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# Mono- and binuclear copper(II) complexes of new hydrazone ligands derived from 4,6-diacetylresorcinol: Synthesis, spectral studies and antimicrobial activity



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## HIGHLIGHTS

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

- Two new hydrazone ligands were synthesized and characterized.
  Copper(II) complexes were
- synthesized and characterized by analytical and spectral methods.
- The spin Hamiltonian parameters of some complexes were calculated and discussed.
- The complexes exhibited octahedral and square planar geometrical arrangements.
- The ligands and some complexes showed antimicrobial activity.

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### ABSTRACT

Two new hydrazone ligands,  $H_2L^1$  and  $H_2L^2$ , were synthesized by the condensation of 4,6-diacetylresorcinol with 3-hydrazino-5,6-diphenyl-1,2,4-triazine and isatin monohydrazone, respectively. The structures of the ligands were elucidated by elemental analyses, IR, <sup>1</sup>H NMR, electronic and mass spectra. Reactions of the ligands with several copper(II) salts, including AcO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>--</sup>, Cl<sup>-</sup> and Br<sup>-</sup> afforded mono- and binuclear metal complexes. Also, the ligands were allowed to react with Cu(II) ion in the presence of a secondary ligand (L') [N,O-donor; 8-hydroxyquinoline, N,N-donor; 1,10-phenanthroline or O,O-donor; benzoylacetone]. Characterization and structure elucidation of the prepared complexes were achieved by elemental and thermal analyses, IR, electronic, mass and ESR spectra as well as conductivity and magnetic susceptibility measurements. The ESR spin Hamiltonian parameters of some complexes were calculated. The spectroscopic data showed that the  $H_2L^1$  ligand acts as a neutral or monobasic tridentate ligand while the  $H_2L^2$  ligand acts as a bis(monobasic tridentate) ligand. The coordination sites with the copper(II) ion are phenolic oxygen, azomethine nitrogen and triazinic nitrogen ( $H_2L^1$  ligand) or isatinic oxygen ( $H_2L^2$ ligand). The metal complexes exhibited octahedral and square planar geometrical arrangements depending on the nature of the anion. The ligands and some metal complexes howed antimicrobial activity. © 2014 Elsevier B.V. All rights reserved.

# Introduction

Hydrazones and their metal complexes form an interesting class of compounds which find extensive applications in antibacterial,

http://dx.doi.org/10.1016/j.saa.2014.02.014 1386-1425/© 2014 Elsevier B.V. All rights reserved. antifungal and antitumor agents [1–3]. Also, they are used in extraction of some metal ions using different buffer solutions [4], micro determination of metal ions [4], determination of titanium in bauxite, Portland cement, amphibolites and granites [5].

Triazine is an important class of heterocyclic compounds found in many synthetic and natural products with a wide range of

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biological activities, such as adenosine receptor antagonist [6], antiamoebic [7], antimalarial [8], antiviral [9], antitubercular [10] and carbonic anhydrase inhibitor [11].

Isatin is a versatile lead molecule for designing potential bioactive agents and its derivatives were reported to possess a broad spectrum of antiviral activities [12]. Ligands containing isatin moiety are known to possess a wide range of pharmacological properties that include antibacterial, antifungal [13], anticonvulsant [14] and anti-HIV [15] activities.

The bifunctional carbonyl compound; 4,6-diacetylresorcinol (DAR) serves as precursor for the construction of different polydentate ligands [16–20]. In our previous studies, metal complexes of polydentate ligands derived from 4,6-diacetylresorcinol [21–27] have been synthesized and fully characterized. The most motivating features of these ligands are the possibility of use them to synthesize polynuclear complexes with different modes of bonding. Also, mixed-ligand complexes including 4,6-diacetylresorcinol as a primary ligand have been studied [28–30].

On the basis of stated facts, the present work is an extension to our work and is devoted to the synthesis of new hydrazone ligands,  $H_2L^1$  and  $H_2L^2$ , by the condensation of 4,6-diacetylresorcinol with 3-hydrazino-5,6-diphenyl-1,2,4-triazine and isatin monohydraz-

one, respectively in the molar ratio 1:2 (DAR:hydrazino). The ligational behavior of the new ligands towards different copper(II) salts was investigated. The structures of the ligands and their metal complexes were characterized by elemental and thermal analyses, IR, <sup>1</sup>H NMR, electronic, ESR and mass spectra as well as conductivity and magnetic susceptibility measurements at room temperature. The biological activity of the ligands and their complexes was screened against selected kinds of bacteria and fungi.

# Experimental

## Materials

4,6-Diacetylresorcinol was prepared as cited in the literature [16]. 3-Hydrazino-5,6-diphenyl-1,2,4-triazine was prepared according to Ref. [31] and isatin monohydrazone was prepared according to Ref. [32]. Benzil, glacial acetic acid, thiosemicarbazide, hydrazine hydrate and isatin were BDH or Merck products. Metal salts, lithium hydroxide, 8-hydroxyquinoline (8-HQ), 1,10-phenan-throline (Phen), benzoylacetone (Bac), EDTA disodium salt, ammonium hydroxide, mureoxide and nitric acid were either Aldrich,

Table 1

Analytical and physical data of the hydrazone,  $H_2L^1$  and  $H_2L^2$ , ligands and their copper(II) complexes.

No. Reaction	Complex M.F. [F. Wt]		Yield <sup>a</sup>	M.P.	Elemental analysis, % found/(calc.)					
			(%)	(°C)	с н	Ν	Cl/S	М		
$H_2L^1$	C <sub>25</sub> H <sub>21</sub> N <sub>5</sub> O <sub>3</sub> [439.48]	Pale brown	89	>300	68.46 4.7 (68.33) (4.82	16.1 ) (15.94)	-	-		
(1) $H_2L^1 + Cu(OAc)_2 \cdot H_2O$	[(HL <sup>1</sup> )Cu(OAc)(H <sub>2</sub> O)]·1.5H <sub>2</sub> O C <sub>27</sub> H <sub>28</sub> N <sub>5</sub> O <sub>7.5</sub> Cu [606.1]	Brown	83	>300	53.57 4.97 (53.51) (4.66	11.8 ) (11.55)	-	10.4 (10.48)		
(2) $H_2L^1 + Cu(NO_3)_2 \cdot 2.5H_2O$	[(HL <sup>1</sup> )Cu(H <sub>2</sub> O)]NO <sub>3</sub> C <sub>25</sub> H <sub>22</sub> N <sub>6</sub> O <sub>7</sub> Cu [582.04]	Dark green	84	>300	51.66 3.8 (51.59) (3.81	14.56 ) (14.44)	-	11.0 (10.92)		
(3) $H_2L^1 + CuSO_4 \cdot 5H_2O$	$[(H_2L^1)Cu(SO_4)(H_2O)_2] \cdot 1.5H_2O \ C_{25}H_{28}N_5O_{10.5}SCu \ [662.14]$	Brown	50	>300	45.42 4.0 (45.35) (4.26	10.47 ) (10.58)	4.6 (4.84)	9.4 (9.6)		
$(4)  H_2L^1 + CuCl_2 \cdot 2H_2O$	[(HL <sup>1</sup> )CuCl]·1.5H <sub>2</sub> O C <sub>25</sub> H <sub>23</sub> N <sub>5</sub> O <sub>4·5</sub> ClCu [564.49]	Green	75	281	52.9 4.2 (53.19) (4.11	12.29 ) (12.41)	6.0 (6.28)	11.1 (11.26)		
(5) $H_2L^1 + CuBr_2$	$[(HL^{1})Cu(H_{2}O)_{3}]Br \cdot H_{2}O C_{25}H_{28}N_{5}O_{7}BrCu [653.98]$	Dark green	60	260	45.84 4.1 (45.92) (4.32	10.88 ) (10.71)	-	9.5 (9.72)		
(6) $H_2L^1 + Cu(OAc)_2 \cdot H_2O + 8-$ HQ	[(HL <sup>1</sup> )Cu(8-HQ)(H <sub>2</sub> O)] C <sub>34</sub> H <sub>28</sub> N <sub>6</sub> O <sub>5</sub> Cu [664.19]	Chocolate brown	96	263	61.47 4.0 (61.49) (4.25	12.9 ) (12.65)	-	9.4 (9.57)		
(7) $H_2L^1 + Cu(OAc)_2 \cdot H_2O + Pher$	n [(HL <sup>1</sup> )Cu(OAc)(Phen)] C <sub>39</sub> H <sub>31</sub> N <sub>7</sub> O <sub>5</sub> Cu [741.27]	Dark brown	71	267	63.4 3.9 (63.19) (4.22	13.5 ) (13.23)	-	8.4 (8.57)		
(8) $H_2L^1 + Cu(OAc)_2 \cdot H_2O + Bac$	[(HL <sup>1</sup> )Cu(H <sub>2</sub> O)(Bac)]·2H <sub>2</sub> O C <sub>35</sub> H <sub>35</sub> N <sub>5</sub> O <sub>8</sub> Cu [717.24]	Dark brown	71	>300	58.3 4.7 (58.61) (4.92	9.9 ) (9.76)	-	8.7 (8.86)		
$H_2L^2$	$C_{26}H_{20}N_6O_4$ [480.49]	Brown	94	>300	64.8 4.5 (64.99) (4.2)	17.2 (17.49)	-	-		
(9) $H_2L^2 + Cu(OAc)_2 \cdot H_2O$	$[(L^2)Cu_2(OAc)_2(EtOH)_2]\cdot 0.5H_2O\cdot 0.5EtOH\ C_{35}H_{40}N_6O_{11}Cu_2\\ [847.83]$	Dark brown	59	>300	49.6 4.5 (49.58) (4.76	9.79 ) (9.91)	-	14.8 (14.99)		
(10) $H_2L^2 + Cu(NO_3)_2 \cdot 2.5H_2O$	$[(L^2)_2Cu_2]\cdot EtOH\ C_{54}H_{42}N_{12}O_9Cu_2\ [1130.10]$	Chocolate brown	17	>300	57.37 3.77 (57.39) (3.75	14.6 ) (14.87)	-	11.20 (11.25)		
(11) $H_2L^2$ + CuSO <sub>4</sub> ·5H <sub>2</sub> O	$[(L^2)_2Cu_2]\cdot 2H_2O\ C_{52}H_{40}N_{12}O_{10}Cu_2\ [1120.07]$	Chocolate brown	23	>300	55.57 3.92 (55.76) (3.6)	15.4 (15.01)	-	11.30 (11.35)		
(12) $H_2L^2$ + CuCl <sub>2</sub> ·2H <sub>2</sub> O + LiOH	$[(L^2)Cu_2Cl_2] \cdot H_2O \cdot EtOH \ C_{28}H_{26}N_6O_6Cl_2Cu_2 \ [740.55]$	Dark brown	58	>300	45.59 3.55 (45.41) (3.54	11.1 ) (11.35)	9.3 (9.57)	17.0 (17.16)		
(13) $H_2L^2$ + CuBr <sub>2</sub>	$[(L^2)Cu_2Br_2] C_{26}H_{18}N_6O_4Br_2Cu_2 [765.37]$	Dark brown	53	>300	40.83 2.29 (40.80) (2.37	10.7 ) (10.98)	-	16.4 (16.61)		
(14) $H_2L^2 + Cu(OAc)_2 \cdot H_2O + 8 - HQ$	$[(L^2)Cu_2(8\text{-}HQ)_2(EtOH)_2] C_{48}H_{42}N_8O_8Cu_2 [986.01]$	Chocolate brown	79	>300	58.39 4.1 (58.47) (4.29	11.1 ) (11.36)	-	12.7 (12.89)		
(15) $H_2L^2 + Cu(OAc)_2 H_2O + Pher$	n [( $L^2$ )Cu <sub>2</sub> (OAc) <sub>2</sub> (Phen) <sub>2</sub> ]·3H <sub>2</sub> O C <sub>54</sub> H <sub>46</sub> N <sub>10</sub> O <sub>11</sub> Cu <sub>2</sub> [1138.12]	Brown	40	>300	57.06 3.8 (56.99) (4.07	12.0 ) (12.31)	-	10.9 (11.17)		
(16) $H_2L^2 + Cu(OAc)_2 \cdot H_2O + Bac$	$[(L^2)Cu_2(H_2O)_2(Bac)_2]\cdot 3H_2O\ C_{46}H_{46}N_6O_{13}Cu_2\ [1018.00]$	Reddish brown	64	>300	54.24 4.3 (54.27) (4.55	8.0 ) (8.26)	-	12.3 (12.48)		

<sup>a</sup> The yield is calculated on the basis of ligands.

BDH or Merck products. Organic solvents (ethanol, absolute ethanol, methanol, isopropanol, diethylether, dimethylformamide (DMF) and dimethylsulfoxide (DMSO)) were reagent grade chemicals and were used without further purification.

#### Measurements

Elemental analyses (C, H, N, S and Cl) were carried out at the Microanalytical Center, Cairo University, Giza, Egypt. Analysis of the copper(II) ion followed the dissolution of the solid complex in concentrated HNO<sub>3</sub>, neutralizing the diluted aqueous solutions with ammonia and titrating the metal solutions with EDTA. Melting points of the ligands and their complexes were determined using a Stuart SMP3 melting point apparatus. IR spectra were recorded using KBr discs on FT IR Nicolet IS10 spectrometer. The electronic spectra were recorded at room temperature on a Jasco model V-550 UV/Vis spectrophotometer as Nujol mulls and/or solutions in DMF. <sup>1</sup>H NMR spectra were recorded using a Mercury-300BB (300 MHz). Dimethylsulfoxide, DMSO-d<sub>6</sub>, was used as a solvent and tetramethylsilane (TMS) as an internal reference. ESR spectra of the complexes were recorded at Elexsys, E500, Bruker company. The magnetic field was calibrated with a 2,2'-diphenyl-1-picrylhydrazyl (DPPH) sample purchased from Aldrich. Mass spectra were recorded on GC-2010 Shimadzu Gas chromatography instrument mass spectrometer. Samples were introduced directly to the probe, and the fragmentations were carried out at 300 °C and 70 eV. The magnetic susceptibility measurements were carried out at room temperature using a magnetic susceptibility balance of the type Johnson Matthey, Alfa product, Model No. (MKI). Effective magnetic moments were calculated and corrected using Pascal's constants for the diamagnetism of all atoms in the compounds [33]. Molar conductivities of  $10^{-3}$  M solutions of the solid complexes in DMF were measured on the Corning conductivity meter NY 14831 model 441. TGA-measurements were carried out from room temperature up to 800 °C at a heating rate of 10 °C/min on a Shimadzu-50 thermal analyzer. The biological activity of the

ligands and their metal complexes was studied using the disc diffusion method [34].

#### Synthesis of the hydrazone ligands

The hydrazone ligands were prepared in two steps. The first step was the formation of 4,6-diacetylresorcinol (DAR) by acetylation of resorcinol [16]. The second step was the condensation of 4,6-diacetylresorcinol stoichiometrically in the molar ratio 1:2 with 3-hydrazino-5,6-diphenyl-1,2,4-triazine or isatin monohydrazone to give the hydrazone ligands: 1-(5-(1-(2-(5,6-diphenyl-1,2,4-triazin-3-yl)hydrazono)ethyl)-2,4-dihydroxyphenyl)ethanone (H<sub>2</sub>L<sup>1</sup>) and 3,3'-(1,1'-(4,6-dihydroxy-1,3-phenylene)bis(ethan-1-yl-1-ylidene))bis(hydrazine-2,1-diylidene)diindoline-2-one (H<sub>2</sub>L<sup>2</sup>), respectively (Structure 1). The use of 1:2 or 1:1 (DAR:hydrazino triazine) molar ratios yielded the same product (1:1) not the desired bis compound. The preparation method is as follows:

A solution of 4,6-diacetylresorcinol (0.5 g, 2.58 mmol) in absolute ethanol or methanol (30 mL) was added to 3-hydrazino-5,6diphenyl-1,2,4-triazine (0.678 g, 2.58 mmol or 1.358 g, 5.16 mmol) in absolute ethanol or isatin monohydrazone (0.831 g, 5.16 mmol) in methanol (30 mL). The reaction mixture was heated under reflux for 8 h which yielded brown products. The precipitate was filtered off, washed several times with absolute ethanol or methanol then with diethylether and finally air-dried. The  $H_2L^1$  and  $H_2L^2$  ligands were recrystallized from acetic acid and methanol–DMF, respectively. The crystals were dried in a desiccator over anhydrous calcium chloride. The analytical and physical data for the ligands and their metal complexes are listed in Table 1.

## Synthesis of the metal complexes

The metal salt and the ligand, both dissolved in ethanol, were mixed in the molar ratio 1:1 in case of  $H_2L^1$  ligand and 2:1 (M:L) in case of  $H_2L^2$  ligand and heated under reflux for 8 h. The resulting precipitates were filtered, washed with ethanol then ether and finally air-dried. The complexes were kept in a desiccator over

#### Table 2

Characteristic IR spectral data of the hydrazone, H<sub>2</sub>L<sup>1</sup> and H<sub>2</sub>L<sup>2</sup>, ligands and their complexes.

No.	Complex	IR spectra (cm) <sup>-1</sup>									
		v(OH) and/or v(NH) triazine or isatin	v(C=N) azomethine	v(C=N) triazine	v(N=N) triazine	v(C=0) isatin	v(M—O)	ν(M—N)	Other bands		
	$H_2L^1$	3429, 3306	1609	1533	1442	-	-	-			
1	$[(HL^1)Cu(OAc)(H_2O)] \cdot 1.5H_2O$	3425, 3254	1593	1505	1428	-	579	474	1553 ν <sub>as</sub> (COO <sup>-</sup> ), 1484 ν <sub>s</sub> (COO <sup>-</sup> ); (bidentate OAc <sup>-</sup> )		
2	$[(HL^1)Cu(H_2O)]NO_3$	3446, 3185	1595	1517	1433	-	494	421	1446; $v(NO_3^-)$ (ionic)		
3	$[(H_2L^1)Cu(SO_4)(H_2O)_2] \cdot 1.5H_2O$	3467	1558	1507	1430	-	495	445	1098, 1048; $v(SO_4^2-)$ (monodentate)		
4	$[(HL^1)CuCl] \cdot 1.5H_2O$	3446, 3188	1599	1517	1432	-	570	418			
5	$[(HL^1)Cu(H_2O)_3]Br \cdot H_2O$	3447, 3187	1595	1516	1427	-	579	427			
6	$[(HL^1)Cu(8-HQ)(H_2O)]$	3341, 3292	1601	1505	1430	-	513	446	1486, v(C=N) 8-HQ		
7	[(HL <sup>1</sup> )Cu(OAc)(Phen)]	3440	1592	1506	1427	_	531	419	1562 v <sub>as</sub> (COO <sup>-</sup> ), 1445 v <sub>s</sub> (COO <sup>-</sup> ); (monodentate OAc <sup>-</sup> ), 1540, v(C=N) Phen		
8	$[(HL^1)Cu(H_2O)(Bac)]\cdot 2H_2O$	3577	1589	1505	1423	-	494	462	1685, v(C=0) Bac		
	$H_2L^2$	3420, 3229	1621	-	-	1716	-	-			
9	$[(L^2)Cu_2(OAc)_2(EtOH)_2] \cdot 0.5H_2O \cdot 0.5EtOH$	3417	1592	-	-	1710	546	469	1548 v <sub>as</sub> (COO <sup>-</sup> ), 1486 v <sub>s</sub> (COO <sup>-</sup> ); (bidentate OAc <sup>-</sup> )		
10	[(L <sup>2</sup> ) <sub>2</sub> Cu <sub>2</sub> ]·EtOH	3402, 3217	1594	-	-	1710	577	469			
11	$[(L^2)_2Cu_2]\cdot 2H_2O$	3402, 3217	1594	-	-	1710	577	469			
12	$[(L^2)Cu_2Cl_2] \cdot H_2O \cdot EtOH$	3442, 3340	1586	-	-	1709	550	459			
13	$[(L^2)Cu_2Br_2]$	3435	1593	-	-	1693	546	491			
14	$[(L^2)Cu_2(8-HQ)_2(EtOH)_2]$	3417	1598	-	-	1710	519	492	1497, v(C=N) 8-HQ		
15	$[(L^2)Cu_2(OAc)_2(Phen)_2]\cdot 3H_2O$	3416	1586	-	-	1695	545	490	1551 v <sub>as</sub> (COO <sup>-</sup> ), 1428 v <sub>s</sub> (COO <sup>-</sup> ); (monodentate OAc <sup>-</sup> ), 1520, v(C=N) Phen		
16	$[(L^2)Cu_2(H_2O)_2(Bac)_2]\cdot 3H_2O$	3440	1589	-	-	1710	510	469	1670, v(C=O) Bac		

Table 3	3
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Electronic si	nectra	magnetic	momente	and mola	r conductivity	/ data /	of the h	vdrazona	H_I 1	and Hal <sup>2</sup>	ligande an	d thair i	complayer	
LIEUTOINC S	pecua,	magnetic	moments	anu moia	Conductivity	y uala i	or the n	yurazone,	T12L	anu ngi	, ligalius all	u men i	complexes.	

No.	Complex	Electronic spectral bands <sup>a</sup> (nm) $\lambda_{max}^{a}$ (nm)/( $\varepsilon_{max}$ )	$\mu_{\rm eff.}$ <sup>b</sup> B.M.	$\mu_{\text{compl.}}$ <sup>c</sup> B.M.	Conductance <sup>a</sup> ( $\Omega^{-1}$ cm <sup>2</sup> mol <sup>-1</sup> )
	$H_2L^1$	281 (0.28), 331 (0.26), 371 (0.14)	-	-	_
1	[(HL <sup>1</sup> )Cu(OAc)(H <sub>2</sub> O)]·1.5H <sub>2</sub> O	474 <sup>e</sup> , 537 <sup>e</sup> sh	2.12	-	8.3
2	$[(HL^1)Cu(H_2O)]NO_3$	543 <sup>d</sup>	1.86	-	107.4
3	$[(H_2L^1)Cu(SO_4)(H_2O)_2] \cdot 1.5H_2O$	500 <sup>e</sup> sh, 550 <sup>e</sup> sh	2.15	-	39
4	$[(HL^1)CuCl] \cdot 1.5H_2O$	538 <sup>d</sup>	1.71	-	34.2
5	$[(HL^1)Cu(H_2O)_3]Br \cdot H_2O$	519 <sup>d</sup> sh, 566 <sup>d</sup>	1.8	-	84.9
6	$[(HL^{1})Cu(8-HQ)(H_{2}O)]$	520 <sup>d</sup> sh, 578 <sup>d</sup> sh	1.31	-	7.2
7	[(HL <sup>1</sup> )Cu(OAc)(Phen)]	457 <sup>d</sup> , 542 <sup>d</sup>	1.83	-	4.5
8	$[(HL^1)Cu(H_2O)(Bac)]\cdot 2H_2O$	486 <sup>e</sup> , 567 <sup>d</sup>	2.1	-	5. 2
	$H_2L^2$	266 (0.3), 342 (0.2), 422 (0.18)	-	-	-
9	$[(L^2)Cu_2(OAc)_2(EtOH)_2]\cdot 0.5H_2O\cdot 0.5EtOH$	493 <sup>d</sup> , 564 <sup>d</sup>	1.4	1.66	6.4
10	$[(L^2)_2Cu_2]$ ·EtOH	530 <sup>d</sup> , 600 <sup>d</sup>	2.1	2.57	11
11	$[(L^2)_2Cu_2]\cdot 2H_2O$	530 <sup>d</sup> , 600 <sup>d</sup>	2.02	2.6	11
12	$[(L^2)Cu_2Cl_2] \cdot H_2O \cdot EtOH$	589 <sup>d</sup>	1.9	2.54	40.3
13	$[(L^2)Cu_2Br_2]$	515 <sup>d</sup>	1.62	2.07	24.5
14	$[(L^2)Cu_2(8-HQ)_2(EtOH)_2]$	519 <sup>d</sup> , 565 <sup>d</sup>	2.01	2.67	10
15	$[(L^2)Cu_2(OAc)_2(Phen)_2]\cdot 3H_2O$	515 <sup>d</sup> , 558 <sup>d</sup>	2.1	2.74	12.5
16	$[(L^2)Cu_2(H_2O)_2(Bac)_2]\cdot 3H_2O$	474 <sup>d</sup> sh, 573 <sup>d</sup>	2.12	2.8	6. 2

Solutions in DMF ( $10^{-3}$  M), values of  $\varepsilon_{max}$  are in parentheses and multiplied by  $10^{-4}$  (L mol<sup>-1</sup> cm<sup>-1</sup>).

 $\mu_{\rm eff.}$  is the magnetic moment of one cationic species in the complex.

 $\mu_{\text{compl.}}$  is the total magnetic moments of all cations in the complex.

<sup>d</sup> Nujol mull.

e Concentrated solutions.

# Table 4

<sup>1</sup>H NMR spectral data of the hydrazone ligands.

(c) Ph (c) Ph	(e) $H$ $N - N =$ $N$ $N$ $(f)$	(a) CH <sub>3</sub> (b) (d)	(a) CH <sub>3</sub> O OH (f) (c)	N N H (e)	(a) (a) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c	(c)
	(H <sub>2</sub> L <sup>1</sup> )				(H <sub>2</sub> L <sup>2</sup> )	
	$\delta_{\rm H}(\rm ppm)$					
	$H^a$	$H^b$	$H^{c}_{aromatic}$	$H^d$	H <sup>e</sup>	Hf
$H_2L^1$	2.57, 2.66 (6H)	6.38 (1H)	7.34–7.54 (10H)	8.08 (1H)	11.62 (1H; exchangeable with D <sub>2</sub> O)	12.58, 14.32 (2H; exchangeable with D <sub>2</sub> O)
$H_2L^2$	2.58, 2.66 (6H)	6.39 (1H)	6.42-8.18 (8H)	8.25 (1H)	10.77 (2H; exchangeable with $D_2O$ )	12.61, 13.54 (2H; exchangeable with $D_2O$ )

anhydrous calcium chloride. The following detailed preparations are given as examples and the other complexes were obtained similarly.

## Synthesis of $[(HL^1)Cu(OAc)(H_2O)] \cdot 1.5H_2O$ , complex (1)

About 0.182 g (0.91 mmol) of copper(II) acetate dissolved in 30 mL ethanol was added gradually to 0.4 g (0.91 mmol) of the ligand, H<sub>2</sub>L<sup>1</sup>, dissolved in 30 mL ethanol. The reaction mixture was heated under reflux for 8 h which resulted a brown precipitate that was filtered off, washed several times with ethanol, diethylether and finally air-dried. The yield was 0.46 g (83%).

## Synthesis of $[(HL^1)Cu(8-HQ)(H_2O)]$ , complex (6)

About 0.182 g (0.91 mmol) of copper(II) acetate dissolved in 30 mL ethanol was added gradually to 0.4 g (0.91 mmol) of the ligand,  $H_2L^1$ , dissolved in 30 mL ethanol. The reaction mixture was heated under reflux for 30 min. and then 0.132 g (0.91 mmol) of 8-hydroxyquinoline (8-HQ) dissolved in ethanol was added to the above mixture. The resulting mixture was heated under reflux for 8 h which resulted a chocolate brown precipitate that was filtered off, washed several times with ethanol, diethylether and finally air-dried. The yield was 0.58 g (96%).

#### Antimicrobial activity

The standardized disc-agar diffusion method [34] was followed to determine the activity of the synthesized compounds against the sensitive organisms Staphylococcus aureus (ATCC 25923) and Bacillus subtilis (ATCC 6635) as Gram positive bacteria, Salmonella typhimurium (ATCC 14028) and Escherichia coli (ATCC 25922) as Gram negative bacteria and Candida albicans (ATCC 10231) and Aspergillus fumigatus as fungus strain. The antibiotic chloramphenicol was used as reference in the case of Gram-positive bacteria. cephalothin in the case of Gram-negative bacteria and cycloheximide in the case of fungi.

The compounds were dissolved in DMF which has no inhibition activity to get concentrations of 100  $\mu$ g mL<sup>-1</sup> and 50  $\mu$ g mL<sup>-1</sup>. The test was performed on medium potato dextrose agars (PDA) which contain infusion of 200 g potatoes, 6 g dextrose and 15 g agar [35]. Uniform size filter paper disks (3 disks per compound) were impregnated by equal volume (10  $\mu$ L) from the specific concentration of dissolved tested compounds and carefully placed on inoculated agar surface. After incubation for 36 h at 27 °C in the case of bacteria and for 48 h at 24 °C in the case of fungi, inhibition of the organisms was measured and used to calculate mean of inhibition zones.

## **Results and discussion**

## Characterization of the ligands

The structures of the ligands were elucidated by elemental analyses, IR, electronic, <sup>1</sup>H NMR and mass spectra. The results of

the elemental analyses (Table 1) are in good agreement with the proposed formula. The IR spectral data of the ligands (Table 2) showed characteristic absorption bands in the ranges 3420–3429, 3229–3306 and 1609–1621 cm<sup>-1</sup> which may be assigned to v(OH)<sub>phenolic</sub>, and v(NH)<sub>triazine or isatin and v(C=N)<sub>azomethine</sub>, respectively. The triazine ligand, H<sub>2</sub>L<sup>1</sup>, showed bands at 1533 and 1442 cm<sup>-1</sup> that may be attributed to v(C=N), v(N=N) of the triazine moiety, respectively [36]. Finally, the isatinic ligand, H<sub>2</sub>L<sup>2</sup>, showed a strong band at 1716 cm<sup>-1</sup> characteristic for v(C=O) of the isatin moiety [13,37,38]. The electronic spectral data of the ligands in DMF (Table 3) showed three bands in the ranges 266–281, 331–342 and 371–422 nm. The higher energy bands may be assigned to  $\pi$ - $\pi$ \* transitions of the triazine or isatin ring and C=C</sub>



Fig. 1. Mass spectra A: H<sub>2</sub>L<sup>1</sup> ligand, B: H<sub>2</sub>L<sup>2</sup> ligand, C: [(HL<sup>1</sup>)Cu(H<sub>2</sub>O)]NO<sub>3</sub> (2) and D: [(L<sup>2</sup>)<sub>2</sub>Cu<sub>2</sub>]·2H<sub>2</sub>O (11).

band. The medium energy band may be composite bands due to charge transfer (CT) transitions involving the whole molecules as well as  $\pi - \pi^*$  transitions involving the triazine, isatin and phenyl rings and/or azomethine groups. Finally, the lower energy band may be attributed to  $n-\pi^*$  transitions of the azomethine groups. <sup>1</sup>H NMR spectral data ( $\delta$  ppm) of the ligands relative to TMS (0 ppm) in DMSO-d<sub>6</sub> are listed in Table 4. The signals observed in the range 12.58-14.32 ppm may be assigned to the hydrogenbonded phenolic –OH groups [13,21–23,27,28]. These signals disappeared in the presence of D<sub>2</sub>O, indicating that these protons are acidic and the hydroxyl groups can participate in the coordination with the metal ions [25,26]. Also, signals observed at 11.62 and 10.77 ppm, which disappeared in the presence of D<sub>2</sub>O, may be assigned to the triazinic and isatinic -- NH protons, respectively [39,40]. Finally, the signals due to aromatic and methyl protons are detected in the ranges 6.38-8.25 and 2.57-2.66 ppm. Moreover, the structures of the ligands were deduced from mass spectral data (Fig. 1) which showed the molecular ion peaks at 439 and 481 a.m.u. for  $H_2L^1$  and  $H_2L^2$  ligands, respectively, confirming their formula weights (F.W. 439.48 and 480.49 respectively).

#### Characterization of the metal complexes

The hydrazone ligands were allowed to react with several Cu(II) salts of AcO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and Br<sup>-</sup> in order to investigate the effect of the counterions on the products. Also, the ligands were allowed to react with copper(II) ion in the presence of secondary ligands (L') [N,O-donor; 8-hydroxyquinoline, N,N-donor; 1,10-phenanthroline or O,O-donor; benzoylacetone]. The prepared complexes are stable at room temperature, non-hygroscopic and insoluble in water and common organic solvents. The obtained complexes are characterized by elemental and thermal analyses, IR, electronic, ESR and mass spectra as well as conductivity and magnetic measurements.

#### IR spectra

The IR spectral data of the complexes are listed in Table 2. Comparison of the IR spectra of the metal complexes with those of the free ligands revealed that all complexes showed broad bands in the range 3185–3577  $\text{cm}^{-1}$  which may be attributed to the stretching frequency of v(NH) and/or the hydroxyl group; v(OH) of the phenolic group, water or ethanol molecules associated with the complexes which are confirmed by elemental and thermal analyses. The bands at 1609 and 1621 cm<sup>-1</sup> assigned to v(C=N) for  $H_2L^1$ and  $H_2L^2$  ligands, respectively were shifted to lower wave number in all complexes, indicating the participation of the azomethine nitrogen in chelation. In case of H<sub>2</sub>L<sup>1</sup> ligand, bands at 1533 and 1442 cm<sup>-1</sup> assigned to v(C=N), v(N=N) of the triazine moiety, respectively were shifted to lower wave number in all complexes, indicating the participation of the triazine nitrogen in chelation. Similarly, the band observed at 1716 cm<sup>-1</sup> characteristic for v(C=0) of the isatin moiety in  $H_2L^2$  ligand was shifted to lower wave number in all complexes, indicating the participation of the isatinic oxygen in chelation [13]. In complexes 1 and 9, the chelating bidentate CH<sub>3</sub>COO<sup>-</sup> group was supported by new bands appeared in the ranges 1548–1553 and 1484–1486 cm<sup>-1</sup>. These two bands are due to  $v_{as}(COO^{-})$  and  $v_{s}(COO^{-})$ , respectively. The separation of the two bands,  $\Delta v = (v_{as} - v_s) = 62 - 69 \text{ cm}^{-1}$ , is comparable to the values cited for the bidentate character of the acetate group [24,29,30,41];  $\Delta v = 75-80 \text{ cm}^{-1}$ . On the other hand, complexes 7 and 15 showed new bands characteristic for  $v_{as}(COO^{-})$ and  $v_s(COO^-)$  of acetate ion in the ranges 1551–1562 and 1428– 1445 cm<sup>-1</sup>. The higher difference (117–123 cm<sup>-1</sup>) between the two bands indicates the monodentate nature of the acetate group [42,43]. Complex **2** showed a new band at  $1446 \text{ cm}^{-1}$  which can be assigned to the ionic  $NO_3^-$  group [22,26] indicating the ionic nature of the complex. These infrared spectral data were supported by coductance data (see latter). Complex 3 showed new bands at 1098 and 1048 cm<sup>-1</sup> which may be assigned to the coordinated sulfate group in a monodentate fashion [42]. Complexes 10 and 11 did not exhibit new bands assigned for nitrate or sulfate anions, respectively indicating the absence of these anions which is consistent with elemental analyses (Table 1). The mode of bonding in these complexes (10 and 11) was suggested to be 2:2 (L:M) which was obtained in our previous work [24] for a related Schiff base ligand derived from 4,6-diacetylresorcinol and benzylamine where this behavior was obtained in case of copper(II) and cerium(III) ions. Furthermore, in our recently work including 4,6-diacetylresorcinol as a ligand, this mode of bonding was obtained in case of alkaline earth metal [28], nickel(II) [29] and copper(II) [30] ions. The mixed-ligand complexes containing 8-hydroxyquinoline (6 and **14**) or 1.10-phenanthroline (**7** and **15**) showed new bands in the ranges 1486–1497 and 1520–1540  $cm^{-1}$  (Table 2) supporting the coordination of the C=N group of the secondary ligand to the metal ion [21-23,26]. Similarly, the mixed benzoylacetone complexes (8 and 16) showed new bands in the range 1670- $1685 \text{ cm}^{-1}$  due to the coordinated C=O group of benzoylacetone [44]. In free benzoylacetone, the v(C=0) band has been reported at  $1724 \text{ cm}^{-1}$  [45]. Thus the shift of v(C=O) band to lower wave number supports the coordination of the C=O group to the metal ion [44]. Finally, the above interpretation is supported by the appearance of the new bands at 494–579 and 428–492  $cm^{-1}$  assigned to v(M-O) and v(M-N) [24-27,46-48], respectively.

## Conductivity measurements

The molar conductance values of the complexes in DMF ( $10^{-3}$  M solutions) were measured at room temperature and the results are listed in Table 3. The values showed that all complexes have non



**Fig. 2.** X-band ESR spectra of the complexes A:  $[(HL^1)CuCl] \cdot 1.5H_2O$  (4), and B:  $[(L^2)Cu_2(OAc)_2(EtOH)_2] \cdot 0.5H_2O \cdot 0.5EtOH$  (9).

#### Table 5

ESR data of some copper(II) complexes at room temperature.

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}\times 10^{-4}(cm^{-1})$	G	$\alpha^2$	$\beta^2$
[(HL <sup>1</sup> )Cu(H <sub>2</sub> O) <sub>3</sub> ]Br·H <sub>2</sub> O <b>(5)</b>	2.19	2.06	111	3.17	0.56	0.89
[(L <sup>2</sup> )Cu <sub>2</sub> (OAc) <sub>2</sub> (EtOH) <sub>2</sub> ]·0.5H <sub>2</sub> O·0.5EtOH <b>(9)</b>	2.17	2.03	113	5.7	0.53	0.85

electrolytic nature except complexes (**2** and **5**) which gave molar conductance value = 107.4 and 84.9  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, respectively, suggesting their 1:1 electrolytic nature [13,21,22,41,49]. This is consistent with the infrared data. In case of complexes **3**, **4**, **12** and **13**, the relatively high values of the molar conductance data may be due to the partial dissociation in their DMF solutions, however, they did not reach the previously reported values for 1:1 electrolytes in DMF solutions (~70–110)  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> [49].

#### Magnetic measurements and electronic spectra

Due to the Jahn-Teller distortion and because of the low symmetry of the environment around Cu<sup>II</sup>-ion (d<sup>9</sup>), detailed interpretations of the spectra and magnetic properties are somewhat complicated [50]. The magnetic moment values of the complexes (except complexes 6 and 9) are in the range 1.62–2.15 B.M., which is consistent with the presence of one unpaired electron [26,30,41]. In case of complexes 6 and 9, the subnormal magnetic moment values (1.31–1.4 B.M.) may be due to anti-ferromagnetic exchange; the smallest  $\mu_{\text{eff}}$  values, the strongest is the exchange [51,52]. The electronic spectra of the complexes (1, 3, 5–11, and 14–16) show two absorption bands in the ranges 457-530 and 537-600 nm which may be assigned to the  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  and  ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ transitions, respectively corresponding to a distorted octahedral geometry [26,41]. On the other hand, complexes (2, 4, 12 and 13) show one band in the range 515-589 nm, respectively, which may be assigned to the  ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$  transition in a square planar geometry [24,26,41,42].

#### ESR spectra

To obtain further information about the stereochemistry and the site of the metal ligand bonding, ESR spectra of the complexes (4, 5 and 9) were recorded in the solid state. Fig. 2 represents the ESR spectra of complexes 4 and 9. The spectrum of complex 4 exhibits one broad band with g = 2.09. The spectra of complexes 5 and 9 exhibit two signals at 2.19, 2.06 for the former complex and at 2.17, 2.03 for the latter one. The shapes of the spectra of complexes are consistent with octahedral geometry around the Cu(II) center in complexes 5 and 9 and square planar in complex 4 [24–26,30,41]. The spin Hamiltonian parameters of complexes

$$[(H_{2}L^{1})Cu(SO_{4})(H_{2}O)_{2}].1.5H_{2}O \xrightarrow{-1.5H_{2}O} [(H_{2}L^{1})Cu(SO_{4})(H_{2}O)_{2}]$$

$$[(H_{2}L^{1})Cu(SO_{4})] \xrightarrow{-2H_{2}O} [(H_{2}L^{1})Cu(SO_{4})] \xrightarrow{-2H_{2}O} [(H_{2}L^{1})Cu(SO_{$$

**Scheme 1.** Thermal degradation pattern of complex (**3**),  $[(H_2L^1)Cu(SO_4)(H_2O)_2]$ - $\cdot$ 1.5H<sub>2</sub>O, in the range of 36–275 °C.

5 and 9 were calculated and summarized in Table 5. The room temperature solid state ESR spectra of the complexes are quite similar and exhibit an axially g-tensor parameters with  $g_{\parallel} > g_{\perp} > 2.0023$ . In axial symmetry, the g-values are related by the expression,  $G = (g_{\parallel} 2)/(g_{\perp}-2) = 4$ , which measures the exchange interaction between copper centers in the solid. According to Hathaway [53,54], if the value of *G* is greater than four, the exchange interaction between copper(II) centers in the solid state is negligible, whereas when G is lower than 4, a considerable exchange interaction is indicated in the solid complex. The calculated G value for complex 5 is 3.17, suggesting a Cu-Cu exchange interaction while in complex **9**, the value is 5.7 indicating a negligible interaction [13,30,41]. Molecular orbital coefficients,  $\alpha^2$  (a measure of the covalency of the in-plane  $\sigma$ -bonding between copper 3d orbital and the ligand orbitals) and  $\beta^2$  (covalent in-plane  $\pi$ -bonding), were calculated by using the following equations [55].

$$\begin{split} \alpha^2 &= \left(\frac{A_{\parallel}}{0.036}\right) + (g_{\parallel} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) + 0.04\\ \beta^2 &= -\frac{(g_{\parallel} - 2.0023)E}{8\lambda\alpha^2}, \end{split}$$

where  $\lambda = -828 \text{ cm}^{-1}$  for the free copper ion and *E* is the electronic transition energy,  $\alpha^2 = 1$  indicates complete ionic character, whereas  $\alpha^2 = 0.5$  denotes 100% covalent bonding, with the assumption of negligibly small values of the overlap integral. The lower values of  $\alpha^2$  (0.53–0.56) compared to  $\beta^2$  (0.85–0.89) indicate that the in-plane  $\sigma$ -bonding is more covalent than the in-plane  $\pi$ -bonding. These data are in good agreement with the data reported earlier [13,30,41].

#### Thermal analysis

Thermal gravimetric analysis (TGA) was mainly used to proof the associated water or solvent molecules to be in the coordination sphere or in the outer sphere of the complex [13,25,26,56]. Complexes **3**, **4** and **9** were taken as representative examples for thermal analysis. The results of thermal analysis of these complexes are in agreement with elemental analyses.

The thermogram of complex (**3**),  $[(H_2L^1)Cu(SO_4)(H_2O)_2]\cdot 1.5H_2O$ , showed two stages of decomposition in the range 36–275 °C. The first one in the range 36–143 °C, is due to the loss of one and half uncoordinated water molecule (weight loss; Calc./Found%; 4.08/ 4.46%). The second stage in the range 143–275 °C and is due to the loss of two coordinated water molecules (weight loss; Calc./Found%; 5.44/5.51%). The decomposition pattern of complex **3** has been explained by the reactions shown in Scheme 1.

In case of complex **4**,  $[(HL^1)CuCl] \cdot 1.5H_2O$ , the weight loss in the range 32–107 °C corresponds to one and half uncoordinated water



Structure 1. Structures of the hydrazone, H<sub>2</sub>L<sup>1</sup> and H<sub>2</sub>L<sup>1</sup>, ligands.



(4)

**Structure 2.** Representative structures of the neutral complexes of  $H_2L^1$  ligand obtained by using AcO<sup>-</sup>,  $SO_4^{2^-}$  and  $CI^-$  anions.



Structure 3. Representative structures of the cationic complexes of  $H_2L^1$  ligand obtained by using  $NO_3^-$  and  $Br^-$  anions.

molecule (weight loss; Calc./Found%; 4.78/4.92%). Finally, the thermogram of complex **9**,  $[(L^2)Cu_2(OAc)_2(EtOH)_2]\cdot 0.5H_2O\cdot 0.5EtOH$  showed a weight loss in the range 27–97 °C that corresponds to half uncoordinated water molecule as well as half uncoordinated ethanol molecule (weight loss; Calc./Found%; 3.77/3.67%). However, the coordinated ethanol molecules are lost during the decomposition of the complex within the next stages.

### Mass spectra

The mass spectra of the complexes **2**, **6**, **11** and **13**, as representative complexes, provide good evidence for the molecular formulas of these complexes. Fig. 1 depicts the mass spectra of complexes **2** and **11**. The mass spectra of the complexes **2**, **6** and **13** showed the highest mass peak with m/z 582, 664 and 765, respectively which agree very well with the formula weights of the complexes [(HL<sup>1</sup>)Cu(H<sub>2</sub>O)]NO<sub>3</sub> (F. Wt = 582.04), [(HL<sup>1</sup>)Cu(8-HQ)(H<sub>2</sub>O)] (F. Wt = 664.19) and [(L<sup>2</sup>)Cu<sub>2</sub>Br<sub>2</sub>] (F. Wt = 765.37). However,



Structure 4. Representative structures of the ternary complexes of H<sub>2</sub>L<sup>1</sup> ligand.



Structure 5. Representative structures of the binary complexes of H<sub>2</sub>L<sup>2</sup> ligand.

complex **11** showed the parent peak at m/z 1084 which compares very well with the calculated formula weights of the non-hydrated complex [(L<sup>2</sup>)<sub>2</sub>Cu<sub>2</sub>] (F. Wt = 1084.07).



Structure 6. Representative structures of the ternary complexes of H<sub>2</sub>L<sup>2</sup> ligand.

Finally, from the interpretation of elemental and thermal analyses and spectral data (infrared, electronic, ESR and mass) as well as conductivity and magnetic susceptibility measurements at room temperature, it is possible to draw up the tentative structures of the metal complexes. Structures 2–6 represent the proposed structures of the metal complexes.

#### Table 6

Antimicrobial activity of the hydrazone ligands and their Cu(II) complexes.

#### Antimicrobial studies

The antimicrobial activity of the ligands and their metal complexes was investigated against the sensitive organisms S. aureus (ATCC 25923) and B. subtilis (ATCC 6635) as Gram-positive bacteria, E. coli (ATCC 25922) and S. typhimurium (ATCC 14028) as Gramnegative bacteria, yeast: C. albicans (ATCC 10231) and fungus: A. fumigatus. The results are listed in Table 6. Inspection of the data given in Table 6 reveals that the ligands and their metal complexes showed a promising activity against C. albicans while some complexes are active against the Gram-positive bacteria; B. subtilis. Few complexes showed an antimicrobial activity against S. aureus, E. coli and A. fumigatus. Finally, the ligands and their metal complexes are inactive against S. typhimurium. It is clear that H<sub>2</sub>L<sup>2</sup> ligand and its complexes are more active than H<sub>2</sub>L<sup>1</sup> ligand and its complexes towards all organisms. Also, the activity of the ligands is enhanced by chelation. This enhancement in activity due to chelation can be explained on the basis of chelation theory [57]. Chelation reduces the polarity of the metal ion considerably, mainly because of the partial sharing of its positive charge with donor groups and the possible  $\pi$ -electron delocalization over the whole chelate ring. Chelation not only reduces the polarity of metal ion, but also increases the lipophilic character of the chelate. As a result of this, interaction between metal ion and the cell walls is favoured resulting in interference with normal cell processes. If the geometry and charge distribution around the molecule are incompatible with the geometry and charge distribution around the pores of the bacterial cell wall, penetration through the wall by the toxic agent cannot take place, preventing toxic reaction within the pores [58]. Finally, some complexes (1, 3, 9 and 13–16) seem to be promising since they showed antimicrobial activity comparable to (and

Organism	Mean <sup>a</sup> of zone diameter, nearest whole mm.											
	Gram-positive bacteria				Gram-negative bacteria				Yeasts and Fungi <sup>b</sup>			
	Staphylococcus aureus (ATCC 25923)		Bacillus subtilis (ATCC 6635)		Salmonella typhimurium (ATCC 14028)		Escherichia coli (ATCC 25922)		Candida albicans (ATCC 10231)		Aspergillus fumigatus	
Concentration	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml
Sample												
$H_2L^1$	-	-	6 L	5 L	-	-	-	-	6 L	4 L	4 L	2 L
$[(HL^{1})Cu(OAc)(H_{2}O)] \cdot 1.5H_{2}O(1)$	-	-	20 I	15 I	-	-	-	-	30 H	24 H	-	-
$[(HL^{1})Cu(H_{2}O)]NO_{3}(2)$	-	-	-	-	-	-	-	-	11 L	8 L	-	-
$[(H_2L^1)Cu(SO_4)(H_2O)_2] \cdot 1.5H_2O(3)$	-	-	24 H	16 I	-	-	-	-	31 H	26 H	-	-
$[(HL^{1})CuCl] \cdot 1.5H_{2}O(4)$	-	-	-	-	-	-	-	-	9 L	7 L	-	-
$[(HL^1)Cu(H_2O)_3]Br \cdot H_2O(5)$	-	-	9 L	7 L	-	-	-	-	9 L	7 L	-	-
$[(HL^1)Cu(8-HQ)(H_2O)]$ (6)	-	-	14 I	9 I	-	-	-	-	15 I	11 I	11 L	8 L
$[(HL^1)Cu(OAc)(Phen)]$ (7)	-	-	-	-	-	-	-	-	11 L	7 L	10 L	7 L
$[(HL^{1})Cu(H_{2}O)(Bac)]\cdot 2H_{2}O(8)$	-	-	10 L	7 L	-	-	-	-	24 H	18 I	-	-
$H_2L^2$	4 L	2 L	7 L	4 L	-	-	6 L	4 L	7 L	5 L	5 L	3 L
$[(L^2)Cu_2(OAc)_2(EtOH)_2] \cdot 0.5H_2O \cdot 0.5EtOH$ (9)	-	-	-	-	-	-	-	-	26 H	21 H	-	-
$[(L^2)_2Cu_2]$ ·EtOH ( <b>10</b> )	-	-	-	-	-	-	-	-	14 I	8 L	-	-
$[(L^2)_2Cu_2] \cdot 2H_2O$ ( <b>11</b> )	-	-	-	-	-	-	-	-	20 I	14 I	-	-
$[(L^2)Cu_2Cl_2] \cdot H_2O \cdot EtOH$ (12)	-	-	-	-	-	-	-	-	13 I	10 I	-	-
$[(L^2)Cu_2Br_2]$ (13)	-	-	31 H	20 H	-	-	-	-	27 H	20 H	11 L	8 L
$[(L^2)Cu_2(8-HQ)_2(EtOH)_2]$ (14)	-	-	28 H	20 H	-	-	24 I	20 H	28 H	23 H	38 H	31 H
$[(L^{2})Cu_{2}(OAc)_{2}(Phen)_{2}]\cdot 3H_{2}O(15)$	27 H	20 H	29 H	24 H	-	-	22 I	20 H	29 H	23 H	-	-
$[(L^2)Cu_2(H_2O)_2(Bac)_2]\cdot 3H_2O$ (16)	28 H	21 H	30 H	23 H	-	-	-	-	25 H	18 I	-	-
Control <sup>c</sup>	35	26	35	25	36	28	38	27	35	28	37	26

– = No effect.

L: Low activity = mean of zone diameter  $\leq 1/3$  of mean zone diameter of control.

I: Intermediate activity = mean of zone diameter  $\leq 2/3$  of mean zone diameter of control.

H: High activity = mean of zone diameter > 2/3 of mean zone diameter of control.

<sup>a</sup> Calculated from 3 values.

<sup>b</sup> Identified on the basis of routine cultural, morphological and microscopical characteristics.

<sup>c</sup> Chloramphenicol in the case of Gram-positive bacteria, cephalothin in the case of Gram-negative bacteria and cycloheximide in the case of fungi.

sometimes higher than) those of chloramphenicol, cephalothin and cycloheximide.

## Conclusion

The condensation reaction of 4,6-diacetylresorcinol with 3hydrazino-5,6-diphenyl-1,2,4-triazine and isatin monohydrazone afforded the hydrazone,  $H_2L^1$  and  $H_2L^2$ , ligands, respectively. Reactions of the  $H_2L^1$  ligand with different copper(II) salts afforded mononuclear complexes including neutral complexes (obtained by using AcO<sup>-</sup>,  $SO_4^{2-}$  and Cl<sup>-</sup> anions as well as ternary complexes) and cationic complexes (obtained by using  $NO_2^-$  and  $Br^-$  anions). The spectroscopic data showed that the  $H_2L^{1}$  ligand acts as a monobasic tridentate ligand in all complexes except the sulfato complex (3) in which the ligand acts as a neutral tridentate. On the other hand, reactions of the H<sub>2</sub>L<sup>2</sup> ligand with different copper(II) salts afforded neutral binuclear complexes in which it acts as a bis(monobasic tridentate) ligand. The coordination sites with the copper(II) ion are phenolic oxygen, azomethine nitrogen and triazinic nitrogen ( $H_2L^1$  ligand) or isatinic oxygen ( $H_2L^2$  ligand). The metal complexes exhibited octahedral and square planar geometrical arrangements. The ligands and some complexes showed antimicrobial activity.

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