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# Physicochemical studies and biological evaluation on (*E*)-3-(2-(1-(2-hydroxy-phenyl)hydrazinyl)-3-oxo-*N*-(thiazol-2yl)propanamide complexes

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#### HIGHLIGHTS

- Schiff base complexes of (H<sub>2</sub>o-HAH) were prepared.
- The complex structure was elucidated using different characterization techniques.
- Calculation of kinetic and thermodynamic parameters.
- Antimicrobial activities of all compounds were studied.

# G R A P H I C A L A B S T R A C T



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# ABSTRACT

Hydrazone complexes of Co(II), Ni(II), Cu(II), Pd(II), Cd(II), Zn(II) and U(VI)O<sub>2</sub> with (*E*)-3-(2-(1-(2-hydroxyphenyl)hydrazinyl)-3-oxo-*N*-(thiazol-2yl)propanamide (H<sub>2</sub>o-HAH) have been synthesized. The complex structure has been elucidated by analysis (elemental and thermal), spectroscopy (<sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, UV-visible, ESR, MS) and physical measurements (magnetic susceptibility and molar conductance). The kinetic and thermodynamic parameters for the different decomposition steps of some complexes have been calculated using the Coats–Redfern equation. Also, the association and formation constants of Co(II) ion in absolute ethanol solutions at 294.15 K have been calculated by using electrical conductance. Moreover, the ligand and its complexes have been screened for their antibacterial (*Escherichia coli* and *Clostridium* sp.) and antifungal activities (*Aspergillus* sp. and *Stemphylium* sp.) by MIC method.

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# Introduction

Hydrazones,  $R_1R_2C=NNH_2$  are a special group of compounds in the Schiff base family which derived from the condensation of hydrazines with carbonyl compounds, namely aldehydes and ketones. Hydrazones are known to function as chelating agents that can form different complexes with transition metals. Several hydrazones are obtained depending on the experimental conditions; which have application as biologically active compounds [1] and as analytical reagents [2]. As biologically active compounds, hydrazones find applications in the treatment of diseases such as anti-tumor [3], tuberculosis [4], leprosy and mental disorder [5]. Tuberculostatic activity is due to the formation of stable chelates with transition metals present in the cell [6]. Thus, many vital enzymatic reactions catalyzed by these transition metals cannot take place in the presence of hydrazones [7]. Hydrazones also act as herbicides, insecticides, nematocides, rodenticides and plant growth regulators [8,9].

We have recently published some bivalent transition metal complexes of hydrazones derived from 3-hydrazinyl-oxo-*N*-(thia-zole-2-)propanamide [10–12]. In continuation of our work on hydrazones, the present work aims to synthesize and characterize

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complexes of (*E*)-3-(2-(1-(2-hydroxyphenyl)hydrazinyl)-3-oxo-*N*-(thiazol-2-yl)propanamide (H<sub>2</sub>o-HAH) with Co(II), Ni(II), Cu(II), Pd(II), Cd(II), Zn(II) and U(VI)O<sub>2</sub> ions. The possible modes of chelations, the geometry and the nature of bonding of the complexes are discussed on the basis of various spectroscopic techniques (<sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, UV-visible, ESR, MS). Also, their antimicrobial activity have been tested.

# Experimental

# Materials and reagents

All chemicals used were of the analytical reagent grade (AR), and of the highest purity available. They included 3-hydrazinyl-oxo-*N*-(thiazole-2-) propanamide; *o*-hydroxyacetophenone (Aldrich); Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, Ni(CH<sub>3</sub>COO)·4H<sub>2</sub>O, Co(CH<sub>3</sub>COO)·4H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, Zn(CH<sub>3</sub>COO)<sub>2</sub>· 2H<sub>2</sub>O and PdCl<sub>2</sub> (Sigma, Merck). Organic solvents used included absolute ethyl alcohol, diethyl ether, and dimethylsulfoxid (DOMS). These solvents were spectroscopic pure from BDH. De-ionized water collected from all glass equipments was usually used in all preparations.

### Instrumentations

Elemental microanalyses of the isolated solid complexes for C, H and N were performed in the Microanalytical Center. The molar conductance of the complexes were determined by preparing  $10^{-3}$  M solutions of the complexes in DMSO at room temperature and measured on a YSI Model 32 conductivity bridge. The IR absorption spectra were recorded on a Mattson 5000 FTIR Spectrophotometer, in the range 4000-400 cm<sup>-1</sup> in KBr disk. Magnetic moment values were evaluated at room temperature (25 ± 1 °C) using a Johnson Matthey magnetic susceptibility balance using Hg[Co(SCN)<sub>4</sub>] as calibrant. ESR spectrum of Cu(II) complex was obtained on a Bruker EMX Spectrometer working in the X-band (9.78 GHz) with 100 kHz modulation frequency. The microwave power was set at 1 mW and modulation amplitude was set at 4 Gauss. The low-field signal was obtained after four scans with a tenfold increase in the receiver gain. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature. Mass spectra were recorded on a Mattson 5000 FTIR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the ligand and Cd(II), Zn(II), Pd(II) and U(VI)O<sub>2</sub> complexes were recorded in DMSO on an EM-390 (200 MHz) spectrometer. The thermal analyses (TG, DTG and DTA) were carried out in dynamic nitrogen atmosphere (20 mL/min) with a heating rate of 10 °C/min using Shimadzu TG-60H and DTA-60H thermal analyzers. Ni(II), Co(II), Cu(II), Pd(II), Cd(II), Zn(II) and U(VI)O<sub>2</sub> contents in the complexes were determined by the well known standard methods [13]. The antifungal and antibacterial activities were carried out at the Microanalytical center. The specific conductivity (Ks) was achieved by using a conductometer of the type (HANNA, H1 8819 N) and a cell constant equal (1). The conductometer was connected with ultra-thermostat of the type (Kottermann 4130) and a digital thermometer. The temperature at which all measurements were achieved, was adjusted at 21 °C.

#### Procedures

# Preparation of (E)-3-(2-(2-hydroxybenzylidene)hydrazinyl)-3-oxon(thiazole-2yl)propanamide

(H<sub>2</sub>o-HAH) was prepared by reflux a mixture of 3-hydrazinyloxo-*N*-(thiazole-2-)propanamide (0.01 mol; 2.00 g) and *o*-hydroxy acetophenone (0.01 mol; 1.36 g) in absolute ethanol for 3 h (Scheme 1). On cooling, yellow crystals were formed, filtered off, washed with EtOH and Et<sub>2</sub>O and recrystallized from EtOH (M.p.: 230 °C; yield 80%; see Table 1). The purity of the compound was checked by thin layer chromatography (TLC).

# Preparation of complexes

The complexes were prepared by mixing equimolar amounts of H<sub>2</sub>o-HAH with ethanolic and/or aqueous solution of acetate salt of Ni(II), Co(II), Cd(II), Cu(II), Zn(II) and U(VI)O<sub>2</sub>; chloride salt of pd(II) as potassium tetrachloropalladate. The reaction mixture was heated on a water bath for 1–3 h. The precipitate was filtered off, washed with hot EtOH and/or H<sub>2</sub>O successfully and finally preserved in a vacuum desiccator over anhydrous CaCl<sub>2</sub>.

#### Conductance measurements

All conductometric titrations were measured using 0.1 mmol of  $H_2o$ -HAH and 1 mmol of  $CoCl_2$  solution as an initial concentration from each. 20 ml of ligand in absolute ethanol was taken and titrated with small addition of metal with 0.5 ml intervals were done and the specific conductances were measured. The specific conductivity (*Ks*) was achieved by using a conductometer of the type (HANNA, H1 8819 N) and a cell constant equal (1).

#### **Biological** activity

#### Antifungal activity

The antifungal activity of the ligand (H<sub>2</sub>o-HAH) and its metal complexes Ni(II), Co(II), Cu(II), Cd(II), Zn(II), Pd(II) and U(VI)O<sub>2</sub> were screened against two types of fungi viz. Aspergillus sp. and Stemphylium sp. These species were isolated from the infected organs of the host plants on potato dextrose agar. The cultures of the fungi were purified by single spore isolation technique. The solution in different concentrations 0.5, 1 and 1.5 mg/ml of each compound in DMSO were prepared for testing against spore germination. A drop of the solution of each concentration was kept separately on glass slides. The conidia, fungal reproducing spores lifted with the help of an inoculating needle, were mixed in every drop of each compound separately. Each treatment was replicated thrice and a parallel DMSO solvent control set was run concurrently on separate glass slides. All the slides were incubated in humid chambers at room temperature for 24 h. Each slide was observed under the microscope for spore germination and percent germination was finally calculated. The results were also compared with a standard antifungal drug Miconazole at the same concentrations.

#### Antibacterial activity

The antibacterial activity of the all isolated compounds were studied against *Clostridium* sp. and *Escherichia coli* bacteria. The solution in different concentrations 0.5, 1 and 1.5 mg/ml of each compound in DMSO were prepared for testing against spore germination. Paper discs of Whatman filter paper of uniform diameter (2 cm) were cut and sterilized in an autoclave. The paper discs soaked in the desired concentration of the complex solutions were placed aseptically in the petridishes containing nutrient agar media seeded with *Clostridium* sp. and *E. coli* bacteria separately. The petridishes were incubated at 37 °C and the inhibition zones were recorded after 24 h of incubation. The antibacterial activity of a common standard antibiotic Ampicillin was also recorded using the same procedure as above at the same concentrations and solvent.

# **Results and discussion**

# IR spectra

In the IR spectrum of  $H_{20}$ -HAH (Scheme 2), the bands observed at 1700, 1670, 1606, 1560, 3201, 3114 and 3446 cm<sup>-1</sup>



Scheme 1. The outline of the synthesis of ligand (H<sub>2</sub>o-HAH) and its complexes.

#### Table 1

Analytical and physical data of H<sub>2</sub>O-HAH and its metal complexes.

Compound	Compound Empirical formula (Molecular mass) Color M Exp. (Calcd.)		MP (°C) Yield (%) % Found (Calcd.)							
					С	Н	Ν	М	$\Lambda_m^{a}$	
Н <sub>2</sub> 0-НАН <b>(1)</b>	C <sub>14</sub> H <sub>14</sub> O <sub>3</sub> N <sub>4</sub> S 318.87 (318.59)	Yellow	230	80	52.85 (52.78)	4.28 (4.43)	17.41 (17.58)	-	-	
[Ni (Ho-HAH)(OAc)(H2O)]·H2O (2	NiC <sub>16</sub> H <sub>20</sub> O <sub>7</sub> N <sub>4</sub> S 472.07 (471.54)	Brown	>300	80	40.78 (40.75)	4.37 (4.28)	11.73 (11.88)	12.39 (12.49)	4	
[Cu(Ho-HAH)(OAc)(H2O)]·H2O (3	) CuC <sub>16</sub> H <sub>20</sub> O <sub>7</sub> N <sub>4</sub> S 476.90 (476.15)	Green	>300	75	40.41 (40.36)	4.23 (4.24)	11.60 (11.76)	13.40 (13.35)	5	
[Pd(Ho-HAH)(H <sub>2</sub> O)]·H <sub>2</sub> O (4)	PdC <sub>14</sub> H <sub>17</sub> O <sub>5</sub> N <sub>4</sub> S 459.59 (460.03)	Brown	>300	85	36.25 (36.55)	3.28 (3.72)	12.25 (12.18)	21.78 (21.41)	3	
[Cd(Ho-HAH)(OAc)(H <sub>2</sub> O)]·H <sub>2</sub> O (5	) CdC <sub>16</sub> H <sub>20</sub> O <sub>7</sub> N <sub>4</sub> S 525.24 (525.02)	Yellowish- white	>300	70	36.82 (36.60)	3.81 (3.84)	10.69 (10.67)	21.65 (21.41)	3	
$[Zn(o-HAH)(H_2O)] \cdot H_2O$ (6)	ZnC <sub>14</sub> H <sub>16</sub> O <sub>5</sub> N <sub>4</sub> S 418.16 (417.98)	Yellowish- white	>300	70	40.17 (40.22)	4.03 (3.85)	13.44 (13.40)	15.62 (15.64)	3	
[Co(o-HAH)(H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O (7)	CoC <sub>14</sub> H <sub>20</sub> O <sub>7</sub> N <sub>4</sub> S 447.86 (447.32)	Brown	>300	80	37.75 (37.59)	4.31 (4.50)	12.60 (12.52)	13.4 (13.12)	4	
[UO <sub>2</sub> ( <i>o</i> -HAH)(H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O (8)	UO <sub>2</sub> C <sub>14</sub> H <sub>20</sub> O <sub>7</sub> N <sub>4</sub> S 658.99 (658.65)	Yellow	>300	75	25.56 (25.52)	3.11 (3.06)	8.57 (8.51)	36.73 (36.14)	4	

<sup>a</sup> In DMSO ( $ohm^{-1} cm^2 mol^{-1}$ ).

are attributed to  $\upsilon(C=O)_1$ ,  $\upsilon(C=O)_2$  [14],  $\upsilon(C=N)_1$ ,  $\upsilon(C=N)_2$  [15],  $\upsilon(NH)_1$ ,  $\upsilon(NH)_2$  [16] and  $\upsilon(OH)$  [17], respectively (see Table 2). The appearance of (OH) as a broad band at lower wavenumber and the two weak broad bands in the 1900–2080 and 2155–

2233  $cm^{-1}$  regions suggest intramolecular hydrogen bonding (O–H $\cdots$ O) [18].

The shifts of the characteristic absorption bands of the free ligand on complexation as well as the appearance of new vibrational



Scheme 2. <sup>13</sup>C NMR spectra of (A) H<sub>2</sub>o-HAH, (B) [Zn(o-HAH)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O.

 Table 2

 Most important IR spectral bands of H<sub>2</sub>o-HAH and its metal complexes.

Compound	υ(OH)	$\upsilon(\text{NH})_1$	$\upsilon(NH)_2$	υ(C=0) <sub>1</sub>	υ(C=0) <sub>2</sub>	$\upsilon(C=N)_1$	$\upsilon(C=N^*)_1$	$\upsilon(C=N^{*})_{2}$	υ( <b>CO</b> ) <sub>1</sub>	υ( <b>CO</b> ) <sub>2</sub>	υ( <b>M</b> —0)	υ(M—N)
1	3446	3201	3114	1700	1670	1606	-	-	-	-	-	-
2	3374	3199	-	1696	-	1595	1640	-	-	1165	530	450
3	3409	3174	-	1700	-	1594	1650	-	-	1163	550	460
4	3443	3227	-	1685	-	1587	1601	-	-	1142	542	468
5	3442	3222	-	1683	-	1590	1606	-	-	1105	522	437
6	3440	-	-	-	-	1589	1604	1596	1128	1083	522	422
7	3372	-	-	-	-	1594	1630	1620	1148	1095	560	455
8	3331	-	-	-	-	1580	1608	1598	1137	1089	552	459

bands indicates  $H_{2}o$ -HAH behaves in a tridentate and/or tetradentate manner depending on the metal salt used and the reaction conditions.

The IR spectra of  $[Cu(Ho-HAH)(OAc)(H_2O)]\cdot H_2O$  and  $[Ni(Ho-HAH)(OAc)(H_2O)]\cdot H_2O$  complexes reflect that the  $(H_2o-HAH)$  acts as a mononegative tridentate ligand coordinating *via* the deprotonated enolized carbonyl oxygen  $(=C-O^-)_2$ , azomethine nitrogen  $(C=N)_1$  and hydroxyl group (OH). This mode of complexation is supported by the following observations: (i) the shift of v(OH) and  $v(C=N)_1$  to lower wave numbers, (ii) the disappearance of both  $v(C=O)_2$  and  $v(NH)_2$  with simultaneous appearance of new bands at 1163, 1165 and 1640, 1650 cm<sup>-1</sup> which assignable to  $v(C-O)_{2(enolic)}$  [19] and  $v(C=N^*)_2$  [15], respectively and (iii) the appearance of new bands in 530–550 and 450–460 cm<sup>-1</sup> which may be attributed to (M-O) and (M-N) [20], respectively.

Also, in  $[Pd(Ho-HAH)(H_2O)]\cdot H_2O$  and  $[Cd(Ho-HAH)(OAc)(H_2-O)]\cdot H_2O$  complexes,  $H_2o$ -HAH acts as a mononegative tridentate ligand coordinating *via* the carbonyl oxygen  $(C=O)_1$ , the azomethine nitrogen  $(C=N)_1$  and the deprotonated enolized carbonyl oxygen  $(=C-O^-)_2$ . This mode of complexation is supported by: (i) the disappearance of  $v(C=O)_2$  and  $v(NH)_2$  with simultaneous appearance of new bands at 1105, 1142 and 1601, 1606 cm<sup>-1</sup> which assignable to  $v(C-O)_{2(enolic)}$  [19] and  $v(C=N^*)_2$  [15], respectively, (ii) shift of azomethine nitrogen  $v((C=N)_1$  and  $(C=O)_1$  to lower wave numbers and (iii) the appearance of new bands in the 522–542 and 437–468 cm<sup>-1</sup> which may be attributed to v(M-O) and v(M-N) [20], respectively. Moreover, the IR spectrum of the  $[Zn(o-HAH)(H_2-O)]\cdot H_2O$  shows that  $H_2O$ -HAH acts as a binegative tridentate ligand coordinating *via* the azomethine nitrogen  $(C=N)_1$ , the two deproto-

nated enolized carbonyl oxygens (=C–O<sup>-</sup>)<sub>1</sub>, (=C–O<sup>-</sup>)<sub>2</sub>. This mode of complexation is supported by (i) the shift of  $\upsilon$ (C=N)<sub>1</sub> to lower wavenumber, (ii) the disappearance of  $\upsilon$ (C=O)<sub>1</sub>,  $\upsilon$ (C=O)<sub>2</sub>,  $\upsilon$ (NH)<sub>1</sub> and  $\upsilon$ (NH)<sub>2</sub> with simultaneous appearance of new band at 1128, 1083, 1604 and 1596 cm<sup>-1</sup> which assignable to  $\upsilon$ (C–O)<sub>1(enolic)</sub>,  $\upsilon$ (C–O)<sub>2(enolic)</sub> [19],  $\upsilon$ (C=N<sup>\*</sup>)<sub>1</sub> and  $\upsilon$ (C=N<sup>\*</sup>)<sub>2</sub> [15], respectively (iii)  $\upsilon$ (C=N)<sub>2</sub> and  $\upsilon$ (OH) vibrations remain more or less at the same position and (iv) the IR spectrum of this complex shows new band at 522 and 422 cm<sup>-1</sup> which may be attributed to  $\upsilon$ (Zn–O) and  $\upsilon$ (Zn–N) [20], respectively.

Finally, for  $[UO_2(o-HAH)(H_2O)_2]\cdot 2H_2O$  and  $[Co(o-HAH)(H_2O)_2]\cdot 2H_2O$  complexes,  $H_2o$ -HAH acts as a binegative tetradentate ligand coordinating through the two deprotonated enolized carbonyl oxygen (=C $-O^-$ )<sub>1</sub>, (=C $-O^-$ )<sub>2</sub>, azomethine nitrogen (C=N)<sub>1</sub> and hydroxyl group (OH). This mode of complexation is supported by the disappearance of (C=O)<sub>1</sub>, (C=O)<sub>2</sub>, (NH)<sub>1</sub> and (NH)<sub>2</sub> with simultaneous appearance of new band at 1137–1148, 1089–1095, 1608–1630 and 1598–1620 cm<sup>-1</sup> region assignable to  $v(C-O)_{1(enOlic)}$ ,  $v(C-O)_{2(enOlic)}$  [19],  $v(C=N^*)_1$  and  $v(C=N^*)_2$  [15], respectively. The negative shift of both  $v(C=N)_1$  and v(OH). Also, the IR spectra of these complexes show new bands in 552–560 and 455–459 cm<sup>-1</sup> regions which may be attributed to v(M-O), v(M-N) [20], respectively.

The complexes which have coordinated water molecules have two sharp bands observed in 851–869 and 542–579 cm<sup>-1</sup> attributed to  $\rho_r(H_2O)$  [21] and  $\rho_w(H_2O)$  [21] vibrations, respectively.

The acetate complexes show two bands in 1513–1557 and 1413–1449 cm<sup>-1</sup> which can be assigned to  $v_{as}(O-C-O)$  and  $v_{s}(-O-C-O)$  of acetate group. The difference between those two bands

**Table 3** The <sup>1</sup>H NMR spectral data of ( $H_2o$ -HAH) and its diamagnetic complexes.

Compounds	(OH)	(NH)1	(NH) <sub>2</sub>	$-CH_2$	$-CH_3$	Aromatic protons
1	13.06	12.89	11.20	3.69	1.88	7.21-7.78
4	12.89	11.95	-	3.54	1.83	7.34-7.89
5	12.49	11.98	-	3.52	1.91	7.31-8.06
6	12.53	-	-	3.45	1.90	7.19-8.12
8	10.25	-	-	3.49	1.86	8.78-9.81

 $(98, 106 \text{ cm}^{-1})$  indicates the bidentate bonding for the acetate group [21].

The IR spectrum of  $[UO_2(o-HAH)(H_2O)_2]\cdot 2H_2O$  complex displays three bands at 921 and 845 cm<sup>-1</sup> assigned to  $\upsilon_3$  and  $\upsilon_1$  vibrations, respectively, of the dioxouranium ion. The  $\upsilon_3$  value is used to calculate the force constant (F) of  $\upsilon(U=O)$  by the method of McGlynn et al. [22]:

$$(\upsilon_3)^2 = (1307)^2 (F_{U-0}) / 14.103 \tag{1}$$

The force constant obtained for uranyl complex was then substituted into the relation given by Jones [23]:

$$R_{U-0} = 1.08(F_{U-0})^{-1/3} + 1.17$$
(2)

to give an estimate of the (U–O) bond length in Å. The calculated  $F_{U=O}$  and  $R_{U=O}$  values are 7.003 mdynes Å<sup>-1</sup> and 1.734 Å, respectively, fall in the usual range for the uranyl complexes [22].

# Nuclear magnetic resonance spectral studies

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of H<sub>2</sub>O-HAH and its Pd(II). Cd(II), Zn(II) and U(VI)O<sub>2</sub> complexes were recorded in d<sub>6</sub>-DMSO. The <sup>1</sup>H NMR spectrum of H<sub>2</sub>O-HAH shows three signals at 13.06, 12.89 and 11.20 ppm assignable to the protons of (OH),  $(NH)_1$ and  $(NH)_2$ , respectively (Table 3). The appearance of the signal attributed to the proton of OH group at a high value downfield from TMS suggests the presence of intramolecular hydrogen bonding. The multiplet signals observed in the 7.21-7.78 ppm region are assigned to the aromatic protons. The sharp singlet observed at 3.69 ppm is assigned to active methylene protons (-CH<sub>2</sub>). Also, the <sup>1</sup>H NMR spectra of the Pd(II) and Cd(II), complexes show the signals attributed to the (NH)<sub>1</sub> and OH protons indicating that these groups play no part in coordination. But, the lack of signal due to (NH)<sub>2</sub> proton emphasizes the deprotonation of the enolized carbonyl oxygen (= $C-O^-$ )<sub>2</sub>. Also, the lack of signals due to (NH)<sub>1</sub> and (NH)<sub>2</sub> protons in the <sup>1</sup>H NMR spectrum of the diamagnetic Zn(II) complex emphasizes the deprotonation of the enolized carbonyl oxygen  $(=C-O^{-})_1$  and  $(=C-O^{-})_2$ . Moreover, in case of  $U(VI)O_2$  complex the protons attributed to  $(NH)_1$  and  $(NH)_2$  are disappear and the (OH) proton showed an upfield shift on complexation.

From <sup>13</sup>C NMR spectral data (Table 4 and Scheme 2), the signals for the C<sub>7</sub>, C<sub>8</sub> and C<sub>10</sub> showed an upfield shift on complexation [24] compared with the free ligand in all diamagnetic complexes. While, C<sub>1</sub> showed an downfield shift on complexation in case of U(VI)O<sub>2</sub> complex. Furthermore, in case of Cd(II) complex the appearance of new signals at  $\delta$  = 175 ppm and  $\delta$  = 52 ppm give strong evidence for the presence of the acetate group. The other ring carbon atoms did not show significant shifts.

Electronic spectra and magnetic moment measurements

The electronic spectrum of [Ni(Ho-HAH)(OAc)(H<sub>2</sub>O)]·H<sub>2</sub>O complex shows two bands at 16949 and 27,778 cm<sup>-1</sup> (see Table 5) assigned to  ${}^{3}A_{2g}^{-} \rightarrow {}^{3}T_{1g}^{-}(F)$  and  ${}^{3}A_{2g}^{-} \rightarrow {}^{3}T_{1g}^{-}(P)$  transitions, respectively, in an octahedral geometry [25]. The calculated values of  $D_q$ , B,  $\beta$  and  $v_2/v_1$  values lie in the range reported for an octahedral structure. The position of  $v_1$  (10527 cm<sup>-1</sup>) is calculated theoretically [25]. The values of the magnetic moments value ( $\mu_{eff.}$  = 3.2 BM) can be taken as an additional evidence for an octahedral geometry.

The electronic spectrum of  $[Co(o-HAH)(H_2O)_2] \cdot 2H_2O$  complex shows two bands at 16,667 and 18,518 cm<sup>-1</sup> attributed to  ${}^{4}T_{1g}^{-} \rightarrow {}^{4}A_{2g}^{-}(F)$  and  ${}^{4}T_{1g}^{-} \rightarrow {}^{4}T_{1g}^{-}(P)$  transitions, respectively, in an octahedral configuration [25]. The calculated values of  $D_q$ , B,  $\beta$ and  $v_2/v_1$  are in good agreement with those reported for octahedral Co(II) complexes. The position of  $v_1$  (7937 cm<sup>-1</sup>) is calculated theoretically [25]. Also, the magnetic moment value (5.1 BM) is consistent with octahedral geometry around the Co(II) ion.

The Cu(II) complex has magnetic moment value (2.1 BM), indicating the presence of Cu(II) ion. The electronic spectrum of [Cu(H<sub>2</sub>O-HAH)(OAc)(H<sub>2</sub>O)]·H<sub>2</sub>O complex shows a broad band at 16891 cm<sup>-1</sup> with a shoulder at 14286 cm<sup>-1</sup> which may be assigned to  ${}^{2}B_{1g}^{-} \rightarrow {}^{2}E_{g}$  and  ${}^{2}B_{1g}^{-} \rightarrow {}^{2}A_{1g}^{-}$  transitions, respectively, in a tetragonally distorted octahedral configuration [25].

The electronic spectrum of  $[UO_2(o-HAH)(H_2O)_2]\cdot 2H_2O$  complex shows two bands at 23,809 and 27,778 cm<sup>-1</sup> may be attributed to  ${}^{1}E_{g}^{+} \rightarrow {}^{2}\pi_{u}$  transition and charge transfer  $n \rightarrow \pi^*$ , respectively [25].

The diamagnetic [Pd(Ho-HAH)(H<sub>2</sub>O)]·H<sub>2</sub>O complex shows a band at 22,223 cm<sup>-1</sup> which is assigned to  ${}^{1}A_{1g}^{-} \rightarrow {}^{2}B_{1g}^{-}$  transition in a square-planar configuration [26].

#### ESR studies

The room temperature solid-state ESR spectrum of  $[Cu(H_2O-HAH)(OAc)(H_2O)]$ ·H<sub>2</sub>O has axially symmetric g-tensor parameters with  $g_{||}(2.40) > g_{\perp}(2.09) > 2.0023$  indicating that the copper site has a  $d_{x^2-y^2}$  ground-state characteristic of tetrahedral, square planar or octahedral stereochemistry [27]. In axial symmetry the *g*-values are related by the expression,  $G = (g_{||} - 2)/(g_{\perp} - 2) = 4$ , where *G* is the exchange interaction parameter. According to Hathaway [28], the calculated *G* value was 4.6 suggesting that there are no copper–copper exchange interactions.

The ability of  $A_{||}$  (160 × 10<sup>-4</sup> cm<sup>-1</sup>) to decrease with increasing of  $g_{//}$  (2.23) is an evidence of an increase of the tetrahedral distortion in the coordination sphere of copper [29,28]. In order to quantify the degree of distortion of the Cu(II) complexes, we selected the *f* factor  $g_{||}/A_{||}$  obtained from the ESR spectrum. Where, the *f* factor is regarded as an empirical index of tetrahedral distortion. For this complex, the  $g_{||}/A_{||}$  quotient is 139, demonstrating the presence of significant dihedral angle distortion in the  $d_{xy}$ -plane and indicating a distorted octahedral geometry. Superhyperfine

Table 4 <sup>13</sup>C NMR Chemical shifts in (ppm) assignments for H<sub>2</sub>O-HAHNH and its diamagnetic complexes.

Compound	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>
1	163	118	134	123	131	120	170	177	46	167	164	112	141
4	164	117	134	123	130	119	163	171	54	158	164	111	140
5	164	118	133	123	129	121	163	170	54	158	164	112	140
6	165	118	133	122	131	1212	162	160	56	151	163	110	141
8	169	122	134	123	130	118	160	162	56	154	164	112	142

Table 5

Compound	$\mu_{eff.}$ (BM)	Band position $(cm^{-1})$	$D_{\rm q}~({\rm cm}^{-1})$	<i>B</i> (cm <sup>-1</sup> )	β	$\upsilon_2/\upsilon_1$
2	3.2	16,949; 27,778	1051	876	0.8	1.6
7	5.1	16,667; 18,518	919	766	0.8	2.1
3	2.1	16,891; 14,286	-	-	-	-
8	Diam.	23,809; 27,778	-	-	-	-
4	Diam.	22,223	-	-	-	-

Magnetic moments, electronic spectra and ligand field parameters of metal complexes of H<sub>2</sub>0-HAH.

structure for this complex was not seen at higher fields, excluding any interaction of the nuclear spins of nitrogen (I = 1) with the unpaired electron density on Cu(II) [30].

Molecular orbital coefficients,  $\alpha^2$  (covalent in-plane  $\sigma$ -bonding) and  $\beta^2$  (covalent in-plane  $\pi$ -bonding) were calculated:

$$\alpha^{2} = \left(\frac{A_{//}}{0.036}\right) + (g_{//} - 2.0023) + \frac{3(g_{\perp} - 2.0023)}{7} + 0.04$$
(3)

$$\beta^2 = \frac{(g_{//} - 2.0023)E}{-8\lambda\alpha^2}$$
(4)

 $\lambda = 828 \text{ cm}^{-1}$  for the free ion and *E* is the  ${}^{2}B_{1g}^{-} \rightarrow {}^{2}A_{1g}^{-}$  transition. As a measure of the covalence, the value of  $\alpha^{2}$  (0.75) and  $\beta^{2}$ 

As a measure of the covalence, the value of  $\alpha^2$  (0.75) and  $\beta^2$  (0.61) for the complex indicate that the in-plane  $\sigma$ -bonding and in-plane  $\pi$ -bonding are appreciably covalent and are consistent with very strong in-plane  $\pi$ -bonding in this complex.

# Thermal analysis

The TG of the isolated complexes was taken as a proof for the existing of  $H_2O$  molecules as well as the anions to be outside and/or inside the coordination sphere [31,32]. The water of crystallization lost in 32–150 °C regions. The complexes show thermal stability rather than the ligand where the beginning of its decomposition shifts to higher temperature (205–294 °C). In general, all complexes are thermally stable but [Ni(Ho-HAH)(OAC)(H<sub>2</sub>O)]·H<sub>2</sub>O is the highest one. It is thermally stable up to 294 °C. In the temperature range 294–350 °C, the TG curve displays 30.0% weight loss which could be ascribed to the elimination of the loosely bound (C<sub>5</sub>H<sub>5</sub>N<sub>2</sub>OS) moiety. The final weight loss of 33.8% ending at 498 °C, is largely attributed to complete decomposition of the organic molecule, alongside rupture of the chelate bond, leaving NiO comprising 15.8% of the initial mass of the complex as shown in Table 4.

Table 6
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Thermal	behavior	of metal	complexes	of (Hao-HAH	Ð
merman	Denavior	or metal	complexes	01 (1120 11/11	1).

Kinetic data

The kinetic and thermodynamic parameters of thermal degradation process have been calculated using Coats–Redfern model [32]. Coats–Redfern relation is as follows:

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}$$
(5)

where  $\alpha$  represents the fraction of sample decomposed at time *t*, defined by:

$$\alpha = \frac{w_o - w_t}{w_o - w_\infty} \tag{6}$$

 $w_o$ ,  $w_t$  and  $w_\infty$  are the weight of the sample before the degradation, at temperature *t* and after total conversion, respectively. *T* is the derivative peak temperature.  $\beta$  is the heating rate = dT/dt, *E* and *A* are the activation energy and the Arrhenius pre-exponential factor, respectively. *A* plot of versus 1/T gives a straight line whose slope (E/R) and the pre-exponential factor (*A*) can be determined from the intercept. (see Table 6)

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]$$

A number of pyrolysis processes can be represented as a first order reaction. Particularly, the degradation of a series of Ho-HAH complexes was suggested to be first order [33], therefore we assume n = 1 for the remainder of the present text. The other thermodynamic parameters of activation can be calculated by Eyring equation [34]:

$$\Delta H = E - RT \tag{7}$$

$$\Delta S = R ln \frac{hA}{k_{\rm B}T} \tag{8}$$

$$\Delta G = \Delta H - T \Delta S \tag{9}$$

 Compound (Molecular mass)	Temp. range, (°C)	Decomposition product(s) loss (Formula mass)	Mass% found (Calcd.)
<b>2</b> (471.54)	35-115	H <sub>2</sub> O (18.02)	3.8 (3.8)
	115-294	$H_2O + C_2H_3O_2$ (77.07)	16.6 (16.5)
	294-350	C <sub>5</sub> H <sub>5</sub> N <sub>2</sub> OS (141.11)	30.0 (29.9)
	350-498	C <sub>9</sub> H <sub>7</sub> N <sub>2</sub> O (159.17)	33.8 (33.8)
	>498	Residue; NiO (74.71)	15.8 (15.9)
<b>3</b> (476.15)	32-150	H <sub>2</sub> O (18.02)	3.8 (3.8)
	150-205	$H_2O + C_2H_3O_2$ (77.07)	16.2 (16.3)
	205-345	C <sub>5</sub> H <sub>5</sub> N <sub>2</sub> OS (141.11)	29.7 (29.6)
	345-575	C <sub>9</sub> H <sub>7</sub> N <sub>2</sub> O (159.17)	33.4 (33.5)
	>575	Residue; CuO (79.54)	16.7 (16.7)
<b>7</b> (447.32)	45-120	2 H <sub>2</sub> O (36.03)	8.1 (8.1)
	120-255	2H <sub>2</sub> O (36.03)	8.1 (8.1)
	255-360	C <sub>3</sub> H <sub>3</sub> N <sub>2</sub> S (99.07)	22.0 (22.1)
	360-580	$C_{11}H_9N_2O_2$ (201.21)	45.1 (45.0)
	>580	Residue;CoO (74.93)	16.7 (16.7)

 Table 7

 Kinetic parameters of complexes evaluated by Coats-Redfern equation.

Complex	Peak	Mid temp. (K)	Ea (kJ/mol)	$A(S^{-1})$	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol K)	$\Delta G$ (kJ/mol)
3	1st	378	119.962	3.17576E14	116.819	30.7338	105.202
	2nd	450	170.849	9.69674E14	167.107	38.564	149.753
	3rd	570	161.280	3.29071E10	156.541	-48.960	184.448
	4rd	753	125.106	6549.09097	118.845	-179.559	254.053
2	1st	340	116.029	6.845E13	113.202	18.855	106.791
	2nd	478	106.962	2.48701E7	102.988	-107.255	154.256
	3rd	613	363.608	4.04323E26	358.512	258.446	200.084
	4rd	715	229.460	1.65781E12	223.515	-18.257	236.569
7	1st	345	89.616	1.21529E9	86.748	-72.211	111.661
	2nd	451	44.116	1.885	40.366	-243.081	149.996
	3rd	606	193.083	2.45602E12	188.045	-13.6144	196.295
	4rd	766	211.620	1.03025E10	205.252	-61.072	252.033



Fig. 1. Coats-Redfern plots of (A) step(1), (B) step(2), (C) step(3) and (D) step(4) of [Cu(Ho-HAH)(OAc)(H<sub>2</sub>O)]·H<sub>2</sub>O.

Thermodynamic parameters such as activation energy (*Ea*), preexponential factor (*A*), entropy of activation ( $\Delta S$ ), enthalpy of activation ( $\Delta H$ ) and free energy of activation ( $\Delta G$ ) of decomposition steps were calculated using Coats–Redfern [32] (see Table 7 and Figs. 1–3). From the results, the following remarks can be pointed out:

The high values of activation energy (*Ea*) reveals the high stability of such chelates due to their covalent bond character [35].

The positive values of the free energy ( $\Delta G$ ) for the investigated complexes indicates that the free energy of the final residue is

higher than that of the initial compound, and all the decomposition steps are non–spontaneous processes. Also, the values of the activation,  $\Delta G$  increases significantly for the subsequent decomposition stages of a given complex. This is due to increasing the values of  $T\Delta S$  significantly from one step to another which overrides the values of  $\Delta H$  [36,37].

The negative values of the entropy ( $\Delta S$ ) for the degradation process indicates slow reaction and the activated complex is more ordered than the reactants [38].



Fig. 2. Coats-Redfern plots of (A) step(1), (B) step(2), (C) step(3) and (D) step(4) of [Ni(Ho-HAH)(OAc)(H<sub>2</sub>O)]·H<sub>2</sub>O.

# Electrical conductance

Interaction of Co(II) with (H<sub>2</sub>o-HAH) in solution

The specific conductance values ( $K_s$ ) of different concentrations of Co(II) solution in the absence and in the presence of ligand (E)-3-(2-(1-(2- hydroxyphenyl)hydrazinyl)-3-oxo-N-(thiazol-2yl)propanamide (H<sub>2</sub>o-HAH) was measured. From the specific conductance values ( $K_s$ ), the molar conductance ( $\Lambda_m$ ) values were calculated [39] according to Eq. (8):

$$\Lambda_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C}$$
(10)

where ( $K_s$ ) and ( $K_{solv}$ ) are the specific conductance of the solution and the solvent, respectively; ( $K_{cell} = 0.99$ ) is the cell constant and (*C*) is the molar concentration of the Co(II) solution.

The concentration dependence on the molar conductance  $(\Lambda_m)$  of different Co(II) concentrations in the absence and presence of ligand where studied by plotting  $(\Lambda_m)$  versus  $(\sqrt{C})$  as shown in Fig. 4. The molar conductance values  $(\Lambda_m)$  decreased linearly by increasing the metal concentration.

Also, the limiting molar conductance  $(\Lambda_o)$  at infinite dilutions were estimated for Co(II) in absence and presence of the ligand by extrapolating the relation between  $(\Lambda_m)$  and  $(\sqrt{C})$  to zero concentration for each line. In addition, the molar conductance  $(\Lambda_m)$ was drawn against the molar ratio (M/L) in the presence of ligand, where (M) is the metal concentration and (L) is the ligand concentration (Fig. 5). Different straight lines were obtained with sharp breaks in presence of ligand representing stoichiometric ratios.

#### The association constants of Co(II) in the presence of H<sub>2</sub>o-HAH

The association constant of Co(II) in the presence of ligand could be calculated by using Eq. (9) for 1:2 asymmetric electrolytes [40,41].

$$K_A = \frac{A_0^2 (\Lambda_0 - \Lambda_m)}{4C_m^2 + \Lambda^3 S(z)}$$
(11)

where  $(\Lambda_m, \Lambda_0)$  are the molar and limiting molar conductance of metal;  $C_m$  is metal concentration; S(z) is Fuoss–shedlovsky factor which equal (1) for strong electrolytes [42].

The Gibbs free energies of association ( $\Delta G_A$ ) [43,44] were calculated from the association constant values by Eq. (10):

$$\Delta G_A = -RT \ln K_A \tag{12}$$

where R is the gas constant and T is the absolute temperature.

# The formation constants $(K_f)$ for Co(II)-H<sub>2</sub>0-HAH complexes

The formation constants ( $K_f$ ) for Co(II)–ligand complexes can be calculated for each line in (M/L) relation against ( $\Lambda_m$ ) in presence of ligand by using Eq. (11) [45,46].



Fig. 3. Coats-Redfern plots of (A) step(1), (B) step(2), (C) step(3) and (D) step(4) of [Co(o-HAH)(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O.



60 55 50 45 40 35 30 < 25 20 15 10 5 0 0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 M/L

**Fig. 4.** The relation between molar conductance and  $(\sqrt{C})$  of Co(II) (A) in absence of H<sub>2</sub>o-HAH, (B) in presence of H<sub>2</sub>o-HAH in absolute ethanol at 294.15 K.

$$K_f = \frac{\Lambda_m - \Lambda_{obs}}{(\Lambda_{obs} - \Lambda_{ML})[L]}$$
(13)

where  $(A_m)$  is the molar conductance of the metal before addition of the ligand,  $(A_{obs})$  is the molar conductance of solution during

**Fig. 5.** The relation between molar conductance ( $\Lambda_M$ ) and the molar ratio (M/L) of Co(II) in presence of (H<sub>2</sub>o-HAH) in absolute ethanol at 294.15 K.

titration and  $(\Lambda_{ML})$  is the molar conductance of the complex. Also, the Gibbs free energy of complex formation were calculated by using Eq. (12).

$$\Delta G_f = -RT \ln K + f \tag{14}$$

#### Table 8

Association co	instants and Gi	bbs free energies	of association f	for Co(II) with	(Hoo-HAH)	) in absolute ethanol at 294 15 K
1 issociation co	motunes und or	bbb nee energies	or association i		11/0 11111	

$\Lambda_m$ (cm <sup>2</sup> ohm <sup>-1</sup> )	C <sub>m</sub>	$\Lambda_o - \Lambda_m$	$\Lambda_o^2(\Lambda_o-\Lambda_m)$	$4C^2 + \Lambda_m^3$	K <sub>A</sub>	$\Delta G_A (kJ/mol)$
49.200	$\textbf{2.439}\times \textbf{10}^{-5}$	21.80	$1.099\times10^5$	$1.191\times10^5$	0.923	+0.197
37.80	$4.762\times10^{-5}$	33.2	$1.67 \times 10^5$	$5.401 \times 10^4$	3.099	-2.765
30.100	$6.976  imes 10^{-5}$	40.90	$2.016  imes 10^5$	$2.727\times 10^4$	7.560	-4.945
26.400	$9.091 \times 10^{-5}$	44.60	$2.248  imes 10^5$	$1.839  imes 10^4$	12.219	-6.186
23.402	$1.111  imes 10^{-5}$	47.60	$2.399  imes 10^5$	$1.281 \times 10^4$	18.728	-7.163
20.700	$1.142\times10^{-5}$	50.30	$\textbf{2.536}\times \textbf{10}^{5}$	$\textbf{8.869}\times 10^3$	28.589	-8.197

 $\Lambda_o = 71 \text{ cm}^2 \text{ ohm}^{-1}$ .

#### Table 9

Formation constants and Gibbs free energies of formation for 1:2 (M/L) Co(II)-(H<sub>2</sub>o-HAH) complexes in absolute ethanol at 294.15 K.

$\Lambda_{obs}$ (cm <sup>2</sup> ohm <sup>-1</sup> )	[ <i>L</i> ]	$(\Lambda_{obs} - \Lambda_{ML}) [L]$	$(\Lambda_M - \Lambda_{obs})$	$K_{f}$	$\Delta G_f(kJ/mol)$
49.200 37.800 30.100	$\begin{array}{l} 9.750\times 10^{-5} \\ 9.523\times 10^{-5} \\ 9.302\times 10^{-5} \end{array}$	$\begin{array}{c} 3.139 \times 10^{-3} \\ 1.028 \times 10^{-3} \\ 2.884 \times 10^{-4} \end{array}$	39.80 51.2 58.9	$\begin{array}{c} 1.268 \times 10^{4} \\ 4.978 \times 10^{4} \\ 2.043 \times 10^{4} \end{array}$	-23.097 -26.441 -29.892

 $\Lambda_M = 89 \text{ cm}^2 \text{ ohm}^{-1}$ ,  $\Lambda_{ML} = 27 \text{ cm}^2 \text{ ohm}^{-1}$ .

#### Table 10 Formation constants and Gibbs free energies of formation for 1:1 (M/L) Co(II)-(H<sub>2</sub>o-HAH) complexes in absolute ethanol at 294.15 K.

$\Lambda_{obs}$ (cm <sup>2</sup> ohm <sup>-1</sup> )	[ <i>L</i> ]	$(\Lambda_{obs} - \Lambda_{ML}) [L]$	$(\Lambda_M - \Lambda_{obs})$	$K_{f}$	$\Delta G_f$ (kJ/mol)
26.400	$9.091\times10^{-5}$	$2.745\times10^{-3}$	62.600	$\textbf{2.280}\times \textbf{10}^{4}$	-24.532
23.402	$8.888 imes 10^{-5}$	$3.913  imes 10^{-4}$	65.598	$1.676 \times 10^{5}$	-29.409
20.700	$8.697 imes10^{-5}$	$1.478  imes 10^{-4}$	68.300	$4.619  imes 10^5$	-31.887
19.476	$\textbf{8.511}\times10^{-5}$	$4.051  imes 10^{-5}$	69.524	$1.716\times10^{6}$	-35.096

 $\Lambda_M = 89 \text{ cm}^2 \text{ ohm}^{-1}$ ,  $\Lambda_{ML} = 19 \text{ cm}^2 \text{ ohm}^{-1}$ .

### Table 11

Formation constants and Gibbs free energies of formation for 2:1 (M/L) Co(II)-(H<sub>2</sub>o-HAH) complexes in absolute ethanol at 294.15 K.

$\Lambda_{obs}$ (cm <sup>2</sup> ohm <sup>-1</sup> )	[ <i>L</i> ]	$(\Lambda_{obs} - \Lambda_{ML}) [L]$	$(\Lambda_M - \Lambda_{obs})$	$K_{f}$	$\Delta G_f(kJ/mol)$
18.607 17.422 17.000 16.227	$\begin{array}{c} 8.333 \times 10^{-5} \\ 8.163 \times 10^{-5} \\ 8.000 \times 10^{-5} \\ 7.843 \times 10^{-5} \end{array}$	$\begin{array}{c} 2.172 \times 10^{-4} \\ 1.161 \times 10^{-4} \\ 8.000 \times 10^{-5} \\ 1.779 \times 10^{-5} \end{array}$	70.393 71.580 72.000 72.773	$\begin{array}{c} 3.240 \times 10^5 \\ 6.166 \times 10^5 \\ 9.000 \times 10^5 \\ 4.089 \times 10^5 \end{array}$	-31.020 -32.593 -33.517 -37.218

 $\Lambda_M = 89 \text{ cm}^2 \text{ ohm}^{-1}$ ,  $\Lambda_{ML} = 19 \text{ cm}^2 \text{ ohm}^{-1}$ .

#### Table 12

Formation constants and Gibbs free energies of formation for 3:1 (M/L) Co(II)-(H<sub>2</sub>o-HAH) complexes in absolute ethanol at 294.15 K.

$\Lambda_{obs}$ (cm <sup>2</sup> ohm <sup>-1</sup> )	[ <i>L</i> ]	$(\Lambda_{obs} - \Lambda_{ML}) [L]$	$(\Lambda_M - \Lambda_{obs})$	$K_{f}$	$\Delta G_f(kJ/mol)$
16.467	$7.690\times10^{-5}$	$1.128\times10^{-4}$	72.533	$\textbf{6.429}\times 10^{5}$	-32.695
16.308	$7.547 imes10^{-5}$	$9.871  imes 10^{-5}$	72.692	$7.364  imes 10^5$	-33.027
15.814	$7.407\times10^{-5}$	$6.029  imes 10^{-5}$	73.186	$1.214\times10^{6}$	-34.248
15.033	$7.273\times10^{-5}$	$2.399  imes 10^{-5}$	73.967	$3.082  imes 10^6$	-36.527
15.050	$7.143\times10^{-5}$	$3.571\times10^{-6}$	73.950	$\textbf{2.071}\times \textbf{10}^{6}$	-41.184

 $\Lambda_{\rm M}$  = 89 cm<sup>2</sup> ohm<sup>-1</sup>,  $\Lambda_{\rm ML}$  = 15 cm<sup>2</sup> ohm<sup>-1</sup>.

From the results, the following remarks can be pointed out:

# **Biological** activity

- The association free energies evaluated for complexes are spontaneous and small (see Table 8), indicating that electrostatic attraction force.
- Different complexes resulted from the interaction of metal with ligand which are 1:2, 1:1, 2:1 and 3:1 (*M*/*L*) complexes with formation constants and formation Gibbs free energies (see Tables 9–12) of the order:

 $K_f(3:1) > K_f(2:1) > K_f(1:1) > K_f(1:2)$  for (M/L), and  $\Delta G_f(3:1) > \Delta G_f(2:1) > \Delta G_f(1:1) > \Delta G_f(1:2)$ .

 The formation constants and formation Gibbs free energies increase by increasing the metal concentration which favors spontaneous processes. Diseases caused by microbial infections are a serious menace to the health of human being and often have connection to some other diseases when the body system gets debilitated. Developing antimicrobial drugs and maintaining their potency in opposition to resistance by different classes of microorganisms as well as a broad spectrum of antibacterial and antifungal activities are some of the major concerns of research in this area.

Minimum inhibitory concentration (MIC) [47,48] was determined for each of the active compounds. All of the tested compounds showed a remarkable biological activity against different types of Gram-positive and Gram-negative bacteria (*Clostridium* sp. and *E. coli*) and against fungi species (*Stemphylium* sp. and



Fig. 6. Effect of ligand and its metal complexes toward (A) Aspergillus sp., (B) Stemphylium sp. (C) E. Coli and (D) Clostridium sp.

Aspergillus sp.) (Fig. 6). On comparing the biological activity of the ligand and its metal complexes with the standard (Miconazole and Ampicillin), from the results, the Ni(II), Co(II), Cu(II), Cd(II), Zn(II), Pd(II) and U(VI)O<sub>2</sub> metal complexes shown potential antimicrobial activities against all the bacterial and fungal strains. Amongst all the compounds tested,  $Pd(Ho-HAH)(H_2O)]$ ·H<sub>2</sub>O complex demonstrated the most potent antibacterial and antifungal activity

(90%) at the higher concentration of 1.5 mg/ml [49]. In general all the metal complexes possess higher antimicrobial activity than the ligand and this may be due to the change in structure due to coordination and chelating tends to make metal complexes act as more powerful and potent bactereostatic agents, thus inhibiting the growth of the microorganisms. Moreover, coordination reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor groups within the chelate ring system formed during the coordination. This process, in turn, increases the lipophilic nature of the central metal atom, which favors its permeation more efficiently through the lipid layer of the microorganism, thus destroying them more aggressively. Increased activity of the metal chelates is due to the lipophilic nature of the metal ion in complexes. Furthermore, the mode of action of Schiff base compounds may involve the formation of a hydrogen bond through the azomethine nitrogen atom with the active center of the cell constituents, resulting in interference with normal cell process [50–54].

#### Conclusion

Schiff base complexes of Co(II), Ni(II), Cu(II), Pd(II), Cd(II), Zn(II) and U(VI)O<sub>2</sub> with (E)-3-(2-(1-(2- hydroxyphenyl)hydrazinyl)-3oxo-N-(thiazol-2yl)propanamide (H20-HAH) were prepared and characterized. It is obvious from this study that the (H<sub>2</sub>0-HAH) behaves in a tridentate and/or tetradentate ligand. The electronic spectra of the complexes as well as their magnetic moments suggest octahedral geometries for all isolated complexes except Pd(II) complex has square planner geometry. The kinetic and thermodynamic parameters (*Ea*, *A*,  $\Delta H$ ,  $\Delta S$ ,  $\Delta G$ ) of all thermal decomposition steps suggested the first order behavior. Also, the association free energies evaluated for Co(II) complexes are spontaneous and small indicating that electrostatic attraction force. Moreover, the biological activities of the ligand and its complexes against bacterial and fungal organisms have been evaluated by using minimum inhibitory concentrations (MICs) method. The [Pd(Ho-HAH)(H<sub>2</sub>O)]·H<sub>2</sub>O was the most active against all strains.

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