

## 2-(Phenylamino)acetohydrazide로부터 유도된 Hydrzone 리간드와 그들의 착물의 합성, 특성 및 항균활성

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## Synthesis, Characterization and Antimicrobial Activities of Hydrazone Ligands Derived from 2-(phenylamino)acetohydrazide and Their Metal Complexes

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**요약.** N'-(2-hydroxybenzyl)-2-(phenylamino)acetohydrazide ( $\mathbf{H}_2\mathbf{L}^1$ , **1**) 및 N'-((3-hydroxy-naphthalen-2-yl)methylene)-2-(phenylamino)acetohydrazide ( $\mathbf{H}_2\mathbf{L}^2$ , **13**)에 대한 VO(II), ZrO(II), Hf(IV), UO<sub>2</sub>(II), Sn(II), V(V)O<sub>3</sub>, Ru(III), Cd(II), Ho(III) 및 Yb(III) 착물을 합성하여 원소분석, <sup>1</sup>H NMR, IR, UV-Vis, 전기전도도 및 열분석 (DTA 및 TG)을 통해 특성을 조사하였다. 이들 리간드는 분광학적 결과에 의하면 중성 이배위, 일열기성 이배위, 일열기성 삼배위 또는 이열기성 삼배위 리간드로 행동한다. 그 결과 azomethine 질소원자, 양성자화 되어있거나 또는 탈양성자화 된 형태의 페놀 하이드록시 그룹 그리고 에놀 또는 케톤형 카르보닐 그룹을 통해 금속이온에 결합한다. 이들 리간드와 그 금속 착물들은 모체 리간드 및 금속이온 용액에 비해 높은 항균 및 항박테리아 저해효과를 보인다. 대부분의 금속 착물은 표준 항균성 시약 (amphotricene B) 보다 더 높은 항균 활성성을 보인다. 또한 이들 리간드와 착물은 항박테리아 활성도보다는 항균활성도에서 더 높은 수치를 보인다.

**주제어:** Acetohydrazide, hydrazone, 금속착물, 생물활성도

**ABSTRACT.** VO(II), ZrO(II), Hf(IV), UO<sub>2</sub>(II), Sn(II), V(V)O<sub>3</sub>, Ru(III), Cd(II), Ho(III) and Yb(III) complexes of N'-(2-hydroxybenzyl)-2-(phenylamino)acetohydrazide ( $\mathbf{H}_2\mathbf{L}^1$ , **1**) and N'-((3-hydroxy-naphthalen-2-yl)methylene)-2-(phenylamino)acetohydrazide ( $\mathbf{H}_2\mathbf{L}^2$ , **13**) have been synthesized and characterized by elemental analyses, <sup>1</sup>H NMR, IR, UV-Vis, conductance, thermal analyses (DTA and TG). The spectral data showed that the ligands behave as neutral bidentate, monobasic bidentate, monobasic tridentate or bibasic tridentate ligand bonded to the metal ions through the azomethine nitrogen atoms, phenolic hydroxyl group in protonated or deprotonated form and enolic or ketonic carbonyl group. The ligands and their metal complexes exhibit higher antifungal and antibacterial inhibitory effects than parent ligands and the solution of metal ions. Most of metal complexes exhibit higher antifungal activity than standard antifungal drug (amphotricene B). It is also clear that the ligands and their metal complexes have higher antifungal activity than antibacterial activity.

**Keywords:** Acetohydrazide, Hydrazone, Metal complexes, Biological activity

### INTRODUCTION

The interest in the study of hydrazone compounds and their metal complexes has recently been grown up due to their biological activities as antifungal,<sup>1-3</sup> antibacterial<sup>1-4</sup> anticonvulsant,<sup>5</sup> anti-inflammatory,<sup>3</sup> anti-malarial,<sup>6</sup> analgesic,<sup>7</sup> anti-platelets,<sup>8</sup> anti-tuberculosis,<sup>9</sup> anticancer,<sup>10</sup> and

a treatment of leprosy and mental disorder diseases.<sup>11</sup> Tuberculostatic activity is attributed to the formation of stable chelates with transition metals present in the cell. Thus, many vital enzymatic reactions catalyzed by these transition metals cannot take place in the presence of hydrazones.<sup>8</sup> Hydrazones also act as herbicides, insecticides, nematocides, rodenticides and plant growth regu-

lators. Also hydrazones are used as plasticizers and stabilizers for polymers, polymerization initiators, anti-oxidants. In analytical chemistry, hydrazones find application in detection, determination and isolation of compounds containing the carbonyl group. More recently, they have been extensively used in detection and determination of several metals.<sup>12</sup> Due to the coordination capability of isonicotinoyl hydrazide, which are a primary anti-tuberculosis drug, and its hydrazones which has been widely exploited for many biochemical and pharmacological applications. Metal complexes of 2-acetylpyridine benzoylhydrazone were synthesized and crystallographically characterized.<sup>13</sup> Manganese(II), iron(III), nickel(II), cobalt(II) and zinc(II) complexes of 2,6-diformyl-4-methylphenoldibenzoylhydrazone have been prepared and characterized by elemental and spectroscopic measurements.<sup>14</sup> Cobalt(II), manganese(II), copper(II) complexes of 2-acetylpyridine salicyloylhydrazone and 2-benzoylpyridine salicyloylhydrazone, have been synthesized and characterized.<sup>15</sup> Zinc(II) complexes of 2-Benzoylpyridine-phenylhydrazone, 2-benzoylpyridine-para-chloro-phenyl hydrazone and 2-benzoylpyridine-para-nitro-phenyl hydrazone have been prepared and characterized elemental, spectral and single-crystal X-ray diffraction analyses.<sup>16</sup> Much work on metal complexes of hydrazones with different functional groups has been reported.<sup>17</sup> The aim of this manuscript is the preparation and characterization of VO(II), ZrO(II), Hf(IV), UO<sub>2</sub>(II), Sn(II), V<sup>(V)</sup>O<sub>3</sub>, Ho(III), Ru(III), Cd(II) and Yb(III) complexes of N'-(2-hydroxybenzyl)-2-(phenylamino) acetohydrazide (**H<sub>2</sub>L<sup>1</sup>**, **1**) and N'-(3-hydroxy naphthalen-2-yl)methylene)-2-(phenylamino) acetohydrazide (**H<sub>2</sub>L<sup>2</sup>**, **13**).

## EXPERIMENTAL

### Instrumentation and measurements

The starting chemicals were of analytical grade. IR spectra of the solid ligand and complexes were recorded on Perkin-Elmer infrared spectrometer 681 or Perkin-Elmer 1430 using KBr disc. The <sup>1</sup>H-NMR spectra were recorded with a JEOL EX-270 MHz FT-NMR spectrometer in CDCl<sub>3</sub> as solvent, where the chemical shifts were determined relative to the solvent peaks. The molar conductivity of the metal complexes in DMSO at 10<sup>-3</sup>M concentration was measured using a dip cell and a Bibby conductimeter MC1 at room temperature. The resistance measured in ohms and the molar conductivities were calculated according to the equation: equation:  $\Lambda_M = V \times K \times g / M_w \times \Omega$  where:  $\Lambda_M$  = molar conductivity (ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>),

$V$  = volume of the complex solution,  $K$  = cell constant (0.92 cm<sup>-1</sup>),  $M_w$  = molecular weight of the complex,  $g$  = weight of the complex,  $\Omega$  = resistance measured in ohms. Electronic absorption spectra were recorded on a Shimodzu 240 using 1 cm quartz cells taking DMSO as solvent. The thermal analyses (DTA and TG) were carried out in the air on a Shimadzu DT-30 thermal analyzer from 27 to 800 °C at a heating rate of 10 °C per minute. Elemental analysis (CHN) was performed in the Analytical Unit within Cairo University (Egypt) by the usual methods of analysis.

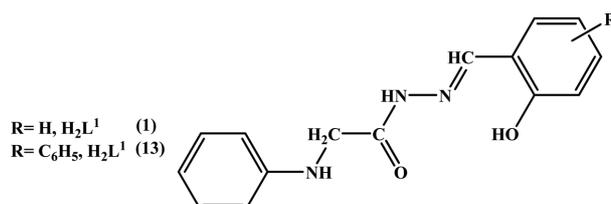
### Preparation of ligands

The acetohydrazide Schiff bases **H<sub>2</sub>L<sup>1</sup>** and **H<sub>2</sub>L<sup>2</sup>** were prepared by refluxing equimolar amounts of salicylaldehyde (1.22 g, 0.01 mol) or 2-hydroxy-1-naphthaldehyde (1.72 g, 0.01 mol) to the solution of 2-(phenylamino)acetohydrazide (1.65 g, 0.01 mol.) in 50 ml absolute ethanol for an hour. The formed solid product was filtered off, washed with ethanol, crystallized from ethanol and dried under vacuum over anhydrous CaCl<sub>2</sub>.<sup>18</sup> <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>, ppm) **H<sub>2</sub>L<sup>1</sup>**:  $\delta(\text{OH})=13.15$  (s, 1H),  $\delta(\text{CONH})=11.88$  (s, 1H)  $\delta(\text{NHCH}_2)=9.8$  (s, 1H),  $\delta(\text{N}=\text{CH})=8.65$  (s, 1H),  $\delta(\text{C}_6\text{H}_5)=8.43-7.10$  (m, 9 H), and  $\delta(\text{CH}_2)=4.05$ ; **H<sub>2</sub>L<sup>2</sup>**:  $\delta(\text{OH})=12.85$  (s, 1H),  $\delta(\text{CONH})=11.80$  (s, 1H)  $\delta(\text{NHCH}_2)=10.1$  (s, 1H),  $\delta(\text{N}=\text{CH})=8.6$ (s, 1H),  $\delta(\text{C}_6\text{H}_5)=8.33-6.90$  (m, 11 H), and  $\delta(\text{CH}_2)=4.25$  (*Fig. 1*).

### Preparation of metal complexes

Complexes **2-7**, **10**, **14**, **17-19** and **21-22** were prepared by adding a solution of metal salts VOSO<sub>4</sub>·3H<sub>2</sub>O, ZrOCl<sub>2</sub>·8H<sub>2</sub>O, UO<sub>2</sub>(OAc)<sub>2</sub>·2H<sub>2</sub>O, SnCl<sub>2</sub>·2H<sub>2</sub>O, Cd(OAc)<sub>2</sub>·6H<sub>2</sub>O, Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O or RuCl<sub>3</sub>·3H<sub>2</sub>O (1 mmol) to the solution of the hydrazone ligands (2 mmol, in ethanol). The mixture was refluxed while stirring for three hours. The resulting solid complexes were filtered off, washed several times with ethanol and dried under vacuum.

Complexes **8**, **9**, **11-12**, **15-16**, **20** and **23-24** were prepared by adding a solution of metal salts HoCl<sub>3</sub>·6H<sub>2</sub>O, RuCl<sub>3</sub>·nH<sub>2</sub>O, NH<sub>4</sub>VO<sub>3</sub>, HfCl<sub>4</sub>, ZrOCl<sub>2</sub>·8H<sub>2</sub>O, and UO<sub>2</sub>(OAc)<sub>2</sub>·2H<sub>2</sub>O (1 mmol) to the solution of the hydrazone ligands (1 mmol, in ethanol). The mixture was refluxed



*Fig. 1.* Structure representation of the ligands.

while stirring for four hours. The resulting solid complexes were filtered off, washed several times with ethanol and dried under vacuum.

### *In-vitro* antibacterial and antifungal activities

The biological activities of the newly synthesized ligands, their metal complexes and metal salts were carried out in the Botany Department, Lab. of microbiology, Faculty of Science, El-Menoufia University. They have been studied for their antibacterial and antifungal activities by disc diffusion method.<sup>19,20</sup> The antibacterial and antifungal activities were done using *Escherichia coli* and *Aspergillus niger* at 1000 ppm concentrations in solvent DMSO. Where DMSO poured disc was used as negative control. The bacteria were subcultured in nutrient agar medium which, prepared using (g.L<sup>-1</sup> distilled water) NaCl (5 g), peptone (5 g), beef extract (3 g), agar (20 g). The fungus was subcultured in Dox's medium which prepared using (g.L<sup>-1</sup> distilled water) yeast extract (1 g), sucrose (30 g), NaNO<sub>3</sub>, agar (20 g), KCl (0.5 g), KH<sub>2</sub>PO<sub>4</sub> (1 g), MgSO<sub>4</sub>·7H<sub>2</sub>O (0.5 g) and trace of FeCl<sub>3</sub>·6H<sub>2</sub>O. These mediums

were then sterilized by autoclaving at 120 °C for 15 min. After cooling to 45 °C the medium was poured into 90 mm diameter Petri dishes and incubated at 37 or 28 °C respectively. After few hours, Petri dishes were stored at 4 °C. Microorganisms were spread over each dish by using sterile bent Loop rod. The test is carried out by placing filter paper disks with a known concentration of the compounds on the surface of agar plates inoculated with a test organism. Standard antibacterial drug (tetracycline), antifungal drug (amphotericin B) and solution of metal salts were also screened under similar conditions for comparison. The Petri dishes were incubated for 48-72 hours at 37 or 28 °C for the two organisms respectively. The zone of inhibition was measured in millimeters carefully. All determination was made in duplicate for each of the compounds. An average of the two independent readings for each compound was record.

## RESULTS AND DISCUSSION

The ligand H<sub>2</sub>L<sup>1</sup>, **1**; H<sub>2</sub>L<sup>2</sup>, **13** and their metal com-

**Table 1.** Analytical and some physical Characteristics for the ligands and their metal complexes

| No. | Compounds  | Color       | M. Wt.  | Calcd (Found) % |             |               | Λ <sup>a</sup> <sub>M</sub> | Yeild (%) |
|-----|--|-------------|---------|-----------------|-------------|---------------|-----------------------------|-----------|
|     |  |             |         | C               | H           | N             |                             |           |
| 1   | H <sub>2</sub> L <sup>1</sup> (C <sub>15</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> )         | Yellow      | 269.31  | 67.20(67.90)    | 5.20(5.50)  | 19.60 (19.40) | --                          | 90        |
| 2   | [(HL <sup>1</sup> ) <sub>2</sub> (VO)]·H <sub>2</sub> O  | green       | 621.55  | 57.97(57.90)    | 4.78(5.10)  | 13.52 (13.70) | 13                          | 70        |
| 3   | [(HL <sup>1</sup> ) <sub>2</sub> ZrO]·5H <sub>2</sub> O  | Yellow      | 735.91  | 48.96 (49.20)   | 5.48(5.60)  | 11.42 (11.60) | 5.3                         | 82        |
| 4   | [(H <sub>2</sub> L <sup>1</sup> ) <sub>2</sub> UO <sub>2</sub> (OAc) <sub>2</sub> ]·4H <sub>2</sub> O  | Orange      | 998.78  | 40.89 (40.9)    | 4.44 (4.10) | 8.41 (9.62)   | 8.4                         | 75        |
| 5   | [(HL <sup>1</sup> ) <sub>2</sub> Sn]·3H <sub>2</sub> O   | Y. White    | 709.35  | 50.8 (51.00)    | 4.83 (4.61) | 11.85 (12.02) | 33.5                        | 70        |
| 6   | [(H <sub>2</sub> L <sup>1</sup> ) <sub>2</sub> Cd(OAc) <sub>2</sub> ]                                  | Y. White    | 767.09  | 53.24(53.00)    | 4.47(4.52)  | 10.96(13.11)  | 12.4                        | 80        |
| 7   | [(HL <sup>1</sup> ) <sub>2</sub> UO <sub>2</sub> ]   | Orange      | 806.62  | 44.67 (45.50)   | 3.50 (3.59) | 10.42 (10.72) | 15.3                        | 73        |
| 8   | [(HL <sup>1</sup> )HoCl <sub>2</sub> (H <sub>2</sub> O)]·4H <sub>2</sub> O                             | Yellow      | 594.21  | 30.32(29.97)    | 4.07(4.25)  | 7.07 (7.32)   | 6.5                         | 77        |
| 9   | [(HL <sup>1</sup> )RuCl <sub>2</sub> (H <sub>2</sub> O)]·6H <sub>2</sub> O                             | Dark Brown  | 566.41  | 31.81(31.70)    | 4.98(4.90)  | 7.43 (7.64)   | 4.7                         | 83        |
| 10  | [(HL <sup>1</sup> ) <sub>2</sub> Yb]·(NO <sub>3</sub> )  | Y. white    | 771.64  | 46.70(47.10)    | 3.66(3.90)  | 12.71 (13.01) | 90.1                        | 80        |
| 11  | NH <sub>4</sub> [(H <sub>2</sub> L <sup>1</sup> )VO <sub>3</sub> ]·2H <sub>2</sub> O                   | Y. White    | 422.31  | 42.66 (43.11)   | 4.54 (4.20) | 13.27 (13.55) | 72.5                        | 77        |
| 12  | [HL <sup>1</sup> HfCl <sub>3</sub> ]·2H <sub>2</sub> O   | Yellow      | 590.18  | 30.53(30.31)    | 3.25 (3.29) | 7.12 (7.31)   | 17.5                        | 65        |
| 13  | H <sub>2</sub> L <sup>2</sup> (C <sub>19</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> )         | Yellow      | 319.36  | 71.46 (71.50)   | 5.37 (5.32) | 13.16 (13.2)  | --                          | 85        |
| 14  | [(HL <sup>2</sup> ) <sub>2</sub> VO]   | green       | 703.65  | 64.8 (64.58)    | 4.58 (4.42) | 11.94 (12.12) | 0.5                         | 73        |
| 15  | [HL <sup>2</sup> ZrOCl]·2H <sub>2</sub> O  | Yellow      | 497.06  | 45.91 (45.49)   | 4.06 (4.05) | 8.45 (8.54)   | 21.1                        | 77        |
| 16  | [(H <sub>2</sub> L <sup>2</sup> ) <sub>2</sub> (UO <sub>2</sub> )(OAc) <sub>2</sub> ]                  | Orange      | 707.48  | 39.05 (38.81)   | 3.28 (3.47) | 5.94 (6.17)   | 30.2                        | 75        |
| 17  | [(HL <sup>1</sup> ) <sub>2</sub> Sn]   | Black       | 755.42  | 60.42 (60.21)   | 4.27 (4.32) | 11.13(11.26)  | 10.5                        | 77        |
| 18  | [(HL <sup>1</sup> ) <sub>2</sub> Cd(OAc) <sub>2</sub> ]  | Yellow      | 869.23  | 58.04 (57.91)   | 4.64 (4.52) | 9.67(10.09)   | 11.5                        | 73        |
| 19  | [(HL <sup>2</sup> ) <sub>2</sub> (UO <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]·2H <sub>2</sub> O | Pale yellow | 1068.79 | 42.70 (42.54)   | 3.58 (3.63) | 10.48 (10.71) | 23.5                        | 76        |
| 20  | [(L <sup>2</sup> )HoCl(H <sub>2</sub> O) <sub>2</sub> ]  | Yellow      | 552.76  | 41.21 (41.93)   | 3.46 (4.41) | 7.59 (7.98)   | --                          | 75        |
| 21  | [(HL <sup>2</sup> ) <sub>2</sub> Ru]·Cl  | Brown       | 773.27  | 59.02 (58.89)   | 4.17 (4.22) | 10.87 (11.02) | 79.3                        | 78        |
| 22  | [(L <sup>2</sup> )Yb(NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]                                | Pale Yellow | 588.42  | 38.78(39.31)    | 3.25 (3.01) | 8.52 (9.75)   | 13.8                        | 79        |
| 23  | NH <sub>4</sub> [(H <sub>2</sub> L <sup>2</sup> )VO <sub>3</sub> ]                                     | Y. White    | 436.34  | 52.30 (51.65)   | 3.93(3.78)  | 12.84 (12.59) | 65.6                        | 65        |
| 24  | [HL <sup>2</sup> HfCl <sub>3</sub> ]·6H <sub>2</sub> O   | Yellow      | 711.30  | 32.08 (31.89)   | 3.97(3.88)  | 5.91 (6.01)   | 9.8                         | 59        |

<sup>a</sup>Molar conductivity as 10<sup>-3</sup> M solutions (ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>), Y. = yellowish

**Table 2.** IR spectral assignment for the ligands and their metal complexes

| No. | Compounds  | $\nu(\text{Coord. H}_2\text{O})$ | $\nu(\text{OH})$ | $\nu(\text{NH})$ | $\nu(\text{C=O})$ | $\nu(\text{C=N})$ | $\nu(\text{C-OH})$ | $\nu(\text{N-N})$ | $\nu(\text{M-O})$ | $\nu(\text{M-N})$ | $\nu(\text{M=O})/\nu\text{NO}_3$ |
|-----|--|----------------------------------|------------------|------------------|-------------------|-------------------|--------------------|-------------------|-------------------|-------------------|----------------------------------|
| 1   | $\text{H}_2\text{L}^1 (\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}_2)$        | ----                             | 3434(br)         | 3320, 3270       | 1675(s)           | 1620              | 1275               | 958               | --                | --                | --                               |
| 2   | $[(\text{HL}^1)_2(\text{VO})]\cdot\text{H}_2\text{O}$                          | 3347(br)                         | -----            | 3306,3267        | 1674(s)           | 1607              | 1310               | 1030              | 688               | 461               | 972                              |
| 3   | $[(\text{HL}^1)_2\text{ZrO}]\cdot 5\text{H}_2\text{O}$                         | 3388(br)                         | -----            | 3300, 3162       | 1670(s)           | 1606              | 1299               | 1030              | 692               | 534               | 912                              |
| 4   | $[(\text{H}_2\text{L}^1)_2\text{UO}_2(\text{OAc})_2]\cdot 4\text{H}_2\text{O}$ | 3350(br)                         | 3388(m)          | 3303,3256        | 1675(s)           | 1611              | 1267               | 1031              | 594               | 509               | 902                              |
| 5   | $[(\text{HL}^1)_2\text{Sn}]\cdot 3\text{H}_2\text{O}$                          | 3400(br)                         | ---              | 3316,3256        | 1676(s)           | 1608              | 1313               | 1033              | 571               | 505               |                                  |
| 6   | $[(\text{H}_2\text{L}^1)_2\text{Cd}(\text{OAc})_2]$                            | -----                            | 3428(w)          | 3308,3267        | 1675(s)           | 1605              | 1266               | 1028              | 627               | 570               |                                  |
| 7   | $[(\text{HL}^1)_2\text{UO}_2]$   | -----                            | -----            | 3300,3170        | --                | 1600              | 1311               | 1021              | 638               | 508               | 897                              |
| 8   | $[(\text{HL}^1)\text{HoCl}_2(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$    | 3410(br)                         | -----            | 3328,3203        | 1646              | 1609              | 1298               | 998               | 515               | 420               |                                  |
| 9   | $[(\text{HL}^1)\text{RuCl}_2(\text{H}_2\text{O})]\cdot 6\text{H}_2\text{O}$    | 3390(br)                         | -----            | 3311,3268        | 1645              | 1595              | 1312               | 1034              | 571               | 506               |                                  |
| 10  | $[(\text{HL}^1)_2\text{Yb}](\text{NO}_3)$                                      | -----                            | 3423(br)         | 3300             | ----              | 1613              | 1290               | 1035              | 581               | 506               | 1385                             |
| 11  | $\text{NH}_4[\text{H}_2\text{L}^1\text{VO}_3]\cdot 2\text{H}_2\text{O}$        | -----                            | 3401(br)         | 3290,3201        | 1693(s)           | 1596              | 1294               | 1027              | 657               | 513               | 944,909                          |
| 12  | $[\text{HL}^1\text{HfCl}_3]\cdot 2\text{H}_2\text{O}$                          | 3480(br)                         | ----             | 3301, 3265       | 1693(s)           | 1596              | 1295               | 1012              | 584               | 489               |                                  |
| 13  | $\text{H}_2\text{L}^2 (\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2)$        | -----                            | 3425(br)         | 3299, 3180       | 1665(s)           | 1606              | 1280               | 979               | 620               | 497               |                                  |
| 14  | $[(\text{HL}^2)_2\text{VO}]\cdot 2\text{H}_2\text{O}$                          | -----                            | ---              | 3298,3191        | 1666(s)           | 1595              | 1305               | 1012              | 612               | 511               |                                  |
| 15  | $[\text{HL}^2\text{ZrOCl}]\cdot 2\text{H}_2\text{O}$                           | 3360(br)                         | --               | 3295, 3206       | 1665(s)           | 1590              | 1298               | 991               | 600               | 505               |                                  |
| 16  | $[(\text{H}_2\text{L}^2)(\text{UO}_2)(\text{OAc})_2]$                          | ---                              | 3398(br)         | 3250,3150        | 1660(s)           | 1588              | 1299               | 1025              | 540               | 480               | 932                              |
| 17  | $[(\text{HL}^1)_2\text{Sn}]\cdot 2\text{H}_2\text{O}$                          | ---                              | ---              | 3289,3200        | 1667(s)           | 1595              | 1285               | 1012              | 560               | 475               |                                  |
| 18  | $[(\text{HL}^1)_2\text{Cd}(\text{OAc})_2]$                                     | ---                              | -----            | 3300,3195        | 1665(s)           | 1585              | 1280               | 1022              | 540               | 468               |                                  |
| 19  | $[(\text{HL}^2)_2(\text{UO}_2)(\text{NO}_3)_2]\cdot 2\text{H}_2\text{O}$       | 3380(br)                         | -----            | 3310,3200        | 1670(s)           | 1599              | 1276               | 1025              | 544               | 447               | 940                              |
| 20  | $[(\text{L}^2)\text{HoCl}(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$       | 3400(br)                         | -----            | 3310             | ---               | 1583              | 1255               | 1027              | 570               | 475               |                                  |
| 21  | $[(\text{HL}^2)_2\text{Ru}]\text{Cl}$  | -----                            | -----            | 3270,3140        | 1655(s)           | 1580              | 1311               | 1031              | 562               | 480               |                                  |
| 22  | $[(\text{L}^2)\text{Yb}(\text{NO}_3)]\cdot 2\text{H}_2\text{O}$                | -----                            | -----            | 3310             | ----              | 1598              | 1271               | 1027              | 575               | 465               |                                  |
| 23  | $\text{NH}_4[(\text{H}_2\text{L}^2)\text{VO}_3]$                               | -----                            | -----            | 3300,3180        | 1665(s)           | 1580              | 1284               | 1024              | 565               | 490               | 970, 918                         |
| 24  | $[\text{HL}^2\text{HfCl}_3]\cdot 6\text{H}_2\text{O}$                          | 3425(br)                         | -----            | 3290,3170        | 1670(s)           | 1605              | 1325               | 1020              | 570               | 510               |                                  |

plexes **2-12** and **14-24** are stable at room temperature. The complexes are insoluble in  $\text{H}_2\text{O}$  but sparingly soluble in common organic solvents such as ethanol, acetone, and chloroform but highly soluble in DMF and DMSO. The elemental analysis confirmed that the complexes **2-7**, **10**, **14**, **17-19** and **21-22** composed form ligand and metal ions with molar ratios equal to 2L:1M, However, the complexes **8**, **9**, **11-12**, **15-16**, **20** and **23-24** composed form ligand and metal ion with molar ratios equal to 1:1 *Table 1*. The analytical, *Table 1* and spectral data *Tables 2* and *3* are compatible with the suggested structure. The structure was formulated as shown in *Figs. 2-7*.

### Mass Spectra of the Ligands

The mass spectra of the Schiff base ligands  $\text{H}_2\text{L}^1$  and  $\text{H}_2\text{L}^2$  revealed the molecular ion peaks at  $m/e$  269 and 319, which are coincident with the formula weights of the two ligands (269.31) and (319.36), respectively, supporting the identity of their structures *Fig. 1*.

### IR spectra

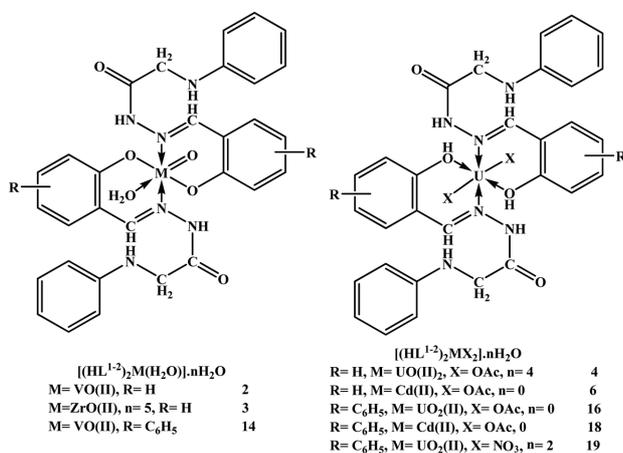
The infrared spectral data of the ligands and their metal

complexes **2-12** and **14-24** were presented in *Table 2*. The infrared spectra of the ligands  $\text{H}_2\text{L}^1$  and  $\text{H}_2\text{L}^2$  showed a strong band at 1680 and 1665  $\text{cm}^{-1}$  which assigned to carbonyl group  $\nu(\text{C=O})$  of the two ligands respectively. The two medium bands in the 3320-3299 and 3270-3180  $\text{cm}^{-1}$  ranges may be assigned to the  $\nu(\text{NH})$  amino groups of  $\text{NHCH}_2$  and  $\text{CONH}$ , indicating that the ligand is present in the ketonic form in the solid state.<sup>21,22</sup> The spectrum showed also broad bands at 3438 and 3425  $\text{cm}^{-1}$  which may be assigned to the stretching vibration of the phenolic hydroxyl associated through an intra-molecular hydrogen bonding.<sup>21-23</sup> The relatively strong bands located in the 1620-1606, 1275-1280, 958-979  $\text{cm}^{-1}$  ranges assigned to the  $\nu(\text{C=N})$  of the azomethine group, phenolic  $\nu(\text{C-OH})$ <sup>18</sup> and  $\nu(\text{N-N})$  respectively.<sup>22</sup>

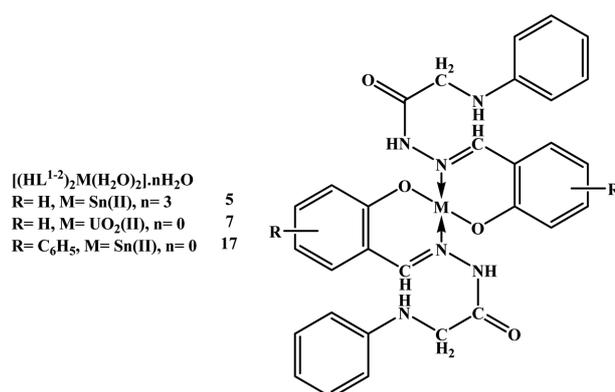
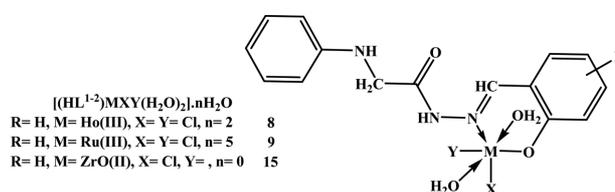
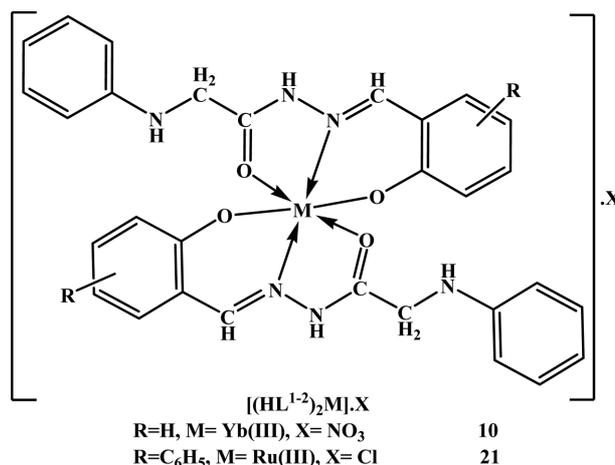
The mode of bonding of the ligands with the metal ions can be predicted by comparison the infrared spectra of the complexes **2-12** and **14-24** with that of the free ligands. In case of complexes **2**, **3**, **5**, **7-9**, **12-15**, **17-20**, **22** and **24** the bands characteristic to the phenolic hydroxyl group disappeared indicating that, it takes part in the bonding to the metal ions in the deprotonated form. In the case of com-

**Table 3.** Electronic spectra of the ligands and their metal complexes

| No. | Compounds                              | Bands in DMF                 |
|-----|--|------------------------------|
| 1   | $H_2L^1$ ( $C_{15}H_{14}N_3O_2$ )      | 335, 315, 255                |
| 2   | $[(HL^1)_2(VO)] \cdot H_2O$            | 690, 580, 535, 340, 325, 260 |
| 3   | $[(HL^1)_2 ZrO] \cdot 5H_2O$           | 465, 390, 330, 320, 260      |
| 4   | $[(H_2L^1)_2 UO_2(OAc)_2] \cdot 4H_2O$ | 450, 375, 330, 320, 260      |
| 5   | $[(HL^1)_2 Sn] \cdot 3H_2O$            | 685, 390, 360, 345, 315, 255 |
| 6   | $[(H_2L^1)_2 Cd(OAc)_2]$               | 345, 325, 255                |
| 7   | $[(HL^1)_2 UO_2]$                      | 335, 315, 255                |
| 8   | $[(HL^1) HoCl_2(H_2O)] \cdot 4H_2O$    | 615, 490, 430, 300, 255      |
| 9   | $[(HL^1) RuCl_2(H_2O)] \cdot 6H_2O$    | 630, 520, 340, 320, 260      |
| 10  | $[(HL^1)_2 Yb] \cdot NO_3$             | 570, 465, 325, 305, 260      |
| 11  | $NH_4[(H_2L^1) VO_3] \cdot 2H_2O$      | 550, 465, 330, 310, 260      |
| 12  | $[HL^1 HfCl_3] \cdot 2H_2O$            | 430, 345, 300, 260           |
| 13  | $H_2L^2$ ( $C_{19}H_{17}N_3O_2$ )      | 390, 375, 360, 345, 310, 255 |
| 14  | $[(HL^2)_2 VO]$                        | 710, 575, 520, 420, 330, 255 |
| 15  | $[HL^2 ZrOCl] \cdot 2H_2O$             | 420, 330, 255                |
| 16  | $[(H_2L^2)(UO_2)(OAc)_2]$              | 530, 350, 320, 260           |
| 17  | $[(HL^2)_2 Sn]$                        | 565, 400, 380, 325, 310, 255 |
| 18  | $[(HL^2)_2 Cd(OAc)_2]$                 | 345, 325, 255                |
| 19  | $[(HL^2)_2(UO_2)(NO_3)_2] \cdot 2H_2O$ | 505, 460, 370, 335, 260      |
| 20  | $[(L^2) HoCl(H_2O)]$                   | 645, 500, 380, 330, 260      |
| 21  | $[(HL^2)_2 Ru] \cdot Cl$               | 610, 500, 400, 335, 255      |
| 22  | $[(L^2) Yb(NO_3)]$                     | 590, 430, 375, 310, 245      |
| 23  | $NH_4[(H_2L^2) VO_3]$                  | 520, 480, 345, 255           |
| 24  | $[HL^2 HfCl_3] \cdot 6H_2O$            | 455, 345, 300, 260           |

**Fig. 2.** structure representation of Cd(II), VO(II), ZrO(II) and UO<sub>2</sub>(II) complexes.

plexes **4**, **6**, **11**, **16** and **23** the characteristic band of the phenolic hydroxyl group is present and shifted to lower wave number by 6-46 cm<sup>-1</sup> indicated that the ligand coordinated to the metal ions through the protonated phenolic hydroxyl oxygen. This suggestion is supported by the higher or lower shifting of the  $\nu(C-O_{phenolic})$  band which

**Fig. 3.** structure representation of Sn(II) and UO<sub>2</sub>(II) complexes **5**, **7** and **17**.**Fig. 4.** structure representation of Ho(III) Ru(III) and ZrO(II) complexes **8**, **9** and **15**.**Fig. 5.** structure representation of Yb(III) and Ru(III) complexes **10** and **21**.

appeared in the spectra of the metal complexes in the 1330-1266 range.<sup>24-26</sup> The bands of carbonyl  $\nu(C=O)$  and  $\nu(NH)$  amino groups are appeared at the same position indicating that these groups do not participate in the coordination to the metal ions except complexes **10** and **21** in which shifted to lower frequency indicating the participation of the carbonyl oxygen in coordination with the Ru(III) or Yb(III) ions. But in case of complexes **20** and **22** the characteristic band of carbonyl  $\nu(C=O)$  and amino  $\nu(NH)$  groups disappeared indicating that, the ligand bonding with Ru(III) and Yb(III) in dibasic form through

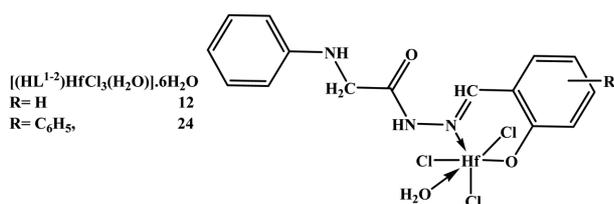


Fig. 6. structure representation of Hf(IV) complexes 12 and 24.

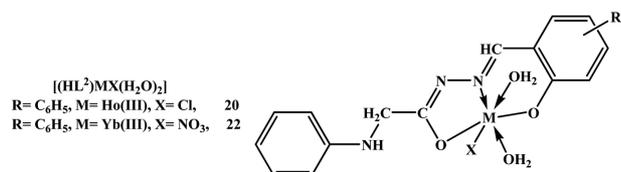


Fig. 7. structure representation of Ho(III) and Yb(III) complexes 20 and 22.

the enolic carbonyl oxygen and deprotonated phenolic hydroxyl oxygen. The characteristic band of the azomethine group  $\nu(C=N)$  was shifted to lower frequency compared to that of the free ligand by a value ranged between 6 and 31  $cm^{-1}$ . This indicated that, the azomethine nitrogen atom coordinated with the metal ions.<sup>17</sup> On the other hand the characteristic band of  $\nu(N-N)$  was shifted from 958 and 979  $cm^{-1}$  in the spectrum of the ligands to 991-1035  $cm^{-1}$  in the spectra of all complexes. The lowering of the C=N frequency and also the increasing in the frequency of N-N confirmed that the azomethine nitrogen atom participated in coordination with the metal ions. This shifting in the  $\nu(N-N)$  band to higher energy region is due to diminished repulsion between the ions pair of adjacent nitrogen atoms upon coordination.<sup>17</sup> The appearance of a new bands appeared in the ranges 504-692 and 420-534  $cm^{-1}$  for different complexes may be assigned to the  $\nu(MO)$  and  $\nu(MN)$  respectively.<sup>27,28</sup> The  $\nu_{as}(CO_2^-)$  and  $\nu_s(CO_2^-)$  of the free acetate ion are ca. 1560 and 1416  $cm^{-1}$  respectively. In unidentate acetate complexes  $\nu(C=O)$  is higher than  $\nu_s(CO_2^-)$  and  $\nu(C-O)$  is lower than  $\nu_{as}(CO_2^-)$ . As a result the separation between the two  $\nu(CO)$  is much larger in unidentate than in free ion but in bidentate the separation is lower than in the free ion while in bridging bidentate the two  $\nu(CO)$  is closer to the free ion.<sup>29</sup> In the case of complexes **4**, **6**, **16** and **18**, there are two new bands appeared in the 1550-1561 and 1348-1377  $cm^{-1}$  ranges which are attributed to the symmetric and asymmetric stretching vibration of the acetate group. The differences between these two bands are in the 169-194  $cm^{-1}$  range which indicates that, the acetate ion coordinates to the metal ion in unidentate manner.<sup>29,30</sup> The infrared spectra of nitrate complexes **10**, **19** and **22** show the presence

of coordinated or ionic nitrates. The two strong bands associated with the asymmetric stretch ( $C_{2v}$  symmetry, coordinated  $NO_3$  group) appear at 1435, 1333 and 1426  $cm^{-1}$  for the complexes **19** and **22** respectively. The difference of the nitrate stretching fundamentals at  $\sim 1400$  and  $\sim 1300$   $cm^{-1}$  ( $\Delta\nu$ ) has been used to distinguish between the degree of covalency of the nitrate coordination. This difference ( $\Delta\nu$ ) increases as the coordination of the nitrate group increases for monodentate to bidentate and/or bridging increases. The magnitude is used to establish the type of nitrate coordination. In these complexes **19** and **22**  $\Delta\nu$  are 99 and 101  $cm^{-1}$  respectively and are typical of unidentate bonding of nitrates. The spectrum of complex **10** shows band at 1385  $cm^{-1}$  which is characteristic for ionic nitrates ( $D_{3h}$  symmetry, free  $NO_3$  ion).<sup>29,31-33</sup>

The infrared spectra of the vanadyl complexes **2** and **14** exhibit a sharp band in the 971-987  $cm^{-1}$  was assigned to  $\nu(V=O)$  stretch.<sup>34</sup> The spectra of zirconyl complexes **3** and **15** show band at 736 and 798 respectively assigned to the  $\nu(Zr=O)$ .<sup>35</sup> The infrared spectra of the uranyl complexes **4**, **7**, **16** and **19** reveal bands in the 940-954  $cm^{-1}$  range which may be attributed to  $\nu(O=U=O)$ .<sup>36,37</sup> The spectra of vanadate complexes **11** and **23** show bands at 3325, 1418 and 3300, 1432  $cm^{-1}$  attributed to the NH stretching and deformation of  $NH_4^+$  group respectively. In addition bands in the 977-946  $cm^{-1}$  assigned to  $\nu(V=O)$ .<sup>34,38,39</sup> In complexes **2-5**, **8-9**, **11-12**, **15**, **19-20** and **24** there are a broad band appeared in the 3347-3480  $cm^{-1}$  range assigned to lattice water molecules.<sup>39</sup>

The spectral and elemental analyses indicated that, the hydrazone ligands behave as neutral bidentate ( $H_2L^{1-2}$ ), monobasic bidentate ( $HL^{1-2}$ ) or monobasic tridentate ligands toward the metal ions, bonded with the metal ion via protonated or deprotonated phenolic hydroxyl oxygen atom, azomethine nitrogen atom or ketonic carbonyl oxygen atom.

### The molar conductivity

The molar conductivity of  $1 \times 10^{-3} M$  solution of the metal complexes in DMSO at room temperature are in the 8.4-90.1  $\Omega^{-1}cm^2mol^{-1}$  range indicating the non electrolytic nature of these complexes except complexes **10**, **11**, **21** and **23**. These confirmed that the anion is coordinated to metal ion. The considerably high values of some complexes may be due to the partial solvolysis by DMSO. However, complexes **10**, **11**, **21** and **23** have values 72.5, 90.1, 79.3 and 65.6  $\Omega^{-1}cm^2mol^{-1}$ , indicating the electrolytic nature of this complex.<sup>40</sup> These data are agreeable with Greenwood *et al.* studies.<sup>41</sup> They have suggested 50-70  $\Omega^{-1}cm^2mol^{-1}$  as the range for 1:1 electrolyte in DMSO.

### Electronic absorption spectra of the ligands and their metal complexes

The electronic absorption spectral bands of the ligands and their metal complexes in DMSO are reported in *Table 3*. The data reveals that, the ligands comprise three sets of bands. The first set of the shortest wave length appeared at 250-265 nm may be assigned to the  $\pi \rightarrow \pi^*$  transition in the benzenoid moieties which nearly unchanged on complexation.<sup>22,42</sup> The second set appears at 310-320 and 345-395 nm may be assigned to  $n \rightarrow \pi^*$  of the azomethine and carbonyl group.<sup>22,39</sup> These bands shifted to higher energy on complexation indicating the participation of these groups in coordination with metal ions. The spectra of vandyl(II) complexes **2** and **14** in DMSO solution show that, there are three bands at 690, 575, 520 and 710, 580, 535 nm respectively which may be assigned to  ${}^2B_2(d_{xy}) \rightarrow E(d_{xz}, d_{yz})$ ,  ${}^2B_2(d_{xy}) \rightarrow {}^2B_1(d_{x^2-y^2})$  and  ${}^2B_2(d_{xy}) \rightarrow {}^2A_1(d_{z^2})$  transitions indicating that, the vanadyl(II) complexes have distorted octahedral structures (*Fig. 2*).<sup>43-45</sup> However the electronic absorption spectra of ruthenium(III) complexes **9** and **21** in DMSO solution displays two bands at 520, 630 and 500, 610 nm. The first band is due to LMCT transition and the second is assigned to  ${}^2T_{2g} \rightarrow {}^2A_{2g}$  transition. The band positions are similar to those observed for other octahedral ruthenium(III) complex (*Fig. 4, 5*).<sup>46</sup> The electronic spectra of the uranyl complexes **4, 7, 16** and **19** exhibit one band in the 490-530 nm which may be assigned to ligand to uranium charge-transfer transitions.<sup>47</sup> The diamagnetic complexes zirconium(II), tin (II), cadmium(II) and hafnium(IV) complexes **3, 5, 6, 12, 15, 17, 18** and **24** do not show d-d transitions. The bands observed in the 420-465 nm range may be due to intraligand transition and (LMCT) (*Table 4*).<sup>48,49</sup> The electronic spectral data of the ytter-

bium(III) and holmium(III) complexes **8, 10, 20** and **22** show weak bands in the 430-645 nm range because of weak f-f transition.<sup>50-52</sup>

### Thermal Analyses (DTA and TG)

The results of TG and DTA analyses of complexes are shown in *Table 4*. The results show good agreement with theoretical formula as suggested from the analytical data (*Table 1*). Complexes **3, 4, 8** and **9** lost hydrate water mol-

**Table 5.** biological activities of the ligands and their metal complexes against bacteria and fungus

|     |   | Inhibition zone in mm   |                          |
|-----|---|-------------------------|--------------------------|
| No. | Compounds   | <i>Escherichia coli</i> | <i>Aspergillus niger</i> |
|     | DMSO  | 0                       | 0                        |
|     | Amphotricene B  | --                      | 17                       |
|     | Tetracycline  | 37                      | --                       |
| 1   | H <sub>2</sub> L <sup>1</sup> (C <sub>15</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> )        | 15                      | 18                       |
| 2   | [(HL <sup>1</sup> ) <sub>2</sub> (VO)]·H <sub>2</sub> O   | 22                      | 25                       |
| 3   | [(HL <sup>1</sup> ) <sub>2</sub> ZrO]·5H <sub>2</sub> O   | 23                      | 25                       |
| 4   | [(H <sub>2</sub> L <sup>1</sup> ) <sub>2</sub> UO <sub>2</sub> (OAc) <sub>2</sub> ]·4H <sub>2</sub> O | 22                      | 25                       |
| 6   | [(H <sub>2</sub> L <sup>1</sup> ) <sub>2</sub> Cd(OAc) <sub>2</sub> ]                                 | 19                      | 20                       |
| 8   | [(HL <sup>1</sup> ) <sub>2</sub> HoCl <sub>2</sub> (H <sub>2</sub> O)]·4H <sub>2</sub> O              | 25                      | 20                       |
| 10  | [(HL <sup>1</sup> ) <sub>2</sub> Yb(NO <sub>3</sub> ) <sub>3</sub> ]                                  | 17                      | 27                       |
| 11  | NH <sub>4</sub> [H <sub>2</sub> L <sup>1</sup> VO <sub>3</sub> ]·2H <sub>2</sub> O                    | 21                      | 18                       |
| 13  | H <sub>2</sub> L <sup>2</sup> (C <sub>19</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> )        | 17                      | 11                       |
| 14  | [(HL <sup>2</sup> ) <sub>2</sub> VO]  | 23                      | 28                       |
| 15  | [HL <sup>2</sup> ZrOCl] <sub>2</sub> ·2H <sub>2</sub> O   | 23                      | 16                       |
| 20  | [(L <sup>2</sup> )HoCl(H <sub>2</sub> O)]   | 25                      | 22                       |
| 21  | [(HL <sup>2</sup> ) <sub>2</sub> RuCl]  | 32                      | 20                       |
| 22  | [(L <sup>2</sup> )Yb(NO <sub>3</sub> ) <sub>3</sub> ]   | 23                      | 25                       |
| 23  | NH <sub>4</sub> [(H <sub>2</sub> L <sup>2</sup> )VO <sub>3</sub> ]                                    | 23                      | 19                       |
| 24  | [HL <sup>2</sup> HfCl <sub>3</sub> ]·6H <sub>2</sub> O  | 18                      | 22                       |

**Table 4.** Thermal data for some metal complexes

| Comp. No. | Temp. (C <sup>o</sup> ) | DAT (peak) | TG (Wt. loss (%)) |         | Assignment   |
|-----------|-------------------------|------------|-------------------|---------|--|
|           |                         |            | Calc.             | (Found) |  |
| (3)       | 90                      | Endo.      | 12.24             | (12.8)  | Loss of hydration water (5 H <sub>2</sub> O)                       |
|           | 540                     | Exo.       | 73.19             | (72.65) | Decomposition with the formation of ZrO <sub>2</sub>               |
| (4)       | 100                     | Endo.      | 9.02              | (9.20)  | Loss of hydration water (5 H <sub>2</sub> O)                       |
|           | 260                     | Endo.      | 11.80             | (12.00) | Loss of two acetate atoms (2HOAc)                                  |
|           | 540                     | Exo.       | 53.93             | (52.86) | Decomposition with the formation of UO <sub>3</sub>                |
| (8)       | 95                      | Endo.      | 9.10              | (8.89)  | Loss of hydration water (3 H <sub>2</sub> O)                       |
|           | 285                     | Endo.      | 3.03              | (3.00)  | Loss of coordinated water (1 H <sub>2</sub> O)                     |
|           | 295                     | Endo.      | 11.93             | (12.20) | Loss of two chloride atoms (2HCl)                                  |
|           | 550                     | Exo.       | 45.32             | (46.20) | Decomposition with the formation of HoO <sub>2</sub>               |
| (9)       | 80                      | Endo.      | 19.08             | (18.90) | Loss of hydration water (6 H <sub>2</sub> O)                       |
|           | 140                     | Endo.      | 3.18              | (2.95)  | Loss of coordinated water (1 H <sub>2</sub> O)                     |
|           | 270                     | Endo.      | 12.52             | (12.25) | Loss of hydrochloride molecules (2 HCl)                            |
|           | 530                     | Exo.       | 47.55             | (47.80) | Decomposition with the formation of Ru <sub>2</sub> O <sub>3</sub> |

ecules in the temperature 75-100 °C range and were accompanied by an endothermic peak. The coordinated water molecules were eliminated from their complexes at relatively higher temperature than those of the hydrate water molecules (Table 4). The removal of an HCl molecule was observed for **8** and **9** complexes in the temperature 240-310 °C range, which was accompanied by an endothermic peak. The complexes decompose through degradation of the hydrazone ligand at a temperature over than 500 °C leaving metal oxides (530-550) range.

### Biological activity

The antibacterial and antifungal activities of the ligand and its metal complexes were screened on bacterial and fungal strains using the disk diffusion method. It is important to note that the ligands and their metal complexes exhibit antifungal and antibacterial inhibitory effects than

parent ligands and the solution of metal ions. Most of metal complexes exhibit more antifungal activity than standard antifungal drug (amphotricene B). It is also clear that the ligand and its metal complexes have more antifungal activity than antibacterial activity. The inhibition zone diameter of the compounds is shown in Figs. 8 and 9. The order of antifungal activity of the compounds is **(14)**>**(10)**>**(4)**>**(2)=(22)**>**(3)**>**(20)**=**(24)**>**(6)**=**(8)**=**(21)**>**(23)**>**(H<sub>2</sub>L<sup>1</sup>)**=**(11)**>**(Amphotricene B)**>**(15)**=**(H<sub>2</sub>L<sup>2</sup>)**, however, the order of antibacterial activity of the compounds is **Tetracycline**>**(21)**>**(8)**=**(20)**>**(3)**>**(14)**=**(15)**=**(22)**=**(23)**>**(2)**=**(4)**>**(11)**>**(6)**>**(24)**>**(10)**=**(H<sub>2</sub>L<sup>2</sup>)**>**(H<sub>2</sub>L<sup>1</sup>)**. The increased activity of the metal complexes can be explained on the basis of chelation theory.<sup>53</sup> It is known that the chelation tends to make the ligand act as more powerful and potent fungicidal and bactericidal agents, thus killing more fungi and bacteria than the ligand. It is known that, in a com-

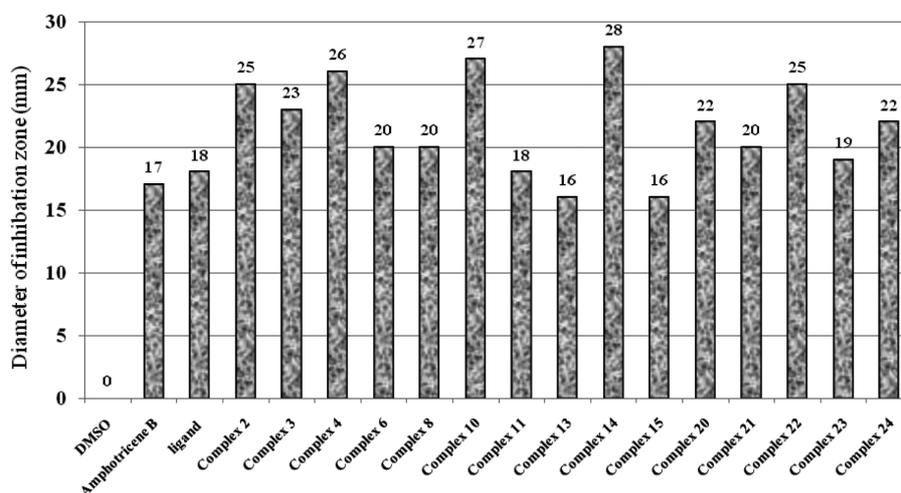


Fig. 8. Antifungal activity of the ligand and its metal complexes against Fungus (*Aspergillums Niger*).

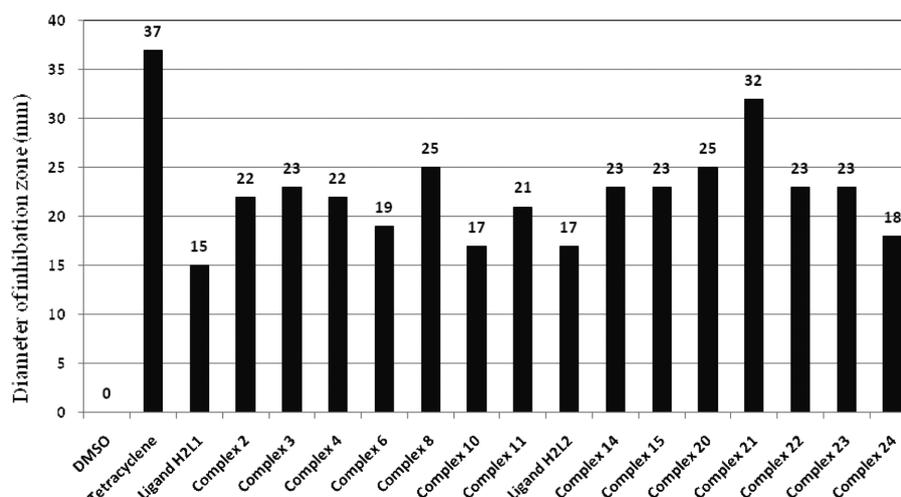


Fig. 9. Antibacterial activity of the ligands and their metal complexes against gram-negative bacterium (*E. coli*).

plex, the positive charge of the metal is partially shared with the donor atoms present in the ligands, and there may be  $\pi$ -electron delocalization over the whole chelating system.<sup>54</sup> This increases the lipophilic character of the metal chelate and favors its permeation through the lipid layer of the membranes. There are other factors which also increase the activity, which are solubility, conductivity, coordination mode and bond length between the metal and the ligand. The variation in the effectiveness of different compound against different organisms also depends either on the impermeability of the cell of the microbes or differences in ribosomes of microbial cells.<sup>55,56</sup> The variation of biological activity of the complexes may be due to change in electronic configuration of the metal and also, the environment around the metal ion.

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