

RESEARCH PAPER

Synthesis and Characterization of some divalent transition metal complexes with acid hydrazone ligand

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ABSTRACT:

Complexes with the general formula $[M(LH)_2]X_2$ where $M=Mn(II), Co(II), Ni(II)$ and $Cu(II)$ $LH= 4$ -acetylpyridine benzoyl hydrazone and $X=$ chloride ion were synthesized. The structures were confirmed by IR spectroscopy, and characterized by elemental analyses, UV-vis, $^1H.n.m.r$ $^{13}C-n.m.r$, and conductivity measurements. Molar conductance values in DMSO indicate that all complexes are electrolytes with mole ratio (1:2) and chloride ions not participate in coordination to central metal ion except Mn complex. The ligand act as bidentate, they coordinates through azomethine nitrogen ($>C=N-$) and carbonyl oxygen's.

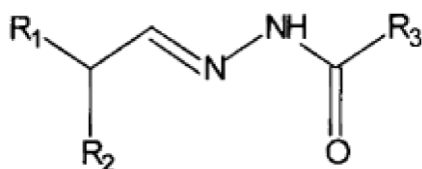
KEY WORDS: Acid hydrazone; complexes; synthesis.

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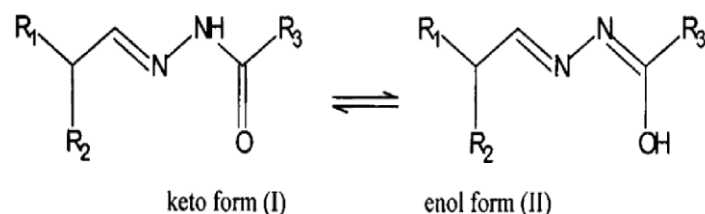
1.INTRODUCTION :

The condensation between substitution acid hydrazide with carbonyl compound (aldehydes, ketones) is the best method for hydrazone preparation or synthesis by the reaction of hydrazine with aldehydes, ketones in ethanol, methanol that have a general formula of $R_1R_2C = NNR_3R_4$ contains (N-N) linkage. The general formula for a substituted acylhydrazone is shown below: (Hamada et al., 2015)



General formula of a substituted acylhydrazo

Hydrazone behave as bidentate ligands and owing of $-NH-C=O$ group in acid hydrazone show keto-enol tautomerism, keto-form was absent in solid state while in solution enol- form is present and they exist as an equilibrium mixture keto and enol forms. (Bessy, 2009)



Tautomerism of acid hydrazone (keto-enol form)

Keto-enol Tautomerism makes it to form a stable complex with different transition metal ions make hydrazone ligand played a great role in inorganic chemistry. (Sreeja, 2004)

The arylhydrazones ligand $R-CO-NH-N=CHR$ act as bidentate or chelating ligands and

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coordinate with transition metal ions through the N atom of azomethine group and O atom of the carbonyl group, a five membered ring being produced. (Aurkie et al., 2008; Sajjad, et al., 2019; Adrian and Jack, 2009)

The most interest hydrazones and its complexes usage in clinical, analytical, biological fields like antibacterial (Ruth et al., 2006) antimicrobial, antifungal, anticonvulsant, (Marisa et al., 1999) anti-analgesic (Rafat et al., 2010), antimalarial, anti-inflammatory (Bhushankumar et al., 2011), anticancer (Basavaraj et al., 2011), antitumor (Wagnat, Naned, and Rafat, 2013), anti-tuberculosis, (Ahmet et al., 2010) antioxidant are some physiologically active of it (Bahaa et al., 2019; Deepa et al., 2015). They show activity against leukemia, sarcomas and other malignant neoplasms. industrially hydrazone used as plasticizers and as polymerization initiators antioxidants. Also play a great role in plant growth regulators, insecticides, rodenticides, herbicides, nematocides. (Livio et al., 2017)

The new complexes of Mn(II),Co(II),Ni(II) and Cu(II) with the ligand 4-acetylpyridine benzoyl hydrazone, having general the formula $[M((LH)_2)Cl_2]$ where $M = Mn(II), Co(II), Ni(II)$ while (H_2O) is participate as ligand in Cu complex. The result indicates that in all complexes, ligand was coordinated to metal via azomethine nitrogen ($>C=N-$) and carbonyl oxygen's.

2. Materials and Methods

2.1 Experimental Notes:

All chemicals used were of reagent grade, supplied by either Merck, Fluka or (B.D.H). Melting Point of the complexes were measured using Electro thermal-IA 9000-England melting point apparatus. Thermo Mattson IR 300 spectrophotometer was used to recorded infrared spectra in the $(400-4000) \text{ cm}^{-1}$ range using KBr discs. The conductivity was measured for the (10^{-3} M) solution of the complexes in (DMSO), using WTW-conductometer inolab 749-Geermany. Electronic spectra were recorded on a UV-Vis. spectrometer, CE -3021- England. Elemental analysis was carried out on Elementary Analyses system GmbH in Kashan University (Iran). $^1\text{H.n.m.r}$ $^{13}\text{C-n.m.r}$ spectra of ligand and complexes were recorded by Bruker ultra-shield 300 MHz with TMS as internal reference, in Kashan University (Iran).

2.2 Preparation of Acid Hydrazone Ligand:

(4.11ml, 0.0375 mol) of 4-acetylpyridine was added to a solution of (5.1 gm, 0.0375 mol) benzoyl hydrazine which is dissolved in (50ml) absolute ethanol, heated to reflux for (1hr.). Filtered off and recrystallized in ethanol, washed with diethyl ether and dried under vacuum.

2.3 Preparation of metal complex:

Solid complexes were prepared by heating of ethanolic solution of metal chloride (0.000418 mol) was added to (0.000836 mol) of prepared ligand in (15 ml) absolute ethanol, heated to reflux for (1 hr.), a colored complex was formed. Filtered off and recrystallized in ethanol, washed with diethyl ether and dried under vacuum.

3. Result and Discussion:

Several methods, traditional and modern are available for elucidating the structure of ligand and their coordination complexes. The complexes are characterized by elemental analysis, Infrared Spectral, $^1\text{HNMR}$, $^{13}\text{C-NMR}$ spectral, Molar conductivity measurement, Electronic Spectra and Magmatic susceptibility measurement.

3.1 Elemental analysis:

The complexes were analyzed for carbon, hydrogen and nitrogen. The results are given in the table (1). The stoichiometry of the complexes data was found to be (1:2) (M:L).

3.2 Infrared Spectral Studies:

The IR spectra of the complexes were analyzed and compared with free hydrazone ligand (LH) that show a strong absorption band at (1644 cm^{-1}) assigned to $\nu (C=O)$ and medium intensity band $\nu (C=N)$ at (1588 cm^{-1}) . Both of these bands shift to lower wave number after complexation indicate that the ligand act as bidentate and coordination occur from oxygen's carbonyl group and nitrogen's azomethine to central metal (Morsy et al.,2011; Samar, 2017), other bands observed at (3200cm^{-1}) and (1448 cm^{-1}) assigned to the $\nu (N-H \text{ cm}^{-1})$ and $\nu (C=N)_{py}$ respectively which is not affected on complexation. A new band appear in complex around (1065 cm^{-1}) , $(469-501 \text{ cm}^{-1})$, $(422-424 \text{ cm}^{-1})$ which are attributed to $\nu (C-O)$, $(M-O)$, $(M-N)$ respectively. (Mariana et al., 2010; Ikechukwu and Peter, 2015; Ganesh, 2016; Abdul hakim and Salima, 2008)

Another broad band appear in Cu complex around (3432 cm^{-1}) due to ν (O-H) absorption band which is for participate H_2O in coordination. (Nakamoto, 1978)

3.3 Molar conductivity measurement:

Conductivity measurement of complexes carried out in 10^{-3} M (DMSO) solution. All molar conductance values are listed in table (2). These values showed that all complexes were electrolyte.

The value of the molar conductance ($\text{cm}^2.\text{ohm}^{-1}.\text{mol}^{-1}$) are in the ranges (71.8-76.5 $\text{cm}^2.\text{ohm}^{-1}.\text{mol}^{-1}$) which correspond to (1:2) electrolytes, this is also confirmed with positive AgNO_3 test for chloride containing complexes except Mn complex which is not electrolyte.

3.4 Electronic Spectra:

Electronic spectra of octahedral manganese (II) complex exhibit six spin- forbidden transition in the visible region, three of the electronic transition bands around (15470) cm^{-1} which assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ (D), (23640) cm^{-1} transition s assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ (D) and (29455) cm^{-1} assignable to the charge transfer respectively for an octahedral geometry for Mn (II) complex. (Lever, 1984; Achut et al., 2010)

In the present work the electronic spectra of cobalt (II) complex was exhibit the electronic transition band at (17120) cm^{-1} which may be attributable to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (P) in tetrahedral environment for cobalt complex, while the band at (23923) cm^{-1} is assigned to the (L \rightarrow M) charge transfer (charge transfer). (Canpolat and Kaya, 2005; Sajid and Qin-han, 2008; Tejraj, 1984)

The electronic spectra of Ni(II) complex show one absorption band at (14710) cm^{-1} which may be assigned to ${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$ (F) transition, suggestion the tetrahedral geometry around Ni (II). Both Co(II), Ni(II) complexes show an intense band at (23923 - 24390) cm^{-1} which can be assigned to charge transfer transition of tetrahedral geometry. (Lever, 1984; Kasuga et al., 1984; George and Christos, 1985; Christian, 1962; Yamada and Takeuchi, 1982).

Finally square pyramidal geometry is proposed for Cu complex 4 based on the presence of two bands at (21978) cm^{-1} and (16393) cm^{-1} . These bands may be assigned to the ${}^2\text{B}_1 \rightarrow {}^2\text{A}_1$ and the ${}^2\text{B}_1 \rightarrow {}^2\text{E}$ transitions, respectively, based on assignments published before (James, 1978; Sudeep et al., 1996)

3.5 Magmatic susceptibility:

The effective magnetic moment values were calculated by using formula, $\mu_{\text{eff}} = 2.83 (\chi_M T)^{1/2}$ BM where, χ_M = molar susceptibility, T = absolute temperature.

The magnetic susceptibility for Mn (II) complex is that found is (1.92) B.M at 300 K compared with theoretical value (1.73B.M) expected for low spin d^5 Mn complex that evidence for octahedral geometry. (Achut et al., 2010)

The magnetic moment value for Co(II) complex was found (3.79) B.M that evidence for paramagnetic and tetrahedral geometry compared with theoretical value (3.84) B.M. (Sajid and .Qin-han, 2008)

Cu(II) complex had a magnetic moment of (1.89) B.M which is higher than the theoretical value of (1.73) B.M. due to John Teller distortion expected for a d^9 ion with one unpaired electron. (Temitope et al., 2019; F. Albert, 1999)

Ni(II) complex had magnetic moment of (2.71) B.M which is lower than theoretical value of (2.82) B.M. that indicate Ni complex is paramagnetic (Mohammed and Mostafa, 2001)

3.6. ${}^1\text{H}$ -NMR and ${}^{13}\text{C}$ -NMR Spectra:

The ${}^1\text{H}$ -NMR spectrums of synthesized ligand were recorded in DMSO-d 6 solution using TMS as internal standard show signals at 10.70 ppm (s, 1H) due to the -NH proton. The two doublet peaks with equal integration at 8.63 and 7.40 ppm belongs to the protons of the pyridine ring, were shown at significant different δ depending on their position to the electronegative nitrogen atom of the pyridine ring. The aromatic protons (Ar-H) show singlets at 7.50- 7.89 ppm. The singlet peak at 2.32 ppm with integration equal to 3 H's clearly belongs to the methyl group (-N=CCH₃) (Rosaleen et al., 2004). Moreover, the ${}^{13}\text{C}$ NMR spectrum of the ligand showed a signal at 163.58 ppm corresponding to the carbonyl group(C=O). The aromatic carbons of the phenyl ring are observed at 127.5, 128.8 ,132.2 and 138.4ppm (Bridson, 2003; El-Saied et al., 2017). The signal of the azomethine carbon(C=N) is observed at 149.14 ppm (Juvansinh et al., 2015). The chemical shift appeared at 14.24 ppm can be assigned to the methyl group (CH₃), and pyridine ring carbon show a signal at 124.1, 138.4and

147.7 ppm. The ^1H and ^{13}C - NMR spectra of ligands is full agreement with their proposed structure.

The essential features of the ^1H -NMR spectrum of the Co(II), Mn(II), Ni(II) and Cu(II) complexes as a representative case is similar to that of ligand. The ^1H -NMR spectrum of ligand shows a signal at (10.70 ppm) is assigned to amide proton (-CONH-), which is downfield in the spectrum of the complex at (10.91)(10.97)(10.95)(11.2) respectively indicating coordination of oxygen of -CONH- with metal ion (Shivakumar et al., 2008). The presence of this signal in the free ligand and the complexes indicating that free ligand is mainly in keto form and coordinated to the metal ion in keto form also. The slight downfield shift of methyl group protons from

(2.32 ppm) in the ligand to (2.45, 2.61, 2.55 and 2.67 ppm) respectively for the complexes may be considered as another evidence of coordination of the ligand through azomethine nitrogen. The signals of the atoms of carbon (C=O) and (C=N) in the ^{13}C -NMR spectrum present shifts of (2.76, 3.01, 2.88 and 2.95) ppm respectively (2.48, 2.55, 3.11 and 2.65) ppm in the complexes, and this downfield in the spectrum of the complex pointed clearly the involvement of the atoms of amide oxygen and azomethine nitrogen in coordination. The atoms of carbon in the pyridine ring have signals in the same region of the spectrum and the shift is very small and in this way is confirmed that the pyridinic nitrogen is not involved in the coordination.

Table 1. Analytical and physical data of the ligand and their complexes

Compd.	Color	M.wt	(M.P) $^{\circ}\text{C}$	AgNO ₃ Test	Molar Conductivity	Analyses Found (Calc.%)		
						C	H	N
C ₁₄ N ₃ H ₁₃ O (LH)	Needly White	239.11	(172.5-172.8)	-----	-----	-----	-----	-----
[Mn(LH) ₂ Cl ₂]	White	604.06	>225 $^{\circ}$ decomp	- Ve	1.9	55.58 (55.66)	4.30 (4.33)	13.87 (13.91)
[Co(LH) ₂ Cl ₂]	Turquoise-Blue	608.06	>165 $^{\circ}$ decomp	+ Ve	74.2	55.24 (55.30)	4.28 (4.31)	13.79 (13.82)
[Ni(LH) ₂ Cl ₂]	Green	607.82	>270 $^{\circ}$ decomp	+Ve	71.8	55.26 (55.32)	4.25 (4.31)	13.73 (13.82)
[Cu(LH) ₂ H ₂ O]Cl ₂	Pale- green	630.67	>145 $^{\circ}$ decomp	+ Ve	76.5	53.28 (53.32)	4.39 (4.47)	13.26 (13.32)

Table 2. The IR spectra of the ligand and complexes and geometrical structure

Compd.	N-H	C-H	C=O	C=N	(C=N) _{py}	C-O	M-O	M-N	Geo. Str
C ₁₄ N ₃ O ₁₃ (LH)	3200	3036	1644	1588	1448	-----	-----	-----	-----
[Mn(LH) ₂ Cl ₂]	3209	3023	1578	1532	1446	1075	477	422	O.h
[Co(LH) ₂ Cl ₂]	3214	3056	1597	1524	1447	1068	501	418	T.h
[Ni(LH) ₂ Cl ₂]	3189	3062	1600	1536	1447	1065	469	424	T.h
[Cu(LH) ₂ H ₂ O]Cl ₂	3211	3058	1599	1506	1437	1068	477	423	Sq.py

Table 3. Magnetic moment and electronic spectral data of the complexes

No.	Complex	Band absorption		Assignment	Magnetic moment B.M
		Cm ⁻¹	Nm		
1	[Mn(LH) ₂ Cl ₂]	43859	228.0	$\pi \rightarrow \pi^*$	(1.92) O.h
		39370	254.0	$n \rightarrow \pi^*$	
		29455	339.5	C.T	
		23640	423.0	$^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g}$	
		15470	646.4	$^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g}$	

2	$[Co(LH)_2]Cl_2$	40176 35273 23923 17120 14710	248.9 283.5 418.0 584.0 679.8	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T ${}^4A_2 \rightarrow {}^4T_1$ (P) ${}^3A_2 \rightarrow {}^3T_2$ (F)	(3.79) T.h
3	$[Ni(LH)_2]Cl_2$	37835 29069 24390 14710	264.3 344.0 410.0 679.8	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T ${}^3A_2 \rightarrow {}^3T_2$ (F)	(2.71) T.h
4	$[Cu(LH)_2H_2O]Cl_2$	34305 26212 23724 21978 16393	291.5 381.5 421.5 455.0 610.0	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T ${}^2B_1 \rightarrow {}^3A_1$ ${}^2B_1 \rightarrow {}^2E$	(1.89) Sq.py

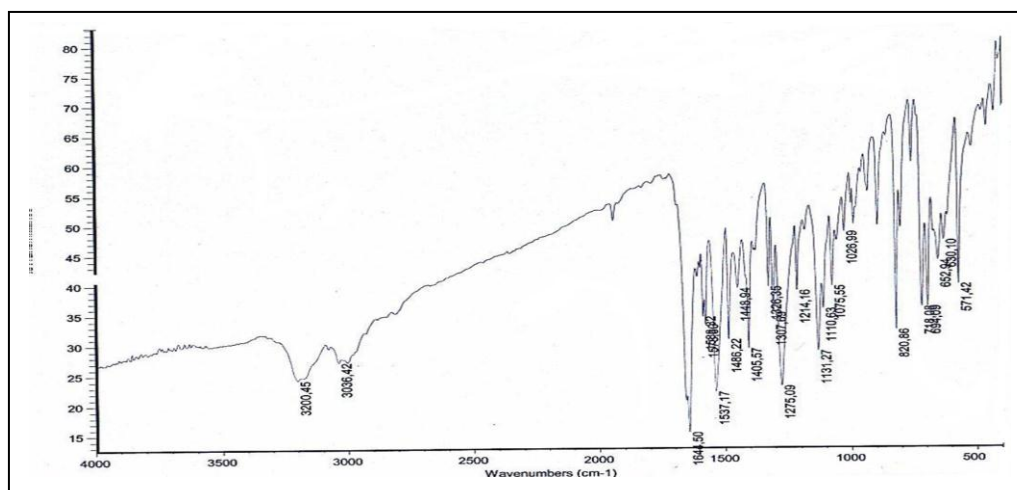


Fig (1) : Infra-red spectra of ligand

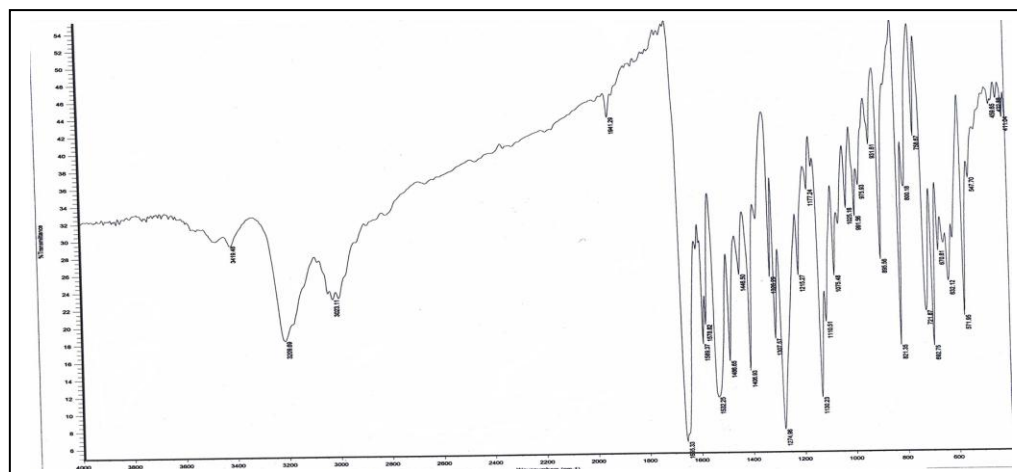


fig (2): Infra-red spectra of Mn complex

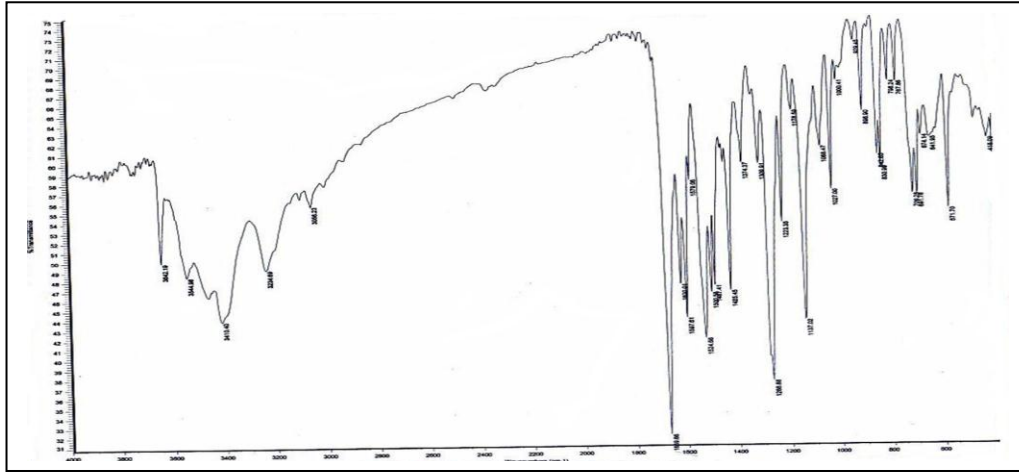


fig (3): Infra-red spectra of Co complex

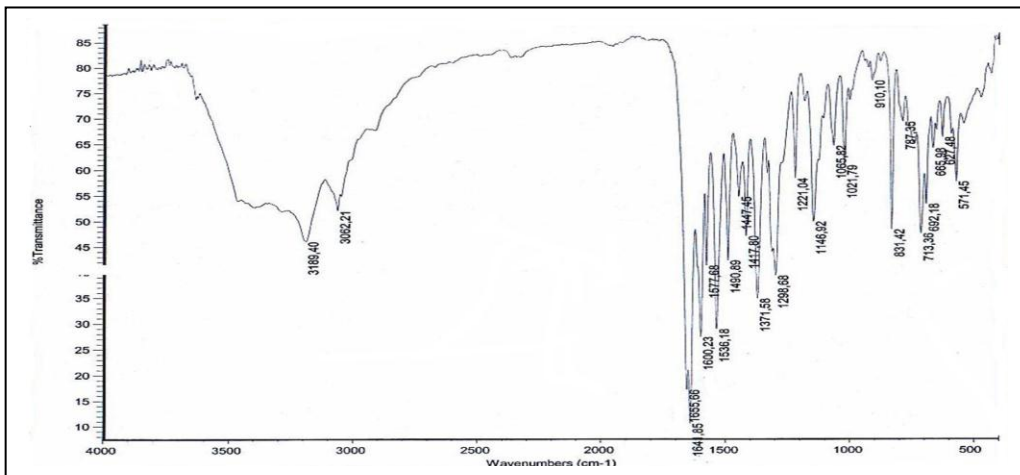


Fig (4): Infra-red spectra of Ni complex

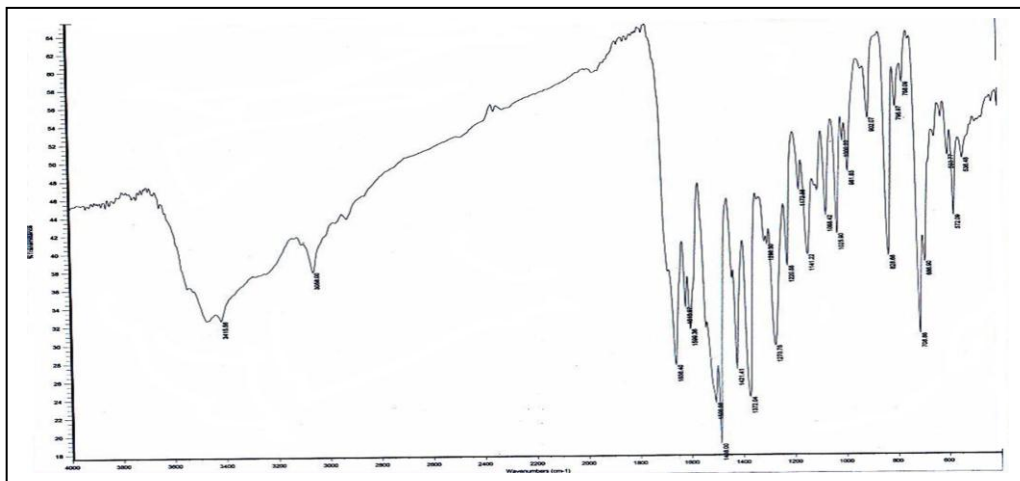


Fig (5): Infra-red spectra of Cu complex

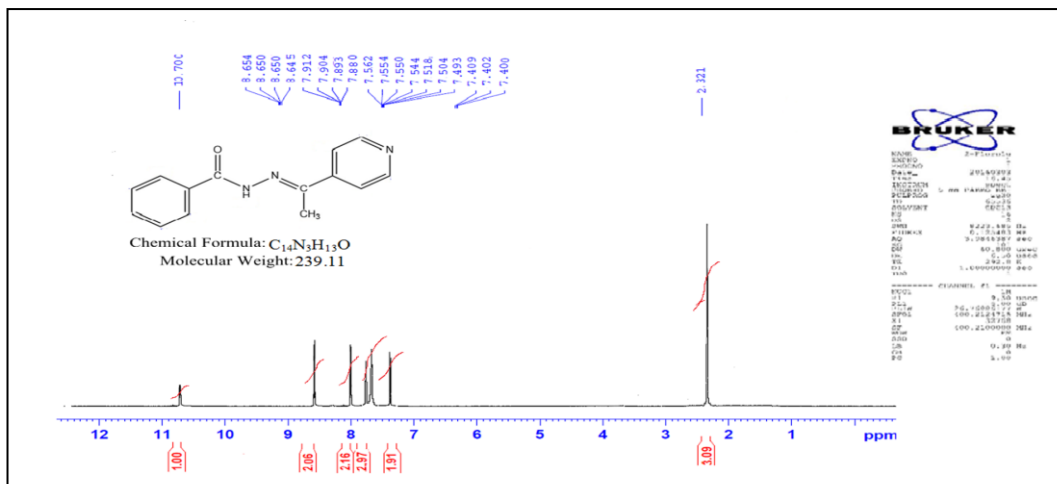


Fig (6) : 1H NMR spectra of ligand

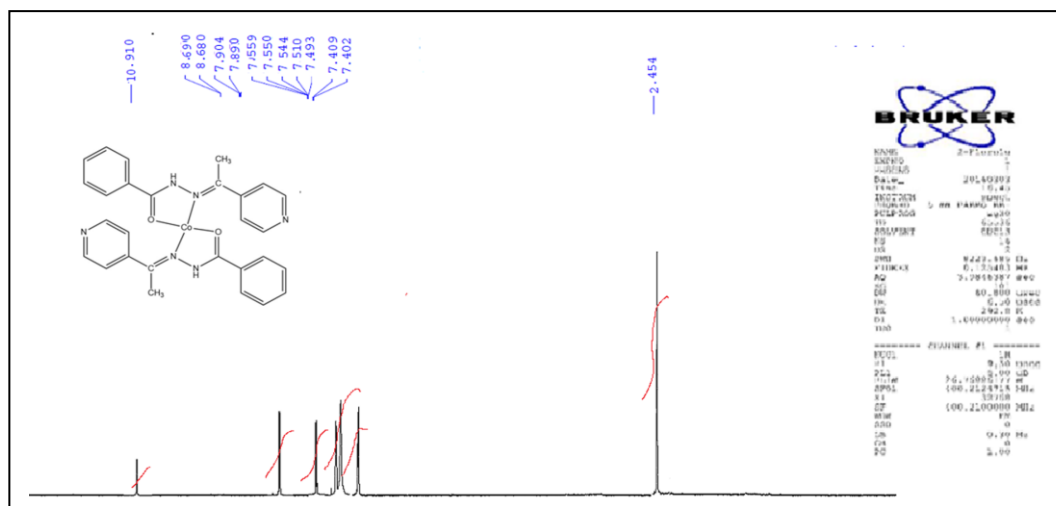


Fig (7) : 1H NMR spectra of $[Co(LH)_2]Cl_2$ complexes

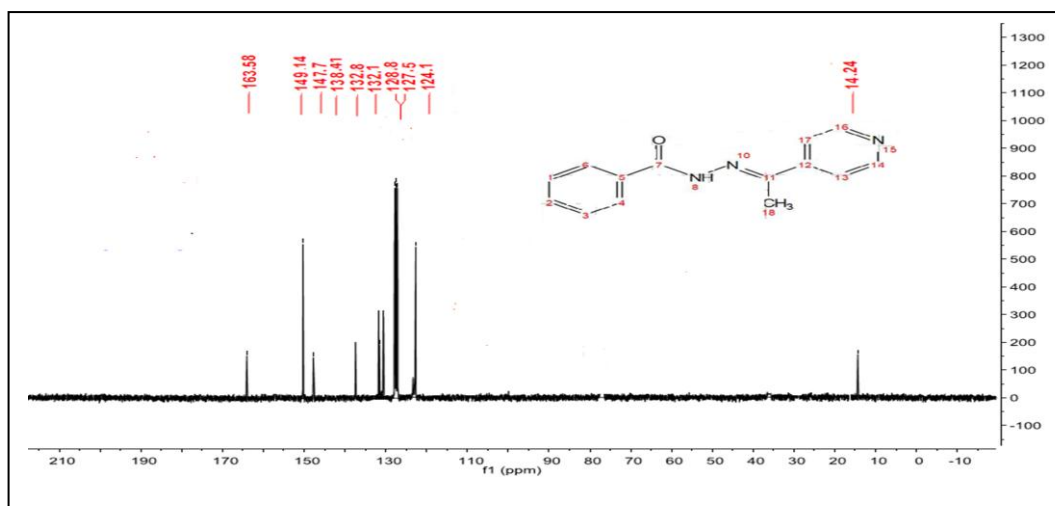


Fig (8) : ^{13}C NMR spectra of ligand

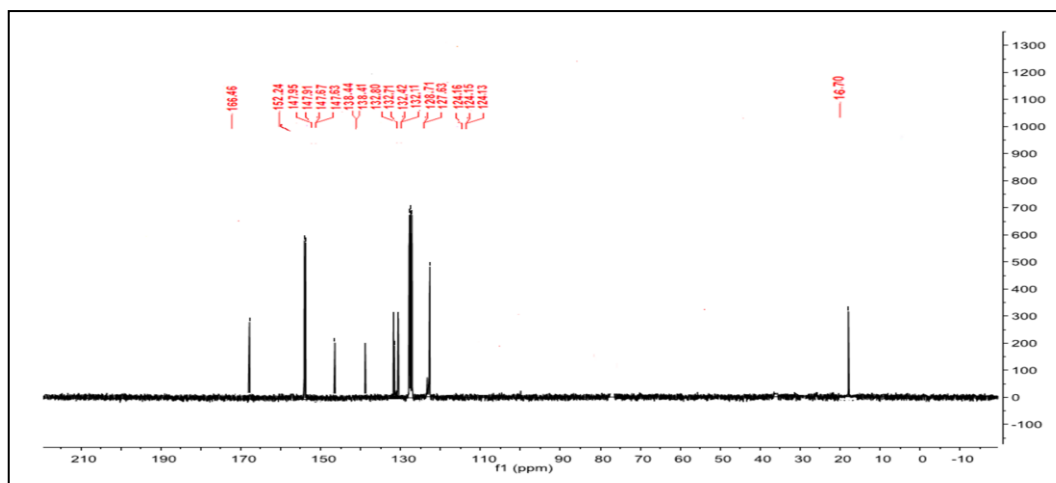
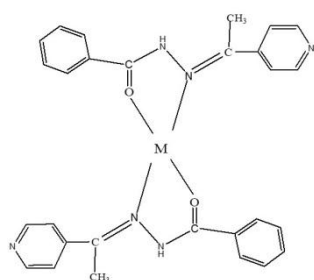


Fig (9) : ^{13}C NMR spectra of $[\text{Ni}(\text{LH})_2]\text{Cl}_2$ complex

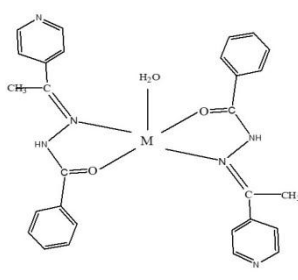
4. Conclusion:

In summary, the work reported involved synthesis and characterization of 4- acetyl pyridine benzoyl hydrazone and Mn(II), Co(II), Ni(II) and Cu(II) complexes have been investigated by spectroscopy and some other

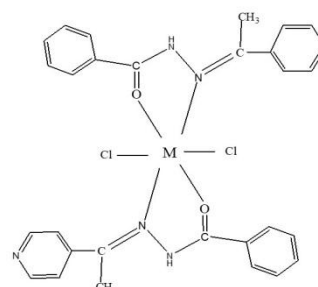
techniques (IR, UV-Vis spectroscopy, ^1H NMR, ^{13}C -NMR spectral molar conductivity and elemental analysis, magnetic susceptibility). In all the complexes, the hydrazone is associated with the metal through the carbonyl oxygen and the azomethine nitrogen to result in different geometrical structures.



Structure of
 $[\text{M}(\text{LH})_2]\text{Cl}_2$ complexes where
 $\text{M}=\text{Co}$ and Ni



Structure of
 $[\text{Cu}(\text{LH})_2\text{H}_2\text{O}]\text{Cl}_2$ complex



Structure of
 $[\text{Mn}(\text{LH})_2]\text{Cl}_2$ complex

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