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New Metal(II) Complexes of 2-Hydroxy-N-(2-Hydroxynaph Thalene-1-yl) Methylene Benzohydrazide: Synthesis and Spectroscopic Studies

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Abstract

The study includes the preparation of complexes Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) with Schiff base ligand ($HNMBH_2$) which is derived from the condensation reaction of 2-hydroxybenzohydrazide with 2-Hydroxy-1-naphthalene carboxaldehyde. The properties of which were characterized by infrared, magnetic measurements, molar conductivity measurements, electronic spectra, nuclear magnetic resonance spectra of ^{1}H and^{13} C, and gas chromatography-mass spectrometry. It is found that the ligand acts as neutral tridentate to give high-stability mononuclear complexes that have a tetrahedral or square planar structure.

Key words: hydrazides, benzohydrazide complexes, Schiff base, transition and non-transition elements.

Introduction

Hydrazones are an important class of organic compounds [1] and they are azomethine compounds that contain the reactive structural unit [2] azomethine ($\rangle C=N-N$) [3] . These compounds have basic properties due to the presence of the pair electrons on the nitrogen atom, as well as the double bond of the azomethine group [4] . Because of the ability of hydrazones to react with electrophilic and nucleophilic groups, this led to their use in the preparation of many organic compounds, especially heterocyclic compounds [5] ,which have proven effective in many pharmaceutical applications. [6] ,agricultural [7] ,and biological [8,9] as it is included in the treatment of tuberculosis [10,11] ,the treatment of cancerous tumors, and the expansion of constricted blood vessels [12].Hydrazones are prepared from the condensation reaction between hydrazide and aldehyde or ketones. where the oxygen atom in the carbonyl group in the carbonyl compound is replaced by the functional group (HN−NH_2−) linked to the hydrazide.[13]

The hydrazones derived from acid hydrazides are polydentate ligands of the most prominent ligands used in coordination chemistry, as they enter into the preparation of a large number of complexes with metal ions in general and transition elements in particular. Through atoms with high electrical negativity such as oxygen and sulfur, and then the formation of complexes with different structures and multiple uses.[14]

Hydrazonate has received great attention for its effectiveness against stopping the division of cancer cells[15], and for being anti-tumors. As well as its effectiveness against leukemia if the chelating compounds are stable with the transition metals present in the cell[16]. Hydrazones were used as analytical reagents, in addition to using them to determine some elements by spectroscopic methods.[17,18]Also, hydrazones have been used as colorants for polymers, stabilizers and initiators of the polymerization process, and anti-oxidants. [19]

They also work as catalysts in organic reactions, as well as in the detection, isolation and identification of carbonyl-containing compounds.[20]

In this research, the new Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes, were prepared with Schiff base ligand which is derived from 2-hydroxy benzohydrazide and 2-hydroxy -1-naphthalenecarboxaldehyde and characterized with chemical , physical and spectral methods.

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 spectrophtometric method using atomic absorption spectroscopy Analytik Jena G mbH-nov AA350-Flame Atomic Absorption Spectrometer, at College of Agriculture and Foresty,University of Mosul.Molar conductivity of the prepared complexes were measured for 10^{-3} M solution in dimethyl formamide (DMF) at 25℃ using HANNA EC214 conductivity meter instrument. Magnetic susceptipility of the prepared complexes were done at 25℃ using Sherwood Sientific (MSB-MK) Magnetic Suceptibility Balance at College of Education of Pure Sciences, Univercty of Tikrit .

In frared absorption spectro of the Schiff base ligand and complexes were recored on Shimadzu FT-IR84005 spectrophotometer , Japan at College of Science , Universty of Salahuddin in ware number range 400-4000 cm^{-1} . Shimdzu UV-Vis spectrophotometer , Uv-1800 was used for electronic spectra measurment for 10^{-3} M solution of the ligand and its complexes in DMF at 25℃ in the ware length rang 190-1100 nm uusing 1 cm qurrts cell .^{1} HNMR and ^{13}CNMR specter of the ligand and complex (4) were recorded at room

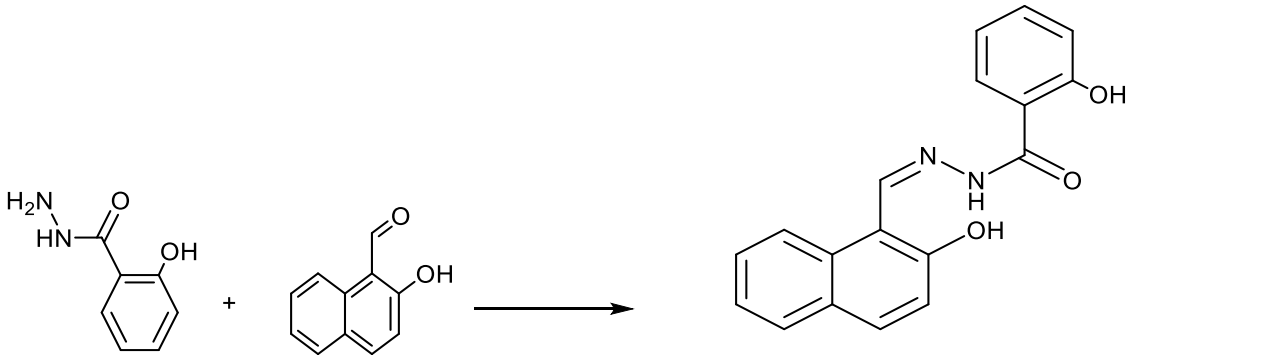
teperature with Bruker DRX system at 400 MHz , using tetamethyl saline (TMS) an internal standard in dimethylsulfoxide (DMSO-d^6) at Colleg of Science , Uinevercty of Basra .

GC-MS-Qp2010 Ultra Gas Chramotogrophy-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 .

Experimental part

Preparation of the ligand (E) -2-hydroxy-n-((2-hydroxynaphthalen-1-yl)methylene)benzohydrazide

Dissolve (0.003mol, 0.45 g) of 2-hydroxy benzohydrazide in 10 ml absolute ethanol, then add to it a solution consisting of dissolving (0.003mol, 0.51 g) 2-hydroxy-1-naphthalene caroxaldehyde in 10 ml absolute ethanol, the addition being gradually in the form of drops for half an hour with continuous stirring. After completing the addition process, the mixture is heated by heating for 6 hours. The solution is cooled in an ice bath, then the formed precipitate is filtered and washed with cold absolute ethanol several times, then diethyl ether and dried at 50 °C in an electric oven. The precipitate is weighed and the percentage of the product is calculated, and the following equation shows the reaction:



2-hydroxybenzohydrazide 2-hydroxy-1-naphthalenecarboxaldehyd (*E*)-2-hydroxy-*N*'-((2-hydroxynaphthalen-1-yl)methylene)benzohydrazide

preparation of the complexes

The all complexes where prepared by the reaction ligand with metals chloride using the following method:

$(0.003\text{mol},\ 0.92\text{g})$ of the ligand $(HNMBH_2)$ dissolved in 10 ml of hot absolute ethanol is added to it (0.003mol) of metal chloride dissolved in 10 ml of absolute ethanol, and the addition process should continue for $10-20$ minutes with continuous stirring, then the mixture is heated by reflux for a period of $(3-6)$ hours. Then, the mixture is cooled in an ice bath to precipitate, after that colored precipitate is filtered and washed with cold ethanol several times, then diethyl ether and dried in an electric oven at a temperature of $50-60°C$, then weighed and the percentage of the product is calculated.

Results and discussion

The complexes of divalent cobalt, nickel, copper, zinc, cadmium, and mercury were studied and characterized with a Schiff base ligand derived from the reaction of $2-$hydroxybenzohydrazide with $2-$hydroxy$-1-$naphthaldehydecarboxaldehyde, then reacting the prepared ligand with chloride ions mentioned above to form metal complexes in a ratio of $1:1$ (metal: ligand), as shown in the following equation:

$$MCl_2.nH_2O+HNMBH_2 \longrightarrow [M(HNMBH_2)Cl]Cl + nH_2O$$

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

n =0 ,2 or 6

The resulting complexes are all solid, colored and stable substances in the air at room temperature. They are insoluble in water and have low solubility in ethanol and methanol, but they have good solubility in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).

The determination of the elements cobalt (II), nickel (II) copper(II) zinc (II) and cadmium (II) by a spectrophotometric method using an atomic absorption spectrometer, [21] after digesting the complexes with concentrated nitric acid and then completing the volume with deionized water, and solution of the complexes were prepared with concentrations that are within the limits of the concentrations of the standard samples compatible with the linear range of the standard curve of the derived elements. through measuring the molar conductivity of the complexes at a concentration of 10^{-3} M, using dimethyl formamide (DMF) as a solvent and after allowing the solution to be of thermal equilibrium at $25℃$,it was found that it agrees with the structural formulas of the proposed complexes, as 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 obtained as shown in the Table(1).

The determination of coordination sites of the prepared Schiff base ligand in this study and its metal complexes in the infrared spectrum is due to the stretching frequencies of the γ (C=N) γ (C=O), γ(OH) groups and the bending frequency of the δ (OH) phenolic group and γ (M−O), γ (M−N) . Since the position of the location is affected by the coordination of the ligands with the metal atoms of their donor atoms, and the following is an explanation of the changes in the infrared spectra and their complexes. The stretching frequency stretching of the azomethine group γ (C = N) ligand fig(1) appeared in the region (1630cm^{-1}). and when it bonds with the metal ion, it shifted to lower frequencies $(1595-1541\text{cm}^{-1})$, which indicates the coordination of the nitrogen atom of the isomethine group with the metal ions [22,23,24].The spectrum of infrared showed the stretching frequency of the group γ (C=O) at the region $(1687\ \text{cm}^{-1})$, and when forming the complexes, the band appeared at a lower frequency than the ligand band at $(1681-1620\text{cm}^{-1})$, which indicates the participation of the oxygen atom of the carbonyl group in coordination with the metal ions of the prepared complexes. [25,26] The stretching frequency of the hydroxyl group γ(OH) appeared as a

band of the ligand in the region ($3229\ cm^{-1}$) and the band located region ($1388cm^{-1}$) is related to the bending frequency of the phenolic hydroxyl group [27-29] .

The stretching and bending frequency bands of the hydroxyl group appeared in the complexes prepared in the regions that are lower than those observed for the ligand in the range ($3219-3209cm^{-1}$) and ($1292-1236cm^{-1}$), respectively. This confirms the coordination of the metal ions with the oxygen atom of the hydroxyl group. [27,28] As for the stretching frequency of the γ (NH) group in the spectrum of the ligand, it appeared at ($3055cm^{-1}$), and an absorption band appeared at ($1571cm^{-1}$) in the ligand, which is attributed to the bending frequency of the bond (NH). Formation of complexes, which indicates that this group does not participate in coordination with any of the metal ions in the prepared complexes. The stretching frequency of the γ (M-O) , γ (M-N) bonds appears in the lower frequency of the infrared spectrum of complex compounds, and these frequencies are not observed in the ligand spectrum. The infrared spectrum showed the stretching frequency of the γ (M-O) and γ (M-N) groups of the prepared complexes in the region confined between ($540-525cm^{-1}$) ($464-424cm^{-1}$), respectively, and confirms their appearance in the complexes and their non-appearance in the ligand spectrum within the ranges. The above determined on the coordination between the metal ions and the ligand through the phenolic and carbonyl oxygen atoms and the nitrogen of the azomethine group. [30-32] The stretching frequency of γ (M-Cl) appears at ($280-200\ cm^{-1}$) and was not observed in the infrared spectrum of chloride ions that are coordinated with the metal ions located inside the coordination sphere because they are outside the range of the infrared spectrophotometer used. It was concluded that its coordinate from measured the molar conductivity of the prepared complex solutions, as well as based on magnetic and electronic spectra measurements of the prepared complexes. [33,34] Table (2) shows the most important bands of prepared of ligand and complexes

Magnetic susceptibility measurements were carried out at 25°C using Gouy method. The prepared Co (II) tetra coordinate complex showed the value of the magnetic moment (4.32 B.M), where the cobalt ion (II) in the $3d^7$ system has three unpaired electrons, which is higher than the theoretical value (3.87B.M) due to the presence of the second orbital contribution, and this is consistent with the value of the moment magnetic Co(II) with tetrahedral structure. [35,36]

The Ni (II) complex showed diamagnetic properties, due to the absence of any unpaired electron, and this indicates that the complex possesses a square planar structure [37,6]. The Cu(II) complex showed a magnetic moment with a value of (2.00 B.M.) and with the electronic spectrum of the complex, it was clear that it was with a tetrahedral structure . [38,39,40] All Zn(II), Cd(II), Hg(II), complexes are diamagnetic because they have an electron-filled $d10$ orbital and are expected to take the most common tetrahedral structure which is the most common depending on the chemical analysis and other physical measurements.[39,41]

The electronic spectra of the ligand and the complexes were measured at a concentration of 10^{-3} M and a temperature of 25°C, using dimethylformamide (DMF) as a solvent, and the results were obtained as in Table (3). The prepared and appears at a wavelength of 37950 cm^{-1} which is attributed to the chromophore. Ligand showed two main bands, the first bands attributed to the electronic transion ($\pi-\pi^*$) (C=N-NH-CO-) and the second band is attributed to the electronic transition ($n-\pi^*$) and appears at a wavelength of 35149 cm^{-1}, which occurs due to nitrogen and oxygen atoms Fig(10) and when forming complexes, these bands show a displacement towards lower frequencies due to coordination with metal ions. [43,42] .The electronic spectrum of the tetra coordinated Co(II) complex Fig (11) showed an absorption band at ($19920cm^{-1}$) and this band is attributed to the electronic transion

$^4A_2(F)$ $^4T_1(P)$ υ_3 as for the ~~two~~ bind that go back to the two electronic trans missions $^4A_2$ (F) $^4T_1$ (F) υ_2 and $\longrightarrow$

$^4A_2$ (F) $\longrightarrow$ $^4T_2$ (F) υ_1 they lie in ranges that are out of the range of device used for measuring the electronic spectroscopy . The charge is at (29069 cm), which indicates that the cobalt complex has a tetrahedral structure [44.45.36]. As for the Ni(II) complex Fig (12), the electronic spectrum showed that it has an absorption band at (12476 cm^{-1}) returns to electronic transition ^1A_1g ^1A_2g(~~υ_1~~) and a second band at (22551cm^{-1}) attributed to electronic transition ^1A_1g ^1B_1g(~~υ_2~~) , and charge transfer at (30303 cm^{-1}) and the appearance of these bands indicating that this complex has a square planar structure around the nickel (II) ion. [6, 37,46-48]

Cu(II) complex Fig (١٣) showed a wide absorption band in the region (12576 cm^{-1}) this band belongs to the $^2T_2(D)$ $\longrightarrow$ $^2E(D)$ electronic transition and the charge transfer band at (30721 cm^{-1}) , it is in agreement with the magnetic measurements of the complex and with the published research that indicates that it is a tetrahedral structure. [52-50,49] As for the complexes of Zn (II), Cd(II), Hg (II) fig (14), they gave absorption bands of the order of (32786-31645cm^{-1}) and these absorption 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 have d^{10} in the outer valence orbital and the above complexes have taken the structure of a tetrahedral[53-50,40,39].

In this study, ^{1}HNMR, ^{13}CNMR spectroscopy was used to study the structural properties of the ligand and the complex (5) Fig (9) in DMSO-d6 solvent and to verify the correctness of its chemical formula. The ligand spectrum showed the aromatic rings protons in the form of double signal at (δH7.06 ppm 2H) It belongs to two protons, as well as a triple signal (δH7.47 ppm1H) due to one proton and a double signal H7.82ppm1H) that belongs to one proton of the aromatic ring. A double signal appeared at (δH 7.34ppm1 H) that belongs to

one proton and a double signal at (δH7.60 ppm2H) belongs to two protons, as well as two triple signals at (δH 7.51ppm1H) (δH 7.9ppm1H) that belongs to two protons, and the spectrum gave double signal at (δh8.03ppm1H) belongs to one proton of the two naphthalene rings. The spectrum of the ligand also showed a single signal at (δH9.03ppm1H) belonging to the azomethine group proton and two single signals at (δH 10.06ppm1H)(δH 11.07ppm1H) belonged to two protons of two phenolic hydroxyl groups, and finally a single signal appeared at (δH 12.76ppm1H) belonging to the proton of the NH group.

The nuclear magnetic resonance spectrum of the carbon $^{13}C-\{^{1}H\}$NMR for the ligand measured in DMSO-d6 solvent and shown in Fig (8) clearly showed the sign as of the prepared Schiff base ligand and the number of carbon atoms present in it according to the proposed formula, where the spectrum showed six signals attributed to the carbon atoms for the aromatic ring at chemical shift (116.20ppm,117.77ppm,121.46ppm,129.29ppm

,133.40ppm,148.15ppm),respectively. The spectrum also showed belongs to the carbon atoms of the naphthalene ring at the chemical shift of (109.05, 119.37, 119.64, 124.05, 128.23, 128.29, 129.41, 131.16, 134.50, 164.41) and the spectrum also showed a chemical shift of the carbon atom of the carbonyl group at (159.22) ppm) and at chemical shift. (158.15 ppm) belongs to the carbon atom of the isomethine group.

The mass spectrum of the complex [Ni(HNMBH_2)Cl]Cl in Fig (15) showed a peak at 435 m/2, corresponding to the theoretically calculated mass of (C_{18} H_{14} N_2O_3 Ni Cl_2) 435 m/2.

Conclusions

From the various physical and chemical studies and various spectroscopic measurements, it was concluded that the ligand, which gives highly stable complexes with different metal ions used in this research, acts as a neutral tridentate, in coordination

through azomethine nitrogen, carbonyl oxygen and phenolic oxygen. Thus, the structure of all tetrahedral symmetric complexes with a tetrahedral structure was proposed, as in Fig (16). Except for the nickel complex that takes the structure of a square planar as in Fig (17)

Acknowledgements

The authors thank the Department of Chemistry, College of Education for Girls, University of Mosul, for the facilities provided to conduct research in chemistry laboratories.

Table1:Analytical and some physical data of the $HNMBH_2$ ligand and its complexes

No.	Chemical formula	Colour	M.P°C	Yield %	M% Calc./(Found)	Λ_M(DMF) (cm^2 .ohm^{-1}.$mole^{-1}$)
	$HNMBH_2$	Light yellow	269-270	87	—	—
1	[Co($HNMBH_2$) Cl]Cl	Orange	313 d*	74	١٣.٥١ 13.47	٨٥.1
2	[Ni($HNMBH_2$)Cl]Cl	Light green	311 d	79	—	٧٩.3

3	$[Cu(HNMBH_2)Cl]Cl$	Green	303–304	80	١٤.٤٢ 14.37	٦٧.2
4	$[Zn(HNMBH_2)Cl]Cl$	Light yellow	312 d	69	١٤.٧5 14.84	٨٢.6
5	$[Cd(HNMBH_2)Cl]Cl$	Orange	316 d	82	—	٧١.1
6	$[Hg(HNMBH_2)Cl]Cl$	Light yellow	265–268	86	—	٦٥.5

d*= decomposition temperature.

Table 2 : selected Infrared band of the ligand and its complexes (cm^{-1})

NO.	Chemical formula	υ(C=O)	υ (C=N)	υ(NH)	δ(NH)	υ (N–N)	(υOH)	δ(OH)	υ (C=C)	υ(M–N)	υ (M–O)
	$(HNMBH_2)$	١٦٨7	1630	٣٠٥٥	١٥٧١	1031	٣٢٢٩	1305	١٦٠٢	----------	----------
1	$[Co(HNMBH_2)Cl]Cl$	١٦٨١	١٥٩٥	٣٠٤٩	١٥٦٢	١٠٣٧	٣٢13	١٢٩٢	١٦٠٤	٤٦٤	٥٢٨
2	$[Ni(HNMBH_2)Cl]Cl$	١٦٢٠	١٥٩٥	٣٠٤٧	١٥٥٨	١٠٣٥	٣٢١٩	١٢٨٨	١٦٠٤	٤٣٦	٥٤0
3	$[Cu(HNMBH_2)Cl]Cl$	1672	1541	٣٠٣٩	1511	٩٧٢	٣٢٠٩	1247	١٦٠٦	٤٦٠	٥٢٥

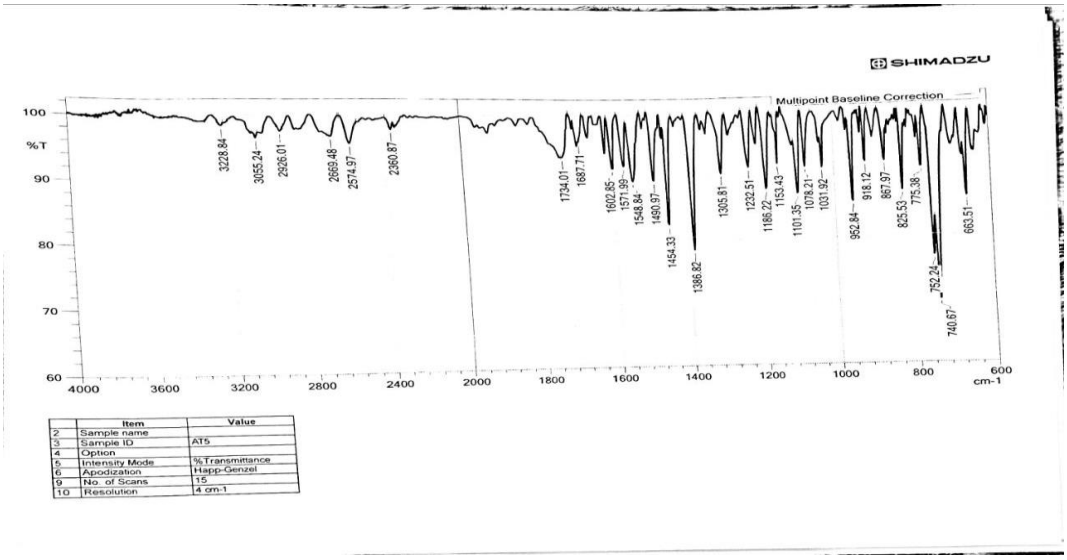
4	[Zn(HNMBH$_2$)Cl]Cl	١٦٤٥	١٥٧٧	٣٠٤1	١٥٦٠	٩٥٥	٣٢٠٩	1238	١٦٠٦	٤٦١	٥٢٦
5	[Cd(HNMBH$_2$)Cl]Cl	١٦٤3	١٥٧5	٣٠٣٩	١٥48	٩٥5	٣٢٠٩	1238	١٦٠٨	٤٣٠	٥٢٦
6	[Hg(HNMBH$_2$)Cl]Cl	١٦٤١	١٥77	3061	١٥50	٩٥٥	٣211	١٢٣٦	١٦٠٢	٤٢٤	٥٢٧

No.	Chemical formula	Absorption region (cm^{-1})	Possible assignments	μ_{eff} (B.M.)	Geometry
	$HNMBH_2$	35149 37950	$n \longrightarrow \pi*$ $\pi \longrightarrow \pi*$	———	———
1	[Co($HNMBH_2$)]Cl_2	19920 29069	$^4A_2$ (F) $\rightarrow$ $^4T_1(v_3)$ Charge transfer(C.T)	4.32	T_d^*
2	[Ni($HNMBH_2$)] Cl_2	12476 22551 30303	$^1A_2g \longrightarrow {}^1A_2g\ \gamma_1$ $^1A_2g \longrightarrow {}^1B_1g\ \gamma_2$ Charge transfer(C.T)	diamagnetic	D4h*
3	[Cu ($HNMBH_2$)] Cl_2	12576 30721	$^2T_2$ (D) $\rightarrow$ ^2E (D) Charge transfer(C.T)	2.00	T_d
4	[Zn($HNMBH_2$)] Cl_2	31847	Charge transfer(C.T)	diamagnetic	T_d

5	[Cd ($HNMBH_2$)] Cl_2	32786	Charge transfer(C.T)	diamagnetic	T_d
6	[Hg ($HNMBH_2$)] Cl_2	31645	Charge transfer(C.T)	diamagnetic	T_d

Table3:Magnetic moment, absorption data, band assignments and structures of the $HNMBH_2$ ligand and complexes .

T_d^* = Tetrahedral Geometry , $D4h^*$= Square Planar



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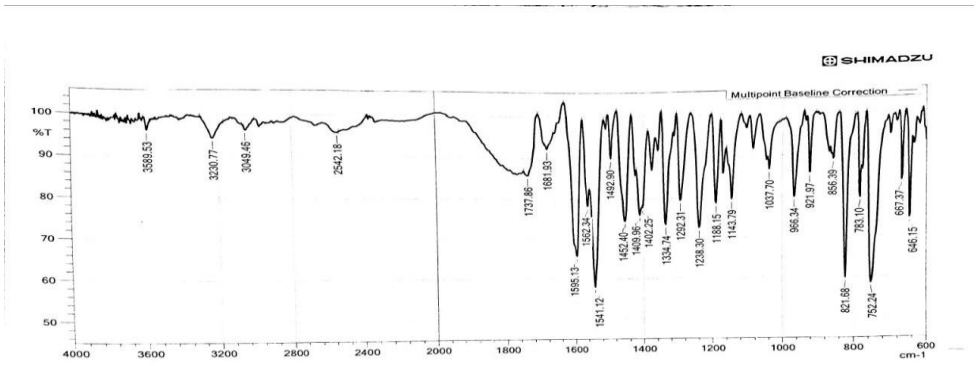
3	Sample ID	AT5
4	Option	
5	Intensity Mode	%Transmittance
6	Apodization	Happ-Genzel
9	No. of Scans	15
10	Resolution	4 cm-1

Fig(1): Infrared spectrum of the ligand ($HNMBH_2$)



	Item	Value
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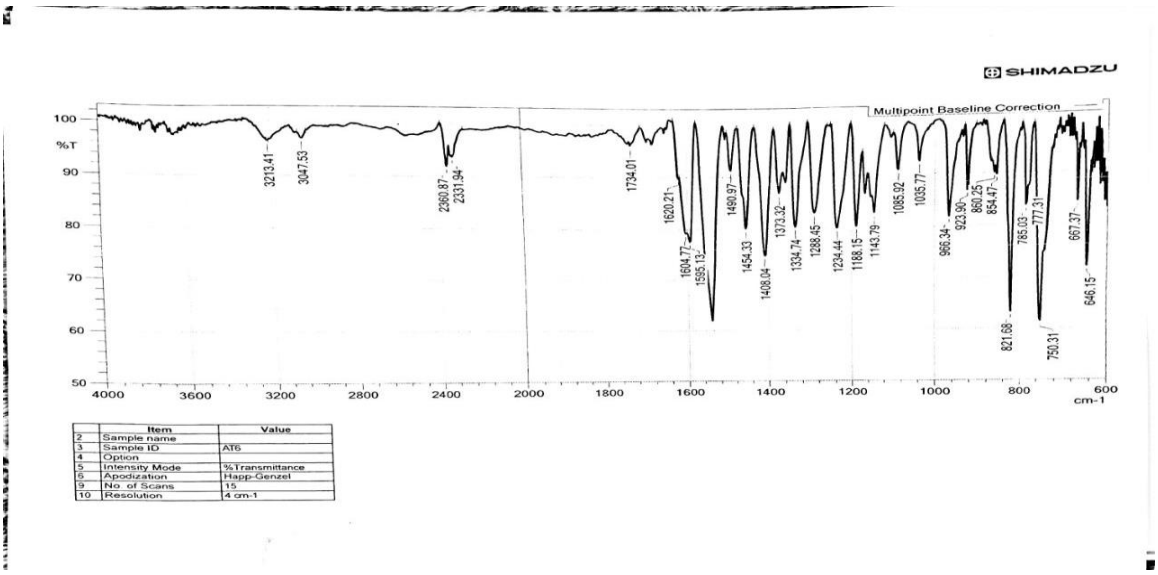
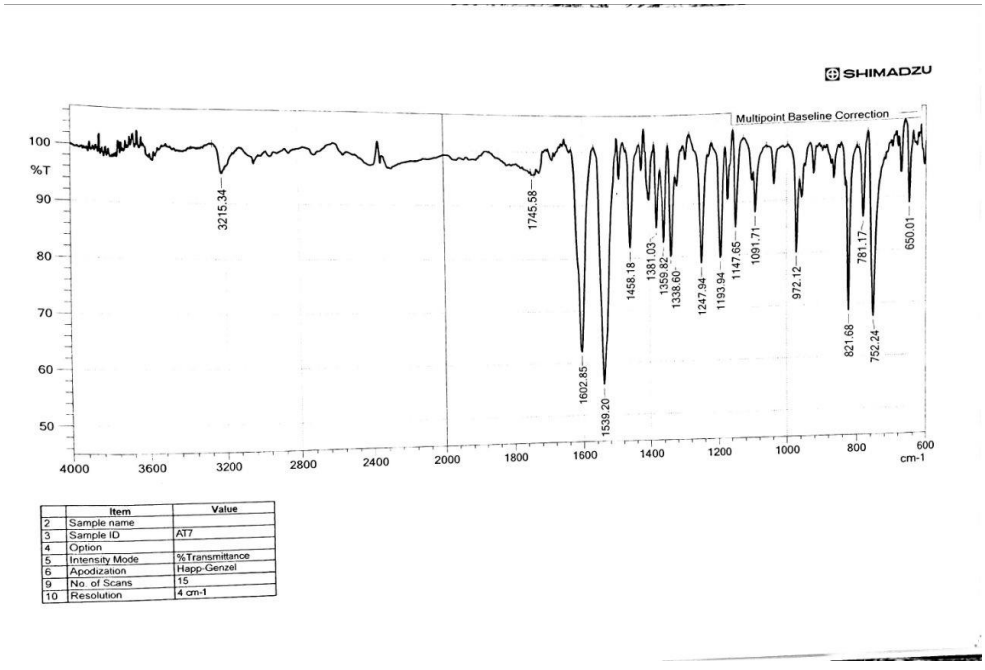
3	Sample ID	AT3
4	Option	
5	Intensity Mode	%Transmittance
6	Apodization	Happ-Genzel
9	No. of Scans	15
10	Resolution	4 cm-1

Fig(2): Infrared spectrum of the complex [$Co(HNMBH_2)Cl]Cl$



	Item	Value
2	Sample name	
3	Sample ID	AT6
4	Option	
5	Intensity Mode	%Transmittance
6	Apodization	Happ-Genzel
9	No. of Scans	15
10	Resolution	4 cm-1

Fig(3): Infrared spectrum of the complex $[Ni(HNMBH_2)Cl]Cl$



	Item	Value
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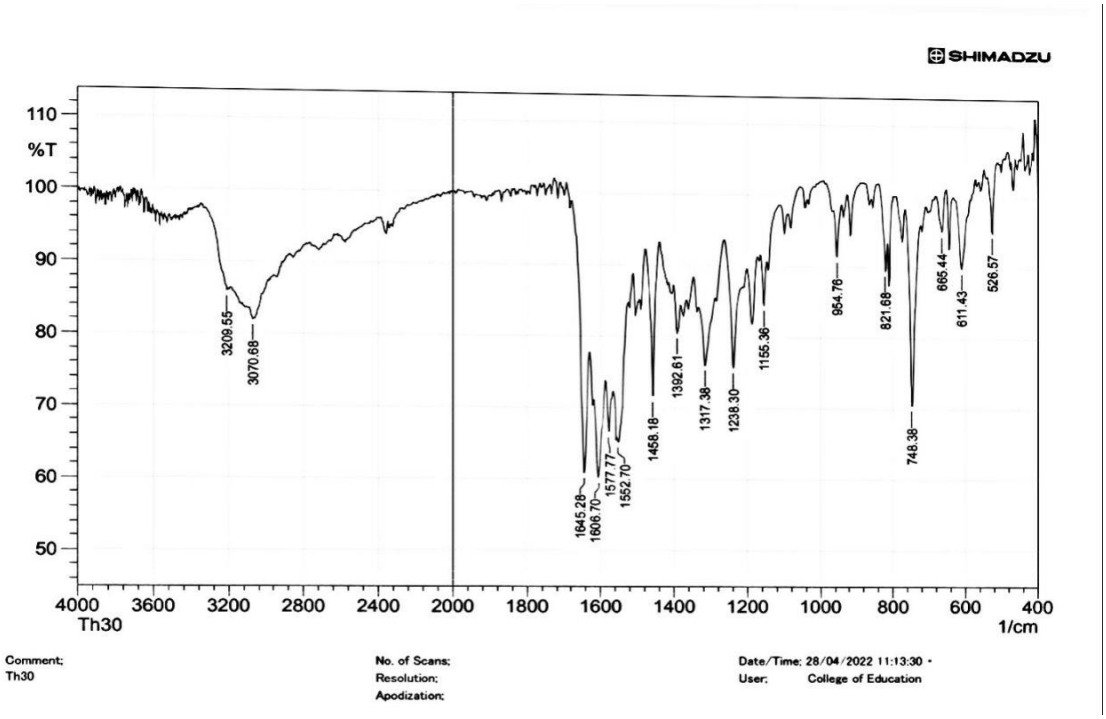
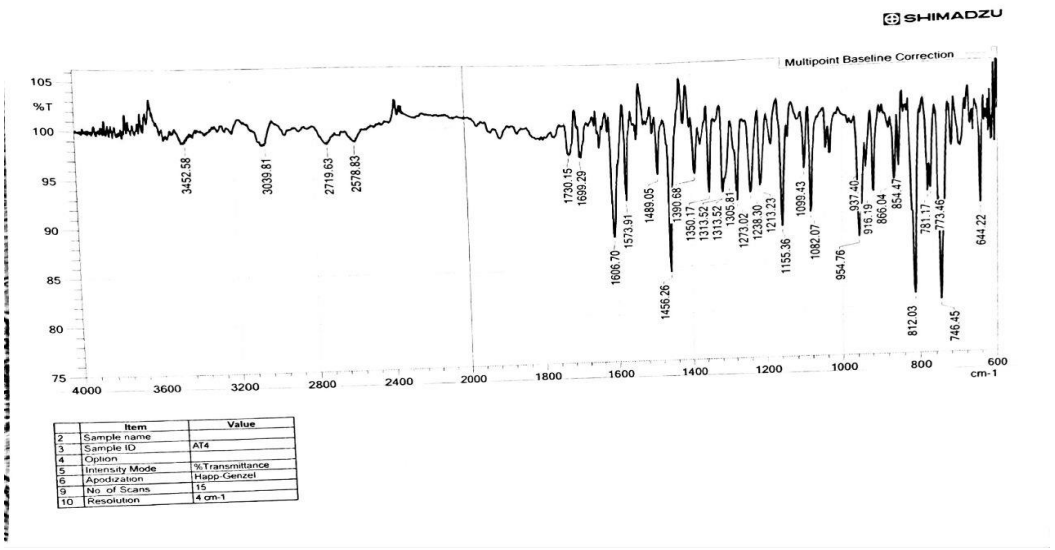
3	Sample ID	AT7
4	Option	
5	Intensity Mode	%Transmittance
6	Apodization	Happ-Genzel
9	No. of Scans	15
10	Resolution	4 cm-1

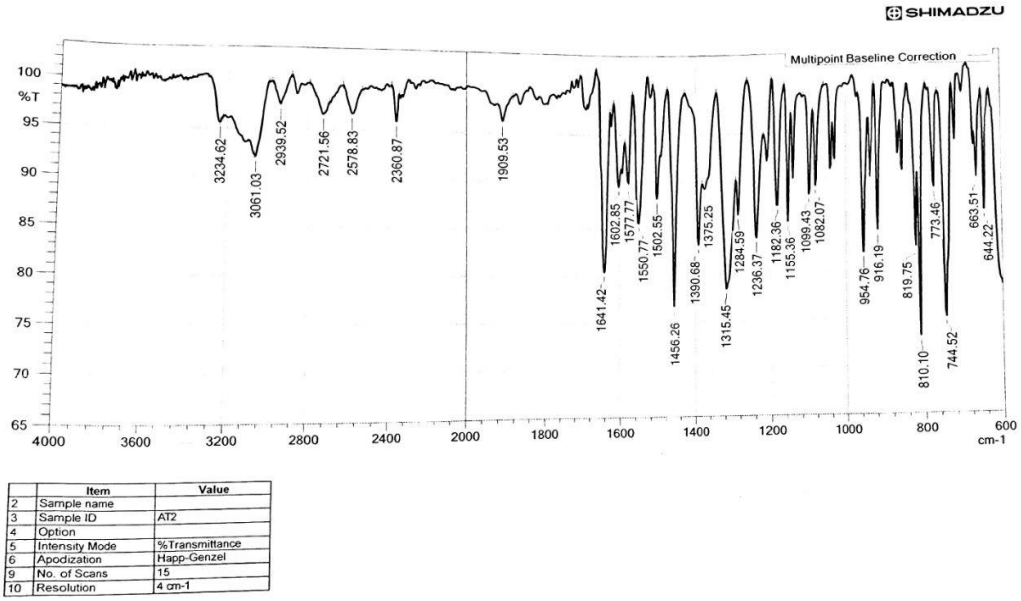
Fig(4): Infrared spectrum of the complex $[Cu(HNMBH_2)Cl]Cl$



Fig(5) : Infrared spectrum of the complex $[Zn(HNMBH_2)Cl]Cl$



Fig(6): Infrared spectrum of the complex [Cd(HNMBH$_2$)Cl]



	Item	Value
2	Sample name	
3	Sample ID	AT2
4	Option	
5	Intensity Mode	%Transmittance
6	Apodization	Happ-Genzel
9	No. of Scans	15
10	Resolution	4 cm-1

Fig(7) : Infrared spectrum of the complex [Hg(HNMBH$_2$)Cl]Cl

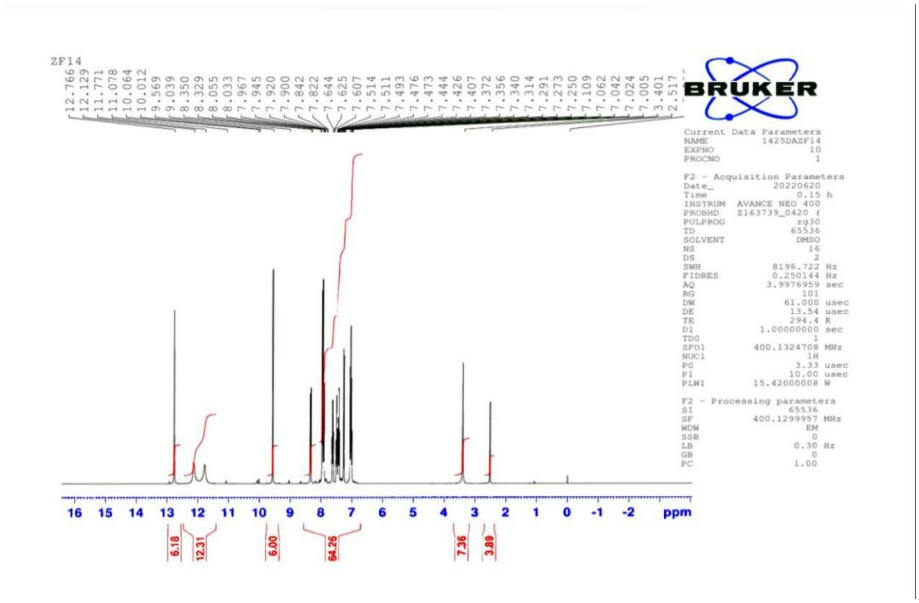


Fig (8)^{1}HNMR spectra of the ligand (HNMBH$_2$)

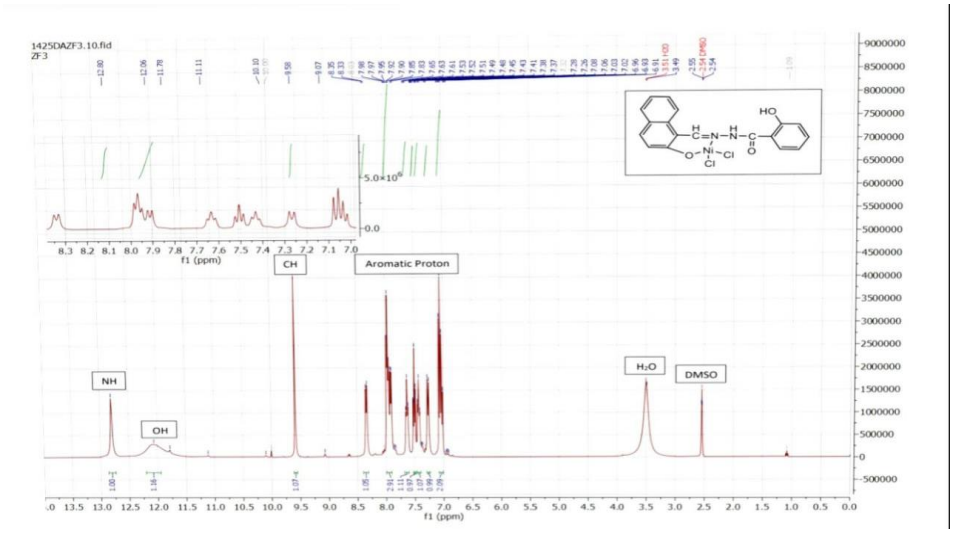


Fig (9)^{13}CNMR spectra of the complexes [Hg(HNMBH$_2$)Cl]Cl

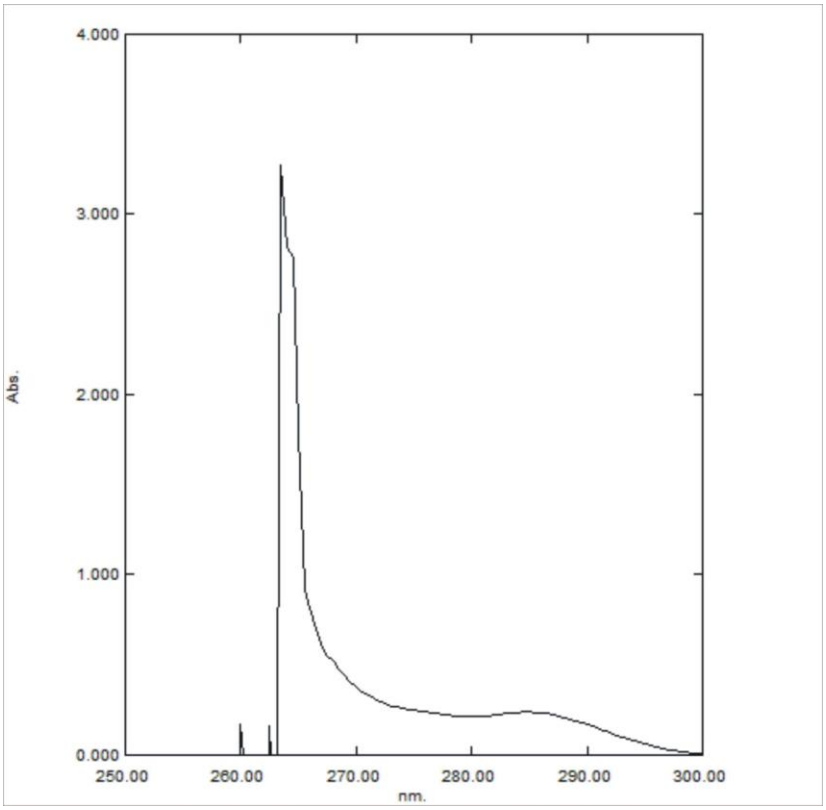
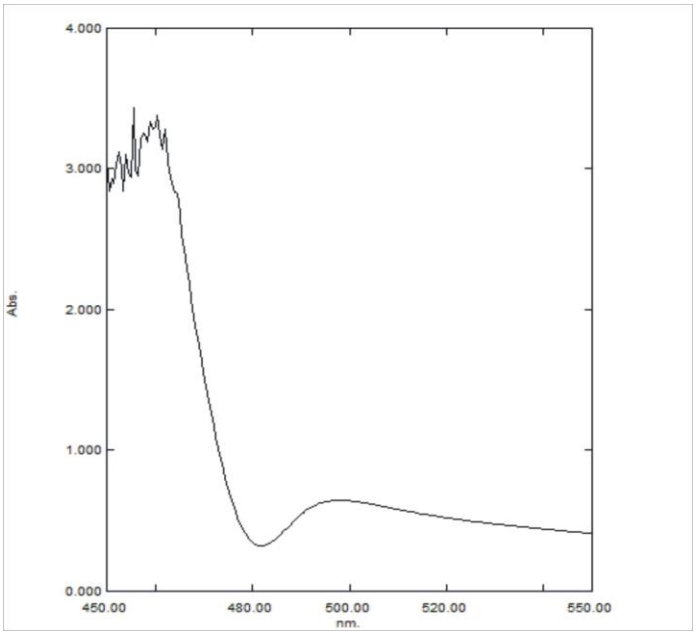
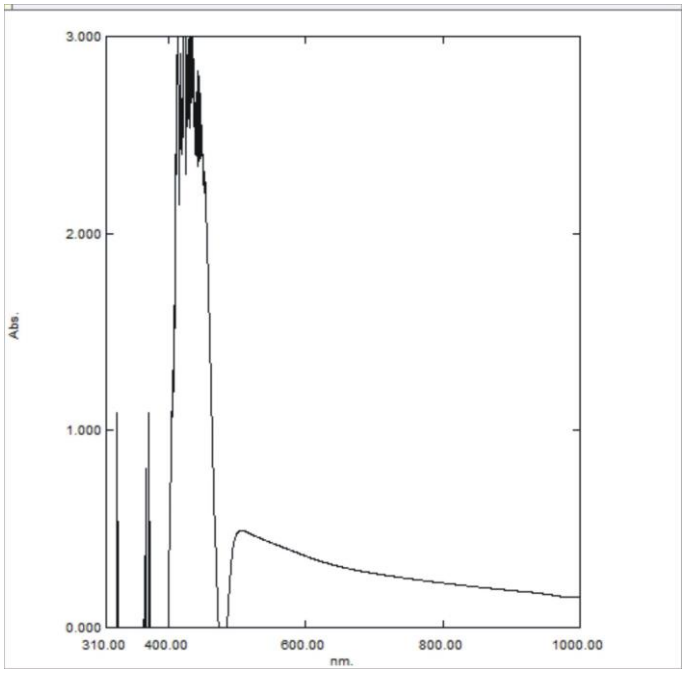


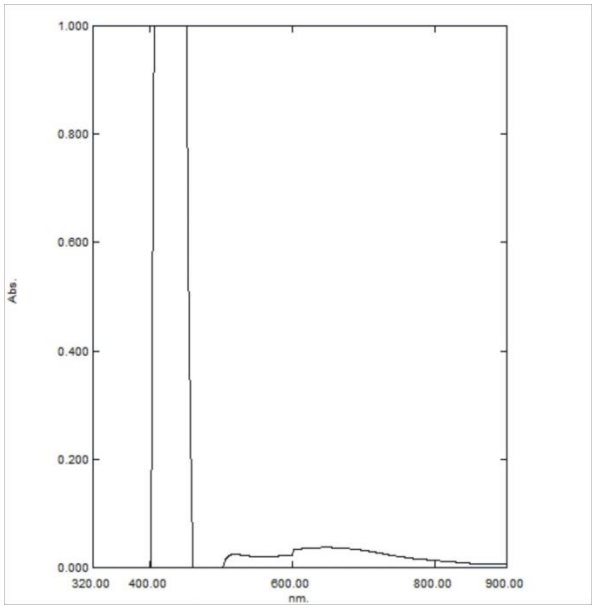
Fig (10): Electronic spectra of the ligand ($HNMBH_2$)



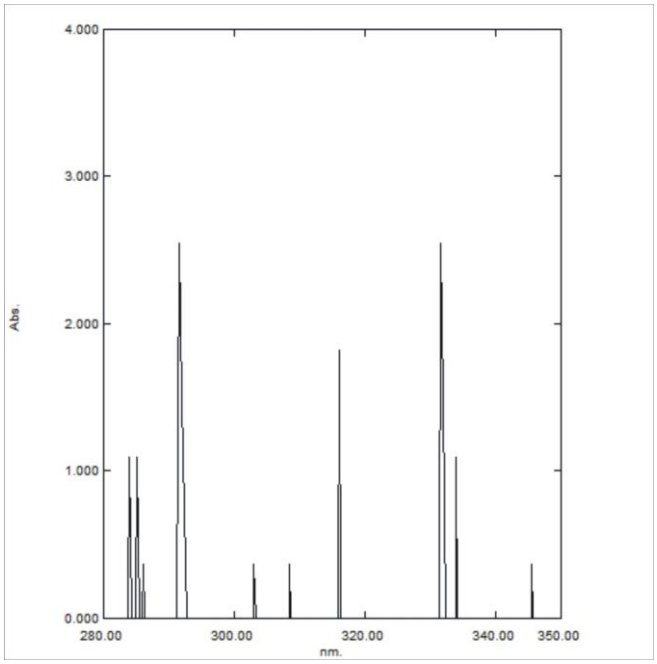
Fig(11) :Electronic spectra of the [Co(HNMBH$_2$)Cl] complex



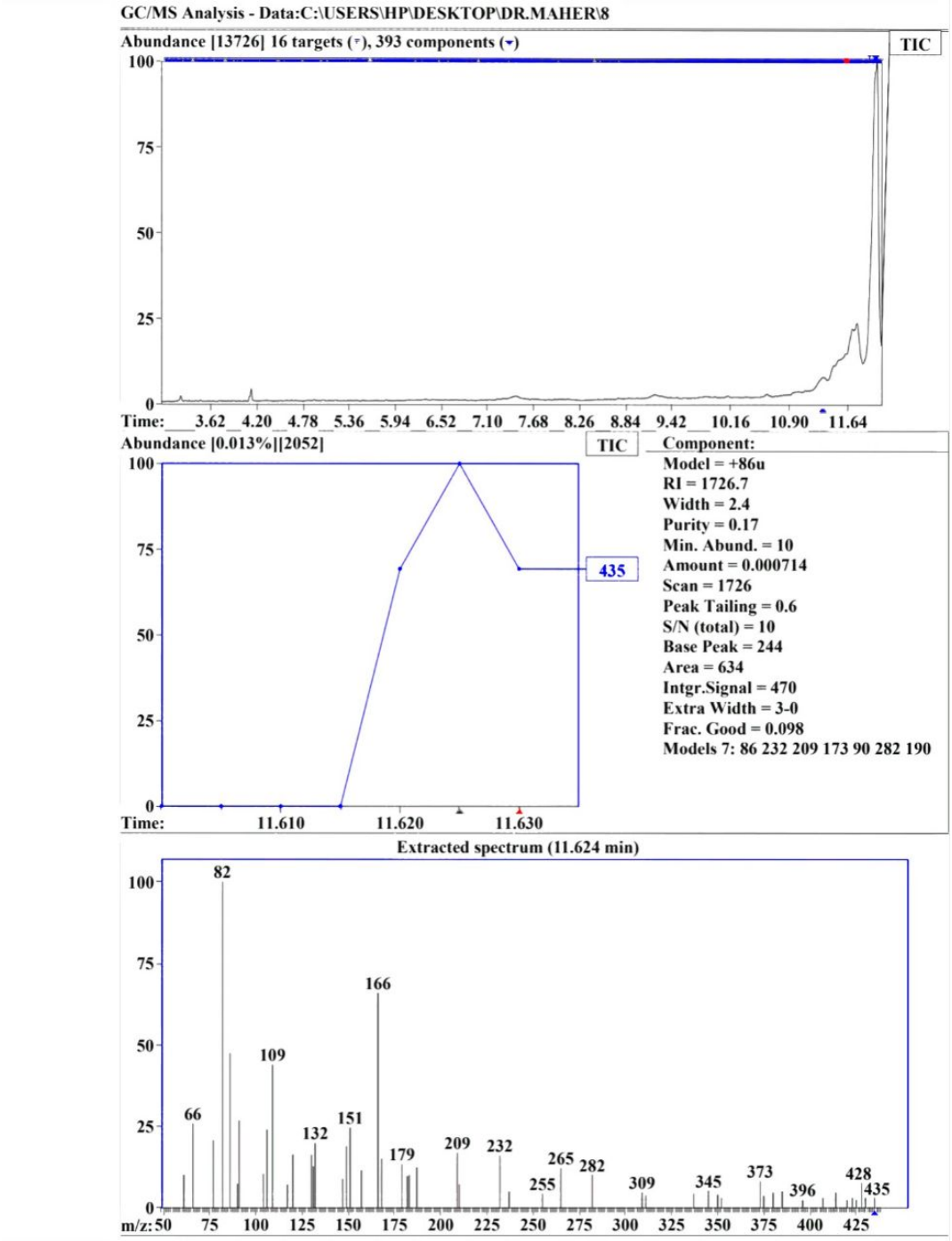
Fig(12): Electronic spectra of the [Ni(HNMBH$_2$)Cl] complex



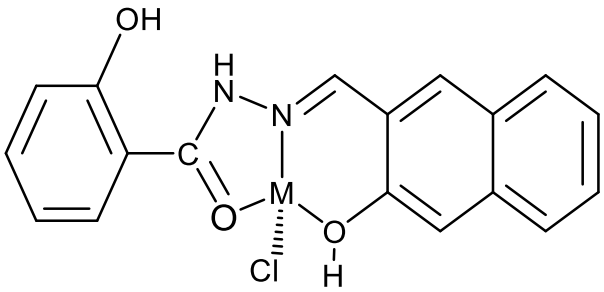
Fig(13) :Electronic spectra of the [Cu(HNMBH$_2$)Cl] complex



Fig(14):Electronic spectra of the [Hg($HNMBH_2$)Cl] complex

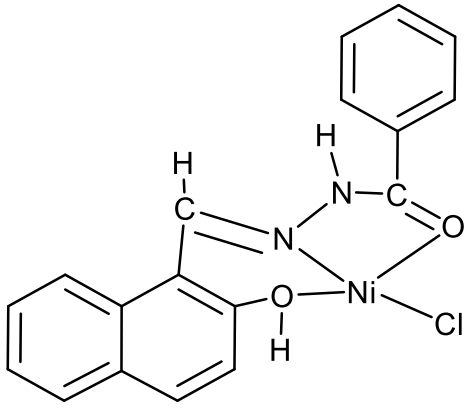


Fig(15) : GC–Mass Spectral data of the complexes [Ni(HMEBH)Cl]Cl



M= Co(ll),Cu(ll) , Cd(ll) , Zn(ll) ,Hg(ll)

Fig(16) :The suggested structure of metal(II)complexes(Td)



Fig(17) : The suggested structure of Ni(II) complexe (D_{4h})

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