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Synthesis, Characterization, and Antibacterial Activity Evaluation of New Co(II),Ni(II),Cu(II) and Zn(II) Complexes with Tridentate Hydrazones

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ABSTRACT

Hydrazones derived from acid hydrazides and 2-benzoylpyridine namely; 2-benzoylpyridineacetyl hydrazine (BPAH),2-benzoylpyridine-4-methylbenzoyl hydrazone (BPMH) and 2-benzoylpyridine picolinoylhydrazone (BPPH) have been synthesized and used to prepar the corresponding Co(II), Ni(II), Cu(II) and Zn(II) complexes. The ligands undergo deprotonation forming neutral mononuclear octahedral bis-complexes of the type $[M(L-H)_2]$ where L-H = deprotonated BPAH, BPMH or BPPH, acting as uni-negative tridentate ligands. The complexes isolated were characterized by elemental analyses, (IR, electronic spectra), molar conductance and magnetic susceptibility measurements. The bonding and probable structure of ,the complexes are discussed depending on the basis of the spectral and magnetic data. The ligands, as well as some of their complexes, screened against eight Gram-positive and Gram-negative bacteria, The tested compound exhibited moderate activity with respect to ceftriaxone antibiotic and higher activity than the free ligands.

Keywords: Hydrazones, Complexes, Transition metals, Antibacterial activity.

تحضير وتشخيص وتقييم الفعالية المضادة للبكتيريا لمعقدات جديده لكل من Co(II) و Ni(II) و Cu(II) و Zn(II) مع هيدرازونات ثلاثية السن

الملخص

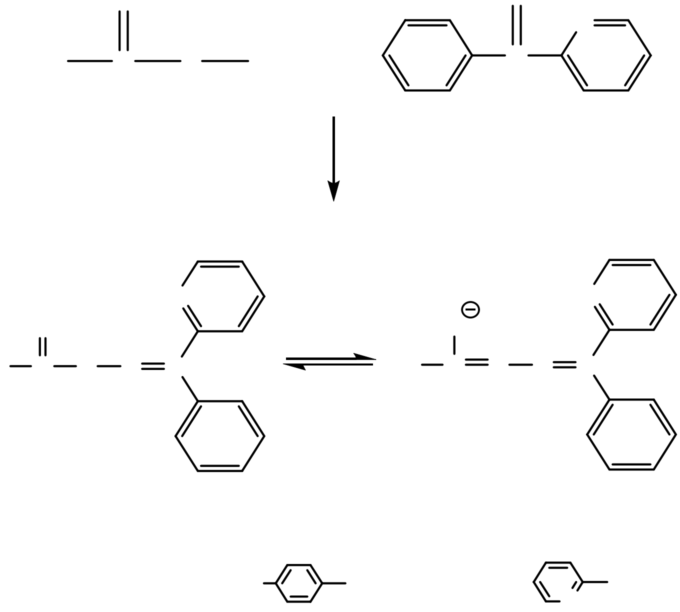
حضرت هيدرازونات مشتقة من هيدرازيدات الحوامض و 2-بنزويل بيريدين وهي: 2-بنزويل بيريدين أسيتايل هيدرازون (BPAH)، 2-بنزويل بيريدين 4-مثيل بنزويل هيدرازون (BPMH)، 2-بنزويل بيريدين بيكولينويل هيدرازون (BPPH) واستخدمت بوصفها ليكاندات لتحضير معقدات جديده للأيونات الفلزية Co(II) و Ni(II) و Cu(II) و Zn(II). فقدت الليكاندات بروتونات خلال عملية التحضير وكونت معقدات ثنائية (-bis) متعادلة احادية النوى ذوات الصيغة العامة $[M(L-H)_2]$ حيث L-H = الليكاندات PBAH و BPMH و BPPH منزوعة البروتون ولها تراكيب ثمانية السطوح سلكت فيها الليكاندات بوصفها ثلاثية السن احادية الشحنة السالبة شخصت المعقدات المحضرة بواسطة تحاليل العناصر واطياف الاشعة تحت الحمراء (IR) والاطياف الالكترونية (UV-Vis) وقياسات التوصيلية المولارية والحساسية المغناطيسية وتم تحديد اسلوب تناسق الليكاندات والتراكيب المتوقعة اعتماداً على البيانات الطيفية والمغناطيسية. قيمت فعالية الليكاندات وبعض معقداتها ضد ثمانية انواع من البكتيريا الموجبة والسالبة وأظهرت المركبات المقيمة أظهرت فعالية متوسطة بالمقارنة مع المضاد الحيوي ceftriaxone و أظهرت المعقدات فعالية أعلى من الليكاندات.

الكلمات الدالة: هيدرازونات، معقدات، عناصر انتقالية، فعالية بايولوجية.

INTRODUCTION

Hydrazones have found wide applications in synthetic chemistry (Gupta *et al.*, 2007) and in numerous pharmacological applications as antimicrobial, anticonvulsant, anticancer, antibacterial, antitumor agents, antiviral and anti-inflammatory agents (Rollas and Kücükgüzel, 2007 ; Marella *et al.*, 2014). Some aroylhydrazones have been widely investigated as one of the orally effective tridentate iron chelators (Richardson and Bernhardt, 1999; Kalinowski *et al.*, 2008). Hydrazones are now being used extensively in detection and quantitative determination of several metals (Suvarapu *et al.*, 2012) and in the preparation of metal complexes having diverse structures (Jing-lin. *et al.,* 2014). Hydrazone-based ligands have received considerable attention due to their unique ligational properties and significant physicochemical properties of their metal complexes (Stadler and Harrowfield, 2009) and the possible applications of these complexes as new therapeutic agents (Rahman *et al.*, 2018). Some aroyl-hydrazone complexes of transition metals are used as models for elucidation the mechanism of enzyme inhibition (Richardson and Bernhardt, 1999). The study of the complexes is also justified by their activity against various bacteria (Suvarapu *et al.*, 2012).

Literature survey of transition metal hydrazone complexes revealed that their coordination behavior depends on the nature of the substituents and also on the position of the imine 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). In view of potential interesting structural features and properties, we considered it worthwhile to attempt synthesis of some transition and non-transition metal complexes of hydrazone ligands derived from acetylhydrazine, 4-methylbenzoyl hydrazine or picolinoyl hydrazine and 2-benzoylpyridine Fig. (1). The complexes have been characterized by various physicochemical methods. Also, the antibacterial (Gram-negative and Gram-positive bacterial strains) have been examined.



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 FT-IR 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 cuvettes. Molar conductances 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 complexes 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 complexmetric titration using standard EDTA solution (Ni and Zn) (Vogel, 1989).

Preparation of the Ligands

Preparation of Acid Hydrazides:

Acetyl hydrazine, 4-methylbenzoyl 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).

Preparation of Hydrazones:

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

To a solution of acid hydrazide (0.02 mole) [1.48 g, acetyl hydrazine, 3.00 g, 4-methylbenzoyl hydrazine, or 2.74 g, picolinoyl hydrazine] in absolute ethanol (25 mL) was added to the solution of benzoyl pyridine (3.66 g, 0.02 mole) in absolute ethanol (25 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).

Preparation of the Metal Complexes

To 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 (0.478g, 0.002 mole) of the ligand (BPAH), (0.630g, 0.002 mole) of the ligand (BPMH) or (0.604g, 0.002 mole) of the ligand (BPPH) in absolute ethanol (10 mL) and(0.2g, 0.002 mole) of 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 2-benzoylpyridine (BPAH,BPMH and BPPH were prepared in good yields by condensation with acid hydrazides (Scheme 1). The reaction of these hydrazones with metal acetates in presence of triethyl amine (Sadhukhan *et al*., 2011) yield bis-complexes in which the ligands enolize and deprotonated during complexation as indicated by analytical data (Table 1 and 2). All the complexes are coloured (except complex No 4,white) non-hygroscopic solids, stable to air and moisture at room temperature. They are generally insoluble in water and non-polar organic solvents, slightly soluble in ethanol, methanol, chloroform, but are more soluble in highly polar organic solvents, like DMF and DMSO. Most complexes melt in temperature range (300-198)ºC which may indicate the non-polymeric nature of the complexes. The low molar conductance values of the solutions of the complexes in absolute ethanol (24.6-3.1) ohm^{-1}mol^{-1}cm^2 and in DMF (26.2-6.5) 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. (^{O}C)**	**Yield %**	**Metal %**		**ohm^{-1}cm^{2}mol^{-1}**	
					Calc.	Found	EtOH	DMF
L_1	BPAH($C_{14}H_{13}N_3O$) M.wt=239	White	92-94	58	……	…….	....	……
1	[C_O (BPAH-H)$_2$]	Brown	248d	52	11.01	11.52	4.5	6.5
2	[Ni (BPAH-H)$_2$]	Red	278-280	57	10.9	11.09	12.5	10.8
3	[Cu (BPAH-H)$_2$]	Green	240-242	54	11.77	12.45	11.3	7.8
4	[Zn (BPAH-H)$_2$]	White	280-282	67	12.0	12.2	6.2	7.7
L_2	BPMH($C_{20}H_{17}N_3O$) M.wt=315	White	118-120	68	……	……	……	……
5	[C_O(BPMH-H)$_2$] .2H_2O	Brown	220-222	89	8.15	9.07	5.4	14.6
6	[Ni(BPMH-H)$_2$]	Brown	298-300	66	8.50	8.1	4.9	17.7
7	[Cu(BPMH-H)$_2$]	Green	232-234	71	9.18	9.93	19.0	16.3
8	[Zn(BPMH-H)$_2$]	Yellow	260-262	61	9.4	10.2	3.1	15.2
L_3	BPPH($C_{18}H_{14}N_4O$) M.wt=302	White	122-124	67	……	……	……	…..
9	[C_O(BPPH-H)$_2$]	Brown	198-200	82	8.91	9.27	5.3	6.8
10	[Ni(BPPH-H)$_2$]	Red	210-212	82	8.88	9.27	24.6	26.2
11	[Cu(BPPH-H)$_2$]	Green	300d	66	9.54	10.27	5.4	10.8
12	[Zn(BPPH-H)$_2$]	Yellow	202-204	86	9.79	9.2	24.4	14.3

*d= decomposition

Table 2: Elemental analyses of ligands and some of complexes

Compd. No.	**Abbreviation**	**Formula**	**Elemental analyses Calculated (Found)**		
			C%	**H%**	**N%**
L_1	BPAH	$C_{14}H_{13}N_3O$	70.29 (69.96)	5.44 (6.03)	17.57 (16.79)
L_2	BPMH	$C_{20}H_{17}N_3O$	76.19 (75.81)	5.40 (4.98)	13.33 (13.69)
L_3	BPPH	$C_{18}H_{14}N_4O$	71.52 (70.90)	4.64 (4.43)	18.54 (18.50)
3	[Cu(BPAH-H)$_2$]	$C_{28}H_{24}N_6O_2Cu$	62.28 (60.95)	4.45 (4.26)	15.57 (15.78)
5	[C_O(BPMH-H)$_2$] .2H_2O	$C_{40}H_{36}N_6O_4C_O$	66.39 (66.11)	4.43 (4.89)	11.62 (11.44)
10	[Ni(BPPH-H)$_2$]	$C_{36}H_{26}N_8O_2Ni$	65.38 (65.50)	3.93 (3.92)	16.95 (16.52)

Infrared spectra

IR spectra usually provide a lot of valuable information on coordination behavior of the ligands with metals. The IR spectra of the free ligands and their corresponding metal complexes were compaired (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 (3303 – 3141), (1695 – 1670), (1648 – 1614) and (991 – 954) cm^{-1} in the spectra of the free ligands are assigned to ν (N-H), ν (C=O), ν (C=N) and ν (N-N) respectively (Singh *et al.*, 2014 ; Sathyadevi *et al.*, 2012). The bands of $\nu_{(N-H)}$ and $\nu_{(C=O)}$ were absent in the spectra of the deprotonated ligands in all complexes suggesting coordination via enol- form, by deprotonation of the N-H proton, during the complexation process. The appearance of anew $\nu_{(c-o)}$ band in these complexes at the region (1305-1245) cm^{-1} suggest bonding of the ligands to the metal ions through deprotonated (C-O) group (Singh *et al.*, 2013).

The stretching vibrations of azomethine group $\nu_{(C=N)}$ are shifted to lower frequencies in all the complexes spectra by (43-6)cm^{-1}, which proves that nitrogen atom of azomethine group is involved in complexation (Mishra *et al.*, 2014). Coordination of nitrogen to the metal atom reduces the electron density in the azomethine group causing a shift in the $\nu_{(C=N)}$ band to lower frequencies (Shit *et al.*, 2009). The $\nu_{(N-N)}$ observed at (991-954) cm^{-1} in the spectra of the ligands, shifts to higher frequencies by (38-21) cm^{-1} in their complexes, indicates the coordination of nitrogen atom of N-N group with metal ions (Singh *et al.,* 2013). This phenomenone 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). These observations were further substantiated by the appearance of non-ligand bands at the ranges (519-450)cm^{-1} and (459-406) cm^{-1} which are tentatively assigned to ν_{M-O} ,ν_{M-N} respectively (El-Boraey and Aly, 2013). The pyridine in-plane deformation mode at (623-611) cm^{-1} in the spectra of the free ligands shifts to (653-623) cm^{-1} in the spectra of all complexes suggesting coordination of the heterocyclic nitrogen atom (Despaigne *et al.*, 2009). Hence, it may be concluded that in all complexes are deprotonated and the ligands BPAH, BPMH and BPPH acts as anionic tridentate ONN donor, chelating through the enolate oxygen, the imine nitrogen and pyridine ring nitrogen atoms. Abroad band at ca.3400 cm^{-1} is observed in complex No.(5) which indicate the presence of lattice water (Sreejith *et al.*, 2018). Isince vibrational modes such as wagging, twisting and rocking activated by coordination to the metal not been found in the expected ranges, it appers that water molecules are not coordinated.

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

Comp. No.	ν(N-H)	ν(C=O)	ν(C=N)	ν(C-O)	ν(N-N)	δ(Py.ring)	ν(M-O)	ν(M-N)
L_1	$3141_{(m)}$	$1670_{(vs)}$	$1628_{(sh)}$	…..	$954_{(m)}$	$617_{(m)}$	……	……
1	……	……	$1598_{(s)}$	$1305_{(s)}$	$989_{(m)}$	$623_{(m)}$	$519_{(w)}$	$459_{(m)}$
2	……	……	$1586_{(m)}$	$1290_{(s)}$	$982_{(m)}$	$632_{(m)}$	$498_{(m)}$	$417_{(m)}$
3	……	……	$1622_{(s)}$	$1255_{(s)}$	$980_{(m)}$	$646_{(m)}$	$487_{(m)}$	$411_{(m)}$
4	……	……	$1600_{(m)}$	$1245_{(s)}$	$982_{(m)}$	$629_{(m)}$	$488_{(m)}$	$408_{(w)}$
L_2	$3303_{(m)}$	$1670_{(vs)}$	$1614_{(s)}$	……	$991_{(m)}$	$611_{(m)}$	……	……
5	……	……	$1593_{(m)}$	$1292_{(s)}$	$1017_{(m)}$	$653_{(m)}$	$450_{(m)}$	$422_{(w)}$
6	……	……	$1582_{(m)}$	$1252_{(s)}$	$1018_{(m)}$	$638_{(m)}$	$473_{(m)}$	$433_{(w)}$
7	……	……	$1589_{(m)}$	$1255_{(sh)}$	$1012_{(m)}$	$640_{(m)}$	$494_{(m)}$	$406_{(w)}$
8	……	……	$1584_{(m)}$	$1254_{(s)}$	$1023_{(m)}$	$638_{(m)}$	$472_{(m)}$	$425_{(w)}$
L_3	$3304_{(s)}$	$1695_{(vs)}$	$1648_{(sh)}$	……	$974_{(m)}$	$623_{(m)}$	……	……
9	……	……	$1626_{(s)}$	$1252_{(s)}$	$1012_{(m)}$	$648_{(m)}$	$453_{(m)}$	$429_{(m)}$
10	……	……	$1622_{(m)}$	$1257_{(m)}$	$997_{(m)}$	$644_{(m)}$	$505_{(w)}$	$422_{(m)}$
11	……	……	$1628_{(s)}$	$1278_{(s)}$	$1012_{(m)}$	$636_{(m)}$	$499_{(m)}$	$418_{(w)}$
12	……	……	$1605_{(m)}$	$1247_{(m)}$	$1008_{(m)}$	$652_{(m)}$	$459_{(m)}$	$415_{(m)}$

w=weak , m=medium , s=strong , vs=very strong , sh=sharp

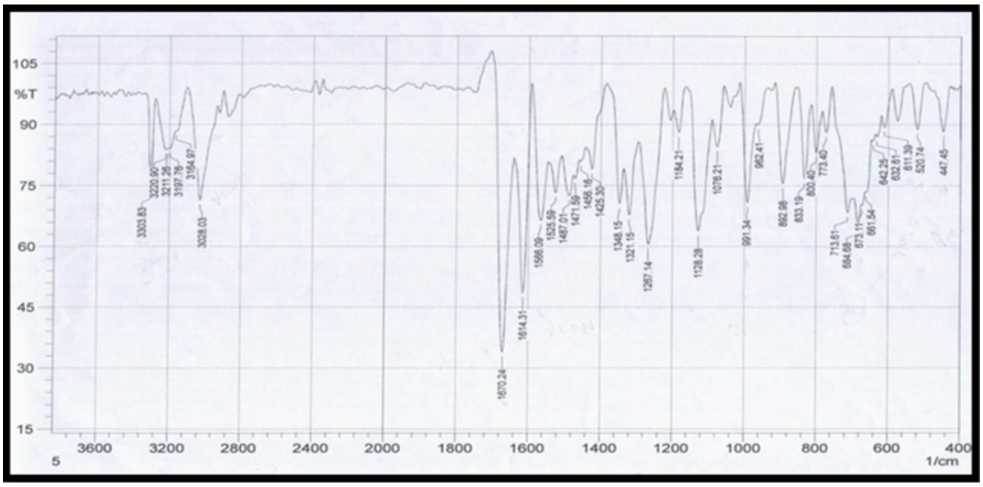


Fig. 1: Infrared spectrum of ligand [BPMH]

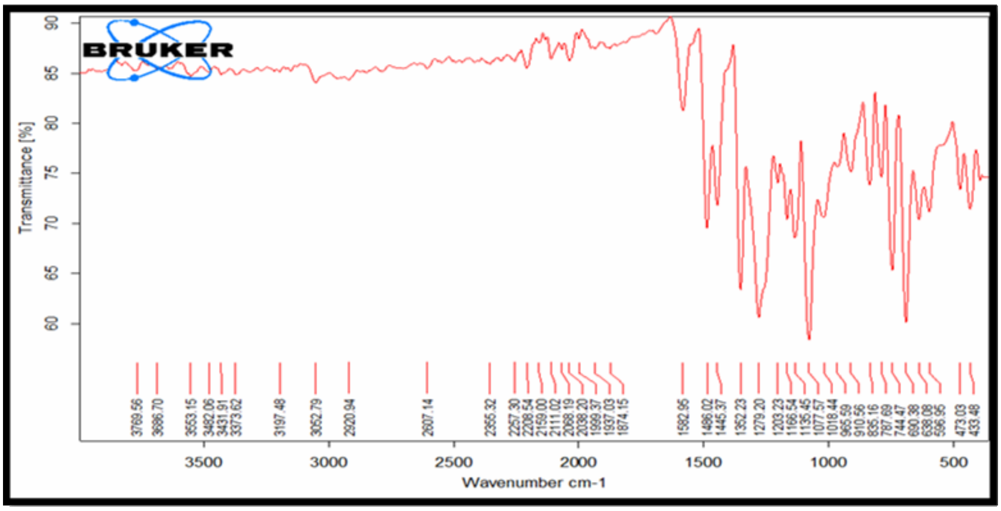


Fig. 2: Infrared spectrum of complex [Ni(BPMH-H)$_2$]

Electronic spectra and magnetic moments 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 (33783-322582) cm^{-1}and (31446-31250) cm^{-1}. The first band probably due to $\pi\rightarrow\pi^*$ transition of the chromophore (-C=N-NH-CO-), and the second band might 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 complexion with metal ions. The new intense band observed in the spectra of all complexes at the region (28169-24096) cm^{-1} may be associated with the charge transfer transitions (LMCT).

The magnetic moment values of Co(II) complexes (1,5,9) are in the range (5.09-4.90) 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 (20833-20325) cm^{-1}, (15625-13550) cm^{-1} and (9433-9216) cm^{-1} indicating an octahedral geometry around the metal ion. These transitions are assigned as $^4T_{1g}(F)\rightarrow{}^4T_{2g}(P)$ (**ν_3**), $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ (**ν_2**) and $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ (**ν_1**) respectively. (Cotton *et al.*, 1999; Singh *et al.*, 2013; Bakale *et al.*, 2018).

The magnetic moment values of Ni(II) complexes (2,6,10) are in the range (3.18-2.73) BM which are very 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 (23255–19880) cm^{-1}, (13245–12004) $cm^{-1}$and (10006–9174) cm^{-1} assignable to $^3A_{2g}(F)\rightarrow{}^3T_{1g}(p)$(**$\nu_3$**), $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ (**ν_2**) and$^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$ (**ν_1**) transitions respectively (Cotton *et al.*, 1999 ; El-Sonbati, *et al.*, 2016 ; Singh *et al.*, 2014).

The electronic spectra of Cu(II) complexes (3,7,11) contains a broad band at (14925–14450) 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 $^2Eg\rightarrow{}^2T_2g$ (Singh, 2008; Rakha *et al.*, 2014). Magnetic moment of these complexes are in range (2.26–2.00) 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}(wave number)
L_1	……	33783,31250
1	4.90	33557,28901,26246,20408,14084,9433
2	2.73	31716,30303,25974,19880,13245,10006
3	2.26	32258,29239,24096,14705
4	dia	32145,29850,26315
L_2	......	32258,31250
5	4.91	32051,29585,27624,20833,13550,9216
6	3.18	32786,31250,26315,20080,12594,9174
7	2.1	31746,29411,27624,14450
8	dia	31645,28169,25316
L_3	……	32787,31446
9	5.09	32278,30440,28169,20325,15625,9302
10	2.96	32185,30489,25641,23255,12004,9259
11	2.0	33112,28571,26455,14925
12	dia	31645,28169,25316

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
L	BPAH	…	……	……	14	…	……	11	…
3	[Cu(BPAH-H)$_2$]	14	16	……	……	13	……	26	…
4	[Zn(BPAH-H)$_2$]	18	……	……	15	…	……	……	…
L$_2$	BPMH	…	11	……	12	…	……	18	…
7	[Cu(BPMH-H)$_2$]	20	16	……	13	…	……	22	…
8	[Zn(BPMH-H)$_2$]	9	12	……	22	…	……	10	…
L$_3$	BPPH	…	……	……	……	…	……	11	…
11	[Cu(BPPH-H)$_2$]	20	11	……	……	…	……	22	…
12	[Zn(BPPH-H)$_2$]	12	12	11	22	…	14	13	…
	Ceftriaxone	…	……	……	32	28	40	30	…

* = Inhibition diameter (mm)

CONCLUSION

Based on stoichiometries and spectro-chemical studies, the hydrazine ligands, acts as a monobasic tridentate ligand ONN in all prepared deprotenated complexes (1-12) coordinating through the enolate oxygen, azommethine group nitrogen and pyridine ring nitrogen atoms. Octahedral geometry proposed for all complexes Fig. (1).

Cu(II) and Zn(II) complexes are tested against six Gram-negative and two Gram-positive bacteria, they exhibited moderate activity with respect to ceftriaxone antibiotic and higher activity than the free ligands.

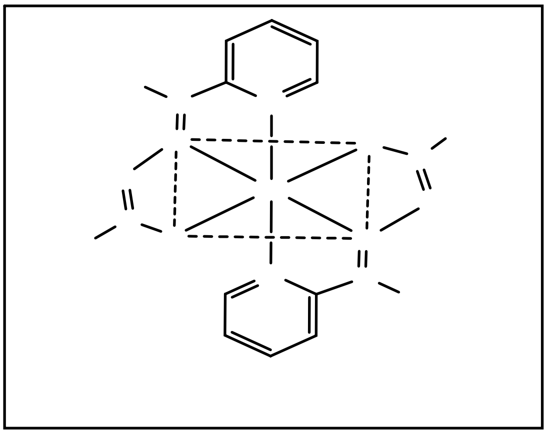


Fig. 3: Proposed structure for the complexes

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