

# Synthesis And Characterization of Some Divalent Metal Complexes of Acid Hydrazine

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## Abstract

Ligand Base Schiff(1-(2-hydroxyphenyl) ethylidene) isonicotinohydrazide (HPENH). is used to prepare several new complexes for some transition elements, like Co (II), Ni (II), and Cu (II), and non-transition elements, like Zn (II), Cd (II), and Hg (II).was synthesis by the condensation reaction of nicotinohydrazide [M(HPENH) Cl] Cl with 1-(2-hydroxyphenyl) ethane-1-one in an neutral medium led to the formation of mononuclear complexes, and the reaction of the ligand with metallic salts in a ratio of 1:1 metal: ligand led to the formation of mononuclear complexes with the formula: M = Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Hg (II).

Measurements of molar conductivity, magnetic measurements, electronic spectra, infrared spectra, proton <sup>1</sup>H and carbon <sup>13</sup>C magnetic resonance spectra, and gas-mass chromatography were used to figure out what the complexes were. These studies have shown that ligand works evenly in triple dentate to make tetrahedral-shaped complexes as likely as possible.

## 1. introduction

Hydrazons are essential organic compounds that contain the active synthetic unit C=N (2) and they are isomethine compounds. The ability of the nitrogen atoms in hydrazones to form them different many types of azomethine compounds, such as oxime and imine (3). Because hydrazones can react with electrophilic and nucleophilic groups, they can form many organic compounds, especially heterocyclic compounds, which have many uses in pharmaceutical, agricultural, and biological fields. Poly dentate ligand compounds with various biological activities, including antispasmodic activity (6,7) and activity against leukemia, schizophrenia, and mild meningitis (8) . These activities work to reduce nervous tension and are also used to treat tuberculosis. Stable chelated complexes can be formed with transition metals that speed up vital processes (9,10, 11). Industrially, they are used as plasticizers, polymer stabilizers, and antioxidants. Agriculturally, they were used pesticides for berbs , parasites, rodents, and insects, and organization for the of some plants (6,10) .

In analytical chemistry, they are also used to estimate a number of ion transition metal ions by colour spectroscopy or measure the intensity of fluorescence (12,13) Researchers are very interested in the ligands of hydrazones that have nitrogen and oxygen as donor atoms. This is especially true when forming hydrazone complexes with metal ions because it is easy to prepare stable complexes with them by giving them electron pairs from metal ions in general and ions of transitional elements in particular (15,14).

Numerous studies have shown that the best way to connect hydrazone with metallic ion is to be bidentate, monobasic neutral form through the nitrogen of the azomethine group C=N and the oxygen of the carbonyl group (C=O) (16). Numerous researches dealt with preparing and

studying hydrazones ligands and complexes and showed the structure of these complexes and how the metallic ion coordinate with the ligand. During this study, new Schiff base ligand complexes were prepared N- (1-(2-hydroxyphenyl) ethylidene) isonicotinohydrazide (HPENH). They characterize by physical, chemical and spectral method to obtain the structure of these complexes with metallic chlorides of the transition elements Cu(II), Ni(II), and Co(II), as well as the non-transition elements Zn(II), Cd(II), and Hg(II).

## 2. Materials & Methods

All chemicals used are high purity and used without additional purification. The melting point or decomposition temperature of ligand and complexes SMP30 apparatus.

The metal contents of Ni (II), Cu(II), Zn(II), Cd(II) were determined spectrophotometric method using atomic absorption spectroscopy Analytik Jena G mbH-nov AA350-Flame Atomic Absorption Spectrometer, at College of Agriculture and Forestry, University of Mosul. Molar conductivity of the prepared complexes were measured for 10<sup>-3</sup> M solution in dimethyl formamide (DMF) at 25°C using HANNA EC214 conductivity meter instrument. Magnetic susceptibility of the prepared complexes were done at 25°C using Sherwood Scientific (MSB-MK) Magnetic Susceptibility Balance at College of Education of Pure Sciences, University of Tikrit.

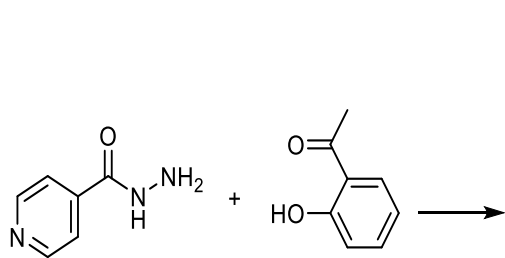
Infrared absorption spectroscopy of the Schiff base ligand and complexes were recorded on Shimadzu FT-IR84005 spectrophotometer, Japan at College of Science, University of Salahuddin in wave number range 400-4000 cm<sup>-1</sup>. Shimadzu UV-Vi's spectrophotometer, UV-1800 was used for electronic spectra measurement for 10<sup>-3</sup> M solution of the ligand and its complexes in DMF at 25°C in the wavelength range 190-1100 nm using 1 cm quartz cell. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the ligand and complex (4) were recorded at room temperature with Bruker DRX

system at 400 MHz, using tetramethyl silane (TMS) an internal standard in dimethylsulfoxide (DMSO-d<sup>6</sup>) at Colleg of Science , Uinevercity of Basra .

GC-MS-Qp2010 Ultra Gas Chromatography-Mass spectroscopy , Shimadzu measure ment drvice was used to masure the mass spectra of the ligand and complex(5) to dermin their molecular weight at central laboratory of Samarra University.

### 3. Experimental part

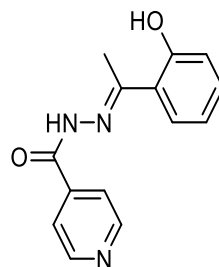
Isonicotinohydrazide (0.003 mol,0.41g ) in absolute



isonicotinohydrazide

1-(2-hydroxyphenyl)ethan-1-one

ethanol 50 ml was added drop wise to an absolute ethanol solution 5 ml of (0.003 mol,0.40g ) of 1-(2-hydroxyphenyl) ethane-1-one . the solution was stirred at room temperature for about 25 minutes in 50 ml round bottomed flask . then the mixture was boiled under reflux for 6 hrs and cooled in an ice bath . then , the formed precipitate is filtered , washed with cold ethanol and recrystallized from ethanol and dried in vacuum. The precipitate was weighed and the percentage calculated . the following equation Shows the ligand preparation .

*(E)-N'-(1-(2-hydroxyphenyl)ethylidene)isonicotinohydrazide*

### 4. 4.preparation of the complexes

The complexes were prepared by reacting metal chloride with the prepared ligand (HPENH) using the following method. An ethanolic 10 ml solution of metal chloride (0.003 mol) was added drop wise with continuous stirring for about 15-20minutes to a hot solution of (0.003 mol ,0.5 g ) of the prepared ligand (HPENH) ethanol 10 ml . the mixture so obtained was boiled under reflux for about 3-6 hrs. then the mixture cooled in an ice bath, and the colour precipitate complexes were filtered off, washed several times with cold ethanol, then with diethyl ether and dried under vacuum. The precipitate was weighed and percentage calculated.

### 5. Results and discussion

Cobalt, nickel, copper, zinc, cadmium, and mercury divalent complexes were studied and characterized with Schiff base ligand derived from the reaction of isonicotinohydrazide with 1-(2-hydroxyphenyl) ethan-1-one, and then the prepared Ligand reacted with the ion chloride of the metals mentioned above to be formed metallic complexes in a mol ratio of (1:1) (metal: ligand) as shown by the following equation:



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

n =0, 2 or 6

The complexes are solid, colored, and stable in air at room temperature. They don't dissolve in water and don't dissolve well in ethanol and methanol, but they dissolve well in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The elements of nickel (II) in the prepared complexes Copper (II), zinc (II), and cadmium (II) elements were determined by spectrophotometric method using atomic absorption spectrometry<sup>(17)</sup>. Table1. The complexes were broken down with concentrated

nitric acid, filling the volume with deionized water. complex solutions were made with concentrations that fall within the range of concentrations of standard samples are compatible with the linear range of the standard curve of derived elements, and that can be used with other measurements to propose synthetic formulas for the prepared complexes. Through molar conductivity measurements of the prepared complexes at a concentration of (10)<sup>-3</sup> M using a dimethylformamide solvent (DMF), and after allowing the solution be in thermal equilibrium at a temperature of 25°C, it was found that it is consistent with the synthetic formulas of the proposed complexes, where it was found that the complexes fall within the complexes with electrolytic behavior in a ratio of 1:1 in the solution, and this is consistent with the results shown in Table (1).

In the infrared spectrum, the determination of coordination is due to the stretching frequencies of the groups  $\nu$  (C=N),  $\nu$  (C=O), and  $\nu$  (OH), the bending frequency of the  $\delta$  (OH) phenolic group,  $\nu$  (M-O), and  $\nu$  (M-N), sites of the Schiff base ligand prepared in this study and its metallic complexes. As the location of the bands is affected by the ligand coordination with the donating metal ions.

The stretching frequency of the isomethine group  $\nu$  (C=N) of the ligand was found to be in the region (1608 cm<sup>-1</sup>), but when it was connected to a metal ion, it moved to a lower frequency range (1593–1541cm<sup>-1</sup>), showing that the isomethine group is consistent with metal ions<sup>(18, 19, 20, 21)</sup>. The infrared spectra showed the stretching frequency of the group  $\nu$  (C=O) at the region (1678 cm<sup>-1</sup>), and when the complexes were formed, the band appeared at a frequency lower than the ligand band (1670–1647 cm<sup>-1</sup>), which showed that the oxygen atom of the carbonyl group was bonded with the metallic ions of the complexes.<sup>(22,23,24)</sup> The hydroxyl group  $\nu$  (OH) stretching frequency showed up as a band in the

prepared ligand in the region (3360 cm<sup>-1</sup>) and the hydroxyl group bending frequency showed up as a band in the region (1373 cm<sup>-1</sup>)(25,26,27). The hydroxyl group stretching and bending frequency bands were observed in the regions that are lower than those for the free ligand in the ranges of (3346-3198 cm<sup>-1</sup>) and (1369-1333 cm<sup>-1</sup>), respectively, and this proves that metallic ions are consistent with the oxygen atom of the hydroxyl group. The stretching frequency of the  $\nu$  (NH) group in the ligand spectrum was found to be (3118 cm<sup>-1</sup>), and the stretching values of this bond were found to be in about the same place in preparation the complexes. This showed that this group did not have any coordinated with any of the metal ions in the complexes. The stretching frequency of the  $\nu$  (M-N)  $\nu$  (M-O) bonds is at the lowest frequency of the infrared spectrum of complex compounds, and these frequencies are not seen in the spectra of ligand.

The infrared spectrum showed that the group  $\nu$  (M-O) and  $\nu$  (M-N) regvn between (580-509cm<sup>-1</sup>) and (464-430cm<sup>-1</sup>) respectively, for the complexes that were prepared. This shows that they are in the complexes but not in the ligand spectrum, which is consistent with what was that the two oxygen atoms in the phenolic group and the nitrogen in the iso methine group (28,29,30,16). The stretching frequency of the (M-Cl) bond appear at (280-200 cm<sup>-1</sup>) in the infrared spectrum of chlorideion, that covalently bonded with the metal ions located inside the coordination sphere because they and is coordination were outside the range of the device used. Was proved through thje molar conductivity of the solution of the prepared complexes and also loy depending on magnetic measurements and electronic spectra (13 ,33, 31, 32, 33), table (2) shows the most important ligand bands and the complexes they are used to prepared.

The Gouy method was used to measure magnetic suseeptibility at (25°C). Tetracoordinate cobalt (II) complex showed magnetic moment value (4.28 B.M.). Where the cobalt ion has 3d<sup>7</sup> system three unpaired electrons, which are higher than the theoretical value (3.87 B.M.) due to the presence of second order orbital contribution, and this is in conformity with magntic moment value of Co(II) tetrahedral complex. (34,35)

The Ni (II) complex revealed a value of magnetic moment (3.50 B.M.) due to the existence of two unpaired electrons, which is more than the theoretical value (2.83 B.M.) due to the presence of the orbital contribution. The electronic spectrum of the complex revealed that it has a tetrahedral structure, Moraver , Cu(II) complex exhibited a magnetic moment value (2.24 B.M. ) and in accordance with electronic sepectrum of the complex ,it was clear that it has a tetra hedral structure.(36,38) All Zn(II), Cd(II) and Hg(II) complexes are diamagnetic because they have d<sup>10</sup> orbital ,which is full of electrons and expected that have a tetrahedral structure which is the most common depending on

the chemical measurements and the other physical studies . (39,40)

The electronic spectra of the ligands and complexes were measured at the concentration of 10<sup>-3</sup>M, temperature 25°C, using dimethylformamide (DMF) as a solvent, and the results were obtained as in Table (3). The prepared ligand showed two main bands, The first band is attributed to the electronic transition ( $\pi$ - $\pi^*$ ). It appears at a wave number 37878 cm<sup>-1</sup> which is attributed to chromophore C=N-NH-CO. The second band is attributed to the electronic transition ( $n$ - $\pi^*$ ) and appears at wave number 35460 cm<sup>-1</sup>, which occurs due to nitrogen and oxygen atoms Fig (10). When forming complexes, these bands show a displacement towards lower frequencies due to coordination with metal ions. (40,33) The complex Co (II) Fig (11). shows absorption band at (14858 cm<sup>-1</sup>) and due to the electronic transition 4A<sub>2</sub>(F)→4T<sub>1</sub> (P)  $\nu$ <sub>3</sub> while the two electronic bands relate to 4A<sub>2</sub>(F)→4T<sub>1</sub> (P)  $\nu$ <sub>2</sub>, 4A<sub>2</sub>(F)→4T<sub>1</sub> (P)  $\nu$ <sub>1</sub> they are located in ranges outside the range of the instrument used for electronic spectrometry. The complex's charge transfer band also appeared at (30101cm<sup>-1</sup>) which indicates a cobalt (II) tetrahedral structure (41,42,34) As nickel (II) the complex Fig. (12) showed that it has an absorption band at (16750 cm<sup>-1</sup>) that belong back to the electronic transition 3T<sub>1</sub>(F)→3T<sub>1</sub> (P)  $\nu$ <sub>3</sub>. As for the two bands that belong to the two-electron transfer, 3T<sub>1</sub>(F)→3T<sub>2</sub> (F)  $\nu$ <sub>1</sub> 3T<sub>1</sub>(F)→3T<sub>2</sub> (F) they were not identified because of their low intensity, which is outside the range of the device used. The band or (charge transition) its value (28328 cm<sup>-1</sup>) indicating that this complex possesses a tetrahedral structure around the nickel (II) ion (43,44,45,46,47). Cu (II) Fig. (13) complex showed a wide absorption band in the region (16863 cm<sup>-1</sup>). This band belongs to the 2T<sub>2</sub>(D)→2E(D) electron transition and the charge transfer band at (33670cm<sup>-1</sup>). It is in agreement with the magnetic measurements of the complex and with the published research that indicates that it is a tetrahedron (48,49,50). The complexes of Hg (II), Cd (II), Zn (II). Table (3) gave absorption bands of the order of (30303cm<sup>-1</sup> – 31347 cm<sup>-1</sup>) and these absorptions probably represent the charge transfer spectra and in a few cases are attributed to the ligand bands. These complexes do not give (d-d) transitions because they do not give d<sup>10</sup> in the outer valence orbital and the above complexes are tetrahedral. (51,52, 36) In the research that we use, nuclear magnetic resonance spectroscopy (<sup>13</sup>CNMR, <sup>1</sup>HNMR) was used to investigate the structural characteristics of the ligand and the complex (5). Fig. (8) in the DMSO-d<sub>6</sub> solvent. This was done in order to validate the accuracy of their respective chemical formulas. The protons of the aromatic ring were seen in the ligand spectrum in the form of a signal multiple at chemical shift ( $\delta$  H 7.56-6.944H), which related to protons for the aromatic ring. A double signal that was detected at ( $\delta$  H 7.65 ppm<sup>2</sup>H) belonged to two protons, and

another double signal that was detected at ( $\delta$  H 8.81 ppm2H) also belonged to two protons of the pyridine ring. In addition, there was a single indication that showed up at ( $\delta$  H 3.42 ppm 3H), and it belonged to the three protons of the methyl group. And there was only one signal that showed up at ( $\delta$  H11.62 ppm 1H), and it belonged to the proton of the NH group as well as the proton of the phenolic hydroxyl group was identified as the source of a single signal that located up at ( $\delta$  H13.25 ppm1H). The nuclear magnetic resonance spectrum of the cadmium complex Cd(II) is figclsh the aromatic ring protons are a multiple signal ( $\delta$  H 7.52 -  $\delta$  H 6.97 ppm4H). belonged to the protons, for the aromatic ring there was an appearance of a double signal at ( $\delta$  H7.61 ppm2H) that belonged to two protons, as well as an appearance of a binary signal at ( $\delta$  H8.82 ppm2H) that belonged to two protons of the pyridine ring. The methyl group appeared as a single signal at ( $\delta$  H3.45 ppm 3H), which returns to three protons, and as a single signal at ( $\delta$  H11.9 ppm 1H), which belonged to one proton of a group NH. Finally, the single sign al found at the location ( $\delta$  H 13.19 ppm 1H) is assigned to the proton of the

phenolic OH group. Display the spectrum of the carbon nuclear magnetic resonance  $^{13}C\{^1H\}$ -NMR of the ligand measured in DMSO-d<sub>6</sub> solvent and shown in the Fig. (9), where the spectrum showed six signals attributed to the carbon atoms of the aromatic ring at the chemical shift (117.83 ppm, 119.09 ppm, 119.33 ppm, 129.19ppm, 132.03 ppm and159.23ppm) respectively. The spectrum also showed five signals belonging to the carbon atoms of the pyrdene ring at anochemical shift (122.50 ppm and 122.50 ppm, 140.57 ppm, 150.65 ppm, and 150.65 ppm). In addition, the spectrum showed a chemical shift of the carbon atom of the carbonyl group at 159.90 ppm, and when the chemical displacement (163.47 ppm) belongs to the carbon atom of the carbonyl group.

The mass spectrum of the prepared Schiff base ligand (HPENH) showed multiple splittings with different relative abundances, figure () , where a peak appeared at 255m/2 at an abundance of 25%, representing the same molecular weight as the chemical formula (C<sub>14</sub> H<sub>13</sub> N<sub>3</sub> O<sub>2</sub>), and the mass spectrum of the complex [Zn(HMEBH)Cl]Cl Fig.() showed a peak at 391m/2 corresponding to the theoretical mass of (C<sub>14</sub> H<sub>13</sub> N<sub>3</sub> O<sub>3</sub> Zn Cl<sub>2</sub>).

Table 1: Analytical and some physical data of the ligand and its complexes

No.	Chemical formula	Colour	M.P. <sup>oC</sup>	Yield %	M% Calc. (Found)	$\Lambda_m(\text{DMF})(\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mole}^{-1})$
	HPENH	238-240	Beige	80	-	-
1	[Co (HPENH) Cl] Cl	314 d*	Brown	71	-	83.0
2	[Ni (HPENH) Cl] Cl	316 d	Light green	60	15,25	71.4
3	[Cu (HPENH) Cl] Cl	158-160	Light brown	83	16.31(16.16)	67.0
4	[Zn (HPENH) Cl] Cl	312 d	Light yellow	61	16.71(16.08)	85.6
5	[Cd (HPENH) Cl] Cl	317 d	Light yellow	88	25,64(25.47)	69.6
6	[Hg (HPENH) Cl] Cl	243-246	Light yellow	70	-	53.9

d\*=decomposition temperature

Table2:Magnetic moment,absorption data,band assignments and structures of the HPENH ligand and complexes

Geometry	$\mu$ eff (B.M)	Possible assignments	Absorption region ( cm-1)	Chemical formula	No.
		$n \pi^* \pi \pi^*$	3546037878	HPENH	
Td*	4.28	$^4A_2 (F) ^4T_1(v_3)$ Chagctransfer(C.T)	1485830101	[Co(HPENH) Cl] Cl	1
Td	3.50	$^3T_1 (F) ^3T_1(p)V3$ Chagctransfer (C.T)	1675028328	[Ni( HPENH) Cl] Cl	2
Td	2.24	$^2T_2 (D) ^2E (D)$ Chagctransfer(C.T)	1686333670	[Cu (HPENH) Cl] Cl	3
Td	diamagnetic	Charetranfcer(C.T)	30581	[Zn( HPENH) Cl] Cl	4
Td	diamagnetic	Charetranfcer(C.T)	30303	[Cd (HPENH) Cl] Cl	5
Td	diamagnetic	Charetranfcer(C.T)	31347	[Hg (HPENH) Cl] Cl	6

Table 3 :Important IR,spectral bands(cm-1)for HPENH and its complexes

No.	C chemical formula	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{NH}$	$\nu_{N-N}$	$\nu_{OH}$	$\delta_{OH}$	$\nu_{C=C}$	$\nu_{(C=N) py}$	$\nu_{M-N}$	$\nu_{M-O}$
	HPENH	1678	1608	3118	1064	3350	1373	1604	1533		
1	[Co (HPENH) Cl] Cl	1653	1551	3147	1020	3269	1333	1604	1550	430	542
2	[Ni (HPENH) Cl] Cl	1651	1552	3167	1022	3271	1354	1606	1552	450	580
3	[Cu (HPENH) Cl] Cl	1647	1564	3143	1064	3198	1339	1600	1535	440	525
4	[Zn (HPENH) Cl] Cl	1670	1593	3099	993	3346	1362	1606	1521	464	509
5	[Cd (HPENH) Cl] Cl	1668	1541	3069	1018	3253	1351	1607	1541	442	516
6	[Hg (HPENH) Cl] Cl	1661	1556	3091	1012	3248	1369	1604	1514	462	509

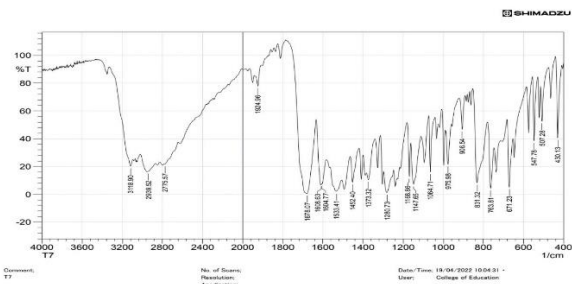


Fig (1): Infrared spectrum of the ligand (HMEBH)

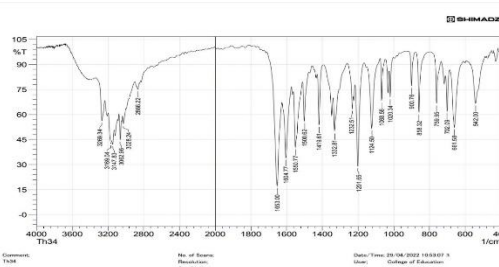


Fig (2): Infrared spectrum of the complex [Co (HMEBH)Cl]Cl

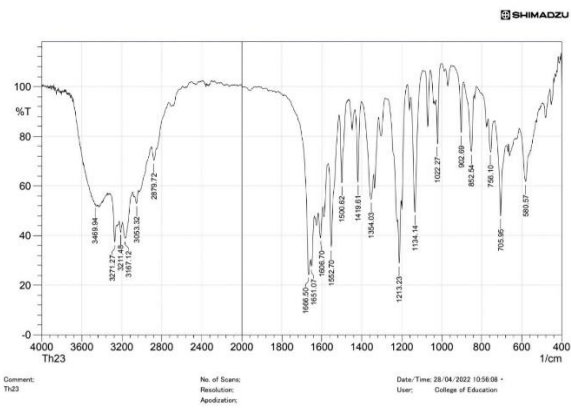


Fig (3): Infrared spectrum of the complex [ Ni (HMEBH)Cl] Cl

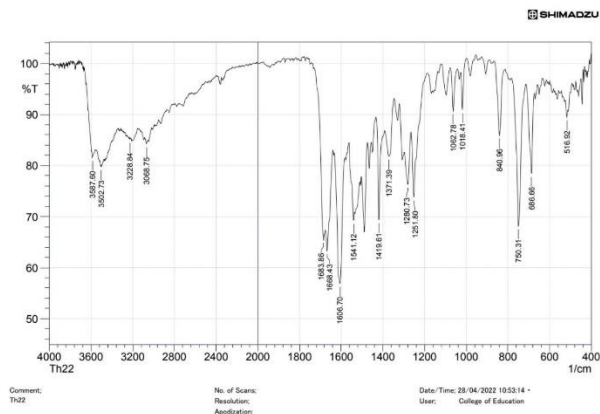


Fig (7): Infrared spectrum of the complex [ Hg (HMEBH)Cl] Cl

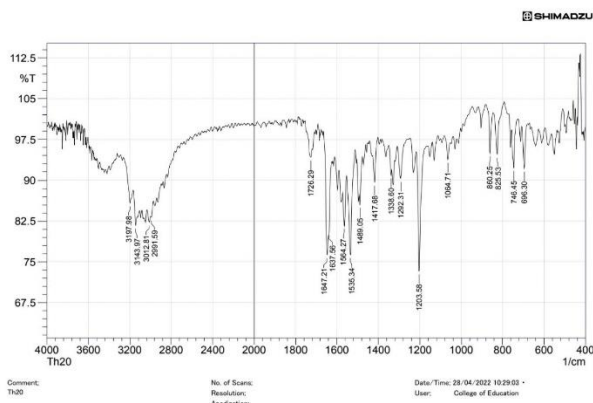


Fig (4): Infrared spectrum of the complex [ Cu (HMEBH)Cl] Cl

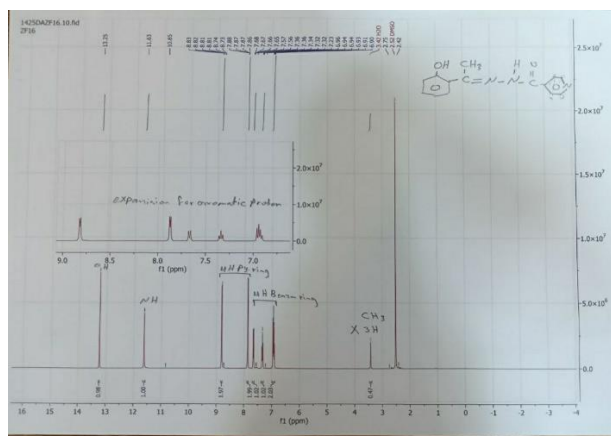


Fig (8) 1H NMR spectra of the ligand (HMEBH)

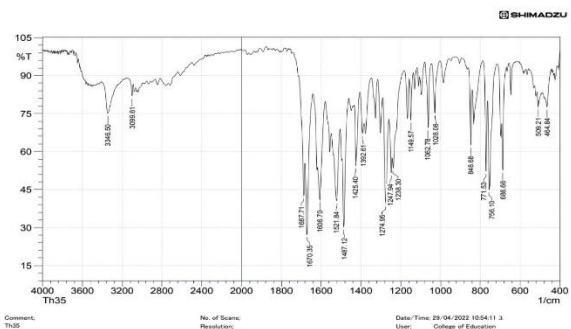


Fig (5): Infrared spectrum of the complex [ Zn (HMEBH)Cl] Cl

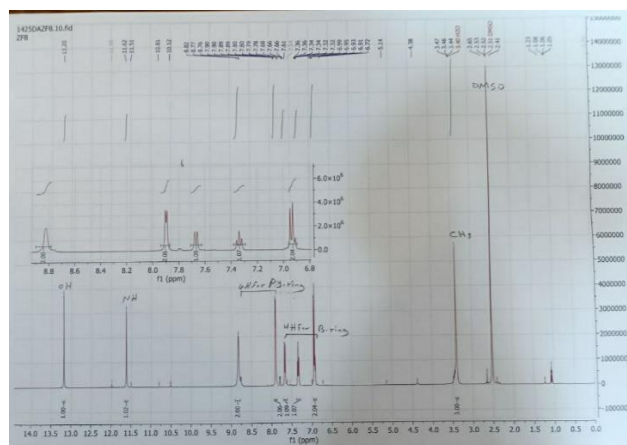
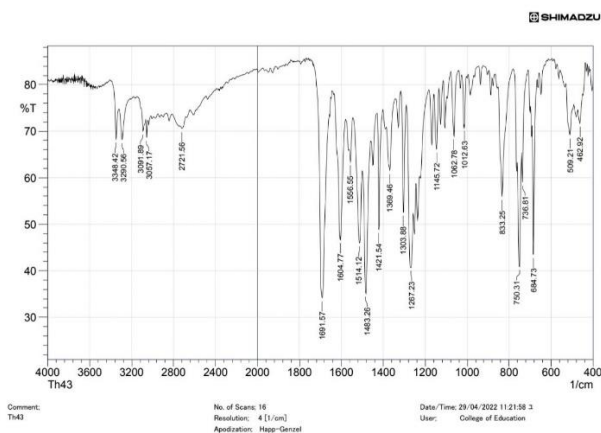


Fig (9) 13C NMR spectra of the complexes [Zn (HMEBH)Cl] Cl



Fig(6): Infrared spectrum of the complex [ Cd (HMEBH)Cl] Cl

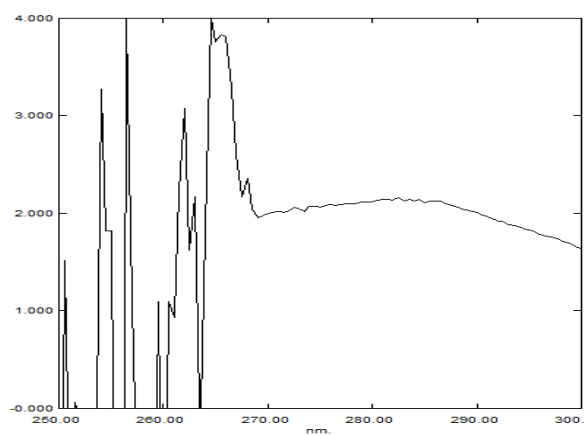


Fig (10): Electronic spectra of the ligand (HMEBH)

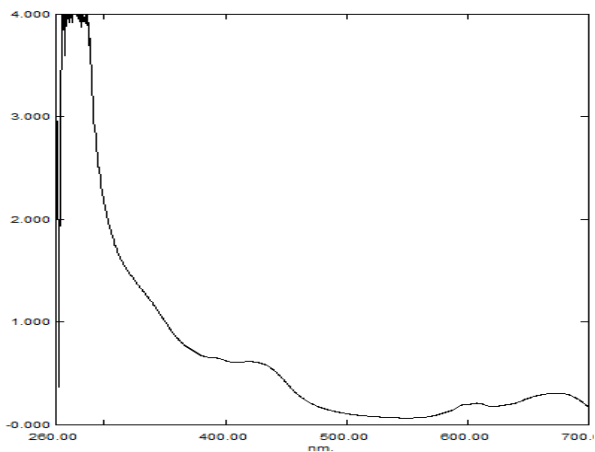


Fig (11): Electronic spectra of the complex [Co (HMEBH)Cl] Cl

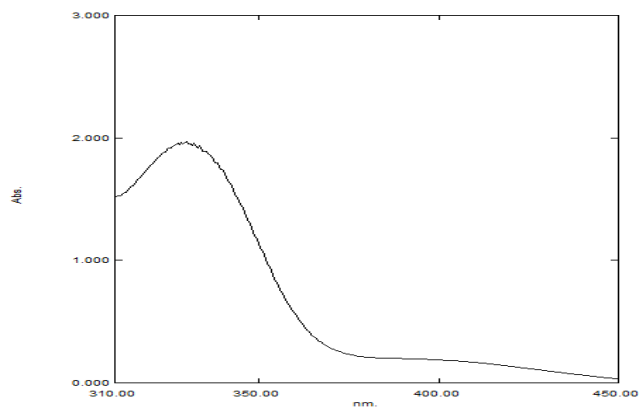


Fig (15): Electronic spectra of the complex [Cd (HMEBH)Cl] Cl

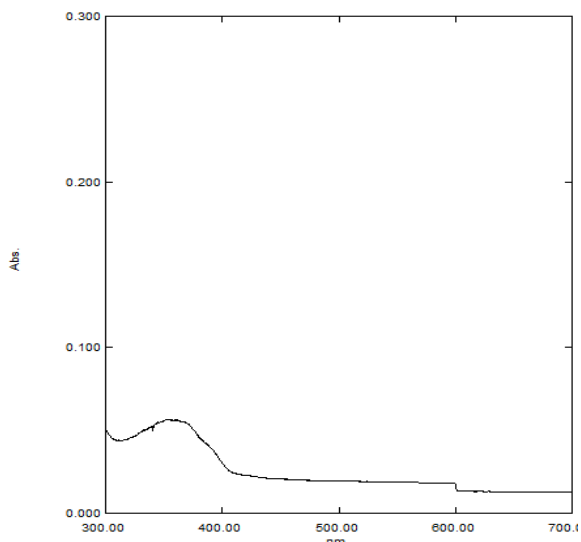


Fig (12): Electronic spectra of the complex [Ni (HMEBH)Cl] Cl

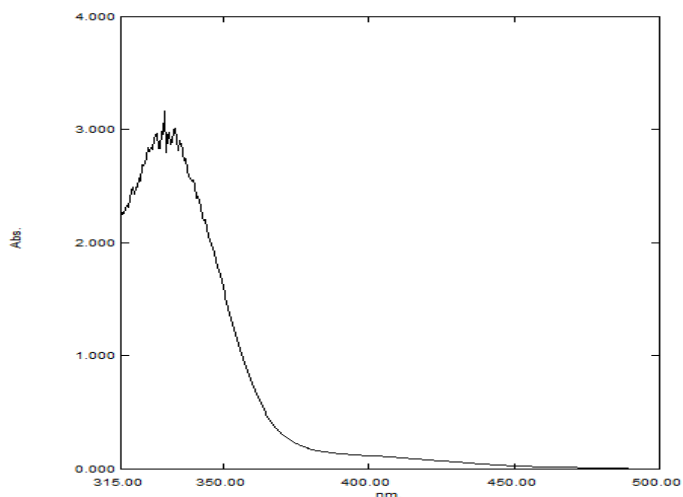


Fig (16): Electronic spectra of the complex [Hg (HMEBH)Cl] Cl

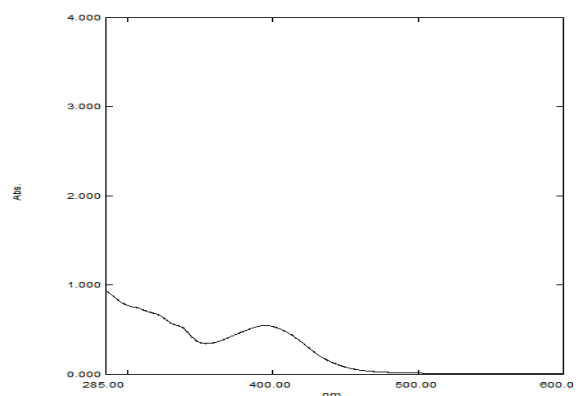


Fig (13): Electronic spectra of the complex [Cu (HMEBH)Cl] Cl

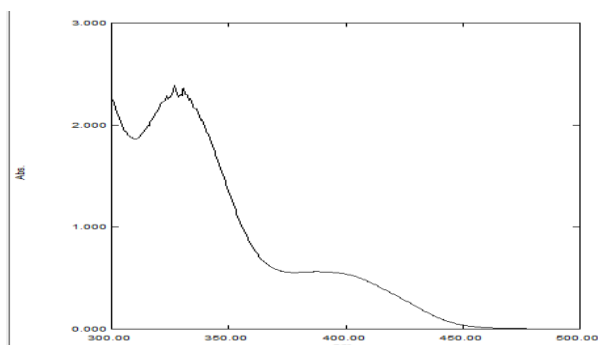


Fig (14): Electronic spectra of the complex [Zn (HMEBH)Cl] Cl

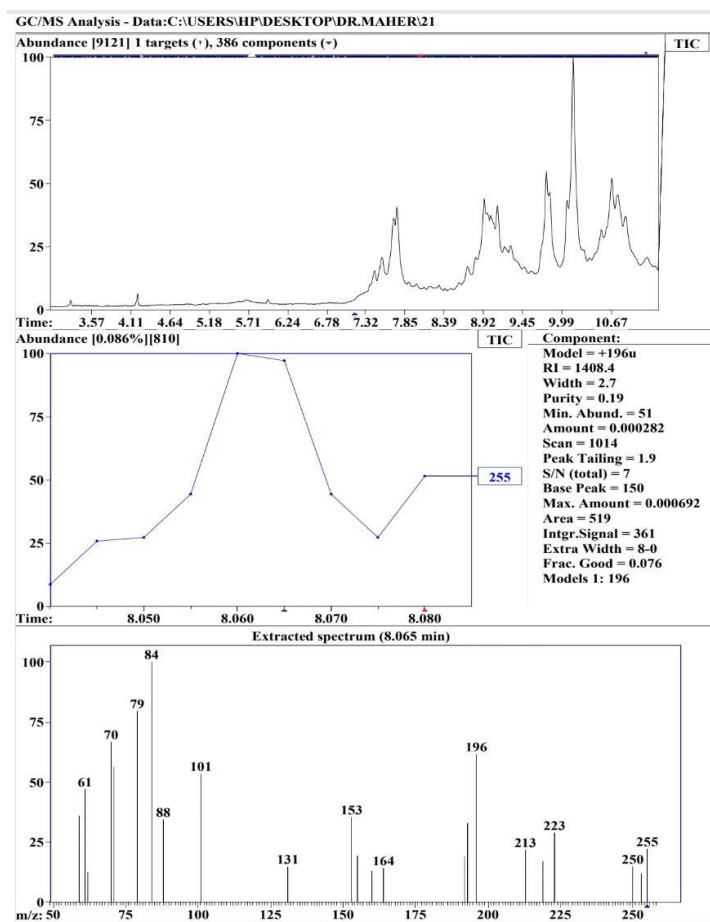


Fig (17): GC-Mass Spectral data of the Ligand (HMEBH)

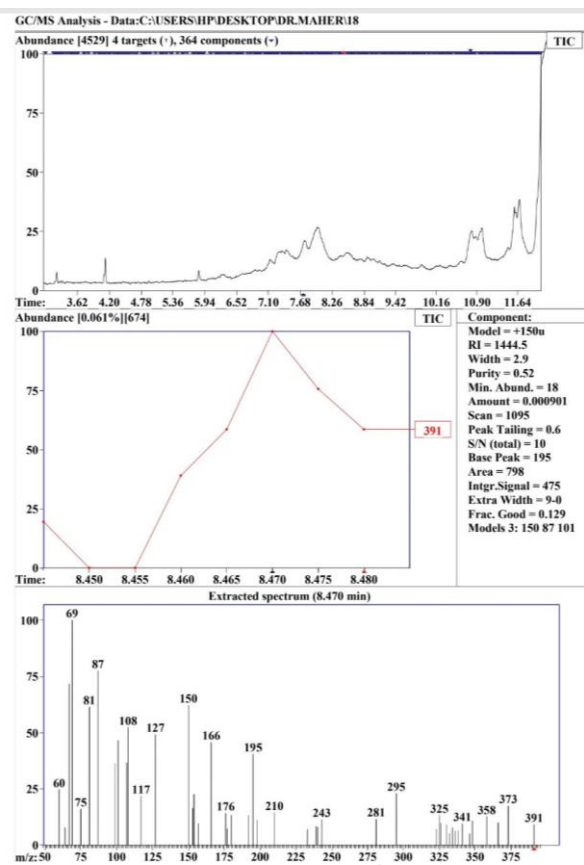


Fig (18): GC-Mass Spectral data of the complexes  $[Zn(HMEBH)Cl]Cl$

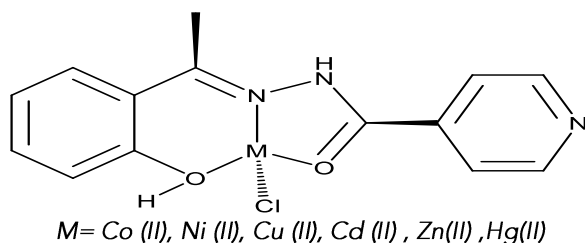


Fig (19): The suggested structure of metal (II) complexes

## 6. Conclusions

From the different physicochemical studies and various spectral measurements, it is concluded that the ligand, which gives very stable complexes with the various metal ions used in that work, acts as neutral tridentate, coordinating through azomethine nitrogen, and carbonyl oxygen and phenolic oxygen atoms. Thus, neutral tetra coordinated complexes were suggested and might have tetrahedral structure. fig (19)

## 7. Acknowledgments

The authors are thankful to Department of Chemistry, College of Education for Girls, University of Mosul, for the facilities provided to carry out the research in chemistry laboratories.

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