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# Synthesis and Characterization of (Fe(II),Co(II),Ni(II) and Cu(II)) Complexes with Schiff Base derived from [benzoyl hydrazine] with [benzyl mono oxime]

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## Abstract

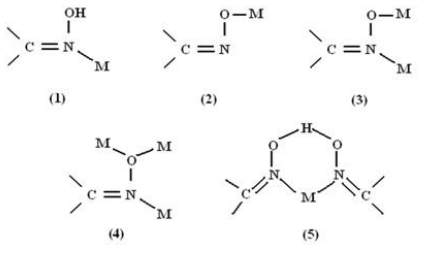
The reaction of [Benzoyl hydrazine] with [Diphenyl mono oxime] and Glacial acetic acid was carried out in methanol gave a new tridentate ligand [Benzoic acid (2-hydroxyimino- 1, 2-diphyneylethylidene) - hydrazide]. This ligand was reacted with some metal ions ($Fe^{(II)}$, $Co^{(II)}$, $Ni^{(II)}$, and $Cu^{(II)}$) in methanol with (1:1) metal : ligand ratio to give a series of new complexes of the general formula $[M(L)Cl_2.H_2O]$, where M= $Fe^{(11)}$, $Co^{(11)}$, $Ni^{(11)}$ and $Cu^{(11)}$.

All compounds were characterized by spectroscopic methods (I.R, UV-Vis), elemental microanalysis (C.H.N), atomic absorption, magnetic susceptibility, and conductivity measurements. From the obtained data the proposed molecular structures were suggested for the complexes of Fe $^{(II)}$, Co $^{(II)}$, Ni $^{(II)}$ and Cu $^{(II)}$ are of geometric octahedral.

**Key words: Bnzoyl hydrazine, Diphenyl mono oxime, Schiff Base, Complexes of Schiff Base .**

## Introduction

Oximes complexes have been found in general inorganic and coordination Chemistries and untypical methods for their synthesis have been reviewed. Oxime or Oximato species can bind a metal in different coordination modes and exhibit versatile reactivity [1] Scheme (1).



**Scheme (1)**

Much information has been accumulated in areas such as structure, stability and reactivity of the molecule, analytical Chemistry and biochemical models [2]. The important roles of such oxime complexes lies in there activity as, polymers catalyses, fungicides and bactericides[3]. Oxime imine complexes played an important role in radiopharmaceutical and related nuclear medicine [4,5]. The chemistry of oxime / oximato metal complexes has been investigated since the beginning of last century[6].This paper reports the synthesis and characterization of new imine oxime ligand derived from the reaction of [benzoyl hydrazine] and diphenyl mono oxime and its nickel, iron, cobalt and copper complexes. Oxime complexes of transition metals were

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used as apower ful Catalysis in organic reactions. Hampl and Co-werkers[7] reported the reactivity of some 2-pyridine ketoximes Complexes in the Cleavage of P-nitrophenyl esters of Carboxylic acidin water. Oxime amine Compounds played an important role in radio pharmaceuticals and related nuclear medicine[8-10].

## Materials and Methods

Reagents were purchased from Fluka and Rediel- Dehenge Chemical Co. I.R spectra were recorded as (KBr) discs using a Shimadzu 8300 FTIR spectrophotometer in the range (4000-400) $cm^{-1}$. Electronic spectra of the prepared compounds were measured in the region (200-900) nm for$10^{-3}$M solution in (Methanol) at 25 $^{0}C$ using a Shimadzu,160 spectrophotometer with1.000+0.001 $cm^{-1}$ matched quartz cell. Elemental microanalyses were preformed on a (C.H.N) analyzer, model 1106 (Carlo-Erba), while metal contents of the complexes were determined by atomic absorption (A.A) technique using a Shimadzu A.A 680G atomic absorption spectrophotometer. Electrical conductivity measurements of the complexes were recorded at 25 $^{0}C$ for $10^{-3}$ M solutions of the samples in (Methanol), using a PW 9526 digital conductivity meter. Magnetic measurements were recorded on Bruker BM6 instrument at 298 K following the Faradays method Chloride contents for complexes were determined by using potrntiometric titration method (686- titroprocessor-665- Dosimat- Metrohm- Swiss).

### Synthesis of the ligand [Benzoic acid ( 2- hydroxyimino -1 ,2-diphyneylethylidene) - hydrazide]

A solution of (benzoyl hydrazine), (0.34 g, 2.59 m mole) in methanol (10 mL) was added slowly to a mixture of diphenyl mono oxime (0.56g, 2.59 m mole) dissolved in methanol (10mL). Then drops of glacial acetic acid were added. The mixture was refluxed for (4 hr.), and then stirred at room temperature for (1 hr). A yellow precipitate was collected by filtration, dried under vacuum for (24 hr), to give (L)as a mustard solid, Yield, (81%), m.p. (220 $^{0}C$)

### 1- Synthesis of [Fe (L) $Cl_2.H_2O$]

To a solution of (0.0869g, 0. 43 m mole) of $FeCl_2.4H_2O$ in (10 mL) methanol. Was added a solution of (0.15g, 0.43 m mole) of the ligand in (15 mL) methanol. The mixture was allowed to reflux for (2 hr.). During this time the colour of the mixture became brown. The solution was allowed for a slow evaporation at room temperature and a brown precipitate was formed. Yield (70 %) m.p (161-164$^{0}C$) .

### 2-Synthesis of [Co (L) $Cl_2.H_2O$]

In (50 mL) round bottom flask (0.103 g, 0.43 m mole) of ($CoCl_2.6H_2.O$) was dissolved in (10 mL) methanol. A solution of (0.15 g, 0.43 m mole) of the ligand in (15 mL)methanol was added to the above mixture. The reaction was allowed to reflux for (2 hr). A yellow precipitate was formed, Yield (68 %) m.p (160$^{0}C$) .

### 3- Synthesis of [Ni (L) $Cl_2.H_2O$]

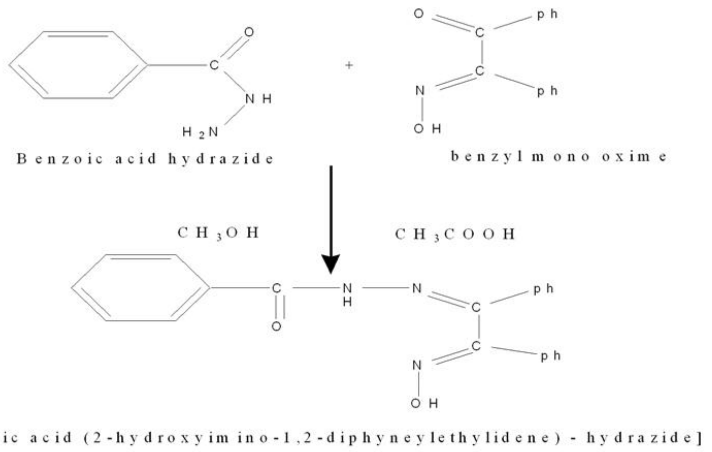
$NiCl_2.6H_2O$ (0.1038 g, 0.43 m mole) as suspended in (10 mL) of ethanol. To this suspension, a mixture of (0.15g,0.43 m mole) of the ligand in (15 mL) ethanol was added and the mixture was allowed to reflux for (2 hr). A pale yellow precipitate was formed Yield(33%)m.p(300$^{O}C$)dec.

### 4- Synthesis of [Cu (L) $Cl_2.H_2O$]

A (0.074g,0.43 m mole )of $CuCl_2.2H_2O$ was dissolved in (10mL) methanol. A solution of (0.15g,0.43m mole )of the ligand in (15mL)methanol was added to the above mixture. The reaction was allowed to reflux for (2hr).A brown precipitate was formed yield (24%)m.p (160 $^{O}C$).

## Results and discussion

The new ligand type ($N_2O$) was prepared according to the general method shown in Scheme (2)



**Scheme (2) the synthesis route of the ligan**

The (I.R) spectrum for the ligand fig (1a) shows two bands at (1625 and 1425) cm$^{-1}$ duo to the $\upsilon$(C=N) stretching for the imine and oxime groups respectively [11]. On the other hand the band at (1650) cm$^{-1}$ assigned to the $\upsilon$(C=O) stretching. The band at (3550) cm$^{-1}$ is attributed to the $\upsilon$ (O─H) stretching of the (OH) group in the oxime group. The bands at (990) and (1100) cm$^{-1}$ are attributed to $\upsilon$ (N─O) stretching. The bands at (3425) and (3100) cm$^{-1}$ is attributed to the $\upsilon$ (N─H) stretching and $\upsilon$ (C─H) aromatic respectively. While (U.V-Vis) spectrum fig (2a) exhibits a high intense absorption peak at (296) nm which assigned to overlap of ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$) transitions, table (2). The most important infrared spectra band that provide conclusive structure evidence for coordination of the ligand to central metal ions ($Fe^{(II)}$, $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$) are given in table (1). The I.R spectra of the metal complexes show that the $\upsilon$(C=N) stretching frequency for the imine group are shifted to lower frequency by (8) cm$^{-1}$ in comparison to that for the free ligand fig (2b,2c). These bands were assigned to the $\upsilon$(C=N) stretching of reduced bond order. This is indicative of nitrogen coordination of the nitrogen to the metal ion [12]. While the $\upsilon$(C=N) stretching frequency for the oxime group are shifted markedly to higher frequency by ca. (25) cm$^{-1}$, it can be attributed to the delocalization of metal ion electronic density into the ligand ($\pi$- system) [13]. The band of (1650) cm$^{-1}$ duo to the $\upsilon$(C=O) in the free ligand shift toward higher value in all complexes at (1685-1680) cm$^{-1}$ indicating that the carbonyl oxygen atom coordinated to the metal ions. The band at (3425) cm$^{-1}$ in the free ligand which can be attributed to $\upsilon$ (N─H) stretching vibration, the position of this band remains at nearly the same frequency in spectra of the metal complexes suggesting the un-coordination of this group. A band at (1080) cm$^{-1}$ corresponds to N-coordination of the oximato group

[11]. Confirms the presence of water molecule in complexes (1), (2), (3), and (4). The υ (N─O) stretching bands at (990) and (1100) cm$^{-1}$ for the ligand are shifted to higher frequencies by (10-30) cm$^{-1}$. The increase of the υ (N─O) is presumably duo to the complexation with metal ions [14]. The band at the range (3228, 1630 shoulder and 840) cm$^{-1}$ due to υ (O─H) δ (H-OH), and δ (OH) bending respectively, suggesting the presence of coordinated water, these results are in agreement with that reported by Nakamoto reports [15]. The new band in the range at (470-625) cm$^{-1}$ assigned to υ (M-O), υ (M-N) stretching respectively. The assignment of characterization bands are summarized in table (1) [16].

**Table (1) I.R. spectra data of the ligand and it's complexes**

| Compound | υ(O─H) oxime<br>υ(O─H) $H_2O$ | υ(N─H) | υ(C─H) aroma | υ(C=N) imine<br>υ(C=N) oxime | υ(N─O) | υ(M─N)<br>υ(M─O) | υ(C=O) | Additional Peaks |
|---|---|---|---|---|---|---|---|---|
| [$C_{21}H_{17}N_3O_2$] | 3550<br>- | 3425 | 3100 | 1625<br>1425 | 990<br>1100 | - | 1650 | υ(C-N) 1123<br>υ(C=C) 1420 ring |
| [Fe(L)$Cl_2$.$H_2O$] | 3550<br>3228 | 3210 | 3010 | 1617<br>1440 | 1000<br>1130 | 470<br>495 | 1685 | υ(C─N) 1370 |
| [Co(L)$Cl_2$.$H_2O$] | 3450<br>3400 | 3320 | 3050 | 1625<br>1450 | 1000<br>1150 | 500<br>550 | 1684 | υ(C─N) 1380 |
| [Ni(L)$Cl_2$.$H_2O$] | 3450<br>3490 | 3250 | 3050 | 1625<br>1450 | 1000<br>1145 | 480<br>625 | 1682 | υ(C─N) 1350<br>υ(C=C) 1320 |
| [Cu(L)$Cl_2$.$H_2O$] | 3450<br>3250 | 3220 | 307 | 1620<br>1450 | 1000<br>1120 | 510<br>520 | 1680 | υ(C─N) 1320<br>υ(C=C)1450 ring |

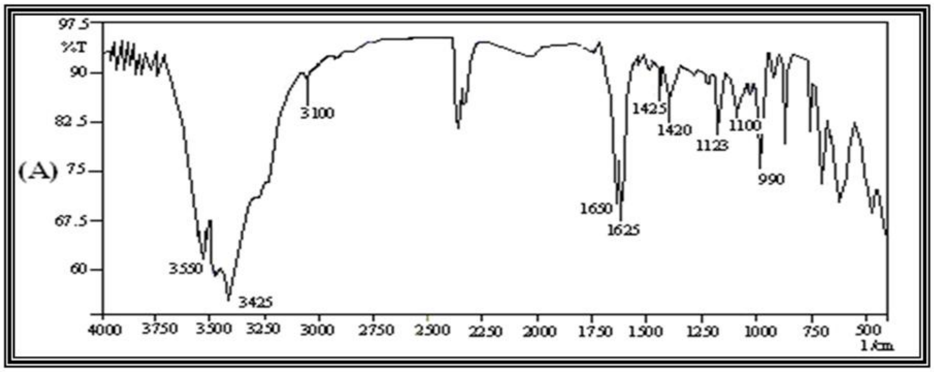


Fig (1-a) the I.R. spectrum of the ligand

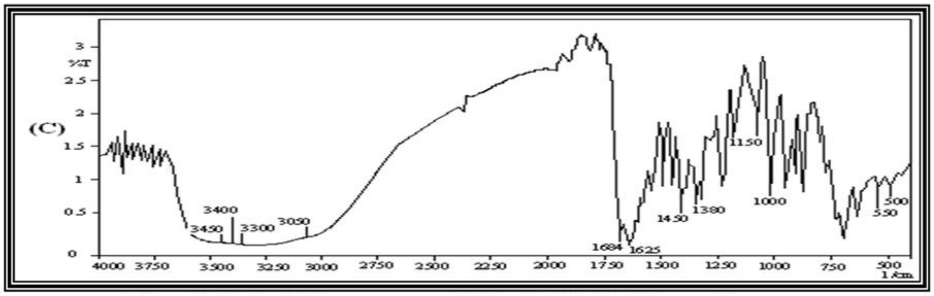


Fig . (1-b) the I.R. spectrum of [Co (L) $Cl_2.H_2O$] complex

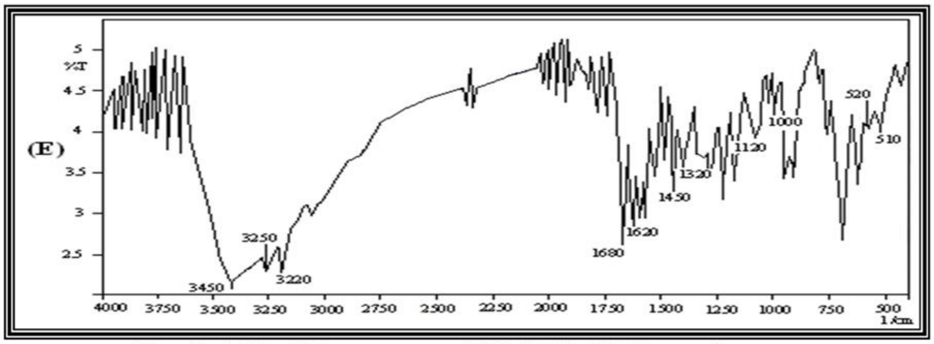


Fig. (1-c) The I.R. spectrum of [Ni $(L)Cl_2.H_2O$] complex

**Table (2): electronic spectral data and conductance measurements for the ligand [L] and it's complexes in methanol ,magnetic moment**

| Compound | λ nm | Wave number $Cm^{-1}$ | $\varepsilon_{max}$ Molar $Cm^{-1}$ | Transitions | Λm $S.cm^2.(Mole^{-1})$ | $\mu_{eff}$ (BM) |
|---|---|---|---|---|---|---|
| [$C_{21}H_{17}N_3O_2$] | 296 | 33783 | 2382 | $(\pi\rightarrow{}^*\pi)$ $(n\rightarrow{}^*\pi)$ | 30 | - |
| [$Fe(L)Cl_2.H_2O$] | 211 | 47393 | 457 |  | 25 | - |
|  | 344 | 29069 | 1669 |  |  |  |
|  | 397 | 25188 | 1386 | $({}^1A_{1g}\rightarrow{}^3T_{1g})$ |  |  |
| [$Co( L) Cl_2.H_2O$] | 342 | 29239 | 2389 |  | 37 | - |
|  | 376 | 26595 | 1378 | $({}^4T_{1g}\rightarrow{}^4T_{1g(P)})$ |  |  |
|  | 610 | 16393 | 220 | $({}^4T_{1g}\rightarrow{}^4A_{2g})$ |  |  |
| [$Ni(L)Cl_2.H_2O$] | 283 | 35335 | 2216 |  | 32 | 3.1 |
|  | 342 | 29239 | 1748 |  |  |  |
|  | 362 | 27624 | 2216 | $({}^3A_{2g}\rightarrow{}^3T_{1g\,(P)})$ |  |  |
| [$Cu(L)Cl_2.H_2O$] | 261 | 38314 | 2465 |  | 29 | 1.8 |
|  | 864 | 11574 | 223 | $({}^2E_g\rightarrow{}^2T_{2g})$ |  |  |

The (U.V-Vis) spectral of the complexes (Fe $^{(II)}$, Co $^{(II)}$, Ni $^{(II)}$ and Cu $^{(II)}$) showed absorption bands at (211,344) nm, (342,376) nm, (238,342) nm and (261, 330) nm which assigned to ligand field and charge transfer transition indicate a shift of ligand band, this is duo to the complexation. In the [$Fe(L)Cl_2.H_2O$], [$Co(L)Cl_2.H_2O$], [$Ni(L)Cl_2.H_2O$] and [$Cu(L)Cl_2.H_2O$]

complexes figs.(3-b,c,d and e), the peaks at (397) nm, (610) nm, (362) nm and (864) nm are attributed to (d-d) electronic transition type ($^1A_{1g}\rightarrow{}^3T_{1g}$), ($^4T_{1g}\rightarrow{}^4T_{1g(P)}$), ($^4T_{1g}\rightarrow{}^4A_{2g}$), ($^3A_{2g}\rightarrow{}^3T_{1g(P)}$) and ($^2E_g\rightarrow{}^2T_{2g}$) respectively, suggesting an octahedral structure about Fe, Co, Ni and Cu ions respectively [17,18]. The molar conductance values were found in the range (25-37) S. $cm^2.mole^{-1}$ table (2) .which indicates that the complexes are non –electrolytes [19]. These were determined in (Methanol) solution ($10^{-3}$ M) .The Magnetic moments for the complexes are shown in table (2) .The Ni (II) (3.1 BM), Cu (II) (1.8) .The nickel complex was paramagnetic indicated that the geometry around Ni (II) was octahedral.

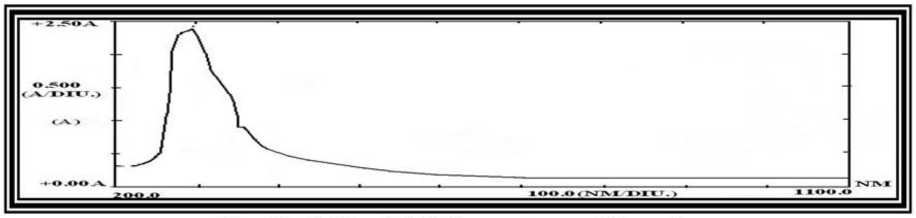


**Fig. (2-A) The U.V-Vis spectrum of ligand**

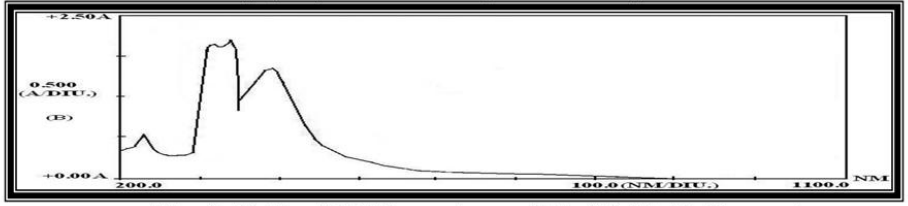


**Fig. (2-B) The U.V-Vis spectrum of [Fe (L) $Cl_2.H_2O$] complex**

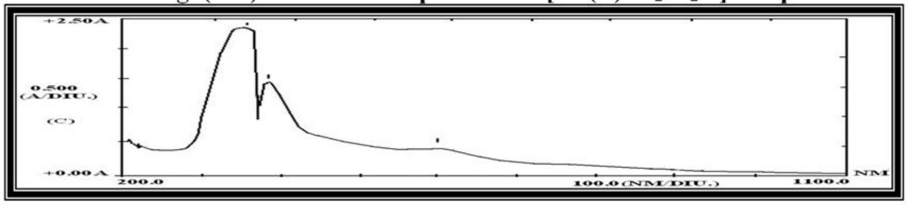


**Fig. (2-C) the U.V-Vis spectrum of [Co (L)$Cl_2.H_2O$] complex**

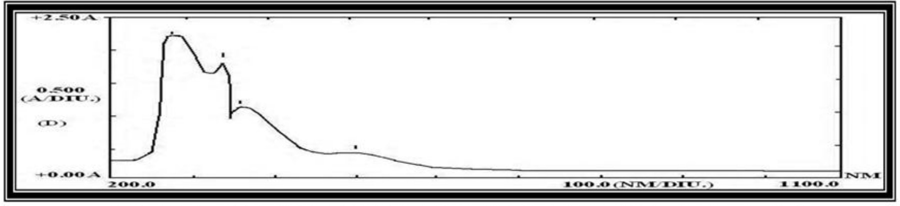


**Fig. (2-D) The U.V-Vis spectrum of the ligand [Ni (L) $Cl_2$. $H_2O$]**

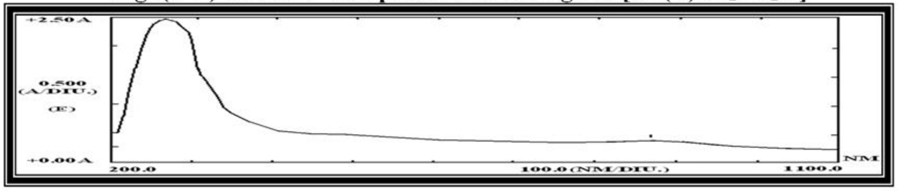


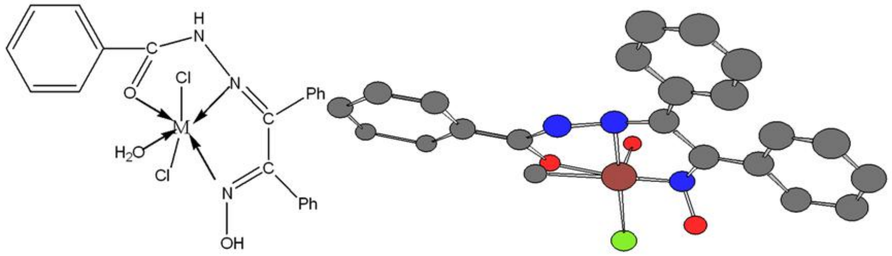
**Fig. (2-E) the U.V-Vis spectrum of [Cu (L)$Cl_2.H_2O$] complex**

The prepared complexes are stable at room temperature, non hygroscopic, insoluble in water, but soluble in methanol, DMF and DMSO. The analytical and physical data table (3) and spectra data table (1) and (2) are compatible with the suggested structure fig(3).

**Table (3) analytical and physical data of the ligand and it's complexes**

| Complexes formula | Color | Mw. | M.P. $^0$C | Yield % | (Found), Calcd. % | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | Metal |
| $[C_{21}H_{17}N_3O_2]$ | Mustard | 343 | 220 | 81 | (73.46)<br>73.11 | (4.95)<br>4.80 | (12.24)<br>12.02 | - |
| $[Fe(L)Cl_2.H_2O]$ | Brown | 487.8 | 164 | 70 | (51.66)<br>51.15 | (3.89)<br>3.47 | (8.61)<br>8.26 | (11.43)<br>11.11 |
| $[Co( L) Cl_2.H_2O]$ | Yellow | 490.9 | 160 | 68 | (51.33)<br>51.00 | (3.87)<br>3.62 | (8.55)<br>8.22 | (11.99)<br>11.82 |
| $[Ni(L)Cl_2.H_2O]$ | Pale yellow | 490.7 | 300 dec | 33 | (51.33)<br>51.20 | (3.87)<br>3.58 | (8.56)<br>8.41 | (11.96)<br>11.62 |
| $[Cu(L)Cl_2.H_2O]$ | Brown | 495.5 | 93 | 24 | (50.85)<br>50.63 | (3.83)<br>3.55 | (8.47)<br>8.61 | (12.81)<br>12.46 |

**dec=decomposition**



**M= Fe $^{(II)}$, Co $^{(II)}$, Ni $^{(II)}$, and Cu $^{(II)}$**
**Figure (3) the suggested structure for the complexes**

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# تحضير وتشخيص معقدات ثلاثي المنح نوع $N_2O$ من تفاعل الليكاند Benzoic acid (2-hydroxy imino – 1,2-di Phyneyl ethylidene) – hydrazide مع ايونات العناصر
# (Fe $^{(II)}$, Co $^{(II)}$, Ni $^{(II)}$, and Cu $^{(II)}$)

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## الخلاصة:

حضر الليكاند [Benzoic acid (2-hydroxyimino- 1,2-diphyneylethylidene)- hydrazide]

من مفاعلة (Benzoylhydrazine ) مع ( Diphenylmonooxime) ثم مفاعلة الليكاند مع بعض العناصر الفلزية باستخدام الميثانول وسطا للتفاعل وبنسبة (1 : 1) بوجود حامض الخليك حيث تكونت معقدات جديدة ذوات الصيغة العامة :

$[M (L) Cl_2 H_2O]$

حيث:

M= Fe $^{(11)}$, Co $^{(11)}$, Ni $^{(11)}$, and Cu $^{(11)}$

شخصت جميع المركبات بالطرق الطيفية التالية ( الاشعة تحت الحمراءوالاشعة فوق البنفسجية –المرئية وكذلك شخصت المركبات بوساطة ,التحليل الكمي الدقيق للعناصر مع التوصيلية المولارية الكهربائية).من نتائج البحث كان الشكل الفراغي المقترح لمعقدات العناصر هي ثماني السطوح.