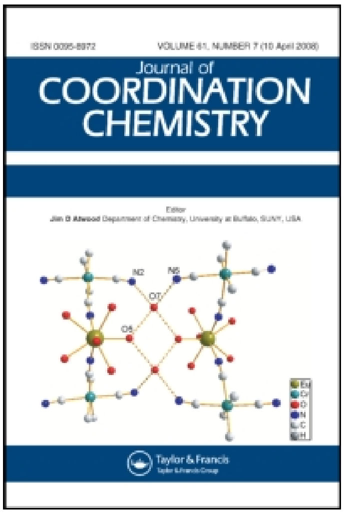

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Synthesis, spectral studies, and antimicrobial activity of binary and ternary Cu(II), Ni(II), and Fe(III) complexes of new hexadentate Schiff bases derived from 4,6-diacetylresorcinol and amino acids

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Synthesis, spectral studies, and antimicrobial activity of binary and ternary Cu(II), Ni(II), and Fe(III) complexes of new hexadentate Schiff bases derived from 4,6-diacetylresorcinol and amino acids

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Two new hexadentate N_2O_4 donor Schiff bases, H_4L^1 and H_4L^2, were synthesized by condensation of 4,6-diacetylresorcinol with glycine and alanine, respectively. The structures of the ligands were elucidated by elemental analyses, IR, ^{1}H NMR, electronic, and mass spectra. Reactions of the Schiff bases with copper(II), nickel(II), and iron(III) nitrates in 1 : 2 molar ratio gave binuclear metal complexes and, in the presence of 8-hydroxyquinoline (8-HQ) or 1,10-phenanthroline (Phen) as secondary ligands (L′), mixed-ligand complexes in two molar ratios 1 : 2 : 2 and 1 : 2 : 1 ($L^1/L^2 : M : L'$). The complexes were characterized by elemental and thermal analyses, IR, electronic, mass, and ESR spectral studies, as well as conductivity and magnetic susceptibility measurements. The spectroscopic data reveal that the Schiff-base ligands were dibasic or tetrabasic hexadentate ligands. The coordination sites with the metal ions are two azomethine nitrogens, two oxygens of phenolic groups, and two oxygens of carboxylic groups. Copper(II) complexes were octahedral and square planar while nickel(II) and iron(III) complexes were octahedral. The Schiff bases, H_4L^1 and H_4L^2, and some of their metal complexes showed antibacterial activity towards Gram-positive (*Staphylococcus aureus* and *Streptococcus pyogenes*) and Gram-negative (*Pseudomonas fluorescens* and *Pseudomonas phaseolicola*) bacteria and antifungal activity towards the fungi *Fusarium oxysporium* and *Aspergillus fumigatus*.

Keywords: Schiff-base ligand; Binuclear complexes; Mixed-ligand; 4,6-Diacetylresorcinol; Amino acid; Binary and ternary complexes

1. Introduction

Schiff bases play an important role in inorganic chemistry forming stable complexes with most transition metal ions. The field of bioinorganic chemistry has increased interest in Schiff-base complexes since many of these complexes serve as models for biologically important species [1–3]. Considerable attention has been given to the

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preparation of transition metal complexes of Schiff bases derived from amino acids due to their biological importance [4–9]. In addition, it has been reported that the complexes of amino acid Schiff base possess antitumor activities [10–12].

The bifunctional carbonyl compound, 4,6-diacetylresorcinol (DAR), has been used as precursor for the formation of different polydentate ligands [13–18] and mixed-ligand complexes [19–21]. In our previous studies, metal complexes of polydentate ligands derived from condensation of DAR with thiosemicarbazide, semicarbazide [22, 23], thiocarbohydrazide [24], and benzylamine [25] have been fully characterized. These ligands can be used to synthesize polynuclear complexes with different modes of bonding. Multimetallic complexes constitute an important part in modern inorganic chemistry due to such compounds as active sites in a variety of metalloenzymes.

The present work is about the synthesis of new polydentate Schiff bases, H_4L^1 and H_4L^2, by condensation of DAR with glycine and alanine, respectively, in molar ratio 1 : 2 and their complexes with copper(II), nickel(II), and iron(III), in ligand : metal 1 : 2 ratio. We have also synthesized mixed-ligand complexes of these Schiff-base ligands with 8-hydroxyquinoline (8-HQ) or 1,10-phenanthroline (Phen). The results of our investigations are presented in this manuscript.

2. Experimental

2.1. *Materials*

DAR was prepared as mentioned in [15]. $Cu(NO_3)_2 \cdot 2.5H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, glycine, alanine, potassium hydroxide, acetic acid, 8-hydroxyquinoline, 1,10-phenanthroline, EDTA disodium salt, ammonium hydroxide, metal indicators, and nitric acid were either Aldrich, BDH, or Merck products. Organic solvents [ethanol, absolute ethanol, diethylether, dimethylformamide (DMF), and dimethylsulfoxide (DMSO)] were reagent grade chemicals and were used without purification.

2.2. *Synthesis of Schiff bases, H_4L^1 and H_4L^2*

The Schiff bases were prepared in two steps. The first step was formation of DAR by acetylation of resorcinol [15]. The second step was condensation of DAR in the molar ratio 1 : 2 with the amino acid (glycine or alanine) to give the Schiff bases H_4L^1 and H_4L^2 as follows.

A solution of the appropriate amino acid (glycine or alanine) (10 mmol) in water (20 mL) containing KOH (0.56 g, 10 mmol) was added to DAR (0.97 g, 5 mmol) in absolute ethanol (20 mL). The reaction mixture was refluxed for 4 h yielding yellow products. After cooling, the pH of the mixture was adjusted to 6.0–7.0 with acetic acid. The precipitate was filtered off, washed several times with 1 : 1 (v/v) ethanol : water then with diethylether, and finally air-dried. The ligands were recrystallized from methanol–DMF. The crystals were dried in a desiccator over anhydrous calcium chloride. The analytical and physical data for H_4L^1 and H_4L^2 and their metal complexes are listed in table 1.

Table 1. Analytical and physical data of H_4L^1 and H_4L^2 and their metal complexes.

Complex	Color	Yield (%)	Decomp. point (°C)	Elemental analysis, % Found/(Calcd)				Magnetic moment (BM)		Conductance[c] ($\Omega^{-1}\,cm^2\,mol^{-1}$)
				C	H	N	M	μ_{eff}[a]	μ_{compl}[b]	
H_4L^1 ($C_{14}H_{16}N_2O_6$) [308.29]	Yellow	88	>300	54.35 (54.54)	5.50 (5.23)	8.82 (9.09)	–	–	–	–
$[(L^1)Cu_2(H_2O)_6] \cdot \frac{1}{2}EtOH$ (**1**)	Dark green	72	>300	31.77 (32.03)	4.57 (4.84)	5.30 (4.98)	22.40 (22.59)	1.97	2.66	Insol.
$[(L^1)Cu_2(8\text{-}HQ)_2(EtOH)_2] \cdot H_2O$ (**2**)	Green	55	292	51.67 (51.98)	4.36 (4.85)	7.00 (6.74)	15.10 (15.28)	2.12	2.87	9.0
$[(H_2L^1)Cu_2(Phen)_2(NO_3)_2] \cdot 5\frac{1}{2}H_2O$ (**3**)	Brown	50	>300	44.50 (44.88)	4.07 (4.06)	10.90 (11.02)	12.30 (12.50)	2.18	2.84	13.0
$[(L^1)Ni_2(H_2O)_6] \cdot 1\frac{1}{2}H_2O$ (**4**)	Pale green	68	>300	30.04 (30.20)	4.48 (4.89)	5.30 (5.03)	20.90 (21.09)	3.20	4.48	Insol.
$[(L^1)Ni_2(8\text{-}HQ)_2(EtOH)_2] \cdot \frac{1}{2}H_2O$ (**5**)	Pale green	66	>300	53.17 (53.18)	4.68 (4.83)	6.70 (6.89)	14.20 (14.44)	3.21	4.50	6.0
$[(H_2L^1)Ni_2(Phen)(NO_3)_2(H_2O)_2] \cdot 2\frac{1}{2}H_2O \cdot EtOH$ (**6**)	Pale green	62	>300	39.37 (39.33)	4.44 (4.36)	9.60 (9.83)	13.60 (13.73)	3.22	4.48	9.0
$[(H_2L^1)Fe_2(NO_3)_2(H_2O)_4](NO_3)_2 \cdot EtOH$ (**7**)	Brownish red	41	>300	24.61 (24.51)	3.35 (3.60)	11.00 (10.72)	14.00 (14.24)	5.81	8.16	130.0
$[(H_2L^1)Fe_2(8\text{-}HQ)_2(NO_3)_2](NO_3)_2 \cdot 4H_2O$ (**8**)	Black	30	>300	37.37 (37.37)	3.89 (3.53)	10.70 (10.90)	10.70 (10.86)	5.86	8.24	140.0
H_4L^2 ($C_{16}H_{20}N_2O_6$) [336.35]	Yellow	62	230	57.00 (57.14)	5.80 (5.99)	8.52 (8.33)	–	–	–	–
$[(L^2)Cu_2(H_2O)_2] \cdot H_2O$ (**9**)	Dark green	83	>300	37.75 (37.43)	4.75 (4.32)	5.10 (5.46)	24.60 (24.75)	1.79	2.40	Insol.
$[(L^2)Cu_2(8\text{-}HQ)_2(EtOH)(H_2O)]$ (**10**)	Olive green	67	269	52.89 (53.13)	4.35 (4.71)	7.10 (6.88)	15.40 (15.62)	1.95	2.63	20.0
$[(H_2L^2)Cu_2(Phen)(NO_3)_2(H_2O)_2]$ (**11**)	Brown	70	>300	42.14 (41.95)	3.66 (3.77)	11.00 (10.48)	15.80 (15.85)	1.98	2.78	20.0
$[(L^2)Ni_2(H_2O)_6]$ (**12**)	Pale green	66	>300	34.50 (34.45)	4.79 (5.06)	5.35 (5.02)	20.80 (21.05)	3.20	4.58	4.0
$[(L^2)Ni_2(8\text{-}HQ)_2(H_2O)_2] \cdot \frac{1}{2}H_2O$ (**13**)	Pale green	80	>300	52.03 (52.02)	4.50 (4.49)	6.95 (7.14)	14.80 (14.96)	3.0	4.20	3.0
$[(H_2L^2)Ni_2(Phen)(NO_3)_2(H_2O)_2] \cdot 2\frac{1}{2}H_2O$ (**14**)	Pale green	86	>300	40.39 (40.18)	4.61 (4.21)	9.80 (10.04)	14.00 (14.03)	3.15	4.30	7.0
$[(H_2L^2)Fe_2(NO_3)_4(H_2O)_2] \cdot 3\frac{1}{2}H_2O$ (**15**)	Brown	60	>300	24.57 (24.23)	3.72 (3.69)	10.30 (10.60)	13.90 (14.08)	5.80	8.30	Insol.
$[(H_2L^2)Fe_2(8\text{-}HQ)_2(NO_3)_2](NO_3)_2 \cdot 2H_2O$ (**16**)	Black	54	>300	40.05 (40.02)	3.50 (3.56)	11.10 (10.98)	10.80 (10.95)	5.41	7.60	163
$[(H_2L^2)Fe_2(Phen)(NO_3)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$ (**17**)	Red	80	>300	35.66 (35.54)	3.67 (3.62)	11.60 (11.84)	11.70 (11.80)	5.30	7.40	151

[a] μ_{eff} is the magnetic moment of one cationic species in the complex.
[b] μ_{compl} is the total magnetic moments of all cations in the complex.
[c] Solutions in DMF (10^{-3} M).

2.3. *Synthesis of metal complexes*

An ethanolic solution of metal nitrate was added to the ligand suspended in ethanol in the molar ratio 2 : 1 (M : L). The reaction mixture was refluxed for 5 h forming a precipitate in the hot solution, then cooled slowly, collected by filtration, washed with ethanol, then diethylether, and finally air-dried. The prepared complexes are stable at room temperature, non-hygroscopic, and insoluble in water and common organic solvents. The following detailed preparations are given as examples and the other complexes were obtained similarly.

2.3.1. Synthesis of $[(L^1)Cu_2(H_2O)_6]\cdot½EtOH$ (1). A total of 0.754 g (3.24 mmol) of $Cu(NO_3)_2 \cdot 2.5H_2O$ dissolved in 30 mL ethanol was added gradually to 0.5 g (1.62 mmol) of H_4L^1, suspended in 30 mL ethanol. The reaction mixture was refluxed for 5 h giving a dark green precipitate which was filtered off, washed several times with ethanol and diethylether, and finally air-dried. The yield was 0.657 g (72%). The binary complexes of Ni(II) and Fe(III) with H_4L^1 and H_4L^2 were synthesized by exactly the same method.

2.3.2. Synthesis of $[(L^1)Cu_2(8\text{-}HQ)_2(EtOH)_2]\cdot H_2O$ (2). A total of 0.754 g (3.24 mmol) of $Cu(NO_3)_2 \cdot 2.5H_2O$ dissolved in 30 mL ethanol was added gradually to 0.5 g (1.62 mmol) of H_4L^1 suspended in 30 mL ethanol. The reaction mixture was refluxed for 30 min and then 0.471 g (3.24 mmol) of 8-hydroxyquinoline dissolved in ethanol was added to the mixture. The resulting mixture was refluxed for 5 h resulting in a green precipitate which was filtered off, washed several times with ethanol and diethylether, and finally air-dried. The yield was 0.743 g (55%). Mixed ligand complexes of Ni(II) and Fe(III) with H_4L^1 and H_4L^2 in the presence of 8-hydroxyquinoline or 1,10-phenanthroline were synthesized in exactly the same manner.

2.3.3. Unsuccessful trials. Several attempts to prepare iron(III) complex of H_4L^1 in the presence of 1,10-phenanthroline (Phen) were unsuccessful with oily products obtained which could not be isolated in a pure form.

2.4. *Analytical and physical measurements*

Elemental analyses (C, H, and N) were performed at the Microanalytical Center, Cairo University, Giza, Egypt. Analyses of metal ions followed dissolution of the solid complex in hot concentrated nitric acid then diluting with doubly distilled water. The solution was neutralized with ammonia solution and then the metal ions were titrated with EDTA following standard literature methods [26–28]. The pH values were measured by a WTW-D-8120 digital pH-meter fitted with a combined glass electrode. Melting points of the ligands and their metal complexes were determined using a Stuart melting point instrument. IR spectra (4000–400 cm^{-1}) were obtained using KBr discs on a Shimadzu 4000 FT-IR spectrophotometer. Electronic spectra were recorded at room temperature on a Jasco model V-550 UV-Vis spectrophotometer as Nujol mulls and/or solutions in DMF. ^1H NMR spectra of the ligands were recorded at room temperature by using a Bruker WP 200 SY spectrometer. Dimethylsulfoxide, DMSO-d_6, was used as a solvent and tetramethylsilane (TMS) as an internal reference.

The spectra were examined from 0 to 18 ppm. The chemical shifts (δ) are given downfield relative to TMS. D_2O was added to every sample to test for deutration. Mass spectra were recorded at 290°C and 70 eV on a Hewlett-Packard mass spectrometer model MS-5988. Magnetic susceptibility measurements were carried out at room temperature using a magnetic susceptibility balance of the type Johnson Matthey, Alfa product, Model No. (MKI). Effective magnetic moments were calculated and corrected using Pascal's constants for diamagnetism of all atoms [29]. Molar conductivities of 10^{-3} M solutions in DMF were measured on a Corning conductivity meter NY 14831 model 441. ESR spectra of the copper(II) complexes were recorded on an Elexsys, E500, Bruker Company, National Research Centre, Dokki, Cairo, Egypt. The thermogravimetric analysis (TGA) of the solid complexes was performed using a Shimadzu-50 thermal analyzer. The biological activity of the Schiff bases and their metal complexes were studied using the disc diffusion method [30].

2.5. *Antimicrobial activity*

The standard disc-agar diffusion method [30] was followed to determine the activity of the synthesized compounds against *Staphylococcus aureus* (ATCC 25923) and *Streptococcus pyogenes* (ATCC 19615) as Gram-positive bacteria, *Pseudomonas fluorescens* (S 97) and *Pseudomonas phaseolicola* (GSPB 2828) as Gram-negative bacteria and the fungi *Fusarium oxysporium* and *Aspergillus fumigatus*. The antibiotic chloramphenicol was used as standard reference for Gram-negative bacteria, cephalothin for Gram-positive bacteria, and cycloheximide as standard antifungal reference.

The tested compounds were dissolved in DMF (which has no inhibition activity) to concentrations of 2 and 1 $\mathrm{mg\,mL^{-1}}$. The test was performed on the medium potato dextrose agar (PDA), which contains infusion of 200 g potatoes, 6 g dextrose, and 15 g agar [31]. Uniform size filter paper disks (three disks per compound) were impregnated by equal volume (10 µL) from the specific concentration of dissolved test compounds and carefully placed on incubated agar surface. After incubation for 36 h at 27°C for bacteria and 48 h at 24°C for fungi, inhibition of the organisms shown by clear zone surrounding each disk was measured and used to calculate mean inhibition zones.

3. Results and discussion

3.1. *The Schiff bases, H_4L^1 and H_4L^2*

The Schiff bases, H_4L^1 and H_4L^2, were prepared by condensation of DAR with glycine or alanine, respectively, in the molar ratio 1 : 2. The structures were elucidated by elemental analyses, electronic, IR, ^{1}H NMR, and mass spectra. The elemental analyses (table 1) are in good agreement with the proposed formula.

IR spectral data of the Schiff bases and their metal complexes are listed in table 2. H_4L^1 and H_4L^2 showed non-ionized COO stretching frequencies at 1725 and 1734 $\mathrm{cm^{-1}}$, respectively [32, 33]. Bands at 1625 $\mathrm{cm^{-1}}$ in H_4L^1 and 1647 $\mathrm{cm^{-1}}$ in H_4L^2 may be attributed to ν(C=O) and ν(C=N) stretching of the keto and imine forms of the ligands [34]. The amino acid Schiff bases have keto and imine tautomeric

Table 2. Characteristic IR spectral data (cm^{-1})[a] of H_4L^1 and H_4L^2 and their metal complexes.

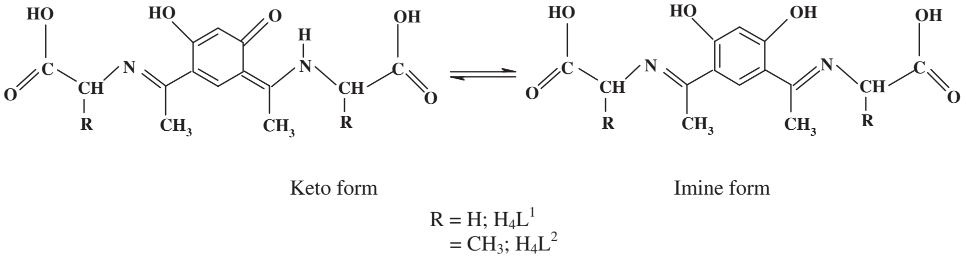
	IR spectra (cm^{-1})							
Complex	ν(OH)	ν(NH)	ν(COOH) (non-ionized)		ν(C=O) ν(C=N)	ν(C–O)		
H_4L^1	3123 m, br	3380 m	1725 w		1625 m	1062 m		
H_4L^2	3074 m, br	3424 m	1734 w		1647 s	1049 s		
	ν(OH) (H_2O/EtOH/phenolic)	ν_{asy}(COO)	ν(C=N)	ν_{sym} (COO)	ν(C–O)	ν(M–O)	ν(M–N)	Other bands
1	3431 s, br	1615 w	1591 vs	1387 s	1070 m	576 w	466 m	
2	3422 m, br	1614 w	1574 vs	1379 s	1078 w	580 w	435 w	1497 s; ν(C=N)(8-HQ)
3	3400 m, br	1612 m	1590 vs	1380 s	1075 m	580 w	444 w	1543 m; ν(C=N)(Phen) 1205 m, 1045 m; $\nu(NO_3^-)$
4	3437 s, br	1610 w	1593 vs	1384 s	1085 w	594 w	470 w	
5	3350 s, br	1604 m	1578 vs	1378 vs	1069 w	557 w	443 w	1502 s; ν(C=N)(8-HQ)
6	3380 s, br	1610 m	1580 vs	1381 s	1072 w	570 w	460 w	1550 m; ν(C=N)(Phen) 1180 m, 1040 m; $\nu(NO_3^-)$
7	3415 m, br	1604 m	1592 vs	1396 s	1074 m	565 w	430 w	1410 w, 1225 m, 1030 m; $\nu(NO_3^-)$
8	3395 s, br	1618 m	1584 vs	1385 s	1077 m	580 w	461 w	1515 s; ν(C=N)(8-HQ) 1240 m, 1050 m; $\nu(NO_3^-)$
9	3412 m, br	1607 m	1579 vs	1380 s	1060 m	565 w	448 w	
10	3419 m, br	1614 w	1576 s	1377 vs	1056 m	521 m	461 w	1497 s; ν(C=N)(8-HQ)
11	3421 m, br	1620 w	1586 s	1382 vs	1070 m	580 w	431 w	1563 m; ν(C=N)(Phen), 1261 m, 1106 m; $\nu(NO_3^-)$
12	3405 s, br	1610 m	1600 vs	1385 s	1064 w	530 w	462 w	
13	3388 m, br	1610 m	1595 vs	1380 s	1058 w	545 w	455 w	1488 m; ν(C=N)(8-HQ)
14	3384 m, br	1625 w	1602 vs	1383 m	1053 m	594 m	425 w	1559 s; ν(C=N)(Phen), 1270 s, 1106 m; $\nu(NO_3^-)$
15	3383 m, br	1612 m	1594 s	1382 s	1060 m	575 w	440 w	1215 m, 1100 m; $\nu(NO_3^-)$
16	3400 m, br	1608 m	1588 vs	1378 s	1064 m	580 w	460 w	1525 m; ν(C=N)(8-HQ), 1425 m, 1230 m, 1085 w; $\nu(NO_3^-)$
17	3410 m, br	1610 m	1588 vs	1380 s	1067 m	560 w	433 w	1560 m; ν(C=N)(Phen), 1420 m, 1250 m, 1096 w; $\nu(NO_3^-)$

[a] s, strong; m, medium; w, weak; vs, very strong; br, broad.

forms [34, 35] (scheme 1), while in complexes they exist only in the imine form [33, 36]. The medium intensity band around 3400 cm^{-1} assignable to –NH vibration [37] confirmed that the ligands are in the keto-imine forms [38]. H_4L^1 and H_4L^2 showed broad bands at 3123 and 3074 cm^{-1}, respectively, which could be assigned to $\nu(OH \cdots N)$ for phenolic group. Finally, bands for H_4L^1 and H_4L^2 were observed at 1062 and 1049 cm^{-1}, respectively, which are assigned to ν(C–O) of the phenolic group.

Electronic spectral data of the Schiff bases, H_4L^1 and H_4L^2, summarized in table 3, have two strong broad bands at ~300 and ~400–420 nm. The existence of two absorption bands for amino acid Schiff bases is attributed to the two tautomeric (keto and imine) forms [39, 40]. The strong broad band at ~300 nm indicates the imine form, and the strong broad band at ~400–420 nm is assigned to the π–π* transition in the keto form [36] (scheme 1).

^{1}H NMR spectral data (δ ppm) of H_4L^1 and H_4L^2 in DMSO-d$_6$ are provided as Supplementary material. The phenolic –OH protons (16.66 and 16.40 ppm for H_4L^1 and

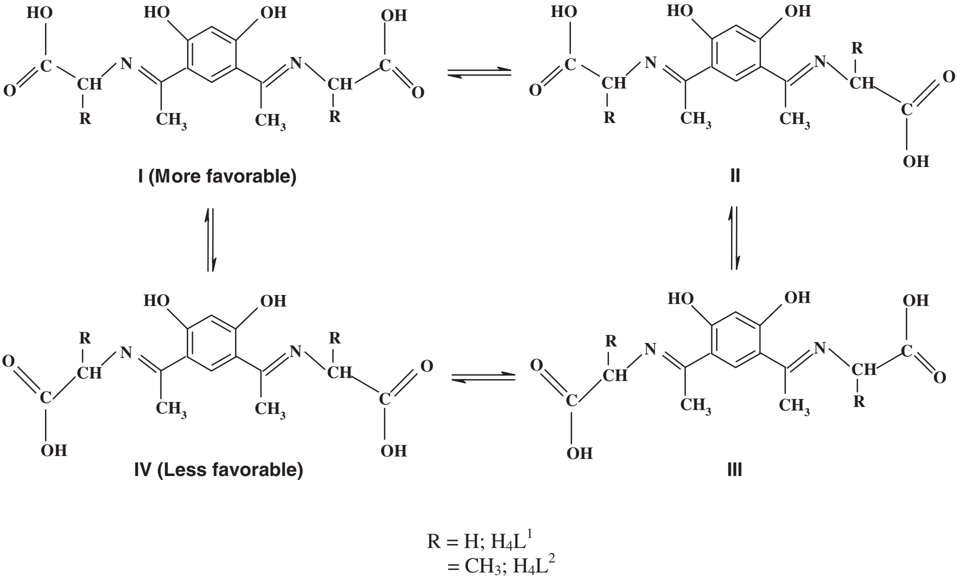


Scheme 1. Keto-imine tautomeric forms of the Schiff base, H_4L^1 and H_4L^2, ligands.

Table 3. Electronic spectral data of H_4L^1 and H_4L^2 and their metal complexes.

Complex	λ_{max}[a] (nm)/ε_{max} (L cm^{-1} mol^{-1})	Assignment
H_4L^1	265 (700), 314 (480), 420 (300)	
1	(570, 675)[b]	$^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2B_{2g}$
2	(540,594)[c]	$^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2B_{2g}$
3	564 (300), 612 (250)	$^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2B_{2g}$
4	(440, 625)[b]	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$
5	456 (250), 607 (210)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$
6	500 (280), 588 (325)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$
7	555 (300)	$^6A_1 \rightarrow {}^4T_2(G)$
8	610 (215)	$^6A_1 \rightarrow {}^4T_2(G)$
H_4L^2	266 (750), 316 (450), 410 (320)	
9	(530)[b]	$^2B_{1g} \rightarrow {}^2A_{1g}$
10	(560, 620)[c]	$^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2B_{2g}$
11	(590, 635)[b]	$^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2B_{2g}$
12	450 (330), 649 (270)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$
13	475 (270), 598 (220)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$
14	435 (340), 603 (290)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$
15	(594)[b]	$^6A_1 \rightarrow {}^4T_2(G)$
16	600 (220)	$^6A_1 \rightarrow {}^4T_2(G)$
17	529 (240)	$^6A_1 \rightarrow {}^4T_2(G)$

[a] Solutions in DMF (10^{-3} M).
[b] Nujol mull.
[c] Concentrated solutions.



Scheme 2. Isomeric structures of the Schiff base, H_4L^1 and H_4L^2, ligands.

H_4L^2, respectively) and carboxylic protons (12.58 and 12.10 ppm for H_4L^1 and H_4L^2, respectively) disappear in the presence of D_2O, indicating that these protons are acidic and the hydroxyl groups participate in coordination with the metal ions. ^{1}H NMR spectra of the ligands in DMSO-d_6 show different isomeric species for the same ligand. Among the proposed isomeric forms (I–IV) of the ligands (scheme 2), form I is more favorable, while form IV is less favorable; forms II and III are in a similar chemical environment and expected to show the same signals. The aromatic proton signals at 5.82 and 8.2 ppm, for H_4L^1, and 5.7 and 7.9 ppm, for H_4L^2, can be used as a probe of these isomeric forms. The integrated ratio of I : (II or III) : IV isomeric forms are 44 : 30 : 2 for H_4L^1 and 40 : 32 : 3 for H_4L^2.

The mass spectra of the H_4L^1 and H_4L^2 ligands showed the molecular ion peaks at *m*/*z* 308 and 336, respectively, confirming their formula weights (FW 308.29 and 336.35, respectively). Supplementary material contains mass spectra of H_4L^1 and some selected complexes. The mass fragmentation pattern of H_4L^1 (Supplementary material) supported the suggested structure.

3.2. *Characterization of the metal complexes*

H_4L^1 and H_4L^2 have two ONO donor sites and reacted with metal ions in the molar ratio 2 : 1 (M : L) [M = Cu(II), Ni(II) or Fe(III); L = H_4L^1 or H_4L^2] yielding binuclear complexes (**1**, **4**, **7**, **9**, **12**, and **15**). Reactions in the presence of secondary ligands (L′) (8-HQ or Phen) in 1 : 2 : 2 (L : M : L′) molar ratio gave mixed-ligand complexes in 1 : 2 : 2 ratio (**2**, **3**, **5**, **8**, **10**, **13**, and **16**) as well as 1 : 2 : 1 complexes (**6**, **11**, **14**, and **17**). The metal complexes were characterized by elemental and thermal analyses, IR, electronic, ESR, and mass spectra, as well as conductivity and magnetic susceptibility measurements at room temperature.

3.2.1. IR spectra.

Comparison of the IR spectra of the metal complexes with those of the free ligands revealed that all complexes have a broad band in the range 3350–3437 cm^{-1} assignable to ν(OH) of water and/or ethanol molecules associated with the complexes; these were confirmed by elemental and thermal analyses. A strong band from 1574 to 1602 cm^{-1} is assigned to coordinated ν(C=N). Bands at 1604–1625 and 1377–1396 cm^{-1} are assigned to ν_{as}(COO) and ν_s(COO), respectively. The difference between ν_{as}(COO) and ν_s(COO), $\Delta\nu$, is in the range 208–242 cm^{-1}, suggesting monodentate coordination of carboxylate [32, 41, 42]. Bands at 1062 and 1049 cm^{-1} characteristic of ν(C–O) in H_4L^1 and H_4L^2, respectively, appeared in their complexes at 1069–1085 and 1053–1070 cm^{-1}, respectively, with reduced intensity, suggesting that the phenolic oxygen is coordinated [43, 44]. The nitrato complexes (**3**, **6**–**8**, **11**, and **14**–**17**) showed two bands, 1180–1270 and 1030–1106 cm^{-1}, assigned to monodentate NO_3^- [45]. Complexes **7**, **16**, and **17** showed bands in the range 1410–1425 cm^{-1} assigned to ionic NO_3^-, indicating the ionic nature of these complexes. These infrared spectral data are supported by conductance data (table 1). The mixed ligand complexes containing 8-hydroxyquinoline (**2**, **5**, **8**, **10**, **13**, and **16**) and 1,10-phenanthroline (**3**, **6**, **11**, **14**, and **17**) showed new bands at 1488–1525 and 1543–1563 cm^{-1}, respectively, suggesting the presence of co-ordinated 8-hydroxyquinoline and 1,10-phenanthroline moieties [46–49]. Bands observed at 521–594 and 425–470 cm^{-1} are assigned to ν(M–O) and ν(M–N), respectively [50].

3.2.2. Conductivity measurements.

Molar conductances of the complexes in DMF (10^{-3} M solutions) were measured at room temperature and the results are listed in table 1. Complexes are non-electrolytes except **7**, **8**, **16**, and **17**, which are 1 : 2 electrolytes. These results agree with IR spectral data (table 2).

3.2.3. Electronic and ESR spectra and magnetic measurements.

Electronic spectra of metal complexes (table 3) were examined as DMF solutions and/or Nujol mulls for sparingly soluble complexes. Comparison of spectra for free ligands with their metal complexes showed persistence of the bands for ligands in all complexes. However, the bands were slightly shifted in complexes. New bands were observed in the spectra of the complexes, which are listed in table 3.

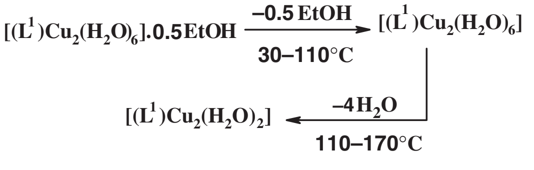
The Cu(II) complexes (**1**–**3**, **10**, and **11**) showed two absorptions at 540–590 and 594–675 nm, assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively, corresponding to a distorted octahedral geometry around copper(II) [50]. Complex **9** showed one band at 530 nm which may be assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition in square planar geometry [51]. The effective magnetic moments of **1**–**3** and **9**–**11** lie in the range 1.79–2.18 B.M., consistent with one unpaired electron (d^9) [52, 53]. X-band ESR spectra of $[(L^1)Cu_2(H_2O)_6] \cdot \frac{1}{2}EtOH$ (**1**) and $[(L^2)Cu_2(H_2O)_2] \cdot H_2O$ (**9**) (Supplementary material) were recorded in the solid state at 25°C. The spectrum of **1** exhibits signals at $g = 2.08$ and $g = 2.21$ and the shape is consistent with octahedral geometry. The spectrum of **9** exhibits one broad band with $g = 1.9$ and the shape is consistent with square-planar Cu(II) [52, 54].

Based on the electronic spectral and magnetic moment data, nickel(II) complexes have octahedral geometry. Electronic spectra showed bands in the regions 435–500 and 588–649 nm, which correspond to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ electronic transitions, respectively, which are consistent with octahedral geometry [55]. The effective magnetic moments of the complexes (**4–6** and **12–14**) are in the range 3.0–3.22 BM, confirming the octahedral geometry [56].

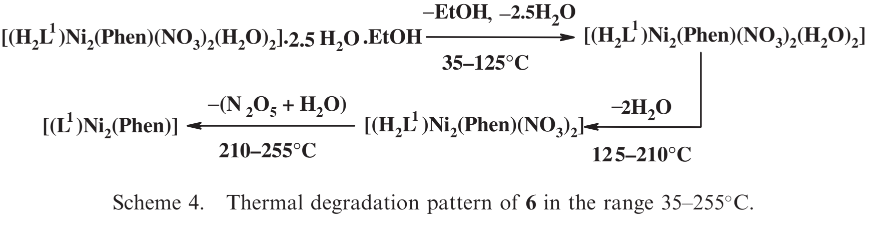
The effective magnetic moment values of the Fe(III) complexes (**7**, **8**, and **15**) in the range 5.80–5.86 BM are consistent with five unpaired electrons in the octahedral geometry [57]. However, the mixed-ligand complexes of H_4L^2 (**16** and **17**) showed magnetic moment values of 5.41 and 5.30 BM, respectively, which are lower than the expected value of the high-spin octahedral arrangement, suggesting a slight antiferromagnetic interaction. The electronic spectra of the iron(III) complexes showed absorption bands in the region 529–610 nm which may be assigned to $^6A_1 \rightarrow {}^4T_2$ (G) electronic transition [51], suggesting octahedral Fe(III).

3.2.4. Thermal analysis. TGA was used to probe associated water or solvent molecules to be in the coordination sphere or crystalline form [16]. Complexes **1** and **6** are representative examples. Thermal analyses of the two complexes are in agreement with elemental analyses. The thermogram of **1** shows two stages of decomposition in the range 30–170°C. The first, 30–110°C, is due to loss of half uncoordinated ethanol molecule (weight loss; Anal. Calcd/Found%; 4.1/4.3%). The second stage in the range 110–170°C is due to loss of four coordinated water molecules (weight loss; Anal. Calcd/Found%; 13.3/13.0%). The last two coordinated water molecules are lost during decomposition in the range 170–220°C. The decomposition pattern of **1** is shown in scheme 3.

The thermogram of **6** shows three stages of decomposition from 35–255°C. The first in the range 35–125°C is loss of 2.5 uncoordinated water molecules and one uncoordinated ethanol molecule (weight loss; Anal. Calcd/Found%; 10.6/10.4%). The second stage from 125 to 210°C corresponds to loss of two coordinated water molecules (weight loss; Anal. Calcd/Found%; 4.7/5.0%). The decomposition in the range 210–255°C corresponds to loss of two molecules of nitric acid (weight loss; Anal. Calcd/Found%; 17.3/17.2%). The decomposition pattern of **6** is shown in scheme 4.



Scheme 3. Thermal degradation pattern of **1** in the range 30–170°C.



Scheme 4. Thermal degradation pattern of **6** in the range 35–255°C.

Table 4. Antimicrobial activity of H_4L^1 and H_4L^2 and their metal complexes.

	Mean* of zone diameter, nearest whole mm											
	Gram-positive bacteria				Gram-negative bacteria				Fungi**			
Organisms	*S. aureus* (ATCC 25923)		*St. pyogenes* (ATCC 19615)		*P. phaseolicola* (GSPB 2828)		*P. fluorescens* (S 97)		*F. oxysporium*		*A. fumigatus*	
Concentration / Sample	$2\,mg\,mL^{-1}$	$1\,mg\,mL^{-1}$	$2\,mg\,mL^{-1}$	$1\,mg\,mL^{-1}$	$2\,mg\,mL^{-1}$	$1\,mg\,mL^{-1}$	$2\,mg\,mL^{-1}$	$1\,mg\,mL^{-1}$	$2\,mg\,mL^{-1}$	$1\,mg\,mL^{-1}$	$2\,mg\,mL^{-1}$	$1\,mg\,mL^{-1}$
H_4L^1	3	2	3	2	4	2	4	2	18	13	20	15
1	–	–	–	–	4	2	5	3	16	10	17	13
2	5	2	4	2	4	2	5	3	22	14	21	16
3	–	–	–	–	4	2	5	3	–	–	–	–
4	–	–	–	–	–	–	–	–	16	10	17	12
5	–	–	–	–	–	–	–	–	15	10	16	13
6	–	–	–	–	6	2	5	3	–	–	–	–
7	–	–	–	–	3	2	4	2	–	–	–	–
8	–	–	–	–	–	–	–	–	14	10	14	11
H_4L^2	3	2	3	2	4	2	4	2	7 L	4	4	2
9	–	–	–	–	5	2	4	2	–	–	–	–
10	–	–	–	–	3	2	5	2	28	23	17	14
11	5	2	4	2	3	2	4	2	26	24	17	14
12	6	3	7	3	4	2	5	3	23	14	21	15
13	–	–	–	–	–	–	–	–	23	15	20	16
14	–	–	–	–	4	2	5	3	24	16	24	15
15	7	3	7	3	5	2	5	3	–	–	–	–
16	7	3	7	3	–	–	–	–	30	22	28	24
17	–	–	–	–	–	–	–	–	28	22	30	24
Control[a]	42	28	38	30	36	25	38	30	40	28	40	31

*Calculated from 3 values.

**Identified depending on morphological and microscopical characteristics.

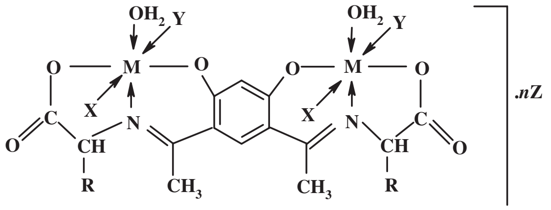
–No effect.

[a] Chloramphenicol in the case of Gram-positive bacteria, cephalothin in the case of Gram-negative bacteria, and cycloheximide in the case of fungi.

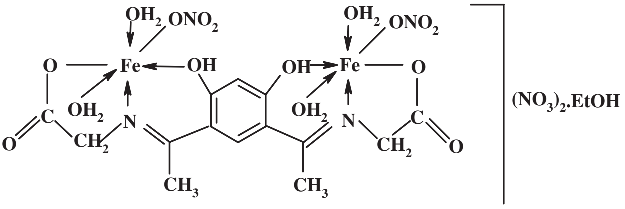
3.2.5. Mass spectra of the metal complexes. The mass spectra of **1**, **12**, **13**, and **14** are shown in Supplementary material. Complex **12** showed the parent peak at *m/z* 560 which compares well with the formula weight of the complex (FW = 557.83). Complexes **1**, **13**, and **14** showed parent peaks at *m/z* 540, 773, and 792, respectively, which compare well with calculated formula weights of the non-hydrated or solvated complexes $[(L^1)Cu_2(H_2O)_6]$ (FW = 539.48), $[(L^2)Ni_2(8\text{-}HQ)_2(H_2O)_2]$ (FW = 776.1), and $[(H_2L^2)Ni_2(Phen)(NO_3)_2(H_2O)_2]$ (FW = 792.04).

3.3. *Antimicrobial studies*

The antimicrobial activities of H_4L^1 and H_4L^2 and their metal complexes were investigated against *S. aureus* (ATCC 25923) and *St. pyogenes* (ATCC 19615) as



R	M	X	Y	*n*	Z	Complex
H	Cu	H_2O	H_2O	0.5	EtOH	**1**
H	Ni	H_2O	H_2O	1.5	H_2O	**4**
CH_3	Cu	nil	nil	1	H_2O	**9**
CH_3	Ni	H_2O	H_2O	nil	nil	**12**



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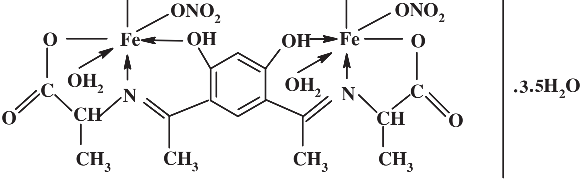
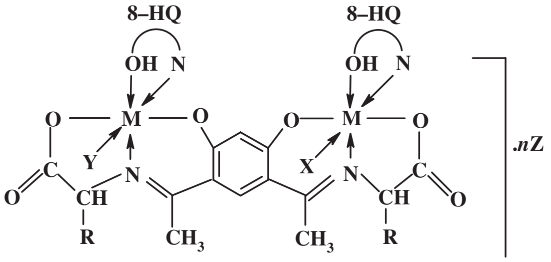
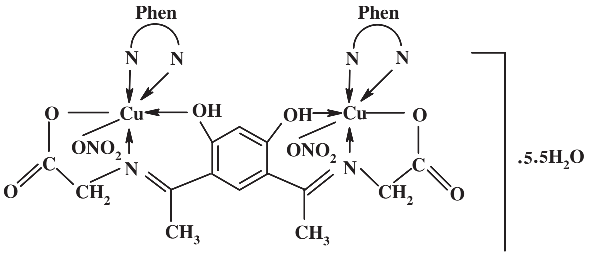


(15)

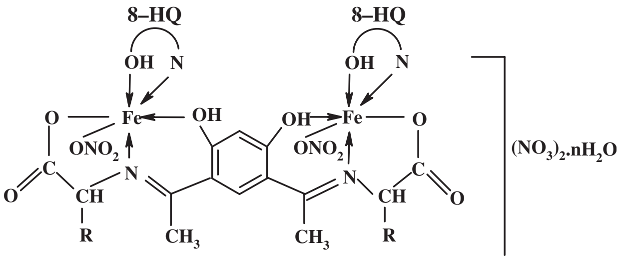
Figure 1. Representative structures of the binary complexes of the amino acid Schiff base, H_4L^1 and H_4L^2, ligands.



R	M	X	Y	*n*	Z	Complex
H	Cu	EtOH	EtOH	1	H_2O	**2**
H	Ni	EtOH	EtOH	0.5	H_2O	**5**
CH_3	Cu	H_2O	EtOH	nil	nil	**10**
CH_3	Ni	H_2O	H_2O	0.5	H_2O	**13**



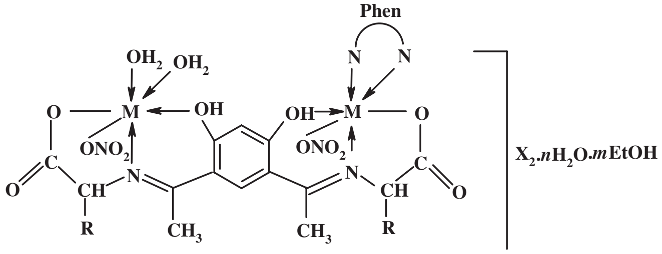
(**3**)



R	*n*	Complex
H	4	**8**
CH_3	2	**16**

Figure 2. Representative structures of the ternary complexes (1 : 2 : 2; L : M : L′) of the amino acid Schiff base, H_4L^1 and H_4L^2, ligands.

Gram-positive bacteria, *P. fluorescens* (S 97) and *P. phaseolicola* (GSPB 2828) as Gram-negative bacteria, and the fungi *F. oxysporium* and *A. fumigatus* (table 4). The Schiff bases, H_4L^1 and H_4L^2, and their metal complexes show low antibacterial activity. Complexes **15** and **16** showed the highest activity towards Gram-positive bacteria while **6** showed the highest activity towards Gram-negative bacteria. The Schiff bases and their metal complexes showed remarkable antifungal activity. Complexes of H_4L^1 showed lower antifungal activity than the ligand itself, except **2**; metal complexes of H_4L^2 showed higher antifungal activity than the ligand.



R	M	X	*n*	*m*	Complex
H	Ni	nil	2.5	1	**6**
CH_3	Cu	nil	nil	nil	**11**
CH_3	Ni	nil	2.5	nil	**14**
CH_3	Fe	NO_3	2	nil	**17**

Figure 3. Representative structures of the ternary complexes (1 : 2 : 1; L : M : L′) of the amino acid Schiff base, H_4L^1 and H_4L^2, ligands.

4. Conclusion

Two new hexadentate Schiff-base ligands were synthesized by condensation of DAR with glycine and alanine. Reactions of these ligands with metal nitrates in 1 : 2 (L : M) molar ratio gave binuclear metal complexes. Reactions in the presence of secondary ligands (L′) yielded mixed-ligand complexes. The prepared complexes were characterized by elemental and thermal analyses, IR, electronic, mass, and ESR spectra as well as conductivity and magnetic susceptibility measurements. The spectroscopic data showed that the Schiff bases are dibasic or tetrabasic hexadentate through the two azomethine nitrogens, two oxygens of phenolic groups and two oxygens of the carboxylic groups. Copper(II) complexes were octahedral except for **9**, which was square planar, while nickel(II) and iron(III) complexes were octahedral. The synthesized ligands and complexes showed antibacterial activity towards Gram-positive bacteria (*S. aureus* and *St. pyogenes*), Gram-negative bacteria (*P. fluorescens* and *P. phaseolicola*), and antifungal activity towards the fungi *F. oxysporium* and *A. fumigatus*. Tentative structures of the complexes are shown in figures 1–3.

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