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Antimicrobial, spectral, magnetic and thermal studies of Cu(II), Ni(II), Co(II), UO₂(VI) and Fe(III) complexes of the Schiff base derived from oxalyldiazide

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Abstract

The Schiff base ligand, oxalic bis[(2-hydroxybenzylidene)hydrazide], H₂L, and its Cu(II), Ni(II), Co(II), UO₂(VI) and Fe(III) complexes were prepared and tested as antibacterial agents. The Schiff base acts as a dibasic tetra- or hexadentate ligand with metal cations in molar ratio 1:1 or 2:1 (M:L) to yield either mono- or binuclear complexes, respectively. The ligand and its metal complexes were characterized by elemental analyses, IR, ¹H NMR, Mass, and UV-Visible spectra and the magnetic moments and electrical conductance of the complexes were also determined. For binuclear complexes, the magnetic moments are quite low compared to the calculated value for two metal ions complexes and this shows antiferromagnetic interactions between the two adjacent metal ions. The ligand and its metal complexes were tested against a Gram + ve bacteria (*Staphylococcus aureus*), a Gram -ve bacteria (*Escherichia coli*), and a fungi (*Candida albicans*). The tested compounds exhibited high antibacterial activities.

Keywords: Schiff base ligand, metal complexes, antimicrobial, IR, magnetic, electronic spectra

Introduction

Considering the constant emergence of antibiotic resistance to clinically used compounds, it is of critical importance to develop novel antibiotic classes, which eventually would target the lipid layer of the organisms and other aspects of the pathogen life cycle. Metal complexes constitute one such possible class with biological activity [1,2]. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species [2–7]. The remarkable biological activity of acid hydrazides, a class of Schiff base, their corresponding aroyldiazones, and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant

interest [7–14]. The coordination compounds of hydrazide and aroyldiazones have been reported to act as enzyme inhibitors and are useful due to their pharmacological applications.[6–13,14]. Isonicotinic acid hydrazide (INH) is a drug of proven therapeutic importance and is used as in bacterial diseases, e.g., tuberculosis [15]. Hydrazones derived from condensation of isonicotinic acid hydrazide with pyridine aldehydes have been found to show better antitubercular activity than INH.[13]. Tri- and terdentate Schiff bases may contain ONO or ONS donor atoms and their metal complexes may be monomeric, dimeric, trimeric or tetrameric with abnormal magnetic properties and characteristic structures [8–16]. The synthesis and biological activity of the Zn(II)-complex of the Schiff base, oxalic bis[(2-hydroxybenzylidene)-hydrazide], has been previously studied [16]. The complex has the formula [Zn(L)Cl₂] (Figure 1) in which the Schiff base functions as a tetradentate ligand [16]. The present

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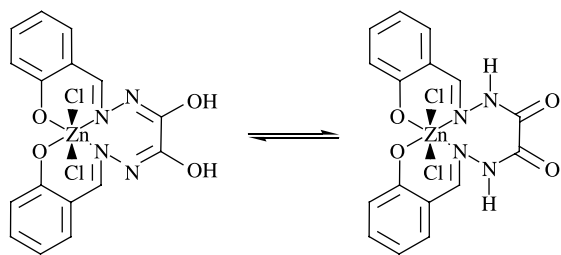


Figure 1. Proposed structure of Zn(II) complex, from Ref. [16].

work was undertaken in order to throw light on the ligational behaviour of the Schiff base derived from oxalylhydrazide towards other metal ions such as Cu(II), Ni(II), Co(II), UO₂(VI) and Fe(III) as well as their biological activity in inhibiting the growth of some pathogenic bacteria.

Experimental

Materials

CuCl₂·2H₂O, NiCl₂·6H₂O, CoCl₂·6H₂O, FeCl₃·6H₂O, UO₂(OCOCH₃)₂·2H₂O were obtained from BDH. Oxaloyldihydrazide, salicylaldehyde were either BDH or Merck products and were used without further purification. Organic solvents used were reagent grade.

Preparation of the schiff base ligand, H₂L

The ligand was prepared according to the previous reported method [14]. Salicylaldehyde (2.4 g., 20 mmol, dissolved in 10 mL absolute ethanol) was added to a stirred hot ethanolic solution of oxaloyldihydrazide (1.2 g, 10 mmol dissolved in 30 mL absolute ethanol). Then 2–3 drops of conc. H₂SO₄ were added and the reaction mixture was refluxed for 8 h. The white solid precipitated was filter off, wash with 5 mL ethanol, and then recrystallized from ethanol (yield 70%, m.p. 169°C).

Preparations of the metal complexes

Preparation of the mononuclear metal complexes. Metal salt (3 mmol in 10 mL ethanol) [CuCl₂·2H₂O, NiCl₂·6H₂O, CoCl₂·6H₂O, FeCl₃·6H₂O or UO₂(acetate)·2H₂O] was heated on a water bath to ensure complete dissolution of the metal salt. To this solution, the ligand (0.978 g, 3 mmol in 10 mL ethanol) was added gradually. The reaction mixture was refluxed for 3 h with constant stirring. The precipitated coloured solid complexes were filtered, washed several times with 50% (v/v) ethanol-water mixture to remove any traces of the unreacted starting materials, then washed with diethyl ether and dried in a vacuum desiccator over CaCl₂. The obtained solid metal complexes and their colours are shown in

Table I. The complexes are stable solids, which decomposed above 250°C without melting and they are insoluble in common organic solvents such as ethanol, methanol, chloroform acetone but soluble in DMSO and DMF.

Preparation of the binuclear metal complexes. Metal salt (6 mmol in 20 mL ethanol) [CuCl₂·2H₂O, NiCl₂·6H₂O, CoCl₂·6H₂O, FeCl₃·6H₂O or UO₂(acetate)·2H₂O] was heated on a water bath to ensure complete dissolution of the metal salt. The metal salt solution was added gradually to a stirred hot solution of the ligand (0.978 g, 3 mmol in 10 mL ethanol). The reaction mixture was refluxed for 12 h under constant stirring. The precipitated solid complexes were filtered, washed several times with 50% (v/v) ethanol-water mixture to remove any traces of the unreacted starting materials, then washed with diethyl ether and dried in air. The obtained metal complexes and their colours are shown in Table I. The complexes are stable solids, which decomposed above 250°C. They are insoluble in common organic solvents such as ethanol, methanol, chloroform and acetone but soluble in DMSO and DMF.

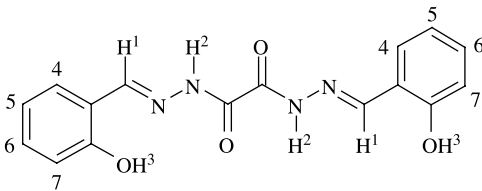
Physical measurements and analyses

Reflectance spectra of the ligand and its metal complexes were recorded as BaSO₄ discs using a model 1601 Shimadzu UV-Visible in the range 190–1100 nm. The solution of the ligand, in ethanol was recorded on a Jasco V-550 UV-Visible spectrometer in the range 200–900 nm. IR spectra were recorded as CsI discs using a FT-IR 4000 Perkin Elmer Spectrometer. ¹H NMR spectra were carried out in DMSO-d₆ at room temperature using TMS as internal standard on a Bruker 250 MHz spectrophotometer. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a model MK1 Johnson Matthey Alpha products magnetic susceptibility balance. The effective magnetic moments were calculated using the relation ($\mu_{eff} = 2.828 (\chi_m T)^{\frac{1}{2}}$ B.M. where χ_m is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds. The TG-DTA measurements were carried out on a Shimadzu thermo gravimetric analyzer in dry nitrogen atmosphere and a heating rate of 10°C/min using the TA-50 WS1 program. Mass spectra were recorded at 70 eV and 300°C on an MS 5988 Hewlett-Packard mass spectrometer. Conductivities were measured in DMF solutions of the complexes (10⁻³ M) using a model LBR, WTWD-812 Wilhelm Conductivity meter fitted with a model LTA100 cell. Analyses of the metals followed decomposition of their complexes with concentrated nitric acid. The resultant solution was diluted with distilled water, filtered to remove the

Table I. Characteristic of H₂L and its corresponding mono- and binuclear metal complexes.

Compound (F.W) ^c	Colour	Yield%	Elemental analysis, Calc. (Found) %				
			C	H	N	Cl	M
H ₂ L C ₁₆ H ₁₄ N ₄ O ₄ (326.0)	Light yellow	70	58.90 (59.10)	4.29 (4.50)	17.18 (17.40)	—	—
(1) [Cu(L)]·EtOH C ₁₈ H ₁₈ N ₄ O ₅ Cu (434.5)	Light green	25	49.71 (50.14)	4.14 (4.63)	12.89 (13.30)	—	14.84 (14.95)
(2) [Ni(L)(OH ₂) ₂]·2EtOH C ₂₀ H ₂₈ N ₄ O ₈ Ni (510.7)	Pale green	30	46.99 (47.22)	5.48 (5.81)	10.97 (11.30)	—	11.49 (12.10)
(3) [Co(L)(OH ₂) ₂]·2EtOH C ₂₀ H ₂₈ N ₄ O ₈ Co (511)	Brown	33	46.97 (47.40)	5.48 (4.82)	10.96 (11.54)	—	11.55 (12.47)
(4) [Fe(L)Cl(OH ₂) ₂]·EtOH C ₁₈ H ₂₀ N ₄ O ₆ ClFe (479.5)	Reddish brown	45	45.05 (45.53)	4.17 (4.56)	11.68 (11.80)	7.40 (7.60)	11.68 (12.02)
(5) [UO ₂ (L)(OH ₂) ₂]·EtOH C ₂₀ H ₂₄ N ₄ O ₆ U (686)	Light red	65	34.99 (35.32)	3.50 (3.75)	8.16 (8.48)	—	34.69 (35.33)
(6) [(Cu) ₂ (L)(Cl) ₂]·EtOH C ₁₈ H ₁₈ N ₄ O ₅ Cl ₂ Cu ₂ (570)	Green	35	37.89 (38.13)	3.16 (3.42)	9.82 (10.20)	12.46 (12.25)	22.63 (22.73)
(7) [(Ni) ₂ (L)(Cl) ₂ (OH ₂) ₄]·2EtOH C ₂₀ H ₃₂ N ₄ O ₁₀ Cl ₂ Ni ₂ (676.4)	Yellowish green	40	35.48 (35.71)	4.73 (4.27)	8.28 (8.45)	10.50 (11.08)	17.37 (17.52)
(8) [(Co) ₂ (L)(Cl) ₂ (OH ₂) ₄]·2EtOH C ₂₀ H ₃₂ N ₄ O ₁₀ Cl ₂ Co ₂ (677)	Brown	38	35.45 (35.81)	4.73 (5.12)	8.27 (8.55)	10.49 (10.70)	17.43 (17.84)
(9) [(Fe) ₂ (L)(Cl) ₄ (OH ₂) ₂]·EtOH C ₁₈ H ₂₂ N ₄ O ₇ Cl ₄ Fe ₂ (660)	Deep violet	55	32.73 (32.82)	3.33 (3.73)	8.48 (8.91)	21.52 (21.93)	16.97 (17.30)
(10) [(UO ₂) ₂ (L)(OH ₂) ₂]·EtOH C ₂₂ H ₂₈ N ₄ O ₁₁ U ₂ (1000)	Red	60	26.40 (26.52)	2.80 (3.21)	5.60 (6.04)	—	47.60 (47.82)

EtOH = C₂H₅OHTable II. ¹H NMR data for the ligand HL in DMSO-d₆.

oxalic bis[(2-hydroxybenzylidene)hydrazide], H ₂ L	
	
Chemical shift, δ _{TMS} (ppm)	Assignment ^a
7.9	[s, 2H] (1)
16.1	[s, 2H] (2)
11.1	[s, 2H] (3)
7.2	[m, 2H] (4)
7.1	[m, 2H] (5)
7.3	[m, 2H] (6)
6.8	[m, 2H] (7)

^as = singlet, d = multiplet.

precipitated ligand. The solution was then neutralized with aqueous ammonia solution and the metal ions titrated with EDTA. Analysis of the uranyl complex was carried out at the Central Laboratory for Environmental Quality Monitoring, CLQM, Kalubia, Cairo, Egypt. The complex was first dried and ground followed by digestion by nitric-HF digestion mixture using Milestone Microwave Digester Model MLS 1200 Mega. The digestible uranium metal was analyzed using a Perkin Elmer ICP OES, Model Optima-3000 coupled with an Ultra Sonic Nebulizer, USN. Microanalyses of carbon, hydrogen, nitrogen and chlorine were carried out at the Micro analytical Center, Cairo University, Giza, Egypt. Chlorine in the Fe(III) complexes was determined by ion chromatography using a (1C) Dionex 500 instrument for anions at the Central Laboratory for Environmental Quality Monitoring, El-Kanater, Cairo, Egypt.

Pharmacology

The *in vitro* evaluation of antimicrobial activity was carried out at Saudi Pharmaceutical industries and Medical Appliance Corporation. The purpose of the screening program was to provide the antimicrobial activity and bacteriostatic and fungistatic efficiency of the investigated metal complexes. The prepared compounds were tested against one strain of Gram +ve bacteria (*Staphylococcus aureus*), Gram -ve bacteria (*Escherichia coli*) and fungi (*Candida albicans*) to provide the MIC's (Minimum inhibitory concentration) for each complex. Bacteriostatic and fungistatic efficiency is the lowest concentration of solution which inhibits the growth of a test organism.

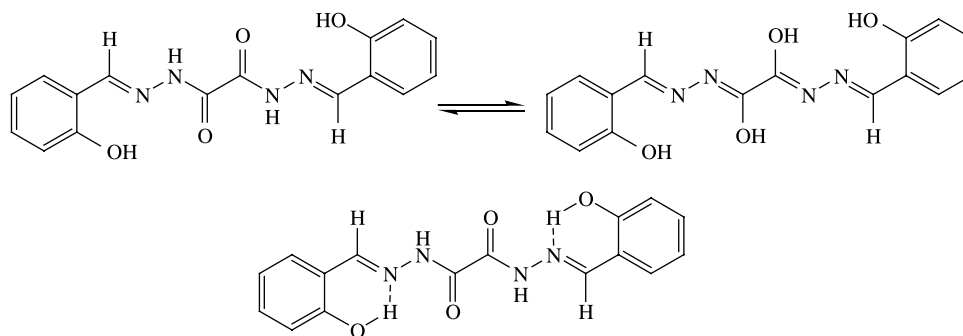
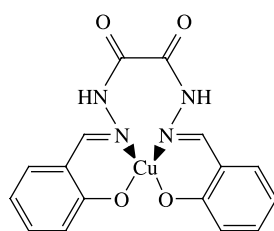
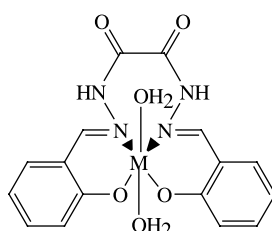
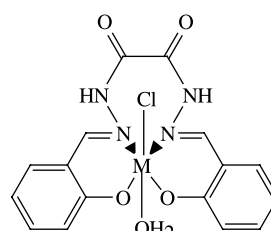
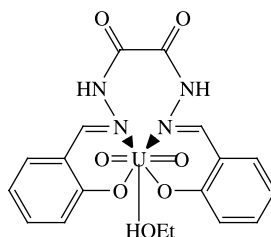


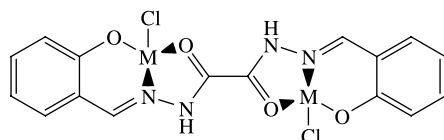
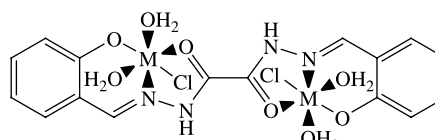
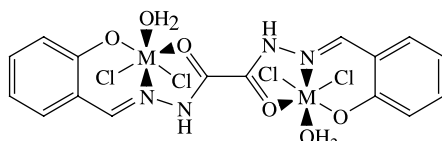
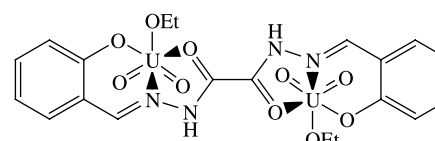
Figure 2. Keto, enol forms and H-bonding occurring in the Schiff base ligand.



Square-planar Cu(II) complex (1)

Octahedral complexes (2) and (3)
(M=Ni(II) or Co(II))Octahedral complex (4)
(M=Fe(III))UO₂(VI) complex (5)

Mononuclear complexes

Binuclear complex (6)
(M=Cu(II))Binuclear complexes (7) and (8)
(M=Ni(II) or Co(II))Binuclear complex (9)
(M=Fe(III))Binuclear complex (10)
(UO₂(VI))

Binuclear complexes

Figure 3. Suggested structures for mono- and binuclear nuclear complexes.

Table III. Infrared frequencies of the ligand and its metal complexes.

Compound (F.W)	$\nu(\text{OH phenolic, H}_2\text{O or alcohol})$	IR frequencies ^{a,b} (cm^{-1})				
		$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{NH})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
H ₂ L C ₁₆ H ₁₄ N ₄ O ₄ (326.0)	3530 m, br ($\nu\text{OH-phenolic}$)	1541 s	1677 vs	3176 s	—	—
(1) [Cu(L)].EtOH C ₁₈ H ₁₈ N ₄ O ₅ Cu (434.5)	3426 m, br ($\nu\text{OH-alcohol}$)	1508 s	1671 vs	3178 m	540 m	420 w
(2) [Ni(L)(OH ₂) ₂].2EtOH C ₂₀ H ₂₈ N ₄ O ₈ Ni (510.7)	3440 m, br ($\nu\text{OH-coordinated water}$). Overlapped with ($\nu\text{OH-alcohol}$)	1512 m	1679 vs	3177 m	520 m	425 w
(3) [Co(L)(OH ₂) ₂]. 2EtOH C ₂₀ H ₂₈ N ₄ O ₈ Co (511)	3440 m, br ($\nu\text{OH-coordinated water}$). Overlapped with ($\nu\text{OH-alcohol}$)	1509 s	1678 vs	3179 m	515 m	410 w
(4) [Fe(L)Cl(OH ₂)].EtOH C ₁₈ H ₂₀ N ₄ O ₆ ClFe (479.5)	3440 m, br ($\nu\text{OH-coordinated water}$). Overlapped with ($\nu\text{OH-alcohol}$)	1501 sh	1677 vs	3177 m	520 w	445 w
(5) [UO ₂ (L)(EtOH)].EtOH C ₂₀ H ₂₄ N ₄ O ₆ U (686)	3440 m, br ($\nu\text{OH alcohol}$)	1507 s	1675 vs	3177 m	520 m	465 w
(6) [(Cu) ₂ (L)(Cl) ₂].EtOH C ₁₈ H ₁₈ N ₄ O ₅ Cl ₂ Cu ₂ (570)	3426 m, br ($\nu\text{OH-alcohol}$)	1512 s	1651 vs	3178 m	540 m	420 w
(7) [(Ni) ₂ (L)(Cl) ₂ (OH ₂) ₄].2EtOH C ₂₀ H ₃₂ N ₄ O ₁₀ Cl ₂ Ni ₂ (676.4)	3440 m, br ($\nu\text{OH-coordinated water}$). Overlapped with ($\nu\text{OH-alcohol}$)	1502 m	1650 vs	3177 m	520 m	425 w
(8) [(Co) ₂ (L)(Cl) ₂ (OH ₂) ₄].2EtOH C ₂₀ H ₃₂ N ₄ O ₁₀ Cl ₂ Co ₂ (677)	3440 m, br ($\nu\text{OH-coordinated water}$). Overlapped with ($\nu\text{OH-alcohol}$)	1519 s	1655 vs	3179 m	515 m	410 w
(9) [(Fe) ₂ (L)(Cl) ₄ (OH ₂) ₂].EtOH C ₁₈ H ₂₂ N ₄ O ₇ Cl ₄ Fe ₂ (660)	3400 m, br ($\nu\text{OH-coordinated water}$). Overlapped with ($\nu\text{OH-alcohol}$)	1515 m	1649 vs	3177 m	520 w	445 w
(10) [(UO ₂) ₂ (L)(OEt) ₂]. EtOH C ₂₂ H ₂₈ N ₄ O ₁₁ U ₂ (1002)	3440 m, br ($\nu\text{OH alcohol}$)	1517 s	1654 vs	3180 sh	520 m	465 w

^aOther bands: H₂L 1558 $\nu(\text{s C}=\text{C})$, 1140 $\nu(\text{s N}-\text{N})$, 1336 $\nu(\text{s C}-\text{N})$, 3107 $\nu(\text{s OH enolic})$, 1228 (δ phenolic OH); (1) 1559 $\nu(\text{s C}=\text{C})$, 1136 $\nu(\text{s N}-\text{N})$, 1337 $\nu(\text{s C}-\text{N})$, 357 m $\nu(\text{s Cu}-\text{Cl})$; (2) 1557 $\nu(\text{s C}=\text{C})$, 1140 $\nu(\text{s N}-\text{N})$, 1332 $\nu(\text{s C}-\text{N})$; (3) 1554 $\nu(\text{s C}=\text{C})$, 1125 $\nu(\text{w N}-\text{N})$, 1321 $\nu(\text{s C}-\text{N})$; (4) 1565 $\nu(\text{s C}=\text{C})$, 1130 $\nu(\text{m N}-\text{N})$, 1325 $\nu(\text{s C}-\text{N})$; (5) 1554 $\nu(\text{s C}=\text{C})$, 1125 $\nu(\text{w N}-\text{N})$, 1320 $\nu(\text{s C}-\text{N})$, 901 $\nu_3(\text{s O}=\text{U}=\text{O})$., (6) 1557 $\nu(\text{s C}=\text{C})$, 1140 $\nu(\text{s N}-\text{N})$, 1337 $\nu(\text{s C}-\text{N})$, 1357 m; (7 and 8) 1557 $\nu(\text{s C}=\text{C})$, 1139 $\nu(\text{s N}-\text{N})$, 1335 $\nu(\text{s C}-\text{N})$, 357 $\nu(\text{m Ni}-\text{Cl})$, 355 $\nu(\text{m Co}-\text{Cl})$; (9) 1558 $\nu(\text{s C}=\text{C})$, 1132 $\nu(\text{w N}-\text{N})$, 1321 $\nu(\text{s C}-\text{N})$, 350 $\nu(\text{m Fe}-\text{Cl})$; (10) (5) 1554 $\nu(\text{s C}=\text{C})$, 1130 $\nu(\text{w N}-\text{N})$, 1325 $\nu(\text{s C}-\text{N})$, 901 $\nu_3(\text{s O}=\text{U}=\text{O})$; ^bv = very, s = strong, m = medium, w = weak, br = broad, ^bsh = shoulder.

Table IV. Magnetic moment, electronic and conductance measurements spectral data (nm) for H₂L and its metal complexes.

Compound	$\mu_{\text{eff.}}$ ^a B.M.	μ_{compl} ^b found (<i>expected</i>) ^c B.M.	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and charge transfer transitions	$d \rightarrow d$ transitions	EC ^d
H ₂ L C ₁₆ H ₁₄ N ₄ O ₄ (326.0)	—	—	244, 360, 395 (sh) ^e	—	—
(1) [Cu(L)].EtOH C ₁₈ H ₁₈ N ₄ O ₅ Cu (434.5)	1.76	—	240,311, 325, 348	665	11.4
(2) [Ni(L)(OH ₂) ₂].2EtOH C ₂₀ H ₂₈ N ₄ O ₈ Ni (510.7)	3.19	—	240,311, 325, 355	670 (sh), 768	11.0
(3) [Co(L)(OH ₂) ₂]. 2EtOH C ₂₀ H ₂₈ N ₄ O ₈ Co (511)	5.20	—	249, 311, 359, 395	656, 477, 414	12.6
(4) [Fe(L)Cl(OH ₂)].EtOH C ₁₈ H ₂₀ N ₄ O ₆ ClFe (479.5)	4.20	—	247, 315, 350, 395	552, 392	38.4
(5) [UO ₂ (L)(EtOH)].EtOH C ₂₀ H ₂₄ N ₄ O ₆ U (686)	—	—	247, 317, 350, 395	552, 392	13.6
(6) [(Cu) ₂ (L)(Cl) ₂].EtOH C ₁₈ H ₁₈ N ₄ O ₅ Cl ₂ Cu ₂ (570)	—	2.82 (3.56)	240, 320, 359, 395	245,315, 330, 350, 670	11.5
(7) [(Ni) ₂ (L)(Cl) ₂ (OH ₂) ₄].2EtOH C ₂₀ H ₃₂ N ₄ O ₁₀ Cl ₂ Ni ₂ (676.4)	—	4.44 (6.40)	250, 322, 350, 369	659, 837	11.5
(8) [(Co) ₂ (L)(Cl) ₂ (OH ₂) ₄].2EtOH C ₂₀ H ₃₂ N ₄ O ₁₀ Cl ₂ Co ₂ (677)	—	7.52 (10.40)	249, 312, 359, 390	675, 477, 414	12
(9) [(Fe) ₂ (L)(Cl) ₄ (OH ₂) ₂].EtOH C ₁₈ H ₂₂ N ₄ O ₇ Cl ₄ Fe ₂ (660)	—	5.94 (8.42)	247, 314, 350, 395	552, 392	48.5
(10) [(UO ₂) ₂ (L)(OEt) ₂]. EtOH C ₂₂ H ₂₈ N ₄ O ₁₁ U ₂ (1002)	—	—	247, 315, 350, 395	580, 567,523, 530	11

^a $\mu_{\text{eff.}}$ is the magnetic moment of only one cationic species in the complex; ^b μ_{compl} is the magnetic moment of all cations in the complex; ^cThe expected values were calculated by adding known susceptibilities of the metal cations present in the complex in the suggested structures; ^dEC = Electrical Conductance, 10⁻³ M solution in DMF, Ohm⁻¹ cm²mol⁻¹; ^esh = shoulder.

Results and discussion

Characterization of the ligand

The Schiff base (Figure 2) was prepared by the reaction of salicylaldehyde with oxaloyldihydrazide in a 2:1 molar ratio [14]. Elemental analysis data shared that the ligand has the molecular formula given in Table I. The ^1H NMR spectrum (Table II) of the ligand in deuterated DMSO- d_6 showed that the aromatic proton signals appeared at δ 6.8–7.3 ppm and the $\text{CH}=\text{N}$ proton signals at δ 7.9 ppm as expected [16–21]. The signals of the NH and the phenolic OH protons appeared at δ 16.1 and 11.1 ppm, respectively [16,20,21].

The IR spectrum of the ligand (Table III) shows a weak broad absorption band at 3530 cm^{-1} assigned for νOH of the phenolic groups. The stretching vibration [20,21] of NH and the enolic groups originating through tautomerism (Figure 2) appeared as weak bands at 3176 and 3107 cm^{-1} , respectively. The low value of the latter bands and their weak intensities are due to H-bonding, which also indicates the tautomerism between the keto and enol forms leading to a conjugated system. H-Bonding appears as a series of weak absorption bands in the range 2414 – 2330 cm^{-1} . Intramolecular H-bonding occurs between the hydrogen atoms of the phenolic OH groups, the imine NH and the oxygen atom of the ketonic groups. The conjugation system of the ligand leads to a decrease in the absorption frequencies of both the ketonic and the azomethine groups. This may be attributed to a decrease of their band orders, and they are better represented as $\text{C} \equiv \text{O}$, $\text{C} \equiv \text{C}$ and $\text{C} \equiv \text{N}$ bonds. The stretching vibrations of these bands appear at 1677 , 1558 and 1541 cm^{-1} , respectively [20,21]. $\nu(\text{C}=\text{O})$ of the phenol moiety appears at 1386 cm^{-1} and $\nu(\text{C}=\text{N})$ appears at 1336 cm^{-1} . The deformation vibration [20,21], δ , of the phenolic OH group appears at 1228 cm^{-1} .

The UV-VIS spectrum of the solid ligand showed two bands at 226 and 365 nm and a shoulder at 422 nm . Its ethanolic solution spectrum showed three absorption bands at 244 , 360 and 394 nm . The differences between the solid and the solution spectra of the ligand are due to the solvent effect. It is also noted that as the extent of conjugation increases, the wavelength of the maximum absorption encroaches on the visible region [22,23]. The first band in the solution spectrum would be assigned to $\pi \rightarrow \pi^*$ transition of the aromatic rings, the second and third bands would be due to $n \rightarrow \pi^*$ transition within the $\text{C}=\text{O}$ and $\text{C}=\text{N}$ groups [20,21] (Table IV).

The mass spectrum of the ligand showed its molecular ion at $m/e = 326$ which coincides with formula weight. Metastable ion(s) were not observed [20,21].

Elemental analyses and IR spectral data of the ligand and its mononuclear (1–5) and binuclear metal

complexes (6–10) are collected in Table. 1. The results showed that the H_2L coordinated with the metal ions as dibasic tetra- or hexadentate depending upon the molar ratios of $\text{M}:\text{L}$.

Metal complexes

The Schiff base ligand H_2L is dibasic and behaves as tetradentate or hexadentate containing O_2N_2 or O_4N_2 coordination sites depending upon the molar ratios of $\text{M}:\text{L}$. In the molar ratio of 1:1 ($\text{M}:\text{L}$), it behaves as dibasic tetradentate yielding mononuclear metal complexes as shown in Figure 3. On the other hand, binuclear metal complexes were obtained using molar ratios of 2:1 ($\text{M}:\text{L}$) in which the ligand acts as dibasic hexadentate (Figure 3).

All metal complexes have octahedral configuration around the metal ions except the Cu(II) and $\text{UO}_2(\text{IV})$ complexes. The Cu(II) -complex has a square-planar configuration distorted toward tetrahedral while the $\text{UO}_2(\text{IV})$ -complex has its favour hepta-coordination.

IR spectra of the metal complexes

Mononuclear metal complexes. The IR spectra of the mononuclear complexes (1–5) (Table 3) showed that the band due to the phenolic OH group that appeared in the spectrum of the ligand at 3530 cm^{-1} , disappeared in the spectra of these complexes. This may be due to the displacement of its proton by the metal ion. Moreover, the spectra showed that the vibrations of the $-\text{C}=\text{N}$ group were shifted to a lower frequency due to the coordination of the nitrogen atom of the azomethine group. The bands due to the imine, NH and $\text{C}=\text{O}$ groups which appeared at 3176 and 1677 cm^{-1} in the IR spectrum of the parent ligand, respectively, remained in the IR spectrum of the complexes. These bands were not significantly affected by complex formation, indicating the non-participation of these groups in complex formation. As a result, the Schiff base hydrazone ligand, H_2L , coordinates in these complexes as monobasic tetradentate with O_2N_2 coordination sites *via* the oxygen atoms of the phenolic OH and the nitrogen atoms of the azomethine groups [24].

Binuclear metal complexes. The IR spectra of the binuclear metal complexes (6–10) (Table III) showed a broad band at ≈ 3440 – 4000 cm^{-1} due to $\nu(\text{OH})$ of the coordinated water or alcohol molecules which replaced the band of the phenolic OH groups observed in the spectrum of the parent ligand. Moreover, the bands due to the imine NH groups remained. The bands due the $\text{C}=\text{N}$ and $\text{C}=\text{O}$ groups are shifted to lower frequencies, indicating the participation of these groups in complexation. As a result, the Schiff base ligand, H_2L , coordinates in

these complexes as dibasic hexadentate with O_4N_2 coordination sites *via* the oxygen atoms of the phenolic OH, the nitrogen atoms of the azomethine and the oxygen atoms of the carbonyl groups as shown in Figure 3. In all spectra, new bands appeared, for all types of the complexes, at 515–540 and 410–465 cm^{-1} that would be assigned to $\nu M-O$ and $\nu M-N$, respectively [24].

The IR spectra of the mono- and binuclear $UO_2(VI)$ complexes, Table 3, showed a broad band at 3440 cm^{-1} assigned to $\nu(OH)$ of the coordinated ethanol group. $\nu(NH)$ of the uncoordinated NH groups appeared as a shoulder at 3176 cm^{-1} , exactly at the same frequency as for the parent ligand. However, no splitting of this band was observed, which may be due to the larger separation of the two ligand moieties, due to the larger volume of the $UO_2(VI)$ cation in the complex molecules. Well-characterized bands appeared at 1517 and 1654 cm^{-1} assigned to the coordinated $C=N$ and $C=O$ groups. The bands occur at a lower frequency compared to that of the parent ligand indicating its involvement in coordinating the $UO_2(VI)$ cation in addition to the phenolic oxygen atoms after replacing their hydrogen ions by the uranyl(VI) cation. The $\nu_3(O=U=O)$ appeared as a strong band at 901 cm^{-1} overlapping with another band already present in the spectrum of the parent ligand and thus gaining higher intensity [23,24].

The IR spectrum of the binuclear Fe(III) complex, Table 3, showed a broad band at 3400 cm^{-1} due to $\nu(OH)$ of the outer-sphere ethanol molecules. Another band appeared at 1515 and 1649 cm^{-1} due to the $C=N$ and $C=O$ groups, respectively. These bands are shifted to lower frequency compared to that of the parent ligand. This shift would be due to the effect of the tripositive ferric ion on decreasing the force constant of the $C=N$ and $C=O$ bonds.

Magnetic moments and electronic spectral data of the metal complexes

The reflectance spectra and magnetic moments data of the metal complexes are listed in Table 4. Generally, in all spectra of the metal complexes, the absorption bands due to $\pi-\pi^*$ and $n-\pi^*$ transitions observed in the spectrum of the free ligand at higher energy have shifted to lower frequencies due to coordination of the ligand with metal ions.

The reflectance spectra of the Cu(II) complexes (1 and 6) (Table 4) showed absorption bands at > 345 , > 311 , > 330 , > 358 and > 665 nm. The first four bands are due to the ligand absorption which are shifted from those of the parent ligand due to complex formation. The bands at > 665 nm are due to $d \rightarrow d$ attributed to the $A_{1g} \rightarrow {}^2B_{1g}$ transitions characterized by Cu(II) ion in a square-planar geometry [24,25,26]. The shift of the $d \rightarrow d$ absorption band to lower energy than

that expected for square-planar geometry, at 550 nm for square-planar N,N' -ethylene bis-(salicylideneimine)-copper(II), Cu(acacen) [24] may be due to the distortion of the square-planar geometry towards tetrahedral. [24,25,26]. The square-planar geometry of Cu(II) ions in the complexes 1 and 6 are confirmed by the measured magnetic moments values, 1.76 and 2.82 B.M. respectively. The value of 2.8 B.M. for the binuclear complex, 6, lower than the expected value of two Cu(II) ions, may be due to antiferromagnetic interactions between the adjacent Cu(II) ions in the complex. The square-planar geometry, in complex 1, is achieved by the coordination of Cu(II) ion with one molecule H_2L through O_2N_2 coordination sites. However, in complex 6, two Cu(II) ions coordinated to one molecule of the ligand each through O_2N coordination sites complete its square-planar geometry by the coordination of a chloride ion [24,25,26].

The reflectance spectrum of the mononuclear Ni(II) complex (2), Table IV, showed a main band at 768 nm and a shoulder at 670 nm. The main band may be due to $A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ electronic transition and may be overlapped [25,26] by the ligand transitions, which appeared at 355 nm. The third transition, $A_{2g}(F) \rightarrow A_{2g}(P)$ is out of the scale of the spectrophotometer used. The magnetic moment of the complex is 3.19 B.M. which agrees with the presence of Ni(II) ion in an octahedral geometry [22,25,26]. This indicates that the Ni(II) ion is coordinated to O_2N_2 sites in an octahedral geometry [25,26,27]. The Ni(II) ion completes its six-coordination sphere by two water molecules.

The reflectance spectrum of the binuclear Ni(II) complex (7) showed a diffuse band in the range 659–837 nm. This indicates that each Ni(II) ion is coordinated to the ligand through O_2N sites in an octahedral geometry [24,25,26]. Each Ni(II) ion completes its six-coordination sphere by two water molecules and chloride ion. The magnetic moment of this complex is 4.44, which is smaller than the calculated value for two Ni(II) ions in octahedral geometries and may indicate antiferromagnetic interactions between adjacent Ni(II) ions in the complex [24,15].

Octahedral, tetrahedral and square-planar cobalt (II) complexes show magnetic moments between 4.7–5.2, 4.2–4.8 and 2.2–2.9 B.M., respectively [25,26]. The μ_{eff} values for the present Co(II) complexes (3 and 8), Table IV, are 5.2 and 7.52 B.M. The magnetic moment of binuclear complex (8) is 7.52 B.M., which is smaller than the calculated value for two Co(II) ions in octahedral geometries and may indicate antiferromagnetic interactions between adjacent Co(II) ions in the complex. The reflectance spectra of complexes 3 and 8 showed the d-d transition, $T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ at 656 and 675 nm, respectively. The two shoulders observed in both spectra at 477 and 414 nm may be due to $T_{1g}(F) \rightarrow {}^4$

Table V. Thermal analyses data for some metal complexes of H₂L.

Compound M.F. (M..W.)	dissociation Stages	Temp range in TG °C	Weight loss Found (Calcd.) %	Decomposition assignment
(1) [Cu(L)].EtOH C ₁₈ H ₁₈ N ₄ O ₅ Cu (434.5)	Stage I	61–110	10.40 (10.61)	1 mol outer sphere EtOH
	Stage II	224–235	25.86 (26.30)	2 CO, N ₂ H ₂ and N ₂
	Stage III	385–450	39.64 (39.20)	C ₂ H ₂ and (C ₆ H ₄) ₂ O
(2) [Ni(L)(OH ₂) ₂].2EtOH C ₂₀ H ₂₈ N ₄ O ₈ Ni (510.7)	Stage I	61–110	26.00 (25.10)	2 mol outer sphere EtOH
	Stage II	130–210	7.57 (7.10)	2 mol coordinated water
	Stage III	228–240	21.94 (22.32)	2 CO, N ₂ H ₂ and N ₂
	Stage IV	385–450	37.73 (38.00)	C ₂ H ₂ and (C ₆ H ₄) ₂ O
(3) [Co(L)(OH ₂) ₂].2EtOH C ₂₀ H ₂₈ N ₄ O ₈ Co (511)	Stage I	61–110	26.00 (25.12)	2 mol outer sphere EtOH
	Stage II	130–210	7.57 (7.11)	2 mol coordinated water
	Stage III	228–240	21.94 (22.33)	2 CO, N ₂ H ₂ and N ₂
	Stage IV	385–450	37.73 (38.03)	C ₂ H ₂ and (C ₆ H ₄) ₂ O
(4) [Fe(L)Cl(OH ₂)].EtOH C ₁₈ H ₂₀ N ₄ O ₆ ClFe (479.5)	Stage I	65–110	9.74 (9.59)	outer sphere EtOH
	Stage II	130–220	7.77 (7.50)	2 mol coordinated water
	Stage III	240–260	38.80 (38.50)	2 CO, N ₂ H ₂ and N ₂ and Cl
	Stage IV	285–465	37.23 (38.80)	C ₂ H ₂ and (C ₆ H ₄) ₂ O
(5) [UO ₂ (L)(EtOH)].EtOH C ₂₀ H ₂₄ N ₄ O ₆ U (686)	Stage I	61–110	6.30 (6.71)	outer sphere EtOH
	Stage II	130–212	6.35 (6.71)	coordinated ethanol
	Stage III	228–246	17.10 (16.62)	2 CO, N ₂ H ₂ and N ₂
	Stage IV	385–450	28.70 (28.30)	C ₂ H ₂ and (C ₆ H ₄) ₂ O
(6) [(Cu) ₂ (L)(Cl) ₂].EtOH C ₁₈ H ₁₈ N ₄ O ₅ Cl ₂ Cu ₂ (570)	Stage I	61–110	8.50 (8.10)	1 mol outer sphere EtOH
	Stage II	238–260	13.20 (12.81)	2 mol HCl
	Stage III	330–370	25.70 (25.30)	2 CO, and 2N ₂
	Stage IV	385–455	37.67 (37.12)	2 C ₇ H ₆ O
(7) [(Ni) ₂ (L)(Cl) ₂ (OH ₂) ₄].2EtOH C ₂₀ H ₃₂ N ₄ O ₁₀ Cl ₂ Ni ₂ (676.4)	Stage I	61–120	13.20 (13.60)	2 mol outer sphere EtOH
	Stage II	125–220	11.20 (10.64)	4 mol coordinated water
	Stage III	238–260	10.73 (10.80)	2 mol HCl
	Stage IV	335–375	22.30 (21.80)	2 CO, and 2N ₂
	Stage V	385–455	31.50 (31.33)	2 C ₇ H ₆ O
(8) [(Co) ₂ (L)(Cl) ₂ (OH ₂) ₄].2EtOH C ₂₀ H ₃₂ N ₄ O ₁₀ Cl ₂ Co ₂ (677)	Stage I	61–120	13.27 (13.58)	2 mol outer sphere EtOH
	Stage II	125–220	10.17 (10.63)	4 mol coordinated water
	Stage III	238–260	10.73 (10.80)	2 mol HCl
(9) [(Fe) ₂ (L)(Cl) ₄ (OH ₂) ₂].EtOH C ₁₈ H ₂₂ N ₄ O ₇ Cl ₄ Fe ₂ (660)	Stage IV	335–375	21.18 (21.30)	2 CO, and 2N ₂
	Stage V	385–455	31.50 (31.31)	2 C ₇ H ₆ O
	Stage I	61–120	6.74 (7.00)	mol outer sphere EtOH
	Stage II	125–220	5.80 (5.5.0)	2 mol coordinated water
	Stage III	238–260	23.21 (21.82)	2 mol HCl, Cl ₂
(10) [(UO ₂) ₂ (L)(OEt) ₂]. EtOH C ₂₂ H ₂₈ N ₄ O ₁₁ U ₂ (1000)	Stage IV	335–375	16.86 (17.00)	2 CO, and 2N ₂
	Stage V	385–455	32.50 (32.12)	2 C ₇ H ₆ O
	Stage I	61–120	4.50 (4.60)	mol outer sphere EtOH
	Stage II	112–130	9.50 (9.00)	mol coordinated EtO-OEt
	Stage III	335–375	14.80 (14.40)	2 CO, and 2N ₂
	Stage IV	385–465	21.56 (21.20)	2 C ₇ H ₆ O

$A_{2g}(P)$ transition indicating that $Co(II)$ ion is coordinated to O_2N_2 (complex **1**) or O_2N (complex **8**) coordination sites of the ligand. In complex **8**, each $Co(II)$ ion completes its six-coordination sphere with two water molecules and chloride ion.

On the other hand, the reflectance spectra of $Fe(II)$ complexes (**4** and **9**) showed broad bands at 552 and 392 nm. These bands may be due to the spin forbidden transition $A_{1g} \rightarrow {}^4T_{2g}(G)$ and $A_1 \rightarrow {}^4A_1$, ${}^4E(G)$ electronic transitions [24] which may gain their intensity as a result of the vibronic mechanism in the octahedral field around ferric ion. The magnetic moment of complex **9** is 5.94 B.M. and that of mononuclear $Fe(III)$ complex **4**, is 4.20 B.M.. These values indicate the presence of antiferromagnetic interactions between adjacent $Fe(III)$ ions in complex **9** [25,26].

The reflectance spectra of the diamagnetic uranyl complexes **5** and **10**, in addition to the ligand bands, showed bands at 580 and 576 nm, respectively, imparting the complexes their colours. The bands observed at 523 and 530 nm are due to the electronic transitions from apical oxygen atom to the f-orbitals of the uranyl atom characteristic of the uranyl moiety. Both complexes are diamagnetic [25,26].

Molar conductance of the metal complexes

The conductance measurements, recorded for 10^{-3} M solutions of the metal complexes in DMF, are listed in Table IV. All complexes are non-conducting indicating their neutrality and that the divalent cations have replaced the phenolic and protons. However, the $Fe(III)$ complexes (**4** and **9**) showed an appreciable amount of conductance which may be through the replacement of a part of the coordinated chloride ions by solvent molecules as previously reported [24]. A phenomenon usually encountered in complexes containing chloride ions.

1H NMR spectrum of the uranyl complexes

The uranyl complexes (**5** and **10**) were selected as they are diamagnetic. Their 1H NMR spectra in $DMSO-d_6$ and after deuteration are discussed. The spectra of the complexes differ from that of the free ligand in the following aspects:

1. The disappearance of the signal due to the phenolic OH groups, in both spectra, is attributed to its involvement in coordinating the uranyl cation, while the signals due to the NH and $-C=H$ groups remained in both spectra, however, with an upfield shift. This may be due to the metal ion indicating that the ligand H_2L acts as a dibasic ligand.
2. The signals due to the aromatic ring showed fine structure and appeared as four separate signals at $\delta = 7.14, 7.53$ and 7.6 ppm.

3. The NH group which did not take part in coordinating the uranyl cation disappeared on deuteration.

Thermal analyses

The TG-DTA results for the solid complexes **1–10** are listed in Table V. The results show good agreement with the formulae suggested from the analytical data, Table 1. A general decomposition patterns was concluded in which the complexes decomposed in three stages. Beside these three stages, complexes, which have coordinated water, ethanol or chloride ion exhibited an additional stage and were decomposed in four stages (Table 5). Complexes with outer sphere ethanol molecules loose these at $61-110^\circ C$. The second stage is the loss of the coordinated water or solvent molecules at 130 to $250^\circ C$. The third to four stages represented the loss of the rest of the organic moiety and, finally, the formation of metal oxides.

Antimicrobial activity and minimum inhibitory concentration, MIC

The tests were performed according to the method previously reported [29]. 0.02 g of each complex was dissolved in 100 mL dimethylsulfoxide, DMSO, to produce 0.02% solutions. To a series of culture tubes containing sterile 5 mL double strength solution of Soyabean Casein Digest Medium (Tryptic Soy Broth), 5 mL of the 0.02% DMSO solution was added and mixed. To determine the bacteriostatic efficiency towards Gram +ve bacterium (*Staphylococcus aureus*) and the Gram -ve bacterium (*Escherichia coli*), 1 mL of a 1:10 diluted solution of Tryptic Soy Broth (TSB) (prepared by pipetting 1 mL of bacterial) was added to each culture tube cultures incubated at $37^\circ C$ for 24 h into 9 mL of sterile Tryptic Soy Broth. For the test for fungistatic efficiency, 0.1 mL of undiluted sample was incubated for 72 h at $37^\circ C$ with a TSB cultivation of *Candida albicans*. All inoculated culture tubes were incubated at $30-35^\circ C$ for 18–24 h. After that, the "MIC" level was assessed visually. MIC was recorded as the first clear tubes after turbidity, starting with the blank broth i.e. the highest dilution of the antiseptic/disinfectant preventing growth is taken as the "MIC" of the test organism. [8–10,28,29].

The tests were conducted for a series of concentrations of 1, 25, 50, 100% DMSO solutions obtained by diluting the stock 0.02% DMSO of each tested compound. The inhibition zones caused by the various compounds on the microorganisms were examined. The results of the preliminary screening test are listed in Table VI. Generally, the results showed that all tested compounds exhibited MIC at a concentration of 25%. However, only two complexes, **4** and **9**, exhibited MIC at a concentration of 1%

Table VI. Anti-microbial activity of the tested complexes.

Compound	MIC**		
	<i>Staphylococcus aureus</i> ATCC* 6538	<i>Escherichia coli</i> ATCC 8739	<i>Candida albicans</i> ATCC 10231
H ₂ LC ₁₆ H ₁₄ N ₄ O ₄ (326)	50%	25%	—
(1) [Cu(L)]·EtOH C ₁₈ H ₁₈ N ₄ O ₅ Cu (433.5)	25%	25%	25%
(2) [Ni(L)(OH ₂) ₂]·2EtOH ^c C ₂₀ H ₂₈ N ₄ O ₈ Ni (510.7)	25%	25%	25%
(3) [Co(L)(OH ₂) ₂]·2EtOH ^c C ₂₀ H ₂₈ N ₄ O ₈ Co (511)	50%	25%	—
(4) [Fe(L)Cl(OH ₂) ₂]·EtOH ^c C ₁₈ H ₂₂ N ₄ O ₇ ClFe (497.5)	1%	25%	1%
(5) [UO ₂ (L)(EtOH)]·EtOH ^c C ₂₀ H ₂₄ N ₄ O ₆ U (686)	25%	50%	25%
(6) [(Cu) ₂ (L)(Cl) ₂]·EtOH C ₁₈ H ₁₈ N ₄ O ₅ Cl ₂ Cu ₂ (568)	50%	25%	—
(7) [(Ni) ₂ (L)(Cl) ₂ (OH ₂) ₄]·2EtOH C ₂₀ H ₂₈ N ₄ O ₈ Cl ₂ Ni ₂ (640)	50%	25%	—
(8) [(Co) ₂ (L)(Cl) ₂ (OH ₂) ₄]·2EtOH C ₂₀ H ₂₈ N ₄ O ₈ Cl ₂ Co ₂ (641)	25%	50%	25%
(9) [(Fe) ₂ (L)(Cl) ₂ (OH ₂) ₂]·EtOH C ₁₈ H ₂₂ N ₄ O ₇ Cl ₂ Fe ₂ (660)	1%	50%	1%
(10) [(UO ₂) ₂ (L)(OEt) ₂]·EtOH C ₂₂ H ₂₈ N ₄ O ₁₁ U ₂ (1000)	25%	50%	25%

*number of strain in the American collection

**MIC is the lowest concentration of the compound solution to inhibit the growth of the microorganism.

reflecting a higher cytotoxic effect. The Schiff base H₂L was found to be biologically active and its metal complexes showed significantly enhanced antibacterial activity against one or more bacterial strains, in comparison to the parent ligand from which they were derived. All metal complexes were found to be the highly active against all organisms and in all concentration while the ligand, H₂L, exhibited its activity at 50 and 100% conc. for *S. aureus* and at 25, 50 and 100% for *E. coli* and did not affect the other tested strain organism, *Candida albicans*, at any concentration tested. A remarkable result is that the complexes, **1** and **2**, were found to have high activity against all strains at most of the concentrations used. On the other hand, complexes **5**, **8**, and **10** were found to have a high activity against *S. aureus* and *C. albicans* at 25 and 50% concentrations.

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