

## Synthesis and Structural Studies of Co(II), Ni(II), Cu(II), Zn(II), Th(IV) and UO<sub>2</sub>(II) Complexes with 2-Acetylpyridine-4'-methylbenzoyl hydrazone

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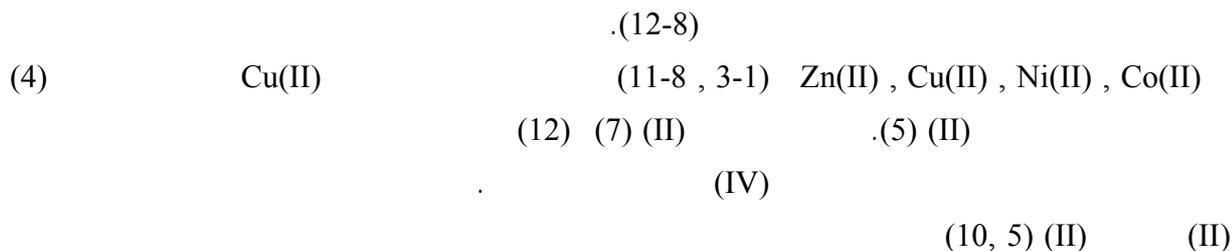
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### ABSTRACT

A number of Co(II), Ni(II), Cu(II), Zn(II), Th(IV) and UO<sub>2</sub>(II) complexes with 2-acetylpyridine-4'-methylbenzoyl hydrazone (APMBH), obtained by the condensation of 2-acetylpyridine with 4-methylbenzoyl hydrazine are reported. The reaction of metal chlorides with APMBH lead to isolation of complexes having the general formulas [M(APMBH)(H<sub>2</sub>O)<sub>n</sub>Cl<sub>2</sub>] (n=1, M=Co(II), Ni(II); n=0, M=Zn(II), UO<sub>2</sub>(II)), [Ni(APMBH-H)Cl(DMSO)]<sub>2</sub>, [Cu(APMBH-H)Cl]<sub>2</sub> and [Th(APMBH)<sub>2</sub>Cl<sub>2</sub>]Cl<sub>2</sub>. The reaction of metal acetate with APMBH in 1:2 molar ratio yields the deprotonated bis-complexes [M(APMBH-H)<sub>2</sub>] (M= Co(II), Ni(II), Cu(II), Zn(II) and UO<sub>2</sub>(II)). The complexes have been characterized by elemental analysis, spectral (IR, UV-Vis) magnetic and molar conductance measurements, which revealed that APMBH act as neutral tridentate NNO-donor ligand in the metal chloride complexes (1, 2, 5-7) and as a monobasic tridentate ligand in the dimeric complexes (3, 4). The ligand also acts as a monobasic NNO-tridentate in the deprotonated bis-complexes (8-12). Octahedral structure is suggested for Co(II), Ni(II), Cu(II) and Zn(II) complexes (1-3, 8-11), dimeric square pyramidal structure for Cu(II) complex (4) and trigonal bipyramidal structure for Zn(II) complex (5). Uranyl complexes 7 and 12 are expected to have pentagonal bipyramidal and hexagonal bipyramidal structures respectively. Eight coordinate structure is proposed for Th(IV) complex (6). The antibacterial activity of Cu(II) and Zn(II) complexes (5 and 10) against Gram-positive and Gram-negative bacteria has been tested and show moderate and high activity respectively.

**Keywords :** Transition metals, Hydrazone, Thorium, Uranium

(II)	(II)	(II)	(II)	(II)	(II)	(IV)
		-4'-		-2		
(II)	(IV)	(II)	(II)	(II)	(II)	
	-4	-2	(APMBH)			-4'- -2
[M(APMBH)(H <sub>2</sub> O) <sub>n</sub> Cl <sub>2</sub> ]			APMBH			
[Ni(APMBH-H)Cl(DMSO)] <sub>2</sub>	(UO <sub>2</sub> (II)	Zn(II) = M	n=0, i(II)	Co(II) =M	n=1	)
			[Th(APMBH) <sub>2</sub> Cl <sub>2</sub> ]Cl <sub>2</sub>	[Cu(APMBH-H)Cl] <sub>2</sub>		
=M	) [M(APMBH-H) <sub>2</sub> ]		APMBH			
	APMBH			(UO <sub>2</sub> (II), Zn(II), Cu(II), Ni(II), Co(II)		(IR, UV-Vis)
(4, 3)				(7-5, 2-1)		



## INTRODUCTION

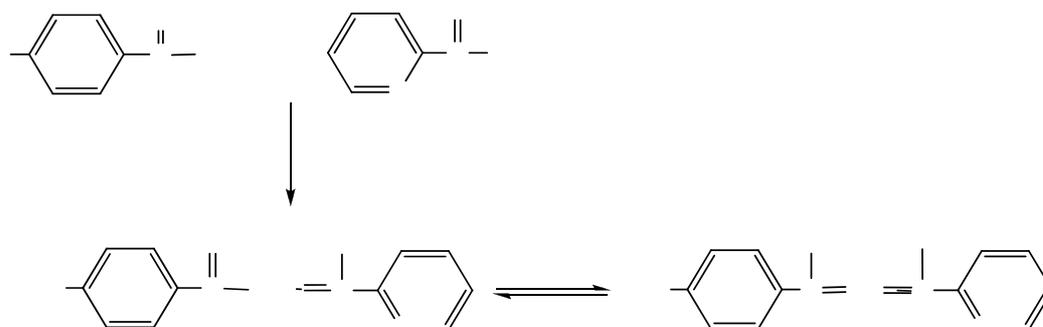
A considerable attention has been paid in the last decade to hydrazones, since they display a variety of coordination mode which leads to different molecular structures metal complexes (Alageson *et al.*, 2013 ; Singh and Singh, 2013 ; Ibrahim *et al.*, 2009; Jang *et al.*, 2005).

Hydrazones are considered an important class of ligands also because the processes pharmacological applications as antimicrobial, anticonvulsant, analgesic, anti-inflammatory, antiplatelet, antitubercular, and antitumoral agenst (Rollas and Kücükgül, 2007). Biological activities of hydrazone metal complexes are also reported for several transitional metals (Alageson *et al.*, 2013 ; Sathyadevi *et al.*, 2012). Moreover, it has recently been shown that hydrazones such as pyradoxal isonicotinoyl hydrazone analogs are effective iron chelators in vivo and in vitro and may be of value for the treatment of iron overload (Bernharat *et al.*, 2008).

The coordination behavior of aroyl hydrazones is known to depend on the pH of the medium, the nature of the substituents and also on the position of hydrazino group relative to other moieties. Moreover, the deprotonation of the NH group which is readily achieved in complexation, results in the formation of tautomeric anionic species having new coordination properties (Al-Daher and Mustafa, 2013; Galic *et al.*, 2012).

Hydrazones have also been proven to show potential applications as catalysts (Hosseini-Monfared *et al.*, 2013), luminescent probes and molecular sensors (Guo *et al.*, 2011; Sun *et al.*, 2009). Many hydrazone complexes show an excellent catalytic activity in various reactions (Sadhukhan *et al.*, 2011). They are also used as analytical reagents for spectrophotometric determination of several metal ions (Bale and Sawant, 2001).

In view of the above mentioned significant importance of hydrazone metal complexes in various fields and on continuation of our studies of hydrazone metal complexes (Al-Daher and Mustafa, 2013; Al-Daher and Hadi, 2013; Al-Daher and Al-Qassar, 2011), we were motivated to synthesis Co(II), Ni(II), Cu(II), Zn(II), Th(IV) and UO<sub>2</sub>(II) Complexes with 2-Acetylpyridine-4'-methylbenzoyl hydrazone (APMBH) (Scheme 1) and to describe their structural and antibacterial properties.



**Scheme 1: Tautomer forms of 2-acetylpyridine-4'-methylbenzoyl hydrazone (APMBH)**

## EXPERIMENTAL

### Materials and Measurements

All chemicals used were reagent grade from B.D.H or Fluka companies, used as supplied.

Infrared spectra were recorded as KBr discs using Tensor 27 Bruker FT-IR spectrophotometer ( $4000-400\text{ cm}^{-1}$ ). Electronic absorption spectra were recorded in DMF  $10^{-2}$  solutions on Shimadzu U V-1650 PC spectrophotometer at room temperature using 1cm cell. Molar conductance was measured at ambient temperature using PMC3 Jeneway conductivity meter. Magnetic susceptibility measurements of the complexes were carried out using Bruker BM6 instrument at room temperature.  $^1\text{H-NMR}$  spectra were recorded in DMF- $d_7$  solution using TMS as an internal standard on BRUKER : AVANCE (III) 400 MHz spectrophotometer. Melting points were obtained on Electro thermal 9300 melting point apparatus in open capillaries.

The metal content of the complexes was determined spectrophotometrically using Shimadzu (AA670) atomic absorption spectrophotometer, Zinc and Nickel were also determined by complexometric titration against standard EDTA solution (Vogel, 1989). Thorium and uranium were determined colourimetrically using thoron and arsinazo III as reagents respectively (Marczenko and Balcezak, 2000). Chloride content was estimated volumetrically using standard  $\text{AgNO}_3$  solution (Vogel, 1989).

### Preparation of ligand

#### a. Preparation of the 4-methylbenzoyl hydrazine :

This was prepared according to literature (Furniss *et al.*, 1989) by the reaction of excess hydrazine hydrate and ethyl toluate in ethanol yield 70%, mp.  $116-117^\circ\text{C}$  (lit. mp.  $117^\circ\text{C}$ ).

#### b. Preparation of 2-Acetylpyridine-4'-methylbenzoyl hydrazone (APMBH):

It was prepared following the general procedure (Sacconi, 1953) by reacting an ethanolic solution (15 mL) of 4-methylbenzoyl hydrazine (4.5 g, 0.03 mole) with (3.63 g, 0.03 mole) 2-Acetylpyridine in ethanol (10 mL) under refluxing with a continuous stirring for 3hr. After the completion of reaction and partial removal of solvent, white crystalline solid was separated on cooling. The solid filtered, washed with cold ethanol (5 mL) and finally dried in an oven at  $70-80^\circ\text{C}$  (yield 90% mp.  $150^\circ\text{C}$ ).

### Preparation of complexes

#### a. Preparation of metal chloride complexes :

The respective metal chloride (0.001 mole, 0.238g,  $\text{CoCl}_2.6\text{H}_2\text{O}$ ; 0.238 g,  $\text{NiCl}_2.6\text{H}_2\text{O}$ ; 0.171 g,  $\text{CuCl}_2.2\text{H}_2\text{O}$ ; 0.136 g,  $\text{ZnCl}_2$ ; 0.377g,  $\text{UO}_2\text{Cl}_2.2\text{H}_2\text{O}$ ) solution in (10 mL) absolute ethanol were heated under reflux with a constant stirring with (0.25 g, 0.001 mole) of the ligand APMBH in (10 mL) absolute ethanol for 2hr. The solid complexes formed were then filtered off washed with hot ethanol (5 mL), ether (5 mL) and finally dried in an oven at  $70-80^\circ\text{C}$ . The complex (3)  $[\text{Ni}(\text{APMBH-H})\text{Cl}(\text{DMSO})_2]$  was prepared in the same way except that DMSO was used as solvent instead of absolute ethanol. In case of Th(IV) complex (6) thorium tetrachloride hydrate,  $\text{ThCl}_4.5\text{H}_2\text{O}$  (0.464 g, 0.001 mole) and (0.50 g, 0.002 mole) of APMBH in ethanol were used.

#### b. Preparation of the deprotonated bis Complexes:

To a stirred solution of APMBH (0.50 g, 0.002 mole) in absolute ethanol (10 mL) was added a hot ethanolic solution (10 mL) of the corresponding metal acetate (0.001 mole 0.249 g,  $\text{Co}(\text{CH}_3\text{COO})_2.4\text{H}_2\text{O}$ ; 0.249 g  $\text{Ni}(\text{CH}_3\text{COO})_2.4\text{H}_2\text{O}$ ; 0.199g,  $\text{Cu}(\text{CH}_3\text{COO})_2.\text{H}_2\text{O}$ ; 0.219g,  $\text{Zn}(\text{CH}_3\text{COO})_2.2\text{H}_2\text{O}$ ; 0.424 g  $\text{UO}_2(\text{CH}_3\text{COO})_2.2\text{H}_2\text{O}$ ). The resulting mixture was refluxed for 3hr upon which solid was formed. The solid complexes were filtered, washed with ethanol (5 mL) then with ether (5 mL) and dried in an oven at  $70-80^\circ\text{C}$ .

**Antibacterial activity:**

This was evaluated using agar diffusion method (Kethcum,1988). Gram-positive bacteria *Staphylococcus aureus* and Gram-negative bacteria *Klebsiella pneumoniae* were cultivated in nutrient agar on petri dishes. The test solution was prepared by dissolving (10 mg) of the tested substances in DMSO (1 mL). A 6 mm diameter filter paper discs were soaked in the tested solutions. After 24h cultivation at 37 °C, diameters of zones of inhibition were determined. DMSO was inactive under applied conditions.

**RESULTS AND DISCUSSION**

The reaction of equimolar amounts of 4-methylbenzoyl hydrazine and 2-acetyl pyridine in ethanol gave the desired hydrazone ligand APMBH (Scheme 1) in excellent yield and purity. The analytical data and some of the physical properties of the prepared ligand and its complexes are shown in (Table 1) which indicates that metal chlorides form 1:1 (M:L) complexes with APMBH of the general formula,  $[M(APMBH)(H_2O)_nCl_2]$  ( $n=1$ ,  $M=Co(II)$ ,  $Ni(II)$ ;  $n=0$ ,  $M=Zn(II)$ ,  $UO_2(II)$ ) and deprotonated dimeric complexes  $[Cu(APMBH-H)Cl]_2$  and  $[Ni(APMBH-H)Cl(DMSO)]_2$ . Deprotonation of metal chloride (1:1) complexes is reported in literature (Despaigne *et al.*, 2009). Thorium(IV) tetrachloride form 1:2 (M:L) complex (6). On the other hand, the reaction of metal(II) acetates with APMBH in 1:2 molar ratio yields the mononuclear deprotonated bis-complexes  $[M(APMBH-H)_2]$  ( $M= Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$ ,  $Zn(II)$  and  $UO_2(II)$ ).

The metal complexes are stable non-hygroscopic insoluble in most common organic solvents like chloroform, benzene, acetone, diethyl ether and slightly soluble in methanol or ethanol but more soluble in DMSO and DMF. Most of the complexes melt or decompose in the temperature range 237-295 °C and few melted above 300 °C Molar conductance data of  $10^{-3}M$  solutions of the complexes (Table 1) at room temperature show low values (1.66-14.92)  $ohm^{-1} mol^{-1} cm^2$  indicating that they are non-electrolytes, except for Th(IV) complex (6) which behaves as 1:2 electrolyte (Geary, 1971).

**Table 1: Physical properties and analysis data of the ligand and its complexes**

Complex No.	Formula	P°C.m	Color	Yield %	$\Omega\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$		calculated/(found)	
					DMF	Ethanol	%M	%Cl
L	APMBH (C <sub>15</sub> H <sub>15</sub> N <sub>3</sub> O)	150	White	90	-----	-----	-----	-----
1	[Co(APMBH)(H <sub>2</sub> O)Cl <sub>2</sub> ]	237	Green	82	13.83	14.92	14.70 (14.48)	17.70 (17.52)
2	[Ni(APMBH)(H <sub>2</sub> O)Cl <sub>2</sub> ]	265d	Green	90	8.64	10.21	14.65 (14.52)	17.71 (17.48)
3	[Ni(APMBH-H)Cl(DMSO)] <sub>2</sub>	288d	Dark green	75	5.46	9.24	13.83 (13.57)	8.36 (8.12)
4	[Cu(APMBH-H)Cl] <sub>2</sub>	260	Dark green	78	1.93	8.08	18.09 (17.85)	10.11 (9.88)
5	[Zn(APMBH)Cl] <sub>2</sub>	237d	White	76	4.49	5.86	16.79 (16.55)	18.23 (17.97)
6	[Th(APMBH) <sub>2</sub> Cl <sub>2</sub> Cl] <sub>2</sub>	295d	White	84	142	81	26.36 (26.56)	16.13 (15.88)
7	[UO <sub>2</sub> (APMBH)Cl] <sub>2</sub>	340	Yellow	92	1.98	6.23	40.06 (39.88)	11.95 (11.72)
8	[Co(APMBH-H) <sub>2</sub> ]	295	Brown	69	5.56	1.66	10.47 (10.25)	
9	[Ni(APMBH-H) <sub>2</sub> ]	230d	Dark green	82	2.56	2.60	10.43 (10.22)	
10	[Cu(APMBH-H) <sub>2</sub> ]	252	Green	76	3.68	3.92	11.18 (11.39)	
11	[Zn(APMBH-H) <sub>2</sub> ]	346	Yellow	84	5.34	3.26	11.48 (11.26)	
12	[UO <sub>2</sub> (APMBH-H) <sub>2</sub> ]	336	Orange	83	1.80	4.42	30.74 (30.56)	

d=decomposition temperature

**Characterization of organic ligand**

The main IR bands of the ligand with their tentative assignments in (Table 2) display a medium intensity band at 3338 cm<sup>-1</sup> due to amide NH stretching vibration  $\nu_{(\text{N-H})}$  of the hydrazone which may be involved in NH...O hydrogen bonding. The strong bands at 1672 and 1610 cm<sup>-1</sup> are assigned to the carbonyl group stretching vibration  $\nu_{(\text{C=O})}$  and azomethine stretching vibration  $\nu_{(\text{C=N})}$  respectively. The low energy of  $\nu_{(\text{C=N})}$  could be attributed to conjugation with neighboring pyridine (Karbouj *et al.*, 2010). The medium band at 623 cm<sup>-1</sup> is assigned to the pyridine ring in plane deformation mode. The spectrum of the ligand displays also a weak band at 993 cm<sup>-1</sup> due to N-N stretching vibration  $\nu_{(\text{N-N})}$  (Despaigne *et al.*, 2009 ; Singh, 2008). IR data suggest keto-form of the ligand in the solid state.

<sup>1</sup>H-NMR spectrum of the free ligand in DMF-d<sub>7</sub> solution shows a weak signal at  $\delta$  10.79 ppm (s, 1H) assigned to NH proton. The aryl protons appeared in their usual position at  $\delta$  7.32-7.86 ppm (m, 4H) and pyridine protons at  $\delta$  7.42-8.62 ppm (m, 4H). The spectrum exhibits additional signals at  $\delta$  2.46 ppm (s, 3H) and  $\delta$  2.39 ppm (s, 3H) characteristic of methyl groups (CH<sub>3</sub>-C=N) and (CH<sub>3</sub>-Ar) respectively (Karbouj *et al.*, 2010; Jang *et al.*, 2005). The number of protons assigned from <sup>1</sup>H-NMR is consistent with the formula.

## Characterization of the complexes

### Infrared spectra:

The FT-IR spectra of the complexes are recorded as KBr discs and the main IR bands with their tentative assignments are given in (Table 2), which shows that the band of  $\nu_{(N-H)}$  in metal chloride complexes (1, 2, 5-7) is either unchanged or shifted to higher frequencies indicating non-involvement in coordination. The band due to carbonyl stretching vibration  $\nu_{(C=O)}$  is shifted to lower frequencies in these complexes by  $31-71\text{cm}^{-1}$  indicating coordination through the oxygen atom of the carbonyl group (i.e. the hydrazone is coordinated in the keto-form) (El-Tabl *et al.*, 2012).

The bands of  $\nu_{(N-H)}$  and  $\nu_{(C=O)}$  were absent in the spectra of the metal chloride 3 and 4) suggesting coordination of the enol-form of the ligand by deprotonation of the N-H proton, during the complexation. This behavior was also observed in the IR spectra of the deprotonated bis-complexes (8-12) in which the  $\nu_{(N-H)}$  and  $\nu_{(C=O)}$  disappeared also, due to the enolization of the carbonyl group on complex formation (Singh and Singh, 2013). The appearance of a new  $\nu_{(C-O)}$  band in these complexes in the range  $(1286-1301)\text{cm}^{-1}$  confirms the coordination of the hydrazone in the enolate form. This mode of bonding is supported by the appearance of another new band in the range  $(1579-1599)\text{cm}^{-1}$  corresponding to  $\nu_{(N=C-O)}$ . (El-Tabl *et al.*, 2012; Hosseini-Mofared *et al.*, 2013).

The azomethine stretching frequency  $\nu_{(C=N)}$  is shifted to lower frequencies by  $(15-52)\text{cm}^{-1}$  in the spectra of the complexes indicating coordination through azomethine group nitrogen atom (Ibrahim *et al.*, 2009). At the same time, the band due to  $\nu_{(N-N)}$  was shifted to a higher frequency. The increase in the frequency of this band is a clear indication of the increase in the double bond character due to the loss of the electron density via electron donation to the metal ions and further confirmation of the coordination of the ligand via the azomethine group. (El-Tabl *et al.*, 2012).

The pyridine in-plane deformation mode  $\delta(\text{py})$  at  $623\text{cm}^{-1}$  in the spectrum of the ligand shifts to higher frequencies  $631-646\text{cm}^{-1}$  in spectra of the complexes suggesting coordination of the pyridine nitrogen atom (Despaigen *et al.*, 2009). The appearance of non-ligand bands in the spectra of the complexes at the ranges  $(519-580)\text{cm}^{-1}$  and  $(415-450)\text{cm}^{-1}$  which may be tentatively assigned to  $\nu_{M-O}$  and  $\nu_{M-N}$  respectively is another evidence for the bonding of the ligand with the metal ions (El-Tabl *et al.*, 2012).

The spectra of the complexes (1 and 2) exhibit a broad band centered around  $3400\text{cm}^{-1}$  due to the symmetric and asymmetric stretching modes of coordinated water molecule. Furthermore, weak bands in the  $887-899, 669-679\text{cm}^{-1}$  ranges may represent the wagging and rocking modes of coordinated water (Singh, 2008).

The IR spectra of uranyl complexes (7) and (12) reveal strong band at  $912-914\text{cm}^{-1}$  is attributed to  $\nu_{(O=U=O)}$  (El-Tabl *et al.*, 2012). The strong band observed at  $1063\text{cm}^{-1}$  in the spectrum of nickel complex (3) is attributed to  $\nu_{(S=O)}$  of the coordinated DMSO molecule through oxygen atom (Nakamoto, 1997).

**Table 2 :Selected infrared frequencies of the ligand and its complexes**

Complex No.	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{N}-\text{H})$	$\nu(\text{C}-\text{O})$	$\delta(\text{Py.ring})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
L	1672(s)	1610(m)	993(w)	3338(m)	-----	623(sh)	-----	-----
1	1618(vs)	1572(s)	1016(m)	3375(w)	-----	640(m)	569(w)	415(w)
2	1618(vs)	1566(s)	1020(m)	3375(w)	-----	644(m)	557(w)	424(w)
3	-----	1599(s) 1579(m)	1020(m)	-----	1286(s)	631(m)	519(w)	430(w)
4	-----	1597(vs) 1558(s)	1020(m)	-----	1290(m)	646(m)	550(w)	415(w)
5	1641(s)	1595(s)	1016(m)	3335(w)	-----	638(sh)	542(m)	424(w)
6	1603(vs)	1560(s)	1012(m)	3342(w)	-----	634(m)	546(m)	418(m)
7	1601(s)	1560(s)	1012(m)	3345(w)	-----	635(m)	552(m)	450(w)
8	-----	1597(vs) 1579(s)	1018(w)	-----	1294(m)	638(m)	519(w)	424(w)
9	-----	1599(vs) 1579(s)	1018(w)	-----	1301(m)	645(sh)	577(w)	430(w)
10	-----	1579(s) 1570(m)	1020(m)	-----	1294(m)	633(m)	580(w)	430(w)
11	-----	1581(s) 1564(s)	1014(m)	-----	1290(m)	640(sh)	567(w)	422(m)
12	-----	1581(s) 1565(s)	1018(w)	-----	1294(m)	640(m)	550(w)	424(w)

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

### Magnetic moments

The magnetic moment of the prepared complexes at room temperature is presented in (Table 3). The results show that Co(II), Ni(II), Cu(II) complexes (1-4 , 8-10) are all paramagnetic, and Zn(II), Th(IV), UO<sub>2</sub>(II) complexes (5-7,11,12) are diamagnetic as expected for d<sup>10</sup> and f<sup>0</sup> configurations.

Cobalt(II) complexes (1) and (8) show values in the 4.97-4.99 BM range indicating that they have three unpaired electrons. This reveals a high-spin octahedral geometry around Co(II) metal center (Singh *et al.*, 2013). Higher magnetic moment value was observed for octahedral Co(II) complexes than the spin-only (3.87 BM) value may be due to a large orbital contribution. Nickel(II) complexes (2) and (9) show values in the range 2.92-3.13 BM which are consistent with two unpaired electron system of octahedral Nickel(II) complexes (El-Tabl *et al.*, 2012). The slightly lower value of magnetic moment (2.75 BM) than the spin only value of nickel(II) complex (3) may be due to the proposed dimeric structure (Sadhukhan *et al.*, 2011) (Fig. 1). Copper(II) complex shows a magnetic value that is equal to 1.84 BM which corresponds to one unpaired electron system in octahedral structure (El-Tabl *et al.*, 2012). The magnetic moment of Cu(II) complex (4) was measured to be 1.49 BM which is below the theoretical value expected for Cu(II) centre  $S=1/2$  and indicative of net antiferromagnetic couple between the copper(II) ions through bridging units in the poly crystalline state, indicating dimeric structure (patel *et al.*, 2013).

### Electronic Spectra

The electronic spectra of the ligand and its metal complexes in the range 200-1100 nm, were carried out in DMF. (Table 3) shows the electronic spectral bands of the current complexes.

The spectrum of the ligand in DMF solution exhibits two absorption bands at 32894 and 30674 cm<sup>-1</sup>. The first band may be assigned to the  $\pi \rightarrow \pi^*$  transition in the benzenoid and pyridine

moieties and intra ligand  $\pi \rightarrow \pi^*$  transition. The second probably due to  $n \rightarrow \pi^*$  of azomethine and carbonyl group (El-Tabl *et al.*, 2012). These bands are shifted to lower wave numbers which may indicate the coordination of the hydrazone to the metal ions. The intense band observed in the spectra of all complexes at the region 28890-25125  $\text{cm}^{-1}$  may be associated with the charge transfer transitions (LMCT).

The electronic spectra of Co(II) complexes (1) and (8) exhibit three bands at the regions 9823-9842  $\text{cm}^{-1}$ , 14749-14925  $\text{cm}^{-1}$  and 18181-18621  $\text{cm}^{-1}$  indicating an octahedral geometry around the metal ion. These transitions are assigned as  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\mathbf{v}_1)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\mathbf{v}_2)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\mathbf{v}_3)$  respectively. (Singh *et al.*, 2013). The electronic spectral bands of Ni(II) complexes (2, 3, 9) observed at the ranges 9652-10869  $\text{cm}^{-1}$ , 14285-15432  $\text{cm}^{-1}$  and 24038-26737  $\text{cm}^{-1}$ . These electronic spectral bands correspond to the transitions  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\mathbf{v}_1)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\mathbf{v}_2)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(p)(\mathbf{v}_3)$ , in an octahedral environment (Singh *et al.*, 2013).

The spectrum of copper(II) complex (10) showed a broad band centered at 14005  $\text{cm}^{-1}$ . The position and the broadness of this band indicated that, Cu(II) ion distorted octahedral geometry. This broad band may consist of three super imposed transitions  ${}^2B_{1g} \rightarrow {}^2E_g$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ . This could be due to the Jahn-Teller effect that operates on the  $d^9$  electronic ground state of six coordinate system (El-Tabl *et al.*, 2012). The electronic spectrum of copper(II) complex (4) involves two ligand field bands appearing at 13623  $\text{cm}^{-1}$  and 9823  $\text{cm}^{-1}$ , corresponding to the transitions  $dz^2 \rightarrow dx^2-y^2$  and  $dxz, dyz \rightarrow dx^2-y^2$  respectively, as expected for distorted square pyramidal geometry (patel *et al.*, 2013).

The diamagnetic uranyl complexes (7) and (12) and Th(IV) complex(6) have  $f^0$  system and zinc(II) complexes (5) and (11) have  $d^{10}$  system, so they do not show  $f \rightarrow f$  or  $d \rightarrow d$  transitions, respectively. The coordination number of these complexes was determined depending upon IR spectra which confirm the behaviour of hydrazone as a tridentate ligand, and molar conductance data, which reveal coordination number 7 and 8 for uranyl complexes (7) and (12) so pentagonal bipyramidal and hexagonal bipyramidal structures, respectively are suggested for these complexes due to linear O=U=O group, Thorium(IV) complex (6) is found to have coordination number 8, so either dodecahedral or square antiprismatic structure is expected (Cotton, 2006). Zinc(II) complexes (5) coordination number 5 and (11) coordination number 6 are proposed to have the more probable trigonal bipyramidal and octahedral structures respectively (Despaigen *et al.*, 2009; Jang *et al.*, 2005).

**Table 3 : Electronic spectra and magnetic moments data of the ligand and its complexes**

Complex No.	$\mu_{\text{eff}}$ B.M	Electronic spectrum $\text{cm}^{-1}$
L(APMBH)	----	32894, 30674
1	4.97	31250, 28571, 25510, 18621, 14749, 9842
2	3.13	32258, 29411, 27932, 25380, 15432, 9652
3	2.75	31446, 29585, 27027, 24038, 14285, 10869
4	1.49	32051, 28901, 25125, 13623, 9823
5	dia	30674, 28571, 26595
6	dia	30487, 27472, 26595
7	dia	30120, 29069, 26881
8	4.99	31055, 29940, 27932, 18181, 14925, 9823
9	2.92	32467, 29850, 28890, 26737, 14534, 9920
10	1.84	32051, 28571, 26315, 14005
11	dia	31250, 28169, 26315
12	dia	31250, 27932, 26178

### Antibacterial activity

The hydrazone, APMBH, ligand and its metal complexes (5) and (10) were evaluated for sensitive organisms (*S.aureus* and *K.pneumoniae* as Gram-positive and Gram-negative bacteria).

The hydrazone ligand and the tested complexes show low activity towards *K.pneumoniae* as Gram-negative bacteria. On the other hand, the ligand exhibits lower activity towards *S.aureus* as Gram-positive bacteria but Zn(II) complex (5) show high activity and Cu(II) complex (10) exhibit moderate activity against *S.aureus* as Gram-positive bacteria (Table 4).

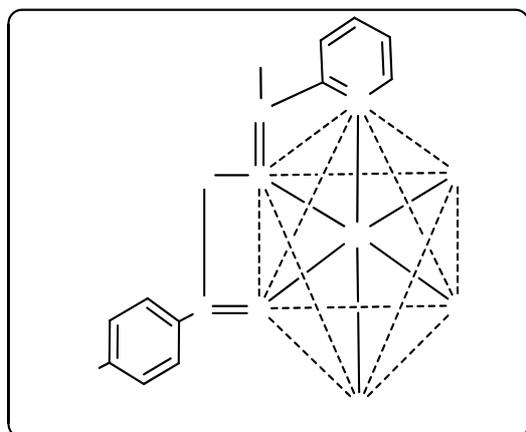
**Table 4: Antibacterial activity of the tested compounds**

Complex No.	Compound	Inhibition zone diameter (mm) <i>K. pneumoniae</i>	Inhibition zone diameter (mm) <i>S.aureus</i>
L	APMBH(C <sub>15</sub> H <sub>15</sub> N <sub>3</sub> O)	7	9
5	[Zn(APMBH)Cl <sub>2</sub> ]	9	21
10	[Cu(APMBH-H) <sub>2</sub> ]	9	15
	Amoxyline	15	17
	Erdhromaycine	11	20

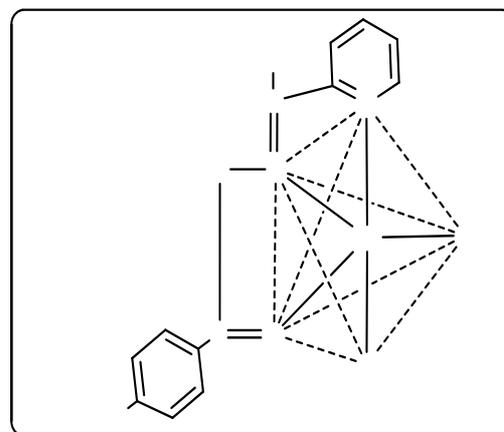
### CONCLUSION

The coordination diversity of the ligand 2-acetyl pyridine-4'-methyl benzoyl hydrazone (APMBH) with Co(II), Ni(II), Cu(II), Zn(II), Th(IV) and UO<sub>2</sub>(II) metal ions showed that the hydrazone acts as neutral or monobasic ONN tridentate ligand, forming stable mononuclear and dinuclear complexes. Molar conductance values indicate that all prepared complexes are non-electrolyte except Th(IV) complex (6) is 1:2 electrolyte. UV/Vis IR and magnetic studies recommended that Co(II), Ni(II), Cu(II) and Zn(II) complexes (1-3, 8-11) have octahedral structures (Fig. 1), including the dimeric Ni(II) complex (3). Square pyramidal geometry around each Cu(II) ions is suggested for the dimeric Cu(II) complex (4), trigonal bipyramidal structure is proposed for [Zn(APMBH)Cl<sub>2</sub>], pentagonal bipyramidal and hexagonal bipyramidal structures for the uranyl complexes (7) and (12) respectively, and eight coordinate structures are suggested for Th(IV) complex (6) (Fig. 1).

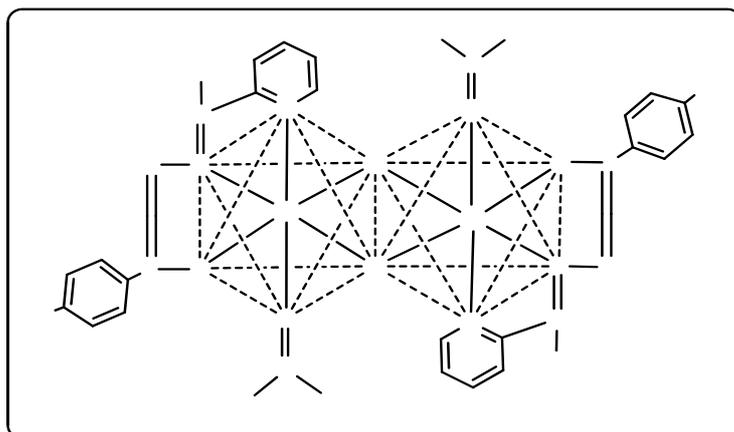
Antimicrobial screening of the free ligand and two of its complexes (5) and (10) in vitro towards Gram-positive and Gram-negative bacteria showed moderate activity, in contrary to the lower activity of the free ligand.



[M(APMBH)(H<sub>2</sub>O)Cl<sub>2</sub>] M=Co(II),Ni(II)  
octahedral  
complexes (1, 2)

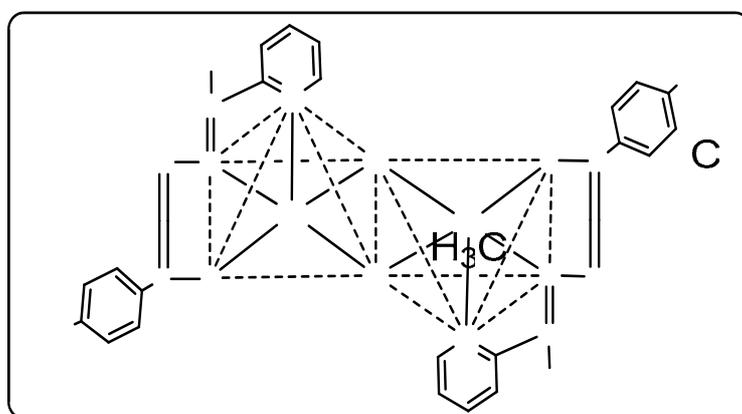


[Zn(APMBH)Cl<sub>2</sub>]  
trigonal bipyramidal  
complex (5)



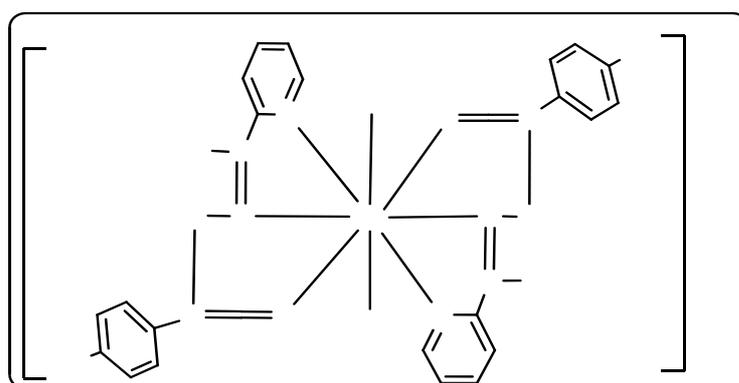
$[\text{Ni}(\text{APMBH-H})\text{Cl}(\text{DMSO})]_2$   
(dinuclear) octahedral  
complex (3)

CH<sub>3</sub>  
C N  
N N Cl



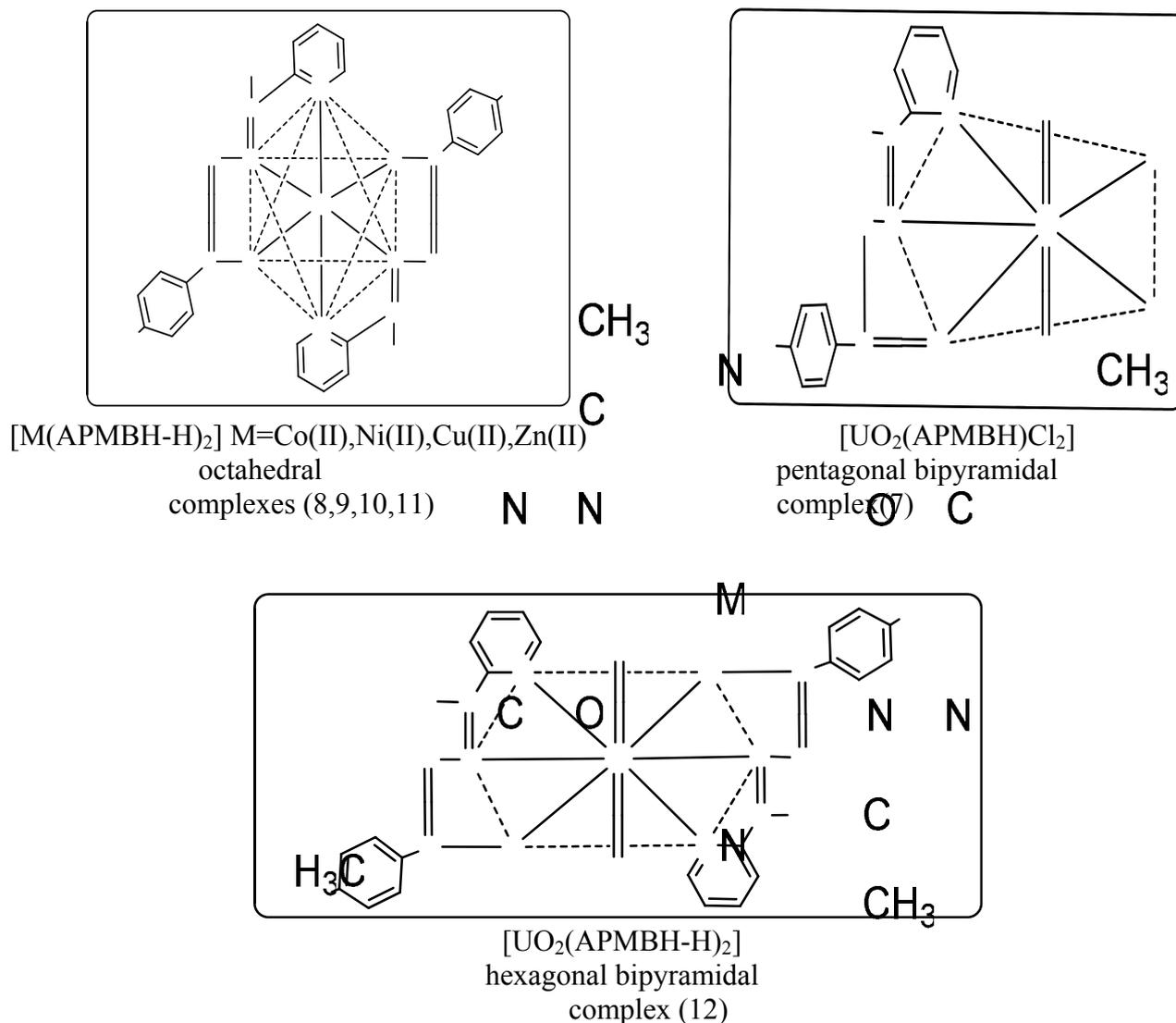
$[\text{Cu}(\text{APMBH-H})\text{Cl}]_2$   
(dinuclear) square pyramidal  
complex (4)

Ni  
C O Cl  
O  
S  
H<sub>3</sub>C CH<sub>3</sub>



$[\text{Th}(\text{APMBH})_2\text{Cl}_2]\text{Cl}_2$   
eight coordinate  
complex(6)

CH<sub>3</sub>  
C N  
N N C  
Cu  
C O C



**Fig. 1: Proposed structures for the prepared complexes**

### REFERENCES

- Alagesan, M.; Bhuvanesh, N.S.P.; Dharmaraj, N. (2013). Potentially cytotoxic new Copper(II) hydrazone complexes: synthesis, crystal structure and biological properties. *J. Chem. Soc., Dalton Trans.*, **42**,7210 - 7223.
- Al-Daher, A.G.M.; Al-Qassar, I.A. (2011). Synthesis and characterization of Co(II), Ni(II), Cu(II), and Zn(II) complexes with 2-furaldehyde 2-thenoyl hydrazone. *Raf. J. Sci.*, **22**(4),109-120.
- Al-Daher, A.G.M.; Mustafa, S.M. (2013). Synthesis and characterization and antibacterial activity of 2-acetylpyridine-2-furoylhydrazone complexes with  $UO_2(II)$ , Th(IV), Co(II), Ni(II), Cu(II), and Zn(II). *Raf. J. Sci.*, **24**(5),72-86.
- Al-Daher, A.G.M.; Hadi, A.A. (2013). Synthesis characterization and antibacterial activity of thorium(IV), dioxouranium(VI), Cobalt(II), Nickel(II), copper(II) and zinc(II) complexes with picolinoyl hydrazones. *Raf. J. Sci.*, accepted for publication.
- Bale, M.N.; Sawant, A.D. (2001). Solvent extraction and spectrophotometric determination of uranium(VI) with pyridine-2-carbaldehyde 2-hydroxy benzoyl hydrazone. *J. Radio. anal. Nucl. Chem.*, **247**, 531-534.
- Bernhardt, P.V.; Wilson, G.J.; Sharpe, P.C.; Kalinowski, D.S.; Richardson, D.R. (2008). Tuning the antiproliferative activity of biologically active iron chelators: characterization of the

- coordination chemistry of 2-acetylpyridine and 2-benzoylpyridine hydrazone ligands. *J. Biol. Inorg. Chem.*, **13**, 107-119.
- Cotton, S. (2006). "Lanthanide and Actinide chemistry". John, Wiley and Sons, England, pp.177-187.
- Despaigne, A.R.; Dasilva, J.G.; Docarmo, A.C.; Piro, O.E.; Castellano, E.E.; Beraldo, H. (2009). Copper(II) and zinc(II) complexes with 2-benzoyl pyridine-methyl hydrazone. *J. Mol. Struct.*, **920**, 97-102.
- El-Table, A.S.; Shakdofa, M.M.E.; Shakdofa, A.M.E. (2012). Metal complexes of N'-(2-hydroxy-5-phenyldiazenyl)benzylidene isonicotino hydrazide. synthesis, spectroscopic characterization and anti bacterial activity. *J. Serb. Chem. Soc.*, **77**, 1-29.
- Furniss, B.S.; Rogers, V.; Smith, P.W.G.; Tatchll, A.R. (1989). "Vogel's Textbook of Practical Organic Chemistry". 5<sup>th</sup> ed. Longman Scientific and Technical, England, 1269 p.
- Galic, N.; Dijaanosic, A.; Kontrec, D.; Miljanic, S. (2012). Structural investigation of aroyl hydrazone in dimethyl sulphoxide, water mixtures. *Spectrochim. Acta.*, **95**, 347-353.
- Geary, W.J. (1971). The use of conductivity measurement in organic solvents for the characterization of coordination compounds. *Coord. Chem. Rev.*, **7**, 81-122.
- Guo, D.; Wu, P.; Tan, H.; Xia, L.; Zhou, W. (2011). Synthesis and luminescence properties of novel 4-(N-carbazole methyl) benzoyl hydrazone Schiff bases. *J. Luminescence.*, **131**(7), 1272-1276.
- Hosseini-Monfared, H.; Asghari-Lalami, N.; Pazio, A.; Wozniak, K.; Janiak, C. (2013). Dinuclear vanadium, copper, manganese and titanium complexes containing O,O,N-dichelating ligands: synthesis, crystal structure and catalytic activity, *Inorg. Chim. Acta.*, **406**, 241-250.
- Ibrahim, K.M.; Gaber, I.M.; Zaky, R.R. (2009). Synthesis and magnetic, spectral and thermal eukaryotic DNA studies of some 2-acetyl pyridine [N-(3-hydroxy-2-naphthoyl)] hydrazone complexes. *J. Coord. Chem.*, **62**(7), 1100-1111.
- Jang, Y.J.; Lee, U.; Koo, B.K. (2005). Synthesis and crystal structures of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) metal complexes with NNO functionalized ligand, *Bull. Korean. Soc.*, **26**(6), 925-929.
- Karbouj, R.; El-Dissouky, A.; Jeragh, B.; Al-Saleh, E. (2010). Synthesis, characterization, and biological activity studies on (E)-N'-[2-hydroxy-1,2-di(pyridine-2-yl) ethylidene] aroyl hydrazides and their copper(II) complexes. *J. Coord. Chem.* **63**(5), 868-883.
- Kethcum, P.A. (1988). "Microbiology: Concept and Applications". John -Wiley and Sons, New York . 384 p.
- Marczenko, Z.; Balcerzak, M. (2000). "Separation, Preconcentration and Spectrophotometry in Inorganic Analysis". Elsevier, pp. 425, 446.
- Nakamoto, K. (1997). "Infrared and Raman Spectra of Inorganic and Coordination Compound". part B, 5<sup>th</sup> ed., , John Wiley and Sons Inc., New York, 270 p.
- Patel, R.N.; Patel, D.K.; Sondhiya, V.P.; Shukla, K.K.; Singh, Y.; Kumar, A. (2013). Synthesis, crystal structure and superoxide dismutase activity of two new bis( $\mu$ -acetato /  $\mu$ -nitrate) bridged copper(II) complexes with N'-[phenyl(pyridine-2-yl) methylidene] benzohydrazone. *Inorg. Chim. Acta.*, **405**, 209-217.
- Rollas, L.; Küçükgülzel, S.G. (2007). Biological activities of hydrazone derivatives. *Molecules*, **12**, 1910-1919.
- Sacconi, L. (1953). Acetylhydrazone of o-Oxy and o-Amino-aldehydes and ketones as tridentate complexing agent. *J. Amer. Chem. Soc.*, **75**, 5434-5435.
- Sadhukhan, D.; Ray, A.; Pilet, G.; Rizzoli, C.; Rosair, G.M.; Gomez-Garcia, C.J.; Signorella, S.; Bellu, S.; Mitra, S. (2011). Weak interaction modulating the dimensionality in superamolecular architectures in three new nickel(II) hydrazone complexes, magnetostructural correlation, and catalytic potential for epoxidation of alkenes under phase transfer conditions., *Inorg. Chem.*, **50**, 8326-8339.
- Sathyadevi, P.; Krishnamoorthy, P.; Algesan, M.; Thanigaimani, K.; Muthiah, P.T.; Dharmaraj, N. (2012). Synthesis crystal structure, electrochemistry and studies on protein binding,

antioxidant and biocidal activities of Ni(II) and Co(II) hydrazone complexes, *Polyhedron*, **31**, 294-306.

Singh, V.P.; Singh, P. (2013). Synthesis, spectral characterization and thermal studies of Co(II), Ni(II), Cu(II), and Zn(II) complexes with 2-amino benzoic acid and 2-hydroxy benzoic acid thiophene 2-methylene hydrazide. *J. Mol. Struct.*, **1035**,363-370.

Singh, V.P. (2008). Synthesis, electronic and ESR spectral studies on copper (II) nitrate complexes with some acylhydrazines and hydrazones. *Spectrochim. Acta*. **A71**,17-72.

Singh, V.P.; Singh, S.; Singh, D.P.; Singh, P.; Tiwari, K.; Mishra, M.; Butcher, R.J. (2013). Synthesis, spectral and single x-ray diffraction studies on Co(II), Ni(II), Cu(II), and Zn(II) complexes with o-amino acetophenone benzoyl hydrazone. *Polyhedron*. **56**,71-81.

Sun, Y.; Liu, Y.; Guo, W. (2009). Fluorescent and chromogenic probes bearing salicylaldehyde hydrazone functionality for cyanide detection in aqueous solution. *Sens. Actuator B: chem.*, **143**(1), 171-176.

Vogel, A.I. (1989). "Vogel's Textbook of Quantitative Analysis". 5<sup>th</sup> ed. Longoman Scientific and Technical, England, pp. 324-329, 349p.