

Synthesis, Characterization and Antibacterial Activity of 2-Acetylpyridine -2-furoylhydrazone Complexes with UO₂(II), Th(IV), Co(II), Ni(II), Cu(II) and Zn(II)

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ABSTRACT

A new heterocyclic hydrazone, 2- acetylpyridine -2- furoyl hydrazone (APFH) and its complexes with UO₂(II), Th(IV), Co(II), Ni(II), Cu(II), and Zn(II) salts, have been prepared. The structure of these compounds has been characterized by elemental analysis, magnetic susceptibility, molar conductance and spectral (IR, UV, H-NMR) measurements. The hydrazone ligand APFH behave as uninegative or neutral tridentate ligand, with ONN donor atoms, towards the metal ions depending on the metal salt used. The magnetic and electronic spectral data indicate octahedral, tetrahedral and pentacoordinate structures for the divalent M(II) ions. Hexagonal bipyramidal structures have been proposed for UO₂(II) complexes, and coordination number (10) geometries have been suggested for Th(IV) complexes. Antibacterial activity of the hydrazone ligand and some of its complexes were studied against gram –positive bacteria: *S. aureus* and gram- negative bacteria: *E. coil*.

Keywords: Hydrazones, Complexes, Thorium, Uranium, Transition metals.

-2-

-2

Ni(II) Co(II) Th(IV) UO₂(II)
Zn(II) Cu(II)

(APFH)

-2-

-2

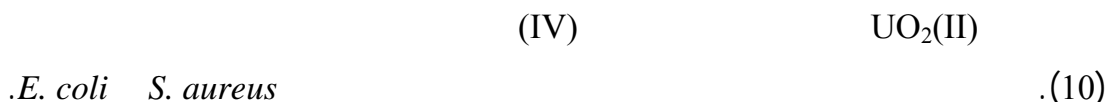
.Zn(II) Cu(II) Ni(II) Co(II) Th(IV) UO₂(II)

UV-Vis, IR)

.(¹H-NMR,

ONN

M(II)



INTRODUCTION

Over the years, much attention has been paid to investigate the chemistry of transition metal complexes with large number of hydrazones as ligands, (Stadler and Harrow field, 2009; Sathyadevi *et al.*, 2012). In particular heterocyclic containing hydrazones (Abd El-Hade *et al.*, 2012, Sathyadevi *et al.*, 2012). Hydrazones ligands create an environment similar to the one present in biological systems usually by making coordination through oxygen and nitrogen atoms. Various important properties of hydrazones, along with their applications in medicine and analytical chemistry, have led to an increased interest, in their complexation of their characteristics with transition metal ions (Bernhardt *et al.*, 2008; Rollas and Kücü Kguzel, 2007; Pinto *et al.*, 2004; Vallinath *et al.*, 2010).

The hydrazones offers a number of attractive features such as degree of rigidity, a conjugated π -system and NH unit that readily participate in hydrogen bonding and may be a site of deprotonation. It is well established that the formation of metal complexes plays an important role in enhancing the biological activity of free hydrazones (Raha *et al.*, 2012).

Heterocyclic hydrazones are promising compounds from the view point of coordination chemistry because of their ability towards complexation and their biological properties. Thus., the chemistry of transition metals with hydrazones has been of interest to coordination as well as bio-inorganic chemists due to their different bonding modes with metal ions (El-Taras *et al.*, 2012).

The structural motif present in heterocyclic hydrazones is a remarkable tool for the development of multifunctional organic receptors that find application in chemical environmental and biological sciences. Heterocyclic hydrazones constitute an important class of active drugs that attracted the attention of medical chemists due to their wide ranging pharmacological properties like antifungal, antibacterial and anticonvulsant compounds (da Silva *et al.*, 2011).

The hydrazones and their transition metal complexes derived from various acid hydrazides and salicylaldehyde have been attracted much attention recently (Maková *et al.*, 2012). On the other hand, the complexes hydrazones derived from 2-furoic acid hydrazide have rarely been reported, (Rao *et al.*, 2007) and expected to have interesting coordination modes and promising biological application.

In the present work we describe the condensation of 2-furoic acid hydrazide and 2-acetyl pyridine to yield the title compound, 2-acetylpyridine 2-furoic hydrazones (APFH). Some transition and actinide metal complexes were synthesized, characterized and evaluated for their antibacterial activities.

EXPERIMENTAL

Materials and methods

All chemicals used were reagent grade from B.D.H. or Fluka companies, used as supplied, except for tetrahydrofuran solvent THF (Perrin *et al.*, 1980).

The infrared spectra ($4000\text{-}400\text{cm}^{-1}$) of the ligand and complexes were recorded on a Tensor 27 Bruker FT-IR spectrophotometer as KBr disc. The UV-Vis spectra of the complexes were recorded at room temperature on Shimadzu U.V-1650 PC-spectrophotometer, using DMF as solvent in 1cm quartz cures. Molar conductances of the complexes were determined in absolute ethanol and DMF (10^{-3}M solutions) at room temperature using a PMC3 Jenway conductivity meter. Magnetic susceptibilities were measured with a Bruker BM6 instrument at ambient temperature. The necessary diamagnetic corrections for ligands were done using Pascal's table. Melting points were obtained on Electro thermal 9300 melting point apparatus in open capillaries. The C.H.N. elemental analysis was performed on Perkin Elmer 2400 analyzer at Al al-Bayt University laboratories, Jordan.

The metal content of complexes was determined spectrophotometrically [Co(II), Cu(II)] using shimadzu AA670 atomic absorption spectrophotometer, Zn(II) and Ni(II) were determined by complexometric titration against standard EDTA (Vogel, 1996). Thorium(IV) and uranium(VI) were determined colourimetrically using thoron and arsinazo(III) as reagents respectively (Marzinko, 2004). Chloride was determined volumetrically using standard AgNO_3 solution (Vogel,1989). $^1\text{H-NMR}$ spectra were recorded in DMSO-d_6 solution using TMS as the internal standard on 300 MHz NMR spectrophotometer at Al al-bayt University, Jordan.

Preparation of the Ligand

Preparation of 2-Furoic acid Hydrazide:

This was prepared by the reaction of ethyl -2-furate with hydrazine hydrate as described previously (Al-Saady and Al-Daher, 2000) m.p. $81\text{ }^\circ\text{C}$.

Preparation of 2-Acetylpyridine- 2-Furoyl Hydrazone (APFH):

This hydrazone ligand was prepared following a general procedure (Sacconi, 1953) as follows:

A solution of 2-furoic acid hydrazide (6.3g, 0.05 mol) in absolute ethanol (20ml) was added to 2-acetylpyridine (6.05g, 0.05 mol) in absolute ethanol (20ml). The reaction mixture was refluxed on a water bath for 3hrs. The hydrazone was separated on cooling in an ice- bath. The light yellowish crystalline solid was filtered, washed with ethanol (5ml) then with ether (5ml) and dried in an oven at ($80\text{-}90\text{ }^\circ\text{C}$) m.p., $130\text{ }^\circ\text{C}$. The reaction is shown in (Fig. 1).

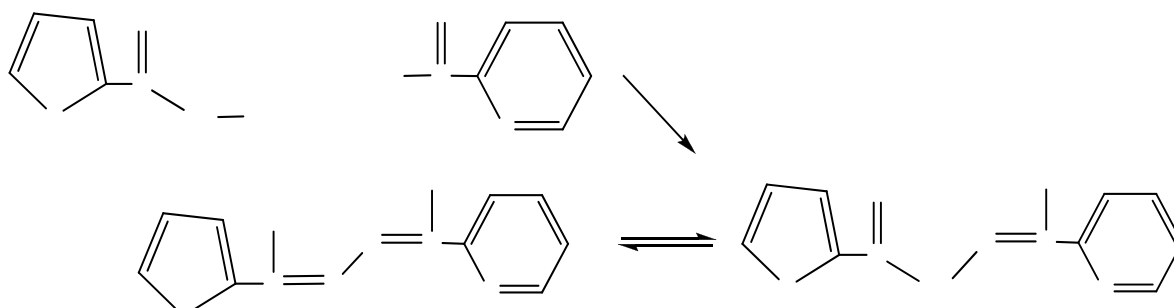


Fig. 1: Synthesis of the ligand APFH

Preparation of Complexes

Preparation of metal chlorides complexes:

The appropriate metal chloride (0.001 mol) [0.24g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.24g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.17g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.14g ZnCl_2] in (10 ml) absolute ethanol were heated under reflux with constant stirring with (0.23g, 0.001 mol) of the ligand APFH in (10 ml) absolute ethanol for 2hrs. The solid complexes formed were then separated by filtration, washed with ethanol (5 ml) and finally dried in an oven at 70-80 °C and kept in a desiccator. In case of thorium(IV) and $\text{UO}_2(\text{II})$ complexes (0.001 mole) [0.46g $\text{ThCl}_4 \cdot 5\text{H}_2\text{O}$, 0.378g $\text{UO}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$] and (0.458g, 0.002 mol) APFH ligand in THF and acetone as solvents, were used respectively.

Preparation of metal nitrate complexes:

The same procedure as in metal chlorides complexes were used except that (0.001 mole) [0.291g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.291g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 0.242g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 0.297g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 0.57g $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, 0.502g $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and (0.46g, 0.002 mol) of APFH were used in absolute ethanol as solvent except that for Th(IV) and $\text{UO}_2(\text{II})$ complex, THF and acetone were used as solvents, respectively.

Preparation of metal thiocyanate complexes:

These were prepared by mixing metal chloride (0.001 mol) in THF (20 ml) and potassium thiocyanate (0.2g, 0.002 mol) with constant stirring at room temperature for 5 hrs. (Agarwal *et al.*, 2006). The precipitated KCl was removed by centrifugation and to the filtrate (0.23g, 0.001 mole) of the ligand (APFH) in (10 ml). THF was added. The solution was heated under reflux for 2hrs. and the formed solid was filtered off, washed with THF (5ml) then dried as above.

In case of Cu(II) complex, it was separated after the evaporation of the resulting solution to half its volume and addition (5 ml) of ether then left to stand overnight in a refrigerator. For Th(IV) complex (0.4g, 0.004 mol) KNCS and (0.46g, 0.002 mole) ligand APFH were used.

Preparation of the deprotonated complexes:

To stirred hot ethanolic solution (20 ml) of the appropriate metal acetate (0.001 mole) [0.25g $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 0.25g $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 0.20g $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, 0.22g $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 0.42g $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] was added (0.46g, 0.002mol) of the ligand APFH in (10 ml) absolute ethanol. The resulting mixture was refluxed for 3hrs., upon which the solid complexes were separated, filtered off and washed with ethanol (5 ml) then dried as above. acetone was used as solvent instead of ethanol in the preparation of Ni(II) and $\text{UO}_2(\text{II})$ complexes.

Antibacterial activity:

This was evaluated using agar diffusion method (Kethcam,1988). Gram-positive bacteria *S. aureus* and Gram-negative bacteria *E.coli* were cultivated in nutrient agar on petri dishes. The test solution was prepared by dissolving (10 mg) of each of the tested compound in (1 ml) DMSO. A 6mm diameter filter paper discs were soaked in the tested

solutions. After 24hrs cultivation at 37C°, diameters of zones of inhibition were determined. DMSO was inactive under applied conditions.

RESULTS AND DISCUSSION

The synthetic route for the ligand (APFH) is shown in (Fig.1) It was prepared by the condensation of 2-furoic acid hydrazide and 2-acetyl pyridine. The reaction of APFH with the metal chlorides, nitrates, or thiocyanates [metal= Co(II), Ni(II), Cu(II), Zn(II), UO₂(II), Th(IV)] in (1:1) or (1:2) molar ratios gave the complexes (1-17) Table (1). The reaction of the ligand with metal acetates in (1:2) molar ratio produced the deprotonated complexes (18-22). The physical properties and chemical analysis of the complexes are given in Table (1,2) and it is in good agreement with the proposed formulas.

All the complexes are non-hygroscopic solids and stable in air. They are sparingly soluble organic solvents like acetone, acetonitrile and moderately soluble in ethanol methanol, DMF and DMSO. The molar conductance values Table (1) of the metal complexes (1-5, 18-22) in ethanol and in DMF are in the ranges (3.4-27.5) and (6.2-27) ohm⁻¹ cm² mol⁻¹ respectively indicating non-electrolyte nature of these complexes. Metal thiocyanate complexes (14-16) molar conductance values in ethanol are in the range (5.3-15) ohm⁻¹ cm² mol⁻¹, but in DMF show higher values probably due to the displacement of weakly bonded one of the thiocyanate groups in these complexes by strong coordinating solvent (DMF) (Vojinovic-Jesic *et al.*, 2008). The molar conductance values reveal that Co(II) thiocyanate complex (13) is (1:1) electrolyte and metal nitrate complexes (7-12) Table (1) are (1:2) electrolyte complexes (Geary, 1971).

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

Complex No.	Formula	Color	m.p C°	Yield %	$\Lambda \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$		M %	Cl %
					Ethanol	DMF	Found /(Calculated)	
L1	APFH (C ₁₂ H ₁₁ N ₃ O ₂)	White	130	76	-----	----	----	----
1	[Co(APFH) (H ₂ O) Cl ₂]	redish brawn	272d	83	27.5	12.2	14.98 (15.63)	19.32 (18.83)
2	[Ni (APFH) (H ₂ O) Cl ₂]	Green	250d	89	15.7	25.3	15.86 (15.58)	18.70 (18.84)
3	[Cu (APFH) (H ₂ O) Cl ₂]	Pale green	124	83	9.2	27.0	16.32 (16.65)	17.82 (18.60)
4	[Zn (APFH) Cl ₂]	White	166	82	4.3	9.4	16.96 (17.89)	19.64 (19.43)
5	[Th (APFH) ₂ Cl ₄]	Pale green	202	65	17.3	23.7	27.19 (27.88)	16.62 (17.06)
6	[UO ₂ (APFH) ₂] Cl ₂	Yellow	218	59	75.0	100.0	30.12 (29.79)	8.51 (8.89)
7	[Co (APFH) ₂] (NO ₃) ₂	Brawn	112	58	79.0	143.2	9.86 (9.19)	
8	[Ni (APFH) ₂] (NO ₃) ₂	Pale green	142	77	76.0	145.3	8.88 (9.19)	
9	[Cu (APFH) ₂] (NO ₃) ₂	Green	190	77	75.0	152.3	9.55 (9.84)	
10	[Zn (APFH) ₂] (NO ₃) ₂	Pale yellow	110	66	78.5	143.6	10.25 (10.09)	
11	[Th(APFH) ₂ (NO ₃) ₂](NO ₃) ₂	White	184	62	78.3	142.3	23.80 (24.73)	
12	[UO ₂ (APFH) ₂] (NO ₃) ₂	Yellow	140	62	71.3	138.2	27.73 (27.93)	
13	[Co (APFH) (NCS)] NCS	Bluish red	200	79	35.7	76.0	15.21 (14.59)	
14	[Ni (APFH) (H ₂ O) (NCS) ₂]	Yellowish green	210d	74	15.0	32.4	13.89 (13.92)	
15	[Cu (APFH) (H ₂ O)(NCS) ₂]	Pale green	157	78	5.3	7.5	15.23 (14.89)	
16	[Zn (APFH) (NCS) ₂]	White	160	82	12	84.0	15.52 (15.93)	
17	[Th (APFH) ₂ (NCS) ₄]	Pale yellow	212d	59	32.5	87.0	25.31 (25.16)	
18	[Co (APFH - H) ₂]	Brown	223	72	5.6	9.2	11.78 (11.44)	
19	[Ni (APFH - H) ₂]	Brawn	242d	97	3.4	6.2	10.92 (11.41)	
20	[Cu (APFH - H) ₂]	Green	258d	73	4.8	9.5	12.65 (12.23)	
21	[Zn (APFH - H) ₂]	Yellow	195	88	4.5	7.8	13.28 (12.53)	
22	[UO ₂ (APFH - H) ₂]	Orange	244d	74	4.8	7.5	31.96 (32.78)	

d = decomposition temperature

Table 2: C.H.N. analyses of some of the prepared complexes

No.	Formula	% C	% H	% N
6	[UO ₂ (APFH) ₂] Cl ₂	35.01 (36.05)	2.231 (2.75)	10.36 (10.51)
8	[Ni (APFH) ₂ (NO ₃) ₂]	45.23 (44.95)	3.56 (3.43)	17.70 (17.48)
11	[Th (APFH) ₂ (NO ₃) ₂](NO ₃) ₂	31.81 (30.70)	3.96 (2.34)	16.56 (14.93)
18	[Co (APFH - H) ₂]	56.07 (55.92)	4.01 (3.88)	15.81 (16.31)
20	[Cu (APFH - H) ₂]	55.01 (55.43)	4.00 (3.85)	16.48 (16.16)

Calculated values in parenthesis

Infrared Spectra

The main frequencies of the i.r. spectra of the ligand and its complexes and their tentative assignments are shown in Table (3). The spectrum of the free ligand showed characteristic absorption bands located at 3141, 1689, 1591, 991, 619 cm⁻¹ which are due to $\nu_{\text{N-H}}$, $\nu_{\text{C=O}}$, $\nu_{\text{C=N}}$, $\nu_{\text{N-H}}$ and the pyridine in plane deformation mode respectively. In the spectra of metal chloride, thiocyanate and nitrate complexes (1-17) the ν_{NH} band is almost unaltered or shifted to higher frequencies indicating non-involvement of this group in coordination and a decrease in hydrogen bonding on complexation may occur. On the other hand, a considerable negative shift (25-86cm⁻¹) in $\nu_{\text{C=O}}$ was observed indicating a decrease in the force constant of (C=O) bond as a consequence of coordination through the carbonyl oxygen atom in these complexes.

In the i.r. spectra of the deprotonated complexes (18-22), the bands due to $\nu_{\text{N-H}}$ and $\nu_{\text{C=O}}$ stretching vibrations were disappeared, which show that the frame H-N-C=O transformed to N=C-OH form followed by deprotonation (Fig.1) and coordinating to the metal ions in the enolate form (Mangalam *et al.*, 2010). A new band due to new $\nu_{\text{C=N}}$ formed as a result of the enolization of the ligand at 1590-1597 cm⁻¹ may be taken as an additional evidence.

Furthermore, another new absorption band appeared in the region 1296-1315 cm⁻¹ in the spectra of the complexes assigned for the $\nu_{\text{C-O}}$ of the enolate from (Sathyadevi *et al.*, 2012). The shift of $\nu_{\text{C=N}}$ to lower wavenumber in all the complexes by about 8-50cm⁻¹ indicates the involvement of the azomethine nitrogen in bonding (Shivakumar *et al.*, 2008). The coordination through the azomethine nitrogen atom was further supported by the shift of the $\nu_{\text{N-N}}$ vibration observed at 991 cm⁻¹. In the spectrum of the ligand to higher frequency in the complexes by 23-50 cm⁻¹. This is due to the reduction of ions pair repulsive forces in the adjacent nitrogen atoms (Nair and Thankamani, 2011).

The pyridine in-plane deformation mode at 619 cm^{-1} in the spectrum of the free ligand shifts to $644\text{--}685\text{ cm}^{-1}$ in the spectra of all complexes suggesting coordination of the heterocyclic nitrogen atom (Despaigne *et al.*, 2009). Conclusive evidence of the bonding is also shown by the observation that new bands appear in the spectra of the complexes at about $540\text{--}579\text{ cm}^{-1}$ and $420\text{--}478\text{ cm}^{-1}$ which are assigned to $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$ stretching vibrations, respectively. The band observed in the spectrum of the free ligand at 1176 cm^{-1} assigned for $\nu_{\text{(C-O-C)}}$ stretching vibration of furan ring (Shivakumar *et al.*, 2008; Halli *et al.*, 2008) is almost unaltered in the spectra of the metal complexes indicating non-participation of the furan ring oxygen atom in bonding with metal. Hence, it may be concluded that in metal chloride, nitrate and thiocyanate complexes (1-17), APFH acts as tridentate ONN donor chelating through the carbonyl oxygen, the imine nitrogen and pyridine ring nitrogen atoms. On the other hand, APFH act as anionic tridentate ligand in the deprotonated complexes (18-22) coordinating through the enolate oxygen atom in addition to the nitrogen atoms of the azomthine group and pyridine ring.

The nitrate complexes (7-10) exhibit a very strong band at the region $1383\text{--}1385\text{ cm}^{-1}$ and medium bands at the region $810\text{--}837\text{ cm}^{-1}$ which are attributed to the ν_3 and ν_2 vibrations, respectively of uncoordinated nitrate ion of D_{3h} symmetry (Kamar and Radhakrishnan, 2011). In the spectrum of the Th(IV) nitrate complex(11), non-ligand bands are observed at $1514, 1279, 1025\text{ cm}^{-1}$, which assigned ν_4, ν_1 and ν_2 vibration modes, respectively of a coordinated nitrate ion, since the magnitude of splitting($\nu_1\text{--}\nu_4$)is 235 cm^{-1} , the nitrate coordinated nitrate ions are in a bidentate fashion (Kuncheria *et al.*, 1989). It is obvious that thorium(IV) nitrate complex (11) containing both ionic and coordinated nitrate ions consistent with conductivity data which suggest 1:2 electrolyte for this complex.

The i.r. spectra of the thiocyanate complexes (13-16) exhibit two strong $\nu_{\text{(CN)}}$ bands at $2092\text{--}2110\text{ cm}^{-1}$ and $2070\text{--}2085\text{ cm}^{-1}$ originating from NCS groups. The first band can unambiguously be ascribed to the coordinated thiocyanate group through nitrogen atom, while the lower energy one suggests a weaker coordination of the other NCS group (Vojinovic-Jesic *et al.*, 2008). The somewhat weaker coordination of one NCS group may be presumed on the basis of their molar conductivity values in DMF Table (1) which suggest 1:1 electrolyte for these complexes, may be due to dissociation of weakly bonded NCS group by strong coordinated solvent DMF. Additional evidence for N-coordinated thiocyanate group is the medium intensity non-ligand band observed at $864\text{--}866\text{ cm}^{-1}$ assigned for $\nu_{\text{(C-S)}}$ (Nakamoto, 1997).

The additional strong band appearing at $918\text{--}928\text{ cm}^{-1}$ in the spectra of uranyl complexes (12, 22) is attributed to the asymmetric stretching vibration of the linear O=U=O group.

Table 3: Characteristic IR spectral bands of the ligand and its complexes

Complex No	ν_{NH}	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{N-N}}$	$\nu_{\text{C-O}}$	$\delta(\text{in-plane py})$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
L	3141(s)	1689(vs)	1591(vs)	911(m)		619(m)		
1	3159(m)	1630(vs)	1556(s)	1036(m)		663(m)	546(m)	478(w)
2	3157(m)	1633(vs)	1556(s)	1036(m)		679(m)	546(m)	460(w)
3	3150(m)	1614(vs)	1541(s)	1036(m)		656(m)	552(m)	465(w)
4	3209(m)	1649(vs)	1556(s)	1018(m)		673(m)	540(m)	455(w)
5	3258(m)	1603(vs)	1552(s)	1016(m)		669(m)	550(m)	452(w)
6	3217(m)	1612(vs)	1552(s)	1024(m)		669(w)	546(m)	449(w)
7	3262(m)	1603(s)	1579(s)	1014(m)		658(w)	552(m)	444(w)
8	3146(m)	1614(vs)	1581(s)	1024(m)		644(w)	546(m)	469(w)
9	3197(m)	1664(vs)	1572(s)	1026(m)		665(w)	579(m)	436(w)
10	3216(m)	1637(vs)	1560(s)	1020(m)		665(w)	540(m)	459(w)
11	3200(m)	1620(vs)	1564(s)	1020(m)		675(w)	544(m)	478(w)
12	3224(m)	1612(vs)	1581(s)	1016(m)		646(w)	552(m)	430(w)
13	3197(m)	1628(vs)	1583(s)	1020(m)		683(w)	542(m)	476(w)
14	3140(m)	1626(vs)	1579(s)	1022(m)		683(w)	542(m)	469(w)
15	3230(m)	1614(vs)	1552(s)	1023(m)		648(w)	557(m)	478(w)
16	3190(m)	1641(vs)	1585(s)	1022(m)		675(w)	542(m)	478(w)
17	3192(m)	1620(vs)	1585(s)	1016(m)		675(w)	546(m)	420(w)
18			1590(m) 1560(m)	1036(m)	1315(s)	681(w)	565(m)	432(w)
19			1597(m) 1560(m)	1022(m)	1308(s)	685(w)	569(m)	469(w)
20			1593(m) 1566(m)	1022(m)	1309(s)	685(w)	571(m)	449(w)
21			1595 1562	1016(m)	1306(s)	681(w)	565(m)	465(w)
22			1595(m) 1560(m)	1041(m)	1296(s)	673(w)	571(m)	449(w)

Electronic Spectra and Magnetic Properties:

The room temperature (25C°) magnetic moments and the electronic spectral data of the complexes are listed in Table (4). The ligand spectrum in DMF shows strong bands at 33003 cm⁻¹ and 29940 cm⁻¹ due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. These bands shift to lower wave numbers in the electronic spectra of most of the complexes at the regions 32894-29820 cm⁻¹ may indicate the coordination of the hydrazone to the metal ions. The new intense band observed in the spectra of all the complexes (1-22) at the region 28362-25153 cm⁻¹ may be associated with the charge transfer transition.

The magnetic moments values of Co(II) complexes (1, 7, 18) are in the range 4.82-4.93 B.M, suggesting octahedral geometry for Co(II)ion (Shivakumar *et al.*, 2008). Their electronic spectra show three bands at the regions 21624-20408 cm⁻¹, 16447-15685cm⁻¹ and 1052-9463 cm⁻¹ corresponding to the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$ transitions respectively, favoring octahedral geometry around the metal ion

(Cotton *et al.*, 1999; Chandra *et al.*, 2009). The electronic spectrum of Co(II) thiocyanate complex (13) exhibits one intense band at 15923 cm^{-1} attribute to the ${}^4A_2 \rightarrow {}^4T_1(p)$ transition, indicating tetrahedral stereo chemistry. The magnetic moment of this complex (4.32 B.M.) supporting the tetrahedral geometry (Cotton *et al.*, 1999).

The Ni(II) complexes (2, 8, 14, 19) show magnetic moment value of 2.93 – 3.19 B.M., slightly higher than the spin only value, indicating an octahedral environmental around Ni(II) ion. The six-coordinated Ni(II) complexes exhibit bands at the regions $25760\text{-}24271\text{ cm}^{-1}$, $16949\text{-}16142\text{ cm}^{-1}$ and $9823\text{-}9368\text{ cm}^{-1}$, assignable to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ transition, respectively. These transitions also reveal an octahedral geometry around the Ni(II) ion (Cotton *et al.*, 1999).

The electronic spectra of Cu(II) complexes (3, 9, 15, 20) contain a board band at $14880\text{-}13623\text{ cm}^{-1}$. This band is characteristic for Cu(II) ion with distorted octahedral stereochemistry and can be assigned to two or three of the transitions ${}^2B_{1g} \rightarrow {}^2E_g$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2A_{2g}$ (Lever, 1984). The magnetic moment of the complexes are in the range 1.78-2.04 B.M, corresponding to one unpaired electron (cotton *et al.*, 1999).

The diamagnetic Zn(II) complexes (4, 10, 16, 21) thorium complexes (5, 11, 17) and uranyl complexes (6, 12, 22) show no prominent absorption in the visible region because of d^{10} and f^0 configuration for Zn(II) and [Th(IV), U(VI)] respectively.

Table 4: Electronic spectral and magnetic susceptibility data of the ligand and its complexes

Complex No.	μ_{eff} B.M.	Electronic spectra cm^{-1}
L		33003, 29940
1	4.82	32674, 29237, 27777, 21624, 16447, 9823.
2	3.19	31026, 28810, 27130, 25760, 15384, 9842.
3	1.78	29820, 27231, 26361, 13623.
4	dia	32467, 28948, 25380.
5	dia	32258, 29585, 28155.
6	dia	32333, 27932, 25510.
7	4.93	31847, 28245, 26332, 20408, 15685, 10452.
8	3.07	30864, 27932, 26144, 24271, 16859, 9780.
9	2.04	31435, 27777, 25252, 14149.
10	dia	30864, 27700, 26530.
11	dia	32467, 29585, 27247.
12	dia	32258, 29069, 26178.
13	4.32	32258, 29522, 25154, 1592.
14	2.93	31645, 28571, 27780, 24390, 16949, 9823.
15	1.86	33783, 29069, 25153, 14880.
16	dia	31055, 28190, 27624.
17	dia	31446, 29325, 28362.
18	4.82	32487, 28571, 27881, 21490, 15673, 9463.
19	3.15	32865, 29572, 28310, 24580, 16142, 9368.
20	1.87	31250, 29364, 28260, 14084.
21	dia	32894, 27777, 26653.
22	dia	33557, 29411, 26175.

¹H-NMR spectra

¹H-NMR spectra of APFH and its Zn(II) complex(4) were recorded in DMSO- d₆, Table (5). The signal at δ (10.70) (s, 1H) is assigned to amide proton (-CONH-) of APFH. This signal is downfield in the spectrum of the complex [Zn(APFH)Cl₂] at δ (10.91) (s,1H) indicating coordination of oxygen of -CONH- with Zn(II) ion. (Shivakumar *et al.*, 2008). The presence of this signal in the free ligand and the complex(4) indicating that free ligand is mainly in keto form and coordinated to the Zn(II) ion in keto form also. The slight downfield shift of methyl group protons furan ring protons and pyridine ring protons may be considered as another evidence of coordination of the ligand through azomethine nitrogen carbonyl group oxygen and pyridine ring nitrogen atoms.

Table 5: ¹HNMR spectra data of APFH and Zn(II) complex(4) [chemical shift in δ (ppm)]

proton	APFH	[Zn(APFH)Cl ₂]
Amide-CONH-,proton	10.70 (s, 1H)	10.91 (s, 1H)
Methyl protons	2.45 (s, 3H)	2.58 (s, 3H)
Furan ring protons	6.71-7.44 (m, 3H)	6.78-7.55 (m, 3H)
Pyridine ring protons	7.84-8.63 (m, 4H)	7.86-8.64 (m, 4H)

s= singlet; m= multiple.

Antibacterial activity

The ligand APFH and two of its complexes (9 and 16) were tested against Gram-positive bacteria *S.aureus* and Gram-negative bacteria *E.coli* Table (6). It is clear that Cu(II) complex is moderately active toward *E. coli*, it is more active than the free ligand but it is less active toward *S.aureus*. On the other hand, Zn(II) complex(16) is less active toward both types of bacteria as compared with the free ligand and Erythromycin.

Table 6: Antibacterial effects of the investigated compound

Complex No.	Compound	Inhibition zone diameter * (mm) <i>S.sureus</i>	Inhibition zone diameter * (mm) <i>E.Coli</i>
L	APFH(C ₁₂ H ₁₁ N ₃ O ₂)	18.0	14.0
9	[Cu(APFH) ₂] (NO ₃) ₂	11.0	17.0
16	[Zn(APFH) (NCS) ₂]	10.0	8.0
	Erythromycin	20.0	12.0

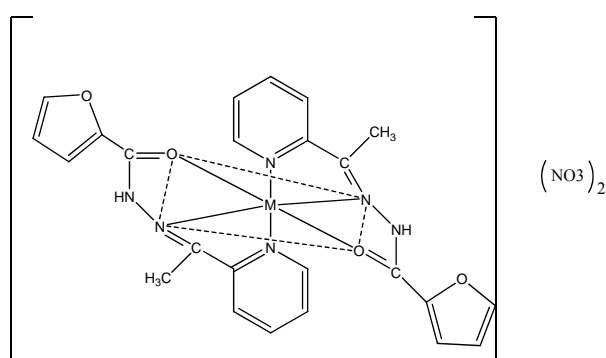
- including diameter of disc (mm).

CONCLUSION

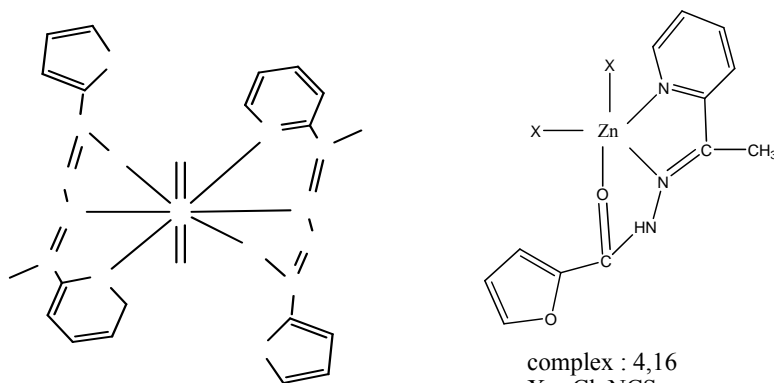
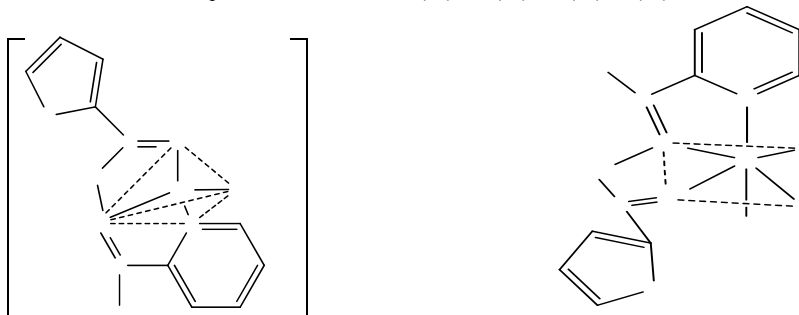
Based on stoichiometries and spectro- chemical studies, the ligand APFH acts as a neutral tridentate ligand ONN in all prepared metal chloride, nitrate and thiocyanate complexes (1-17) coordinating through the carbonyl group oxygen, azomethine group nitrogen and pyridine ring nitrogen atoms. In the deprotonated complexes (18-22), the

ligand was uninegative tridentate ONN coordinating through the enolic oxygen atom in addition to the azomethine and pyridine ring nitrogen atoms. Tetrahedral geometry is suggested for the (1:1) Co(II) thiocyanate complex(13) and octahedral geometry for all the synthesized Co(II), Ni(II), Cu(II), Zn(II) complexes (1, 3, 7-10, 14-15, 18-21) except for Zn(II) chloride (4) and thiocyanate (16) complexes which are expected to have five-coordinated geometry (pentagonal bipyramidal or square pyramid). (Fig. 2).

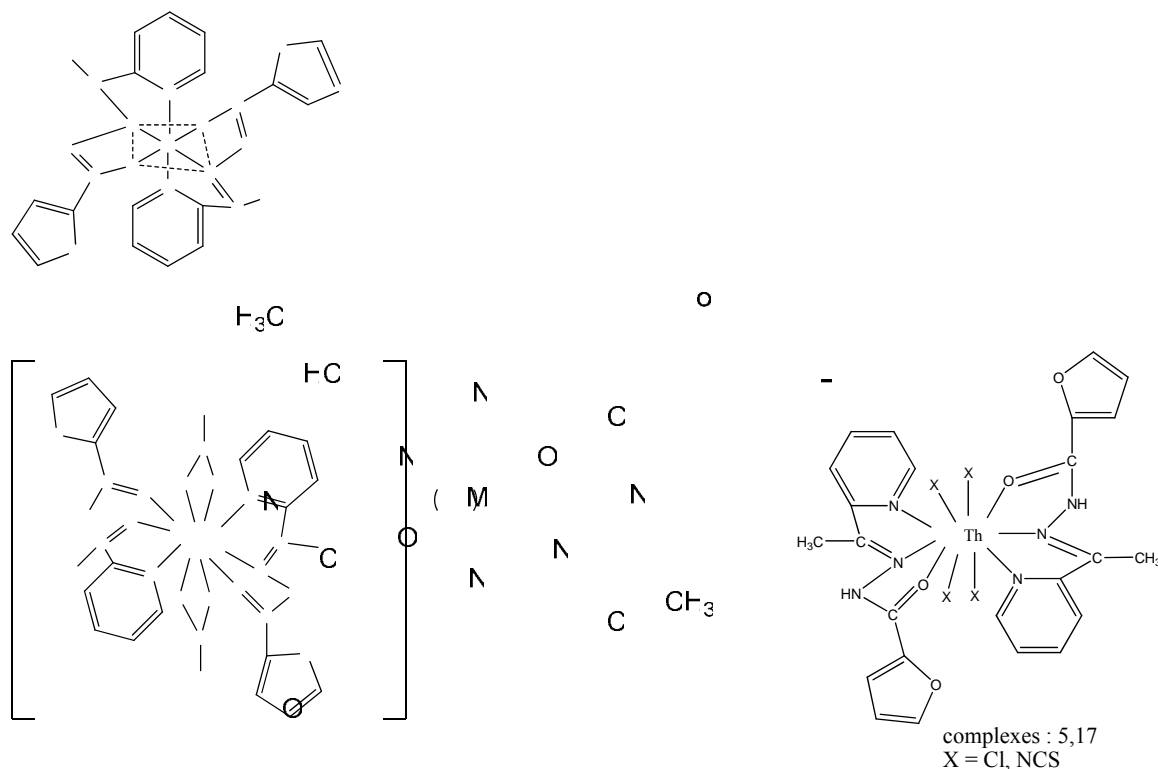
UO₂(II) complexes (6, 12 and 22) are eight coordinated and hexagonal bipyramidal geometry is proposed (Fig. 2). Thorium(IV) complexes (4, 11, and 17) are expected to have low symmetry geometry of coordination number (10) Cu(II) complex (9) is more active against Gram-negative bacteria *E.coli* as compared with the free ligand but less active against Gram-positive bacteria *S.aureus*. Zn(II) complex (16) is less active than APFH ligand against both types of bacteria.



complexes 7,8,9,10 M= Co (II) , Ni (II) , Cu (II) Zn (II)



complex : 4,16
X = Cl, NCS



complexes 18,19,20,21
Fig.2: Proposed structures for the prepared complexes
 Cu(II), Ni (II), Zn(II)

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