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# Synthesis, characterization and extraction studies of some metal (II) complexes containing (hydrazoneoxime and bis-acylhydrazone) moieties

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#### HIGHLIGHTS

- ► We synthesis (hydrazoneoxime L<sub>1</sub>H<sub>2</sub> and bis-acylhydrazone L<sub>1</sub>H<sub>2</sub>) ligands and their complexes.
- ► These compounds characterized by CHN, AAS, IR, <sup>1</sup>H, <sup>13</sup>C NMR, UV-vis spectra and µ<sub>eff</sub>.
- ► The L<sub>1</sub>H<sub>2</sub> act as monoanionic O,N,Ntridentate, but the L<sub>2</sub>H<sub>2</sub> act as dianionic O,N,N,O-tetradentate.
- We examine the extraction ability of ligands in chloroform by the liquid– liquid extraction.
- Strong affinity of ligands towards several metal (II) ions have been studied in aqueous phase.

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#### G R A P H I C A L A B S T R A C T

Synthesis and characterization of the mononuclear metal (II) complexes  $[M(L_1H)_2]$  and polymeric dinuclear metal (II) complexes  $[\{M_2(L_2)_2\}_n]$ ; n = 0, 1, 2...; M = Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) derived from synthesized ligands diacetylmonoximebenzoylhydrazone  $(L_1H_2)$  and 1,4-diacetylbenzene-bis(benzoylhydrazone)  $(L_2H_2)$  respectively. The <sup>1</sup>H NMR, <sup>13</sup>C NMR, elemental analysis(CHN), FT-IR infrared spectra, Magnetic susceptibility measurements and UV-vis. electronic absorption spectra of the  $(L_1H_2)$  and  $(L_2H_2)$  ligands and their metal (II) complexes were reported and investigated.



#### ABSTRACT

In this study, diacetylmonoximebenzoylhydrazone (L1H2) and 1,4-diacetylbenzene bis(benzoyl hydrazone) (L<sub>2</sub>H<sub>2</sub>) were synthesized by the condensation of benzohydrazide with diacetyl monoxime and 1,4-diacetylbenzene, respectively. Complexes of these ligands with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) inos were prepared with a metal:ligand ratio of 1:2 for L<sub>1</sub>H<sub>2</sub> ligand, and 1:1 for L<sub>2</sub>H<sub>2</sub> ligand. The ligands and their complexes were elucidated on the basis of elemental analyses CHN, AAS, FT-IR, <sup>1</sup>H- and  $^{13}$ C NMR spectra, UV-vis spectra and magnetic susceptibility measurements. Results show the  $L_1H_2$ ligand act as monoanionic O,N,N-tridentate and coordination takes place in the enol form through the oxime nitrogen, the imine nitrogen and the enolate oxygen atoms with a  $N_4O_2$  donor environment, while the  $L_2H_2$  ligand act as a dianionic O,N,N,O-tetradentate and coordination takes place in the enol form through the enolate oxygen and the azomethine nitrogen atoms with a N<sub>2</sub>O<sub>2</sub> donor environment. These results are consistent with the formation of mononuclear metal (II) complexes  $[M(L_1H)_2]$ , and binuclear polymeric metal (II) complexes [{M<sub>2</sub>(L<sub>2</sub>)}<sub>n</sub>]. The extraction ability of both ligands were examined in chloroform by the liquid–liquid extraction of selected transition metal [Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup>] cations. The effects of pH and contact time on the percentage extraction of metal (II) ions were studied under the optimum extraction conditions. The (L1H2) ligand shows strong binding ability toward copper(II) and lead(II) ions, while the (L<sub>2</sub>H<sub>2</sub>) ligand shows strong binding ability toward nickel(II) and zinc(II) ions.

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#### Introduction

Oximes and hydrazones are the two important classes of compounds owing to their wide applications in industry, medicine, detection and determination of various metal ions [1–9]. These compounds have a number of potential bonding sites such as carbonyl oxygen, azomethine and imine nitrogens. Therefore, hydrazone and oxime as well as their coordination compounds have been studied extensively [10–15].

Hydrazoneoxime and dihydrazone moieties can react with copper(II) and nickel(II) salts to produce either mono- and binuclear complexes. The keto hydrazone moiety may coordinate to metals in the keto-amide or deprotonated enol-imine form. Such compounds containing both oxime and hydrazone groups typically act as tridentate, dianionic ligands coordinating through the amide oxygen, imine and oxime nitrogens [14–18], but compounds containing dihydrazone act as tetradentate dianionic ligands and coordination takes place in the enol tautomeric form with the enolic oxygen and the azomethine nitrogen atoms [19–24] depending on the reaction conditions.

Solvent extraction is one of the most versatile procedures among the separation techniques used for the removal and separation of metals from aqueous phase. The development of selective extractants has expanded the use of solvent extraction for metal recovery and purification. Oximes have been widely used as extractants for metal ions in solvent extraction. As yet, reports on solvent extraction with the complexes of hydrazoneoxime and dihydrazone compounds are scarce [18,19,25,26]. Therefore, we have investigated the solvent extraction of metal cations through hydrazoneoxime and dihydrazone compounds.

We report herein the synthesis of the free ligands diacetylmonoximebenzoylhydrazone ( $L_1H_2$ ), 1,4-diacetylbenzene bis (benzoylhydrazone) ( $L_2H_2$ ) and their metal complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) inos, and also we investigate the effectiveness of these synthesized ligands in transferring the transition metals Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> cations from the aqueous phase into the organic phase by the liquid–liquid extraction.

#### Experimental

#### Materials

All the chemicals used were purchased from Aldrich–Sigma and Merck companies, and used without further purification.

#### Apparatus

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 MHz spectrometer in DMSO-d<sub>6</sub>. FT-IR spectra were recorded using Bruker-ALPHA (FTIR-4100). CHN analyzer were measured on Euro-vetor-AC-3000 (Italy). Magnetic susceptibility measurements (Bruker 6 B.M) were performed at room temperature by Faraday method at room temperature using Hg[Co(SCN)<sub>4</sub>] as a calibrate; diamagnetic corrections were calculated from Pascal's constants. UV-visible spectra were measured on Jasco Japanese companies V-350 Spectrophotometer in the regions (50,000–9090 cm<sup>-1</sup>). Atomic absorption spectrophotometer (AAS) used to determine metal ion concentration in the aqueous phase was Spectra AAS-Phoenix-986 [Biotech Engineering Management CO Ltd. (UK)]. pH measurements were made on a Hanna Instruments HI 8314 pH meter with a combined glass electrode.

#### Synthesis of $L_1H_2$ , $L_2H_2$ ligands

Benzohydrazide was prepared by refluxing ethyl benzoate (1.5 g, 10 mmol) with hydrazine hydrate (1.5 ml) for 4 h. The compound precipitated on standing over night, filtered and washed with distilled water. The pure hydrazide was obtained by recrystallization from hot ethanol. The ligands synthesized in this work are shown in Schemes 1 and 2 and their syntheses are described as follows:

#### diacetylmonoximebenzoylhydrazone (L1H2)

To a 30 ml methanolic solution of diacetyl mono-oxime (1.01 g, 10 mmol), benzohydrazide (1.36 g, 10 mmol) in 50 ml methanol was added and the reaction mixture was stirred while refluxing for 3 h. On reducing the volume to  $\sim$ 30 ml, the resultant solid was filtered and thoroughly washed with ethanol (2 × 5 ml) followed by diethyl ether (2 × 5 ml). The solid was recrystallised from hot ethanol. Some properties of the synthesized of ligands and complexes are given in Table 1.

#### 1,4-diacetylbenzenebis(benzoylhydrazone) $(L_2H_2)$

A solution of benzohydrazide (10 mmol, 1.36 g) in 30 ml of hot ethanol was added to solution 1,4-diacetylbenzene (5 mmol, 0.81 g) with (3-5) drops of glacial acetic acid in 20 ml of ethanol. The reaction mixture was stirred while refluxing for 3 h. The resultant precipitated were filtered off and washed with water and hot ethanol, and dried under reduced pressure (Table 1).

#### Preparation the complexes

 $[M(L_1H)_2]$  (M = Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup>)

To a 50 ml methanol solution of the  $(L_1H_2)$  ligand (2.19 g, 10 mmol) Et<sub>3</sub>N (1.01 g, 10 mmol) was added with stirring. When the initially colorless solution turned yellow. Addition of anhydrous salts MCl<sub>2</sub> (5 mmol) when [M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)] to the yellow solution produced colored solution was changed immediately. After 5 h of stirring the volume of the solution was reduced to ~20 ml and filtered. The resultant solid was obtained and washed with methanol (3 × 3 ml), followed by diethyl ether (2 × 5 ml), Scheme 1.

#### $[\{M_2(L_2)_2\}_n]$ (M = Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup>)

A hot solution of potassium hydroxide (KOH) (1.12 g, 20 mmol) in ethanol (15 ml) was added to a suspension of the  $(L_2H_2)$  ligand (10 mmol) in ethanol (50 ml) respectively [24]. To the resulting yellow solution, a hot solution of metal (II) chloride anhydrous (10 mmol) when  $[M = Ni^{II}, Co^{II}, Cu^{II}, Zn^{II}, Cd^{II}]$  in ethanol (25 ml)





Scheme 1.



was added. The mixture was then refluxed, with constant stirring, for 4 h. The isolated complex was then filtered off and washed with water and ethanol, followed by dry diethyl ether, then dried in a vacuum oven, Scheme 2.

#### Solvent extraction

A 10 ml aqueous solution containing  $(1 \times 10^{-4} \text{ M})$  metal nitrate and an appropriate buffer by diluted solutions of NH<sub>3</sub> and HNO<sub>3</sub> pure (pH = 2.1–9.1) was contacted with an equal volume 10 ml of the chloroform solution containing  $(1 \times 10^{-3} \text{ M})$  L<sub>1</sub>H<sub>2</sub> or L<sub>2</sub>H<sub>2</sub> ligand by shaking in a mechanical shaker at 25 °C. The ionic strength of the aqueous phase was kept  $\mu$  = 0, 1 by adding appropriate amount of KNO<sub>3</sub>. The extraction mixtures were shacked for 2 h at 25 ± 1 °C. The extractabilities were not affected by further shaking indicating that the distribution equilibrium was attained within 2 h and finally left standing for phase separation for 15 min at room temperatures. After phase separation, metal ions remaining in the aqueous phase were then determined from the decrease in the metal concentration in the aqueous phase by AAS. The extractability was calculated by using the equation below:

$$E(\%) = [(A_{before} - A_{after})/A_{before} \times 100]$$

where  $A_{before}$  is the absorbance in the absence of ligand.

 $A_{\text{after}}$  denotes the absorbance in the aqueous solution phase after extraction.

Fable 1	
Color, melting points, yields, and elemental analytical results of the ligands and their metal co	mplexes.



Fig. 1. Tautomric forms of the aroylhydrazoneoxime ligand.

#### **Results and discussion**

#### Stereo electronic nature of the ligands

The ligands can undergo deprotonation from enolised amide oxygen as well as from the oxime oxygen. When the aroylhydrazoneoxime  $(L_1H_2)$  ligand is reacted with metal (II) ions the ligand get deprotonated from the hydrazone amide moiety and the metal (II) complex is formed (Fig. 1).

While the bis-acylhydrazone  $(L_2H_2)$  ligand is reacted with metal (II) ions, the ligand get deprotonated from the two hydrazone amide moiety and the metal (II) complex is formed (Fig. 2).

Thus the aroylhydrazoneoxime  $(L_1H_2)$  ligand is tridentate uninegative, where as the bis-acylhydrazone  $(L_2H_2)$  ligand is tetradentate bi-negative [27–29].

#### Syntheses

The  $(L_1H_2 \text{ and } L_2H_2)$  ligands were prepared according to the methods described above. These ligands were obtained in good yield and purity, as confirmed by the spectroscopic data (<sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, Magnetic susceptibility, UV–visible spectra and CHN analysis). All the complexes of  $L_1H_2$  ligand were obtained easily by stirring the reactants at room temperature in methanol. Use of one equivalent of base for each equivalent of ligand left the oxime –OH unaffected. But the complexes of  $L_2H_2$  ligand were

Compounds	Empirical formula (formula weight)	Color	M.p <sup>a</sup> (°C)	$\mu_{eff}$ (B.M)	Yield (%)	Calculated/(Found) (%)		
						С	Н	N
$L_1H_2$	C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> (219.24)	White	189	-	84	60.26 (59.67)	5.98 (5.13)	19.17 (18.81)
$L_2H_2$	C <sub>24</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub> (398.46)	White	294	-	82	72.34 (70.95)	5.57 (4.89)	14.06 (13.71)
$[Co(L_1H)_2]$	C <sub>22</sub> H <sub>24</sub> N <sub>6</sub> O <sub>4</sub> Co (495.4)	Brown-reddish	290 <sup>a</sup>	5.1	77	53.34 (52.98)	4.88 (4.03)	16.96 (16.78)
$[Ni(L_1H)_2]$	C <sub>22</sub> H <sub>24</sub> N <sub>6</sub> O <sub>4</sub> Ni (495.16)	Brown	279 <sup>a</sup>	2.81	82	53.36 (52.89)	4.89 (4.12)	16.97 (16.63)
$[Cu(L_1H)_2]$	C <sub>22</sub> H <sub>24</sub> N <sub>6</sub> O <sub>4</sub> Cu (500)	Dark Green	269 <sup>a</sup>	1.75	69	52.85 (52.78)	4.84 (4.21)	16.81 (16.32)
$[Zn(L_1H)_2]$	C <sub>22</sub> H <sub>24</sub> N <sub>6</sub> O <sub>4</sub> Zn (501.87)	Yellow	218	Dia	70	52.65 (52.34)	4.82 (4.30)	16.75 (16.52)
$[Cd(L_1H)_2]$	C <sub>22</sub> H <sub>24</sub> N <sub>6</sub> O <sub>4</sub> Cd (548.87)	Yellow	143	Dia	93	48.14 (47.98)	4.41 (4.18)	15.31 (14.33)
$[{Co_2(L_2)_2}_n]$	C <sub>24</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub> Co <sub>2</sub> (910.74)	Green yellowish	357 <sup>a</sup>	5.95	87	63.30 (62.67)	4.43 (4.33)	12.30 (11.98)
$[{Ni_2(L_2)_2}_n]$	C <sub>48</sub> H <sub>40</sub> N <sub>8</sub> O <sub>4</sub> Ni <sub>2</sub> (910.27)	Dark Green	291	3.29	81	63.33 (62.71)	4.43 (4.21)	12.31 (11.91)
$[{Cu_2(L_2)_2}_n]$	C <sub>24</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub> Cu <sub>2</sub> (919.98)	Olive	268	2.63	75	62.67 (61.88)	4.38 (4.02)	12.18 (11.77)
$[{Zn_2(L_2)_2}_n]$	$C_{24}H_{20}N_4O_2Zn_2$ (923.7)	Yellow	>360	Dia	80	62.41 (61.92)	4.36 (4.01)	12.13 (11.75)
$[{Cd_2(L_2)_2}_n]$	$C_{24}H_{20}N_4O_2Cd_2\ (1017.7)$	Bright Yellow	353	Dia	92	56.65 (55.34)	3.96 (3.78)	11.01 (10.99)

<sup>a</sup> Decomposition.

prepared by refluxing the reactants with constant stirring in ethanol. Use of two equivalent of base (KOH) for each one equivalent of ligand.

The elemental analyses (CHN) suggest that the complexes of  $L_1H_2$  ligand possess 1:2 stoichiometry with general formula  $[M(L_1H)_2]$  as shown in (Fig. 3), and the complexes of  $L_2H_2$  ligand possess 1:1 stoichiometry with compositions of  $[\{M_2(L_2)_2\}_n]$  as shown in (Fig. 4).

#### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the Schiff base ligands

In the <sup>1</sup>H NMR spectrum of the  $L_1H_2$  ligand showed peaks corresponding to (NH) proton of ligand appear as a singlet at  $\delta$  10.74 (s, 1H) ppm. The characteristic oxime OH proton is observed at  $\delta$  11.62 ppm (s, 1H). These chemical shifts are characteristic value for hydrazones and oximes [30–32] (Table 2).

As expected, the aromatic protons of compounds appear at  $\delta$  7.42–7.57 (t, 3H) ppm and  $\delta$  7.86–7.98 (d, 2H) ppm. Additionally, two peaks are present for the CH<sub>3</sub> protons neighboring on oxime group (<u>H</u><sub>3</sub>C–C=NOH) and imine group (<u>H</u><sub>3</sub>C–C=N–NH) appears as a singlet at  $\delta$  2.05 and 2.19 (s, 3H) ppm respectively, [13]. These data are in agreement with previously reported for similar compounds [5,30–32], (Table 2).

In the <sup>1</sup>H NMR spectra of the  $(L_2H_2)$  ligand the amide (NH) resonance appear as singlets at  $\delta$  10.82 ppm (s, 2H). The ring proton resonances of the 1,4-diacetylbenzene moiety of this ligand is observed as a singlet at  $\delta$  8.49 ppm (s, 4H), while that of the benzenoid moiety appears as two different triplet and doublet peaks at  $\delta$  7.43–7.58 (t, 4H),  $\delta$  7.70–7.89 (t, 2H) and  $\delta$  8.07–8.17 (d, 4H) ppm, also the protons of methyl groups (CH<sub>3</sub>) is observed as a singlet at  $\delta$  2.51 (s, 6H) ppm [20,22] (Table 2). These data are in agreement with that previously reported for similar compounds [3,5,6,32,33].

In the <sup>13</sup>C NMR spectrum of L<sub>1</sub>H<sub>2</sub> ligand different signals, which were observed at  $\delta$  150.90 ppm and  $\delta$  155.29 ppm due to (–<u>C</u>=N–NH) and (–<u>C</u>=N–NOH), respectively, show asymmetrically substituted for hydrazone and oxime [3,10]. The signals of the C<sub>aromatic</sub> were observed at  $\delta$  127.45, 128.78, 132.05 and 134.41 ppm corresponding to C-(7,11), C-(8,10), C-(9) and C-(6), respectively. Spectra of (–<u>C</u>=O) appear at  $\delta$  165.77 ppm, as expected[34]. The signals of CH<sub>3</sub> were shown at  $\delta$  9.77, 12.43 ppm. Furthermore, <sup>13</sup>C NMR spectrum at two different frequencies in each case indicates that corresponding to C-(1,4) of CH<sub>3</sub> groups respectively show asymmetrically substituted for hydrazone and oxime [10,31]. The detailed <sup>13</sup>C NMR spectral data are given in Table 3.



Fig. 2. Tautomeric forms of the bis-acylhydrazone ligand.



Fig. 3. Intramolecular hydrogen bonding of ligands.



Fig. 4. s-Cis conformation of ligands.

Table 2<sup>1</sup>H NMR spectral of the ligands in DMSO-d<sub>6</sub>.

Comp.	Chemical Shift ppm, $\delta$ (ppm)					
	Groups	<sup>1</sup> H NMR				
L <sub>1</sub> H <sub>2</sub>	$C\underline{H}_{3}-C=NOH C\underline{H}_{3}-C=N-NH Ar-H (8-10) Ar-H (7,11) -NH -NOH (oxime) -$	2.05 (s, 3H) 2.19 (s, 3H) 7.42–7.57 (t, 3H) 7.86–7.98 (d, 2H) 10.74 (s, 1H) 11.62 (s, 1H)				
$L_2H_2$	$2(C\underline{H}_{3}C=N)$ Ar- <u>H</u> (14, 14',16, 16') Ar- <u>H</u> (15, 15') Ar- <u>H</u> (13, 13', 17, 17') Ar- <u>H</u> (2, 3, 5, 6) 2(-NH)	2.51 (s, 6H) 7.43–7.58 (t, 4H) 7.70–7.89 (t, 2H) 8.07–8.17 (d, 4H) 8.49 (s, 4H) 10.82 (s, 2H)				

In the <sup>13</sup>C NMR spectrum of L<sub>2</sub>H<sub>2</sub> ligand different signals is appeared at  $\delta$  147.22 ppm due to 2(—<u>C</u>=N—NH). The signals of the carbon ring (Ar—<u>C</u>) appears at  $\delta$  127.25, 128.76, 129.48, 133.06, 134.76, 139.62 ppm for C-(13,13',17,17'), C-(2,3,5,6), C-(14,14',16,16'), C-(15,15'), C-(12,12') and C-(1,4), respectively, Table 3. Furthermore, spectra of 2(—<u>C</u>=O) appears at  $\delta$  169.69 ppm, as expected[6]. However, the signal of primary carbon of methyl groups appear at 22.20 ppm Table 2. These data are in agreement with that previously reported for similar compounds [22,32,34–36].

#### IR spectra of the $L_1H_2$ and $L_2H_2$ ligands and their metal (II) complexes

In the IR spectra of the  $L_1H_2$  ligand, the characteristic amide I [ $\nu C=0$ ] band appears at 1667 cm<sup>-1</sup>. The stretching vibration of the (C=N<sub>imine</sub>) and (C=N<sub>oxime</sub>) are observed at 1595, 1579 cm<sup>-1</sup> respectively. The broad medium intensity band appearing at 3180 cm<sup>-1</sup> is assigned to the characteristic (oxime) OH absorptions. The other bands observed in the IR spectra of the ligand are given in Table 4. These values are in accord with the previously reported hydrazone and oxime derivatives [10–14,30].

The IR spectra of  $L_1H_2$  exhibits a very broad medium intensity peak 3400–2600 cm<sup>-1</sup> region, which are assigned to the

**Table 3** <sup>13</sup>C NMR spectral of the ligands in DMSO-d<sub>6</sub>.

Compounds	Chemical Shift ppm, $\delta$ (ppm)				
	Groups	<sup>13</sup> C NMR			
$L_1H_2$	<u>C</u> H <sub>3</sub> −C=NOH	9.77			
	$\underline{C}H_3 - C = N - NH$	12.43			
	Ar— <u>C</u> (7, 11)	127.45			
	Ar— <u>C</u> (8, 10)	128.78			
	Ar— <u>C</u> (9)	132.05			
	Ar— <u>C</u> (6)	134.41			
	— <u>C</u> ==N—NH	150.90			
	— <u>C</u> ==N—NOH	155.29			
	<u>C</u> =0	165.77			
$L_2H_2$	2( <u>C</u> H <sub>3</sub> C=N) (8, 8')	22.20			
	Ar— <u>C</u> (14, 14',16, 16')	129.48			
	Ar— <u>C</u> (15, 15')	133.06			
	Ar– <u>C</u> (13, 13', 17, 17')	127.25			
	Ar— <u>C</u> (2, 3, 5, 6)	128.76			
	Ar— <u>C</u> (12, 12′)	134.76			
	Ar— <u>C</u> (1, 4)	139.62			
	2(CH <sub>3</sub> <u>C</u> =N) (7, 7')	147.22			
	2(– <u>C</u> =0) (11,11′)	169.69			

intramolecular H-bonding vibration  $(O-H\cdots N)$  [37]. Also the amide NH stretching band of this ligand was not observed in the IR spectra probably due to overlapping with the intermolecular hydrogen-bonded OH stretching frequency, or maybe buried under broad band of OH. Since, in the <sup>1</sup>H NMR spectra of ligand, two absorption bands, which are assigned the OH group, and amide NH proton, appear at lower field, at  $\delta$  10.74, 11.62 ppm due to hydrogen bonding and the isomer which have intramolecular hydrogen bonding can be possible for the synthesized aroylhydrazone-oxime compound (L<sub>1</sub>H<sub>2</sub>) in this study (Fig. 3).

However, the shift of the amide NH proton absorption to relatively lower field cannot be explained by the intramolecular hydrogen bonding but may be explained by the intermolecular hydrogen bonding since the amide and carbonyl groups of ligand can bond by intermolecular hydrogen bonding to produce dimmer with an *s*-cis conformation [37,38] (Fig. 4).

In the IR spectra of  $L_2H_2$  ligand, the bands appearing at 1636 cm<sup>-1</sup> corresponding the characteristic amide I  $\nu$ (C=O) band. The absorption band of the  $\nu$ (C=N<sub>imine</sub>) group is observed at 1600 cm<sup>-1</sup>. Also the amide  $\nu$ (NH) stretching band of these compounds is observed in the IR spectra at 3171 cm<sup>-1</sup>. These values are in accord with that previously reported hydrazone derivatives[20–23,25,32,38,39]. The other characteristic IR peaks of hydrazone compounds synthesized in this work are given in Table 5.

The IR absorption bands of the complexes derived from  $L_1H_2$  ligand are given and assigned in Table 4. The bands due to amide I, v(C=O) and amide v(NH) are absent in the IR spectra of the complexes, but new band appear at ~1060 cm<sup>-1</sup> probably due to C–O stretching, suggesting that the NH proton is likely lost via deprotonation and the resulting enolic oxygen and the azomethine

Table 4	
IR spectral data of the L <sub>1</sub> H <sub>2</sub> ligand	and their metal complexes $(cm^{-1})$ .

nitrogen take place in coordination[20,21,24,30]. Comparing these
data with those of the free ligand it is obviously seen that
v(C=N) <sub>imine</sub> , v(C=N) <sub>oxime</sub> and v(N-O) bands shifted to lower
frequencies, whereas v(C-N) absorptions are moved to higher
frequencies [23]. The shift of $v(N-N)$ stretch of the complexes to
higher energy comparing to that of free ligand can be another
evidence for the involvement of azomethine nitrogen in coordina-
tion [16].

The oxime OH absorption band in the IR spectra of the complexes becomes narrow and shifts to higher frequency that indicating non-participation of hydroxyl group in coordinate with metal (II) ions, therefore, suggesting disappearance of intramolecular hydrogen bonding and non-involvement of this group in coordination [20,21].

The characteristic IR frequency values of the complexes derived from  $L_2H_2$  ligand are given in Table 5. The IR spectra of the complexes show significant differences from the free ligand. The bands due to amide I, v(C=O),  $v(C=N_{imine})$  and amide v(NH) are absent in the IR spectra of the complexes, but two new bands appear between ~1586 cm<sup>-1</sup> and ~1145 cm<sup>-1</sup> probably due to C=N–N=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 [20,22]. The shift of v(N-N) stretch of the complexes to higher energy by ~15–31 cm<sup>-1</sup> comparing to that of free ligand can be another evidence for the involvement of azomethine nitrogen in coordination[21,23,24].

#### Magnetic studies of metal (II) complexes

The magnetic moment data of the solid-state complexes at room temperature derived from  $L_1H_2$  ligand are reported in (Table 1), and showed each of Co(II), Ni(II) and Cu(II) complexes are paramagnetic while Zn(II) and Cd(II) complexes are diamagnetic at 298 K. Nickel (II) complex, however, are mononuclear since their effective magnetic moments correspond to the spin value for one unpaired electron, while these magnetic moment values of copper(II) and cobalt(II) complexes are higher than expected for mononuclear copper(II) and cobalt(II) complex [theoretical value of 3.87B.M for one d<sup>7</sup> Co(II) ion and 1.73 B.M for one d<sup>9</sup> Cu(II) ion] were may be explained by (spin–orbital coupling) for copper(II) complexes, and may be due to orbital contribution for cobalt(II) complex. However, all these data (Table 1) are in agreement with previously reported for similar octahedral complexes [40–42].

The magnetic susceptibility measurements of the complexes derived from  $L_2H_2$  ligand (Table 1) shows cobalt(II), nickel(II) and copper(II) complexes are paramagnetic, while zinc(II) and cadmium(II) complexes are diamagnetic at 298 K. However, these results can be observed the magnetic moment values of these complexes are higher than the theoretical value for one ion. Furthermore, these magnetic moment values 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

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Comp.	<i>v</i> (OH)	v(C=0)	v (C=N) imine, oxime	ν (C—N)	ν (N—N)	v (N—O)	v (C—O)
$L_1H_2$	3180	1667	1595, 1579	1311	1039	1019	-
$[Ni(L_1H)_2]$	3191	-	1586, 1553	1352	1053	1006	1296
$[Co(L_1H)_2]$	3227	-	1559, 1535	1368	1060	1021	1293
$[Cu(L_1H)_2]$	3136	-	1585, 1560	1363	1065	1013	1299
$[Zn(L_1H)_2]$	3277	-	1587, 1558	1347	1052	1006	1293
$[Cd(L_1H)_2]$	3262	-	1576, 1529	1365	1060	1012	1285

#### Table 5

IR spectral data of the ligands and their metal complexes as KBr pellets cm<sup>-1</sup>.

Comp.	(NH)	(C=0)	(C=N)	C=N-N=C	(CN)	(C0)	(N-N)
$L_2H_2$	3171	1636	1600	-	-	-	1053
$[{Co_2(L_2)_2}_n]$	-	-	-	1588	1308	1146	1065
$[{Ni_2(L_2)_2}_n]$	-	-	-	1587	1309	1144	1068
$[{Cu_2(L_2)_2}_n]$	-	-	-	1586	1280	1149	1068
$[{Zn_2(L_2)_2}_n]$	-	-	-	1589	1299	1145	1068
$[{Cd_2(L_2)_2}_n]$	-	-	-	1586	1297	1149	1068

#### Table 6

Electronic spectral data  $\lambda_{max}$  nm,  $\nu$  (cm<sup>-1</sup>) of the ligands and their metal complexes in DMF (10<sup>-2</sup>M).

Compounds	Electronic spectra data $\lambda_{max}(cm^{-1})$
$L_1H_2$	320 (31250), 308 (32467), 292 (34246)
$[Co(L_1H)_2]$	864 (11574), 756 (13227), 514 (19455), 356 (28089), 314
	(31847), 292 (34246)
$[Ni(L_1H)_2]$	1022 (9784), 918 (10893), 552 (18115), 385 (25974), 356
	(28089), 292 (34246)
$[Cu(L_1H)_2]$	614 (16286), 432sh (23148), 392 (25510), 290 (34482)
$[Zn(L_1H)_2]$	390 (25641), 342 (29239), 298 (33557)
$[Cd(L_1H)_2]$	360 (27777), 324 (30864), 298 (33557)
$L_2H_2$	356 (28089), 328 (30487), 295 (33898)
$[{Co_2(L_2)_2}_n]$	724 (13812), 364 (27472), 325 (30769), 278 (35971)
$[{Ni_2(L_2)_2}_n]$	850 (11764), 387 (25839), 339 (29498), 316 (31645),
	269 (37174)
$[{Cu_2(L_2)_2}_n]$	819 (12210), 376 (26595), 346 (28901), 331 (30211),
	272 (36764)
$[{Zn_2(L_2)_2}_n]$	391 (25575), 337 (29673), 296 (33783)
$[{Cd_2(L_2)_2}_n]$	395 (25316), 360 (27777), 297 (33670)



**Fig. 5.** Electronic absorption spectra of  $Co^{2*}$  and  $Cu^{2*}$  complexes in DMF  $(10^{-2} \text{ M})$ : (a)  $[Co(L_1H)_2]$ ; (b)  $[Cu(L_1H)_2]$ ; (c)  $[\{Co_2(L_2)_2\}_n]$ ; (d)  $[\{Cu_2(L_2)_2\}_n]$ .



**Fig. 6.** Electronic absorption spectra of  $Ni^{2+}$  complexes in DMF  $(10^{-2} \text{ M})$ : (e)  $[Ni(L_1H)_2]$ ; (f)  $[\{Ni_2(L_2)_2\}_n]$ .



**Fig. 7.** Electronic absorption spectra of  $Zn^{2+}$  and  $Cd^{2+}$  complexes in DMF ( $10^{-2}$  M): (g)  $[Zn(L_1H)_2]$ ; (h)  $[Cd(L_1H)_2]$ ; (i)  $[\{Zn_2(L_2)_2\}_n]$ ; (j)  $[\{Cd_2(L_2)_2\}_n]$ .

#### Table 7

Extraction of metal nitrate with the ligands synthesized <sup>a</sup>.

The extracted metal cations (%)						
Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Pb <sup>2+</sup>		
10.7	8.1	3.1	18.2	19.7	2.1	
16.9	9.3	24.2	28.4	28.1	3.2	
30.7	20.9	93.1	30.7	38	5.0	
61.5	61.6	100	35.2	39.4	6.2	
66.2	95.3	100	44.3	100	7.3	
61.5	95.3	100	88.6	100	9.1	
12.3	11.6	13.6	13.6	5.6	2.1	
13.8	11.6	9.9	22.7	12.7	3.2	
13.8	12.8	24.2	26.1	15.5	5.0	
18.4	12.8	38.5	22.7	23.9	6.2	
10.7	15.1	44.0	31.8	69	7.3	
26.1	94.1	47.2	81.8	66.2	9.1	
	The extr           Co <sup>2+</sup> 10.7           16.9           30.7           61.5           66.2           61.5           12.3           13.8           13.8           13.8           13.8           13.7           26.1	$\begin{tabular}{ c c c c } \hline The extracted meta \\ \hline Co^{2+} $ Ni^{2+} \\ \hline 10.7 $ 8.1 \\ 16.9 $ 9.3 \\ 30.7 $ 20.9 \\ 61.5 $ 61.6 \\ 66.2 $ 95.3 \\ 61.5 $ 95.3 \\ 12.3 $ 11.6 \\ 13.8 $ 11.6 \\ 13.8 $ 11.6 \\ 13.8 $ 12.8 \\ 18.4 $ 12.8 \\ 10.7 $ 15.1 \\ 26.1 $ 94.1 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c } \hline The extracted metal cations (%) \\ \hline \hline Co^{2+} & Ni^{2+} & Cu^{2+} \\ \hline 10.7 & 8.1 & 3.1 \\ 16.9 & 9.3 & 24.2 \\ 30.7 & 20.9 & 93.1 \\ 61.5 & 61.6 & 100 \\ 66.2 & 95.3 & 100 \\ 61.5 & 95.3 & 100 \\ 61.5 & 95.3 & 100 \\ \hline 12.3 & 11.6 & 13.6 \\ 13.8 & 11.6 & 9.9 \\ 13.8 & 12.8 & 24.2 \\ 18.4 & 12.8 & 38.5 \\ 10.7 & 15.1 & 44.0 \\ 26.1 & 94.1 & 47.2 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c } \hline The extracted metal cations (%) \\ \hline Co^{2+} & Ni^{2+} & Cu^{2+} & Zn^{2+} \\ \hline 10.7 & 8.1 & 3.1 & 18.2 \\ \hline 16.9 & 9.3 & 24.2 & 28.4 \\ \hline 30.7 & 20.9 & 93.1 & 30.7 \\ \hline 61.5 & 61.6 & 100 & 35.2 \\ \hline 66.2 & 95.3 & 100 & 44.3 \\ \hline 61.5 & 95.3 & 100 & 88.6 \\ \hline 12.3 & 11.6 & 13.6 & 13.6 \\ \hline 13.8 & 11.6 & 9.9 & 22.7 \\ \hline 13.8 & 12.8 & 24.2 & 26.1 \\ \hline 18.4 & 12.8 & 38.5 & 22.7 \\ \hline 10.7 & 15.1 & 44.0 & 31.8 \\ \hline 26.1 & 94.1 & 47.2 & 81.8 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c } \hline The extracted metal cations (%) \\ \hline \hline Co^{2+} & Ni^{2+} & Cu^{2+} & Zn^{2+} & Pb^{2+} \\ \hline 10.7 & 8.1 & 3.1 & 18.2 & 19.7 \\ 16.9 & 9.3 & 24.2 & 28.4 & 28.1 \\ 30.7 & 20.9 & 93.1 & 30.7 & 38 \\ 61.5 & 61.6 & 100 & 35.2 & 39.4 \\ 66.2 & 95.3 & 100 & 44.3 & 100 \\ 61.5 & 95.3 & 100 & 88.6 & 100 \\ 12.3 & 11.6 & 13.6 & 13.6 & 5.6 \\ 13.8 & 11.6 & 9.9 & 22.7 & 12.7 \\ 13.8 & 12.8 & 24.2 & 26.1 & 15.5 \\ 18.4 & 12.8 & 38.5 & 22.7 & 23.9 \\ 10.7 & 15.1 & 44.0 & 31.8 & 69 \\ 26.1 & 94.1 & 47.2 & 81.8 & 66.2 \\ \hline \end{tabular}$	

 $^a$  Aqueous phase; [metal nitrate] =  $1\times10^{-4}$  M; organic phase; chloroform [ligand] =  $1\times10^{-3}$  M; at 25 °C for 2 h contact time.



**Fig. 8.** The effect of pH on the extraction percentage of metal (II). [metal ions] =  $1 \times 10^{-4}$  M, [L<sub>1</sub>H<sub>2</sub> ligand] =  $1 \times 10^3$  M in chloroform at 25 °C for 2 h contact time.

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 polynuclear complex [14,30,43,44].

#### Electronic absorption spectra

Electronic spectra of the ligands and their metal complexes recorded in DMF solvent( $10^{-2}$  M) are given in (Table 6). In the electronic spectra of the ( $L_1H_2$  and  $L_2H_2$ ) ligands, the band of shortest wavelength appearing at 34246 cm<sup>-1</sup> for  $L_1H_2$  and 33898 cm<sup>-1</sup> for  $L_2H_2$ , may be attributed  $\pi \rightarrow \pi^*$  transition of benzenoid moiety of these ligands and intraligand  $\pi \rightarrow \pi^*$  transition.

The other two bands observed at 32467, 31250 cm<sup>-1</sup> for  $L_1H_2$  and 30487, 28089 cm<sup>-1</sup> for  $L_2H_2$  are most probably due to  $n \rightarrow \pi^*$  electronic transitions of imine and carbonyl groups [18,31,32,45].

In the complexes derived from  $L_1H_2$  ligand, the appearance of three bands in the electronic spectra of  $[Co(L_1H)_2]$  complex at 11574, 13227 and 19455 cm<sup>-1</sup> may be assigned to  ${}^{4}T_1g(F) \rightarrow 4T_2$ . g(F)( $v_1$ ),  ${}^{4}T_1g(F) \rightarrow 4A_2g(F)(<math>v_2$ ) and  ${}^{4}T_1g(F) \rightarrow 4T_1g(P)(v_3)$  transitions, respectively (Fig. 5), also the  $[Ni(L_1H)_2]$  complex (Fig. 6) exhibit three electronic spectral bands at 1022, 10893 and 18115 cm<sup>-1</sup> which may be assigned to  ${}^{3}A_2g \rightarrow 3T_2g(F)(v_1)$ ,  ${}^{3}A_2$ . g  $\rightarrow 3T_1g(F)(v_2)$  and  ${}^{3}A_2g \rightarrow 3T_1g(P)(v_3)$  transitions, respectively, suggesting an octahedral geometry around the Co<sup>2+</sup> and Ni<sup>2+</sup> ions [41,46]. The  $[Cu(L_1H)_2]$  complex (Fig. 5) shows a broad band on the low energy side at 16286 cm<sup>-1</sup> which may be ascribed to  ${}^{2}B_1g \rightarrow 2A_1g$ ,  ${}^{2}B_1g \rightarrow 2B_2g$  and  ${}^{2}B_1g \rightarrow 2Eg$  transitions, and attributed to a distorted octahedral geometry around the Cu<sup>2+</sup> ion [46].

Furthermore, show a broad and very strong band in the UV–visible region at 23148–28089 cm<sup>-1</sup> which are assigned to a ligand  $\rightarrow$  metal (LMCT) charge transfer excitation. Thus both of Zn<sup>2+</sup> and Cd<sup>2+</sup> complexes (Fig. 7) shows disappear bands in the visible region as expected for d<sup>10</sup> systems [47]. Additionally, a broad absorptions exhibit in the range 25974–34482 cm<sup>-1</sup> and which may be due to the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  intraligand transitions (Table 6).

In the complexes derived from  $L_2H_2$  ligand, the electronic spectrum of the  $[Co_2(L_2)_2]_n]$  complex (Fig. 5) shows one band at 13812 cm<sup>-1</sup>, may be assigned to  ${}^{4}A_2(F) \rightarrow 4T_1(P)(\nu_3)$  transition, while the electronic spectrum of  $[Ni_2(L_2)_2]_n]$  complex (Fig. 6), the band at 11764 cm<sup>-1</sup> is attributed to the  ${}^{3}T_1(F) \rightarrow 3T_1(P)(\nu_3)$  transition [48]. These two bands are characteristic for tetrahedral symmetry. As expected, in the tetrahedral compounds (high spin) the  ${}^{4}A_2(F) \rightarrow 4T_2(F)(\nu_1)$ ,  ${}^{4}A_2(F) \rightarrow 4T_1(F)(\nu_2)$  and  ${}^{3}T_1(F) \rightarrow 3T_2(F)(\nu_1)$ ,  ${}^{3}T_1(F) \rightarrow 3A_2(F)(\nu_2)$  transitions for Co(II) and Ni(II) complexes, respectively, are probably located above 1000 nm, which is beyond the detection range of our instrument. In addition to the ligand bands, the  $[Cu_2(L_2)_2]_n]$  complex (Fig. 5) shows a distinct d–d band at 12210 cm<sup>-1</sup>, may be assigned to  ${}^{2}T_2 \rightarrow {}^{2}E$  transition, suggesting an tetrahedral environment around the Cu<sup>2+</sup> ion [49].

The spectrum of the Zn(II) and Cd(II) complexes (Fig. 7) exhibits a strong intense charge transfer transition (LMCT) at 25316– 25575 cm<sup>-1</sup>, these bands are characteristic for tetrahedral symmetry [50,51]. The electronic absorption spectra for the bis-acyl-hydrazone ligands and their metal (II) complexes recorded in DMF solvent are given in Table 6.

#### Extraction ability of the ligands

Solvent extraction of metal ions has become an important process. Several commercial reagents some of which are phenolic oximes derived from salicylaldehyde or ketophenols have been used for copper recovery from sulfate, chloride, nitrate or ammonia media [1,2,4,8,9,37].

To the best of our knowledge, the stability of a transition metal complex with a polydentate chelate ligand in organic phase depends on a range of factors including: number and type of the do-



**Fig. 9.** The effect of pH on the extraction percentage of metal (II). [metal ions] =  $1 \times 10^{-4}$  M, [L<sub>2</sub>H<sub>2</sub> ligand] =  $1 \times 10^{-3}$  M in chloroform at 25 °C for 2 h contact time.

nor atoms present, the number and size of the chelate rings formed on complexation [52]. In addition, the stability and selectivity of complexations strongly depend on the donor ability [53].

In order to confirm whether these ligands can be used for extraction reagent, we studied the complexation ability of the synthesized diacetylmonoximebenzoyl-hydrazone  $(L_1H_2)$  and 1,4-diacetylbenzenebis(benzoyl-hydrazone)  $(L_2H_2)$  by the liquid-liquid extraction of selected transition metal  $[Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}]$  and Pb<sup>2+</sup>. The results are given in Table 7, these data were obtained by using CHCl<sub>3</sub> solutions of the ligands to extract metal nitrates from aqueous solution. The concentration of metals remaining in the aqueous phase was then determined by Spectra AAS-Phoenix-986.

#### Effect of pH on the Extraction

The effect of the pH on the percentage extraction of [Co(II), Ni(II), Cu(II), Zn(II) and Pb(II)] cations by  $L_1H_2$  and  $L_2H_2$  in chloroform was studied in the range of 2.1–9.1 under the optimum



**Fig. 10.** Extraction percentage of the metal nitrate with ligands. ( $L_1H_2$  and  $L_2H_2$ ),  $H_2O$ /CHCl<sub>3</sub> = 10/10 (v/v):[ligand] = 1 × 10<sup>-3</sup> M, [metal nitrate] = 1 × 10<sup>-4</sup> M, at 25 °C for 2 h contact time.



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





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

**Fig. 12.** Suggested structure for the polymeric dinuclear complexes  $[{M_2(L_2)_2}_n]$ ; n = 0, 1, 2...

extraction conditions, (Table 7). As shown in Figs. 8 and 9, the highest extraction percentage of Cu(II) and Pb(II) by  $L_1H_2$  ligand were observed at pH = 6.2–7.3, while the highest extraction percentage of Ni(II) and Zn(II) by  $L_2H_2$  ligand were observed at pH = 7.3–9.1, respectively.

Therefore, the experiments were carried out by using suitable buffer solutions with 0.1 M KNO<sub>3</sub> ionic strength.

It is clear from Table 7 that the extractability results of  $(L_1H_2)$  and  $L_2H_2$ ) ligands were different. Furthermore, the results shown that extraction of metals ions by  $L_1H_2$  ligand were in the order:

$$\mathbf{Cu}^{2+} \ge \mathbf{Pb}^{2+} > \mathbf{Ni}^{2+} > \mathbf{Zn}^{2+} > \mathbf{Co}^{2+}$$

While the extraction percentage of metals ions by  $L_2H_2$  ligand were in the order:

$$Ni^{2+} > Zn^{2+} > Pb^{2+} > Cu^{2+} > Co^{2+}$$

However, It is seen that the diacetylmonoxime-benzoylhydrazone ( $L_1H_2$ ) shows selectivity toward Cu<sup>2+</sup> and Pb<sup>2+</sup> cations, while the 1,4-diacetylbenzene bis(benzoylhydrazone) ( $L_2H_2$ ) shows selectivity toward Ni<sup>2+</sup> and Zn<sup>2+</sup> cations (Fig. 10). These results can be explained by the hard soft acid-base principle. The -C=N-OH and -C=N-NH-CO- groups is a soft base owing to its contribution to cation- $\pi$  interaction; therefore, shows a high affinity toward soft acidic metal (II) cations [8,9,26,54,55]. On the other hand, that N and O donors (the presence of the lone electron pair on the nitrogen and oxygen atoms in ligands provides their basic properties) increases the percentage of the extraction of the metal ions.

#### Conclusion

In this research the synthesis and characterization of the mononuclear metal (II) complexes derived from diacetylmonoximebenzoylhydrazone  $(L_1H_2)$  and polymeric dinuclear metal (II) complexes derived from 1,4-diacetylbenzene bis(benzoylhydrazone)  $(L_2H_2)$ . The reaction of  $(L_1H_2)$  ligand and equivalent molar of  $Et_3N$  with  $MCl_2$  [M = Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)] anhydrous yields the complex  $[M(L_1H)_2]$  where the  $(L_1H_2)$  ligand act as a monobasic O,N,N-tridentate and the coordination takes place in the enol form, suggesting, to be six-coordination with a N<sub>4</sub>O<sub>2</sub> donor environment; each ligand is coordinated through the oxime nitrogen, the imine nitrogen and the enolate oxygen. Furthermore, The reaction of  $(L_2H_2)$  and two equivalent molar of base (KOH) with anhydrous metal chlorides yields the complex  $[\{M_2(L_2)_2\}_n]; n = 0, 1, 2...$  where the ligand act as dinegative, tetradentate and the coordination takes place in the enol tautomeric form, suggesting, to be four-coordination with a N<sub>2</sub>O<sub>2</sub> donor environment; each ligand is coordinated through the azomethine nitrogen and the enolic oxygen atoms.

The <sup>1</sup>H NMR, <sup>13</sup>C NMR, elemental analysis(CHN), FT-IR infrared spectra, Magnetic susceptibility measurements and UV–vis. electronic absorption spectra of the  $(L_1H_2)$  and  $(L_2H_2)$  ligands and their metal (II) complexes were recorded and investigated. However, the elemental analysis results and spectral data are proposed the monomeric complexes  $[M(L_1H)_2]$  an octahedral geometry around the metal (II) ions (Fig. 11), and the polymeric dinuclear metal (II) complexes  $[\{M_2(L_2)_2\}_n\}$ ; n = 0, 1, 2... an tetra-hedral geometry around the metal (II) ions (Fig. 12).

The results of the liquid–liquid extraction study towards selected transition metal  $[Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} \text{ and Pb}^{2+}]$  presented in this work show that  $(L_1H_2)$  ligand has strong affinity towards all transition metal (II) ions, in particular  $Cu^{2+}$  (100%) and Pb<sup>2+</sup> (100%) in aqueous phase with 0.1 M KNO<sub>3</sub> in the pH = 6.2–7.3 rang at 25 °C and 2 h contact time, whereas the results indicate that  $(L_2H_2)$  ligand in organic phase extracts efficiently towards Ni<sup>2+</sup> (94.1%) and Zn<sup>2+</sup> (88.6%) in aqueous phase with 0.1 M KNO<sub>3</sub> in the pH = 7.3–9.1 rang at 25 °C and 2 h contact time, but the  $(L_2H_2)$  ligand is little extractant for the other transition metals. This can make the  $(L_1H_2)$  ligand suitable selectively separating Cu(II) and Pb(II) ions and the  $(L_2H_2)$  ligand suitable selectively separating Ni(II) and Zn(II) ions.

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#### Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.10.046.

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