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一些含三氮杂茂偶氮染料 O,N 供体的 Zr(Ⅱ)配合物的合成、表征和抗微生物活性

Abdalla M Khedr*,[1,2] Mohamed Gaber[1] Khalil M Saad-allah[3](埃及)
([1]Chemistry Department, Faculty of Science, Tanta University, Tanta 31111, Egypt)
([2]Chemistry Department, College of Applied Sciences, Umm Al-Qura University, Makkah, Saudi Arabia)
([3]Botany Department, Faculty of Science, Tanta University, Tanta 31527, Egypt)

摘要: 合成了 9 种 3-(2-羟基萘基-1-偶氮)-1,2,4-三氮唑(HL^1),3-(2,4-二羟苯基-1-偶氮)-1,2,4-三氮唑(HL^2),3-(2-羟基-3-羧基萘基-1-偶氮)-1,2,4-三氮唑(HL^3),3-(2-羟基-5-溴苯基-1-偶氮)-1,2,4-三氮唑(HL^4)和 3-(2-羟基-5-甲基苯基-1-偶氮)-1,2,4-1,2,4-三氮唑(HL^5)的 Zr(Ⅱ)配合物并用元素分析,摩尔电导,磁矩,IR,UV-Vis,^{1}H-NMR 以及热分析(TGA 和 DTA)对其进行了表征。结果表明 HL^1-HL^5 以二齿一元配体方式通过偶氮的氮原子和羟基基团的氧原子与 Zr(Ⅱ)离子配位生成单核配合物。用 4 种革兰氏阴性菌, 即大肠杆菌(Escherichia coli),粘质沙雷氏菌(*Serratia marcescens*),阴沟肠杆菌(*Enterobacter cloacae*)和普通变形杆菌(*Proteus vulgaris*),以及 2 种真菌,即白色念珠菌(*Candida albicans*)和黑曲霉菌(*Aspergillus niger*)对配体及其配合物的生物学活性进行了研究。最小抑菌浓度(MICs)用纸上杯碟琼脂扩散法测定,结果表明在大多数情况下,金属化的配合物的抗微生物活性与自由配体相比有所增强。

关键词: 配位方式; 生物学活性; 锆配合物; 三氮唑偶氮染料; 光谱表征; 热分析
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Synthesis, Characterization and Antimicrobial Efficiency of Some Zirconyl(Ⅱ) Complexes Involving O, N-Donor Environment of Triazole-Based Azodyes

Abdalla M Khedr*,[1,2] Mohamed Gaber[1] Khalil M Saad-allah[3]
([1]*Chemistry Department, Faculty of Science, Tanta University, Tanta* 31111, *Egypt*)
([2]*Chemistry Department, College of Applied Sciences, Umm Al-Qura University, Makkah, Saudi Arabia*)
([3]*Botany Department, Faculty of Science, Tanta University, Tanta* 31527, *Egypt*)

Abstract: Nine zirconyl(Ⅱ) complexes of 3-(2-hydroxynaph-1-ylazo)-1,2,4-triazole (HL^1), 3-(2,4-dihydroxyphen-1-ylazo)-1,2,4-triazole (HL^2), 3-(2-hydroxy-3-carboxynaph-1-ylazo)-1,2,4- triazole (HL^3), 3-(2-hydroxy-5-bromophen-1-ylazo)-1,2,4-triazole (HL^4) and 3-(2-hydroxy-5-methylphen-1-ylazo)-1,2,4-triazole (HL^5) have been synthesized and characterized by elemental analysis, molar conductance, magnetic moment and spectroscopic data (IR, electronic and ^{1}H-NMR) as well as thermal analyses (TGA and DTA). The results show that HL^1-HL^5 coordinate to zirconyl(Ⅱ) ions as bidentate monobasic ligands through the azo nitrogen and the oxygen of hydroxyl group yielding mononuclear complexes. The biological activity of the ligands and their complexes were studied on four Gram-negative bacteria *Escherichia coli*, *Serratia marcescens*, *Enterobacter cloacae* and *Proteus vulgaris* and two Gram-positive bacteria *Bacillus subtilis* and *Staphylococcus aureus* as well as two fungi *Candida albicans* and *Aspergillus niger*. The minimum inhibitory concentrations (MICs) of the prepared compounds were determined by agar diffusion assay using filter paper disc diffusion method. In most cases, metallization increases the antimicrobial activity compared with the free ligand.

Key words: Coordination modes,biological activity, Zirconyl complexes, triazole azodyes, spectral and thermal studies

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Supported by Tanta University.
*通讯联系人。E-mail:abkhedr2010@yahoo.com (A M Khedr)

0 Introduction

The compounds containing azo group (-N=N-) are known as azo dyes. They are versatile molecules and have received much attention in both fundamental research and applied research[1-2].

Also, heterocyclic azodyes have been used as chromogenic indicators for the spectrophotometric determination of several metal ions such as manganese, cobalt, nickel and zinc[5-15] as well as in extraction and separation of these metal ions[16-18]. They have wide applications in catalysis of disproportion of H_2O_2[19], nonlinear optics, optical storage media and chemosensors[20-23]. Furthermore, azodye ligands are potentially capable of forming with most transition metal ions stable complexes, which serve as model compounds for biologically important species. Azodyes accommodate different metal centers involving various coordination modes thereby allowing successful synthesis of metallic complexes with varied stereochemistry[24]. 1,2,4-triazoles and their derivatives represent an interesting class of compounds possessing a wide spectrum of biological activities such as antiviral[25], antifungal[26-28], anticancer[29-31], anti-inflammatory[32-33], antilubercular[34], antibacterial[35-37], and antitumor properties[38]. Moreover, the metal complexes of 1,2,4-triazole derivatives have been extensively investigated[39-43]. In view of these facts and in continuation of our consistent effort towards synthesis and characterization of such type of azo based compounds and their applications[44-51], the present investigation was undertaken to study zirconyl complexes of five triazole based ligands HL^1-HL^5 (Fig. 1). The prepared ligands and their zirconyl (Ⅱ) complexes were characterized by elemental and thermal analyses as well as spectroscopic measurements in addition to conductance and magnetic studies. Keeping in view the antiviral activity and therapeutic effect of the compounds containing triazole moiety[28-38] and the biological activity of the metal ion complexes[52]. The antimicrobial activities of the ligands and their complexes were examined against different bacterial and fungal pathogens.

1 Experimental

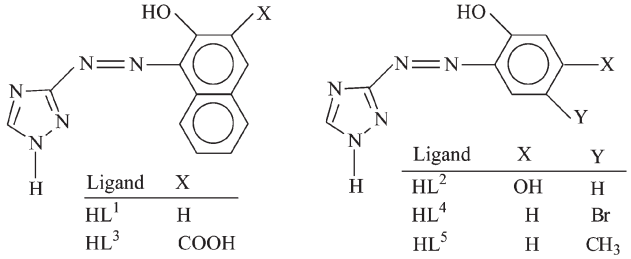
Reagent grade chemicals were used in the present study. The solvents were purified before use by standard methods.

1.1 Preparation of azo dye ligands

In order to prepare the ligands HL^1-HL^5, 3-amino-1,2,4-triazole (0.84 g, 0.01 mol) was dissolved in hydrochloric acid, cooling to 0~5 ℃, and adding an equivalent amount of ice-cooled sodium nitrite solution (0.69 g in 20 mL distilled water) with vigorous stirring. The so formed diazonium salt solution was then coupled with 2-naphtol (1.44 g, 0.01 mol), resorcinol (1.10 g, 0.01 mol), 3-hydroxy-2-naphtoic acid (1.88 g, 0.01 mol), *p*-bromophenol (1.73 g, 0.01 mol) or *p*-hydroxytoluene (1.08 g, 0.01 mol) according to the recommended method for preparation of azo compounds[52]. The product was filtered off, recrystallized from ethanol and subjected to melting point measurements, elemental and spectral analyses to confirm their high purity. Structures of the azodyes HL^1-HL^5 are presented in Fig.1.

1.2 Synthesis of ZrO(II) complexes

Complexes **1**~**9** were prepared by the dropwise addition of a hot (60 ℃) methanolic solution of $ZrOCl_2 \cdot 2H_2O$ to a hot (60 ℃) methanolic solution of ligand (HL^1, HL^2, HL^3, HL^4 or HL^5) in molar ratio of 1∶1 or 1∶2 (metal/ligand). The mixture was refluxed for 8 h. The



Ligand	X
HL^1	H
HL^3	COOH

Ligand	X	Y
HL^2	OH	H
HL^4	H	Br
HL^5	H	CH_3

Fig.1 Structures of the azodye ligands (HL^1-HL^5)

precipitates formed after cooling were filtered off, washed with ethanol, then with diethyl ether and dried under vacuum over anhydrous $CaCl_2$.

1.3 Analysis and physical measurements

Elemental analyses for C, H and N of the ligands and zirconyl (Ⅱ) complexes were performed using a Perkin Elmer 2400 elemental analyzer at the Micro-analytical Unit of Cairo University, Egypt. The metal contents were determined gravimetrically by converting the compounds into ZrO_2. Molar conductance was measured on a conductivity bridge of the type 523 conductometer using 10^{-3} mol·L^{-1} DMF solutions. IR spectra of the ligands and their metal complexes were measured using KBr discs with a Perkin-Elmer (model 1430) infrared spectrophotometer covering the range 4 000 ~200 cm^{-1}. Electronic absorption spectra in the 200 ~700 nm region were recorded on a Shimadzu UV-Vis 240 spectrophotometer. Magnetic susceptibilities were measured at 25 ℃ by the Gouy method using mercuric tetrathiocyanato-cobaltate(Ⅱ) as the magnetic susceptibility standard. Molar susceptibilities were corrected for diamagnetism of the component atoms applying the Pascals constants [54]. ^{1}H NMR spectra were measured in DMSO on a VARIAN UNITY-INOVA 400 (400 MHz) spectrometer using tetramethylsilane as internal reference. Chemical shifts of ^{1}H NMR were expressed in parts per million (ppm, δ units), and coupling constant was expressed in units of hertz (Hz). Thermal analyses (TGA and DTA) were carried out under nitrogen using a Shimadzu TG-50 and DT-50 thermal analyzers with heating rate of 10 ℃·min^{-1} from ambient temperature up to 800 ℃.

1.4 In-vitro antibacterial and antifungal activities

The investigation of the biological activities of the synthesized azodye ligands and their zirconyl complexes were carried out in the Botany Department, Faculty of Science, Tanta University.

1.4.1 Test microorganisms

After Gram-staining procedure, Gram-negative cells appear pink. The Gram-negative bacteria used in this study were Escherichia coli, Serratia marcescens, Enterobacter cloacae and Proteus vulgaris. The thick cell wall of a Gram-positive organism retains the crystal violet dye used in the Gram-staining procedure, so the stained cells appear purple under magnification. Gram-positive bacteria used in this study were *Bacillus subtilis* and *Staphylococcus aureus*. *B. subtilis* is mostly involved in Urinary infection, wound, ulceration and septicemia. *S. aureus* is the mild stone of Gram-positive bacteria and it is a causative agent of pneumonia, meningitis and food poisoning. The tested bacteria were obtained from the culture collection of Bacteriology Unit, Department of Botany, Faculty of Science, Tanta University. Pathogenic fungi are responsible for a number of diseases in human and animals. A number of pathogenic strains of fungi are represented in *Candida albicans* and *Aspergillus niger*. A. niger is less likely to cause human disease than some other Aspergillus species, but, if large amounts of spores are inhaled, a serious lung disease, aspergillosis can occur. The tested fungi were obtained from the culture collection of Mycology Unit, Department of Botany, Faculty of Science, Tanta University.

1.4.2 Media used and antimicrobial assay

Nutrient and Mannitol salt agar media were used for growing and maintaining the tested bacteria and Saparouds-agar ~medium was used for growing and maintaining the tested fungi. The antimicrobial spectra of the prepared ligands and their complexes were determined as powdered samples by the cut-plug method on plates seeded with the tested bacteria (*E. coli*, *S. marcescens*, *P. vulgaris*, *En. Cloacae* and *B. subtilis*.) on nutrient agar (which contained per liter: peptone (3 g), beef extract (5 g), NaCl (5 g) and agar (20 g) at pH value of 7), but *S. aureus* was seeded on Mannitol salt agar medium (which contained per liter: enzymatic digest of casein (5 g), enzymatic digest of animal tissue (5 g), beef extract (1 g), *D*-mannitol (10 g), NaCl (5 g), phenol red (0.025 g) and agar (15 g) at pH value of 7.4). Also, the antimicrobial spectrum of the synthetic compounds was determined as powdered samples by the cut-plug method on plates seeded with the tested fungi (*C. albicans* and *A. niger*) on

Saparouds agar medium (which contained per liter: glucose (40 g), peptone (10 g) and agar (20 g) at pH 6.0). After solidification, the wells were made using cork borer and each was filled with powdery compounds (10 mg). The plates were then incubated at 37 ℃ for 24 h, after which the diameters of the inhibition zones were measured. Compounds produced the highest inhibition zones were selected and assayed further at different concentrations in suspensions to quantify their inhibitory effects[55].

1.4.3 Determination of minimum inhibitory concentrations (MICs)

The minimum inhibitory concentrations (MICs) for synthetic compounds were determined by agar diffusion assay using filter paper disc diffusion method [56]. It was carried out by impregnation of different concentrations of synthesized compounds (0, 10, 25 and 50 $\mu g \cdot mL^{-1}$) in DMSO as a solvent and then placed on filter paper discs of the same diameter (6 mm). The agar plate dilution method was used to inoculate the bacteria in the plate. The medium was seeded with 100 μL of inoculum size 5×10^5. The impregnated discs containing the tested samples of different concentrations were placed on the agar medium seeded with tested microorganisms. Standard antibiotic discs (Ampicillin, 5 $\mu g \cdot mL^{-1}$) and antifungal discs (Itraconazole 50 $mg \cdot mL^{-1}$) were used as positive controls and blank discs (impregnated with DMSO) were used as negative control. The plates were then incubated at 37 ℃ for 24 h to allow maximum growth of the microorganisms. The antimicrobial activities of the tested samples were determined by measuring the diameter of zone of inhibition expressed in millimeter. The inhibition zones were measured in triplicates and expressed as mean±SD[57].

2 Results and discussion

All the prep ared compounds are colored, non-hygroscopic, crystalline solid and stable at room temperature. The complexes are insoluble in water and common organic solvents but moderately soluble in DMF and DMSO. They are highly stable under normal conditions. The purity of the prepared compounds are confirmed using thin layer chromatography (TLC) technique and the spots are visualized under UV light and by spraying with iodine vapor.

2.1 Elemental analysis and molar conductance data

The complexes were formulated from the analytical and physical data which support the suggested formulae listed in Table 1. The molar conductance values of the complexes in DMF (1 $mmol \cdot L^{-1}$) at 25 ℃ lie in the 0.42~2.21 $S \cdot cm^2 \cdot mol^{-1}$ range, indicating that, all the complexes are not electrolytes. These confirm that the anions are coordinated to the metal ion[58]. The results obtained are in good agreement with those calculated for the suggested formulae (Fig. 2) and confirm the high purity of all obtained compounds.

2.2 IR spectra and bonding modes

IR spectral data of the ligands (HL^1~HL^5) and their ZrO(Ⅱ) complexes are summarized in Table 2. Based on the obtained spectroscopic and analytical data, the mode of bonding in the formed zirconyl complexes can be represented as in Fig.2.

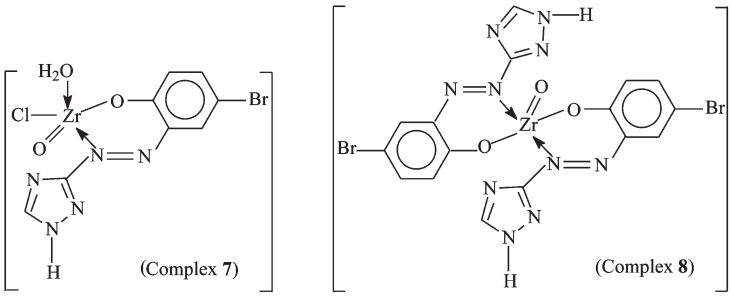


Fig.2 Structure representation of zirconyl(Ⅱ) complexes **7** and **8**

Table 1　Analytical and physical data of HL^1-HL^5 and their ZrO(Ⅱ) complexes[a] (1~9)

Ligand/complexes Molecular formula (Empirical formula)	Mol. Wt. (Calcd.)	Color (Δ_m)	Microanalysis Found (Calcd.) / %				
			C	H	N	Cl	M
HL^1	239.5	Orange	60.6	3.8	29.2	—	—
($C_{12}H_9N_5O$)	(239.24)	(—)	(60.25)	(3.79)	(29.27)		
[$ZrOL^1Cl(H_2O)$]	399.2	Red	36.45	2.56	17.22	9.43	23.12
($C_{12}H_{10}ClN_5O_3Zr$)(**1**)	(398.92)	(0.42)	(36.13)	(2.53)	(17.56)	(9.02)	(22.87)
[$ZrO(L^1)_2$]	584.5	Red	48.99	2.75	12.26	5.87	15.95
($C_{24}H_{16}N_{10}O_3Zr$)(**2**)	(583.68)	(0.51)	(49.39)	(2.76)	(12)	(6.07)	(15.63)
HL^2	205	Yellow	46.98	3.13	33.78	—	—
($C_8H_7N_5O_2$)	(205.18)	(—)	(46.83)	(3.44)	(34.13)		
[$ZrOL_2Cl(H_2O)$]	365.22	Brown	26.69	2.24	18.82	9.55	25.46
($C_8H_8ClN_5O_4Zr$)(**3**)	(364.86)	(0.9)	(26.34)	(2.21)	(19.2)	(9.72)	(25)
[$ZrO(L_2)_2$]	515.98	Brown	37.65	2.38	13.11	7.22	17.33
($C_{16}H_{12}N_{10}O_5Zr$)(**4**)	(515.56)	(0.76)	(37.28)	(2.35)	(13.58)	(6.89)	(17.69)
HL^3	283.5	Red	55.62	3.32	24.83	—	—
($C_{13}H_9N_5O_3$)	(283.25)	(—)	(55.13)	(3.2)	(24.73)		
[$ZrOL^3Cl(H_2O)$]	423.45	Buff	36.66	2.36	17.01	7.97	22.01
($C_{13}H_{10}ClN_5O_5Zr$)(**5**)	(422.93)	(1.26)	(36.92)	(2.38)	(16.56)	(8.38)	(21.57)
[$ZrO(L^3)_2$]	672.11	Buff	46.21	2.46	10.85	5.64	13.92
($C_{26}H_{16}N_{10}O_7Zr$)(**6**)	(671.7)	(1.42)	(46.49)	(2.4)	(10.43)	(5.29)	(13.58)
HL^4	269	Red	35.96	2.23	26.52	—	—
($C_8H_6N_5OBr$)	(268.07)	(—)	(35.84)	(2.26)	(26.13)		
[$ZrOL^4Cl(H_2O)$]	428.32	Brown	22.95	1.64	16.73	7.85	21.79
($C_8H_7BrClN_5O_3Zr$)(**7**)	(427.75)	(2.21)	(22.46)	(1.65)	(16.37)	(8.29)	(21.33)
[$ZrO(L^4)_2$]	641.76	Brown	29.65	1.49	11.33	6.02	14.62
($C_{16}H_{10}BrN_{10}O_3Zr$)(**8**)	(641.35)	(2.18)	(29.96)	(1.57)	(10.92)	(5.53)	(14.22)
HL^5	203.54	Yellow	53.43	4.43	34.48	—	—
($C_9H_9N_5O$)	(203.02)	(—)	(53.2)	(4.46)	(34.47)		
[$ZrOL_5Cl(H_2O)$]	363.41	Brown	30.12	2.82	19.68	20.11	25.49
($C_9H_{10}ClN_5O_3Zr$)(**9**)	(362.88)	(0.75)	(29.79)	(2.78)	(19.3)	(19.3)	(25.14)

[a]All the synthesized complexes decompose with out melting above 270 ℃. Yield=81~83%

The ligands spectra show bands at 3 402~3 325, 3 178~3 119 and 1 452~1 400 cm^{-1} ranges due to ν(OH), ν(NH) and ν(N=N) groups, respectively[59]. The low values of ν(OH) are attributed to the intra-molecular hydrogen bonding between -OH and -N=N groups [59]. Thus, the higher frequency band is associated with a weaker hydrogen bond and the lower frequency band with a stronger hydrogen bond [60]. The spectra of solid complexes were compared with those of the ligands in order to know the mode of bonding. The IR spectra show that the ligands behave as monobasic bidentate ligands, coordinating through OH and nitrogen atom of N=N group. The mode of coordination is suggested by the following evidences: the stretching vibration band; ν(OH), of the hydroxyl group is hidden under the broad bands at 3 419~3 394 cm^{-1} in the spectra of the complexes as a result of the presence of coordinated water molecules which is in turns make it difficult to confirm the deprotonation of the hydroxyl group. The ν(N=N) of the azo group appears at 1 468~1 388 cm^{-1} after complexation indicating the coordination of the azo nitrogen to the metal ions[61]. The (H_2O)

Table 2 IR data of the ligands (HL^1~HL^5) and their ZrO(Ⅱ) complexes 1~9

Comp.	IR spectra / cm^{-1}							
	ν(OH) and /or $\nu(H_2O)$	ν(NH)	ν(C=O)	ν(N=N)	δ(OH)	γ(OH)	ν(M–O)	ν(M–N)
HL^1	3 375	3 119	–	1 400	–	–	–	–
1	3 403	3 120	–	1 439	1 210	847	584	464
2	–	3 118	–	1 468	–	–	583	463
HL^2	3 389	3 178	–	1 407	–	–	–	–
3	3 405	3 180	–	1 395	1 225	850	565	426
4	–	3 179	–	1 453	–	–	589	490
HL^3	3 325	3 134	1 620	1 452	–	–	–	–
5	3 398	3 132	1 622	1 398	1 195	840	585	480
6	3 419	3 133	1 623	1 397	–	–	584	479
HL^4	3 380	3 150	–	1 400	–	–	–	–
7	3 394	3 152	–	1 398	1 200	849	580	499
8	–	3 151	–	1 396	–	–	582	488
HL^5	3 402	3 154	–	1 405	–	–	–	–
9	3 407	3 152	–	1 388	1 230	820	586	486

and (H_2O) IR bands of the coordination water appear at 1 230~1 195 and 850~820 cm^{-1}, indicating the binding of water molecules to the metal ions. The simultaneous appearance of new bands in the 499~426 and 589~565 cm^{-1} regions are due to the ν (M-N) and ν (M-O) vibrations[62], respectively. The stretching C=O bands at 1 620 cm^{-1} of HL^3 appear at 1 622 and 1 623 cm^{-1} in the IR spectra of its complexes **5** and **6**, respectively, indicating that the carboxylic group of the ligand does not participate in complex formation [24]. The zirconyl complexes exhibit one strong band in the region ≈900~870 cm^{-1} which can be attributed to the ν(Zr=O) indicating the presence of $(Zr=O)^{2+}$ moiety in these complexes[63].

2.3 Electronic spectra and magnetic moment measurements

The UV-Vis spectral data of the ligands (HL^1~HL^5) and their ZrO (Ⅱ) complexes in DMF solution are summarized in Table 3.

HL^1~HL^5 show four bands; the first band appears within 220~258 nm range due to the moderate energy π-π* transition corresponding to $^1L_a \leftarrow {}^1A$ state, while the second band appears within 270~325 nm range due to the low energy π-π* transition corresponding to $^1L_b \leftarrow {}^1A$ state of the phenyl ring[64]. The ligands spectra display the third and forth bands at 360~390 and 440~500 nm ranges which can be assigned to the n-π* and charge transfer (CT) transitions within the whole molecule. The electronic spectra of ZrO(Ⅱ) complexes exhibit only highly intensive additional band in the region 510~620 nm attributable to the charge transfer transition besides the ligand bands. Also, ZrO (Ⅱ) complexes **1**~**9** do not show any d-d transitions as expected [65]. All zirconyl complexes **1**~**9** show diamagnetic properties[59].

2.4 ^{1}H NMR spectra

A comparative study between the ^{1}H NMR spectra of the free ligands (HL^1~HL^5) and those of their zirconyl complexes **1**~**9** was made in order to determine the center of chelation and the replaceable hydrogen upon complex formation (Table 3). ^{1}H NMR spectra of HL^1~HL^5 display a multiplet signal at 6.83 ~8.16 for hydrogens of the aromatic rings. In the spectra of ZrO(Ⅱ) complexes, these peaks have downfield shifts attributed to the increased conjugation upon complex formation[66]. The signal for the hydroxyl proton appearing as a singlet at 8.50~8.95 in the spectra of ligands is disappeared from the spectra of the ZrO(Ⅱ) complexes **1**~**9** denoting that, complex formation occurs via proton displacement from the hydroxyl group [67], *i.e.* the ^{1}H NMR spectra confirm the conclusions derived from the IR spectra (Fig.2). The spectrum of HL^3 shows a signal at 9.50

Table 3　UV-Vis and ^{1}H NMR data of HL^1~HL^5 and their ZrO(Ⅱ) complexes (1~9)

Comp.	Electronic spectra (λ_{max} / nm)		^{1}H NMR spectra / ppm	
	Intra-ligand transitions	CT transitions	δ_{Ar-H}	δ_{OH}
HL^1	250, 316, 397, 457	—	6.83~7.80	8.5
1	270, 320, 390, 480	520	6.92~7.87	—
2	265, 325, 385, 485	525	6.90~7.88	—
HL^2	255, 295, 380, 450	—	6.94~7.34	8.72
3	268, 285, 375, 480	620	7.02~7.42	—
4	260, 290, 360, 490	600	7.04~7.43	—
HL^3	261, 324, 350, 473	—	7.72~8.16	8.95
5	270, 290, 360, 480	510	7.83~8.27	—
6	276, 295, 372, 490	515	7.82~8.25	—
HL^4	258, 325, 390, 457	—	6.92~7.56	8.87
7	263, 340, 470	605	7.01~7.65	—
8	262, 335, 395, 465	595	7.03~7.67	—
HL^5	257, 320, 360, 495	—	7.06~7.65	8.82
9	264, 340, 510	606	7.15~7.74	—

assignable to the carboxylic proton. This signal has a very small shifts in the spectra of ZrO(Ⅱ) complexes revealing that the carboxylic group does not participate in complex formation. The changes and downfield shifts in the spectra of zirconyl complexes are good indications for participation of these functional groups of the ligands in coordination with the metal ions.

2.5　Thermal gravimetric analysis (TGA)

TGA gives excellent confirmation for the structure of the coordination compounds as well as their properties, nature of intermediate and final products of their thermal decomposition [68]. The results obtained from TGA curves are collected in Table 4.

The correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in terms of the proposed formulae of the complexes. The obtained results are used in the calculation of the metal content and molecular weight of the formed complexes where the percent of metallic residue are represented in the form of metal oxide. The initial weight loss occurred at 99~139 ℃ is interpreted as the loss of coordinated water molecules (for complexes containing H_2O). The TGA curves show partial decomposition of the organic part of the chelates in the second decomposition step within the temperature range of 200~400 ℃. At the

Table 4　Thermal data obtained from TGA curves of ZrO(Ⅱ) complexes (1~9)

Complex	Loss of coordinated water		Partial decomposition of the ligand		Metallic residue	
	T / ℃	Wt. loss / %	*T* / ℃	Wt. loss / %	*T* / ℃	Residue / %
$[ZrOL^1Cl(H_2O)]$(**1**)	100	4.52	400	30	590	30.89
$[ZrO(L^1)_2]$(**2**)	—	—	200	31	600	21.11
$[ZrOL_2Cl(H_2O)]$(**3**)	110	4.94	360	40	560	33.77
$[ZrO(L^2)_2]$(**4**)	—	—	365	28	570	23.9
$[ZrOL^3Cl(H_2O)]$(**5**)	125	4.26	340	38	700	29.14
$[ZrO(L^3)_2]$(**6**)	—	—	325	25	750	18.35
$[ZrOL^4Cl(H_2O)]$(**7**)	99	4.21	370	25	650	28.81
$[ZrO(L^4)_2]$(**8**)	—	—	400	30	742	19.21
$[ZrOL^5Cl(H_2O)]$(**9**)	139	4.97	271	20	660	33.96

final stage (560~750 ℃), the metal oxide is formed after decomposition of whole molecule from which the metal content is calculated. Also, the results of the molecular weights obtained by TGA are in good agreement with the values calculated using the results of microanalysis for these complexes and with those obtained from determination of the metal ion content after thermal decomposition of the metal chelates.

2.6 Differential thermal analysis and activation energy

DTA can be used to solve problems concerning the structure of the coordination compounds as well as to calculate the kinetic and thermodynamic data for the solid state reactions[69]. The results obtained from DTA curves are presented in Table 5.

The DTA curves of metal-complexes under investigation are characterized by the presence of one endothermic peak at the temperature range of 77 ~ 99 ℃. At these temperatures, water molecules are expelled followed by exothermic peak at 158~178 ℃. At these temperatures a phase change is liable to occur due to the change in crystal structure of the complex, *i.e.*, crystallographic phase transition. At temperature range of 356~629 ℃, exothermic peaks are observed since decomposition and combustion start followed by decarbonization of the organic material in presence of nitrogen and formation of the metallic residue (Table 5). All these data support the data obtained from TGA curves. According to the kinetic data obtained from the DTA curves (Table 5), the activation energy relates the thermal stability of the metal complexes, i.e., the values of activation energies increase as the maximum temperature of the decomposition increases reflecting higher stability of the complexes.

Table 5 Thermal data obtained from DTA curves ZrO(Ⅱ) complexes 1~9

Complex	1st peak			2nd peak			3rd peak		
	T	*E**	Δ*H**	*T*	*E**	Δ*H**	*T*	*E**	Δ*H**
1	87	−5.02	−8.01	172	4.51	0.81	428	43.5	37.67
2	77	−4.42	−7.33	168	2.74	−0.93	506	15.4	8.92
3	93	−7.08	−10.12	178	6.6	2.85	514	40.53	33.99
4	87	−7.78	−10.77	177	6.51	2.77	366	7.82	2.51
5	86	−4.81	−7.8	163	3.47	−0.16	629	32.29	24.79
6	78	−3.93	−6.84	166	3.93	0.28	476	22.08	15.85
7	78	−3.65	−6.57	158	2.32	−1.26	530	9.38	2.7
8	86	−5.16	−8.15	165	3.65	0.01	625	28.28	20.81
9	99	−5.49	−8.58	172	3.46	−0.24	356	6.58	1.35

T: temperature (℃), *E**: activation energy (kJ·mol^{-1}), Δ*H**: activation enthalpy (kJ·mol^{-1})

2.7 Antimicrobial activities

The antimicrobial activity (inhibition zones) of the tested compounds against different types of organisms are measured in triplicates and are reported in Table 6.

The antimicrobial agents available on the market have various drawbacks such as toxicity, narrow spectrum of activity and some also exhibit drug-drug interactions. In view of the high incidence of infections in immune compromised patients, demands for new antimicrobial agents with a broad spectrum of activity and good pharmacokinetic properties have increased[70]. To contribute in the field of medicinal and bioinorganic chemistry, consequently, the compounds synthesized have been evaluated for their antibacterial and antifungal activities against *Escherichia coli*, *Serratia marcescens*, *Enterobacter cloacae* and *Proteus vulgaris* as Gram-negative bacteria, *Bacillus subtilis* and *Staphylococcus aureus*, as Gram-positive bacteria and *Candida albicans* and *Aspergillus niger* as fungi. The obtained data shows that complexes **1**, **3** and **9** are the most active compounds against all organisms, except *A. niger*. Complexes **2**, **4**, **5**, **6**, **7** and **8** display high to

Table 6 Antimicrobial activity (inhibition zones mm) of ligands and their ZrO(Ⅱ) complexes 1~9

Comp.	Inhibition zone diameter / mm							
	P. vulgaris	*S. marcescens*	*En. cloacae*	*S. aureus*	*E. coli*	*B. subtilis*	*A. niger*	*C. albicans*
HL^1	—	8.0±0.1	11.2±0.2	—	—	—	8.0±0.2	—
1	10.8±0.1	12.3±0.1	13.2±0.4	8.0±0.2	11.5±0.3	14.0±0.5	17.3±0.7	—
2	—	9.0±0.3	12.2±0.2	7.0±0.3	—	9.0±0.4	12.0±0.3	—
HL^2	—	7.0±0.2	—	—	—	—	—	—
3	11.0±0.7	12.0±0.2	12.2±0.4	15.0±0.8	10.0±0.1	11.0±0.4	11.2±0.4	—
4	8.5±0.3	11.0±0.2	8.6±0.2	—	10.0±0.2	8.0±0.0	—	—
HL^3	—	8.0±0.2	8.0±0.2	—	—	—	8.0±0.4	—
5	—	10.0±0.4	11.0±0.3	—	—	—	10.0±0.3	—
6	—	9.0±0.3	10.0±0.4	—	—	—	9.0±0.4	—
HL^4	—	10.3±0.2	13.0±0.3	—	—	11.0±0.1	—	—
7	13.0±0.2	12.0±0.3	17.0±0.6	9.5±0.3	13.7±0.6	14.2±0.2	—	—
8	9.0±0.2	11.0±0.4	15.5±0.5	—	11.0±0.4	13.0±0.1	—	—
HL^5	9.0±0.5	11.0±0.1	11.8±0.4	15.2±1.1	8.6±0.3	8.2±0.3	—	—
9	12.0±0.0	16.5±0.4	28.0±1.2	23.0±0.5	13.0±0.4	10.0±0.3	8.0±0.1	—

DMSO was added to different organisms as control and showed no inhibition zone.

moderate activities against bacteria and fungi. All ligands show only moderate activities against the tested organisms. The minimum inhibitory concentrations (MICs) of the synthesized compounds are determined for each antimicrobial agent by using agar diffusion method (Table 7).

The great inhibition activity of HL^2, HL^3 and their complexes against some organisms compared with other compounds is attributed to the presence of the hydroxyl group which binds with the organisms cell wall or cell membrane[71]. It can be seen from Tables 6 and 7 that the antibacterial and antifungal of HL^1~HL^5 ligands may

Table 7 Minimum inhibitory concentrations (MICs) for ligands and their ZrO(Ⅱ) complexes 1~9

Comp.	Minimum inhibitory concentration (MIC) / ($\mu g \cdot mL^{-1}$)							
	P. vulgaris	*S. marcescens*	*En. cloacae*	*S. aureus*	*E. coli*	*B. subtilis*	*A. niger*	*C. albicans*
HL^1	—	50±2.2	25±2.2	—	—	—	50±2.2	—
1	50±0.1	25±2.1	10±2.4	50±2.2	50±2.3	25±2.3	10±2.1	—
2	—	50±1.3	10±2.1	50±2.3	—	50±2.4	25±2.3	—
HL^2	—	50±2.2	–	—	—	—	—	—
3	25±2.1	25±2.2	25±2.4	10±2.2	25±2.1	25±2.4	25±2.4	—
4	50±2.3	50±2.2	50±2.2	—	50±2.2	50±2.1	–	—
HL^3	—	50±2.2	50±2.2	—	—	—	50±2.4	—
5	—	50±2.4	50±2.3	—	—	—	50±2.3	—
6	—	50±2.3	50±2.4	—	—	—	50±2.4	—
HL^4	—	50±2.2	25±2.3	—	—	25±2.1	—	—
7	25±2.2	25±2.3	25±2.6	50±2.3	25±2.2	25±2.2	—	—
8	50±2.1	50±2.4	25±2.5	—	50±2.3	25±2.1	—	—
HL^5	50±2.2	25±2.1	25±2.2	25±1.1	25±2.1	50±2.2	—	
9	25±2.0	10±2.4	10±2.2	10±2.1	25±2.1	25±2.1	50±2.1	—

The standard antibiotic was Ampicillin (MIC=5 $\mu g \cdot mL^{-1}$).

The standard antifungal was Itraconazole (MIC=50 $mg \cdot mL^{-1}$).

be significantly enhanced on chelation. This increase in the antimicrobial activities upon coordination can be explained on the basis of overtone concept and Tweedys chelation theory[72].

3 Conclusions

In conclusion, five triazole azo dye ligands are used to prepare nine new mononuclear zirconyl complexes. The satisfactory analytical data and all the studies presented above indicate that HL^1-HL^5 coordinate to zirconyl(Ⅱ) ions as bidentate monobasic ligands through the azo nitrogen and the oxygen of hydroxyl group. The prepared ligands and their zirconyl complexes are screened *in-vitro* for their antimicrobial activity against different types of bacteria and fungi. In most cases, the ligands and complexes are active against both tested bacteria and fungi, thus giving a new trust of these compounds in the field of mettalo-drugs (medicinal and bio-inorganic chemistry). Metallaization increases the antimicrobial activity compared with the free ligands. All results underscore the futuristic aspects of developing metal ion complexes as frames for formulations in antimicrobial chemotherapy and disease management.

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