (9)	C <sub>58</sub> H <sub>48</sub> Cl <sub>2</sub> Co <sub>2</sub> N <sub>10</sub> O <sub>4</sub> (1137.84 g.mol <sup>-1</sup> )	Red-brown	239	4.11	116	80	61.22 (61.35)	4.25 (4.29)	12.31 (12.01)	6.23 (6.45)	10.36 (10.03)
[Ni <sub>2</sub> (LH <sub>2</sub> )(phen) <sub>2</sub> ]Cl <sub>2</sub> (10)	C <sub>58</sub> H <sub>48</sub> Cl <sub>2</sub> Ni <sub>2</sub> N <sub>10</sub> O <sub>4</sub> (1137.36 g.mol <sup>-1</sup> )	Greenish yellow	269	4.20	119	79	61.25 (61.41)	4.25 (4.05)	12.32 (12.45)	6.23 (6.31)	10.32 (10.44)
[Cu <sub>2</sub> (LH <sub>2</sub> )(phen) <sub>2</sub> ]Cl <sub>2</sub> (11)	C <sub>58</sub> H <sub>48</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>10</sub> O <sub>4</sub> (1147.06 g.mol <sup>-1</sup> )	Brown	224	2.31	121	71	60.73 (60.79)	4.22 (4.09)	12.21 (11.72)	6.18 (6.10)	11.08 (10.67)
[Zn <sub>2</sub> (LH <sub>2</sub> )(phen) <sub>2</sub> ]Cl <sub>2</sub> (12)	C <sub>58</sub> H <sub>48</sub> Cl <sub>2</sub> Zn <sub>2</sub> N <sub>10</sub> O <sub>4</sub> (1150.79 g.mol <sup>-1</sup> )	Pale yellow	256	Dia	124	76	60.53 (60.62)	4.20 (3.89)	12.17 (11.92)	6.16 (5.22)	11.37 (11.41)

<sup>a</sup> with decomposition

## SYNTHESIS OF COMPLEXES

**Synthesis of complexes [M(LH<sub>2</sub>)Cl<sub>2</sub>] [M= Co(II), Ni(II), Cu(II) and Zn(II)].** A solution of (1 mmol) metal(II) chloride [CoCl<sub>2</sub>·2H<sub>2</sub>O (0.237 g); NiCl<sub>2</sub>·6H<sub>2</sub>O (0.238g); CuCl<sub>2</sub>·2H<sub>2</sub>O (0.17 g); and anhydrous ZnCl<sub>2</sub> (0.136 g)] in MeOH (10 ml) was added to a hot solution containing bishydrazone (LH<sub>4</sub>= 0.590 g, 1 mmol) in MeOH (25 ml) with stirring. The reaction

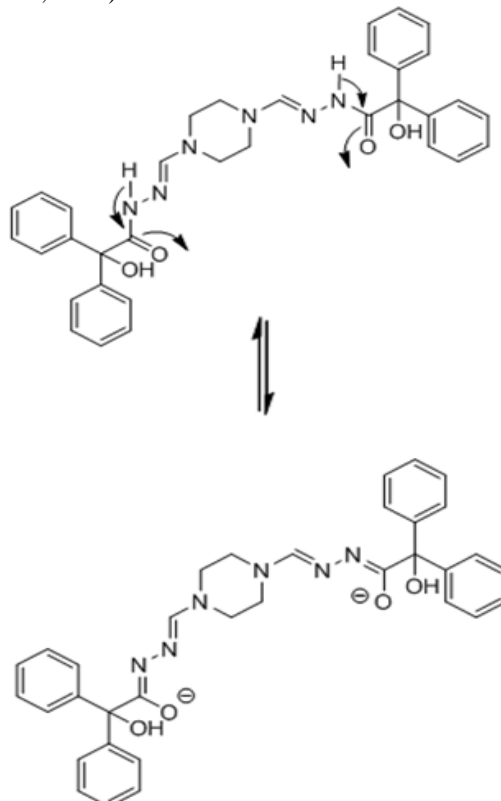
mixture was refluxed for 5 h, and then the volume was reduced to ~10 ml volume under reduced pressure. On standing overnight, the complexes separated, collected by filtration, washed with benzene and chloroform and finally water.

**Synthesis of complexes  $[M_2(LH_2)Cl_4]$   $[M= Co(II), Ni(II), Cu(II) \text{ and } Zn(II)]$ .** A solution of (2 mmol) metal chloride  $[CoCl_2 \cdot 2H_2O$  (0.474 g);  $NiCl_2 \cdot 6H_2O$  (0.476 g);  $CuCl_2 \cdot 2H_2O$  (0.341 g); and anhydrous  $ZnCl_2$  (0.272 g)] in MeOH (10 ml) was added by dropwise to a solution containing bishydrazone ( $LH_4 = 0.590$  g, 1 mmol) in acetone (40 ml) with stirring. The reaction mixture was refluxed for 5 h. The precipitated complexes were filtered off, washed with water and chloroform.

**Synthesis of complexes  $[M_2(LH_2)(phen)_2]Cl_2$   $[M= Co(II), Ni(II), Cu(II) \text{ and } Zn(II)]$ .** The complexes  $[M_2(LH_2)(phen)_2]Cl_2$  were prepared by the following general method. To a solution of (2mmol) metal(II) chloride  $[CoCl_2 \cdot 2H_2O$  (0.474 g);  $NiCl_2 \cdot 6H_2O$  (0.476 g);  $CuCl_2 \cdot 2H_2O$  (0.341 g); and anhydrous  $ZnCl_2$  (0.272 g)] in MeOH (10 ml), a solution of 1,10-phenanthroline (phen = 0.47 g, 2 mmol) in 10 ml MeOH was added dropwise with constant stirring. The resulting colored solution, which was a suspension in the case of copper complexes, was stirred and heated for 15 min. ( $LH_4 = 0.590$  g, 1 mmol) of ligand dissolved in the same solvent (25 ml) was added and refluxed for 3h. The precipitate was filtered, washed with water and ethanol, and then dried in at room temperature.

## RESULTS AND DISCUSSION

Bis-hydrazone such as synthesized in this study may exist in the keto or in the enol tautomeric form in the solid state, Fig. 1. The observation of strong  $\nu(C=O)$  absorption band around  $1658\text{ cm}^{-1}$  in the infrared spectra of the ligand suggest that the ligand is in the keto form in the solid state. The tautomeric keto form of compound was also indicated by  $^1H$ -NMR spectroscopy since the enolic OH signal of enol forms since OH signal of enol form of ligand was not observed, while amide NH signal of keto form appeared at 10.73 ppm (Gup and Kirkan, 2005; Dinda *et al.*, 2002; Dinda *et al.*, 2003; Ainscough *et al.*, 1999; Lee *et al.*, 2003).



**Fig.1. Tautomeric forms of the ligand  $LH_4$**

The reaction of metal(II) chlorides with the 1,4-diformyl piperazine bis(2-hydroxy-2,2-diphenylacetohydrazone ( $LH_4$ ), in a molar ratio of 1:1 using methanol as solvent gave a mononuclear complexes of the type,  $[M(LH_2)Cl_2]$   $[M=Co(II), Ni(II), Cu(II) \text{ and } Zn(II)]$ . The formulation were in accordance with the data of elemental analysis and physicochemical measurements (Tables 1-4). The molar conductance determined at concentration of  $1 \times 10^{-3}$  M, in DMF of the complexes (**1-4**) show small values in the range  $7.7\text{-}11.2\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ , indicating that the complexes are non-electrolytes in nature and

that no inorganic anions such as  $\text{Cl}^-$  ions are present in outer sphere coordination (Shayma *et al.*, 2009; Chandra and Kumar, 2005).

On the other hand, metal(II) chlorides reacted with the same ligand ( $\text{LH}_4$ ) in a 2:1 molar ratio in methanol and acetone, respectively, producing dinuclear complexes (**5-8**) of the type  $[\text{M}_2(\text{LH}_2)\text{Cl}_4]$ . Metal analysis and molar conductance data (Table 1) confirmed these formulas complexes (**5-8**) were non-electrolytes. The non-conducting character reveals the presence of ( $\text{Cl}^-$ ) and metals ions in the coordination sphere (Shayma *et al.*, 2009; Chandra and Kumar, 2005; Rani *et al.*, 2012).

Moreover, The reaction of metal(II) chlorides with the solution containing ligand ( $\text{LH}_4$ ) and 1,10-phenanthroline in a molar ratio of 2:1:2 respectively, using methanol as solvent gives mixed-ligand dinuclear metal(II) complexes with general formula  $[\text{M}_2(\text{LH}_2)(\text{phen})_2]\text{Cl}_2$ , producing complexes (**9-12**). Metal analysis and molar conductance data (Table 1) show values in the range  $116\text{--}124\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ , indicating that the complexes were 1:2 electrolytes (Geary, 1971).

All the synthesized metal complexes were colored, solid and stable towards air and moisture at room temperature. They decomposed on heating at high temperatures and were more or less soluble in common organic solvents (DMF, DMSO, methanol, ethanol, acetone, chloroform, ether).

**$^1\text{H-NMR}$  and IR spectra of the ligand.** In the  $^1\text{H-NMR}$  spectra of the 1,4-diformyl piprazine bis(2-hydroxy-2,2-diphenylacetohydrazone) ( $\text{LH}_4$ ) (Fig. 2) the resonance of the (NH) protons appears as a singlet at  $\delta$  10.73 ppm. The ring protons resonances of the 1,4-diformyl piprazine moiety ( $\text{N-CH}_2\text{CH}_2\text{-N}$ ) of this ligand is observed as a triplet peak at  $\delta$  2.76–2.84 ppm (t, 8H), while that of the benzenoid moiety appears as two different triplet and doublet peaks at  $\delta$  7.31–7.46 (t, 12H), and  $\delta$  7.57–7.60 (d, 8H) ppm, also the protons of ( $=\text{C-H}$ ) next to imine groups were observed as a singlet at  $\delta$  7.65 ppm (s, 2H); the protons of alcoholic (OH) groups were observed as a singlet at  $\delta$  3.77 (s, 2H) ppm (Dinda *et al.*, 2002; Dinda *et al.*, 2003) (Table 2). These data are in agreement with that previously reported for similar compounds (Naskar *et al.*, 2004; Koh *et al.*, 1998).

The  $^{13}\text{C-NMR}$  spectra of ( $\text{LH}_4$ ) (Fig. 3) ligand showed different signals, which were observed at  $\delta$  170.93 ppm belonging to carbonyl group  $2(\text{C=O})$  as expected, and spectra of  $2(-\text{HC=N})$  appear at  $\delta$  146.22 ppm, while the singlet of the  $\text{C}_{\text{aromatic}}$  carbon ( $\text{Ar-C}$ ) were observed at  $\delta$  127.29, 128.76, 129.47, 142.62 ppm for C-(12,18,12',18'), C-(10,14,16,20,10',14',16',20'), C-(11,13,17,19,11',13',17',19'), C-(9,15,9',15'), respectively, (Table 2). Furthermore, the signal of a secondary carbon ( $\text{CH}_2$ ) of diformylpiprazine moiety appears at  $\delta$  53.55 ppm. The obtained values for  $^{13}\text{C-NMR}$  chemical shifts of these compounds are given Table 2. These data are in agreement with that previously reported for similar compounds (Al-Neaimi and Al-Khuder, 2013; Dinda *et al.*, 2003; Lee *et al.*, 2003; Naskar *et al.*, 2004).

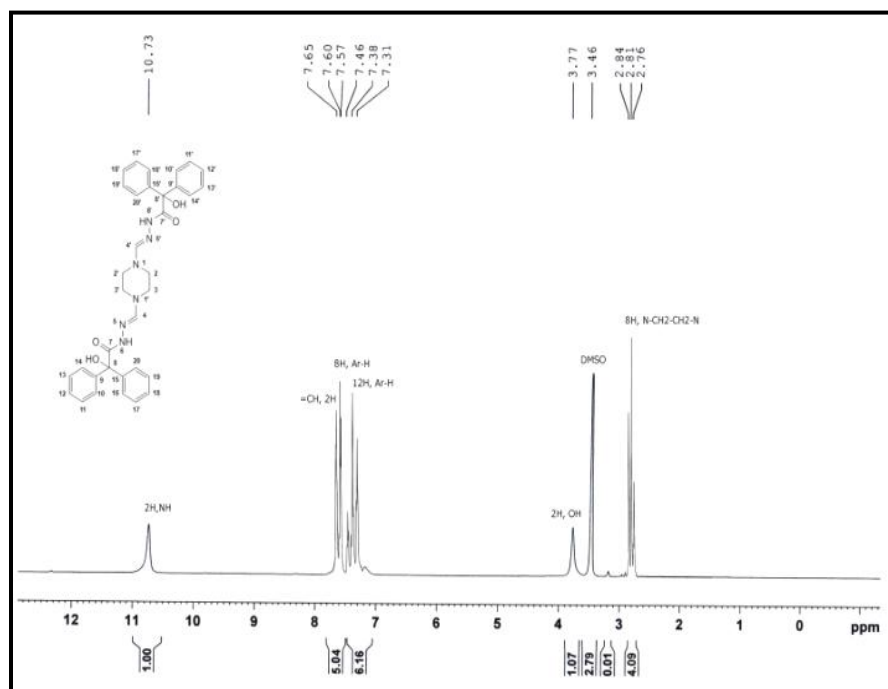
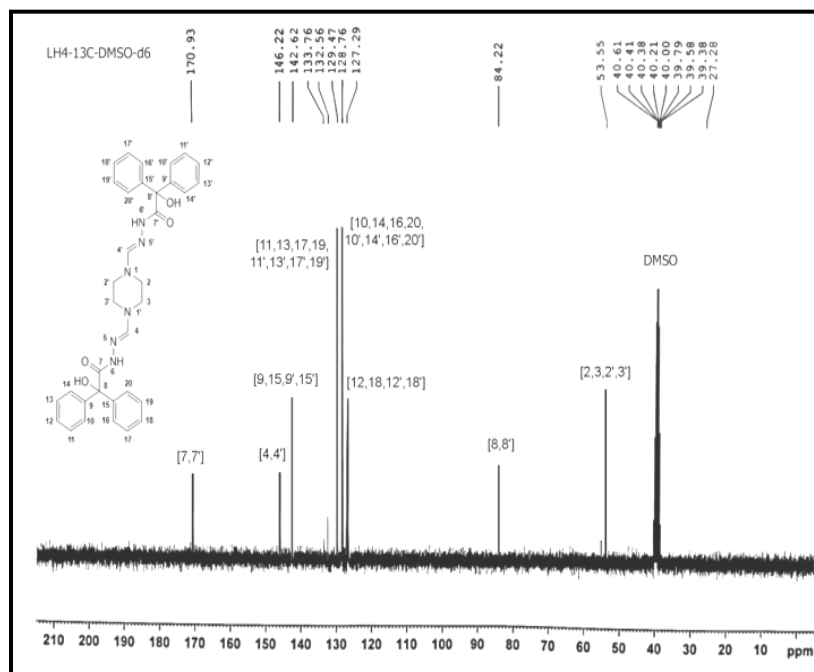


Fig.2.  $^1\text{H-NMR}$  spectrum of  $\text{LH}_4$



**Fig.3.  $^{13}\text{C}$ -NMR spectrum of  $\text{LH}_4$**

**Table 2:  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of the ligand in DMSO- $\text{d}_6$  in  $\delta$  (ppm)**

Comp .	Chemical Shift ppm, $\delta$		Chemical Shift ppm, $\delta$	
	Groups	$^1\text{H}$ -NMR	Groups	$^{13}\text{C}$ -NMR
LH <sub>4</sub>	2(-N-CH <sub>2</sub> -) <sub>2</sub>	2.76-2.84 (t, 8H)	2(-N-CH <sub>2</sub> -) <sub>2</sub>	84.22
	2(C-OH)	3.77 (s, 2H)	2(-HO-C-C=O)	53.55
	Ar-H (11,12,13,17,18,19, 11',12',13',17',18',19')	7.31–7.46 (t, 12H)	Ar-C (12,18,12',18')	
	Ar-H (10,14,16,20, 10',14',16',20')		Ar-C (10,14,16,20,10',14',16',20')	127.29
		7.57–7.60 (d, 8H)	Ar-C (11,13,17,19,11',13',17',19')	128.76
			Ar-C (9,15,9',15')	129.47
			Ar-C (9,15,9',15')	142.62
	2(-HC=N)	7.65 (s, 2H)	2(-HC=N)	146.22
	2(-NH)	10.73 (s, 2H)	2(-C=O)	170.93

**IR spectra of the ligand.** In the IR spectra of ligand, (Fig. 4), the band appearing at  $1658\text{ cm}^{-1}$ , is attributed to the characteristic amide I,  $\nu(\text{C}=\text{O})$  band. The absorption band of the  $\text{C}=\text{N}_{\text{imine}}$  group is observed at  $1606\text{ cm}^{-1}$ . A very broad peak is observed in the  $3285\text{--}2578\text{ cm}^{-1}$  region which is assigned to the intramolecular H-bonding vibration ( $\text{O-H}\cdots\text{O}$ ) between an alcoholic hydroxyl group and adjacent carbonyl oxygen atom (Bagrov and Vasil'eva, 2002; Sadler, 1961). Also, the amide NH stretching band of this compound is not observed in the IR spectra probably because of overlapping with intramolecular hydrogen bonded OH stretching frequency.

For derivatives of ligand (LH<sub>4</sub>) two isomers that have intramolecular hydrogen bonding can be possible (Fig. 5). However, the lower frequency of amide I,  $\nu(\text{C}=\text{O})$  band of (LH<sub>4</sub>) ligand compared with the other bis-hydrazone compounds may be explained that the carbonyl group of bis-hydrazone derivatives (LH<sub>4</sub>) bond to the alcoholic OH group by intermolecular hydrogen bonding (Atkinson *et al.*, 1965; Rollas *et al.*, 1988). Therefore, the isomer (II) is more suitable owing to the position of strong intermolecular hydrogen bonding (O-H...O) (Fig.5).

The other characteristic IR peaks of hydrazone compound synthesized in this work are given in (Table 3). These values are in accord with those previously reported hydrazone derivatives (Lee *et al.*, 2003; Naskar *et al.*, 2004; Rao *et al.*, 2002; Sreekanth *et al.*, 2004; Issa *et al.*, 2001).



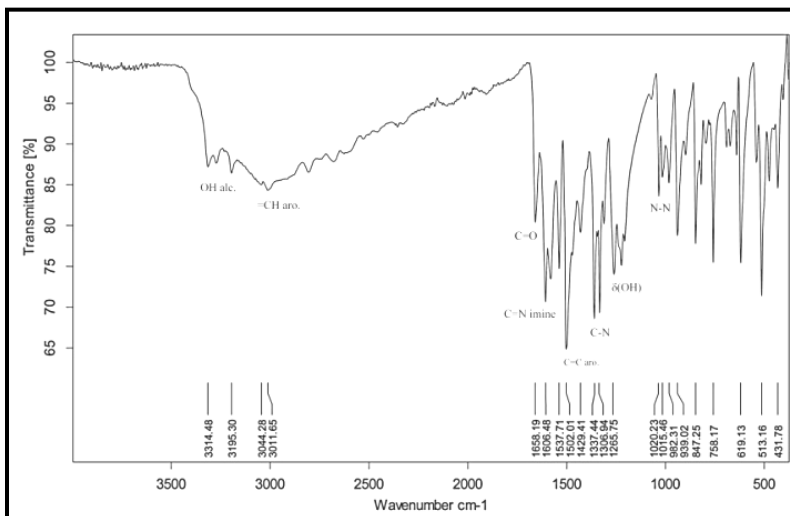


Fig.4. IR spectrum of LH<sub>4</sub>

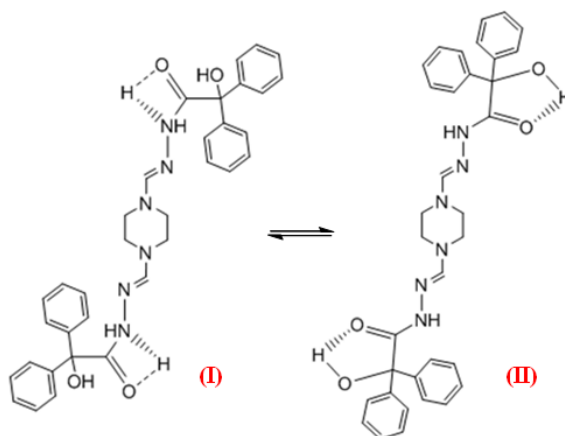


Fig.5. Intramolecular hydrogen bonding of ligand (LH<sub>4</sub>)

**IR spectra of the complexes and coordination mode.** The data of the IR spectra of (LH<sub>4</sub>) ligand and their metal complexes are given in (Table 3). The IR spectra of the complexes show significant differences from the free ligand. The bands due to amide I,  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}=\text{N}_{\text{imine}})$  and amide  $\nu(\text{NH})$  are absent in the IR spectra of all the complexes, but two new bands appear between  $1594\text{--}1586\text{ cm}^{-1}$  and  $\sim 1170\text{ cm}^{-1}$  probably due to  $>\text{C}=\text{N}-\text{N}=\text{C}<$  and C-O stretching, respectively, suggesting that the NH proton is likely lost via deprotonation induced by the metal and the resulting enolic oxygen and the azomethine nitrogen take place in coordination (Ainscough *et al.*, 1999; Rao *et al.*, 2002; Sreekanth *et al.*, 2004; Sreeja *et al.*, 2003). Furthermore, the ligand gets deprotonated from the two hydrazone amide moiety (Fig. 1). Thus the synthesized ligand acting as tetradentate di-negative (Uppadine *et al.*, 2004; Uppadine and Lehn, 2004).

The shift of  $\nu(\text{N}-\text{N})$  stretch of all the complexes to higher energy by  $\sim 25\text{--}30\text{ cm}^{-1}$  comparing to that of free ligand can be another evidence for the involvement of azomethine nitrogen in coordination. Furthermore, the IR spectra of complexes shows a broad band around  $\sim 3370\text{ cm}^{-1}$ , which can be attributed to the free O-H stretching mode indicating non-participation of alcoholic OH group in coordination.

In the spectrum of the 1,10-phenanthroline appeared the band at  $1620\text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  azomethine group. On complexation, this band was shifted to lower frequency in range  $1614\text{--}1608\text{ cm}^{-1}$  for the mixed complexes (9-12) which suggest that the  $\nu(\text{C}=\text{N})$  azomethine group is involved in coordination with 1,10-phenanthroline compound. However, In the far IR spectra of all the complexes, show two new bands at  $419\text{--}456\text{ cm}^{-1}$  and  $505\text{--}554\text{ cm}^{-1}$  maybe due to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$  respectively (Ram *et al.*, 2007; Demir *et al.*, 2008; Nakamoto, 1997).

Table 3: IR spectral data of the ligand and their metal complexes as KBr pellets  $\text{cm}^{-1}$ .

Comp .	$\nu(\text{OH})$ <i>alc.</i>	$\nu(\text{C=O})$	$\nu(\text{C=N})$ ligand/ phen.	$\nu(\text{C=N-N=C})$	$\nu(\text{C-N})$	$\nu(\text{C-O})$	$\nu(\text{N-N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
LH <sub>4</sub>	2500-3314	1658	1606 / 1620	---	1337	---	1020	---	---
(1)	3418	---	---	1589	1367	1172	1035	513	432
(2)	3372	---	---	1590	1361	1156	1044	505	422
(3)	3472	---	---	1587	1358	1171	1025	538	419
(4)	3474	---	---	1592	1371	1167	1040	554	456
(5)	3323	---	---	1586	1354	1171	1032	521	438
(6)	3375	---	---	1591	1347	1167	1042	525	454
(7)	3361	---	---	1588	1352	1185	1053	540	450
(8)	3377	---	---	1592	1374	1148	1043	554	436
(9)	3312	---	--- / 1614	1594	1347	1188	1033	516	451
(10)	3423	---	--- / 1616	1594	1350	1184	1057	527	429
(11)	3355	---	--- / 1614	1587	1347	1174	1052	521	448
(12)	3405	---	--- / 1608	1590	1380	1142	1033	517	422

**Electronic Spectra and Magnetic properties.** Absorption spectra of the ligand and their metal complexes were obtained in DMF at  $25^\circ\text{C}$  for  $10^{-2}$  M and the resulting data are given in (Table 4). The electronic spectrum of the (LH<sub>4</sub>) ligand presents an absorption maxima at  $31847\text{ cm}^{-1}$  and  $27932\text{ cm}^{-1}$  due to  $\pi \rightarrow \pi^*$  of the aromatic rings and to  $n \rightarrow \pi^*$  transition in the C=O and C=N groups, respectively (Al-Neaimi, 2012; Maiti *et al.*, 2004; Rageh, 2004). These transitions were found in the spectra of the complexes but shifted to lower frequencies, indicating coordination of the ligand to the metal ions.

The electronic spectra of Co(II) complex (1) shows three bands at  $11627$ ,  $14430$  and  $19570\text{ cm}^{-1}$  may be assigned to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})(\nu_1)$ ,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})(\nu_2)$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{p})(\nu_3)$  transitions, respectively, (Fig. 6) suggesting an octahedral geometry around the Co(II) ion. The magnetic moment of the Co(II) complex (1) lies at (4.92) B.M. corresponding to the three unpaired electrons and is larger than the spin-only value (3.87 B.M.) for six coordinate geometry. This value is indicative of an appreciable orbital contribution to the magnetic moment of high-spin Co (II) in octahedral surrounding (Singh *et al.*, 2010; Cotton *et al.*, 1999; Agarwal *et al.*, 2006).

The electronic spectra of the Ni(II) complex (2) is consistent with the formation of an octahedral geometry with the appearance of three bands at  $10893$ ,  $14124$  and  $19348\text{ cm}^{-1}$ . These bands refer to the:  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})(\nu_1)$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})(\nu_2)$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})(\nu_3)$  transitions, respectively (Table 4) (Fig. 7). The nickel (II) complex (2) shows  $\mu_{\text{eff}}$  value of (3.10) B.M. This value in tune with a high spin configuration and shows the presence of an octahedral environment around the Ni(II) ion (Al-Neaimi and Al-Khuder, 2013; Lever, 1984). Also, the observed value for the complex (2) is higher than that of the spin-only value (2.83 B.M.) for octahedral complex. This indicates spin-orbit coupling contribution in magnetic moment value (Lever, 1984; Khan *et al.*, 2010).

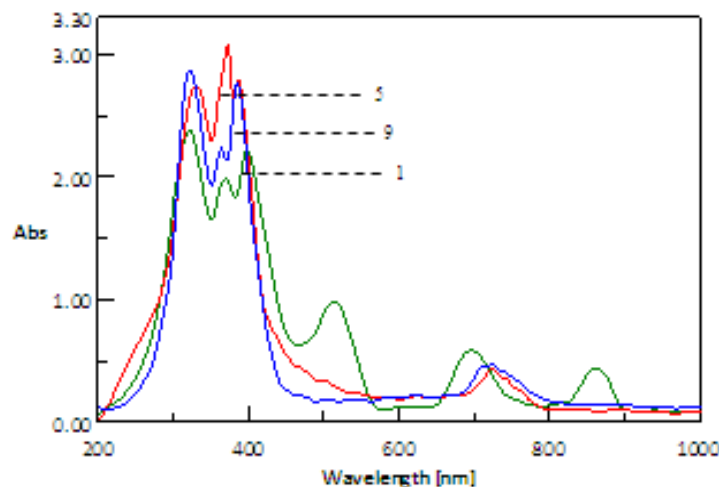


Fig.6. Electronic absorption spectra of Cobalt complexes [Co(LH<sub>2</sub>)Cl<sub>2</sub>] (1) , [Co<sub>2</sub>(LH<sub>2</sub>)Cl<sub>4</sub>] (5) and [Co<sub>2</sub>(LH<sub>2</sub>)(phen)<sub>2</sub>]Cl<sub>2</sub> (9) in DMF (10<sup>-2</sup>)M



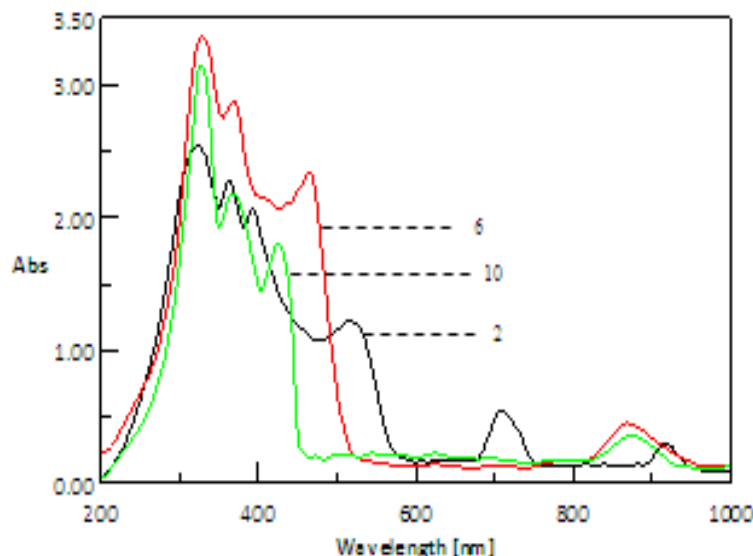


Fig.7. Electronic absorption spectra of Nickel complexes  $[\text{Ni}(\text{LH2})\text{Cl}_2]$  (2),  $[\text{Ni}_2(\text{LH2})\text{Cl}_4]$  (6) and  $[\text{Ni}_2(\text{LH2})(\text{phen})_2]\text{Cl}_2$  (10) in DMF (10-2)M

The electronic spectra of the Cu(II) complex (3) (Table 3) shows a broad band on the lower energy side at  $16339 \text{ cm}^{-1}$  due to the  $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ ,  $^2\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$  and  $^2\text{B}_{1g} \rightarrow ^2\text{E}_g$  transitions, suggesting a distorted octahedral structure (Al-Hazmi *et al.*, 2005) (Fig. 8). The complex (3) shows magnetic moment at (1.92) B.M. suggests that the complex (3) is monomeric in nature, the absence of metal-metal interaction (Karekal and Mathada, 2013; Halli and Sumathi, 2013) and confirming an octahedral geometry. All the spectra of metal (II) complexes (1-3) show a broad and very strong band in the UV-visible region at  $22522\text{-}25575 \text{ cm}^{-1}$  which are assigned to a ligand  $\rightarrow$  metal (LMTC) charge transfer excitation (Lever, 1984; Dianu *et al.*, 2010).

The absorption spectra of Zn(II) complex (4) shows disappear bands due to (d-d) transitions in the visible region as expected for  $d^{10}$  systems (Dianu *et al.*, 2010). However, the complex (4) shows a band at  $26178 \text{ cm}^{-1}$  (Table 3), which is attributed to the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  intraligand transitions. The Zn (II) complex (4) is diamagnetic and on the basis of all the data belonging to the complex (4), it appears that the most probable structure for this complex is an octahedral geometry (Cotton *et al.*, 1999) (Fig. 9).

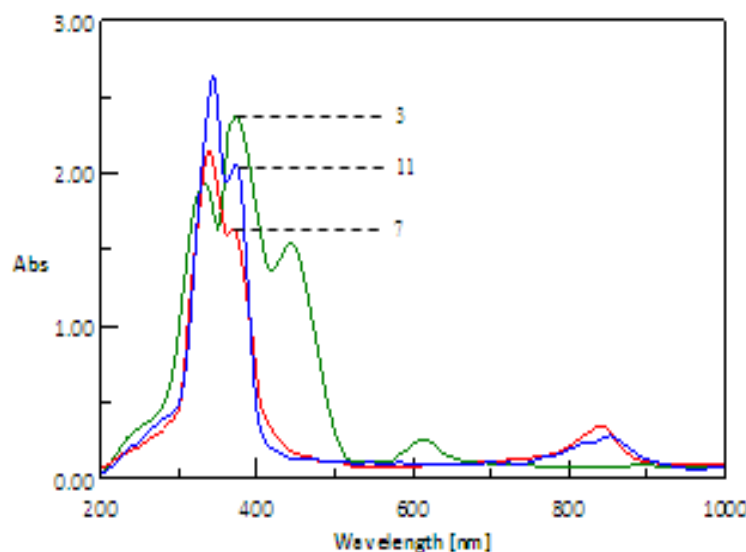
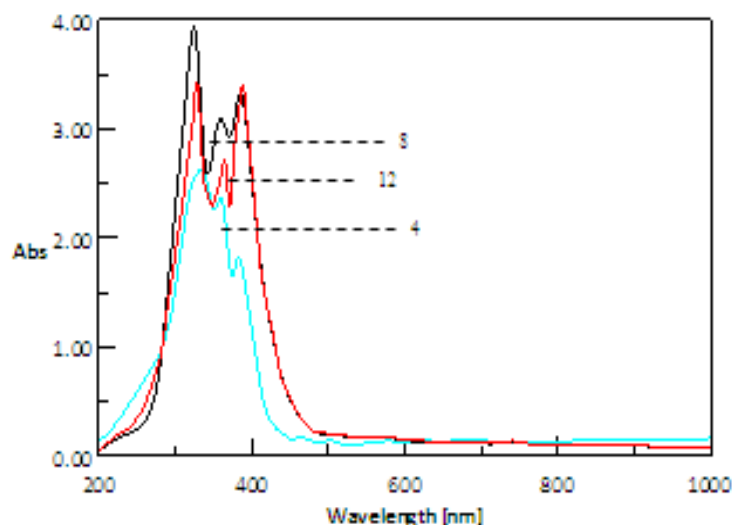


Fig.8. Electronic absorption spectra of Copper complexes  $[\text{Cu}(\text{LH2})\text{Cl}_2]$  (3),  $[\text{Cu}_2(\text{LH2})\text{Cl}_4]$  (7) and  $[\text{Cu}_2(\text{LH2})(\text{phen})_2]\text{Cl}_2$  (11) in DMF (10-2)M



**Fig.9. Electronic absorption spectra of Zinc complexes [Zn(LH<sub>2</sub>)Cl<sub>2</sub>] (4) , [Zn<sub>2</sub>(LH<sub>2</sub>)Cl<sub>4</sub>] (8) and [Zn<sub>2</sub>(LH<sub>2</sub>)(phen)<sub>2</sub>]Cl<sub>2</sub> (12) in DMF (10<sup>-2</sup>)M**

The electronic spectra of the Co(II) complexes (**5** and **9**) (Fig. 6) shows intense band in the high energy region at (25906 and 26118) cm<sup>-1</sup> respectively, which can be assigned to charge transfer band (Table 4). The (d-d) transition was observed at visible region at (13812 and 13825) cm<sup>-1</sup> respectively, may be assigned to <sup>4</sup>A<sub>2</sub>(F)→<sup>4</sup>T<sub>1</sub>(P)(v<sub>3</sub>) transition, further support the presence of tetrahedral environment around the Co(II) ion (Huggi *et al.*, 1982; Hughes and Rutt, 1970). The magnetic moment values for the Co(II) complexes (**5** and **9**) are (4.39 and 4.11) B.M., respectively, corresponding a high spin tetrahedral environment around the Co(II) ion (Al-Neaimi, 2012; Buttrus *et al.*, 2013).

In the electronic spectra of Ni(II) complexes (**6** and **10**) (Fig. 7), the band at (11494 and 11415) cm<sup>-1</sup> is attributed to the <sup>3</sup>T<sub>1</sub>(F)→<sup>3</sup>T<sub>1</sub>(P)(v<sub>3</sub>) transition, this band are characteristic for tetrahedral symmetry. Also a strong high energy band appears at (21551 and 23632) cm<sup>-1</sup> may be assigned to a charge transfer band (Table 4). The observed magnetic moment for the Ni(II) complex (**6** and **10**) are (3.59 and 4.2) B.M., respectively, corresponding a high spin tetrahedral environment around the Ni (II) ion (Buttrus *et al.*, 2013; Abdalrazaq *et al.*, 2010). As expected, in the tetrahedral compounds (high spin) the <sup>4</sup>A<sub>2</sub>(F)→<sup>4</sup>T<sub>2</sub>(F)(v<sub>1</sub>), <sup>4</sup>A<sub>2</sub>(F)→<sup>4</sup>T<sub>1</sub>(F)(v<sub>2</sub>) and <sup>3</sup>T<sub>1</sub>(F)→<sup>3</sup>T<sub>2</sub>(F)(v<sub>1</sub>), <sup>3</sup>T<sub>1</sub>(F)→<sup>3</sup>A<sub>2</sub>(F)(v<sub>2</sub>) transitions for Co(II) and Ni(II) complexes (**5,9** and **6,10**), respectively, are probably located above 1000 nm, which is beyond the detection range of our instrument (Wilkinson, 1987).

In addition to the ligand bands, the Cu(II) complexes (**7** and **11**) (Fig. 8) show a distinct d-d band at (11876 and 11695) cm<sup>-1</sup> (Table 4), may be assigned to <sup>2</sup>T<sub>2</sub>→<sup>2</sup>E transition (Al-Neaimi, 2012; Abdalrazaq *et al.*, 2010) suggested an tetrahedral environment around the Cu(II) ion. The magnetic moment value of the Cu (II) complexes (**7** and **11**) are (2.28 and 2.31) B.M. and in tune with a high spin configuration and shows the presence of a tetrahedral environment around the Cu (II) ion (Sabah, 2013).

The spectra of the Zn(II) complexes (**8** and **12**) (Table 4) exhibits a strong intense band at (26054 and 25706) cm<sup>-1</sup>, which are assigned to a ligand→metal (LMTC) charge transfer excitation. Both of Zn(II) complexes (**8** and **12**) show no bands in the visible region as expected for d<sup>10</sup> systems due to diamagnetic properties of the complexes (Abdalrazaq *et al.*, 2010; Al-Mahrouqi, 2009; Aggarwal *et al.*, 1985). On the basis of all the data belonging to the complex (**8** and **12**), it appears that the most probable structure for these complexes are an tetrahedral geometry (Fig. 9).

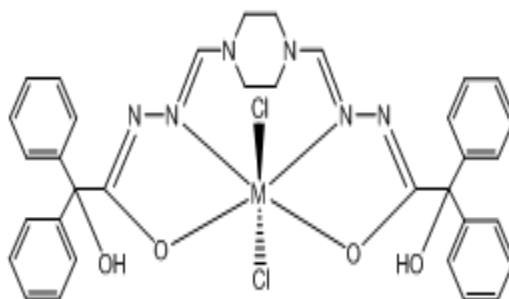
However, these magnetic moment values for Co(II), Ni(II) and Cu(II) complexes [(**5,9**), (**6,10**) and (**7,11**)] respectively, are higher than the theoretical value, and in same time are lower than expected for dinuclear cobalt(II), nickel(II) and copper(II) complexes. These data (Table 1) are in agreement with previously reported for similar to (high spin, Tetrahedral) complexes. These subnormal magnetic moment values of the dinuclear complexes may be explained by weak antiferromagnetic intramolecular interaction since this situation can occur when two equivalent metal ions are coupled via on exchange interaction in a dinuclear complex (Naskar *et al.*, 2004; Al-Mahrouqi, 2009; Baligar *et al.*, 2006; Perlepes *et al.*, 1986).

**Table 4:** Electronic spectral data  $\lambda_{\max}$  nm,  $\nu(\text{cm}^{-1})$  of the ligand and their metal complexes in DMF ( $10^{-2}\text{M}$ ).

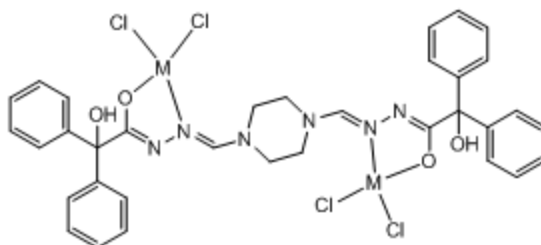
Comp.	Electronic spectra data ( $\lambda_{\max}$ ) $\text{cm}^{-1}$
LH <sub>4</sub>	(314) 31847, (358) 27932
(1)	(320) 31250, (367) 27247, (398) 25125, (511) 19570, (693) 14430, (860) 11627
(2)	(322) 31056, (363) 27548, (391) 25575, (517) 19342, (708) 14124, (918) 10893
(3)	(334) 29940, (372) 26881, (444) 22522, (612) 16339
(4)	(333) 30030, (360) 27777, (382) 26178
(5)	(330) 30303, (372) 26881, (386) 25906, (724) 13812
(6)	(328) 30487, (368) 27173, (464) 21551, (870) 11494
(7)	(338) 29585, (367) 27233, (842) 11876
(8)	(325) 30703, (361) 27248, (383) 26054
(9)	(324) 30834, (366) 27321, (382) 26118, (723) 13825
(10)	(327) 30581, (369) 27094, (423) 23632, (876) 11415
(11)	(341) 29239, (374) 26737, (855) 11695
(12)	(326) 30603, (363) 27531, (389) 25706

## CONCLUSION

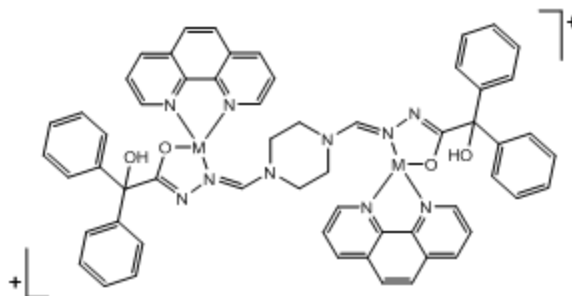
1,4-diformyl piprazine bis (2-hydroxy-2,2-diphenylacetohydrazone (LH<sub>4</sub>) reacts with metal (II) chlorides in a molar ratio of 1:1 using methanol as solvent forming a mononuclear complexes of the type  $[\text{M}(\text{LH}_2)\text{Cl}_2]$   $[\text{M}=\text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$  and  $\text{Zn}(\text{II})]$ . On the other hand, metal(II) chlorides reacted with the same ligand (LH<sub>4</sub>) in a 2:1 molar ratio in methanol and acetone, respectively, producing dinuclear complexes of the type  $[\text{M}_2(\text{LH}_2)\text{Cl}_4]$ , where as the reaction of metal (II) chlorides with the solution containing ligand (LH<sub>4</sub>) and 1,10-phenanthroline in a molar ratio of 2:1:2 respectively, using methanol as solvent gives mixed-ligand dinuclear metal(II) complexes with general formula  $[\text{M}_2(\text{LH}_2)(\text{phen})_2]\text{Cl}_2$ . On the basis of IR and <sup>1</sup>H-NMR spectral data, synthesized ligand are in the keto tautomeric form in the solid state. However, in the IR spectra of the complexes  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}=\text{N})$ , and  $\nu(\text{N}-\text{H})$  stretching vibrations disappears but two new bands are observed due to  $>\text{C}=\text{N}-\text{N}=\text{C}<$  and C-O stretching, respectively, suggesting that the coordination takes place in enol tautomeric form, and the ligand (LH<sub>4</sub>) deprotonated from the two hydrazone amid moiety and acts as dibasic N<sub>2</sub>O<sub>2</sub> tetradentate, bonding to the metal (II) ions through the enolic oxygen and azomethine nitrogen atoms (Fig. 1). Furthermore, the observation of alcoholic hydroxyl group  $\nu(\text{O}-\text{H})$  stretching vibration in the IR spectra of the complexes is concluded as non-involvements of this group in coordination. Considering the elemental analysis results and spectral data, the structures proposed for mononuclear  $[\text{M}(\text{LH}_2)\text{Cl}_2]$ , dinuclear  $[\text{M}_2(\text{LH}_2)\text{Cl}_4]$  and mixed-ligand  $[\text{M}_2(\text{LH}_2)(\text{phen})_2]\text{Cl}_2$  complexes are given in Figs. 10a, 10b and 10c.



**A. mononuclear complexes  $[\text{M}(\text{LH}_2)\text{Cl}_2]$**



**B. dinuclear complexes  $[M_2(LH_2)Cl_4]$**



**C. mixed-ligand dinuclear complexes  $[M_2(LH_2)(phen)_2]Cl_2$**

**M= Co(II), Ni(II), Cu(II), Zn(II)**

**Fig. 10. Suggested structure for the complexes**

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