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Synthesis and Spectral Study of 2-(1-hydrazonoethyl) Pyridine Ligand and Their Complexes with Some Transition Metal (II)

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Abstract

In this study, new novel[APH=2-(1-hydrazonoethyl)pyridine] ligand; which have contained hydrazone group, and their transition metal complexes of [NiII, , ZnII and CdII] were synthesized.The (APH) ligand was synthesized by condensation of 2-Acetyl pyridine with hydrazine monohydrate, and the reaction of (APH) ligand with metal ions ratio of (2:1) respectively, were formed a mononuclear complexes with a metal(II) ions of types [M(APH)2]Cl2and [$Ni(APH)_2Cl_2$] when [M= NiII, ZnII, CdII].The ligand and their complexes were characterized and study on the basis of FT-IR and U.V.–visible. Some physical properties and spectral data for ligands and their complexes are given in Table 1 and 2.

Keywords : metal complexes ; (APH) ; 2-Acetyl pyridine .

1. Introduction

Cobalt thiosemicarbazone complexes exhibit interesting biological properties specially anti-proliferative effects. For instance, furane containing cobalt complexes have demonstrated potent cytotoxicity against the growth of leukemias, lymphomas, human lung, colon, ovary and uterine carcinoma cell cultures [1]. Some pyridoxal thiosemicarbazone cobalt (III) complexes have shown antileukemic activity toward humancell lines U937 and CEM [2]. In another study, the 9,10-phenanthrenequinone cobaltcomplexes have exhibited antiproliferative activity in the human breast cancer cell-line,T47D [3,4].

Due to the anti-proliferative properties of cobalt-thiosemicarbazone complexes, the production of [55Co](III)-bis-(2-acetylpyridine thiosemicarbazone)

([^{55}Co](III)[APTS]2) was investigated. Co-55 (T1/2=17.53 h) was produced by 150 μA irradiation of a natural nickel target by 15 MeV protons.

Co-incidenceimaging also demonstrated tumor uptake from 21–35 h however at 35 h tumoruptake is more specific and significant[5].

A new heterocyclic hydrazone, 2- acetylpyridine -2- furoylhydrazone (APFH) and its complexes with UO2(II), Th(IV), Co(II), Ni(II), Cu(II), and Zn(II) salts, have been prepared[6].

The structure of these compounds has been characterized by elemental analysis, magneticsusceptibility, molar conductance and spectral (IR, UV, H-NMR) measurements. Thehydrazone ligand APFH behave as uninegative or neutral tridentate ligand, with ONN donoatoms, towards the metal ions depending on the metal salt used. the divalent M(II) ions. Hexagonal bipyramidal structures have been proposed for UO2(II)complexes, and coordination number (10) geometries have been suggested for Th(IV)complexes. Antibacterial activity of the hydrazone ligand and some of its complexes werestudied against gram –positive bacteria: S. aureus and gram-negative bacteria: E. coil[7].

The reaction of zinc chloride with 2-acetylpyridine-4-phenylsemicarbazone and nitrogen–sulphurmonodentate ligands such as thiophene, pyridine, picoline ,aniline and ammonia; yielded five novel mixed -ligand complexes: $Zn(2\text{-}Ac.4\text{-}Psc.Th)Cl_2$,$Zn(2\text{-}Ac.4\text{-}Psc.Py)Cl_2$, $Zn(2\text{-}Ac.4\text{-}Psc.Pi)Cl_2$, Zn(2Ac.4-Psc.An)Cl2 and $Zn(2\text{-}Ac.Psc.Am)Cl_2$. These were characterized by elemental analysis,molar conductivity,1H and ^{13}C-NMR, IR and electronic absorption spectroscopic studies.All the complexes possess tetrahedral geometries. The antimicrobial activities were evaluated against staphylococcus aureus, Bacillus anthracis,Aspergillusnigers andCandida albicans.The result of significant inhibition of growth and proliferation of these microbes by the chelates were obtained particularly with the highest efficiency shown by thethiophene and aniline incorporated complexes[8]

The Schiff base (E)-1-(1-(pyridin-2-yl)ethylidene)thiourea was prepared from 2-acetylpyridine and thiourea by microwave oven method using standard procedure. Anti-inflammatory and CNS activities of (E)-1-(1-(pyridin-2-yl)ethylidene)thiourea were studied using albino rats of both the sexes. Animals were divided into four groups, each consisting of four animals[9].

Nicotinic acid (NA) or vitamin B3 is essential for many biological processes namely for theproduction of energy [10], signal transduction, regulation of gene expression [11] and involvement in thesynthetic pathway of lipids [12]. The oxidation of lipoproteins, low density lipoprotein and very lowdensity lipoprotein, by free radical, particularly superoxide radical ($O_2^{\bullet-}$), causes vascularinflammation, which is involved in the early stage development of atherosclerosis, a disease affectingarterial blood vessels [13]. In developed countries such as the United States, atherosclerosis is theleading cause of illness and death accounting for 44% of deaths and morbidity

[14].

2. Experimental

2-1- materials & tolls

- Melting points were determined by using a micro-melting point apparatus without any corrections.
- Infera Red spectra pattern FT-IR-410 prducdeJasco – Japan . reported relative in KBr stretch bonds in cm^{-1}.
- X-ray of the company (PHILIPS) in the Department of Physics - Faculty of Science - University of the expedition.
- A spectral analysis of metals on the principle of optical spark electric version of the company Oxford Instruments in the Department of Physics - Faculty of Science - University of the expedition.
- All chemical materials from Sigma Aldrich .

2-2-Preparation of the ligand (APH):

To a solution of 2-nactyl pyridine (0.01 mole) in methanol (25ml) followed by addition of hydrazine hydrate (0.01 mole) in methanol (10ml), The mixture was refluxedfor 6h. The formed solid product was separated by filtration, purified by crystallization from petroleum ether. Ligand as white crystals was obtained with a yield of (73%) and m.p=117-119^{o}C.

2-3-General Synthesis of metal Complexes;

A solution of ligand (APH) (0.02mol) in ethanol (50ml) was added to a solution of metal (II) chloride hydrous (0.01mol) when [M= Zn(II), Ni(II) and Cd(II))] in ethanol (10 ml) ,andrefluxed for 5h by using a water bath. By cooling the contents, the colored complex separated out in each case.

The same was filtered, then washed with ethanol and washed several times with diethyl ether.

Some properties of the synthesized of ligand and complexes are given in **Table1**.

Compounds	**Formulas**	**Color**	**m.p^{o}C**	**Yield (%)**
APH(L)	$C_7H_9N_3$	yellow	117-119	73
[Zn(APH)$_2$]Cl$_2$	$C_{14}H_{32}N_6O_7ZnCl_2$	White	194-dec	45
[Cd(APH)$_2$]Cl$_2$	$C_{14}H_{32}N_6O_7CdCl_2$	White	283-dec	77
[Ni(APH)$_2$]Cl$_2$	$C_{14}H_{32}N_6O_7NiCl_2$	green	263-dec	58

3. Results and Discussion and Discussion

3-1- Elemental analysis and characterization for ligands and their complexes:

The bidentate Schiff base (APH) was prepared by the condensation of 2- acetyl pyridine and hydrazine hydrate in their 2:1 molar ratio.

The Schiff bases were subjected to elementalanalyses. The results of elemental analyses (C, H, N) of ligand and complexes are given in T in Table 2.

Table 2. Elemental analysis, of ligand and their complexes

compound	**Elemental Analysis % Found (% Calc.)**			
	C	**N**	**M**	**Cl**
APH	**62.22** **61.3**	**31.11** **30.8**	**-**	**-**
[Zn(APH)$_2$]Cl$_2$	**41.37** **40.2**	**20.68** **20.20**	**16** **15.4**	**17.48** **16.94**
[Cd(APH)$_2$]Cl$_2$	**37.16** **36.9**	**18.58** **18.30**	**24.55** **23.80**	**15.70** **14.90**
[Ni(APH)$_2$]Cl$_2$	**42.21** **41.89**	**21.10** **20.8**	**14.32** **13.78**	**17.83** **17.30**

3-2- IRspectra of the (APH) ligand and their complexes

The infrared spectra for the present compounds taken in the range 400-4000 cm^{-1} help to indicate regions ofabsorption vibrations. The main stretching modes are for ν(C=N), ν(C=C) and ν(N-N). The IR data of the spectraof Schiff base ligands (APH) and their complexes are presented in Table 3. The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may beinvolved in chelation.

Spectrum of the APH ligand shows a sharp band at (1677cm^{-1}) due to ν(C=N) azomethine groupwhich has shifted to lower frequency about (70cm^{-1}) in the complexes indicating its participation in chelationthrough azomethine nitrogen. The lowering of band is due to the reduction of electron density in the azomethinelink. Pyridine ν(C-N) shows absorption band at (1298cm^{-1}) in the Schiff base spectrum. These band risesshift by

(1271cm^{-1}) in the complex. Azomethine group in the Schiff base APH hanged after complication.with Zn(II) from (1677cm^{-1}) to (1620cm^{-1}) this indicate that involvement of Azomethine group in complications.

Table 3. Characteristic infrared absorption frequencies (cm^{-1}) of the ligand and complexes.

compounds	ν(NH)	ν(C=N)	ν(C=N) (C=N)$_{Py}$	ν(N-N)	ν(C-N)Py	ν(C-H)SP^2	ν(C-H)Sp^3
APH	3429$_{st}$	1677$_{st}$	1465$_m$	1105$_m$	1298$_m$	3194$_W$	2925$_w$
[Zn(APH)$_2$]Cl$_2$	3342$_{st}$	1620$_{st}$	1460$_m$	1170$_m$	1311$_m$	3069$_W$	2930$_w$
[Cd(APH)$_2$]Cl$_2$	3413$_{st}$	1634$_{st}$	1463$_m$	1179$_m$	1272$_m$	3126$_W$	3008$_w$
[Ni(APH)$_2$]Cl$_2$	3490$_{st}$	1594$_{st}$	1478$_m$	1146m	1271$_m$	3062$_W$	3000$_w$

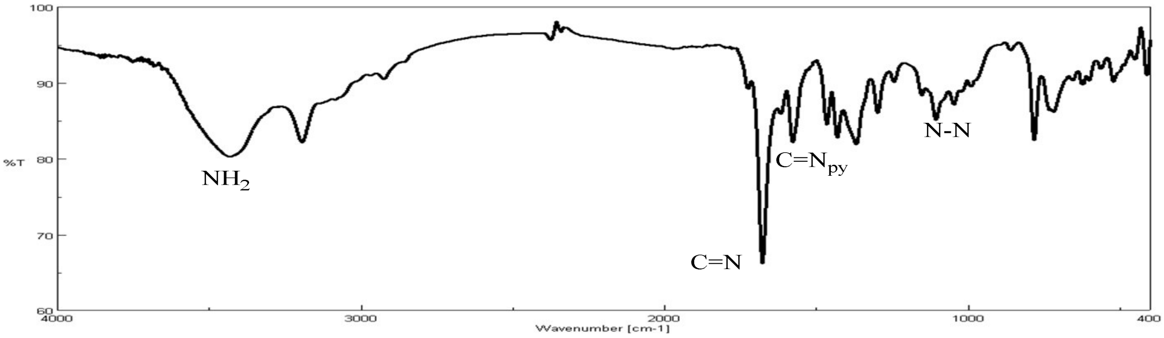


Figure 1: IR spectrum of ligand (APH)

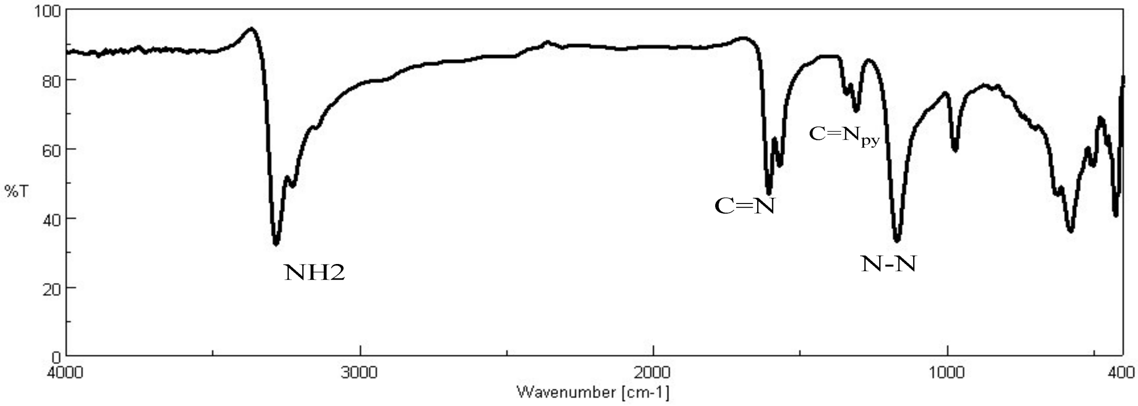


Figure 2: IR spectrum of complex [Zn(APH)$_2$]Cl$_2$

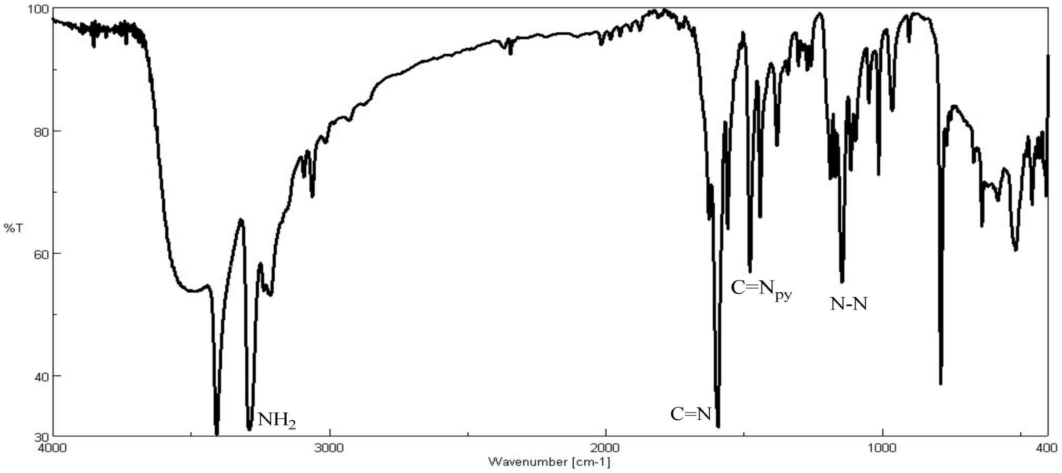


Figure 3: IR spectrum of complex [Cd(APH)$_2$]Cl$_2$

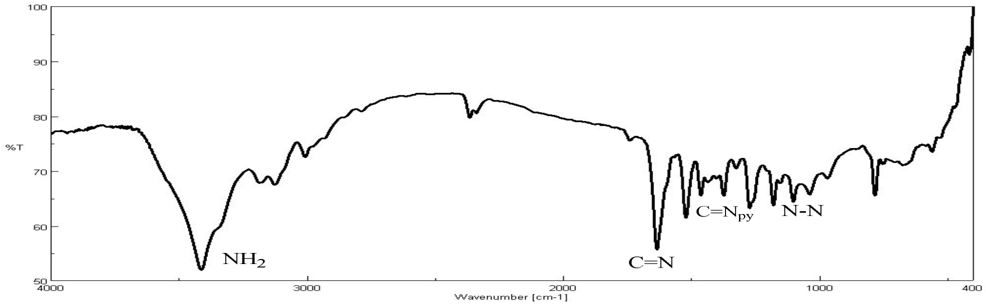


Figure 4: IR spectrum of complex [Ni(APH)$_2$]Cl$_2$

3.3. Electronic spectral data:

The data of the electronic spectra of the ligand and its complexes are given in Table 3. The spectrum of Schiffbase (APH) presented two bands in the UV interval at 235nm and 290nm , assigned to ($\pi \longrightarrow \pi^*$) and ($n \longrightarrow \pi^*$)transitions respectively.

The electronic spectra of the complexes in methanol solution has two bands at (305,356)nm Thesebands may be assigned to the charge transitions (LMTC)of the form ($n \longrightarrow \pi^*$)for azomethine group(C=N) and the pyridine ring was to metal ion$L \longrightarrow M$[15].

The position of these bands suggests an octahedralenvironment to Zn$^{(II)}$,Cd$^{(II)}$ andNi$^{(II)}$ **Scheme1**.

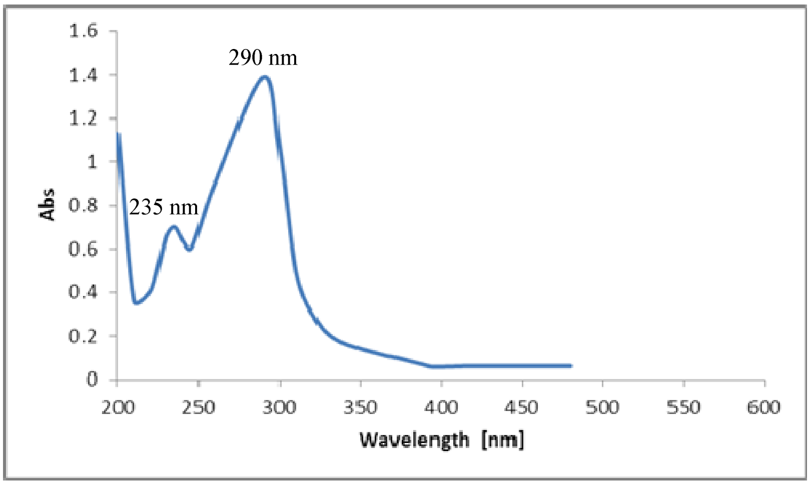


Figure 5: UV absorption spectrum of ligand (APH)

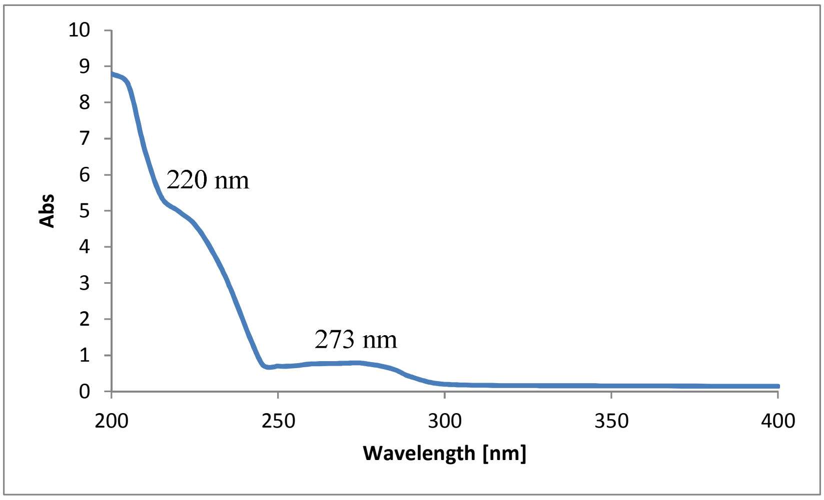


Figure 6: UV absorption spectrum of [Zn(APH)$_2$Cl$_2$]

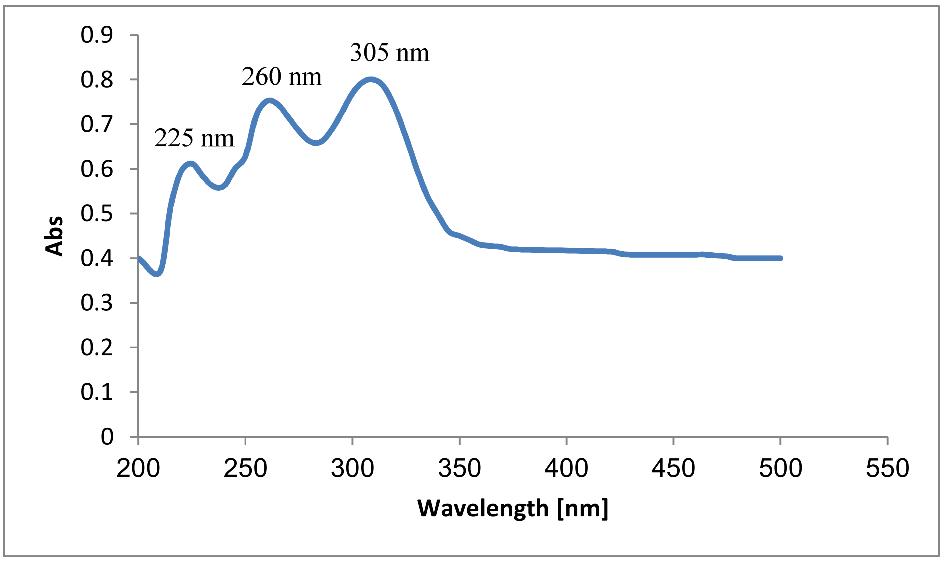


Figure 7: UV absorption spectrum of [Cd(APH)$_2$Cl$_2$]

Table 4: Magnetic moments, electronic bands and ligand filed parameters of APH and its metal complexes[16].

compound	**π→π* (nm)**	**n→π*** (nm)	**L→M (nm)**	d-d (nm)	Assignment
APH	235	290	---	---	---
Zn(APH)$_2$Cl$_2$	220	273	.---	---	---
Cd(APH)$_2$Cl$_2$	225	260	305	---	---
Ni(APH)$_2$Cl$_2$	256	311	356	401 620	$^3A_{2g} \rightarrow {}^3T_{1g}$ (p) $^3A_{2g} \rightarrow {}^3T_{1g}$ (f)

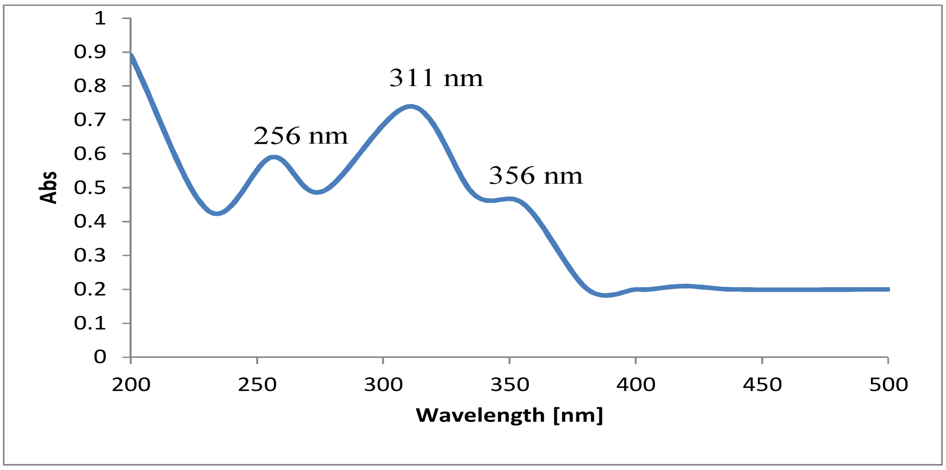


Figure 8: UV absorption spectrum of [Ni(APH)$_2$Cl$_2$]

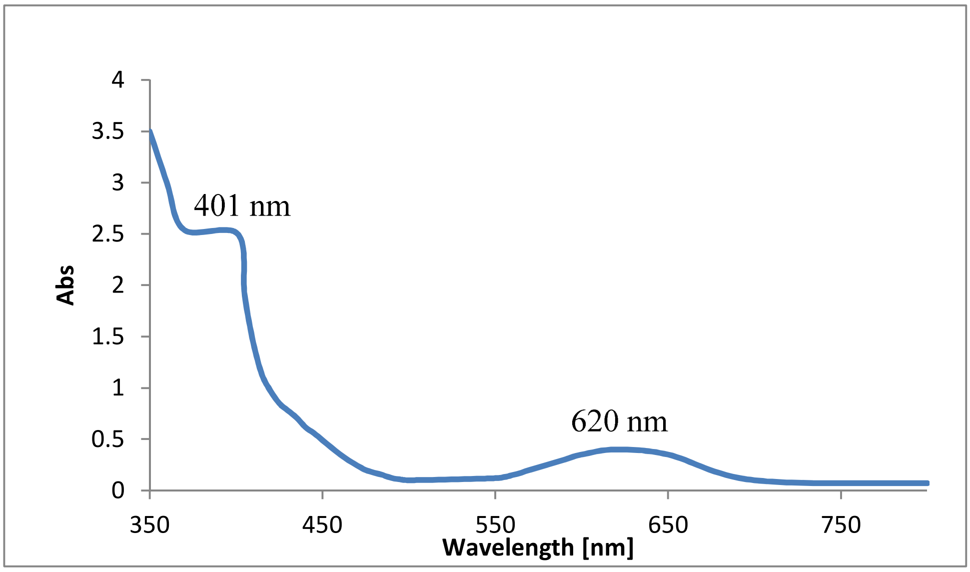
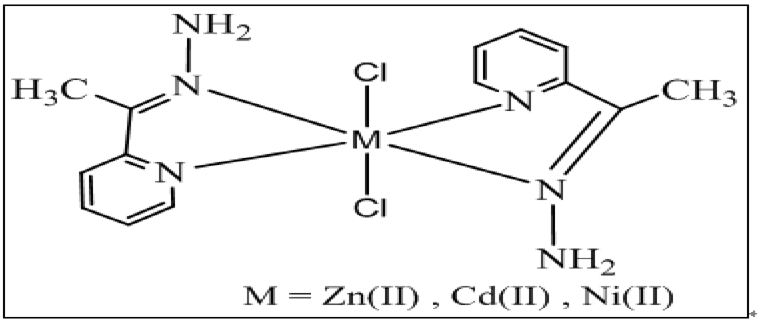


Figure 9: VIS absorption spectrum of $[Ni(APH)_2Cl_2]$



Scheme1: Suggested structures for the APH complexes

13C and1HNMRspectroscopic measurements:

(1H-NMR) spectra of the Schiff base ligand APH. the (13CNMR) of the APH ligand exhibits signals at (δ=145.6 ppm) These signal assigned to carbon azomethine group[17-18].

The (13C and 1H-NMR)spectroscopic measurement of APH Schiff bases are given in **Table 5.**

Table 5. The (13C and 1H-NMR) spectroscopic measurementSchiff basec.

Signal number	13C-NMR (δ ppm)	1H-NMR (δ ppm)
$-C-CH_3$	$-C-CH_3$ 12.73	$-C-CH_3$ 2.380
a	CH-Ar 121.12	CH-Ar 8.61
b	CH-Ar 124.29	CH-Ar 8.34
c	CH- Ar 136.65	CH-Ar 7.92
d	CH-Ar 155.29	CH-Ar 7.48
e	CH-Ar 157.62	NH_2 4.87

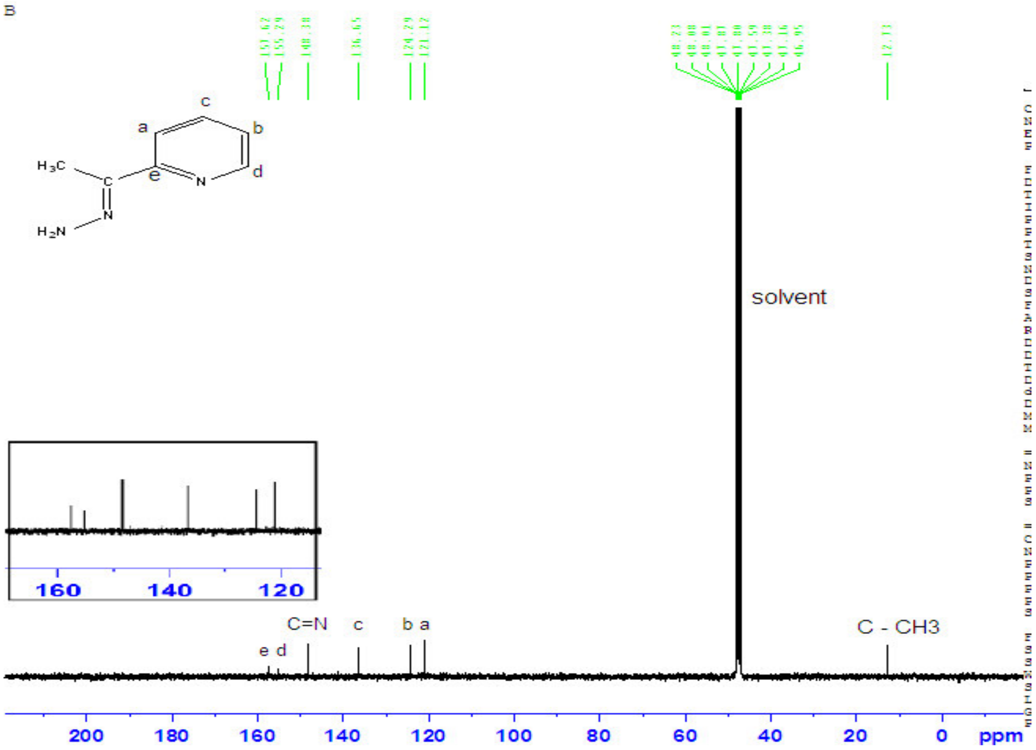


Figure 10 : 13CNMR spectrum of APH

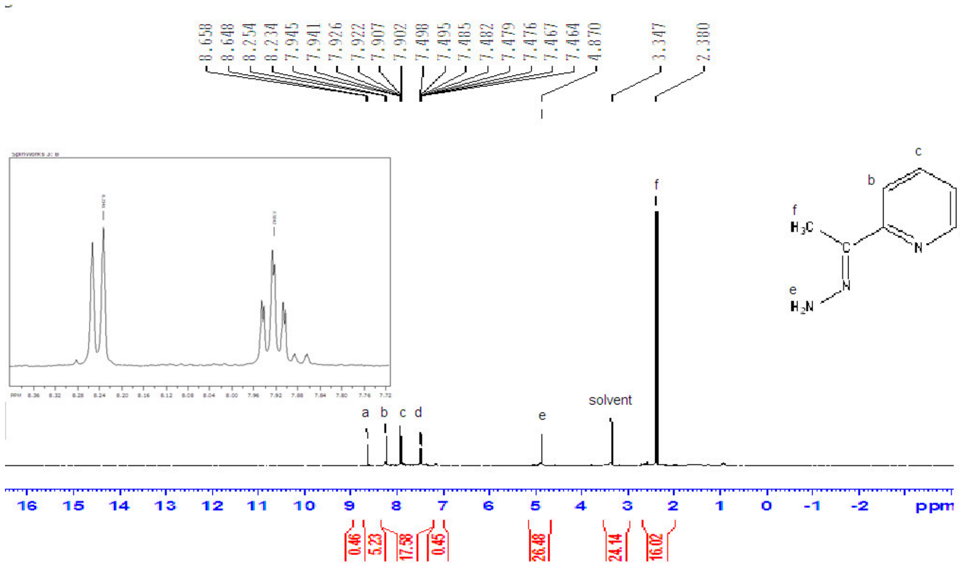


Figure 11 : 1HNMR spectrum of APH

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