

N¹,N²-bis(3-((3-hydroxynaphthalen-2-yl)methylene-amino)propyl)phthalamide의 크롬(III), 망간(II), 철(III), 코발트(II), 니켈(II), 구리(II), 루테튬(III) 및 산화 지르코늄(II) 착물에 대한 합성과 분광학 및 생물학적 연구

Ahmed N. Al-Hakimi[†], Mohamad M. E. Shakdofa[‡], Ahemd M. A. El-Seidy[‡], and Abdou S. El-Tabl^{*,§}

[†]Department of chemistry, Faculty of science, Ibb University, Ibb, Yemen

[‡]Inorganic Chemistry Department, National Research Center, P.O. 12622 Dokki, Cairo, Egypt

[§]Department of chemistry, Faculty of science, El-Menoufia University, Shebin El-Kom, Egypt.

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Synthesis, Spectroscopic, and Biological Studies of Chromium(III), Manganese(II), Iron(III), Cobalt(II), Nickel(II), Copper(II), Ruthenium(III), and Zirconyl(II) Complexes of N¹,N²-Bis(3-((3-hydroxynaphthalen-2-yl)methylene-amino)propyl)phthalamide

Ahmed N. Al-Hakimi[†], Mohamad M. E. Shakdofa[‡], Ahemd M. A. El-Seidy[‡], and Abdou S. El-Tabl^{*,§}

[†]Department of chemistry, Faculty of science, Ibb University, Ibb, Yemen

[‡]Inorganic Chemistry Department, National Research Center, P.O. 12622 Dokki, Cairo, Egypt

[§]Department of chemistry, Faculty of science, El-Menoufia University, Shebin El-Kom, Egypt.

*E-mail: asaeltabl@yahoo.com

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요 약. N¹,N²-bis(3-((3-hydroxynaphthalen-2-yl)methylene-amino)propyl)phthalamide (H₄L, **1**) 의 새로운 크롬(III), 망간(II), 철(III), 코발트(II), 니켈(II), 구리(II), 루테튬(III) 및 산화 지르코늄(II) 착물을 합성하여 원소분석, 물리적 성질 및 분광학적 으로 특성을 규명하였다. 분광학적 결과를 통해 이 리간드는 [H₄LMX₂(H₂O)]·nH₂O (M = Cu(II), Ni(II), Co(II), X = Cl 또는 NO₃)의 일반식을 갖는 착물 **2-5**에서는 중성의 삼배위 리간드로 행동한다. 또는 [H₄L(ZrO)₂Cl₂]·8H₂O 의 일반식을 갖는 착물 **6-9**에서는 이염기성 육배위 리간드로 행동한다. DMF 용액에서의 몰전기전도도 실험결과 이들 착물은 비이온성을 나타낸다. 고체 구리착물 **2**, **5** 및 **6** 의 ESR 스펙트럼에서 g_{||} > g_⊥ 을 보이는데, 이는 일그러진 팔면체구조와 큰 공유결합 성을 갖는 d_{x²-y²} 오비탈에 비공유 전자쌍이 존재함을 의미한다. 이합체 구리(II) 착물 [H₂LCu₂Cl₂(H₂O)₄]·3H₂O (**6**)에 대해 두 구리원자 사이의 거리를 ESR 스펙트럼으로부터 추정된 parallel component 의 field zero splitting 파라메타를 이용하여 계산하였다. 이들 화합물의 항박테리아 및 항균 활성도를 측정한 결과, 몇가지 금속 착물의 경우 표준시약인 tetracycline (박테리아) 및 Amphotricene B (균류)보다 더 큰 저해효과를 보였다.

주제어: 착물, 합성, Schiff 염기, 자성, 생물학적 연구

ABSTRACT. Novel chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), ruthenium(III), and zirconyl(II) complexes of N¹,N²-bis(3-((3-hydroxynaphthalen-2-yl)methylene-amino)propyl)phthalamide (H₄L, **1**) have been synthesized and characterized by elemental, physical, and spectral analyses. The spectral data showed that the ligand behaves as either neutral tridentate ligand as in complexes **2-5** with the general formula [H₄LMX₂(H₂O)]·nH₂O (M=Cu(II), Ni(II), Co(II), X = Cl or NO₃), neutral hexadentate ligand as in complexes **10-12** with the general formula [H₄LM₂Cl₆]·nH₂O (M=Fe(III), Cr(III) or Ru(III)), or dibasic hexadentate ligand as in complexes **6-9** with the general formula [H₂LM₂Cl₂(H₂O)₄]·nH₂O (M = Cu(II), Ni(II), Co(II) or Mn(II), and **13** with general formula [H₄L(ZrO)₂Cl₂]·8H₂O. Molar conductance in DMF solution indicated the non-ionic nature of the complexes. The ESR spectra of solid copper(II) complexes **2**, **5**, and **6** showed g_{||} > g_⊥, indicating distorted octahedral structure and the presence of the unpaired electron in the d_{x²-y²} orbital with significant covalent bond character. For the dimeric copper(II) complex [H₂LCu₂Cl₂(H₂O)₄]·3H₂O (**6**), the distance between the two copper centers was calculated using field zero splitting parameter for the parallel component that was estimated from the ESR spectrum. The antibacterial and antifungal activities of the compounds showed that, some of metal complexes exhibited a greater inhibitory effect than standard drug as tetracycline (bacteria) and Amphotricene B (fungi).

Keywords: Complexes, Synthesis, Schiff base, Magnetism, Biological studies

INTRODUCTION

Schiff base transition metal complexes have been of great interest for many years since they are becoming increasingly important as biochemical, analytical and antimicrobial reagents.¹ Many of metal complexes were showed anticancer and antimicrobial activities.²⁻⁴ It was reported that, some drugs have greater activity when administered as metal complexes than that as free organic compounds.⁵ So, Schiff base complexes might an untapped reservoir for drugs. Synthetic model studies involving magnetically coupled binuclear transition metal systems had attracted much interest because these studies provided deeper insights into complex biological processes. Also, homo binuclear lanthanide(III) complexes with isonicotinoyl hydrazone ligand had been prepared and characterized.⁶ Polyamino carboxylate groups had been used for the design of polydentate ligands such as ethylenediamine tetraacetic acid and diethylenetriamine penta acetic acid, generally showed high affinity for metal cations.⁷ These ligands were widely used as chelating agents in fundamental research⁸ or as diagnostic tools in the pharmaceutical industry⁹ and they are particularly suitable for magnetic resonance imaging (MRI).^{10,11} A majority of Schiff base complexes incorporating five- or six-membered metallocycles are represented by N. O- ligand environment have been published.¹² The aim of this work is the preparation, characterization and antimicrobial activity of chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), ruthenium(III), and zirconyl(II) complexes of N¹,N²-bis(3-((3-hydroxynaphthalen-2-yl)methylene amino)propyl)phthalamide (H₄L).

EXPERIMENTAL

All chemicals and solvents were reagent grade commercial material and used as received. Elemental analyses for (C, H, N, Cl) were determined at the Analytical Unit of Cairo University, Egypt. Standard analytical methods were used to determine the metal ion content.¹³ IR spectra of the ligand and its metal complexes were measured using KBr discs with a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 400-4000 cm⁻¹ and in the 500-100 cm⁻¹ region using polyethylene-sandwiched Nujol mulls on a Perkin Elmer FT-IR 1650 spectrophotometer. Mass spectrum of the ligand recorded using a JEOL JM-S-AX-500 massspectrometer. Electronic absorption spectra in the 200-900 nm regions were recorded on a Perkin-Elmer 550 spectrophotometer.

Magnetic susceptibilities were measured at 25 °C by the Gouy method using mercuric tetrathiocyanato-cobaltate(II) as the magnetic susceptibility standard. The magnetic moments were calculated from the equation: $\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr}} \cdot T}$. Molar conductance was measured on a Tacussel type CD₆NG conductivity bridge using 10⁻³ M DMF solutions. Thermal analyses (DTA and TG) were carried out in air using a Shimadzu DT-30 thermal analyzer. The ESR spectra of the solid complexes at room temperature and at 77 K were recorded using a Varian E-109 spectrophotometer (Leicester University, England). DPPH was used as the marker. TLC was used to confirm the purity of the prepared compounds.

Preparation of the ligand

Ethylphthalate was prepared using a published procedure.¹⁴

Preparation of N¹,N²-bis(3-aminopropyl)phthalamide:

The N¹,N²-bis(3-aminopropyl)phthalamide was prepared (Fig. 1) by the dropwise addition of ethanol solution (50 cm³) of ethyl phthalate (5.0 g, 0.22 mol) to the ethanol-solution (25 cm³) of 1,3-diaminopropane (3.33 g, 0.044 mol) with gentle warming and stirring for one hour. The white precipitate formed was filtered off, washed with

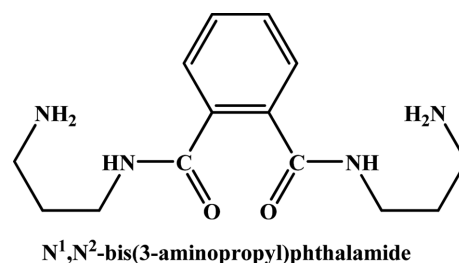


Fig. 1.

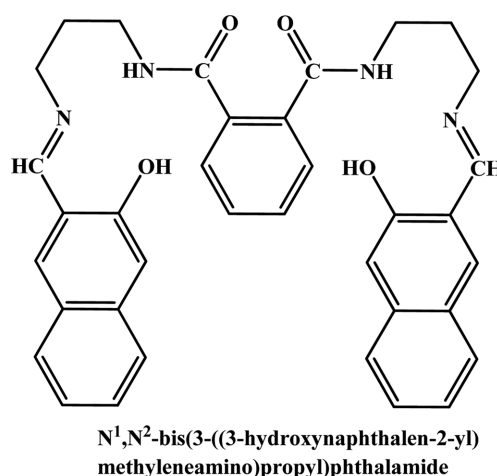


Fig. 2. Structure representation of the ligand.

ethanol, and dried under vacuum over anhydrous CaCl_2 .

Preparation of the ligand (H_4L , 1): The ligand (H_4L , 1) (Fig. 2) was prepared by adding hot ethanol solution (50 cm^3) of N^1, N^2 -bis(3-aminopropyl)phthalamide (5.0 g, 0.018 mol) to a hot ethanol solution (50 cm^3) of naphthaldehyde (6.19 g, 0.036 mol). The mixture was refluxed for two hours and left to cool at room temperature. The yellow product was filtered off, washed with ethanol and dried under vacuum over anhydrous CaCl_2 .

Preparation of metal complexes

Complexes 2-5 were prepared by the dropwise addition of a hot (60°C) methanol solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ to a hot (70°C) ethanol solution of the ligand in molar ratio 1:1M/L (Metal/Ligand). The mixture was refluxed for four hours. The precipitates formed after cooling were filtered, washed with ethanol, then with diethyl ether and dried under vacuum over anhydrous CaCl_2 .

Complexes 6-13 were prepared by mixing a hot (60°C) methanol solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{Cl})_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ with a hot (70°C) ethanol solution of the ligand in molar ratio 2:1 M/L (Metal/Ligand). The mixture was refluxed for four hours. The precipitates formed after cooling were filtered, washed with ethanol, then with diethyl ether and dried under vacuum over anhydrous CaCl_2 .

In-vitro antibacterial and antifungal activities

The investigation of the biological activities of the newly synthesized Schiff base ligand, its metal complexes and their corresponding metal salts were carried out in the Botany Department Lab. of microbiology, Faculty of Science, El-Menoufia University. The antibacterial and antifungal activities were investigated by disc diffusion method.^{15,16} The antibacterial activities were done using *Escherichia coli* and *Aspergillusniger* at 2000 ppm concentrations in DMSO. DMSO poured disc was used as negative control. The bacteria were subcultured in nutrient agar medium which was prepared using ($\text{g} \cdot \text{L}^{-1}$ distilled water) NaCl (5 g), peptone (5 g), beef extract (3 g), agar (20 g). The fungus was subcultured in Dox's medium which was prepared using ($\text{g} \cdot \text{L}^{-1}$ distilled water) yeast extract (1g), sucrose (30 g), NaNO_3 , agar (20 g), KCl (0.5 g), KH_2PO_4 (1 g), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 g) and trace of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. These mediums were then sterilized by autoclaving at 120°C for 15 min. After cooling to 45°C the medium was poured into 90 mm diameter Petri dishes and incu-

bated at 37°C or 28°C , respectively. After few hours, Petri dishes were stored at 4°C . Microorganisms were spread over each dish by using sterile bent loop rod. The test is carried out by placing filter paper disks with a known concentration of the compounds on the surface of agar plates inoculated with a test organism. Standard antibacterial drug (tetracycline), antifungal drug (Amphotericine B) and solution of metal salts were also screened under similar conditions for comparison. The Petri dishes were incubated for 48 h at 37°C or 28°C , respectively. The zone of inhibition was measured in millimeters carefully. All determinations were made in duplicated manner for each of the compounds. An average of the two independent readings for each compound was record.

RESULT AND DISCUSSION

All the prepared compounds are colored, non-hygroscopic, crystalline solid and stable at room temperature. The complexes are insoluble in non-polar solvents but soluble in polar coordinating solvents such as DMSO and DMF. Elemental analyses, physical data, Table 1, and spectral data, Tables 2 and 3 are compatible with the proposed structures shown in Fig. 4. To date, no diffractable crystals have been grown.

N^1, N^2 -bis(3-((3-hydroxynaphthalen-2-yl)methylene-amino)propyl)phthalamide (H_4L) can exist in the keto form (I), keto-enol form (II), enol form (III), Fig. 3.

^1H - and ^{13}C -NMR spectra of 1

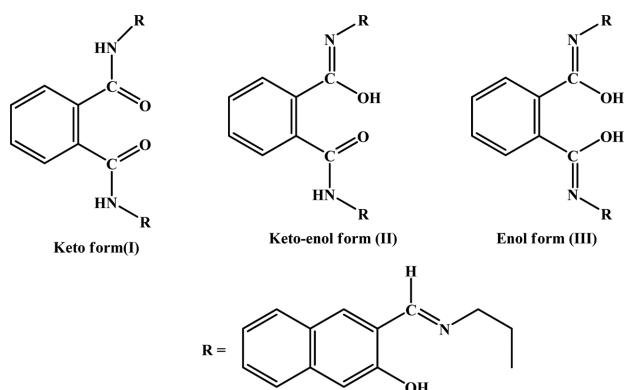
The ^1H -NMR spectrum of the ligand (H_4L , 1) in d^6 -DMSO shows signals consistent with the proposed structure (Fig. 2) and indicated that, the ligand is present in its ketonic form.¹⁷ This conclusion was supported by the presence of peaks due to NH groups appearing at 8.62 ppm (s, 2H)^{18,19} and azomethine group $\text{HC}=\text{N}$ appearing at 8.12 ppm (s, 2H).²⁰ The peak appeared at 10.1 ppm, may be due to the proton of hydroxyl groups (s, 2H).²¹ The peaks appearing in the 7.04-7.85 ppm range may correspond to protons of the aromatic hydrogen (16H). The signals at 3.96, 3.51 and 2.1 ppm may be assigned to terminal $-\text{CH}_2-\text{N}=\text{C}$, terminal $-\text{CH}_2-\text{NH}$ and middle $-\text{CH}_2-$ groups. The ^{13}C -NMR spectrum showed different peaks appearing at 182.1 and 160.23 ppm. These peaks can be due to $-\text{CH}=\text{N}-$ and $-\text{C}-\text{OH}$ groups respectively,²¹ however the peaks at 127.63-140.2 ppm range assigned to the carbon of aromatic ring.²¹ The peaks appearing at 60.22 and 31.52 ppm may be due to terminal $-\text{CH}_2-\text{N}-$ and middle $-\text{CH}_2-$ group carbons.²²

Table 1. Elemental analyses and physical properties of the ligand (H₄L) and its metal complexes

No.	Ligand/complexes	Colour	Yield %	M.P (C ⁰)	$\Omega^{-1}\text{mol}^{-1}\text{cm}^{-2}$	μ_{eff} (B.M)	Found (Calc.) %				
							C	H	N	Cl	M
(1)	[(H ₄ L)] [C ₃₆ H ₃₄ N ₄ O ₄]	Yellow	90	200	----	-----	73.54(73.70)	5.64(5.84)	9.60 (9.55)	----	-----
(2)	[(H ₄ L)CuCl ₂ (H ₂ O)]	Green	85	295	15	1.73	58.40(58.50)	5.11(4.91)	7.70(7.58)	9.40(9.59)	8.50(8.60)
(3)	[(H ₄ L)NiCl ₂ (H ₂ O)].H ₂ O	D. green	80	>300	12	2.8	57.35(57.48)	5.22(5.09)	7.80(7.45)	9.60(9.43)	7.90(7.80)
(4)	[H ₄ LCuCl ₂ H ₂ O].2H ₂ O	Brown	87	280	23	4.8	56.00(56.13)	5.30(5.23)	7.50(7.27)	9.00(9.20)	7.40(7.62)
(5)	[(H ₄ L)Cu(NO ₃) ₂ (H ₂ O)].2H ₂ O	Brown	80	300	21	1.7	52.00(52.20)	5.16(4.87)	10.3(10.15)	-----	7.70(7.67)
(6)	[(H ₂ L)Cu ₂ Cl ₂ (H ₂ O) ₄].3H ₂ O	Brown	81	245	22	1.5	47.49(47.58)	5.20(5.10)	6.40(6.17)	8.30(7.80)	14.2(13.99)
(7)	[(H ₂ L)Ni ₂ Cl ₂ (H ₂ O) ₄].H ₂ O	D. green	77	290	15	1.87	50.00(50.10)	5.00(4.91)	6.70(6.49)	8.30(8.22)	13.51(13.60)
(8)	[(H ₂ L)Co ₂ Cl ₂ (H ₂ O) ₄].2H ₂ O	Brown	75	285	23	2.83	48.90(49.08)	5.11(5.03)	6.70(6.36)	8.00(8.05)	13.51(13.32)
(9)	[(H ₂ L)Mn ₂ Cl ₂ (H ₂ O) ₄].H ₂ O	Brown	82	280	15	3.8	50.40(50.54)	5.06(4.95)	6.90(6.55)	8.40(8.29)	12.90(12.84)
(10)	[(H ₄ L)Fe ₂ Cl ₆].H ₂ O	D. brown	75	>300	18	3.69	46.60(46.54)	4.07(3.91)	6.20(6.03)	22.50(22.89)	11.79(12.04)
(11)	[(H ₄ L)Cr ₂ Cl ₆].2H ₂ O	D. brown	83	>300	12	2.85	45.90(46.00)	4.20(4.08)	6.20(5.96)	22.50(22.64)	10.89(11.07)
(12)	[(H ₄ L)Ru ₂ Cl ₆].3H ₂ O	Black	80	290	14	2.1	40.83(40.96)	3.88(3.82)	5.60(5.31)	20.40(20.15)	19.00(19.15)
(13)	[(H ₂ L)(ZrO) ₂ Cl ₂].8H ₂ O	Yellow	85	>300	20	Dia.	42.40(42.64)	5.03(4.77)	5.60(5.52)	7.00(6.99)	20.91(21.15)

D = Dark $\Omega^{-1}\text{mol}^{-1}\text{cm}^{-2}$ in 10^{-3} M DMF**Table 2.** IR spectra (assignments) of the ligand (1) and its metal complexes

NO.	H ₂ O _{hydr./coord.}	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$
(1)	-	3360s	3252s	1656v.s	1620s	1315m	---	---	---
(2)	3452br	3361s, 3341m	3254s, 3239m	1655v.s	1621s, 1609m	1317m, 1325m	680m	570m	402w
(3)	3580-3445br	3362s, 3338m	3250s, 3237m	1654v.s	1623s, 611m	1316m, 1325m	656m	565	382w
(4)	3620-3450br	3358s, 340m	3249s, 3241m	1655v.s	1621s, 607m	1314m, 1321m	690m	565m	398w
(5)	3610-3440br	3359s, 3346m	3250s, 3235m	1653v.s	1624s, 1606m	1315m, 1328m	660m	560m	----
(6)	3625-3454br	-	3239m	1655v.s	1605m	1325m	670m	550m	385m
(7)	3605-3449br	-	3235m	1657v.s	1608m	1330m	690m	590m	410m
(8)	3600-3455br	-	3225m	1656v.s	1611m	1338m	675m	565m	380w
(9)	3612-3450br	-	3231m	1655v.s	1604m	1335m	680m	565m	380w
(10)	3580br	3349m	3236m	1657v.s	1606m	1330m	670m	605m	375m
(11)	3590br	3344m	3239m	1656v.s	1605m	1325m	650m	570m	365m
(12)	3585br	3347m	3239m	1658v.s	1610m	1329m	670m	595m	405m
(13)	3605br	-	3235m	1655v.s	1612m	1339m	650m	570m	413m

**Fig. 3.****Mass spectra**

The mass spectrum of the ligand reveals the molecular ion peak (m/z) 587 a.m.u consistent with the molecular

weight of the ligand. The most fragments appear at (m/z) 77, 144, 163, 170, 248 and 417 a.m.u corresponding to [C₆H₅], [C₁₀H₈O], [C₁₀H₁₃NO], [C₁₁H₈NO], [C₁₄H₂₀N₂O₂], and [C₂₅H₂₇N₃O₃], respectively (Fig. 5). However copper(II) complexes **2** and **6** show molecular ion peaks (m/z) at 739 and 908 a.m.u., consisted with the molecular weights of 739.15 and 908.79 respectively.

Conductivity measurements

The molar conductance values of the complexes in DMF (10^{-3} M), lie in the 12-23.2 $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$ range, Table 1, indicating that, all the complexes are not electrolytes. These confirmed that the anion is coordinated to metal ion.^{23,24}

IR spectra

The IR spectral data for the ligand (H₄L, **1**) and its metal

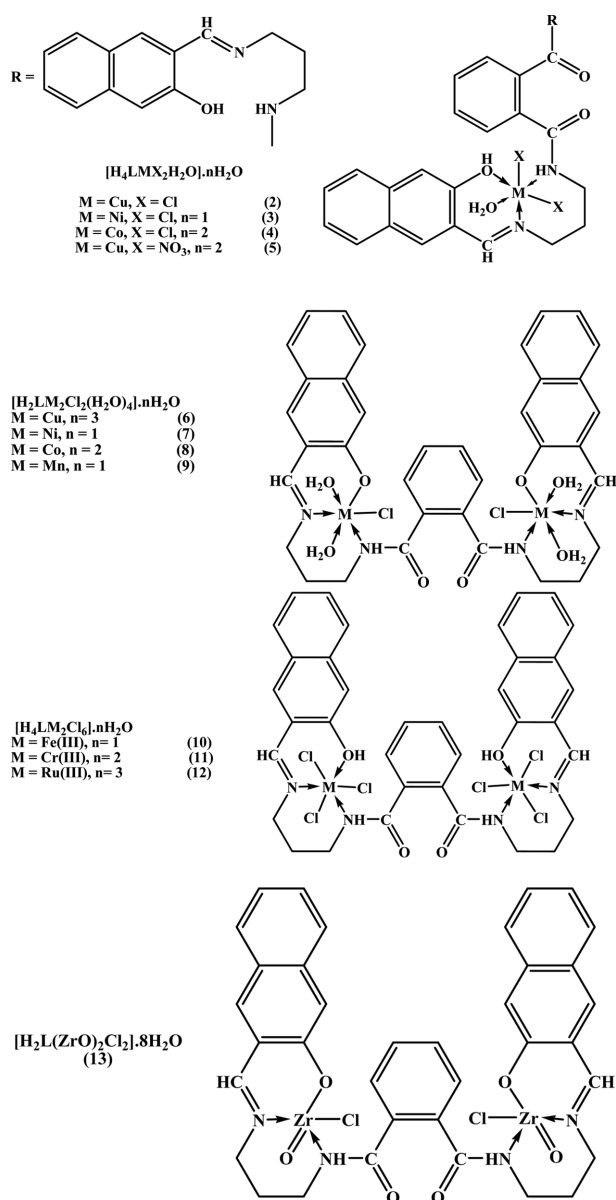


Fig. 4. Structure representation of metal complexes.

complexes are presented in Table 2. The IR spectrum of the ligand showed bands at 3360 and 3252 cm^{-1} may be due to $\nu(OH)$ and $\nu(NH)$ group.¹⁹ However, broad, medium bands were observed in the 3450-3200 and 3180-2600 cm^{-1} ranges, attributed to intra- and intermolecular hydrogen bonding between $-OH$ and $-C=N$, $-NH$ and $-C=O$ groups respectively^{19,25} thus, the higher frequency band is associated with a weaker hydrogen bond and the lower frequency band with a stronger hydrogen bond. Also, the spectrum shows bands at 1656 and 1620 and 1586 cm^{-1} which were assigned to $\nu(C=O)$, $\nu(C=N)$ and $(C=C)_{Ar}$ respectively.^{26,27} The spectra of solid complexes are com-

pared with those of the ligand in order to know the mode of bonding. The spectra showed that the ligand behaved either as:

Neutral tridentate ligand, coordinating through OH , $C=N$, and NH of one arm of the ligand as in case of complexes 2-5, the mode of coordination was suggested by the following evidence: i) the bands due to OH , $C=N$, and NH were shifted to lower wave number with decreasing their intensities, while the other ones found almost at their original place, indicating that, only one of each pair were involved in the coordination,^{19,25,28-30} ii) one band of the two $C-O$ bands was shifted to a higher wave number while the other is found almost at its original place, indicating that, only one phenolic oxygen was involved in the coordination,²⁸ iii) the band of both carbonyl groups found as one band almost at its original place in the ligand indicating that they are not involved in the coordination,^{18,26,27} iv) the simultaneous appearance of new bands in the 656-690 and 560-570 cm^{-1} regions are due to the $\nu(M-N)$ and $\nu(M-O)$ vibrations,^{31,32} respectively.

Bibasic hexadentate ligand, coordinating through all O^- , $C=N$ and NH groups as in case of complexes 6-9 and 13, the mode of coordination was suggested by the following evidence: i) the disappearance of the band of the two OH groups,²⁸ ii) the bands of $C=N$ and NH groups were shifted to lower wave number with decreasing their intensities, indicating that, all $C=N$ and NH groups were involved in the coordination,^{19,25,29,30} iii) the band of two $C-O$ groups were shifted to higher wave number, indicating that, both phenolic oxygen atoms were involved in the coordination,²⁸ iv) the bands of both carbonyl groups were observed as single band at its original place in the ligand indicating that, they are not involved in the coordination,^{18,26,27} iv) the simultaneous appearance of new bands in the 650-690 and 550-590 cm^{-1} regions are due to the $\nu(M-N)$ and $\nu(M-O)$ vibrations, respectively.^{31,32}

Neutral hexadentate ligand, coordinating through all OH , $C=N$ and NH groups as in case of complexes 10-12, the mode of coordination was suggested by the following evidence: i) the bands of $C=N$, OH and NH groups were shifted to lower wave number with decreasing their intensities, indicating that, all $C=N$, OH and NH groups were involved in the coordination,^{19,25,28-30} iii) the band of both $C-O$ groups were shifted to higher wave number, indicating that, all hydroxyl groups were involved in the coordination,²⁸ iv) the bands of both carbonyl groups were observed as single band at its original place in the ligand indicating that, they are not involved in coordination,^{18,26,27} iv) the simultaneous appearance of new bands in the 650-670 and

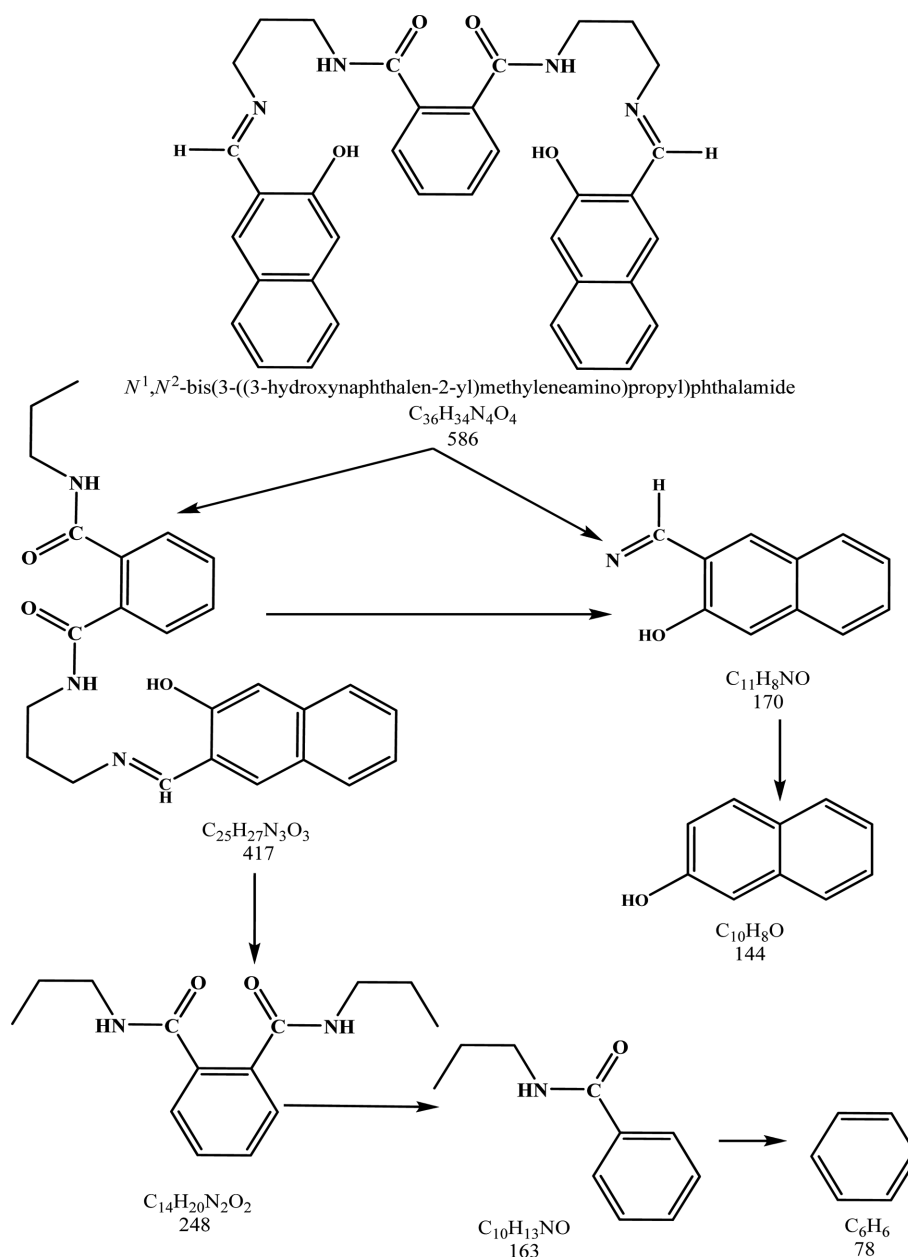


Fig. 5. The fragmentation pattern of the ligand.

570-605 cm^{-1} regions are due to the $\nu(\text{M-N})$ and $\nu(\text{M-O})$ vibrations, respectively.^{31,32} All complexes except complex **5**, show band in the 375-413 region, assignable to $\nu(\text{M-Cl})$.^{19,28} The broad bands in the 3600-3400 cm^{-1} region are due to coordinated water or water of crystallization. Complexes **2-9** showed a band in the 400-600 cm^{-1} region indicating the presence of coordinated water, but the absence of these bands in the spectra of complexes **10-13** indicate the presence of hydrated water rather than coordinated ones. The presence of water molecules within the coordination sphere in the hydrated complexes **2-9** is

further supported by the presence of bands in the 3480-3494, 1605-1610, 940-950 and 613-630 cm^{-1} regions due to OH stretching, HOH deformation, H_2O rocking and H_2O wagging, respectively.^{33,34} The spectrum of the complex **5** showed bands at 1465 cm^{-1} (ν_1), 1050 cm^{-1} (ν_2), 1377 cm^{-1} (ν_4) and 710 cm^{-1} (ν_5) with ν_1 - ν_4 separation of 88 cm^{-1} , characteristic of monodentate nitrato group.³⁵ Zirconyl(II) complex **13** shows band at 825 cm^{-1} assigned to Zr=O .¹⁹

Electronic spectra

The electronic spectral data of the ligand (H_4L , **1**) and

Table 3. UV-Vis. spectra of the ligand, (H₄L) and its metal complexes

No.	Compounds	λ_{max} , nm (ϵ mol ⁻¹ cm ⁻¹)
(1)	[(H ₄ L)] [C ₃₆ H ₃₄ N ₄ O ₄	320(3684), 370(2787)
(2)	[(H ₄ L)CuCl ₂ (H ₂ O)]	315(2320), 345(2966), 450(791), 590(232), 640(58)
(3)	[(H ₄ L)NiCl ₂ (H ₂ O)].H ₂ O	305(1699), 345(2295), 490(476), 580(188), 610(151), 865(189)
(4)	[H ₄ LCuCl ₂ H ₂ O].2H ₂ O	315(2360), 455(3654), 610(370), 665(190)
(5)	[(H ₄ L)Cu(NO ₃) ₂ (H ₂ O)].2H ₂ O	315(2464), 345(1947), 430(992), 585(66)
(6)	[(H ₂ L)Cu ₂ Cl ₂ (H ₂ O) ₄].3H ₂ O	305(3497), 345(2057), 460(764), 580(257), 625(170)
(7)	[(H ₂ L)Ni ₂ Cl ₂ (H ₂ O) ₄].H ₂ O	305(3236), 345(2330), 510(497), 600(388), 870(104)
(8)	[(H ₂ L)Co ₂ Cl ₂ (H ₂ O) ₄].2H ₂ O	300(2457), 475(1654), 590(296), 650(135)
(9)	[(H ₂ L)Mn ₂ Cl ₂ (H ₂ O) ₄].H ₂ O	325(3714), 430(2844), 480(636), 590(85)
(10)	[(H ₄ L)Fe ₂ Cl ₆].H ₂ O	290(2204), 310(5176), 400(1390), 600(92)
(11)	[(H ₄ L)Cr ₂ Cl ₆].2H ₂ O	315(2153), 460(3700), 500(429), 540(38)
(12)	[(H ₄ L)Ru ₂ Cl ₆].3H ₂ O	305(4097), 430(3465), 460(969), 665(25)
(13)	[(H ₂ L)(ZrO) ₂ Cl ₂].8H ₂ O	320(2885), 370 (4464), 430(594)

its metal complexes in DMF solution are summarized in Table 3. The ligand (H₄L, **1**) showed two bands at 370 and 320 nm which may be assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively.³² In the metal complexes, the spectra showed bands in the 345-290 nm range, due to intraligand transitions. Copper(II) complexes **2**, **5**, and **6** in DMF solution showed bands in the 430-460, 580-590 and 625-640 nm range, which were assigned to ligandcopper(II) charge transfer, ${}^2B_1 \rightarrow {}^2E$ and ${}^2B_1 \rightarrow {}^2B_2$ transitions indicating a distorted octahedral structure.^{36,37} Nickel(II) complexes **3** and **7** showed bands in 490-510, 600-610 and 865-870 nm ranges respectively, which are attributable to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1) transitions indicating octahedral nickel(II) complexes.^{38,39} The ν_2/ν_1 ratio for these complexes were 1.41 and 1.45 respectively, which is less than the usual range of 1.5-1.75, indicating distorted octahedral nickel(II) complexes.³⁷ The cobalt(II) complexes **4** and **8** showed bands at 455-475, 590-610 and 650-665 nm ranges, which were assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions respectively, corresponding to high spin cobalt(II) octahedral complexes.^{19,40} Manganese(II) complex **9** showed bands at 430, 480 and 590 nm, these bands were corresponding to ${}^6A_{1g} \rightarrow {}^4E_g$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transitions which are compatible to an octahedral structure for manganese(II) complexes.^{41,42} Iron(III) complex **10** gave bands at 400 and 600 nm are due to charge transfer and ${}^6A_1 \rightarrow {}^4T_1$ transitions, suggesting octahedral structure.^{19,36,42} Chromium(III) complex **11** showed bands at 460 and 540 nm which are attributed to charge transfer and ${}^4A_2 \rightarrow {}^4T_1$ transitions of six coordinate chromium(III) complex.^{43,44} Ruthenium(III) complex **12** showed bands at 460 and 665 nm, are due to LMCT tran-

sition and the other one is assigned to ${}^2T_{2g} \rightarrow {}^2A_{2g}$ transition. These band were similar to those observed for octahedral ruthenium(III) complexes.^{19,45,46} Zirconyl(II) complex **13** shows bands (Table 3) were due to intraligand transitions.

Magnetic moments

The room temperature magnetic moments of complexes **2-14** are present in Table 1. Copper(II) complexes **2**, **5** and **6** show values 1.73, 1.7 and 1.5 B.M.. These values are correspond to one unpaired electron in an octahedral structure.¹⁹ Nickel(II) complexes **3** and **7** show values 2.8 and 1.87 B.M., indicating octahedral nickel(II) complexes.^{19,47,48} Cobalt(II) complexes **4** and **8** show values 4.8 and 2.83 B.M., indicating high spin octahedral cobalt (II) complexes.^{19,38} Manganese(II) complex **9** shows 3.8 B.M., suggesting octahedral geometry around the manganese(II) ion.^{19,38} Iron(III) complex shows 3.69 B.M., indicating high spin iron(III) octahedral geometry.^{19,50} Chromium(III) complex **11** shows 2.85 B.M., which is lower than the spin-only value, implying an operation of spin-exchange interactions take place between chromium (III) ions.⁴⁴ The ruthenium(III) complex **12** shows a magnetic value of 1.67 B.M., indicating an octahedral ruthenium(III) structure.^{19,51} Zirconyl(II) complex **13** shows diamagnetic property.¹⁹ The complexes **6-11** showed low magnetic moment values indicating spin exchange interactions take place between the two ion centers.^{19,47,49}

ESR spectra

The ESR spectra of solid copper(II) complexes **2**, **5** and **6** at room and at liquid nitrogen temperatures were characteristic of a d^9 system and having an axial symmetry type of a $d_{x^2-y^2}$ ground state.⁵² On lowering the tempera-

ture to liquid nitrogen, the spectra were not changed, suggesting that, the geometry of the complexes is not changed on cooling. The g-values suggest octahedral geometry for complexes **2**, **5** and **6**. The complexes show $g_{\parallel} > g_{\perp} > g_e$, indicating a $d_{x^2-y^2}$ ground state, and spectral features were characteristic of axial symmetry.⁵³ The ESR parameters for **2** is $g_{\parallel} = 2.27$, $g_{\perp} = 2.05$, $g_{iso} = 2.13$, $G = 5.4$, $K_{\perp}^2 = 0.64$, $K_{\parallel}^2 = 0.68$, $K^2 = 0.65$ and $K = 0.81$, for **5** is $g_{\parallel} = 2.24$, $g_{\perp} = 2.06$, $g_{iso} = 2.12$, $G = 4.0$, $K_{\perp}^2 = 0.81$, $K_{\parallel}^2 = 0.61$, $K^2 = 0.74$ and $K = 0.86$, for **6** is $g_{\parallel} = 2.26$, $g_{\perp} = 2.08$, $g_{iso} = 2.14$, $G = 3.25$, $K_{\perp}^2 = 1.02$, $K_{\parallel}^2 = 0.67$, $K^2 = 0.9$ and $K = 0.95$. Kivelson and Neiman⁵⁴ show that, the g_{\parallel} -value in the copper(II) complexes can be used as a measure of covalent character of the metal-ligand bond. If this value is greater than 2.3, the environment is essentially ionic and the value less than this limit indicate a covalent environment. All complexes showed covalent bond character.^{19,54,55} The g-values were related by the expression,⁵⁶ $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, if $G > 4.0$ then local tetragonal axes were aligned parallel or only a slightly misaligned, if $G < 4.0$, significant exchange coupling is present. Complexes **2** and **5** show value ≥ 4.0 , however complex **6** shows $G = 3.25$, indicating spin-exchange interactions take place between the copper(II) ions, which is furthered confirmed from the magnetic moment value (Table 1). Also, the g-values of copper(II) complexes with a $^2B_{1g}$ ground state ($g_{\parallel} > g_{\perp}$) may be expressed.^{35,57}

$$K_{\perp}^2 = (g_{\perp} - 2.002)\Delta E_{xz}/2\lambda^o \quad (1)$$

$$K_{11}^2 = (g_{11} - 2.002)\Delta E_{xy}/8\lambda_o \quad (2)$$

$$K^2 = (K_{11}^2 + 2K_{\perp}^2)/3 \quad (3)$$

Where K_{\parallel} and K_{\perp} were the parallel and perpendicular components respectively of the orbital reduction factor (K), λ^o is the spin-orbit coupling constant for the free copper, ΔE_{xy} and ΔE_{xz} were the electron transition energies. From the above relations, the orbital reduction of covalency^{35,57} can be calculated for an ionic environmental, $K=1$ and for a covalent environment $K<1$, the lower the value of K, the greater is the covalent character. The K-values of the complexes **2**, **5**, and **6** were lower than 1.0, confirming covalent bond character.^{19,35,58} The ESR spectra of **4**, **9**, and **10** showed isotropic type with $g_{iso} = 2.21$, 2.012 and 2.0035, indicating octahedral geometry around Co(II), Mn(II), and Fe(III) ions respectively.^{54,57}

The zero field splitting parameter (D) for the parallel components of the dimmer complex **6** was estimated from the spectrum, and is equal to 414. The distance between two copper centers was calculated using the following

equation.⁵⁹

$$D = (3\mu_B / 2R^3) * (3 \cos^2 \theta - 1) \quad (4)$$

Where μ_B is the magnetic moment of the electron and R is the distance (Å) between two electrons. For parallel component (D), $\theta=0$, by substitution in equation 4, D is equal to $3 \mu_B / 2R^3$. For a diradical system in the triplet-state, it is found that, D for the parallel components is equal to 402 G and the distance between the two radicals is equal to 5.2 Å. From these data, the distance between the two copper(II) centers was calculated and is equal to 5.3 Å. This value is close to that for a dimeric copper(II) compound in the triplet state.⁶⁰

Thermal analyses (DTA and TG)

The results of TG and DTA analyses of complexes were shown in Table 4. The results showed good agreement with theoretical formula as suggested from the analytical data (Table 1). All complexes except complex **2**, lost hydration water molecules in the temperature 78-90 °C range and were accompanied with an endothermic peak. The coordinated water molecules were eliminated from these complexes at relatively higher temperature; 110-142 °C, than those of the hydrate water molecules (Table 4). The removal of HCl molecules was observed for all complexes in the temperature 190-240 °C range, which was accompanied by an endothermic peak. The complexes decompose through degradation of the Schiff base ligand at a temperature over than 400 °C leaving metal oxides (480-590) range.

Biological activity

The antibacterial and antifungal activities of the ligand and its metal complexes were screened on bacterial and fungal strains using the disk diffusion method. It is important to note that the ligand and most of its metal complexes exhibit more antifungal inhibitory effects than the Standard antifungal drug (amphotericin B) and most of the metal complexes more active than parent ligands and the solution of metal ions. It is also clear that the ligand and its metal complexes have more antifungal activity than antibacterial activity. The inhibition zone diameter of the compounds is shown in Figs. 6 and 7. The order of antifungal activity of the compounds is **9**, **10** > **6**, **11** > **12** > **5** > Ligand > Amphotericin B > **7**, however, the order of antibacterial activity of the compounds is Tetracycline > **11**, **12** > **9** > **6** > **5** > **7**. The increased activity of the metal complexes can be explained on the basis of chelation theory.⁶¹ It is known that the chelation tends to make the

Table 4. Thermal data for the metal complexes

No.	Temp. (C°)	DTA (peak)		TGA (Wt. loss %)		Assignment
		Endo	Exo	Calc.	Found	
(2)	119	endo	---	2.4	2.5	Loss of coordinated water (1 H ₂ O)
	230	endo ----	exo	9.6	9.5	Loss of chloride atom (2Cl)
	450					
	590	----	exo	10.8	10.7	Decomposition with the formation of CuO
(3)	90	endo	----	2.5	2.6	Loss of hydration water (1H ₂ O)
	142	endo	----	2.5	2.5	Loss of coordinated water (1H ₂ O)
	240	endo	----	9.7	9.5	Loss of chloride atom (2Cl)
	350	-----	exo			
	420	----	exo			
	550	----	exo	10.2	10.1	Decomposition with the formation of NiO
(4)	85	endo	----	4.7	4.6	Loss of hydration water (2H ₂ O)
	118	endo	----	2.3	2.3	Loss of coordinated water (1H ₂ O)
	225	endo	----	9.2	9.1	Loss of chloride atom (2Cl)
	350	----	exo			
	570	----	exo	9.7	9.6	Decomposition with the formation of CoO
(6)	80	endo	----	6.1	6.0	Loss of hydration water (3H ₂ O)
	140	endo	-----	8.1	8.1	Loss of coordinated water(4H ₂ O)
	220	endo	-----	8.0	8.1	Loss of chloride atom (2Cl)
	450	----	exo			
	550	----	exo	17.9	18.0	Decomposition with the formation of (2CuO)
(7)	78	endo	----	2.1	2.3	Loss of hydration water (H ₂ O)
	115	endo	-----	8.4	8.5	Loss of coordinated water(4H ₂ O)
	210	endo	-----	8.2	9.1	Loss of chloride atom (2Cl)
	450	----	exo			
	500	----	exo	17.3	17.1	Decomposition with the formation of (2NiO)
(9)	80	endo	----	2.1	2.3	Loss of hydration water (H ₂ O)
	110	endo	-----	8.4	8.5	Loss of coordinated water(4H ₂ O)
	190	endo	-----	8.2	9.1	Loss of chloride atom (2Cl)
	450	----	exo			
	480	----	exo	16.6	16.3	Decomposition with the formation of (2MnO)
(10)	85	endo	----	1.9	2.0	Loss of hydration water (H ₂ O)
	215	endo	-----	22.5	22.3	Loss of chloride atom (6Cl)
	450	----	exo			
	580	----	exo	33.7	33.5	Decomposition with the formation of (2Fe ₂ O ₃)
(13)	90	endo	----	14.2	14.5	Loss of hydration water (8H ₂ O)
	205	endo	-----	1.1	0.9	Loss of chloride atom (2Cl)
	450	----	exo			
	540	----	exo	24.3	24.9	Decomposition with the formation of (2ZrO ₂)

ligand act as more powerful and potent fungicidal and bactericidal agents, thus killing more fungi and bacteria than the ligand. It is known that, in a complex, the positive charge of the metal is partially shared with the donor atoms present in the ligands, and there may be π -electron delocalization over the whole chelating system,⁶² this increases the lipophilic character of the metal chelate and favors its permeation through the lipid layer of the membranes. There are other factors which also increase the

activity, which are solubility, conductivity, coordination mode and bond length between the metal and the ligand. The variation in the effectiveness of different compound against different organisms also depends either on the impermeability of the cell of the microbes or differences in ribosomes of microbial cells.^{63,64} The variation of biological activity of the complexes may be due to change in electronic configuration of the metal and also, the environment around the metal ion.

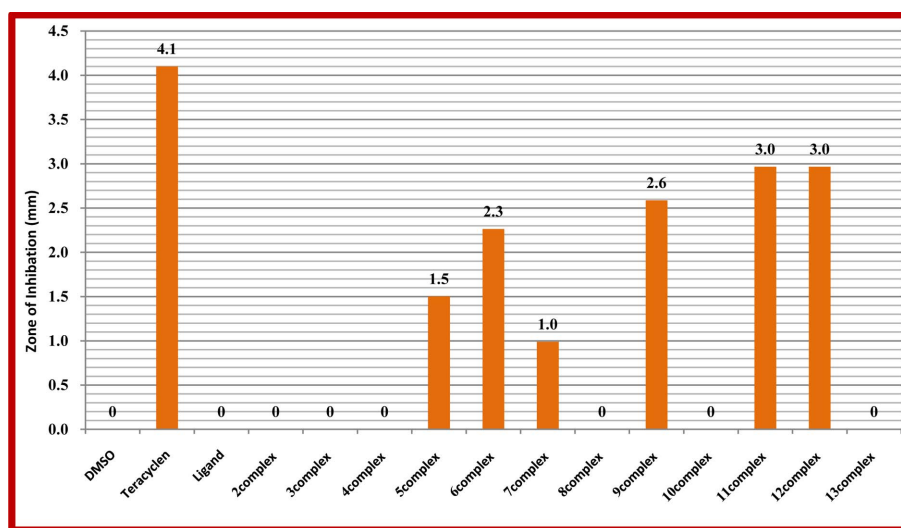


Fig. 6. Antibacterial activity of the ligand and its metal complexes against gram-negative bacterium (*E. coli*).

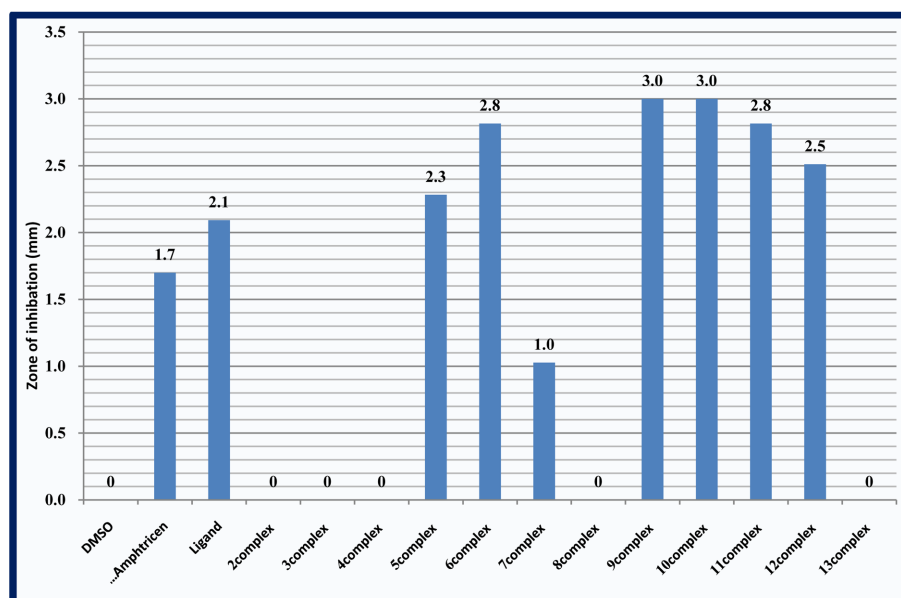


Fig. 7. Antifungal activity of the ligand and its metal complexes against Fungus (*Aspergillusniger*).

SUMMARY

The chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), ruthenium(III) and zirconyl(II) complexes of N¹,N²-bis(3-((3-hydroxynaphthalen-2-yl)methyleneamino)propyl) phthalamide has been synthesized and characterized by elemental and thermal analyses as well as spectroscopic techniques. The analyses data showed that, the ligand behaves as a neutral tridentate, neutral hexadentate, dibasic tridentate or dibasic hexadentate ligand bonded to the metal ion/ions through azomethine nitrogen atoms, protonated or deprotonated hydroxyl groups

and protonated or deprotonated amine groups. The metal complexes have a distorted octahedral, square planer or octahedral geometry. The ESR spectra of solid copper(II) complexes **2**, **5**, and **6** show $g_{\parallel} > g_{\perp} > g_e(2.0023)$, indicating octahedral structure with significant covalent bond character. The biological studies showed that the ligand biologically in active against Gram negative bacterium (*Escherichia coli*), and its metal complexes have mild activity in comparing with Standard antibacterial drug (Tetracycline) but has strongly biological activity against Fungus (*Aspergillusniger*) in comparing with Standard antifungal drug (Amphotricene B).

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