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Synthesis, spectroscopic characterization and biological activity of the metal complexes of the Schiff base derived from phenylaminoacetohydrazide and dibenzoylmethane

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Abstract

A new series of mono and binuclear Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), La(III), Ru(III), Hf(IV), ZrO(II) and UO₂(II) complexes of phenylaminodibenzoylhydrazone have been synthesized and characterized by elementals analyses, IR UV–vis spectra, magnetic moments, conductances, thermal analyses (DTA and TGA) and electron spin resonance (ESR) measurements. The IR spectral data show that, the ligand behaves as a neutral bidentate type (**15** and **16**), monobasic bidentate type (**6**), or monobasic tridentate type (**5**, **7**, **8**, **10**, **11**, **13**, **14**, **17–21**) or dibasic tridentate type **2–4**, **9** and **12** towards the metal ion. Molar conductances in DMF solution indicate that, the complexes are non-electrolytes. The ESR spectra of solid complexes (**9** and **10**) show axial and non-axial types indicating a $d_{(x^2-y^2)}$ ground state with significant covalent bond character. However, complexes (**11** and **12**), show isotropic type, indicating manganese(II) octahedral geometry. Antibacterial and antifungal tests of the ligand and its metal complexes are also carried out and it has been observed that the complexes are more potent bactericides and fungicides than the ligand. © 2007 Elsevier B.V. All rights reserved.

Keywords: Complexes; Spectroscopic studies; Conductivity; Thermal analyses; Syntheses; Magnetism; Biological activity

1. Introduction

Hydrazones and their coordination compounds are well known to be biologically important and interest for their antibacterial, antitumour and antitubercular activities [1]. Also, it has been used as analytical reagent [2], polymer-coating, ink, pigment [3] and fluorescent materials [4]. Metal complexes of a bishydrazone derived from isatin monohydrazone and 2hydroxy-1-naphthaldhyde have been reported and they possess interesting biological properties [5,6]. Transition metal complexes of salicyladehyde thiazolyl hydrazone were prepared and characterized [7]. Number of copper(II) complexes of acylhydrazones had been extensively studied [8–10]. Copper(II) and iron(III) complexes of phenylhydrazoacetylacetone isonicotinoyl hydrazone were synthesized and spectrally characterized [2]. They were able to mimic bimetallic sites in various enzymes

* Corresponding author. *E-mail address:* asaeltabl@yahoo.com (A.S. El-Tabl). [11,12]. These compounds showed antifungal and antibacterial activities [11–13]. Metal(II) complexes of 2-acetypyridine benzoylhydrazone ligand were synthesized and crystallographically characterized [14]. Extensive investigations of this kind of complexes have been undertaken recently, however, we have reported the synthesis and characterterization of metal complexes of phenylaminodibenzoylhydrazone tridentate ligand.

2. Experimental

Reagent grade chemicals were used. Phenylaminoacetohydrazide was prepared by a published method [15]. Elemental analyses were determined by the Analytical Unit of Cairo, University of Egypt. Standard methods were used to determine the metal ion content. All metal complexes were dried in vacuo over anhydrous CaCl₂. The IR (as KBr pellets) spectra were measured using a PerkinElmer 683 spectrophotometer (4000–200 cm⁻¹). Electronic spectra in DMF solutions were recorded on a PerkinElmer 550 spectrophotometer. The conductances of 10^{-3} M solution of the complexes in DMF were

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measured at 25 °C with a Bibby conductometer type MCl. The ¹H NMR spectrum of the ligand in DMSO- d_6 was recorded using a 300 MHZ Varian NMR spectrometer. The thermal analyses (DTA and TGA) 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/min. Magnetic moments were measured by Gouy method using $\mu_{eff} = 2.84(X_M T)^{1/2}$. All electron spin resonance (ESR) measurements of solid complexes at room temperature were made using a Varian E-109 spectrophotometer. DPPH was used as a standard material.

2.1. Preparation of the ligand (1) $[H_2L]$

Phenylaminoacetohydrazide (1.7 g, 0.01 mol) was dissolved in 25 mL of EtOH and dibenzoylmethane (2.3 g, 0.01 mol) in 15 mL EtOH was added dropwise. The reaction mixture was refluxed with stirring for 3 h and, then cooled to room temperature. The product was filtered off, washed several times with EtOH and dried over anhydrous CaCl₂.

2.2. Preparation of metal complexes

(a) 2, 5, 8, 11, 17 and 21

These complexes were prepared by mixing stiochiometric ratios (1L:1M) of the ligand (30 mL EtOH) and metal acetate (50 mL) EtOH. Ni(OAc)₂·4H₂O (2), Co(OAc)₂·4H₂O (5), Cu(OAc)₂·H₂O (8), Mn(OAc)₂·4H₂O (11), Zn(OAc)₂·4H₂O (17) and UO₂(OAc)₂ (21). The mixture was refluxed on a hot plate with stirring for 1–2 h, and then left it to cool to room temperature. Fine crystals which separated were filtered off, washed several times with EtOH and dried over anhydrous CaCl₂.

(b) 3, 6, 9 and 18

These complexes were prepared by using the above procedure, using Ni(NO₃)₂·6H₂O (**3**), Co(NO₃)₂·6H₂O (**6**), Cu(NO₃)₂·3H₂O (**9**) [few drops of TEA] and Zn(NO₃)₂·XH₂O (**18**). The mixture was refluxed on a hot plate with stirring for 1–2 h. The precipitate which formed was filtered off, washed several times with EtOH and dried over anhydrous CaCl₂.

(c) 4, 7, 10, 12–16, 19 and 20

These complexes were prepared by using the above procedure, using NiCl₂· $6H_2O$ (4), CoCl₂· $6H_2O$ (7), CuCl₂· XH_2O (10), MnCl₂· $4H_2O$ (12) [few drops of TEA], FeCl₃· $6H_2O$ (13), RuCl₃ (14), ZrOCl₂· $8H_2O$ (15), HfCl₄· $8H_2O$ (16), ZnCl₂· $4H_2O$ (19) and LaCl₃· $7H_2O$ (20). The mixture was refluxed on a hot plate with stirring for 1–2 h and then left it to cool to room temperature. Fine crystals which separated were filtered off, washed several times with EtOH and dried over anhydrous CaCl₂.

3. Microbiology

3.1. Fungus media

Czapek Dox agar medium was prepared by standard method [16]. *Aspergillus niger* was spread over each dish by using sterile

bent loop rod. Disks were cut by sterilized cork borer and then taken by sterilized needle. The resulted pits are sites for the tested compounds. The plates are incubated at $30 \degree$ C for 24–48 h and then any clear zones present were detected.

3.2. Bacteria media

Nutrient agar medium was prepared by standard method [16]. *E. coli* was spread over each dish by using sterile bent loop rod. Disks were cut by sterilized cork borer and then taken by sterilized needle. The resulted pits are sites for the tested compounds. The plates are incubated at 37 °C for 24–48 h and then any clear zones present were detected.

4. Results and discussion

The reaction of phenylaminoacetohydrazide with dibenzoylmethane in EtOH 1:1, molar ratio, led to the formation of H_2L , as shown in Scheme 1.

The IR spectra of the H_2L and its metal complexes show that, the H_2L has tautomeric forms (I–III) as shown below:



The reaction of the H_2L with metal salts using (1:1) or (2:1) molar ratios, led to the formation of metal complexes with different geometries. All the compounds are intensely

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11. <i>2)</i>	90
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(2.9)	6

Table 1 Elemental analyses and physical properties of the H_2L and its metal complexes

Comp no.	Molecular formula	Colour	Yield (%)	m.p. (°C)	$\Omega^{-1}\textrm{mol}^{-1}\textrm{cm}^2$	$\mu_{\mathrm{eff}}\left(\mu_{\mathrm{B}}\right)$	Found (Calc.) (%)				
							C	Н	Ν	Cl	М
1	$[(H_2L)][C_{23}H_{21}N_3O_2]$	Pink	85	70	_	_	74.1(74.4)	5.7(5.7)	11.0(11.3)	_	_
2	[(HL)Ni(OAc)]·3H ₂ O	Yellow	79	170	2.3	Dia.	55.7(55.4)	5.5(5.4)	7.8(7.8)	-	10.2(10.8)
3	$[(L)Ni(H_2O)]$	Pale green	80	118	2	Dia.	61.8(61.9)	5.3(4.7)	9.0(9.4)	-	13.0(13.2)
4	$[(HL)NiCl(H_2O)_2] \cdot (3/2)H_2O$	Yellow	76	280	1.3	2.85	53.4(53.2)	5.2(5.2)	7.9(8.1)	6.3(6.8)	10.9(11.3)
5	[(HL)Co(OAc)(H ₂ O) ₂]H ₂ O	Black	78	105	2	4.8	55.4(55.4)	5.6(5.4)	7.9(7.8)	-	11.0(10.9)
6	$[(HL)_2Co(H_2O)_2] \cdot (1/2)H_2O$	Pale brown	77	110	3.2	4.9	65.9(66.0)	5.3(5.4)	9.6(10.0)	-	7.0(7.0)
7	$[(HL)CoCl(H_2O)_2]\cdot 2H_2O$	Brown	80	300	1.2	3.9	51.7(51.5)	4.9(5.2)	7.6(7.8)	6.8(6.6)	10.8(11.0)
8	[(HL)Cu(OAc)]·H ₂ O	Brown	81	245	1.2	1.73	58.9(58.8)	4.7(4.9)	8.3(8.2)	-	12.3(12.4)
9	$[(L)Cu_2(NO_3)_2(H_2O)]$	Green	77	190	1.2	1.2	43.3(43.3)	3.8(3.3)	11.0(11.0)	-	19.7(19.9)
10	$[(HL)Cu(Cl)(H_2O)_2]$	Dark green	82	160	1.8	1.74	54.5(54.7)	4.5(4.8)	8.5(8.3)	7.0(7.0)	12.6(12.6)
11	$[(HL)Mn(OAc)(H_2O)_2] \cdot (3/2)H_2O$	Brown	75	115	1.2	5.96	55.9(55.7)	5.7(5.6)	7.4(7.8)	-	12.6(10.2)
12	$[(L)_2Mn_2(H_2O)_4]$	Pale brown	79	110	1.4	3.7	60.5(60.0)	5.6(5.0)	9.0(9.13)	-	12.2(11.9)
13	$[(HL)FeCl_2(H_2O)]$	Brown	76	225	5.4	5.72	53.1(53.6)	4.5(4.3)	8.2(8.2)	13.5(13.8)	10.9(10.8)
14	[(HL)Ru(OH)Cl(H ₂ O)]·3H ₂ O	Black	77	>300	2.1	1.73	46.1(46.3)	5.1(4.9)	7.0(7.0)	5.9(6.0)	17.0(17.0)
15	$[(H_2L)ZrOCl_2]\cdot 7H_2O$	Yellow	82	220	4	Dia.	40.7(40.9)	5.3(5.2)	6.8(6.22)	10.9(10.5)	13.5(13.5)
16	$[(H_2L)HfCl_4]6H_2O$	Green	80	240	3.8	Dia.	34.6(34.5)	4.1(4.1)	5.3(5.3)	17.5(17.8)	22.3(22.3)
17	$[(HL)Zn(OAc)(H_2O)_2] \cdot 3H_2O$	Pink	79	220	1.82	Dia.	51.3(51.3)	5.5(5.6)	7.2(7.2)	-	11.2(11.2)
18	$[(HL)_2Zn(H_2O)]$	Pink	81	138	2.3	Dia.	67.1(67.0)	5.1(5.1)	10.2(10.2)	-	8.0(7.9)
19	$[(HL)ZnCl(H_2O)_2]$	Pink	84	145	1.9	Dia.	54.5(54.5)	4.7(4.7)	8.3(8.3)	7.0 (7.0)	12.9(12.9)
20	$[(L)(HL)La_2Cl_3(H_2O)]\cdot 4H_2O$	Pale green	75	250	2.8	Dia.	44.9(45.5)	3.8(4.0)	7.0 (6.9)	8.7(8.8)	22.8(22.9)
21	$[(HL)UO_2(OAc)] \cdot 2H_2O$	Orange	80	165	3.2	Dia.	40.5(40.9)	3.8(3.5)	5.6 (5.7)	-	32.9(32.4)



coloured, crystalline solids, and stable at room temperature and not decomposing after prolonged storage. The complexes are insoluble in non-polar and polar solvents but soluble in polar coordinating solvents such as DMSO and DMF. Elemental analyses and physical data (Table 1), and spectral data (Tables 2 and 3), are compatible with the proposed structures (Fig. 1). To date, no diffractable crystals have been grown. The reaction of phenylaminoacetohydrazide, dibenzoylmethane and metal salts (1:1:1), molar ratios in ethanol led to the formation of the same complexes (**2–21**).

4.1. ¹H NMR spectrum of the ligand

The ¹H NMR spectrum of the H₂L in DMSO-*d6* shows signals, confirmed with the suggested structure (II). The peaks at 8.19–8.16 ppm range, are assignable to the proton of NH group (s, 1H, NH) [17]. Multiplet signals at 6.62–6.59 and 7.32–7.06 ppm ranges are observed due to the aromatic protons (m, 6H, Ar–H) and (m, 9H, Ar–H), respectively. The resonances at 4.87 and 4.3 ppm are corresponding to –CH=C– and methylene groups (s, 1H, CH) and (s, 2H, CH₃), respectively [14,17,18].

4.2. Conductivity measurements

The molar conductance values of the complexes are in the $(1.2-4.0 \ \Omega^{-1} \ cm^2 \ mol^{-1})$ range (Table 1), the low values indicate the non-electrolytic nature of the complexes [19,20]. This confirms that, the anion is coordinated to the metal ion.

4.3. IR spectra

Important spectral bands of the H₂L and its metal complexes are presented in Table 2. The IR spectrum of the H₂L shows a broad medium bands in the 3450–3200 and 3100–2600 cm⁻¹ ranges, which attributed to inter- and intramolecular hydrogen bondings [21]. The spectrum shows broad strong bands at 3396 and 3250 and strong bands at 1662 and 1600 cm⁻¹, are assigned to the ν (NH), ν (C=O) and ν (C=N), respectively [22–26]. Also, the strong and medium bands appear at 1570, 1508 and 1326 cm⁻¹, correspond to ν (C=C)_{Ar}, ν (CH=C)_{Al} and ν (C–O), respectively [25,27]. In order to know, the mode of

Table 2

IR spectra	(assignments)	of the H ₂ L an	d its metal complexes
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Comp. no.	OH/H2Ohydr./H2Ocoord.	ν (H-bonding)	ν (NH)	v(CO)	$\nu(C-N)$	$\nu(C-C)_{Ar}$	v(CH-C) _{Al}	ν(C-O)	$\nu(OAc)$	ν(M -O)	ν(M —N)	$\nu(M-Cl)$
1	-	3450-3200(br), 3100-2600(br)	3300, 3250 (m), (m)	1662(s)	1600(m)	1570(s)	1508(s)	1326(s)	-	-	-	-
2	-/3570-3300(br)	3280-2850(br), 2800-2460(br)	3300, 3240 (m), (m)	1630(s)	1605, 1599 (m)	1552(s)	1516(s)	1227(m)	1600, 1370 (m), (m)	631(m)	521(m)	-
3	-/-/3250-3050(br)	3000-2830(br), 2820-2400(br)	3352, 3270 (m), (m)	-	1606, 1596 (m)	1550(s)	1523(s)	1228(m)	-	631(m)	525(m)	-
4	3375(s)/3450-3200(br)/3180-2950(br)	3150-2950(br), 2900-2500(br)	3275, 3215 (m), (m)	-	1629, 1599 (m)	1555(s)	1518(s)	1317, 1222 (m), (m)	-	693(m)	517(m)	410(m)
5	-/3560-3250(br)/3200-3030(br)	3000-2820(br), 2800-2380(br)	3334, 2250 (m), (br)	1702(s)	1595(m)	1547(s)	1522(s)	1316, 1226 (m), (m)	1605, 1388 (m), (m)	689, 619 (m), (m)	514(m)	-
6	-/3560-3300(br)/3250-3070(br)	3050-2820(br), 2800-2370(br)	3372, 3275 (m), (m)	1661(s)	1595(m)	1548(s)	1523(s)	1308, 1229 (m), (m)	-	687, 625 (m), (m)	523(m)	-
7	3550(s)/3560-3320(br)/3280-3100(br)	3080-2780(br), 2760-2425(br)	3400, 3263 (m), (m)	-	1632(m)	1550(s)	1517(s)	1308, 1226 (m), (m)	-	692, 625 (m), (m)	519(m)	420(m)
8	-/3530-3280(br)	3100-2800(br), 2780-2380(br)	3389, 3175 (m), (m)	1655(s)	1596(m)	1572(s)	1525(s)	1312, 1230 (m), (m)	1600, 1399 (m), (m)	688, 656 (m), (m)	570(m)	-
9	-/-/3350-3120(br)	3100-2820(br), 2800-2450(br)	3325, 3250 (m), (m)	-	1629, 1595 (m)	1548(s)	1527(s)	1314, 1208 (m), (m)	-	689, 636 (m), (m)	566, 523 (m), (m)	-
10	-/-/3380-3190(br)	3150-2960(br), 2950-2520(br)	3265, 3234 (m), (m)	1726(s)	1593(m)	1575(s)	1522(s)	1311, 1270 (m), (m)	-	692, 630 (m), (m)	538(m)	420(m)
11	-/3520-3260(br)/3230-3030(br)	3000-2800(br), 2780-2450(br)	3325, 3245 (m), (m)	1650(s)	1595(m)	1550(s)	1515(s)	1306, 1224 (m), (m)	1625, 1393 (m)	691, 651 (m), (m)	518(m)	-
12	-/-/3350-3100(br)	3080-2820(br), 2800-2450(br)	3300, 3185 (m), (m)	-	1606, 1599 (m), (m)	1553(s)	1517(s)	1310, 1227 (m), (m)	-	631, 691 (m), (m)	521	-
13	3380-3190(br)	3150-2850(br), 2825-2450(br)	3325, 3261 (m), (m)	1648(s)	1612(m)	1575(s)	1523(s)	1345(m)	-	686, 649 (m), (w)	617(m)	421(m)
14	-/3580-3280(br)/3250-3125(br)	3100-2780(br), 2770-2380(br)	3391, 3260 (m), (m)	1633(s)	1593(m)	1550(s)	1518(s)	1311, 1230 (m), (m)	-	694, 617 (m), (m)	545(m)	410(m)
15	3363(s)/3600-3200(br)	3180-2720(br), 2700-2380(br)	3330, 3250 (m), (m)	-	1595(m)	1560(s)	1524(s)	1318, 1224 (m), (m)	-	685, 612 (m), (m)	540(w)	410(m)
16	3390/3580-3225(br)	3170-2720(br), 2700-2380(br)	3296, 3235 (m), (m)	-	1612, 1596 (m), (m)	1551(s)	1531(s)	1321, 1225 (m), (m)	-	685, 613 (m), (m)	542(m)	420(m)
17	-/3580-3250(br)/3180-3080(br)	3070-2850(br), 2830-2480(br)	3396, 3286 (m)	1662(s)	1629(m)	1551(s)	1533(s)	1341, 1225 (m), (m)	1603, 1395 (m), (m)	677, 637 (m), (w)	520(m)	-
18	-/-/3350-3190(br)	3180-2860(br), 2850-2450(br)	3406, 3289 (m), (m)	1660(s)	1597(m)	1551(s)	1520(s)	1309, 1225 (m), (m)	-	686, 625 (m), (m)	532(m)	-
19	-/-/3325-3200(br)	3190-2870(br), 2850-2460(br)	3437, 3289 (m), (m)	1655(s)	1597(m)	1551(s)	1520(s)	1308, (m)	-	687, 625 (m), (m)	528(m)	407(m)
20	-/3500-3320(br)/3300-3180(br)	3170-2930(br), 2900-2450(br)	3406, 3280 (m), (m)	1650(s)	1598(m)	1552(s)	1519(s)	1308, 1223 (m), (m)	-	689, 608 (m), (m)	519(w)405, 375 (m	.), (m)
21	-/3570-3320(br)	3200-2800(br), 2780-2400(br)	3466, 3190 (m), (m)	1650(s)	1594(m)	1545(s)	1518(s)	1311, 1223 (m), (m)	1600, 1365 (m), (m)	688, 617 (m), (m)	514(m)	-

Strong = (s), medium = (m), broad = (br) and weak = (w).

Table 3	
UV-vis spectra of the H ₂ L and its metal complexes	

Comp no.	Molecular formula	λ_{\max} (nm)
1	[(H ₂ L)]	$370 (\varepsilon = 8.9 \times 10^{-3} \text{ mol}^{-1} \text{ cm}^{-1})$
	$[C_{23}H_{21}N_{3}O_{2}]$	$320 (\varepsilon = 7.7 \times 10^{-3} \text{ mol}^{-1} \text{ cm}^{-1})$
2	[(HL)Ni(OAc)]·3H ₂ O	$550 (\varepsilon = 5 \times 10^{-3} \text{ mol}^{-1} \text{ cm}^{-1}), 420 (\varepsilon = 2.6 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 350, 315$
3	$[(L)Ni(H_2O)]$	$565 \ (\varepsilon = 1 \times 10^{-2} \text{ mol}^{-1} \text{ cm}^{-1}), 420 \ (\varepsilon = 2.8 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 360, 315$
4	$[(HL)NiCl(H_2O)_2] \cdot (3/2)H_2O$	725, ($\mathbb{C} = 6.2 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}$), 525 ($\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}$), 450, 360, 315
5	[(HL)Co(OAc)(H ₂ O) ₂]H ₂ O	715 ($\varepsilon = 5 \times 10^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$), 560 ($\varepsilon = 5 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}$), 460, 365, 315
6	$[(HL)_2Co(H_2O)_2]\cdot(1/2)H_2O$	$690 (\varepsilon = 6.6 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 410 (\varepsilon = 2.3 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 355, 295 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 505 (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} $
7	$[(HL)CoCl (H_2O)_2] \cdot 2H_2O$	695, 500, 420 ($\varepsilon = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}$), 350, 300
8	[(HL)Cu(OAc)]·H ₂ O	$580 \ (\varepsilon = 1 \times 10^{-2} \text{ mol}^{-1} \text{ cm}^{-1}), 430 \ (\varepsilon = 1.7 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 390, 345, 300$
9	$[(L)Cu_2(NO_3)_2(H_2O)]$	$570 \ (\varepsilon = 6.2 \times 10^{-4} \ \text{mol}^{-1} \ \text{cm}^{-1}), 480 \ (\varepsilon = 2.5 \times 10^{-4} \ \text{mol}^{-1} \ \text{cm}^{-1}), 395 \ (\varepsilon = 2.8 \times 10^{-5} \ \text{mol}^{-1} \ \text{cm}^{-1}), 345, 315 \ \text{mol}^{-1} \ \text{cm}^{-1}), 345, 315 \ \text{mol}^{-1} \$
10	$[(HL)Cu(Cl)(H_2O)_2]$	660, 545 ($\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}$), 450 ($\varepsilon = 4.0 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}$), 340, 315
11	$[(HL)Mn(OAc)(H_2O)_2] \cdot (3/2)H_2O$	$625, 520 \ (\varepsilon = 3.3 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}), 470 \ (\varepsilon = 2.3 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 330, 310$
12	$[(L)_2Mn_2(H_2O)_4]$	660, 490 ($\varepsilon = 6.6 \times 10^{-4} \text{ mol}^{-1} \text{ cm}^{-1}$), 415 ($\varepsilon = 3.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}$), 340, 305
13	$[(HL)FeCl_2(H_2O)]$	$680, 520 \ (\varepsilon = 2 \ \times 10^{-3} \text{ mol}^{-1} \text{ cm}^{-1}), 420 \ (\varepsilon = 5.5 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 345, 315$
14	$[(HL)Ru(OH)Cl(H_2O)]\cdot 3H_2O$	$620 (\varepsilon = 6.6 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 360, 305 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 360, 305 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 360, 305 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 360, 305 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 360, 305 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 360, 305 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 360, 305 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 360 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 360 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 470 (\varepsilon = 2.2 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = 4.7 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^{-1}), 560 (\varepsilon = $
15	$[(H_2L)ZrOCl_2]\cdot7H_2O$	390, 345, 300
16	$[(H_2L)HfCl_4]\cdot 6H_2O$	390,350, 300
17	$[(HL)Zn(OAc)(H_2O)_2] \cdot 3H_2O$	355, 315
18	$[(HL)_2Zn(H_2O)]$	350, 320
19	$[(HL)ZnCl(H_2O)_2]$	350, 315
20	$[(L)(HL)La_2Cl_3(H_2O)]\cdot 4H_2O$	320, 315
21	[(HL)UO ₂ (OAc)]·2H ₂ O	460 ($\varepsilon = 2.3 \times 10^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$), 330, 310

coordination between the ligand and the metal ion, the IR spectrum of the H₂L is compared with that of the metal complexes. The $\nu(OH)$ of complexes (4), (7), (15 and 16) observed as strong band at 3375, 3550, 3363 and $3390 \,\mathrm{cm}^{-1}$, respectively. The complexes show broad bands in the 3250-2720 and $2950-2370 \,\mathrm{cm}^{-1}$, ranges are due to intermolecular and intramolecular hydrogen bondings. Also, the complexes show a broad band in the $3600-3200 \text{ cm}^{-1}$ range, which is assigned to hydrated water molecules except complexes (3), (9, 10), (12, 13), (18 and 19). However, the broad band due to the coordinated water molecules appears in the $3380-2950 \text{ cm}^{-1}$ range except complexes (2), (8), (15, 16) and (21) [27,28]. The v(NH) appears medium bands at 3466-3296 and 3289-3175 cm⁻¹ ranges [27,28]. The complexes show a strong band in the 1726–1633 cm⁻¹ range (Table 2), which is assigned to ν (C=O) group except complexes (2–4), (7), (9), (12), (15 and 16) [29,30], however, the medium and strong bands appear in the 1632–1593, 1575–1545 and 1533–1508 cm⁻¹ ranges is due to ν (C=N), ν (C=C)_{Ar} and ν (CH=C) vibrations, respectively [25,31]. Complexes (2), (5), (8), (11), (17) and (21) show $v_a(CO_2) = 1600$, 1605, 1600, 1625, 1603 and 1602 cm^{-1} and $v_s(\text{CO}_2) = 1370$. 1388, 1399, 1393, 1395 and 1365 cm⁻¹, respectively suggesting monodentate acetate group [32–34]. Complex (9) shows strong and medium bands at 1410, 1360, 1208, 823 and 763 cm^{-1} (Table 2), which is assigned to a bridging and terminal nitrate group [33,35,36]. The medium band appears at 1345-1208 cm⁻¹ range corresponds to $\nu(CO)$ group [25,27]. The complexes (4), (7), (10), (13-16), (19 and 20) show a medium band at 421–405 and $390-375 \text{ cm}^{-1}$ ranges, corresponding to terminal and bridging chloride atoms, however, complex (15) shows a medium band at $760 \,\mathrm{cm}^{-1}$ is assigned to $\nu(\text{ZrO})$ vibration [37]. Complex (21) shows a medium band at 940 cm^{-1} is due to O=U=O group [37]. The bonding of the metal ions to the H₂L

through the oxygen and nitrogen atoms is further supported by the presence of new medium and weak bands at 694–608 and 566–514 cm⁻¹ranges, are due to ν (M–O) and ν (M–N), respectively [33,38]. The above results together with the elemental analyses indicated that, the hydrazone coordinated to the metal ion, via the carbonyl oxygen of the hydrazide moiety, carbonyl oxygen of the dibenzoylmethane moiety in enolic or ketonic form and azomethine nitrogen atom.

4.4. Magnetic moments

The room temperature magnetic moments of the complexes (2-21) are shown in Table 1. Nickel(II) complexes (2 and 3) show diamagnetic values confirming square planar geometry around the nickel(II) ion However, complex (4) shows value 2.85 $\mu_{\rm B}$, indicating octahedral geometry [33,37–41]. Cobalt(II) complexes (5–7) show values in the 4.8–3.9 μ_B range (Table 1), indicating high-spin octahedral cobalt(II) complexes [16]. The magnetic moments for the copper(II) complexes (8, 9 and 10) are 1.73, 1.2 and 1.74 $\mu_{\rm B}$, respectively. The value of complex (9) is well below the spin-only value $(1.73\mu_B)$, indicating spinexchange interactions take place between the copper(II) ions [38]. However, the values of the other complexes correspond to one unpaired electron in a square planar or octahedral structure [16]. The magnetic moment values for manganese(II) complexes (11 and 12) are 5.69 and 3.7 $\mu_{\rm B}$, suggest octahedral geometry around the manganese(II) ion [16]. The low moment of (12) may be ascribed to superexchange takes place between manganese(II) ions. Iron(III) complex (13) shows value 5.4 $\mu_{\rm B}$, indicating a high-spin iron(III) octahedral geometry [5]. Ruthenium(III) complex (14) shows a magnetic value 2.1 $\mu_{B.}$, indicating an octahedral structure [42]. Zirconium(IV) complex (15), hafnium(IV) complex (16), zinc(II) complexes (17-19),

lanthanum(III) complex (20) and uranyl complex (21) show diamagnetic values.

4.5. Electronic spectra

The electronic spectral data of the H₂L and its metal complexes are summarized in Table 3. The H₂L shows two bands at 370 nm ($\varepsilon = 8.9 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 320 nm ($\varepsilon = 7.7 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$), which may be assigned to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively, the complexes

show two bands in the 295–315 and 330–365 nm ranges which are assigned to intraligand transition [16,43]. The nickel(II) complexes (**2**) and (**3**) show two bands at 420 and 550 nm and 420 and 565 nm are due to ${}^{3}T_{1} \rightarrow {}^{3}T_{2}$ and ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{2}(P)$ transitions, indicating square planar environment around the nickel(II) ion [44,45]. However, complex (**4**), shows bands at 450, 525 and 725 nm, which are attributable to ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)(\upsilon_{3})$, ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)(\upsilon_{2})$ and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)(\upsilon_{1})$ transitions, respectively indicating an octahedral nickel(II) complex [16,46,47]. The $\upsilon_{2}/\upsilon_{1}$ ratio for the complex is 1.38 which is less



Fig. 1. Structural representation of the complexes.



Fig. 1. (Continued).

than the usual range of 1.5–1.75, indicating distorted octahedral nickel(II) complexes [33,37,40,48,7]. The cobalt(II) complexes (5-7) show bands in the 410-460, 500-550 and 690-715 nm ranges, are assigned to ${}^{4}T_{1g}$ (F) $\rightarrow {}^{4}T_{1g}$ (P), ${}^{4}T_{1g}$ (F) $\rightarrow {}^{4}A_{2g}$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$, transitions, respectively, corresponding to high-spin cobalt(II) octahedral complexes [40,49]. The copper(II) complexes (8) and (9) show different bands (Table 3) at 390, 430 and 580 nm and 395, 480 and 570 nm, corresponding to ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$, ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$, respectively, suggesting square planar geometry [50,51]. However, copper(II) complex (10) shows bands at 450, 545 and 660 nm, are assigned to ligand \rightarrow metal charge transfer, ${}^{2}B_{1} \rightarrow {}^{2}E$ and ${}^{2}B_{1} \rightarrow {}^{2}B_{2}$ transitions respectively, indicating a distorted octahedral structure [10,44,52]. Manganese(II) complexes (11) and (12) show bands at 470, 520 and 625 nm and 415, 490 and 660 nm, respectively are corresponding to $^6A_{1g} \rightarrow {}^4E_g, {}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$ transitions which are compatible to an octahedral geometry around the manganese(II) ion [53]. Iron(III) complex (13) shows bands at 420, 520 and 680 nm, are due to charge

transfer transition while the last band is considered to arise from the ${}^{6}A_{1} \rightarrow {}^{4}T_{1}$ transition, these bands suggest, distorted octahedral geometry around the iron(III) [52,54]. Ruthenium(III) complex (14), shows bands at 470, 560 and 620 nm, respectively, are due to LMCT transition and the last band is assigned to ${}^{2}T_{2g} \rightarrow {}^{2}A_{2g}$ transition. The band position are similar to those observed for other octahedral ruthenium(III) complexes [55–58]. Zirconium(IV) complex (15), hafnium(IV) complex (16), zinc(II) complexes (17–19), lanthanum(III) complex (20) and uranyl(VI) complex (21) show bands (Table 3) corresponding to intraligand transitions [59,60].

4.6. Electron spin resonance

The ESR spectra of solid copper(II) complexes (9) and (10) at room temperature are characteristic of d^9 , configuration and having an axial and non-axial types of a $d_{(x^2-y^2)}$ ground state [61,62]. The *g*-values suggest square planar or octahedral geometries [30] and the complex (9) shows $g_{\parallel} > g_{\perp} > 2.0023$,

Table 4			
Thermal	data for	the metal	complexes

Comp. no.	Temperature (°C)	DTA (peak)		TGA (Wt. loss %)		Assignment
		Endo	Exo	Calc.	Found	
4	70	endo	-	5.2	5.0	Loss of hydrated water $(1.5 \cdot H_2O)$
	210	endo	-	14.5	15.1	Loss of coordinated water $(2H_2O)$ + one chlorine atom
	370	_	exo			
	450	_	exo			
	490	_	exo	17.78	18.1	Decomposition with the formation of NiO
14	65	endo	-	9.0	8.65	Loss of hydrated water $(3H_2O)$
	215	endo	-	13.43	13.8	Loss of coordinated water, chloride atom and hydroxyl group
	300	-	exo			
	350	_	exo			
	420	_	exo			
	600	_	exo	39.51	39.43	Decomposition with the formation of Ru ₂ O ₃
15	90	endo	_	18.66	19.2	Loss of hydrated water $(7H_2O)$
	200	endo	-	12.92	13.2	Loss of chloride atom (2Cl)
	350	_	exo			
	450	-	exo			
	550	_	exo	25.76	25.5	Decomposition with the formation of ZrO ₂
16	85	endo	-	13.5	14.0	Loss of hydrated water $(6H_2O)$
	220	endo	-	20.53	21.0	Loss of, chloride atom (4Cl)
	450	_	exo			
	600	_	exo	38.3	38.1	Decomposition with the formation of HfO ₂
17	75	endo	_	9.24	9.63	Loss of hydrated water $(3H_2O)$
	140	endo	-	6.78	6.9	Loss of coordinated water (2H ₂ O)
	320	endo	_	11.93	12.0	Loss of acetate group
	380	_	exo			
	450	-	exo			
	550	-	exo	18.69	18.5	Decomposition with the formation of ZnO

indicating square planar geometry around the copper(II) ion [21,63,64], however, complex (10) shows non-axial type $g_x > g_y > g_z > 2.0023$ with $(g_y - g_z)/(g_x - g_y) < 1 = 0.23$, indicating a $d_{(x^2-y^2)}$ ground state [21]. The ESR parameters for complex (9) are $g_{\parallel} = 2.22$, $g_{\perp} = 2.09$ and $g_{iso} = 2.13$, $A_{\parallel} = 160 \ G, A_{\perp} = 15 \ G \text{ and } A_{\text{iso}} = 63.3 \ G, \ G = 2.44, \ \alpha^2 = 0.71,$ $g_{\parallel}/A_{\parallel} = 134.5 \text{ cm}^{-1}, K_{\parallel} = 0.76, K_{\perp} = 1.05 \text{ and } K = 0.96, \beta_1^2 =$ 0.80 and $\beta^2 = 1.5$, 2B = -156 and $a_d^2 = 66\%$ and for complex (10), are $g_x = 2.21$, $g_y = 2.08$ and $g_z = 2.05$ [65]. Complex (9) shows G is 2.44, indicating spin-exchange interactions take place between the copper(II) ions [65]. This is confirmed from the magnetic moment. The $g_{\parallel}/A_{\parallel}$ value for complex (9) is (134.5 cm^{-1}) lies just within the range expected for square planar complexes [66]. The g_{\parallel} -value reported here is 2.22 in complex (9) indicating considerable covalent bonding character [30,63,67]. The calculated value of α^2 of complex (9) is 0.71, suggesting considerable covalent bonding [21,68,69]. Kvalue for the complex (9) is 0.96, which confirmed covalent nature [69,70]. Also, the complex (9) shows $\beta_1^2 = 0.8$, indicating a moderate degree of covalancy in the in-plane π -bonding, while $B^2 = 1.5$, indicates the ionic character of the out-of plane π -bonding [71,72]. In complex (9) the isotropic coupling constant is $A_{iso} = -63.3 G$, and the parallel component of the dipolar coupling is 2B = -156G, giving orbital population 66%, indicating a $d_{(x^2-y^2)}$ ground state [66]. However, the ESR spectrum of manganese(II) complexes (11 and 12) show isotropic type with $g_{\rm iso} = 2.022$ and 2.033, respectively typical to manganese(II) octahedral structure.

4.7. Thermal analyses (DTA and TGA)

The DTA and TGA dehydrating curves for complexes (4, and 14–17) show that, the complexes are thermally stable up to 50 °C. Dehydration is characterized by endothermic peaks within the temperature 65–90 °C range [58,73,74]. Complexes (4, 14 and 17) show endothermic peak at 210, 215 and 140 °C, respectively is due to the loss of coordinated water molecules. Another endothermic peak was observed around 200 °C (Table 4), corresponds to the loss of chlorine atoms, however complex (17) shows endothermic peak at 320 °C, is due to the loss of acetate group. The results were confirmed by TGA data (Table 4). The product is stable up to 300 °C when the organic constituents, of the complexes start decomposing, finally leaving the metal oxides (490–600 °C) [75]. The thermal decomposition of complex (4) can be represented as follows:

$$[(HL)NiCl(H_2O)_2]_2^3 H_2O \xrightarrow{70 \,^{\circ}C} [(HL)NiCl(H_2O)_2] + \frac{3}{2}H_2O,$$

$$[(HL)NiCl(H_2O)_2] \xrightarrow{210 \,^{\circ}C} [(HL)Ni] + 2H_2O + Cl,$$

$$[(HL)Ni] \xrightarrow{490 \,^{\circ}C} NiO + volatile organic residue$$

The thermal data of the complexes are shown in Table 4.

4.8. Antibacterial and antifungal screening

The results obtained are presented in Table 5. It is observed that, the activity of the metal complexes increases with increase

n	0
У	0

Table 5

No. of comp	At 250 µg/mL		At 200 μg/mL		At 175 μg/mL		At 150 μg/mL		At 125 μg/mL	
	Fungi	Bacteria								
1	25	50	19	41	12	30	0	24	0	17
3	32	43	25	35	18	28	12	20	0	15
5	31	54	26	45	20	39	14	27	0	20
6	32	48	26	39	19	28	13	17	0	13
8	52	35	45	28	37	20	30	15	20	11
9	35	38	28	30	19	24	13	18	11	13
11	29	43	23	35	18	28	13	23	0	15
18	37	52	31	45	25	37	18	29	14	22

The percent effect of the H₂L and its metal complexes on microorganisms at different concentrations

The percent effect = (diameter of zone/diameter of Petri dish) × 100; Fungi, Aspergillus niger; Bacteria, E. coli; DMF was used as antimicrobial inert solvent.

in the concentration of the solutions. All the metal complexes are more potent bactericides and fungicides than the H₂L. This enhancement in the activity can be explained on the basis of chelation theory [76,77]. The results showed that, copper(II) complex (8) shows higher antifungal activity than the other complexes in all concentrations, however, cobalt(II) complexes (5) shows higher antibacterial activity than the other complexes in all concentrations except at low concentration ($125 \,\mu g/mL$). Zn(II) complex (18) shows higher antibacterial at 200 μ g/mL and $125 \,\mu$ g/mL concentrations. The order of activity of the all complexes is 18 > 5 > 6 > 8 > 9 > 11 > 3 > 1. The variation in the activity of different complexes against different microorganisms depends either on the impermeability of the cells of the microbes or differences in ribosome's in microbial cells [78]. The antibacterial and antifungal activities of the hydrazone ligands and their metal complexes are screened using the disk diffusion [79].

5. Short conclusion

Metal complexes of new hydrazone derived from diketone have been prepared and characterized by elemental, spectral, thermal and magnetic measurements. Modes of coordination depend into the nature of metal ion and the medium of the reaction. The complexes are non-electrolytes and have covalent bond character. Antibacterial and antifungal tests have been carried out.

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