

Synthesis, Characterization and Antibacterial Activity of Thorium(IV), Dioxouranium(VI), Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes with Picolinoyl Hydrazones

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(Received 7 / 7 / 2013 ; Accepted 23 / 9 / 2013)

ABSTRACT

A series of metal complexes of Th(IV), UO₂(II), Co(II), Ni(II), Cu(II) and Zn(II) with 2-acetyl furan picolinoyl hydrazone (AFPH) and 2-thiophen carboxaldehyde picolinoyl hydrazone (TCPH) have been synthesized. The complexes were characterized by elemental analyses (metal and Cl), molar conductance, magnetic susceptibility and spectral (IR, UV-Vis) measurements.

The ligands act as neutral tridentate in metal chloride complexes of the general formula [ML(H₂O)Cl₂], [L=AFPH, M=Co(II), Ni(II), Cu(II). L = TCPH, M = Co(II), Ni(II), Zn(II)] and [UO₂LCl₂] (L = AFPH, TCPH) coordinated through carbonyl oxygen, azomethine nitrogen and pyridine nitrogen atoms. The physico-chemical studies suggest octahedral and pentagonal bipyramidal geometries respectively. On the other hand, the ligands act as monobasic tridentate coordinated through the enolic oxygen, the azomethine nitrogen and the pyridine nitrogen atoms in the deprotonated complexes of the types [M(L-H)Cl]₂, [L=AFPH, M=Zn(II); L=TCPH, M=Cu(II)], [Th(L-H)₂Cl₂] (L=AFPH, TCPH), and [M(L-H)₂] [L=(AFPH, TCPH), M=Co(II), Ni(II), Cu(II), Zn(II), UO₂(II)] forming binuclear square pyramidal and octahedral mononuclear metal complexes. Hexagonal bipyramidal geometry proposed was for the dioxouranium(VI) complexes and square antiprismatic or dodecahedral geometries for Th(IV) complexes.

Keywords: Hydrazones, complexes, transition metals, Thorium, Uranium.

(VI)

(IV)

(II)

(II)

(II)

(II)

-2 (AFPH)

-2

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

(TCPH)

(IR, UV-Vis)

NNO

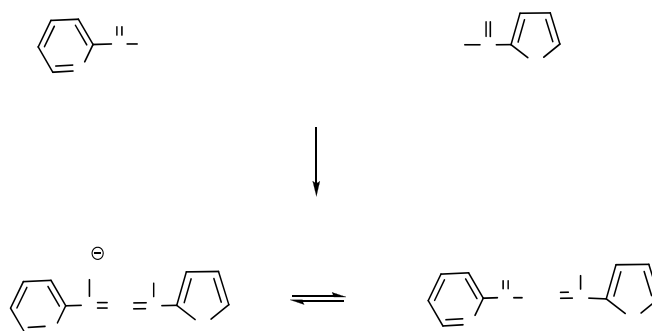
TCPH AFPH

Th(IV), U(VI)

INTRODUCTION

Aroylhydrazones are an important class of ligands, coordinating through protonated/deprotonated amide oxygen and the imine nitrogen of hydrazone moiety, very often an additional donor site (N, O, or S) is provided by the aldehyde or ketone forming the hydrazone ligand. (Singh *et al.*, 2011). The ligand deprotonation state depends upon condition and metal employed (Monfared *et al.*, 2013).

Hydrazones, especially heterocyclic aroylhydrazones are multipurpose ligands having a range of biological and chemical activities (Suvarapu *et al.*, 2012, Rollas and Kucukguzel, 2007). They are well known for their metal binding ability and interesting coordination behaviour (Mondal *et al.*, 2013). Aroylhydrazones containing heterocyclic moieties have proved to be strong chelating agents for transition metals (Singh *et al.*, 2013, Algesan *et al.*, 2013), lanthanides (Anwar *et al.*, 2012), and non-transition metals, (Saadeh *et al.*, 2012). In our laboratory we have investigated the structural diversity of heterocyclic aroylhydrazones along with their magneto-structural properties and antibacterial activities (Al-Daher and Al-Qassar, 2011; Al-Daher and Mohammed, 2011; Al-Daher and Mustafa, 2013). In view of the significant role played by the heterocyclic hydrazones and their metal complexes in biological systems and in various other fields we motivated to synthesize Co(II), Ni(II), Cu(II), Zn(II), UO₂(II) and Th(IV) complexes with 2-thiophene carboxaldehyde and 2-acetyl furan picolinoyl hydrazone (Scheme 1) and study their physico-chemical properties, coordination behavior and antibacterial activity.



EXPERIMENTAL

Material and Measurements

All chemicals used were reagent grade from B.D.H and Fluka companies, used as supplied, except for 2-acetyl furan and 2-thiophene carboxaldehyde purified according to literature (Perrin *et al.*, 1980).

The IR spectra were Performed between 4000 and 400 cm⁻¹ using KBr pellets on a Teson 27 Brucker FT-IR, the intensity of reported IR bands is defined as s=strong, m=medium, w=weak. Metal analyses were carried out by spectrophotometric methods [Co(II), Ni(II), Cu(II), and Zn(II)] using Shimadzu (AA670) atomic absorption spectrophotometer and Jasco V-630 to determine Th(IV) and U(VI) colourimetrically by the reagents thoron and arsinszo(III) respectively (Marczenko and Balcerzak, 2000). Ni(II) and Zn(II) are also determined by complexometric titration against standard EDTA solution, Chloride was determined volumetrically by Mhor's method (Vogel, 1989).

Melting points were obtained on Electrothermal 9300 melting point apparatus in open capillaries. Electronic absorption spectra (190-1100 nm) were recorded in DMF 10⁻²M solutions on Shimadzu U.V-1650 PC spectrophotometer at room temperature using 1cm cell. Molar conductance was measured at room temperature for 10⁻³M solutions in methanol and in DMF using

picolinoyl hydrazide

+

PMC3 Jeneway conductivity meter. Magnetic susceptibility measurements of the complexes were performed on Bruker BM6 instrument at ambient temperature.

Preparation of the ligands

a. Preparation of 2-Picolinic acid hydrazide

This was prepared by the reaction of ethyl picolinate and hydrazine hydrate as reported by (Zareef *et al.*, 2006) (m.p 144 - 145°C).

b. Preparation of the ligand 2-Acetyl Furan Picolinoyl hydrazon (AFPH):-

This was prepared according to literature method (Abd El-Motaleb *et al.*, 2005). To a solution of picolinic acid hydrazide (6.85g, 0.05 mole) in absolute ethanol (20 mL) was added a solution of 2-acetyl furan (5.5g, 0.05 mole) in absolute ethanol (20 mL). The reaction mixture was stirred and boiled under reflux for 3hrs. On cooling in an ice-bath, the white crystalline solid that precipitated was separated by filtration, washed with cold ethanol (5 mL) then with ether (5 mL) and dried in an oven at (80 - 90 °C) m.p 164°C.

c. Preparation of the ligand 2-Thiophen carboxaldehyde Picolinoyl hydrazon (TCPH):-

This was prepared by the same procedure reported in (b) above using (6.85g, 0.05 mole) picolinic acid hydrazide and (5.5g, 0.05 mole) 2-thiophen carboxaldehyde. The hydrazone separated on cooling in an ice-bath as light yellowish crystalline product was filtered, washed and dried as above (m.p 190°C).

Preparation of the Metal Complexes

a. Preparation of metal chloride Complexes

The appropriate metal chloride (0.001 mole) [0.238g, CoCl₂.6H₂O; 0.238g, NiCl₂.6H₂O; 0.171g, CuCl₂.2H₂O; 0.136g, ZnCl₂; 0.377g, UO₂Cl₂.2H₂O] in (10 mL) absolute ethanol was heated under reflux with constant stirring with (0.229g, 0.001 mole) of the ligand (AFPH) or (0.231g, 0.001 mole) of the ligand (TCPH). 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 desiccator. In case of thorium(IV) complexes (0.001 mole) [0.464g, ThCl₄.5H₂O] and (0.458g, 0.002 mole) of the ligand (AFPH) or (0.462g, 0.002 mole) of the ligand (TCPH) were used in absolute ethanol respectively.

b. Preparation of the deprotonated bis Complexes

To stirred hot ethanolic solution (20 mL) of the appropriate metal acetate (0.001 mole) [0.249g, Co(CH₃COO)₂.4H₂O; 0.249g, Ni(CH₃COO)₂.4H₂O; 0.199g, Cu(CH₃COO)₂.H₂O; 0.219g, Zn(CH₃COO)₂.2H₂O; 0.424g UO₂(CH₃COO)₂.2H₂O] was added (0.458g, 0.002 mole) of the ligand (AFPH) or (0.462g, 0.002 mole) of the ligand (TCPH) in absolute ethanol (10 mL). The reaction mixture was then heated under reflux with constant stirring for 3hrs upon which the solid complexes were separated, filtered off and washed with ethanol (5 mL) and dried as above.

Antibacterial activity

Antibacterial activity was evaluated using agar diffusion method (Kethcum, 1988). Gram-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). 6 mm diameter filter discs were soaked in the tested solutions. After 24h cultivation at 37°C, the diameters of zones of inhibition were determined. DMSO was inactive under applied conditions.

RESULTS AND DISCUSSION

It appears from the analytical data Table (1). That reaction between metal chlorides and the ligands AFPH or TCPH occur in 1:1 (M:L) molar ratio, and the reactions of metal acetates with the same ligands take place in (1:2) molar ratio, forming bis-deprotonated complexes in which the ligands enolize and deprotonate during complexation. The complexes are colored powdery solids.

They are sparingly soluble in common organic solvent, ethanol, methanol, DMF and DMSO but are in soluble in chloroform, acetone and diethylether. Most of the complexes melt or melt with decomposition at relatively low temperatures which may indicate the non-polymeric nature of the complexes. The low molar conductance values at room temperature of 10^{-3} M solution in ethanol ($2.08\text{--}18.32\text{ ohm}^{-1}\text{mol}^{-1}\text{cm}^2$) and in DMF ($1.56\text{--}29.48\text{ ohm}^{-1}\text{mol}^{-1}\text{cm}^2$) indicate that they are non-electrolytes (Geary, 1971).

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

Complex No.	Formula	Color	m.PC ^o	Yield %	$\Omega\text{ohm}^{-1}\text{Cm}^2\text{mol}^{-1}$		M%	Cl%
					Ethanol	DMF		
L1	AFPH($\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_2$)	White	163	86				
1	[Co(AFPH) (H_2O) Cl_2]	Brown	280d	60	2.08	15.09	15.20 (15.63)	19.36 (18.83)
2	[Ni(AFPH) (H_2O) Cl_2]	Green	232	71	8.88	12.93	15.82 (15.58)	18.31 (18.84)
3	[Cu(AFPH) (H_2O) Cl_2]	Green	236	67	10.12	19.59	17.04 (16.64)	18.46 (18.61)
4	[Zn(AFPH-H) Cl] $_2$	Yellow	269	74	14.34	11.07	19.32 (19.87)	10.24 (10.79)
5	[Th(AFPH-H) $_2$ Cl_2]	Yellowish Orang	300d	57	13.40	20.29	31.10 (30.56)	9.02 (9.35)
6	[UO $_2$ (AFPH) Cl_2]	Pale yellow	275	85	10.70	21.99	42.16 (41.75)	12.15 (12.45)
7	[Co (AFPH-H) $_2$]	Pale brawn	100	82	7.33	4.94	11.85 (11.44)	
8	[Ni(AFPH-H) $_2$]	Pale green	138	75	9.36	7.44	11.06 (11.40)	
9	[Cu(AFPH-H) $_2$]	Dark green	150	68	11.93	6.07	11.81 (12.22)	
10	[Zn(AFPH-H) $_2$]	Yellow	110	68	7.35	4.52	12.81 (12.53)	
11	[UO $_2$ (AFPH-H) $_2$]	Yellow	295d	72	7.65	9.55	32.36 (32.78)	
L2	TCPH($\text{C}_{11}\text{H}_9\text{N}_3\text{OS}$)	Yellowish Orang	192	75				
12	[Co(TCPH) (H_2O) Cl_2]	Pink	290	75	13.16	21.98	16.02 (15.55)	18.25 (18.73)
13	[Ni(TCPH) (H_2O) Cl_2]	Green	320	76	15.50	17.28	15.96 (15.50)	18.29 (18.74)
14	[Cu(TCPH-H) Cl] $_2$	Pale green	221	72	18.14	29.48	18.87 (19.30)	10.23 (10.79)
15	[Zn(TCPH) (H_2O) Cl_2]	Yellow	203	63	16.21	11.26	16.65 (16.96)	19.04 (18.42)
16	[UO $_2$ (TCPH) Cl_2]	Yellow	280d	87	17.56	20.18	41.25 (41.60)	11.83 (12.41)
17	[Th(TCPH-H) $_2$ Cl_2]	Yellow	305d	85	18.32	24.78	30.02 (30.40)	9.59 (9.30)
18	[Co(TCPH-H) $_2$]	Brown	300d	80	2.44	7.21	11.05 (11.35)	
19	[Ni (TCPH-H) $_2$]	Pale green	112	80	3.72	7.65	11.78 (11.31)	
20	[Cu (TCPH-H) $_2$]	Pale green	240d	66	3.42	1.56	12.64 (12.12)	
21	[Zn(TCPH-H) $_2$]	White	328	78	3.82	7.75	12.12 (12.44)	
22	[UO $_2$ (TCPH-H) $_2$]	Yellowish Orang	240d	73	10.20	5.71	32.22 (32.60)	

d=decomposition temperature

Infrared spectra

The IR spectra of the free ligands and their metal complexes were compared to get information about the coordination behavior of the ligands with the metals (Table 3).

In the IR spectra of the ligands, the vibration bands $\nu_{(N-H)}$, $\nu_{(C=O)}$, $\nu_{(C=N)}$, $\nu_{(N-N)}$ and δ_{py} were observed at 3325, 1685, 1618, 997 and 621 cm⁻¹ respectively for the ligand AFPH and at 3234, 1676, 1622, 997 and 619 cm⁻¹ respectively for the ligand TCPH.

In the IR spectra of the metal chloride complexes (1,2,3,6,12,13,15,16) the bands of $\nu_{(N-H)}$ is either unchanged or shifted to higher frequencies indicating non-involvement in coordination. The band due to $\nu_{(C=O)}$ is shifted to lower frequencies in these complexes by 36-55 cm⁻¹ indicating coordination through the oxygen atom of the carbonyl group (i.e the ligands are coordinated in the keto-form). The bands of $\nu_{(N-H)}$ and $\nu_{(C=O)}$ were absent in the spectra of the metal chloride complexes (4, 5,14,17) suggesting coordination via enol- form, by the deprotonation of the N-H proton, during the complexation process similar observation were noticed in the IR spectra of the deprotonated bis-complexes (7-11,18-22) in which the $\nu_{(N-H)}$ and $\nu_{(C=O)}$ are not observed due to enolization of carbonyl group of the ligands due to complex formation. The appearance of anew $\nu_{(C-O)}$ band in these complexes at the region 1286-1302 cm⁻¹ suggest bonding of the ligands to the metal ions through deprotonated (C-O) group (Abu Affan *et al.*, 2009).

The stretching vibrations of azomethine group $\nu_{(C=N)}$ are shifted to lower frequencies in all the complexes spectra and this proves that nitrogen atom of azomethine group is involved in complexation, coordination of nitrogen to the metal atom reduces the electron density in the azomethine causing a shift in the $\nu_{(C=N)}$ band (Sharma *et al.*, 2006). The spectra of the deprotonated complexes show two bands due to $\nu_{(C=N)}$ in the ranges 1608-1581 cm⁻¹ and 1579-1541 cm⁻¹, the first one is due to the enolization of the ligands $\nu_{(O-C=N)}$ whereas the second one result is due to down shift of $\nu_{(C=N)}$ on coordination with metal (Singh and Sing, 2013). The $\nu_{(N-N)}$ observed at 997 cm⁻¹ in the spectra of AFPH and TCPH, shifts to higher frequencies by 12-27 cm⁻¹ in their complexes. This indicates the coordination of one of the nitrogen atom of N-N group with metal (Singh *et al.*, 2013). This phenomenon is owing to the diminution of the lone pair electrons repulsion which come from the two adjacent nitrogen atoms, by sharing the electrons out to the metal ion (Abu Affan *et al.*, 2009).

The pyridine in-plane deformation mode $\delta_{(py)}$ at the region 619-621 cm⁻¹ of the ligands spectra shifts to higher frequencies 625-669 cm⁻¹ in spectra of the complexes the suggesting the coordination of the heterocyclic nitrogen atom (Despaigen *et al.*, 2009).

The metal complexes also show non-ligand bands in the ranges 507-573 cm⁻¹ and 476-420 cm⁻¹ which are tentatively assigned to ν_{M-O} , ν_{M-N} respectively.

Many workers (Halli and Malipatil, 2011) have reported ν_{C-O-C} stretching vibrations of furan ring in the region 1020-1250 cm⁻¹ in the present case the band at 1090 cm⁻¹ in the spectrum of the AFPH ligand assigned as $\nu_{(C-O-C)}$ stretching, which almost remain unaltered in the metal complexes Table (2) indicating non-participation of the furan ring oxygen atom in bonding with metal.

The medium intensity band observed at 850 cm⁻¹ in the spectrum of the ligand TCPH due to $\nu_{(C-S-C)}$ of thiophene ring is also unaffected by coordination and remains almost at the same position in the metal complexes, which indicates the non-involvement of thiophene sulfur atom in bonding (Singh *et al.*, 2011; Abu Affan *et al.*, 2009).

The spectra of the complexes (1, 2, 3,12,13,15) exhibit a broad band centered around 3400 cm⁻¹ due to the symmetric and asymmetric stretching modes of coordinated water molecule. The H-O-H bending modes occur in the 1630-1610 cm⁻¹ range. Weak bands in the 940-900, 770-750 and 660-640 cm⁻¹ ranges represent the wagging, twisting and rocking modes of coordinated water (Singh, 2008).

The additional band appearing at the region $899\text{--}930\text{ cm}^{-1}$ in the spectra of uranyl complexes (6,11,16, 22) is attributed to the symmetric stretching vibration of $\text{O}=\text{U}=\text{O}$ group. The absence of the ν_1 mode of the $\text{O}=\text{U}=\text{O}$ indicating the linearity of the $\text{UO}_2(\text{II})$ species is maintained in the complexes (Gandi *et al.*, 2001).

On the basis of the above observations, it was found that the ligands AFPH and TCPH are coordinated in the keto-form in the metal chloride complexes (1, 2, 3, 6,12,13,15,16) acting as neutral tridentate ligands through the carbonyl oxygen, imine nitrogen and pyridine nitrogen atoms. In the deprotonated complexes (4, 5, 7, 8, 9, 10, 11, 14, 17, 18, 19, 20, 21,22) AFPH and TCPH coordinated to the metals in the enolate form acting as monobasic tridentate coordinating through the enolic oxygen in addition to imine and pyridine nitrogen atoms (Fig. 1).

Table 2:Characteristic IR spectral bands of the ligands and their complexes

Complex No.	ν_{NH}	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{N-N}}$	$\nu_{\text{C-O}}$	$\delta\text{Py inplane}$	$\nu_{\text{C-O-C}}$	$\nu_{\text{C-S-C}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
L1(AFPH)	3325m	1685s	1618m	997m	----	621sh	1090m	----	-----	-----
1	3384m	1635s	1597s	1020m	----	660m	1111m	----	567m	428w
2	3392m	1638s	1593s	1020m	----	656m	1107m	----	548m	430w
3	3380m	1649s	1601s	1020m	----	648m	1102m	----	513m	461w
4	----	-----	1597s 1552s	1018s	1298m	625w	1111m	----	565m	463w
5	----	-----	1601m 1566m	1012w	1302m	656m	1093m	----	515m	430w
6	3328m	1630s	1603m	1009m	-----	634sh	1101m	----	561m	430w
7	----	----	1591m 1550s	1018m	1294m	669m	1101m	----	513m	465w
8	----	----	1585s 1552m	1020m	1286m	644m	1101m	----	538m	476w
9	----	----	1597s 1579s	1018m	1294m	650sh	1099m	----	573m	474w
10	----	----	1604s 1541s	1024m	1296s	630sh	1109m	----	563m	420w
11	----	----	1608m 1566s	1024m	1296s	642m	1103m	----	528m	420w
L2(TCPH)	3234m	1676s	1622m	997s	-----	619m	----	850m	-----	-----
12	3248s	1637s	1601s	1014m	-----	640sh	----	856m	513m	428w
13	3248m	1637s	1601s	1020m	-----	650m	----	854m	507m	426w
14	-----	-----	1597s 1564s	1018m	1294m	650sh	----	860m	530m	438w
15	3263m	1635vs	1595s	1020m	-----	642s	----	858m	519m	430w
16	3260m	1637m	1589s	1011m	-----	634m	----	854w	528m	428w
17	----	----	1595s 1562m	1011m	1298m	636m	----	862m	538m	430w
18	----	----	1601s 1547s	1009m	1298m	640w	----	860w	507m	428w
19	----	----	1604s 1570m	1011m	1298m	669m	----	860w	560m	420w
20	----	----	1581s 1560m	1018m	1288s	656m	----	865m	534m	428w
21	----	----	1604m 1541s	1016m	1296m	654m	----	856w	536m	440w
22	----	----	1595s 1556m	1018m	1294s	638sh	----	856m	523m	426w

Electronic Spectra and Magnetic moments

The electronic spectra of ligands and their metal complexes in the rang 190-1100nm,were carried out in DMF. Table (3) shows the electronic spectral bands and magnetic moments of the prepared complexes.

The spectra of the ligands in DMF solution exhibit two main absorption bands at 37593-33112 cm^{-1} and 32679-29940 cm^{-1} . The first band probably is due to $\pi \rightarrow \pi^*$ transition of the chromophore (-C=N-NH-CO-), and the second band might be attributed to the $n \rightarrow \pi^*$ transitions resulting from nitrogen, oxygen and sulfur atoms. In the spectra of the complexes, the shift of the ligand transitions to a longer wavelength (red shift) is ascribed to the ligand complexation with metal ions. The new intense band observed in the spectra of all complexes at the region 28901-24752 cm^{-1} may be associated with the charge transfer transitions (LMCT).

The magnetic moment values of Co(II) complexes (1,7,12,18) are in the range 4.81-5.05B.M, which are fairly close to the values reported for three unpaired electrons in an octahedral environment (Singh *et al.*, 2013). These complexes exhibit three bands in their spectra at the regions 19230-18181 cm^{-1} , 16722-14836 cm^{-1} and 10526-9803 cm^{-1} indicating an octahedral geometry around the metal ion .These transitions are assigned as $^4T_{1g} \rightarrow ^4T_{1g}(P)$ (ν_3) , $^4T_{1g} \rightarrow ^4A_{2g}(F)$ (ν_2) and $^4T_{1g} \rightarrow ^4T_{2g}(F)$ (ν_1) respectively. (Cotton *et al.*,1999).

The magnetic moment values of Ni(II) complexes (2,8,13,19) are in the range 2.94-3.13 BM which are slightly higher than the spin only value of two unpaired electrons, indicating octahedral environment around Ni(II) ion. It is further confirmed by their electronic spectral bands observed at the regions 26315-24509 cm^{-1} , 17182-14686 cm^{-1} and 10845-9823 cm^{-1} assignable to $^3A_{2g}(F) \rightarrow ^3T_{1g}(p)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ transitions respectively (Cotton *et al.*, 1999).

The electronic spectra of Cu(II) complexes (3,9,20) contains a broad band at 13812-13405 cm^{-1} . These bands are typical of d-d band of Jahn-Teller distorted Cu(II) complexes in distorted octahedral geometry, and can be assigned to two or three of the transitions $^2B_{1g} \rightarrow ^2E_g$, $^2B_{1g} \rightarrow ^2B_{2g}$ and $^2B_{1g} \rightarrow ^2A_{1g}$ (Singh, 2008). Magnetic moment of these complexes are in range 1.95-2.05 BM correspond to one unpaired electron and suggesting a monomeric octahedral geometry(Cotton *et al.*, 1999). The relatively low magnetic moment of 1.46 BM of the copper(II) complex (14) support the antiferromagnetic behavior of the proposed dimeric structure (Filipovic *et al.*, 2009). The electronic spectrum of this complex exhibit a broad band at 9800-12195 cm^{-1} region. This band is characteristic of square pyramidal geometry (Mondal *et al.*, 2013).

The diamagnetic Zn(II) complexes (4,10,15, 21). Thorium(IV) complexes (5,17) and uranyl complexes (6,11,16, 22) show no prominent absorption in the visible region because of d^{10} and f^0 configurations of Zn(II), Th(IV) and U(VI) ion respectively.

Table 3: Electronic spectra and magnetic susceptibility data of the ligands and their complexes

Complex No.	μ_{eff} B.M.	Electronic Spectra cm^{-1}
L1(AFPH)	----	33112, 29940
1	4.96	32679, 29585, 28571, 19230, 16722, 10526
2	3.13	30864, 29239, 27777, 24509, 14686, 9823
3	1.95	31055, 29498, 27027, 13405
4	dia	29761, 28735, 27397
5	dia	30674, 29585, 25773
6	dia	30487, 29411, 28409
7	4.87	32679, 29585, 26315, 18248, 16666, 9803
8	3.10	31847, 29411, 28571, 24630, 16666, 10845
9	1.98	32467, 28735, 27777, 13812
10	dia	32894, 29585, 25252
11	dia	29411, 28818, 27932
L2(TCPH)	----	37593, 32679
12	4.81	32894, 31250, 27472, 18181, 14836, 9803
13	2.98	34013, 29585, 27624, 24630, 15625, 9852
14	1.46	30303, 26385, 24752, 12195, 9800
15	dia	31055, 29411, 27932
16	dia	31847, 29585, 25906
17	dia	32894, 29411, 28409
18	5.05	31250, 29411, 28901, 18520, 15230, 10331
19	2.94	32467, 29761, 27472, 26315, 17182, 9823
20	2.05	30120, 29069, 26455, 13586
21	dia	31250, 29585, 25510
22	dia	32894, 30303, 27932

Antibacterial activity

The synthesized hydrazones AFPH and TCPH and some of their metal complexes (3, 4, 14, 21) were tested for their antimicrobial activity against selected bacteria, Gram-positive *S.aureus* and Gram-negative *K.pneumoniae*. The results are presented in Table (4). It is clear that they have moderate antibacterial activity at the used concentration (10 mg/ mL) except for the ligand AFPH and its Zn(II) complex (21), which were inactive against *S.aureus*. The higher activity of the metal complexes may be due to the presence of metal ions in the complexes.

Table 4: Antibacterial effects of the investigated compounds

Complex No.	Compound	Inhibition zone diameter *(mm) <i>S.aureus</i>	Inhibition zone diameter *(mm) <i>K.pneumoniae</i>
L1	AFPH($\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_2$)	6	8
L2	TCPH($\text{C}_{11}\text{H}_9\text{N}_3\text{OS}$)	8	7
3	$[\text{Cu}(\text{AFPH})\text{H}_2\text{OCl}_2]$	9	11
4	$[\text{Zn}(\text{AFPH-H})\text{Cl}]_2$	10	7
14	$[\text{Cu}(\text{TCPH-H})\text{Cl}]_2$	7	9
21	$[\text{Zn}(\text{TCPH-H})_2]$	6	7
	Amoxyline	17	15
	Erythromycin	20	11

CONCLUSION

The present work describes the synthesis of 2-acetylfuran picolinoyl hydrazone (AFPH) and 2-thiophen carboxaldehyde picolinoyl hydrazone (TCPH) and the Co(II), Ni(II), Cu(II), Zn(II), UO₂(II) and Th(IV) complexes. The structural characterization of the synthesized compounds were

made by using the elemental analyses, spectroscopic methods, magnetic and conductance studies. From the spectroscopic characterization, it is concluded that the heterocyclic hydrazones AFPH and TCPH act as neutral or monobasic tridentate ligands coordinating through carbonyl group oxygen, azomethine nitrogen and pyridine nitrogen atoms in the keto-form or enolate-form via deprotonation depending on the condition of the reaction and the type of metal salt used. Based on phesicochemical evidence, the proposed structures of the prepared complexes are exhibited in (Fig.1).

The antibacterial activity screening of the ligands and some of their complexes against two type of bacteria showed moderate antibacterial activity.

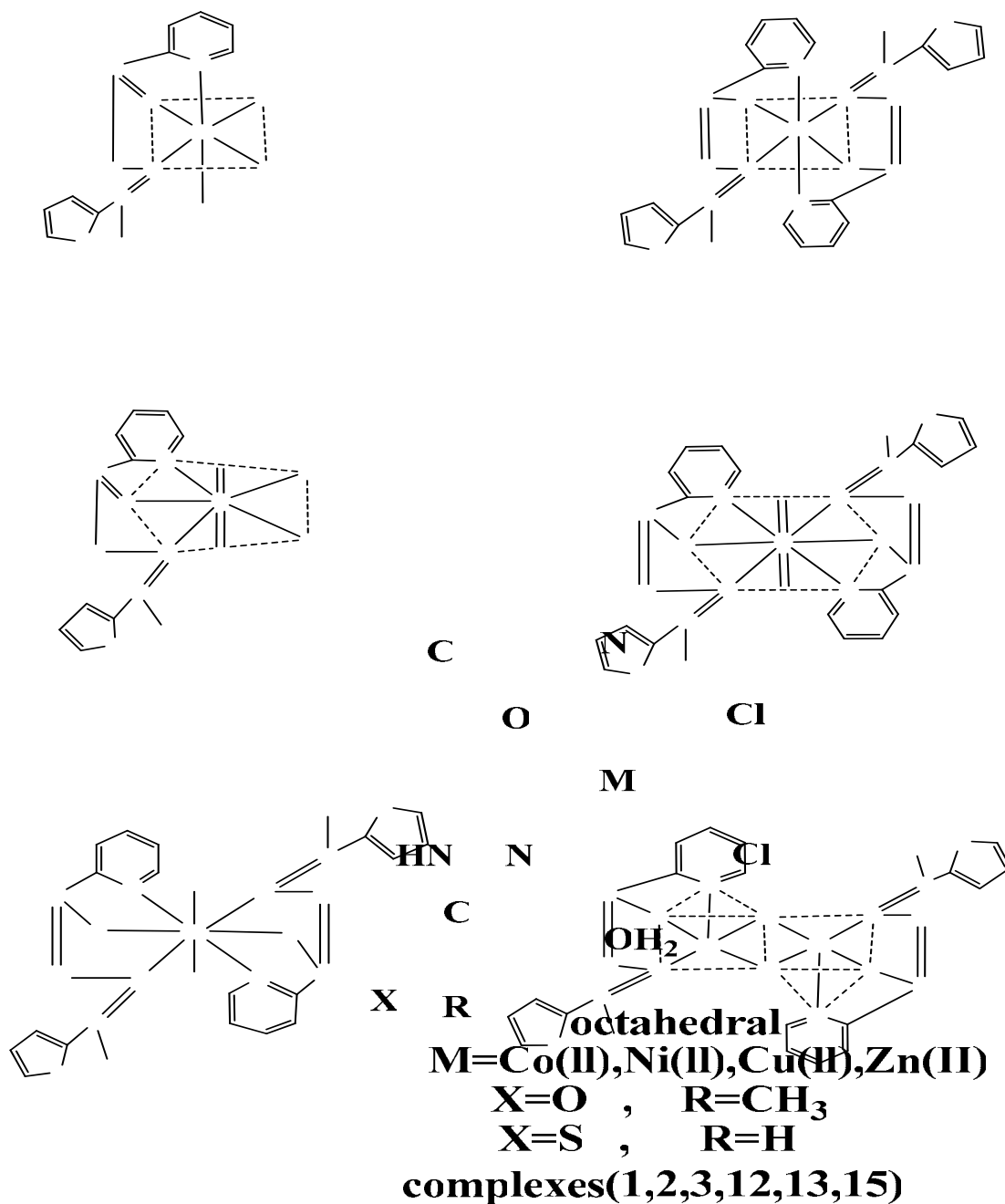


Fig. 1: Proposed structures for the prepared complexes.

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