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# Cobalt(II), nickel(II), copper(II), zinc(II) and hafnium(IV) complexes of N'-(furan-3-ylmethylene)-2-(4-methoxyphenylamino)acetohydrazide

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#### ABSTRACT

Cobalt(II), nickel(II), copper(II), zinc(II) and hafnium(IV) complexes of furan-2-carbaldehyde 4-methoxy-N-anilinoacetohydrazone were synthesized and characterized by elemental and thermal (TG and DTA) analyses, IR, UV-vis and <sup>1</sup>H NMR spectra as well as magnetic moment and molar conductivity. Mononuclear complexes are obtained with 1:1 molar ratio except complexes **3** and **9** which are obtained with 1:2 molar ratios. The IR spectra of ligand and metal complexes reveal various modes of chelation. The ligand behaves as a neutral bidentate one and coordination occurs via the carbonyl oxygen atom and azomethine nitrogen atom. The ligand behaves also as a monobasic tridentate one and coordination occurs through the enolic oxygen atom, azomethine nitrogen atom and the oxygen atom of furan ring. Moreover, the ligand behaves as a neutral tridentate and coordination occurs via the carbonyl oxygen, azomethine nitrogen and furan oxygen atoms as well as a monobasic bidentate and coordination occurs via the enolic oxygen atom and azomethine nitrogen atom. The electronic spectra and magnetic moment measurements reveal that all complexes possess octahedral geometry except the copper complex **10** possesses a square planar geometry. The thermal studies showed the type of water molecules involved in metal complexes as well as the thermal decomposition of some metal complexes.

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#### 1. Introduction

Hydrazones and their metal complexes possessing pronounced biological and pharmaceutical activities as antitumor [1-3], antimicrobial [4], antituberculosis [5] and antimalarial agents [6]. Hydrazones play an important role in improving the antitumor selectivity and toxicity profile of antitumor agents by forming drug carrier systems employing suitable carrier proteins [7]. They also employe as extracting agents in spectrophotometric determination of some ions [8-10] and spectrophotometric determination of some species in pharmaceutical formulations [11], as well as uses in catalytic processes [12,13] and wastewater treatment [14]. Hydrazones, such as pyridoxal isonicotinoylhydrazone, salicylaldehyde benzoylhydrazone and 2-pyridyl carboxaldehyde-2-thiophene carboxaldehyde hydrazone, act as orally effective drugs for the treatment of iron overload diseases or genetic diseases  $\beta$ -thalassemia [15,16]. Metal complexes of hydrazones have found applications in various chemical processes like nonlinear optics, sensors, etc. [17], and have been used in the separation and concentration of palladium and platinum in road dust [18].

\* Corresponding author. E-mail address: Fathi\_Elsaied@yahoo.com (F.A. El-Saied). In the present article a number of new metal complexes of cobalt(II), nickel(II), copper(II), zinc(II) and hafnium(IV) with a new hydrazone ligand N'-(furan-3-ylmethylene)-2-(4-methoxyphe-nylamino)acetohydrazide (HL). The chemical formulations for ligand and its metal complexes were characterized using various analytical, spectroscopic techniques such as infrared, nuclear magnetic resonance, electronic spectra and magnetic moment measurements as well as molar conductance measurements and thermal analyses.

#### 2. Experimental

#### 2.1. Instrumentation and measurements

Elemental microanalyses (C,H) were determined in the micro analytical unit of Cairo University, Egypt. Metals were determined by complexmetric methods [19]. The IR spectra were measured using KBr discs of FT-IR 1650 Perkin-Elmer spectrophotometer. Electronic spectra were recorded in Nujol mulls using Perkin-Elmer 550. The molar conductivity measurements of complexes in  $(1 \times 10^{-3} \text{ M})$  DMF solution were measured at 25 °C with a Bibby conductometer type MCl. The <sup>1</sup>H NMR spectrum of the ligand was recorded using varian unity-300 MHz spectrometer DMSO $d_6$  using. The thermal analyses (DTA and TG) were carried out in air using a Shimadzu DT-30 thermal analyzer in air from

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Fig. 1. Infrared spectrum of ligand HL.

room temperature to 800 °C at a heating rate of 10 °C/min. Magnetic susceptibilities were measured at 27 °C using the modified Gouy method with a Johnson Matthey magnetic susceptibility balance. Magnetic moments were calculated using equation: $\mu_{eff} = 2.84\sqrt{X_{M}^{COTT}T}$ 

#### 2.2. Preparation of the ligand and its metal complexes

#### 2.2.1. Preparation of ethyl 2-(4-methoxyphenylamino)acetate

4-Methoxyaniline (1.23 g, 1 mmol in 5 mL EtOH) was added to a solution of ethylchloroacetate (1.22 g, 1 mmol in 10 mL of EtOH). Sodium acetate trihydrate (1.36 g, 1 mmol) dissolved in 15 mL distilled water was added to the mixture, then, it was refluxed with stirring for 6 h. The product was poured on crushed ice, and the solid precipitate which is formed was filtered off, washed several times with distilled water and dried over anhydrous CaCl<sub>2</sub>.

#### 2.2.2. Preparation of 2-(4-methoxyphenylamino)acetohydrazide

Hydrazine hydrate (2.5 g, 5 mmol) was added drop wise to a solution of ethyl 2-(4-methoxyphenylamino)acetate (2.09 g, 1 mmol) in 30 mL EtOH. The mixture was refluxed with stirring for 3 h, and then left to cool at room temperature. The formed precipitate was filtered off, washed several times with EtOH and dried over anhydrous CaCl<sub>2</sub>.

#### 2.2.3. Preparation of the hydrazone ligand 2-(4-methoxyphenylamino)-N'-(furan-2-yl-methylene)acetohydrazide

N'-(furan-3-ylmethylene)-2-(4-methoxyphenylamino)acetohydrazide was prepared by mixing an eqimolar amounts of 2-(4-methoxy phenylamino)acetohydrazide with furan-2carbaldehyde. The reaction mixture was heated at 60 °C with stirring for 4 h. The obtained product was filtered off, washed with ethanol and dried under vacuum over anhydrous CaCl<sub>2</sub>.

#### 2.2.4. Preparation of metal complexes

The metal complexes were prepared by the addition of a hot ethanol solution of ligand (HL) to an equimolar amount of the metal salt. The appropriate reaction mixture was stirred and heated at  $80 \,^{\circ}$ C for 3 h. The separated complex was filtered off, washed several times with ethanol, and dried under vacuum in the presence of anhydrous CaCl<sub>2</sub>.

#### 2.3. Microbiology: bacteria media

Nutrient agar medium was prepared (g/L distilled water) with 5 g NaCl, 5 g peptone, 3 g beef extract, 15 g agar. The pH of the medium at 7, this medium was then sterilized by autoclaving at  $120 \degree C$  for 15 min. After cooling to  $45 \degree C$  the medium was poured into 90-mm diameter Petri dishes (approximately

#### Table 1

Elemental analysis, colour and molar conductivity for ligand and its metal complexes.

No.	Compounds	Colour	Salt and molar ratio (ML)	$\Lambda_{\mathrm{M}}^{\mathrm{a}}(\mathrm{ohm^{-1}cm^{2}mol^{-1}})$	Elemental analysis (calcd.) (%)		
					C%	H%	M%
1	HL	Pale brown	-	-	61.0(61.5)	5.3(5.5)	-
2	$[Co(L)Br(H_2O)_2] \cdot 2H_2O$	Dark brown	CoBr <sub>2</sub> (1:1)	36.0	34.8(34.8)	4.4(4.6)	11.8(12.2)
3	$[CO(HL)_2(NO_3)_2]$	Dark brown	$Co(NO_3)_2(1:1)$	10.2	46.6(46.1)	4.8(4.1)	9.0(8.1)
4	[Co(L)(OAc)(H <sub>2</sub> O) <sub>2</sub> ](1/4)H <sub>2</sub> O	Brown	$Co(OAc)_2(1:1)$	23.0	43.7(44.6)	4.8(5.0)	13.2(13.7)
5	$[Ni(HL)Cl_2(H_2O)_2] \cdot H_2O$	Brown	NiCl <sub>2</sub> (1:1)	38.0	36.7(36.8)	4.6(4.6)	12.4(12.9)
6	[Ni(HL)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]·3H <sub>2</sub> O	Dark brown	Ni(NO <sub>3</sub> ) <sub>2</sub> (1:1)	38.0	30.9(30.8)	4.6(4.6)	10.2(10.8)
7	$[Ni(HL)(OAc)_2(H_2O)] \cdot H_2O$	Dark brown	$Ni(OAc)_2(1:1)$	38.5	44.4(44.5)	5.3(5.1)	12.4(12.1)
8	$[Cu(HL)Cl_2(H_2O)_2]\cdot H_2O$	Dark brown	$CuCl_2(1:1)$	18.3	37.0(36.4)	4.0(4.6)	12.9(13.8)
9	$[Cu(HL)_2(NO_3)_2] \cdot 5H_2O$	Brown	$Cu(NO_3)_2(1:1)$	38.4	40.4(40.8)	4.6(4.9)	8.3(7.7)
10	$[Cu(L)(OAc)(H_2O)] \cdot H_2O$	Dark brown	$Cu(OAc)_2(1:1)$	18.4	44.5(45.5)	4.7(4.9)	15.2(14.8)
11	$[Zu(HL)_2(NO_3)_2] \cdot H_2O$	Brown	$Zn(NO_3)_2(1:1)$	38.0	45.2(44.6)	4.9(4.2)	9.2(8.7)
12	[Hf(HL)Cl <sub>4</sub> ]	Brown	HfCl <sub>4</sub> (1:1)	27.3	29.1(28.3)	3.2(2.5)	-

Table 2
Infrared spectral bands for ligand and its metal complexes.

No.	Compounds	v(H <sub>2</sub> O)	ν(N-H)	ν(C=0)	ν(C=N)	$v(OAc/NO_3)$	v(furan)	ν(M-O)	ν(M-N)
1	HL	-	3388, 3203, 3120	1672	1625	-	590	-	-
2	$[Co(L)Br(H_2O)_2] \cdot 2H_2O$	3390	3390, 3196	-	1609,1560	-	561	531	450
3	$[Co(HL)_2(NO_3)_2]$	-	3390, 3215, 3140	1619	1551	1384, 1305	590	523	450
4	[Co(L)(OAc)(H <sub>2</sub> O) <sub>2</sub> ](1/4)H <sub>2</sub> O	3380	3380, 3217	-	1600,1556	1585, 1405	562	500	460
5	$[Ni(HL)Cl_2(H_2O)_2] \cdot H_2O$	3380	3380, 3200, 3120	1617	1546	-	590	525	426
6	[Ni(HL)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]·3H <sub>2</sub> O	3380	3380, 3250	1622	1560	1383, 1290	590	524	450
7	$[Ni(HL)(OAc)_2(H_2O)] \cdot H_2O$	3390	3380, 3200, 3120	1631	1560	1580, 1403	618	521	450
8	$[Cu(HL)Cl_2(H_2O)_2] \cdot H_2O$	3420	3200, 3120	1617	1575	-	590	510	470
9	$[Cu(HL)_2(NO_3)_2] \cdot 5H_2O$	3423	3350, 3220, 3127,	1620	1565	1385, 1300	592	560	460
10	$[Cu(L)(OAc)(H_2O)] \cdot H_2O$	3421	3135	-	1605,1580	1600, 1396	593	523	417
11	$[Zn(HL)_2(NO_3)_2] \cdot H_2O$	3390	3390, 3200, 3208	1622	1550	1385, 1304	591	523	440
12	[Hf(HL)Cl <sub>4</sub> ]	-	3390, 3230, 3160	1655	1615	-	591	519	450

20 mL for each) and incubated at 37 °C. After a few hours, Petri dishes were stored at 4°C. *Esherichia coli* was spread over each dish by using sterile bent loop rod. Disks were cut by sterilized cork borer and then taken by sterilized needle. The resulted pits are sites for the tested compounds. The plates are incubated at 37 °C for 48–72 h and then any clear zones present were detected.

#### 3. Results and discussion

The most diagnostic infrared spectral bands of the ligand HL are listed in Table 2. The spectrum of the ligand (Fig. 1) reveals bands at 3388, 3203, 3120, 1672, 1625 and 590 cm<sup>-1</sup>. The first three bands are assigned to  $\nu$ (NH) groups while the last three bands are assigned to  $\nu$ (C=N) and furan ring, respectively.

The <sup>1</sup>H NMR spectrum of the ligand shows signals at 11.43, 11.36, 8.15, 7.9 and multiple signals within 7.81–6.53 ppm. These signals are assigned, to  $\delta(H$ –NCH<sub>2</sub>),  $\delta(H$ –N–N),  $\delta(N$ =CH) as well as aromatic and furan protons, respectively.

The elemental analyses (Table 1), infrared spectral bands (Table 2) and  $^{1}$ H NMR data are compatible with the structure of HL as shown in Fig. 2.

The reaction of the ligand HL with different metal salts: Co(II), Ni(II), Zn(II) and Hf(IV) ions in 1:1 molar ratio in ethanol produced 1:1 metal complexes with stoichiometric is shown in Table 1 and chemical formulations are shown in Fig. 3. These air stable metal complexes are non-hygroscopic, partially soluble in water and most organic solvents except, in DMF and DMSO are freely soluble. The values of molar conductivities in DMF ( $10^{-3}$  M) solutions are depicted in Table 1. These values show that all metal complexes



N'-(furan-2-ylmethylene)-2-(4-methoxyphenylamino)acetohydrazide

Fig. 2. N'-(furan-2-ylmethylene)-2-(4-methoxyphenylamino)acetohydrazide.

behave as non-electrolytes, indicating that the anions are directly attached to the metal ion [20,21].

The most important spectral bands and their assignments for metal complexes are depicted in Table 2. Table 2 shows that, the infrared spectra of complexes 3, 5, 6, 8, 9, 11 and 12 (Figs. 4 and 5) display the bands corresponding to  $\nu$ (C=O) and  $\nu$ (C=N) in the ranges 1655–1617, 1615–1644 cm<sup>-1</sup>, respectively, which are lower than that of the free ligand, indicating that the carbonyl oxygen atom and the azomethine nitrogen atoms are involved in coordination. Moreover, the spectra of these complexes show that the bands corresponding to NH groups and furan ring slightly affected or remain at the some positions on complexation indicating that the NH groups and furan oxygen atom do not participate in coordination. The above arguments indicate that the ligand behaves as a neutral bidentate one and coordination occurs via the carbonyl oxygen and azomethine nitrogen atoms. The infrared spectra of metal complexes 2, 4 and 10 reveal that the band due to the carbonyl group disappears upon complexation. Moreover a band corresponding to one of the N-H groups also disappears and a new band appears in the range 1609–1600 cm<sup>-1</sup>, assigned to  $\nu$ (O–C=N). This could be explained on the basis that the ligand reacts entirely in its enol form. The spectra also show that the band due to furan ring does not show any shift in the spectra of complexes 2 and 4, whereas in the spectrum of complex 10 this band shows a slight shift. This indicating that the furan oxygen atom does not participate in the coordination in the former complexes whereas it is involved in coordination in the latter complex. Table 2 also shows that the spectrum of complex 7 shows bands in the ranges 3380-3200 and 3120, 1631, 1560 and  $618 \text{ cm}^{-1}$  the first three bands assigned to uncoordinated NH groups and the latter three bands assigned to coordinated  $\nu$ (C=O), coordinated  $\nu$ (C=N) and coordinated oxygen furan atom, respectively. This indicates that the ligand in this complex behaves as a neutral tridentate one, coordinating via the carbonyl oxygen, azomethine nitrogen and furan oxygen atoms. The presence of water molecules within the coordination sphere in the hydrate complexes 2, 4–8 and 10 is supported by the appearance of infrared spectral bands in the ranges 3423-3380, 960-820 and 670-640 cm<sup>-1</sup>, assigned to OH stretching, H<sub>2</sub>O rocking and H<sub>2</sub>O wagging, respectively [22]. The absence of the latter two bands in the spectra of the rest complexes 2, 9 and 11 indicating that the water in these complexes is lattice rather than coordinated [23]. Extensive infrared spectral studies reported on metal acetate complexes, indicate that the acetate ligand may coordinate to a metal ion in either a monodentate, bidentate or bridging manner. The  $v_a(COO)$  and  $v_s(COO)$  of the free acetate ions are at 1560 and 1416 cm<sup>-1</sup>, respectively. In monodentate  $\nu$ (C=O) is found at higher energy than  $v_s(C-O)$  is lower than  $v_s(CO_2)$ . As a result, the separation between the two  $\nu$ (C=O) bands is much larger in monodentate complexes than the free ion. The opposite trend is observed in



Fig. 3. Structural representation of the complexes.

bidentate acetate coordination; the separation between  $\nu$ (COO) bands is smaller than of the free ion. For bridging acetate with both two oxygen atoms coordinated as in copper(II) acetate, however the two  $\nu$ (COO) bands are close to the free ion values [21,24]. The infrared spectra of the acetate complexes reveal two bands in the ranges 1600–1580 and 1405–1396 cm<sup>-1</sup>, assignable to  $\nu_a$ (COO) and  $\nu_s$ (COO) in monodentate coordination. Further the acetato complexes exhibit  $\delta$ (COO) near 720 cm<sup>-1</sup> which is considered a diagnostic for monodentate acetate groups.

The infrared spectra of nitrato metal complexes **3**, **6**, **9** and **11** show two bands at 1305–1290 and 1385 cm<sup>-1</sup>, assigned to  $v_1$  and  $v_4$  modes of nitrate group, indicating that the nitrate group is terminally bonded monodentate nitrate group. The infrared spectra of complexes show two new bands at 560–500 and 470–417 cm<sup>-1</sup>, assigned to v(M-O) and v(M-N), respectively [21].

## 3.1. Magnetic moments and electronic spectral data for metal complexes

The electronic absorption spectral bands as well as the room temperature magnetic moments ( $\mu_{eff}$  B.M.) per a metal atom of the metal complexes are listed in Table 3.

Octahedral, tetrahedral and square planar cobalt(II) complexes show magnetic moment values between 4.7–5.2, 4.2–4.8 and 2.2–2.9 B.M., respectively. The values of  $\mu_{eff}$  of cobalt(II) complexes **2–4** at room temperature were 4.8, 4.9 and 4.5 B.M., respectively. These values are consistent with an octahedral geometry around the cobalt(II) ion. The considerably high values ruled out spin–spin interaction between cobalt(II) ions. The electronic spectra of cobalt(II) complexes display two bands in the ranges 702–700 and 650–602 nm (Fig. 6). These bands may be assigned to



Fig. 4. Infrared spectrum of complex (3)

 Table 3

 Magnetic moment values and electronic spectral bands for metal complexes.

No.	Compounds	$\mu_{ m eff}$ (B.M.) (per metal atom)	d-d transitions (nm)
2	$[Co(L)Br(H_2O)_2] \cdot 2H_2O$	4.80	700(w, br), 650
3	[Co(HL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	4.90	702(w, br), 602
4	[Co(L)(OAc)(H <sub>2</sub> O) <sub>2</sub> ](1/4)H <sub>2</sub> O	4.50	600, 558
5	$[Ni(HL)Cl_2(H_2O)_2] \cdot H_2O$	2.85	610(br), 518
6	[Ni(HL)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]·3H <sub>2</sub> O	2.90	630(br), 540
7	$[Ni(HL)(OAc)_2(H_2O)] \cdot H_2O$	3.20	615(br), 504
8	$[Cu(HL)Cl_2(H_2O)_2]\cdot H_2O$	1.95	800(br), 605
9	[Cu(HL) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·5H <sub>2</sub> O	1.97	708, 626, 604
10	$[Cu(L)(OAc)(H_2O)] \cdot H_2O$	2.31	584, 568

the electronic  ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$  and  ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$  transitions, respectively, suggesting a tetragonally distorted octahedral geometry around cobalt(II) ion [22,25].

The room temperature magnetic moment values for nickel(II) complexes **5–7** were 2.85, 2.9 and 3.2 B.M., respectively. These values are consistent with two unpaired electron configuration. The considerably high values also ruled out spin–spin interaction between nickel(II) complexes and ruled out square planar geometry around nickel(II) ion. The electronic spectra of nickel(II) complexes (Fig. 7) reveal two bands in the ranges 630–610 and 540–504 nm, assigned to  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)(\upsilon_{2})$  and  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)(\upsilon_{3})$  transitions, respectively, in pseudo-octahedral nickel(II) complexes [26].

The room temperature magnetic moment values for copper(II) complexes **8–10** were 1.95, 1.97 and 2.31 B.M., respectively. These values close to the spin-only value for an unpaired spin ( $\sim$ 1.73 B.M.). The electronic spectra of copper(II) complexes **8** and **9** exhibit a





Fig. 6. The electronic spectrum of complex (3).



Fig. 7. The electronic spectrum of complex (6).

broad band at 800–708 and a shoulder at 626–605 nm, assigned to  ${}^{2}B_{1} \rightarrow {}^{2}E$  and  ${}^{2}B_{1} \rightarrow {}^{2}B_{2}$  transitions, respectively, indicating a distorted tetragonal structure [27,28]. The electronic spectrum of copper(II) complex **10** shows a broad structured bands at 584–568 nm which suggesting a square planar geometry around the copper(II) ion [29].

#### Table 4

TGA and DTA data for some metal complexes.

#### 3.2. ESR spectra of copper(II) complexes

The ESR spectra of the copper(II) complexes 8 and 10 were recorded in polycrystalline state at room temperature. The ESR spectrum of the copper(II) complex **10** exhibited unresolved only one isotropic signal at high field. The isotropic g value of the complex is 2.117 [30]. The ESR spectrum of the copper(II) complex 8 exhibited anisotropic signals with  $g_{\parallel}$  = 2.379 and  $g_{\perp}$  = 2.091, which is characteristic for a  $d^9$  system with an axial symmetry type of  $d_{x^2-y^2}$ ground state. The g values for the copper(II) complexes denote to octahedral geometries around copper(II) ions [31]. The trend  $g_{\parallel} > g_{\perp} > g_{e}$  (2.0023) shows that the unpaired electron is localized in the  $d_{x^2-y^2}$  orbital [32,33]. In addition exchange coupling interaction between two copper(II) ions explained by Hathaway expression  $G = (g_{\parallel} - 2)/(g - 2)$ . If G > 4.0, the exchange interaction is negligible which is typically the case for complex 8 (G=4.2). Kivelson and Neiman noted that for an ionic environment,  $g_{\parallel}$  is normally 2.3 or larger but for covalent environment,  $g_{\parallel}$  is less than 2.3. The  $g_{\parallel}$  value for copper(II) complexes was larger than 2.3 (2.379) consequently the environment is essentially ionic [32,33].

#### 3.3. Thermal analysis

The TG–DTA results for some solid complexes **4–9** are depicted in Table 4. The results are in good agreement with the formulae shown in Fig. 2.

Table 4 concludes that there is a general decomposition pattern, whereby, the complexes decompose in three main stages. The first stage for all studied complexes is the loss of hydrated water molecules at 32-150 °C, followed in a second decomposition stage by the loss of the coordinated water, chloride, nitrate or acetate ions at 70-420 °C, after that, the deligation process started at a temperature range of 180–1000 °C, finally metal oxide formation takes place.

#### 3.4. Antibacterial activity

The antibacterial activities of the ligand and its metal complexes were screened using the disk diffusion method [33,34]. The variation in the effectiveness of different compounds against different organisms depends either on the impermeability of the cell of the

	•				
No.	Complex	Temperature range in TGA (°C)	Weight loss found (calcd.) (%)	DTA peaks	Disassociation assignment
4	[Co(L)(OAc)(H <sub>2</sub> O) <sub>2</sub> ](1/4)H <sub>2</sub> O	40–70 150–180 180–630	0.7(1.0) 9.1(8.4) -	51 °C 170 °C 284, 336, 488, 550 °C	Loss of 0.25 mole of hydrated water Loss of 2 mole of coordinated water Deligation
5	$[Ni(HL)Cl_2(H_2O_2)]\cdot H_2O$	50–90 90–170 170–270 270–800	3.2(3.9) 7.5(7.9) 15.5(14.3) -	70 °C 150 °C 240 °C −	Loss of 1 mole of hydrated water Loss of 2 mole of coordinated water Loss of two coordinated chloride ions. Deligation
6	$[Ni(HL)(NO_3)_2(H_2O)_2] \cdot 3H_2O$	35–85 85	9.9(9.9)	40 °C 132, 414 °C	Loss of 3 mole of hydrated water Start of deligation
7	[Ni(HL)(OAc) <sub>2</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O	32–70 70–171 173–361 361–520	4.1(3.7) 3.9(3.7) 23.9(24.3)	150 °C 150 °C 210 °C	Loss of 1 mole of hydrated water Loss of 1 mole of coordinated water Loss of two coordinated acetate groups Deligation
8	$[Cu(HL)Cl_2(H_2O)_2]\cdot H_2O$	40–95 165–205 205–420 420–100	3.2(3.9) 8.5(7–8) 14.9(15.4)	55 °C -	Loss of 1 mole of hydrated water Loss of 2 mole of coordinated water Loss of two coordinated chloride ions Complete deligation
9	$[Cu(HL)_2(NO_3)_2]\cdot 5H_2O$	45–150 150–210 210–500	6.0(6.6) 5.0(4.4) -	77 °C 200 °C 321, 350,416,444	Loss of 3 mole of hydrated water Loss of 2 mole of coordinated water Complete deligation

#### Table 5

Antimicrobial activities of HL ligand and its metal complexes.

No.	Compound	Diameter of inhibition zone (mm)				
		Fusarium Oxysporum	Esherichia coli	B. Cereus	Candida	
1	HL	ND <sup>a</sup>	ND	ND	ND	
8	$[Cu(HL)Cl_2(H_2O)_2] \cdot H_2O$	ND	ND	ND	ND	
10	$[Cu(L)(OAc)(H_2O)] \cdot H_2O$	ND	ND	3.0	ND	
11	$[Zn(HL)_2(NO_3)_2] \cdot H_2O$	ND	ND	2.3	ND	
12	[Hf(HL)Cl <sub>4</sub> ]	ND	ND	3.9	ND	

<sup>a</sup> ND: non-detected.

microbes or difference in ribosome's of microbial cells [35–37]. The in vitro antimicrobial activity of the synthesized compounds was assayed on bacteria. All compounds showed a good antibacterial activity against Gram negative bacteria (*Bacillus cereus*) and do not show any effect on bacteria (*E. coli, Candida* and *Fusarium oxysporum*). Complex **12** proved to be the most effective one (Table 5).

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