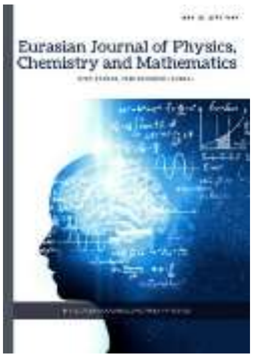


Synthesis and Characterization Zn(II),Cd(II) and Hg(II) complexes with hydrazone Schiff base derived from Benzohydrazide and 4-acetyl pyridine

Bayan Attalla Faiq1
shahla.jamal@uokirkuk.edu.iq
1Department of Chemistry, Collage of Science, Salahaddin University, Erbil, Iraq

Shahla Jamal Shakkor2,*
2 Department of Chemistry, Collage of Science , Kirkuk University, Kirkuk , Iraq

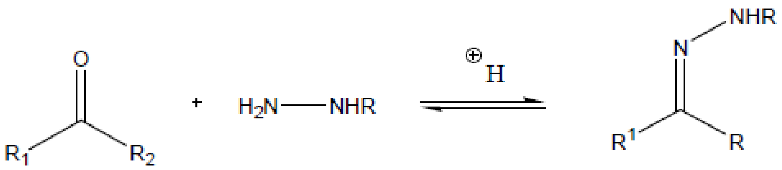
Safa Rida Shakkor2
2 Department of Chemistry, Collage of Science , Kirkuk University, Kirkuk , Iraq

[M(LH) X_2] general complex formula where M= divalent metal of Zn, Cd and Hg ;LH = Schiff base 4-acetylpyridinen benzoyl hydrazone and X = chloride ion, were synthesized . All complexes structures were analyzed by Infrared spectroscopy , and characterized by (C,H,N) analysis, uv-visible and conductivity measurements. The values of molar conductance in dimethyl sulfoxide indicate non-electrolytes properties. The spectral studies indicate that all complexes are distorted tetrahedral geometry. The ligand (LH) coordinates through nitrogen′s imine group (>C=N-) and oxygen's carbonyl group.

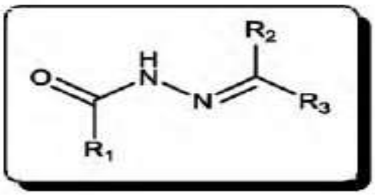
Keywords: hydrazone Schiff base, d^{10} complexes, synthesis.

Introduction:

In organic chemistry the elimination molecule of water in hydrazone synthesis that involves condensation of aromatic an aldehyde or ketones with aromatic or aliphatic acid hydrazide or substitute hydrazine in acid medium.[1]

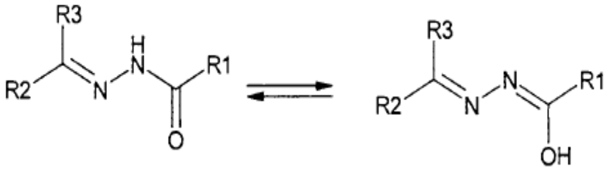


The interesting hydrazone compounds in coordination chemistry having azomethine group (-C=NN-) with the chemical formula $R_1R_2C{=}N{-}NR_3R_4$ and admission of C=O group in the hydrazide part will increase the delocalization of electron and denticity and the produced compound will have general formula $R_1C(=O)NHN=CR_2R_3$ called arylhydrazone.[2,3]



General structure of aroylhydrazones

An aroylhydrazone mode coordination depends on many factors like tatomerism , reaction conditions , stability of the complex formed , and the acid hydrazone show keto-enol form (tautomerism) [4,5] .



(Enol- Keto) form aroyl hydrazone (Tautomerism)

Hydrazone play a great role in biology and pharmacology field as, anti-cancer, anti-tumor agents[6] antimicrobial [7], antiviral, antimalarial [8] fungal [9] anti-inflammatory [10] due to chelating with transition metals to form complexes in addition in analytical chemistry which have many application by acting as polyidentate with transition elements.[11,12]

In this work a new Lewis base hydrazone ligand (4-acetyl benzoyl pyridine hydrazone) prepared ,the ligand containing nitrogen and oxygen and it's complex with divalent heavy metals (Zn,Cd,Hg) are reported in this paper.

Experimental:

Preparation of ligand hydrazone Schiff base:

(0.075 mol,8.22ml) of 4- acetyl pyridine was added to a solution of (0.075 mol, 10.2 ml) benzoyl hydrazine that dissolved in (100ml) absolute C_2H_5OH, and heated to reflux for (1 hour). The reaction filtered1off and recrystallized in C_2H_5OH ,washed the precipitate with $C_2H_5OC_2H_5$ and dried using vaccume.

Metal complex preparation :

Ethanolic solution of d^{10} metal chloride (0.000836mol) was added to (0.001672 mol) of prepared ligand in (30 ml) absolute C_2H_5OH, heated to reflux for (1 hour), a pale coulored complex were precipitate. Filtered off and recrystallization in C_2H_5OH,washing several times with $C_2H_5O\ C_2H_5$ and dried using vaccume.

Result Data and Discussion:

Analytical data:

Elemental analysis of (C,H,N) are shown in given table below table (1). The mole ratio of metal to ligand was (1:1) (M:L) and (Cl^-)chloride ions was share in coordination to central atom.

Table(1) : Analytical and physical data of the ligand and it´s complexes

Ligand & Complexes	***Coulor***	***M.wt***	***(M.P)°C***	***Test of $AgNO_3$***	***Conduct-ivity in molar***	***%element %Found(%Calc.)***		
						C	***H***	***N***
$C_{14}N_3H_{13}O$ (LH)	Needly White	239.11	(172.5-172.8) °C	-------	--------	------	-------	--------
[$Zn(LH)Cl_2$]	Pale-yellow	375.4	>149° Decomp.	- Ve	18.3	44.69 (44.78)	3.38 (3.49)	11.00 (11.19)
[$Cd(LH)Cl_2$]	Milky white	422.42	>325° Decomp.	- Ve	11.9	39.62 (39.80)	3.06 (3.10)	9.88 (9.94)
[$Hg(LH)Cl_2$]	White	510.6	>194° Decomp.	- Ve	8.8	32.79 (32.92)	2.50 (2.56)	8.17 (8.22)

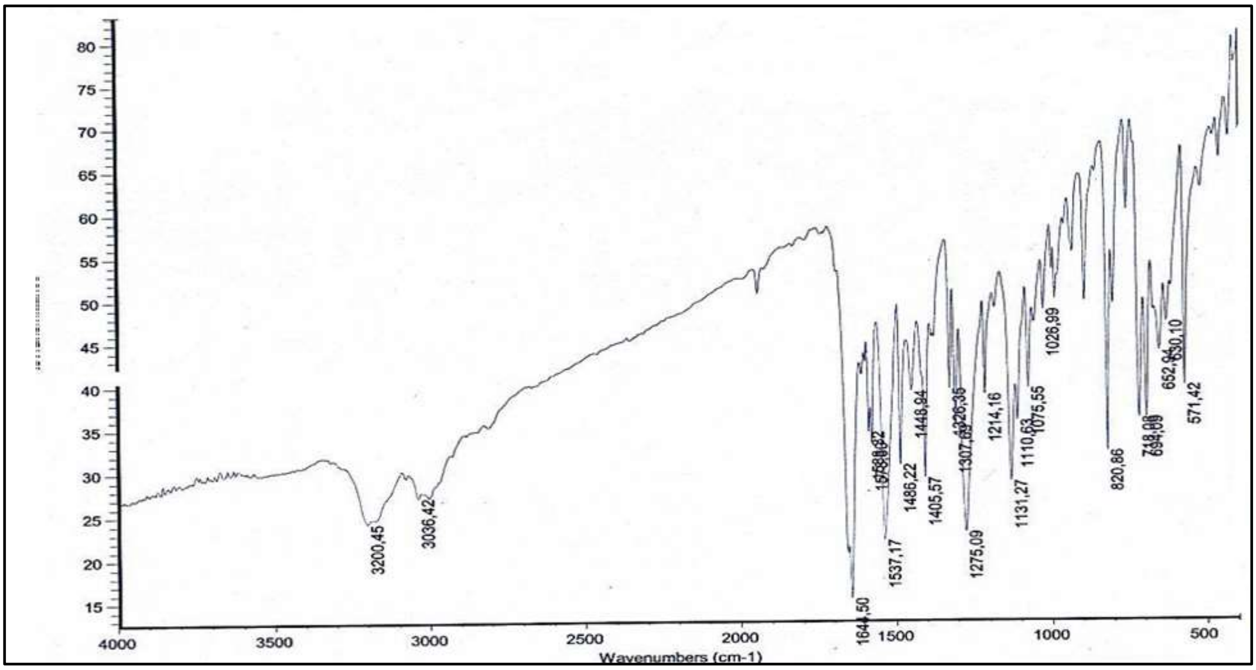
IR Spectra Studies:

All complexes were characterized by infrared spectra and compare with the prepared free ligand (LH) that show a clear and strong absorption peak band at υ. (1644)cm $^{-1}$ which assign to frequency of carbonyl group (C=O) and medium intensity band for imine group (C=N) at (1588)cm $^{-1}$ in free hydrazone (LH) respectively. Both of these bands shift to lower wave number after complexation indicate that the coordination occur through nitrogen of imine group and oxygen of carbonyl group to (Zn,Cd,Hg) metals.

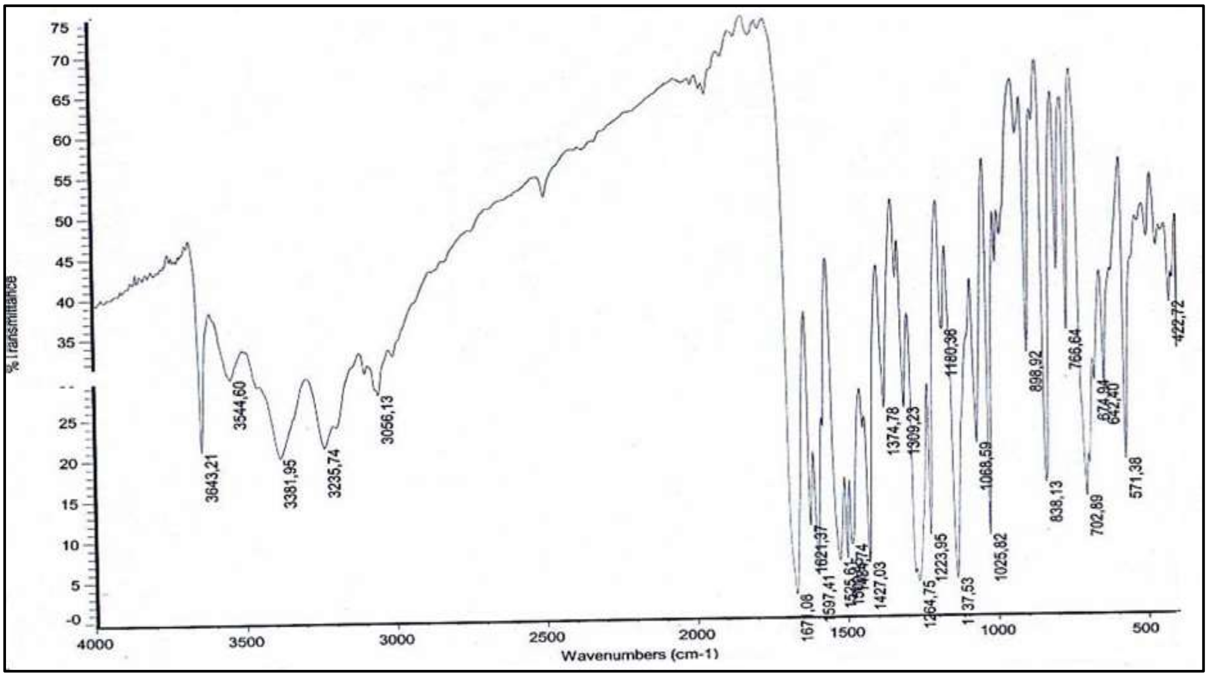
Also other bands observed at (3200) cm $^{-1}$and (1448)cm^{-1} assigned to the υ (N-H) and υ (C=N)$_{py}$ stretching vibration frequency respectively which is not affected after complexation . A new bands appear in d^{10} complexes around (1061-1674) cm^{-1} , ,(421-429) cm^{-1} (468-497) cm^{-1} which are attributed to υ (C-O),(M-N) , (M- O) respectively as shown in table (2) .[13,14,15,16]

Table (2): Infrared spectra of prepared ligand(LH) and it's complexes

Ligand & complexes	**N-H**	**C-H Ar.**	**C=O**	**C=N**	**C=N$_{py}$**	**C-O**	**M-O**	**M-N**	**Comp-lex Str**
$C_{14}N_3OH_{13}$	3200	3036	1644	1588	1448	-----	------	------	-----
[$Zn(LH)\ Cl_2$]	3203	3056	1621	1524	1428	1068	497	422	T.h
[$Cd(LH)Cl_2$]	3205	3047	1617	1577	1448	1061	468	421	T.h
[$Hg(LH)Cl_2$]	3199	3057	1612	1519	1441	1074	488	429	T.h



Fig(1): Structure of (LH) ligand



Fig(2): Structure of Zn complex

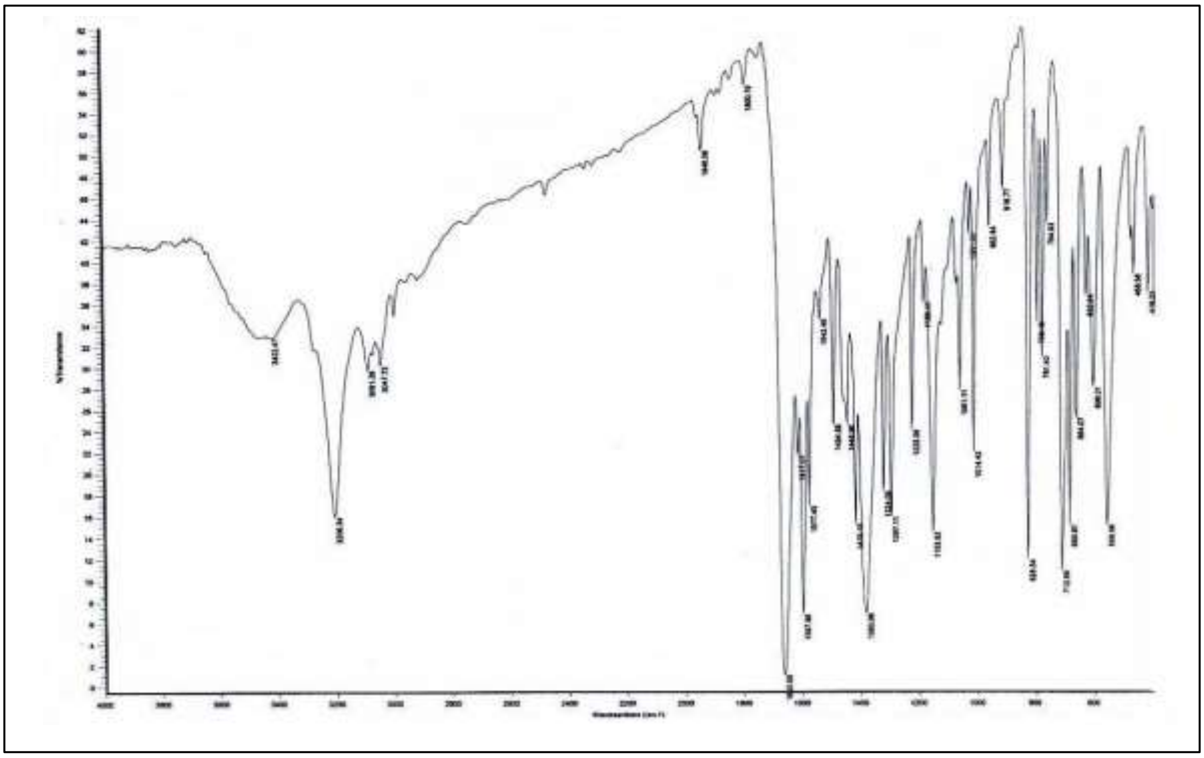
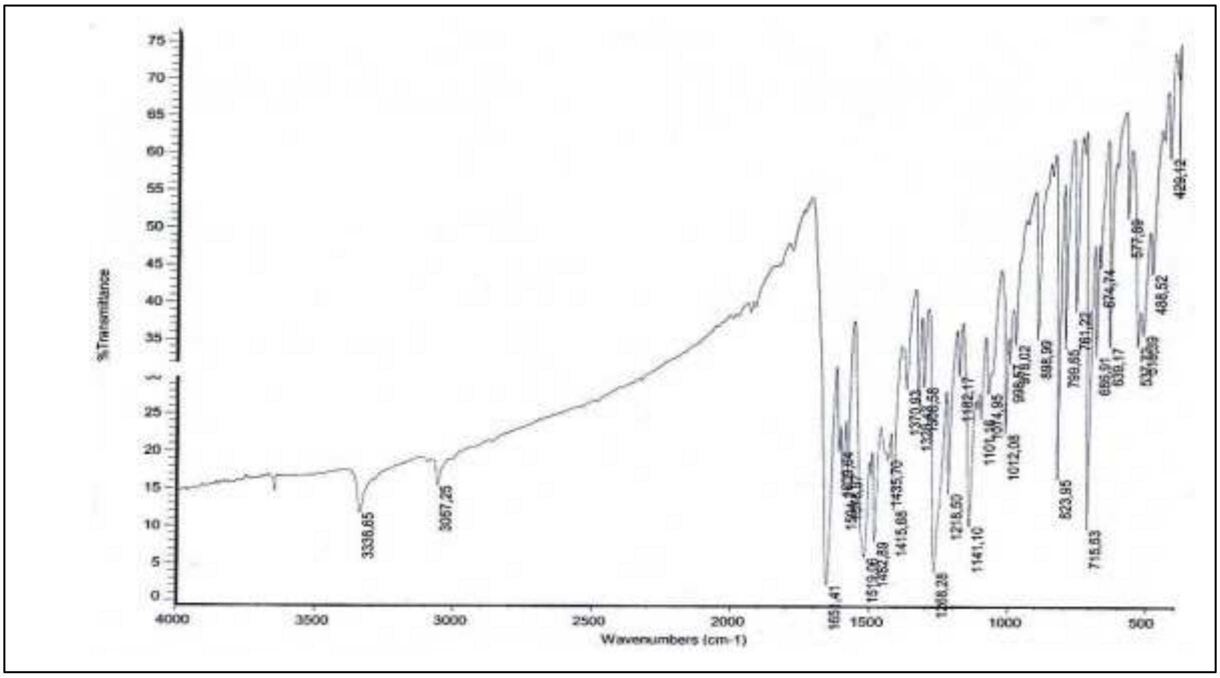


Fig.(3) : Structure of Cd complex



Fig(4): Structure of Hg complex

Measurement of molar conductivity :

Conductivity measurement of d^{10} complexes carried out in 10^{-3} M (dimethyl sulfoxide) solution . All molar conductance values are listed in table (1).These values showed that all complexes were non-electrolytes.

The range value of the molar conductance are in (8.8- 18.3) $cm^2/ohm.mol$ which is correspond to (1:1) non-electrolytes , this is also confirmed with negative $AgNO_3$ test for (Cl^-) chloride ions in outer coordination sphere.

Magnetic susceptibility:

Diamagnetic divalent of (Zn, Cd, and Hg) complexes are zero value of magnetic. This agreement with d^{10} transition metals group that give tetrahedral geometrical structure for all complexes.[17,18]

Electronic Spectra:

The electronic spectra of divalent d^{10} metal complexes show no bands in the visible region as expected for d^{10} group except a broad and sharp absorptions exhibit in the range (29498- 44052) cm^{-1} and which are either assigned to charge transfer or internal ligand transitions ($n\rightarrow\pi^*$) and($\pi\rightarrow\pi^*$) as shown in (Table 3).[19,20,21] .

Table (3): Electronic spectral bands of prepared complexes:

No.	Complex	Band absorption		Assignment
		Cm^{-1}	nm	
1	*[Zn(LH)Cl$_2$]*	43668 35971 30864	229.0 278.0 324.0	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ C.T
2	*[Cd(LH)Cl$_2$]*	43668 36231 30441	229.0 276.0 328.5	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ C.T
3	*[Hg(LH)Cl$_2$]*	44052 36036 29498	227.0 277.5 339.0	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ C.T

Conclusion:

This work report involve synthesis of (LH) and characterization of d10 group divalent metals complexes with 4- acetyl pyridine benzoyl hydrazone that have been analyzed by spectroscopy's dives and some other techniques (Infrared , UV-Visible spectroscopy, molar conductance and elemental analysis). The complexes were tetrahedral structure and acid hydrazone ligand is associate to the metal through oxygen's of carbonyl in addition of nitrogen's of azomethine group.

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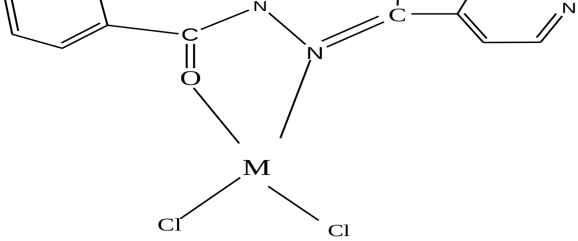

Suggested geometrical Structure of prepared Complex.

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