New Tridentate Hydrazone Metal Complexes Derived from 2-Hydroxy-4-Methoxyacetophenone and some Acid Hydrazides: Synthesis, Characterization and Antibacterial Activity Evaluation

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ABSTRACT

A new series of complexes of Co(II), Ni(II), Cu(II), and Zn(II) with three hydrazones ligands(L) derived from 2-hydroxy-4-methoxy acetophenone (Paeonol) and 4-methylbenzoylhydrazide (AMBH), acetyl hydrazine (AAH), or picolinoyl hydrazine (APH) with the general formula $[M(L-H)_2].nH_2O$ (n= 0, 1, or 2) where L-H = deprotonated AMBH, AAH or APH, have been prepared and characterized by elemental analyses, spectral (FT-IR, UV–visible) as well as molar conductance and magnetic measurements. The data revealed that the ligands AMBH and AAH act as mono-negative ONO chelates coordinated through the carbonyl group and the phenoxy oxygen atoms and azomethine nitrogen atom, while APH acts as NNO chelate, coordinated through the pyridine and azomethine nitrogen atoms and the phenoxy oxygen atom. On the basis of electronic spectral and magnetic moment data, an octahedral geometry is suggested for all complexes. Also, the ligands and some of their complexes were screened for antibacterial activities.

Keywords: Hydrazones, Complexes, Transition metals, Antibacterial activity.
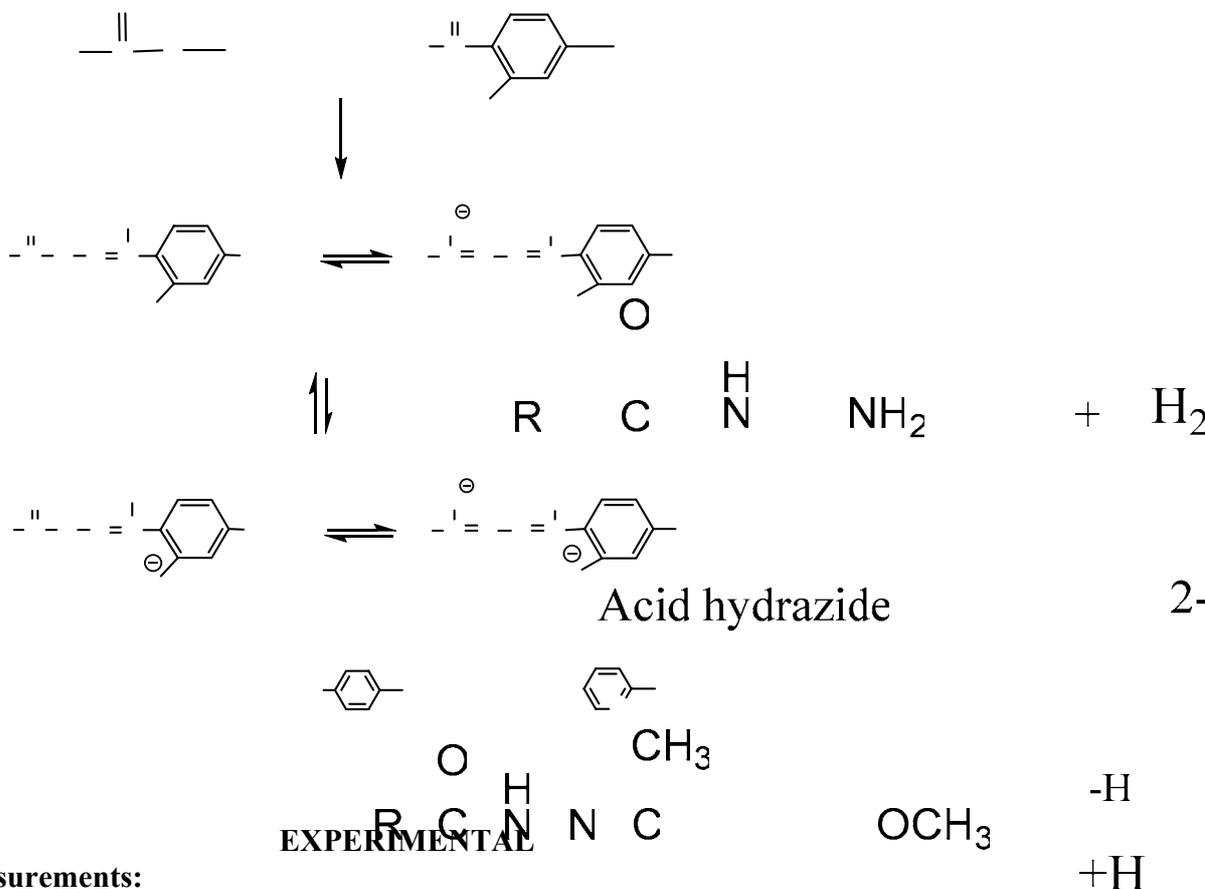
-4-   -2

:

(L)   Zn(II)   Cu(II)   Ni(II)   Co(II)

-4   -4-   -2:   (   )   -4-   -2

-4-   -2   (AAH)   -4-   -2   (AMBH)

AMBH   = L-H   [M(L-H)₂]. nH₂O   (APH)

(IR)   .   APH   AAH

(UV-Vis)

AAH   AMBH   .

(ONO)

APH

.   (NNO)

.

.

.   :

INTRODUCTION

Hydrazones of carboxylic acid hyraziedes (RCONHN=CHR′) are versatile ligands and have applications in many fields. Aroyl hydrazones are quite interesting ligands as they present a combination of donor sites, such as amide oxygen atom, imine nitrogen atom of the hydrazone moiety and an additional donor site (usually N or O) provided from the aldehyde or ketone forming them. Hydrazones have interesting ligation properties due to the presence of these several coordination sites, hence they display versatility in metal coordination (Li *et al*., 2016 ; Singh *et al*., 2015). The mode of coordination depends on the nature of the central metal atom, the pH of the medium, the nature of the substituents and also on the position of the hydrazone group relative to other moieties. Moreover, deprotonation of the –NH group, which is readily achieved in the complexed ligand in particular, results in the formation of tautomeric anionic species, having new coordination properties (Singh, *et al*., 2013). They can act as bidentate, tridentate or tetradentate ligands depending on the nature of substituents attached to the hydrazone unit. Metal complexes of aroylhydrazone ligands have an attractive area of research because of their versatile coordination chemistry and a capability to generate varied molecular architecture and geometry (Banerjee *et al*., 2008; Kobayashi *et al*., 2014; Cindrić *et al*., 2017; Kendur *et al*., 2018).

Hydrazones readily form stable complexes with transition metals (Singh *et al*., 2013 ; Saif, *et al*., 2016), lanthanides (Ajlouni, *et al*., 2016), as well as main group elements (Pilóa *et al*., 2015). They form a wide variety of complexes with chemical, structural, biological and industrial importance. Metal complexes of hydrazones have been proven to show potential applications as catalysts (Sadhukhan *et al*., 2011), luminescent probes (Guo *et al*., 2011) and fluorescent sensors (Mukherjee *et al*., 2011). Their complexes with transition metal ions are known to provide useful models for elucidation of the mechanism of enzyme inhibition by hydrazine derivatives and for their pharmacological applications (Dilworth, 1976)**.** They also have a variety of applications in biological, analytical and clinical fields, such as anti-bacterial, anti-fungal, anti-convulsing,anti-inflammatory, anti-malarial, analgesic, anti-platelets, anti-tuberculosis, anti-cancer and insecticidal activities (Rollas and Kücükgüzel, 2007; Suvarapu *et al*., 2012 ; Marella *et al*., 2014 ; Saif *et al*., 2016). Furthermore, metal complexes with hydrazones present DNA binding and cleavage activities (Banerjee *et al*., 2009 ; Gama *et al*., 2011). In view of the significant role played by the metal complexes of aroylhydrazones in biological systems, catalysis and in various other fields, we were motivated to synthesize Co(II), Ni(II), Cu(II) and Zn(II) complexes with hydrazones derived from 4-methyl benzoyl hydrazine, acetyl hydrazine, and picolinoyl hydrazine with the biologically active ketone (Paeonol), 2-hydroxy-4-methoxy acetophenone, (Fukuhara and Yoshida, 1987) (Scheme 1), and to describe their structures, spectroscopic, and magnetic properties.

$$R \quad C \quad \overset{H}{N} \quad NH_2 \quad + \quad H_2$$

Acid hydrazide 2-

$$R \quad \overset{O}{C} \quad \overset{H}{N} \quad N \quad C \quad \overset{CH_3}{} \quad OCH_3$$

Keto form

$$R \quad \overset{O}{C} \quad \overset{H}{N} \quad N \quad C \quad \overset{CH_3}{} \quad OCH_3$$

Pheñolate for

$$R = CH_3-, AAH ; \quad R = H_3C$$

EXPERIMENTAL

Material and measurements:

All chemicals used were reagent grade from B.D.H., Fluka or Merck chemical companies, used as supplied. The infrared spectra (4000-400) cm^{-1} of the ligands and complexes were recorded on Tensor 27 Bruker spectrophotometer as KBr discs. The UV-Vis spectra (1100-200) nm were recorded at room temperature on Labo Med, inc 1650Pc spectrophotometer using DMF as solvent in 1cm quartz curettes. Molar conductance's of the complexes were determined in absolute ethanol and DMF (10^{-3} M solutions) at room temperature using PMC3 Jenway conductivity meter. Magnetic susceptibilities were measured with Gouy balance Sherwood scientific Cambridge at ambient temperature. The necessary diamagnetic corrections for ligands were done using Pascal's tables. Melting points were obtained on 9300 Electrothermal melting point apparatus in open capillaries. The C.H.N. elemental analyses were performed on Euoro EA 3000 Instrument. The metal content of complexes was determined spectrophotometrically using SENSAA, GBC scientific equipment atomic absorption spectrometer (Co and Cu) and complex metric titration using standard EDTA solution (Ni and Zn) (Vogel, 1989).

- **Synthesis of acid hydrazides**

4-Methylbenzoyl hydrazine and acetyl hydrazine, were prepared by the reaction of the corresponding ethyl esters with hydrazine hydrate as described previously (Al-Saady and Al-Daher, 2000). Picolinoyl hydrazine was prepared from ethyl picolinate as described by (Zareef *et al*., 2006).

- **Synthesis of hydrazones**

These were prepared according to the literature method (Abd El-Motaleb *et al*., 2005), by reacting equimolar amounts of 2-hydroxy-4-methoxy acetophenone and acid hydrazide in absolute ethanol as shown in Scheme 1.

A solution of acid hydrazide (0.01 mole) [1.55 g, 4-methylbenzoyl hydrazine,.0.8 g, acetyl hydrazine, or 1.37g, picolinoyl hydrazine] in absolute ethanol (15 mL) was added to the solution of 2-

Scheme 1 (Synthesis and dep

hydroxy-4-methoxy acetophenone (1.66 g, 0.01 mol) in absolute ethanol (15 mL) and few drops of glacial acetic acid as catalyst. The reaction mixture was stirred and boiled under reflux for 3hrs.After completion of reaction and partial removal of solvent, the white crystalline solids that precipitated on cooling were separated by filtration, washed with cold ethanol (5 mL) then with ether (5 mL) and dried in an oven at (80 - 70 °C).

Synthesis of the Metal Complexes

To the stirred hot ethanolic solution (20 mL)of the appropriate metal acetate (0.001 mole) [0.249g, $Co(CH_3COO)_2.4H_2O$; 0.249g, $Ni(CH_3COO)_2.4H_2O$; 0.199g, $Cu(CH_3COO)_2.H_2O$; 0.219g, $Zn(CH_3COO)_2.2H_2O$] was added (0.596 g, 0.002 mole) of the ligand (AMBH) , (0.444 g, 0.002 mole) of the ligand (AAH) or (0.57 g, 0.002 mole) of the ligand (APH) in absolute ethanol (10 mL) and(0.2g, 0.002 mole) of the organic base triethylamine. The reaction mixture was then heated under reflux with constant stirring for 3hrs upon which the solid complexes were separated, filtered off and washed with ethanol (5 mL) and dried as above.

Antibacterial Activity:

Antibacterial activity was evaluated using agar diffusion method (Kethcum, 1988). gram-negative bacteria viz. *Salmonella typhi, Aeromonas, Klebsiella, Escherichia coli, Pseudomonas acruginosa and Morganella morganii* as well as gram-positive bacteria viz. *Staphylococcus aureus and Enterococcus faecalis* were cultivated in nutrient agar on petri dishes. The test solution was prepared by dissolving (100 mg) of the tested substances in DMSO (1 mL). A 6 mm diameter filter discs were socked in the tested solutions. After 2 h cultivation at 37 °C, diameter of zones of inhibition was determined. DMSO was inactive under applied conditions.

RESULTS AND DISCUSSION

The hydrazones of acid hydrazides (4-methylbenzoyl hydrazine, acetyl hydrazine and picolinoyl hydrazine) (AMBH, AAH, and APH respectively) were prepared in good yields by condensation with 2-hydroxy-4-methoxy acetophenone (Scheme 1). The reaction of these hydrazones with metal acetates in presence of triethyl amine (Sadhukhan *et al*., 2011) yield bis-complexes of the general composition $[M(L-H)_2].nH_2O$ (L= AMBH, AAH, APH; n= 0,1,2), in which the ligands deprotonated during complexation with the metals (II) as indicated by analytical data (Table 1 and 2). Most of the metal complexes are colored powdery non-hygroscopic solids. They are generally insoluble in water and non-polar organic solvents, like chloroform, benzene and diethyl ether, but are slightly soluble in ethanol and methanol, and more soluble in highly polar organic solvents, like DMF and DMSO. The low molar conductance values of the solutions of the complexes in absolute ethanol (2.2-11.5 $ohm^{-1}mol^{-1}cm^2$) and in DMF (7.2-24.5 $ohm^{-1}mol^{-1}cm^2$) indicating that they are non-electrolyte (Geary, 1971).

Table 1 : Some physical properties and analysis data of the ligands and their complexes

Comp. No.	Formula	Color	Mp. (C^0)	Yield %	Metal %		Ωohm^{-1}cm^2 mol^{-1}	
					Calc.	Found	EtOH	DMF
L$_1$	AMBH(C$_{17}$H$_{18}$N$_2$O$_3$) M.wt=298	White	88-90	58	……	…….	....	……
1	[C$_O$ (AMBH-H)$_2$].H$_2$O	Brown	210-212	52	8.78	9.49	6.9	9.7
2	[Ni (AMBH-H)$_2$]	Orange	258-260	71	8.9	8.4	6.4	13.4
3	[Cu (AMBH-H)$_2$] .H$_2$O	Grey	290d	83	9.66	10.17	5.4	8.8
4	[Zn (AMBH-H)$_2$]	White	300d	62	9.9	10.4	4.6	15.2
L$_2$	AAH(C$_{11}$H$_{14}$N$_2$O$_3$) M.wt=222	Yellow	168-170	91	------	------	------	------
5	[C$_O$(AAH-H)$_2$]	Orange	250d	89	11.76	12.14	8.6	9.6
6	[Ni(AAH-H)$_2$] .2H$_2$O	Green	258d	85	11.7	11.9	7.4	10.9
7	[Cu(AAH-H)$_2$] .H$_2$O	Green	274d	87	12.14	12.09	3.2	7.9
8	[Zn(AAH-H)$_2$]	White	290d	94	12.8	13.3	5.1	23.6
L$_3$	APH(C$_{15}$H$_{15}$N$_3$O$_3$) M.wt=285	Yellow	178-180	80	------	------	------	------
9	[C$_O$(APH-H)$_2$]	Brown	230-232	95	9.39	9.84	11.5	24.5
10	[Ni(APH-H)$_2$]	Yellow	200d	78	9.36	9.1	2.8	12.8
11	[Cu(APH-H)$_2$].H$_2$O	Green	276d	84	10.02	9.67	2.2	8.6
12	[Zn(APH-H)$_2$]	Yellow	250d	86	10.3	10.5	2.2	7.2

d= decomposition temperature

Table 2: Elemental analyses of some of the synthesized complexes

Compd. No.	Abbreviation	Formula	Elemental analyses Calculated/(Found)		
			C%	H%	N%
3	[Cu (AMBH-H)$_2$] .H$_2$O	C$_{34}$H$_{34}$N$_4$O$_7$Cu	60.3 (59.22)	5.3 (5.31)	10.28 (10.80)
6	[Ni(AAH-H)$_2$] .2H$_2$O	C$_{22}$H$_{34}$N$_4$O$_8$Ni	49.2 (49.16)	5.9 (5.26)	10.44 (10.49)
11	[Cu(APH-H)$_2$].H$_2$O	C$_{30}$H$_{30}$N$_6$O$_7$Cu	55.42 (54.72)	4.61 (4.04)	12.93 (12.43)

Infrared Spectra

In order to study the bonding mode of ligand to metal in the complexes, IR spectrum of the free ligand was compared with the spectra of metal complexes. The structurally significant IR bands for free ligands and their complexes have been reported in (Table 3). Remarkable differences between the IR spectra of the ligands and those of the corresponding complexes were observed. The IR spectral bands observed at the ranges (3336-3198), (3145 – 3076), (1695 – 1663), (1625 – 1610), (1263-1259) and (974 – 951) cm^{-1} in the spectra of the free ligands are assigned to the phenolic υ(O-H), υ (N-H), υ (C=O), υ (C=N), υ (C–O) and υ (N-N) respectively (Swathy *et al*., 2016 ; Ramesh *et al*., 2012). The disappearance of phenolic υ (OH) band in all the metal complexes indicates the deprotonation of the phenolic-OH group and coordination through a phenolate oxygen. The appearance of υ (C–O)$^-$ bands in the spectra of the complexes in the range (1349- 1311) cm^{-1}, suggests the bonding of ligand through a deprotonated (C–O)$^-$ phenolate group to the metal (Singh *et al*., 2013 ; Swathy *et al*., 2016). The υ (C=O) band observed at (1664 and 1663) cm^{-1} in the spectra of the ligands AMBH and AAH, are shifted considerably to lower wave number by (54-8) cm^{-1}, in its metal complexes, suggesting coordination through carbonyl oxygen (Singh *et al*., 2013 ; Guo *et al*., 2011). The υ (C=O) band in the spectra of the complexes of the ligand APH display no change or shift to higher frequency upon complexation with respect to free ligand. This denotes that the carbonyl oxygen atom is not involved in

coordination in these complexes (El-Taras *et al*., 2012). The pyridine in-plane deformation mode observed at (617) cm^{-1} in the spectrum of the free ligand APH shifted to higher frequencies by (31-18) cm^{-1} in the spectra of its complexes suggesting coordination of the heterocyclic nitrogen atom (Despaigne *et al*., 2009). The υ (C=N) band observed in the spectra of the free ligands shifted to lower frequency by(42-6) cm^{-1} in their metal complexes, indicating the involvement of the azomethine nitrogen in chelation with the metal ion (Singh *et al*., 2015). Coordination of nitrogen to the metal atom reduces the electron density in the azomethine group causing a shift in the $v_{(C=N)}$ band to lower frequencies (Shit *et al*., 2009).

Furthermore, a medium band due to υ (N–N) observed in the spectra of the free ligands is shifted to higher frequencies by (42-6) cm^{-1} in their metal complexes indicating the coordination of one of the nitrogen atom of >N–N< group with metal (Gawande *et al*., 2015 ; Singh *et al*., 2015). This phenomenon is owing to the diminution of the lone pair electrons repulsion which come from the two adjacent nitrogen atoms ,by sharing the electrons out to the metal ion (Shit *et al*., 2009). The v(NH) bands appearing at (3145 – 3076) cm^{-1} in the spectra of the free ligands shifted to higher frequencies in its metal complexes, probably due to decrease in hydrogen bonding on complexation, suggesting non-participation of –NH group in bonding. Their existence of υ (C=O) in the spectra of the complexes indicate that the ligands coordinated in the keto-form and enolization of the ligands on complexation is does not occur. The metal complexes also show a non-ligand bands in the (549– 454) and (462-411) cm$^{–1}$, ranges are tentatively assigned to υ (M–O) and υ (M–N), respectively (Singh *et al*., 2013). A broad band at ca.3400 cm^{-1} is observed in the spectra of the complexes (1,3,6,7, and 11) which indicate the presence of lattice water (Sreejith *et al*., 2018). Since vibrational modes such as wagging, twisting and rocking activated by coordination to the metal have not been found in the expected ranges, it shows that water molecules are not coordinated (El-Taras *et al*., 2012).

On the basis of the above discussion, it may be concluded that in the complexes (1-8), of the ligands AMBH and AAH acts as anionic tridentate ONO donors, chelating through the carbonyl oxygen, the imine nitrogen and phenolate oxygen atoms. On the other hand, APH act as anionic tridentate ONN ligand in its complexes (9-12) coordinating through the phenolate oxygen atom in addition to the nitrogen atoms of the azomethine group and pyridine ring. A general structure for the metal complexes has been proposed Fig. (6).

Table 3 : Selected infrared frequencies of the ligands and their complexes

Comp.No.	v(O-H)	v(N-H)	v(C=O)	v(C=N)	v(C-O)	v(N-N)	δ(Py.ring)	v(M-O)	v(M-N)
L$_1$	3234$_{(s,b)}$	3145$_{(sh)}$	1664$_{(s)}$	1616$_{(s)}$	1263$_{(s)}$	951$_{(m)}$	......	......	......
1	-	3168$_{(m)}$	1648$_{(s)}$	1593$_{(s)}$	1356$_{(s)}$	989$_{(m)}$	......	466$_{(m)}$	424$_{(w)}$
2	-	3168$_{(m)}$	1656$_{(s)}$	1610$_{(vs)}$	1328$_{(m)}$	987$_{(m)}$	......	549$_{(m)}$	422$_{(m)}$
3	-	3181$_{(m)}$	1651$_{(sh)}$	1608$_{(s)}$	1354$_{(s)}$	982$_{(m)}$	......	498$_{(m)}$	462$_{(m)}$
4	-	3191$_{(m)}$	1656$_{(m)}$	1588$_{(vs)}$	1335$_{(s)}$	978$_{(m)}$	......	465$_{(m)}$	443$_{(m)}$
L$_2$	3198$_{(s,b)}$	3101$_{(m)}$	1663$_{(vs)}$	1625$_{(s)}$	1259$_{(s)}$	974$_{(m)}$	......	......	......
5	-	3184$_{(m)}$	1622$_{(s)}$	1604$_{(vs)}$	1342$_{(s)}$	980$_{(m)}$	......	505$_{(m)}$	414$_{(m)}$
6	-	3171$_{(m)}$	1617$_{(sh)}$	1595$_{(s)}$	1311$_{(s)}$	985$_{(m)}$	......	507$_{(m)}$	448$_{(w)}$
7	-	3192$_{(m)}$	1609$_{(s)}$	1583$_{(sh)}$	1335$_{(m)}$	989$_{(m)}$	......	489$_{(m)}$	456$_{(w)}$
8	-	3157$_{(m)}$	1620$_{(s)}$	1593$_{(vs)}$	1312$_{(s)}$	993$_{(sh)}$	......	507$_{(m)}$	434$_{(m)}$
L$_3$	3336$_{(s)}$	3076$_{(m)}$	1695$_{(s)}$	1610$_{(s)}$	1261$_{(s)}$	954$_{(m)}$	617$_{(m)}$	......	......
9	-	3188$_{(m)}$	1711$_{(m)}$	1597$_{(s)}$	1335$_{(w)}$	985$_{(m)}$	635$_{(w)}$	457$_{(m)}$	411$_{(m)}$
10	-	3210$_{(m)}$	1696$_{(m)}$	1596$_{(s)}$	1349$_{(s)}$	987$_{(m)}$	638$_{(m)}$	530$_{(m)}$	451$_{(m)}$
11	-	3076$_{(m)}$	1695$_{(sh)}$	1602$_{(s)}$	1338$_{(sh)}$	996$_{(m)}$	648$_{(m)}$	536$_{(w)}$	462$_{(m)}$
12	-	3207$_{(m)}$	1691$_{(m)}$	1597$_{(s)}$	1341$_{(m)}$	984$_{(m)}$	639$_{(w)}$	454$_{(m)}$	422$_{(m)}$

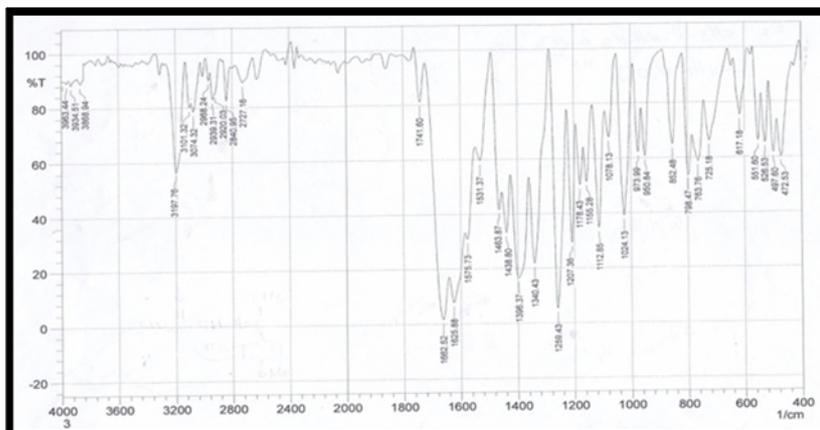vs=very strong, s=strong, sh= sholder, m=medium, w=weak, b=broad

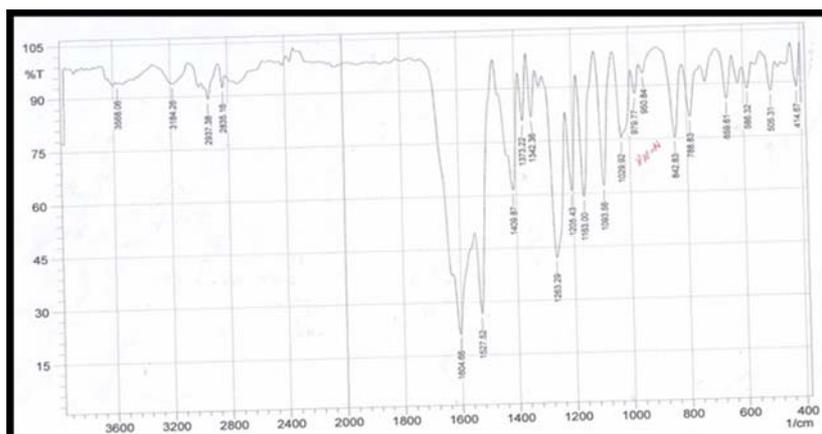**Fig. 1: Infrared spectrum of the ligand [AAH]**

Fig. 2: Infrared spectrum of the complex [Co(AAH-H)$_2$]

Electronic Spectra And Magnetic Moment Properties:

The electronic spectra of ligands and their metal complexes in the rang (1100-200) nm, were carried out in DMF. Table (4) shows the electronic spectral bands and magnetic moments of the prepared complexes.

The spectra of the ligands in DMF solution exhibit two main absorption bands at (34602–32894) cm^{-1} and (31055–29940) cm^{-1}. The first band probably is due to $\pi \rightarrow \pi^*$ transition of the chromophore (-C=N-NH-CO-), and the second band might be attributed to the $n \rightarrow \pi^*$ transitions resulting from nitrogen and oxygen atoms. In the spectra of the complexes, the shift of the ligand transitions to a longer wavelength (red shift) is ascribed to the ligand complextion with metal ions (El-Taras *et al*., 2012). The new intense band observed in the spectra of all complexes at the region (27548–23148) cm^{-1} may be associated with the charge transfer transitions (LMCT) (Ghosh *et al*., 2007).

The magnetic moment values of Co(II) complexes (1,5,9) are in the range (5.11-4.85) B.M, which are fairly close to the values reported for three unpaired electrons in an octahedral environment (Singh *et al*., 2013). These complexes exhibit three bands in their spectra at the regions (20366-19083)

cm^{-1}, (14925–14044) cm^{-1} and (10204–9250) cm^{-1} indicating an octahedral geometry around the metal ion. These transitions are assigned as $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (v_3), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (v_2) and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (v_1), respectively (Bakale *et al*., 2018).

The magnetic moment values of Ni(II) complexes (2,6,10) are in the range (3.3-2.92) BM which are close to the spin only value of two unpaired electrons, indicating octahedral environment around Ni(II) ion. It is further confirmed by their electronic spectral bands observed at the regions (23310–20080) cm^{-1}, (16949–11235) cm^{-1} and (9523–9216) cm^{-1} assignable to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(p)(v_3)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (v_2) and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (v_1) transitions, respectively (El-Sonbati *et al*., 2016).

The electronic spectra of Cu(II) complexes (3,7,11) contain a broad band at (14814–13793) cm^{-1}. These bands are typical of d-d band of Jahn-Teller distorted Cu(II) complexes in distorted octahedral geometry, and can be assigned to two or three of the transitions $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ that resulted from splitting of the $^2E_g \rightarrow {}^2T_2g$ (Rakha *et al*., 2014). Magnetic moment of these complexes are in range (2.01–1.74) B.M correspond to one unpaired electron and suggesting a monomeric octahedral geometry (Cotton *et al*., 1999).

The diamagnetic Zn(II) complexes (4,8,12) show no prominent absorption in the visible region and the Zn(II) complexes were found to be diamagnetic in nature consistent because of d^{10} configuration of Zn(II); therefore, the structures of the prepared Zn(II) complexes were proposed depending on the data of other measurements namely metal content and I.R spectra (Cotton *et al*., 1999; Mishra *et al*., 2014).

Table 4 : Electronic spectra and magnetic moments data of the ligands and their complexes

Complex No.	*Meff* **B.M**	Electronic spectrum cm^{-1}
L_1	……	32894 ,30864
1	4.85	31446, 28490, 27173, 20366, 14925, 10204
2	3.3	31746, 28571, 23148, 20080, 11235, 9216
3	1.87	32258, 28089, 25575,13985
4	diamagnetic	32670, 29850, 26246
L_2	……	34602, 31055
5	5.04	33557, 28735, 26881, 19083, 14814, 9389
6	2.93	33112, 28089, 25510, 20876, 16129, 9302
7	2.01	34482, 31446, 24691, 14814
8	diamagnetic	33898, 27932, 26525
L_3	……	33112, 29940
9	5.11	32051, 28571, 27027, 19920, 14044, 9250
10	2.92	32786, 29069, 24570, 23310, 16949, 9523
11	1.74	32894, 28409, 27548, 13793
12	diamagnetic	29850, 27472, 26178

Antibacterial Test

The anti-bacterial studies were carried out using the disc diffusion method. All results are tabulated in (Table 5). Six types of gram-negative bacteria viz. *Salmonella typhi*, *Aeromonas*, *Klebsiella*, *Escherichia coli*, *Pseudomonas acruginosa* and *Morganella morganii* as well as two types of gram-positive bacteria viz. *Staphylococcus aureus* and *Enterococcus faecalis* were used as the test organisms. Based on the results, the ligands show low activity towards the bacteria. Generally, all of the complexes show higher antibacterial properties compared to the free hydrazone ligands and moderate activity compared to the antibiotic Ceftriaxone.

It is suggested that the antimicrobial activity of the complexes is due to either killing the microbes or inhibiting their multiplication by blocking their active site.

Table 5 : Antibacterial activity of the tested compounds

Comp. No.	Abbriv .	* Sal.typh.	* Aeromonas	* klebsiella	* E. Coli	* P. acruginosa	* Morga morganii	* S. aureus	* E. faecalis
L₁	AMBH	R	R	R	R	R	R	S(30)	R
3	[Cu(AMBH- H)₂] .H₂O	R	R	R	R	R	R	S(11)	R
4	[Zn(AMBH-H)₂]	R	R	R	R	R	R	S(20)	R
L₂	AAH	R	R	R	R	R	R	R	R
7	[Cu(AAH-H)₂].H₂O	S(9)	R	R	S(20)	R	R	S(22)	R
8	[Zn(AAH-H)₂]	S(21)	S(12)	R	S(13)	R	R	R	R
L₃	APH	R	R	R	S(22)	R	S(14)	S(13)	R
11	[Cu(APH-H)₂].H₂O	R	R	R	R	R	R	R	R
12	[Zn(APH-H)₂]	R	R	R	R	R	R	R	R
	Ceftriaxone	R	R	R	S(32)	S(28)	S(40)	S(30)	R

* = Inhibition diameter (mm), R= Resistant, S= Susceptible

Fig.3: Photograph showing the (*S.aureus*) screening of the complexes 3,4,7,8,11,12

Fig.4: Photograph showing the antibacterial antibacterial (*E.Coli*) screening of the complexes 3,4,7,8,11,12

CONCLUSION

Based on stoichiometries and spectro-chemical studies, the AMBH and AAH hydrazone ligands, act as a monobasic tridentate ligand ONO in their prepared deprotenated complexes (1-8) coordinating through the phenolate oxygen, azommethine nitrogen and carbonyl oxygen atoms. The ligand APH acts as a monobasic tridentate ligand ONN in its complexes (9-12) coordinating through the phenolate oxygen, azommethine nitrogen and pyridine ring nitrogen atoms. Octahedral geometry was proposed for all complexes Fig. (5), Fig. (6)

Cu(II) and Zn(II) complexes are tested against six Gram-negative and two Gram-positive bacteria. The exhibited moderate activity with respect to ceftriaxone antibiotic and higher activity than the free ligands.
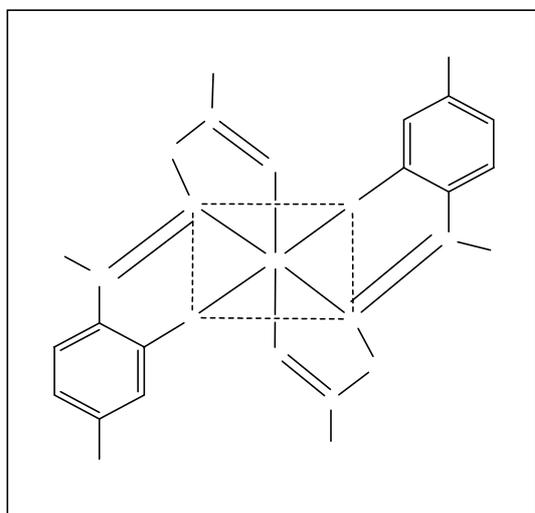
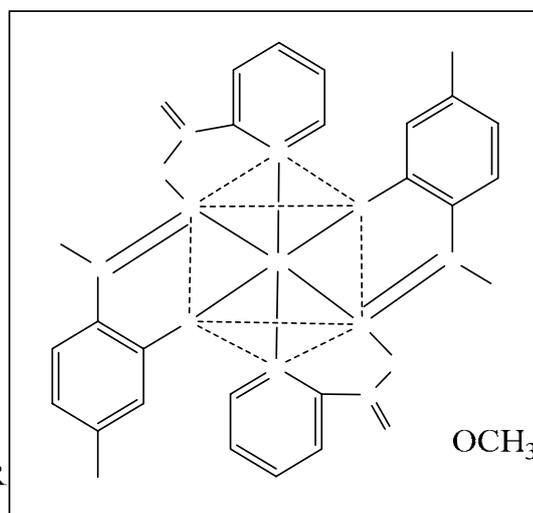**Fig. 5: Proposed structure for the complex (AMBH,AAH)**

Fig. 6: Proposed structure for the complexes (APH)

M= C₀ (II)**,** Ni (II), Cu(II), Zn(II)

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