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Structural, spectral and biological studies of binuclear tetradentate metal complexes of N_3O Schiff base ligand synthesized from 4,6-diacetylresorcinol and diethylenetriamine

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ABSTRACT

The binuclear Schiff base, H_2L , ligand was synthesized by reaction of 4,6-diacetylresorcinol with diethylenetriamine in the molar ratio 1:2. The coordination behavior of the H_2L towards Cu(II), Ni(II), Co(II), Zn(II), Fe(III), Cr(III), VO(IV) and UO₂(VI) ions has been investigated. The elemental analyses, magnetic moments, thermal studies and IR, electronic, ¹H NMR, ESR and mass spectra were used to characterize the isolated ligand and its metal complexes. The ligand acts as dibasic with two N₃O-tetradentate sites and can coordinate with two metal ions to form binuclear complexes. The bonding sites are the nitrogen atoms of the azomethine and amine groups and the oxygen atoms of the phenolic groups. The metal complexes exhibit either square planar, tetrahedral, square pyramid or octahedral structures. The Schiff base ligand and its metal complexes were tested against four pathogenic bacteria (*Staphylococcus aureus and Streptococcus pyogenes*) as Gram-positive bacteria, and (*Pseudomonas fluorescens and Pseudomonas phaseolicola*) as Gram-negative bacteria and two pathogenic fungi (*Fusarium oxysporum and Aspergillus funigatus*) to assess their antimicrobial properties. Most of the complexes exhibit mild antibacterial and antifungal activities against these organisms.

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1. Introduction

Schiff base ligands played central role as chelating ligands in the main group and transition metal coordination chemistry [1,2]. Transition metal complexes of tetradentate Schiff base ligands find applications as model analogues of certain metal enzymes [3] and catalyst in oxidative addition reactions [4,5], modifier for selective electrodes, and different uses in material chemistry [6]. A bimetallic core is versatile at the active site of many metalloenzymes and plays an essential role in biological systems by the interplay of a pair of metal ions [7]. In the last decade, a large number of bimetallic Schiff base complexes of different structural types have been synthesized and characterized [8,9]. These complexes span the gamut in their new applications, donating types, structures [10] and biological activities [11].

Recently, a wide varieties of the Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff base derivatives including compartmental and macrocyclic ligands were tested in vitro for their antibacterial activities against human pathogenic bacteria (using disc diffusion (DD) method [12–15,19] or minimum inhibitory concentration (MIC) method [16,17,20,21]), fungal activities [13,14,16–18,20–23] and

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cytotoxic activity [15,20], where the metal complexes have higher antimicrobial and antifungal activities than the free ligands. Also, a survey highlights structural properties and biological studies of transition metal complexes derived from 4-aminoantipyrine were reported [24]. The most important results of extensive studies (syntheses, spectral, magnetic, redox, structural characteristics, antimicrobial and DNA cleavage) of the metal complexes with heterocyclic Schiff bases of 4-aminoantipyrine with some aldehydes and oximes are reviewed.

In the present work, this field is extended in synthesis of novel tetradentate binuclear Schiff base complexes, which could be used in numerous applications. The ligand was prepared by the condensation of 4,6-diacetylresorcinol (DAR), as starting material, with diethylenetriamine (DET) to afford the corresponding Schiff base, H₂L, ligand. The reaction of this ligand with copper(II), nickel(II), cobalt(II), cadmium(II), zinc(II), iron(III), chromium(III), oxovanadium(IV) and dioxouranium(VI) ions, in the 1:2 molar ratio (ligand:metal ion) was studied. The newly prepared metal complexes of this ligand were identified by different physicochemical and spectroscopic techniques.

The H_2L ligand acts as dibasic with two N_3O -tetradentate sites and can coordinate with two metal ions to form binuclear complexes. Copper(II), cobalt(II), iron(III) and Cr(III) complexes are octahedral. Nickel(II) is square planar while zinc(II) is tetrahedral. Oxovanadium(IV) complex is square pyra-

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Fig. 1. Formation of Schiff base, H₂L, ligand.

midal, while the dioxouranium(VI) complex is an octahedral [25].

The Schiff base, H₂L, ligand and its metal complexes were investigated for antibacterial and antifungal properties. Two Gram-positive bacteria (*Staphylococcus aureus* and *Streptococcus pyogenes*), two Gram-negative bacteria (*Pseudomonas fluorescens* and *Pseudomonas phaseolicola*) and two fungi (*Fusarium oxysporum* and *Aspergillus fumigatus*) were used in this study to assess their antimicrobial properties. Most of the complexes exhibit mild antibacterial and antifungal activities against these organisms and some of them were more effective than the free ligand.

2. Experimental

2.1. Materials

4,6-Diacetylresocinol (DAR) was synthesized according to the literature method [26]. Diethylenetriamine and triethylamine were Merck. Copper(II), nickel(II), cobalt(II), cadmium(II), zinc(II), iron(III) and chromium(III) were used as nitrate salts and were Merck or BDH. Oxovanadium(IV) sulfate monohydrate and dioxouranium(VI) acetate dihydrate were Fluka. Organic solvents (ethanol, absolute ethanol, methanol, diethylether, dimethylformamide and dimethylsulfoxide) were reagent grade and were used as supplied.

2.2. Synthesis of the Schiff base, H_2L , ligand

The ligand was synthesized by adding 4,6-diacetylresorcinol (DAR) (3.88 g, 20 mmol) dissolved in hot absolute ethanol (30 mL) to diethylenetriamine (DET) (3.00 g, 40 mmol) in absolute ethanol (30 mL). The reaction mixture was heated to reflux for 4 h. The yellow product was filtered off and washed with a few amount of ethanol then ether and air dried. Fine crystals were obtained by recrystallization from ethanol. The ligand was kept in a desiccator until used. The yield was 4.98 g (80.4%), m.p. > 250 °C. The Schiff base, H₂L, ligand was characterized by elemental analyses, ¹H NMR and electronic spectra in DMF solution and in the solid state by IR and mass spectra. The formation of H₂L ligand is illustrated in Fig. 1.

2.3. Synthesis of the Schiff base metal complexes

A methanolic solution of the metal salt (30 mL) was added gradually to a methanolic solution of the deprotonated ligand (60 mL) in the molar ratio 2:1. Triethylamine was used to affect the deprotonation of the ligand. The reaction mixtures of the deprotonated H₂L ligand with metal salts were stirred on cold for 30 min, and then heated to reflux, for 3 h. The resulting precipitates were filtered off, washed with methanol then ether. The complexes are insoluble in most common solvents and soluble only in DMF and DMSO.

In each case, triethylamine (0.610g, 10.0 mmol) dissolved in methanol (20 mL) which was added to the ligand (1.822 g, 5.00 mmol) in methanol (30 mL), i.e., in the molar ratio 2:1 (triethylamine:ligand) and heated to reflux for 30 min. The appropriate weight of 10.00 mmol of the metal salts was added to the ionic deprotonated ligand to form the metal complexes.

The following detailed preparation is given as an example and the other complexes were obtained similarly.

2.3.1. Reaction of Cu(II) with H_2L ligand

Copper(II) nitrate tetrahydrate, Cu(NO₃)₂·4H₂O (2.596 g, 10.0 mmol) in methanol (30 mL) was added gradually with constant stirring to a solution of the deprotonated, H₂L, ligand (1.822 g, 5.0 mmol) in methanol (60 mL). The pH of the mixture was 2.2. The stoichiometry of the metal ion to ligand was 2:1. The solution was heated to reflux for 3 h. A green precipitate was formed and washed with small amount of methanol then ether. The yield was 2.307 g (75.6%), m.p. > 250 °C.

2.4. Physical measurements

Carbon, hydrogen and nitrogen contents were carried out at the Microanalytical Center, Cairo University. Analyses of metal ions after the dissolution of the solid complex in hot concentrated nitric acid, HNO₃, then diluting with distilled water and filtering to remove the precipitated ligand. The solution was neutralized with ammonia solution and the metal ions were then titrated with EDTA [27–29]. The FT-IR spectra (4000–400 cm⁻¹) of the compounds were recorded as KBr discs using FT-IR (Shimadzu) spectrophotometer model 4000. ¹H NMR spectra (TMS was used as an internal standard reference) were recorded using a Varian spectrometer, EM-390, 90 MHz. Electronic spectra of the ligand and its metal complexes were carried out in 10⁻³ M DMF solution on a JASCO model V-550 UV-Visible spectrophotometer in the range 200-900 nm. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a magnetic susceptibility balance (Johnson Matthey, Alfa product, Model No. (MKI)). Effective magnetic moments were calculated from the expression $\mu_{eff} = 2.828 (\chi_M T)^{1/2}$ B.M., where χ_M is the molar susceptibility corrected using Pascal's constants for the diamagnetism of all atoms in the compounds and T is the absolute temperature [30]. ESR spectra of compounds were recorded on a Bruker model EMX, X-band spectrometer (9.78 GHz) with 100 kHz modulation frequency. Mass spectra of the compounds were recorded on a Hewlett Packard mass spectrometer model MS 5988. Samples were introduced directly to the probe and the fragmentations were carried out at 300 °C and 70 eV. Thermal gravimetric analysis (TGA) data were measured from room temperature to 800 °C at a heating rate 20 °C/min in dynamic N₂ atmosphere. The data were obtained using a Shimadzu TGA-50H instrument. Thermal analyzer equipped with a thermo-balance. The sample was contained in a boat-shaped platinum pan suspended in the center of a furnace. Molar conductance of millimolar solutions of the solid complexes in DMF was measured on Corning conductivity meter model NY 14831 (USA). Melting points were not corrected and were measured using a Stuart melting point instrument.

2.5. Antimicrobial activities

The in vitro evaluation of antimicrobial activity was carried out at Faculty of Agricultural, Al-Azhar University. The standardized disc-agar diffusion method [31] was followed to determine the activity of the synthesized compounds against the sensitive organisms *S. aureus* (ATCC 25923) and *S. pyogenes* (ATCC 19615) as Gram-positive bacteria, *P. fluorescens* (S 97) and *P. phaseolicola* (GSPB 2828) as Gram-negative bacteria and the fungi *F. oxysporum* and *A. fumigatus*.

The antibiotic chloramphencol was used as standard reference in the case of Gram-negative bacteria, cephalothin was used as standard reference in the case of Gram-positive bacteria and cycloheximide was used as standard antifungal reference.

The tested compounds were dissolved in DMF (which have no inhibition activity), to get concentrations of 2 and 1 mg mL⁻¹. The test was performed on medium potato dextrose agar (PDA) which contains infusion of 200 g potatoes, 6 g dextrose and 15 g agar [32,33]. Uniform size filter paper disks (3 disks per compound) were impregnated by equal volume (10 μ L) from the specific concentration of dissolved tested compounds and carefully placed on incubated agar surface.

After incubation for 36 h at 27 °C in the case of bacteria and for 48 h at 24 °C in the case of fungi, inhibition of the organisms which evidenced by clear zone surround each disk was measured and used to calculate mean of inhibition zones.

The activity of tested compounds was categorized as (i) low activity = mean of zone diameter is $\leq 1/3$ of mean zone diameter of control, (ii) intermediate activity = mean of zone diameter $\leq 2/3$ of mean zone diameter of control and (iii) high activity = mean of zone diameter >2/3 of mean zone diameter of control.

3. Results and discussion

3.1. Schiff base ligand

The structure of the Schiff base, H_2L , ligand is identified by elemental analysis, infrared, UV–Visible, ¹H NMR and mass spectra. Table 1 lists the physical and analytical data of the Schiff base, H_2L , ligand and its metal complexes. From the investigation, H_2L ligand can be represented as shown in Fig. 1.

The infrared spectrum is consistent with the formation of H₂L ligand. The vibrational assignments were aided by comparison with the vibrational frequencies of the related compounds, such as, the Schiff bases of 2-hydroxy-acetophenone [34]. The fundamental stretching mode of the azomethine moiety, ν (–C=N–), is readily assigned by comparison with the infrared spectra of 4,6-diacetylresorcinol (DAR) and diethylenetriamine (DET). The absorption band of the C=O in the 4,6-diacetylresorcinol disappeared, but the absorption band of the NH₂ in the diethylenetriamine, still persists, which may be due to the condensation of the one NH₂ has occurred while the other NH₂ still as it is. The most intense band at 1578 cm⁻¹ is assigned to the -C=N- stretching frequency of the H₂L ligand and is characterized for the azomethine moiety of most Schiff base compounds. On the other hand, other fundamental bands were assigned in the infrared spectrum of the H₂L ligand.

The mass spectrum of the Schiff base, H_2L , ligand, revealed the molecular ion peak at m/e 364 which is coincident with the formula weight (364.4) and support the identity of the structure. Fig. 2 depicts the mass spectrum of the H_2L ligand.

¹H NMR spectra of H₂L ligand in DMSO- d_6 , shows the chemical shifts of the proton signals. Table 2 lists the ¹H NMR chemical shifts (ppm) of the Schiff base, H₂L, ligand and its [Zn₂(L)](NO₃)₂ complex (**4**) in DMSO- d_6 and their assignments. The signals of the –NH and –NH₂ for the diethylenetriamine moiety (4.62 and 10.12 ppm) and

Table 1

- r	c		0									
	Reaction/ligand/complex ^a	Weight; g(mr	nol)	Molecular	pH of the	Yield g; (%)	m.p.(°C)	Color	Elemental analy	ses; Calcd. (Fou	nd)%	
		Ligand	Metal salt	formula (M.Wt.)	mixture				С	Н	N	M
	H ₂ L		I	C ₁₈ H ₃₂ N ₆ O ₂ 364.40	I	4.98(80.4)	>250	Yellow	59.34 (59.11)	8.79(8.88)	22.08 (22.37)	I
-	$H_2L + 2Cu(NO_3)_2 \cdot 4H_2O \rightarrow [Cu_2(L)(NO_3)_2]$	1.822 (5.0)	2.596 (10.0)	C ₁₈ H ₃₀ N ₈ O ₈ Cu ₂ 613.00	2.2	2.307 (75.6)	>250	Green	35.23 (35.02)	4.89 (4.95)	18.27 (18.12)	20.73 (20.95)
7	$H_2L + 2Ni(NO_3)_2 \cdot 6H_2O \rightarrow [Ni_2(L)](NO_3)_2$	1.822 (5.0)	2.908 (10.0)	C ₁₈ H ₃₀ N ₈ O ₈ Ni ₂ 603.40	3.2	1.400(46.4)	>250	Brown	35.80 (35.95)	4.97 (4.94)	18.56 (18.46)	19.46 (19.65)
ŝ	$H_2L + 2Co(NO_3)_2 6H_2O \rightarrow [Co_2(L)(NO_3)_2]$	1.822 (5.0)	2.910 (10.0)	C ₁₈ H ₃₀ N ₈ O ₈ Co ₂ 603.80	2.6	1.528 (57.2)	>250	Brownish-rose	35.77 (35.86)	4.97 (4.88)	18.55 (18.37)	19.51 (19.72)
4	$H_2L + 2Zn(NO_3)_2 \cdot 6H_2O \rightarrow [Zn_2(L)](NO_3)_2$	1.822 (5.0)	2.965 (10.0)	C ₁₈ H ₃₀ N ₈ O ₈ Zn ₂ 616.74	2.3	1.783 (57.8)	>250	Pale yellow	35.02 (34.96)	4.86(4.93)	18.16 (18.00)	21.20 (21.42)
ŝ	$H_2L + 2Fe(NO_3)_3 \cdot 9H_2O \rightarrow [Fe_2(L)(NO_3)_4] \cdot 2H_2O$	1.822 (5.0)	4.040 (10.0)	C ₁₈ H ₃₄ N ₈ O ₁₀ Fe ₂ 633.69	4.1	2.073 (65.4)	>250	Dark brown	34.09 (34.12)	5.37 (5.26)	17.67 (17.51)	17.63 (17.71)
9	$H_2L + 2Cr(NO_3)_3 \cdot 9H_2O \rightarrow [Cr_2(L)(NO_3)_4] \cdot 3H_2O$	1.822 (5.0)	4.000 (10.0)	C ₁₈ H ₃₆ N ₈ O ₁₁ Cr ₂ 644.37	3.8	2425(76.5)	>250	Green	33.52 (33.81)	5.63(5.34)	17.39 (17.71)	16.14(16.22)
2	$\begin{array}{l} H_2L + 2VOSO_4 \cdot H_2 \\ \rightarrow [(VO)_2(L)]SO_4^{b,c} \end{array}$	1.822 (5.0)	1.810 (10.0)	C ₁₈ H ₃₀ N ₆ O ₈ SV ₂ 591.88	5.1	1.823 (61.6)	>250	Green	36.49 (36.17)	5.07 (4.93)	14.19 (14.24)	I
8	$H_2L + 2UO_2(OAc)_2 \cdot 2H_2O \rightarrow [(UO_2)_2(L)](OAc)_2$	1.822 (5.0)	4.241 (10.0)	C ₁₈ H ₃₀ N ₈ O ₁₂ U ₂ 1026.06	2.4	2.498 (48.7)	>250	Yellow	21.05 (20.96)	2.92 (2.81)	10.92 (11.11)	I
a Ai	I reactions were heated to refu	lux for 2–4 h, exc	cept in the forma	ition of Zn(II) and VO(IV) complexes	where the reaction v	as heated to	reflux for 10 h.				

Elemental analysis for sulfur: Calcd. (Found)%: 5.41 (5.43).

The oxovanadium(IV) sulfate was dissolved in a least amount of water then 30 mL methanol was added



Fig. 2. Mass spectrum of the Schiff base, H₂L, ligand.

Table 2

 1 H NMR chemical shifts (ppm)^a of the Schiff base, H₂L, ligand and [Zn₂(L)(NO₃)₂] complex in DMSO-d₆ and their assignments.

Chemical shifts (ppm)		Assignments
H ₂ L	$[Zn_2(L)](NO_3)_2 \text{ complex } (4)$	
1.59 1.79, 2.41 and 3.20 4.62 ^b 5.86 8.17 10.12 ^b 17.28 ^b	1.58 1.80, 2.41 and 3.23 3.31 ^b 5.65 8.00 10.11 ^b -	[s, 6H, 2CH ₃] [m, 8H, 4CH ₂] [s, br, 4H, 2NH ₂] [s, 1H, Ar-H] [s, 1H, Ar-H] [s, 2H, NH] [s, 2H, 2OH]

^a Chemical shifts (ppm) were referenced internally at 25 °C with respect to TMS; s = singlet, br = broad, m = multiplet.

^b The bands disappeared after the addition of D₂O.

the –OH phenolic (17.28 ppm) protons disappear in the presence of D_2O , which indicates that the –OH phenolic groups are acidic and can participate in the coordination with the metal ions. The signals of the CH₃ and CH₂ groups were observed in the range 1.59–3.20 ppm [35]. The two aromatic protons were observed at

5.86 and 8.17 ppm. The signal at 5.86 ppm is shifted to down field based on the shielding by electrons due to the electron-repelling effect of the two hydroxyl groups, i.e., mesomeric (+M) effect. The other proton which observed at 8.17 ppm which is in the metaposition for the two hydroxyl groups and have no mesomeric effect, was deshielded by the inductive (-I) effect of the two acetyl groups and two hydroxyl groups. These two protons did not disappear in the presence of D₂O. On the other hand, each of these two bands showed related bands in slightly higher frequency which is due to the tautometric isomers of the H₂L ligand in solution. This is interpreted by the presence of three different tautometric isomers for the H₂L ligand.

Electronic spectral data of the ligand were recorded in DMF solution and four absorption bands at 272, 324, 335 and 417 nm were characterized. The former and third bands correspond to ${}^{1}L_{a} \rightarrow {}^{1}A_{1}$ and ${}^{1}L_{b} \rightarrow {}^{1}A_{1}$ transitions of the phenyl ring [36]. The second band corresponds to the $\pi \rightarrow \pi^{*}$ transition of the azomethine group, and the last band corresponds to the $n \rightarrow \pi^{*}$ transitions of the oxygen and nitrogen atoms which are overlapped with the intermolecular CT from the phenyl ring.

3.2. Schiff base complexes

The Schiff base, H_2L , ligand behaves as a dibasic ligand with two N₃O-tetradentate sites. The ligand reacted with Cu(II), Ni(II), Co(II), Zn(II), Cr(III), Fe(III), VO(IV) and UO₂(VI) ions to yield the corresponding binuclear transition metal complexes. The geometrical structures of the complexes were identified and characterized using elemental analyses and infrared, UV–Visible, ¹H NMR, ESR and mass spectra. Also, TGA and molar conductivity measurements were conducted to add more proofs in identifying the structures.

3.2.1. IR spectra

The characteristic vibrational frequencies and their tentative assignments for the H_2L ligand and its transition metal complexes are listed in Table 3. The assignments were aided by comparison with the vibrational frequencies of the free ligand and its related compounds [26,37,38].

The shift of the stretching frequencies of the azomethine $\nu(-C=N-)$ group of the metal complexes to lower frequencies which lie in the range of 1570–1530 cm⁻¹, compared with the free lig-

Table 3

Characteristic of the vibrational frequencies (cm⁻¹) of the Schiff base, H₂L, ligand and its metal complexes and their assignments.

	-	, ,			•			
Ligand/complex	$\nu(OH) H_2O$	$v_{as}(NH_2)$ and $v_s(NH_2)$	$v_{\rm s}(\rm NH)$	$\delta(H_2O)$	ν (C=C) and ν (C=N)	ν(M–O)	ν(M–N)	Other bands
H ₂ L	-	3357 s, 3293 s	3275 s	-	1578 vs, br	-	-	_
1	-	3315 s, 3274 s	3167 m	-	1570 s, br	596 w	510 w	1546 m, 1350 vs, 812 w; bidentate NO ₃ groups.
2	-	3312 s, br, 3254	3222 m	-	1567 vs, br	601w	496 w	1742 s, 1357 s, 1055s, 810 w, sh; NO ₃ groups.
3	-	3309 s, 3251 s, br,	3146 m	-	1546 vs	598 w	519 w	1542 m, 1352 vs, 810 w, sh; bidentate NO ₃ groups.
4	-	3310 s 3252 s, br	3210 m	-	1567 vs	598 w	498 w	1755 s, 1356 s, 1054 s, 810 w; NO ₃ groups.
5	3445 s, br	3298 s, 3258 s, br	3198 m	1578 vs, br	1556 s, sh	580 w	492 w	1420 s, sh, 1311 s, br, 810 w, sh; unidentate NO ₃ groups.
6	3415 s, br	3305 m 3255 m, br	3187 m	1599 s, br	1540 s, br	561 m	484 m	1381 vs, 1356 s, 810 w, sh; unidentate NO ₃ groups.
7	-	3293 s 3208 s, br	3144 m	-	1564 vs	591 sh	500 w, sh	1124 s, 1095 s, sh, 1056 s, sh, 625 m,; SO ₄ groups, 942 m, sh: ν(V=O).
8	-	3250 s, sh 3210 s, br	3176 m	-	1530 s, sh	587 vw	419 w	1575 vs, 1428 s, sh, 811 w; OAc groups and 897 m; $v_3(UO_2)$.

s, strong; m, medium; w, weak; vs, very strong; sh, shoulder; br, broad; v, stretching.

and band at 1578 cm⁻¹, may be due to the coordination of the two azomethine groups to metal ions [26,37]. The broad bands in the range of 3445–3415 cm⁻¹ is assigned to the stretching frequencies of the ν (OH) of the water molecules associated to the complexes which are also confirmed by the elemental analyses and TGA data. The two bands at the ranges 3315–3293 and 3293–3210 cm⁻¹ are due to the stretching frequencies, ν_{as} (NH₂) and ν_{s} (NH₂), of the NH₂ groups. Also, the stretching frequency of the ν (NH) for the NH groups in the metal complexes were observed as one sharp band at 3222–3144 cm⁻¹. The weak bands in the two ranges 601–561 and 519–419 cm⁻¹ are assigned to the stretching frequencies of the ν (M–O) [39] and ν (M–N) bands [40], respectively, supporting that the bonding of the ligand to the metal ions is achieved by the phenolic oxygen atoms and the azomethine and amine nitrogen atoms of the ligand.

The NO₃⁻ ions are coordinated to the metal ion as unidentate for the complexes (**5**) and (**6**) with $C_{2\nu}$ symmetry. Each unidentate nitrate group possesses three non-degenerated modes of the vibrations (ν_s , ν_s and ν_{as}), which appeared at 1420–1381, 1356–1311 and 810 cm⁻¹, respectively. The $\nu_s(NO_3^-)$ of the unidentate NO₃⁻ is markedly shifted to lower frequencies compared to that of the free nitrate (1700–1800 cm⁻¹) [41]. This could be a factor measuring the covalent bond strength which is formed due to the transfer of an electron density from NO₃⁻ to the metal ion. In complexes (**1**) and (**3**), two NO₃⁻ ions behave as bidentate ligand. These nitrate groups possesses three non-degenerated modes of the vibrations (ν , ν_a and ν_s), which appeared at *ca*. 1546–1542, 1352–1352 and 812–810 cm⁻¹. Beside, there are two ionic NO₃⁻ groups in the Ni(II) (**2**) and Zn(II) (**4**) complexes, where their vibrations appeared at 1755–1742, 1357–1356 and 1055–1054 cm⁻¹.

In oxovanadium(IV) complex (**7**), several bands were observed at 1124, 1095, 1056 and 625 cm⁻¹ which are assigned to the coordinated sulfate group [42]. In $[(UO_2)_2(L)(OAc)_2]$ complex (**8**), the bands observed at 1575, 1428 and 811 cm⁻¹ are assigned to the acetate group in the complex and overlapped by the ligand vibrations.

The IR spectrum of VO(IV) complex displays a band at 942 cm⁻¹ which has no counterpart in the spectrum of the ligand and is assigned to the stretching frequency of the ν (V=O) [43]. Also, the IR spectrum of the UO₂(VI) complex displays a strong band at 897 cm⁻¹ which is assigned to the stretching frequency of the ν (UO₂) [44].

3.2.2. Electronic spectra, magnetic and molar conductance measurements

It is possible to draw up the electronic transitions and predict the geometry with the aid of magnetic moments of most metal ions. Table 4 lists the characteristic electronic absorption bands, magnetic moments and molar conductance of the H₂L ligand and its metal complexes in DMF solutions. The electronic transitions due to the organic ligand in the metal complexes, showed the absorption bands of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions results from the C=N and C=O groups and appeared at 318-315 and 412-407 nm regions, respectively. These values are lower than the corresponding absorption bands for the H₂L ligand, which observed at 324 and 417 nm, respectively. This may be due to the coordination of the nitrogen and oxygen atoms of the ligands to the metal ions. Also, other two bands were observed in all electronic spectra of the complexes, which persist at the same positions compared to the electronic spectra of the free H₂L ligand, which are the two bands due to the ${}^{1}L_{a} \rightarrow {}^{1}A$ and ${}^{1}L_{b} \rightarrow {}^{1}A$ transitions of the phenyl ring transitions which were observed at 273-272 and 337-334 nm, respectively.

The electronic spectrum of the green Cu(II) complex (1) showed one unsymmetrical band at 712 nm which is assigned to ${}^{3}T_{2g}(G) \leftarrow E_{g}$ transition in distorted octahedral geometry. The mea-

Ligand/complexes	Electronic absorption band	ds and their assigr	iments (nm) ^a				Magnetic momen	ıts	${}^{\mathrm{q}V}$
	$^{1}L_{a} \rightarrow ^{1}A$ (phenyl ring)	¥+ ↑ ד	$^{1}\mathrm{L}_{b} \rightarrow ^{1}\mathrm{A}(\mathrm{phenyl\ ring})$	u → ת*	d-d transition	d-d transition assignments	$\mu_{\text{compl.}^{c}}(\mu B)$	$\mu_{\mathrm{eff}^{\mathrm{d}}}(\mu\mathrm{B})$	
H ₂ L	272(0.74)	324(0.83)	335(0.48)	417(0.55)	ı	1	ı	1	ı
1	272(0.88)	318(0.85)	337 (0.43)	410(0.54)	712(0.35)	${}^{3}T_{2g}(G) \leftarrow E_{g}$	2.68	1.81	130
2	272(0.87)	315(0.74)	335 (0.49)	412(0.53)	525(0.57)	$^{1}A_{2g} \leftarrow ^{1}A_{1g}$	Diamagnetic		135
3	272(0.89)	317(0.92)	337(0.38)	409(0.49)	647(0.26)	${}^{4}A_{2g}(F) \leftarrow {}^{4}T_{1g}(F)$	5.85	4.90	131
					463(0.12)	${}^{4}\mathrm{T}_{1\mathrm{g}}(\mathrm{P}) \leftarrow {}^{4}\mathrm{T}_{1\mathrm{g}}(\mathrm{F})$			
4	273 (0.78)	318(0.82)	336(0.53)	408(0.37)	ı)) 	Diamagnetic		145
5	272(0.85)	316(0.88)	334(0.46)	410(0.55)	830 (0.21)	Charge transfer	7.70	5.94	230
					519 (0.47)	tailing from UV to			
						visible region			
9	272(0.85)	318(0.82)	335(0.51)	409(0.42)	572(0.29)	${}^{4}\mathrm{T}_{\mathrm{2g}}(\mathrm{F}) \leftarrow {}^{4}\mathrm{A}_{\mathrm{2g}}(\mathrm{F})$	5.47	3.87	235
7	273(0.92)	319(0.88)	335(0.39)	407(0.64)	587(0.36)	$\mathbf{b}_1 \leftarrow \mathbf{b}_2$	3.17	1.41	95
8	272(0.85)	315(0.91)	336(0.55)	411(0.48)	600(0.28)	Charge transfer	Diamagnetic		170
^a Electronic spectra ir. ^b Molar conductivities	the visible region recorded in were measured in DMF at $1 \times$	DMF and the values at 10 ⁻³ M. Values at	les of ε_{max} are in parentheses , re in Ω^{-1} cm ² mol ⁻¹ .	and multiplied b	y 10 ⁻⁴ (Lmol ⁻¹ cm ⁻¹)				

Table 4

Magnetic moment values, $\mu_{compl.}$ are the magnetic moment of all metal ions present in the complex. Magnetic moment values, $\mu_{eff.}$ are the magnetic moment of one metal ions present in the complex. sured value of the magnetic moment for Cu(II) complex was 1.81 B.M., which confirm the octahedral structure [45].

The electronic spectrum of the red Ni(II) complex (2) showed a band at 525 nm and is assigned to the ${}^{1}A_{2g} \leftarrow {}^{1}A_{1g}$ transition. The diamagnetic value of the Ni(II) complex agrees with the square planar structure.

The electronic spectrum of the brownish-rose Co(II) complex (3) in DMF solution showed that the complex has an octahedral geometry. Two bands were observed in the visible region, the former one is due to ${}^{4}A_{2g}(F) \leftarrow {}^{4}T_{1g}(F)$ transition, which is observed at 647 nm. The second band due to ${}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}(F)$ transition is observed at 463 nm. The Co(II) complex showed the magnetic moment at 4.90 B.M. at room temperature where the usual octahedral complexes are around 4.8-5.2 B.M.

The electronic spectrum of the dark brown Fe(III) complex (5) showed a strong band at 519 and a weak band at 830 nm. It was not possible to identify the type of the d-d transition. This is due to a strong charge transfer (CT) band tailing from the UV-region to the visible region. Generally, from the elemental analyses and infrared spectrum which gives a significant proof for the nitrate anion to act as a unidentate ligand, it is expected that the Fe(III) complex has the octahedral arrangement. Magnetic moment of the Fe(III) complex (5) was measured and gives 5.94 B.M. This value is the range of the magnetic moment of the high spin octahedral, $t_{2g}^3 e_g^2$ arrangement, which has the amounts to 5.92 B.M. [46].

The electronic spectrum of the green Cr(III) complex (6) showed that it has an octahedral geometry. The transition can be interpreted using Tanab-Sugano diagram. In the Cr(III) octahedral complexes, the splitting of the free ion ground F term along with the presence of the excited P term of the same multiplicity provides the possibility of three spin allowed d-d transition [47]. The first band which observed at 572 nm is due to ${}^{4}T_{2g}(F) \leftarrow {}^{4}A_{2g}(F)$ transition, while the second band due to ${}^{4}T_{1g}(F) \leftarrow {}^{4}A_{2g}(F)$ transition was not observed. The third band which is due to ${}^{4}T_{1g}(P) \leftarrow {}^{4}A_{2g}(F)$ transition lies in the range of the ligand transitions and is not possible to identify. The magnetic moment is expected to be very close to the spin-only value for three unpaired electrons (3.87 B.M.) and also because of the absence of any orbital contribution. In the present work, the magnetic moment of the Cr(III) complex is 3.87 B.M.

The electronic spectrum of the green VO(IV) complex(7) showed one band at 587 nm which corresponds to $b_1 \leftarrow b_2$ electronic transition. With the aid of the elemental analysis and the infrared spectrum, the VO(IV) complex (7) structure is 5-coordinate, thus its geometry would be square pyramidal. Although most oxovanadium(IV) complexes are magnetically simple which having virtually 'spin-only' moments of 1.73 B.M. corresponding to one unpaired electron. In this study, the actual magnetic moment was 1.41 B.M. This value is less than the expected and is less easily understood. But, this could be due to antiferromagnetic effect between vanadium atoms of adjacent molecules linked together through oxygen atoms. The mass spectrum of the VO(IV) complex, $[(VO)_2(L)]SO_4$, showed the molecular ion peak at m/e 495 which agree well with the formula weight of the cationic complex after releasing the SO_4^{2-} anions.

The electronic spectrum of the yellow $UO_2(VI)$ complex (8) arise from the electronic transition of metal \rightarrow ligand charge transfer. This is an allowed transition and produces broad, intense absorption at 600 nm tailing into the visible region which produce the intense yellow color. The $UO_2(VI)$ complex is diamagnetic as expected [47].

Zn(II) complex (4) is diamagnetic as expected and its geometry is most probably tetrahedral. The ¹H NMR spectrum of $[Zn_2(L)](NO_3)_2$ complex (4) in DMSO- d_6 showed the chemical shifts of the proton signals in the spectrum. The assignments are listed in Table 2. It is worthnoting that the proton signals of the phenolic group were not observed in the ¹H NMR spectrum of the Zn(II) complex, which

0 -5000 20000 -25000

Fig. 3. X-bands of the ESR spectra of (a) Cu(II) and (b) VO(IV) complexes of the Schiff base, H₂L, ligand.

means that all the phenolic groups in the ligand were deprotonated to coordinate with the Zn(II) ions. The mass spectrum of the Zn(II) complex, $[Zn_2(L)](NO_3)_2$, showed the molecular ion peak at m/e 491 which agree well with the formula weight of the cationic complex after releasing the NO_3^- anions.

The values of the molar conductivity for all complexes were measured within the range 95–235 Ω^{-1} cm² mol⁻¹, for complexes (1)–(8), which are higher than the expected value for most cases. This may be due to the fact that the DMF solvent replaced the coordinated anions in the complexes, which results in the higher electrolytes due to the uncoordinated anions [48].

3.2.3. ESR spectra and thermal analysis

X-band ESR spectra of $[Cu_2(L)(NO_3)_2]$ complex (1) and $[(VO)_2(L)]SO_4$ complex (7) were recorded in the solid state at 25 °C (Fig. 4). The Cu(II) spectrum exhibited two bands. One of them is strong sharp band with $g_{\parallel} = 2.1081$ and the other is weak with g_{\perp} = 2.1120 (Fig. 3a). The shape of the spectrum is consistent with the octahedral geometry around each Cu(II) ion in the complex [49,50].

The g_{||} value is an important function for indicating the covalent character of (M–L) bonds. For ionic character, the g_{||} value is <2.0023 and for covalent characters the $g\parallel$ value is >2.0023. In the present complex, gll is more than 2.0023 indicating covalent character for Cu-L bond. In axial symmetry, the g-values are related



Table 5	
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Antimicrobial activity of the Schiff base, H₂L, ligand and **1–8** complexes.

Organisms	Mean o	f zone diame	ter ^a (mm)									
	Gram-p	ositive bacte	ria ^b		Gram-negative bacteria ^b				Fungi ^c			
	S. aureu (ATCC 2	ıs 25923)	S. pyoge (ATCC 1	enes 9615)	P. phase (GSPB 2	eolicola 2828)	P. fluore (S 97)	escens	F. oxysp	orum	A. fumiş	zatus
	A	В	A	В	A	В	A	В	A	В	A	В
H ₂ L	22	13	18	11	28	22	22	12	27	10	23	16
1	18	11	15	9	22	14	24	16	15	10	20	12
2	30	20	34	26	26	18	28	23	27	20	29	20
3	19	14	22	14	23	16	20	10	18	10	20	12
4	18	10	16	8	22	15	22	13	15	16	16	10
5	20	14	20	13	23	16	20	13	29	20	31	23
6	10	4	10	6	12	7	10	5	9	4	8	4
7	18	12	18	13	10	7	12	6	20	14	23	15
8	32	22	31	25	32	28	35	30	22	15	22	17
Control #	42	28	38	30	36	25	38	30	40	28	40	31

^a Chloramphencol in the case of Gram-positive bacteria, cephalothinin in the case of Gram-negative bacteria, and cycloheximide in the case of fungi. The concentration of A is 2 mg mL⁻¹ and B is 1 mg mL⁻¹. ^b Calculated from 3 values.

^c Identified depending on morphological and microscopical characteristics.



Fig. 4. Representative structures of the metal complexes of the Schiff base, H₂L, ligand.

to the *G*-factor by the expression $G = (g \parallel -2)/(g_{\perp} - 2) = 4$. According to Hathaway [51], if *G*>4, the exchange interaction between Cu(II) centers in the solid state is negligible, on the other hand, when *G*<4, a considerable exchange interaction is indicated. The *G* value of the complex (0.965) suggests the exchange coupling between Cu(II) centers in the solid state [51]. The powder ESR spectrum of Cu(II) complexes is typical of the octahedral [52]. The value of the magnetic moment (1.81 B.M), beside, the spectral data (712 nm) agrees well with the proposed structures.

Oxovanadium(IV) complex (7) (μ_{eff} = 1.41 B.M. at room temperature) exhibits three bands, g_1 = 2.1081, g_2 = 2.041 and g_3 = 2.144 (Fig. 3b). The resolution of the ESR spectra may be due to superexchange interaction between two oxovanadium(IV) ions which lead to a configuration in which the two electron spins have an antiferromagnetic character. The shape of the spectrum as well as the spectral studies agreed with the square pyramid structure.

Thermal gravimetric analysis for $[Fe_2(L)(NO_3)_2]$ - $2H_2O$ (**5**) and $[Cr_2(L)(NO_3)_2]$ - $3H_2O$ (**6**) complexes were obtained to give information concerning the thermal stability of the complex and to decide whether the water molecules are in the inner or outer coordination sphere of the central metal ion [37,53]. TGA/DrTGA studies were carried out from 25 to 800 °C, which showed four stages of weight loss and the complete decomposition at 670 °C. TGA for the Fe(III) complex showed a weight loss at 90 °C for the two water molecules, Calcd. (Found)%; 5.68 (5.69)%, also, the first stage in the TGA in Cr(III) complex showed a weight loss at 108 °C for three water molecules, Calcd. (Found)%; 8.37%; 8.39%.

From the interpretation of elemental analysis and infrared, electronic spectra, ESR and molar conductivity, it is possible to draw up the tentative structures of the transition metal complexes. Fig. 4 depicts the representative structures of the metal complexes.

3.3. Antimicrobial activity

The Schiff base, H₂L, ligand and its metal complexes were evaluated for antimicrobial activity against two strain Gram-positive bacteria (S. aureus and S. pyogenes), Gram-negative bacteria (P. fluorescens and P. phaseolicola) and fungus (F. oxysporum and A. *fumigatus*). The obtained antimicrobials are presented in Table 5. The Schiff base, H₂L, ligand was found to be biologically active. Table 5 shows, also, that all metal complexes exhibit antimicrobial activity in one or more strain and enhanced it comparing with the parent Schiff base. Although Ni(II) complex (2) showed high activity as antimicrobial activity, the Cr(III) complex (6) showed a dramatic low activity for all Gram-positive, Gramnegative and fungi. Uranyl complex (8) showed high activity in Gram-positive and Gram-negative bacteria in high and low concentrations and intermediate activity for fungi cases. Fe(III) complex (5) showed high activity in fungi only and intermediate activity for bacteria.

It is known that the chelation tends to make the ligand acts as more powerful and potent bacterial agent. A possible explanation for this increase in the activity upon chelation is that, in chelated complex, the positive charge of the metal is partially shared with donor atoms present on the ligands and there is an electron delocalization over the whole chelated ring. This, in turn, increases the lipoid layers of the bacterial membranes. Generally, it is suggested that the chelated complexes deactivate various cellular enzymes, which play a vital role in various metabolic pathways of these microorganisms. Other factors such as solubility, conductivity and dipole moment, which affected by the presence of metal ions, which may also be possible reasons for increasing the biological activity of the metal complexes as compared to the ligand from which they are derived.

4. Conclusions

In the present study, the Schiff base, H₂L, ligand is dibasic with two sets of N₃O-tetradentate sites. The Schiff base, H₂L, ligand was allowed to react with copper(II), nickel(II), cobalt(II), zinc(II), cadmium(II), iron(III), chromium(III), oxovanadium(IV) and dioxouranium(VI) ions, with 1:2 molar ratio (ligand:metal ion). All reactions afforded binuclear complexes except cadmium(II) for H₂L, which gave oily product which was difficult to isolate. For this ligand, nickel(II) complex exhibits a square planar geometry and zinc(II) complex exhibits tetrahedral geometry while copper(II), cobalt(II), iron(III) and chromium(III) complexes exhibit an octahedral geometry which contain coordinated nitrate ions as either unidentate or bidentate ligands. The oxovanadium(IV) complex showed a square pyramidal geometry and dioxouranium(VI) complex is an octahedral. The bonding sites are the azomethine nitrogen and the amino nitrogen atoms and the phenolic oxygen atoms. The ligand and its metal complexes enhanced a significant antimicrobial activity compared with standard antifungal and antibacterial agents.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.04.036.

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