Synthesis and Structural Studies of Co(II), Ni(II), Cu(II), Zn(II), Th(IV) and UO$_2$(II) Complexes with 2-Acetylpyridine-4'-methylbenzoyl hydrazone

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ABSTRACT

A number of Co(II), Ni(II), Cu(II), Zn(II), Th(IV) and UO$_2$(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$_2$O)$_n$Cl$_2$] (n=1, M=Co(II), Ni(II); n=0 , M=Zn(II), UO$_2$(II)), [Ni(APMBH-H)Cl(DMSO)]$_2$, [Cu(APMBH-H)Cl]$_2$ and [Th(APMBH)$_2$Cl$_2$]Cl$_2$. The reaction of metal acetate with APMBH in 1:2 molar ratio yields the deprotonated bis-complexes [M(APMBH-H)$_2$] (M= Co(II), Ni(II), Cu(II), Zn(II) and UO$_2$(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) complexe (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

842.0
52
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 agent (Rollas and Küçükgüzel, 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 (Sadhu khan 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$_2$(II) Complexes with 2-Acetylpyridine-4'-methylbenzoyl hydrazone (APMBH) (Scheme 1) and to describe their structural and antibacterial properties.

Scheme 1: Tautomeric 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 Brucker FT-IR spectrophotometer (4000-400 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. \(^1\)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 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\(^\circ\)C (lit. mp.117\(^\circ\)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\(^\circ\)C (yield 90% mp.150\(^\circ\)C).

Preparation of complexes

a. Preparation of metal chloride complexes:
The respective metal chloride (0.001 mole, 0.238g, CoCl\(_2\).6H\(_2\)O; 0.238 g, NiCl\(_2\).6H\(_2\)O; 0.171 g, CuCl\(_2\).2H\(_2\)O; 0.136 g, ZnCl\(_2\); 0.377g, UO\(_2\)Cl\(_2\).2H\(_2\)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 \(^\circ\)C. The complex (3) [Ni(APMBH-H) Cl (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, ThCl\(_4.5H_2O\) (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, Co(CH\(_3\)COO)\(_2\).4H\(_2\)O; 0.249 g Ni(CH\(_3\)COO)\(_2\).4H\(_2\)O; 0.199g,Cu(CH\(_3\)COO)\(_2\).H\(_2\)O; 0.219g, Zn(CH\(_3\)COO)\(_2\).2H\(_2\)O; 0.424 g UO\(_2\)(CH\(_3\)COO)\(_2\).2H\(_2\)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 \(^\circ\)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 % | ρ Ωcm⁻¹cm²mol⁻¹ | calculated (found) |
|-------------|---------------------------------------------|-------|--------|---------|-----------------|-------------------|
|             | DMF | Ethanol | %M | %Cl |
| L           | APMBH (C₁₅H₁₅N₃O) | 150   | White | 90 | ----- | ----- | ----- | ----- |
| 1           | [Co(APMBH)(H₂O)Cl] | 237   | Green | 82 | 13.83 | 14.92 | 14.70 (14.48) | 17.70 (17.52) |
| 2           | [Ni(APMBH)(H₂O)Cl] | 265d  | Green | 90 | 8.64  | 10.21 | 14.65 (14.52) | 17.71 (17.48) |
| 3           | [Ni(APMBH-H)Cl(DMSO)]₂ | 288d  | Dark green | 75 | 5.46  | 9.24  | 13.83 (13.57) | 8.36 (8.12)    |
| 4           | [Cu(APMBH-H)Cl] | 260   | Dark green | 78 | 1.93  | 8.08  | 18.09 (17.85) | 10.11 (9.88)   |
| 5           | [Zn(APMBH)Cl] | 237d  | White | 76 | 4.49  | 5.86  | 16.79 (16.55) | 18.23 (17.97)  |
| 6           | [Th(APMBH)₂Cl₂] | 295d  | White | 84 | 142   | 81    | 26.36 (26.56) | 16.13 (15.88)  |
| 7           | [UO₂(APMBH)Cl] | 340   | Yellow | 92 | 1.98  | 6.23  | 40.06 (39.88) | 11.95 (11.72)  |
| 8           | [Co(APMBH-H)₂] | 295   | Brown | 69 | 5.56  | 1.66  | 10.47 (10.25) |             |
| 9           | [Ni(APMBH-H)₂] | 230d  | Dark green | 82 | 2.56  | 2.60  | 10.43 (10.22) |             |
| 10          | [Cu(APMBH-H)₂] | 252   | Green | 76 | 3.68  | 3.92  | 11.18 (11.39) |             |
| 11          | [Zn(APMBH-H)₂] | 346   | Yellow | 84 | 5.34  | 3.26  | 11.48 (11.26) |             |
| 12          | [UO₂(APMBH-H)₂] | 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⁻¹ due to amide NH stretching vibration ν(N-H) of the hydrazone which may be involved in NH...O hydrogen bonding. The strong bands at 1672 and 1610 cm⁻¹ are assigned to the carbonyl group stretching vibration ν(C=O) and azomethine stretching vibration ν(C=N) respectively. The low energy of ν(C=N) could be attributed to conjugation with neighboring pyridine (Karbouj et al., 2010). The medium band at 623 cm⁻¹ is assigned to the pyridine ring in plane deformation mode. The spectrum of the ligand displays also a weak band at 993 cm⁻¹ due to N-N stretching vibration ν(N-N) (Despaigne et al., 2009; Singh, 2008). IR data suggest keto-form of the ligand in the solid state.

¹H-NMR spectrum of the free ligand in DMF-d₇ solution shows a weak signal at δ 10.79 ppm (s, 1H) assigned to NH proton. The aryl protons appeared in their usual position at δ 7.32-7.86 ppm (m, 4H) and pyridine protons at δ 7.42-8.62 ppm (m, 4H). The spectrum exhibits additional signals at δ 2.46 ppm (s, 3H) and δ 2.39 ppm (s, 3H) characteristic of methyl groups (CH₃-C=N) and (CH₃-Ar) respectively (Karbouj et al., 2010; Jang et al., 2005). The number of protons assigned from ¹H-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 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) 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) 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) 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 $\delta$(py) at 623 cm$^{-1}$ in the spectrum of the ligand shifts to higher frequencies 631-646 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) cm$^{-1}$ and (415-450) 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 cm$^{-1}$ due to the symmetric and asymmetric stretching modes of coordinated water molecule. Furthermore, weak bands in the 887-899, 669-679 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 cm$^{-1}$ is attributed to $\nu$(O=U=O) (El-Tabl et al., 2012). The strong band observed at 1063 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. | \(\nu(C=O)\)  | \(\nu(C=N)\)  | \(\nu(N-N)\)  | \(\nu(N-H)\)  | \(\delta(Py\text{-}ring)\)  | \(\nu(M-O)\)  | \(\nu(M-N)\)  |
|-------------|----------------|----------------|----------------|----------------|------------------------|----------------|----------------|
| 1           | 1618(vs)       | 1572(s)        | 1016(m)        | 3375(w)        | 644(m)                 | 557(w)         | 424(w)         |
| 2           | 1618(vs)       | 1566(s)        | 1020(m)        | 3375(w)        | 644(m)                 | 557(w)         | 424(w)         |
| 3           | 1603(vs)       | 1560(s)        | 1012(m)        | 3342(w)        | 634(m)                 | 546(m)         | 418(w)         |
| 4           | 1601(s)        | 1560(s)        | 1012(m)        | 3345(w)        | 635(m)                 | 552(m)         | 450(w)         |
| 5           | 1641(s)        | 1595(s)        | 1016(m)        | 3335(w)        | 638(sh)                | 542(m)         | 424(w)         |
| 6           | 1597(vs)       | 1558(s)        | 1020(m)        | 3290(w)        | 629(m)                 | 519(w)         | 430(w)         |
| 7           | 1597(vs)       | 1558(s)        | 1020(m)        | 3290(w)        | 629(m)                 | 519(w)         | 430(w)         |
| 8           | 1597(vs)       | 1558(s)        | 1020(m)        | 3290(w)        | 629(m)                 | 519(w)         | 430(w)         |
| 9           | 1597(vs)       | 1558(s)        | 1020(m)        | 3290(w)        | 629(m)                 | 519(w)         | 430(w)         |
| 10          | 1597(vs)       | 1558(s)        | 1020(m)        | 3290(w)        | 629(m)                 | 519(w)         | 430(w)         |
| 11          | 1597(vs)       | 1558(s)        | 1020(m)        | 3290(w)        | 629(m)                 | 519(w)         | 430(w)         |
| 12          | 1597(vs)       | 1558(s)        | 1020(m)        | 3290(w)        | 629(m)                 | 519(w)         | 430(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$_2$(II) complexes (5-7, 11, 12) are diamagnetic as expected for d$^{10}$ and f$^0$ 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 of octahedral Nickel(II) complexes (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$^{-1}$. The first band may be assigned to the $\pi \rightarrow \pi^*$ transition in the benzenoid and pyridine
moieties and intra ligand π→π* transition. The second probably due to n→π* 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 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 cm⁻¹, 14749-14925 cm⁻¹ and 18181-18621 cm⁻¹ indicating an octahedral geometry around the metal ion. These transitions are assigned as 4T₁g(F)→4T₂g(F)(v₁), 4T₁g(F)→4A₂g(F)(v₂) and 4T₁g(F)→4T₁g(P)(v₃) respectively. (Singh et al., 2013). The electronic spectral bands of Ni(II) complexes (2, 3, 9) observed at the ranges 9652-10869 cm⁻¹, 14285-15432 cm⁻¹ and 24038-26737 cm⁻¹. These electronic spectral bands correspond to the transitions 3A₂g(F)→3T₂g(F)(v₁), 3A₂g(F)→3T₁g(F)(v₂) and 3A₂g(F)→3T₁g(P)(v₃), in an octahedral environment (Singh et al., 2013).

The spectrum of copper(II) complex (10) showed a broad band centered at 14005 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 2B₁g→2E₂g, 2B₁g→2B₂g and 2B₁g→2A₁g. This could be due to the Jahn-Teller effect that operates on the d⁹ 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 cm⁻¹ and 9823 cm⁻¹, corresponding to the transitions dz²→dx²-y² and dxz,dyz→dx²-y² 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 f⁰ system and zinc(II) complexes (5) and (11) have d¹⁰ system, so they do not show f→f or d→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. | µ_eff B.M | Electronic spectrum cm⁻¹ |
|-------------|-----------|--------------------------|
| L(APMBH)    | 4.97      | 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) K. pneumoniae | Inhibition zone diameter (mm) S.aureus |
|------------|---------------------------------|---------------------------------------------|----------------------------------------|
| L          | APMBH(C_{15}H_{15}N_{3}O)      | 7                                           | 9                                      |
| 5          | [Zn(APMBH)Cl_{2}]              | 9                                           | 21                                     |
| 10         | [Cu(APMBH-H)_{2}]              | 15                                          | 17                                     |
|            | Amoxyline                      | 11                                          | 17                                     |
|            | Erthromaycine                  | 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_{2}(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_{2}], 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.
[Ni(APMBH-H)Cl(DMSO)]$_2$ (dinuclear) octahedral complex (3)

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

[Th(APMBH)$_2$Cl$_2$]Cl$_2$ eight coordinate complex (6)
[M(APMBH-H)$_2$] $M=$Co(II),Ni(II),Cu(II),Zn(II) octahedral complexes (8,9,10,11)

[UO$_2$(APMBH)$_2$Cl$_2$] pentagonal bipyramidal complex (7)

[UO$_2$(APMBH-H)$_2$] hexagonal bipyramidal complex (12)

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

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