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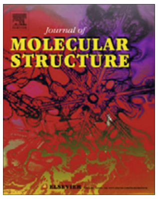

Synthesis, spectroscopic characterization and antimicrobial activity of mono-, bi- and tri-nuclear metal complexes of a new Schiff base ligand

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ABSTRACT

Condensation of *o*-acetoacetylphenol and 1,2-diaminopropane in 1:1 molar ratio under condition of high dilution yielded the mono-condensed dibasic Schiff base ligand with a N_2O_2 donors. The mono-condensed ligand has been used for further condensation with 2-hydroxy-5-nitrobenzaldehyde to obtain the new asymmetrical dicompartmental Schiff base ligand, H_3L, with N_2O_3 donors. The structure of the ligand was elucidated by analytical and spectroscopic tools (IR, ^{1}H and ^{13}C NMR spectra) which indicated that the coordinating sites are oxygen atoms of the phenolic OH groups, nitrogen atoms of the azomethine groups and the oxygen atom of the ketonic group. Reactions of the ligand with metal salts yielded mono- and homo-bi-nuclear complexes formulated as [M(HL)], where M=Co(II), Ni(II) and Cu(II), $[Fe(H_2L)Cl_2(H_2O)]\cdot 2\frac{1}{2}H_2O$, $[Fe_2(HL)(ox)Cl_3(H_2O)_2]\cdot 5H_2O$, $[UO_2(H_2L)(OAc)(H_2O)_2]$, $[VO(H_3L)(SO_4)(H_2O)]\cdot H_2O$, $[M_2(L)Cl(H_2O)_2]\cdot \frac{1}{2}H_2O$, where M=Co(II) and Ni(II) and $[Cu(H_2L)Cl]$. The mononuclear Ni(II) complex, [Ni(HL)], was used to synthesize homo- and hetero-bi- and tri-nuclear complexes with the molecular formulae $[Ni_2(L)Cl(H_2O)_2]$, $[Ni_2(L)_2FeCl(H_2O)]\cdot H_2O$ and $[Ni_2(HL)_2CoCl_2]$. The structures of the complexes were characterized by various techniques such as elemental and thermal analyses, IR, ^{1}H and ^{13}C NMR, mass and electronic spectra as well as conductivity and magnetic moment measurements. Square-planar and octahedral geometries are suggested for the Cu(II), Co(II) and Ni(II) complexes, octahedral geometry for the Fe(III) and VO^{2+} complexes while uranium(VI) ion is octa-coordinated in its complex. The Schiff base and its metal complexes were evaluated for antimicrobial activity against Gram positive bacteria (*Staphylococcus aureus*), Gram negative bacteria (*Escherichia coli*) and fungi (*Candida albicans* and *Aspergillus flavus*). The ligand and some of its complexes were found to be biologically active.

1. Introduction

Schiff base ligands are considered privileged ligands, because they are easily prepared by a simple one-pot condensation of aldehydes and primary amines in an alcohol solvent. Metal complexes of these bases have numerous applications including antibacterial, antifungal [1–6] and antiviral activities [7,8] as well as other biological applications [9–12]. Several applications have been related for these complexes in chemical analysis [13], absorption and transport of oxygen [14], in pesticides [15] and heterogeneous and homogeneous catalysis for oxidation and polymerization of organic compounds [16–19]. The term "dinucleating ligands" was first introduced in 1970 by Robson [20] to describe the class of polydentate chelating ligands which able to bind simultaneously two metal ions. Among many different types of dinucleating ligands, the phenol-based compartmental ligands attracted particularly wide attention of scientists. The term "compartmental" was introduced to indicate a ligand containing two adjacent, but dissimilar coordinating sites [21]. Particular interest in this type of ligands resulted from the recent recognition of the asymmetric nature of a number of bimetallic biosites [22,23].

Thus, in the present work, a new asymmetric dicompartmental Schiff base ligand, H_3L, which contains N_2O_3 coordinating sites was synthesized. Using this dicompartmental ligand, mono-, homo- and hetero-bi- and tri-nuclear complexes were synthesized and characterized. Indeed, the biological activity of the ligand and its complexes was screened against selected kinds of bacteria and fungi.

2. Experimental

2.1. Reagents and materials

$CuCl_2\cdot 2H_2O$, $NiCl_2\cdot 6H_2O$, $CoCl_2\cdot 6H_2O$, $FeCl_3\cdot 6H_2O$, $Cu(OAc)_2\cdot H_2O$, $Ni(OAc)_2\cdot 4H_2O$, $Co(OAc)_2\cdot 4H_2O$, $UO_2(OAc)_2\cdot 2H_2O$, $VOSO_4\cdot H_2O$,

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$LiOH{\cdot}H_2O$, oxalic acid, ethylacetate, sodium metal, *o*-hydroxyacetophenone, 1,2-diaminopropane and 2-hydroxy-5-nitrobenzaldehyde were either BDH or Merck chemicals. *o*-Acetoacetylphenol was prepared following the literature procedure [24]. Organic solvents were spectroscopic grade and used without further purification.

2.2. Synthesis of the ligand

2.2.1. Synthesis of o-acetoacetylphenol

o-Acetoacetylphenol was prepared as cited in the literature [24].

2.2.2. Synthesis of [(E)-3-(1-aminopropan-2-ylimino)-1-(2-hydroxyphenyl)butan-1-one] (H.U.)

A solution of *o*-acetoacetylphenol, 15 g (84.3 mmol) in 250 mL chloroform was added dropwise to a solution of 1,2-diaminopropane, 6.24 g (84.3 mmol) in 150 mL chloroform. After complete addition, the solution was stirred for an additional 18 h and chloroform was removed under reduced pressure, yielding the half-unit ligand as a viscous liquid which solidifies to form yellow precipitate upon addition of heptane. The yellow solid was filtered off, washed with least amount of chloroform and air-dried. Yield: 16.5 g, 83.7%, m.p. 78 °C.

2.2.3. Synthesis of the asymmetric Schiff base ligand

The new Schiff base (*E*)-3-(1-((*E*)-2-hydroxy-5-nitrobenzylideneamino)propan-2-ylimino)-1-(2-hydroxyphenyl)butan-1-one (H_3L) was prepared by condensation of (*E*)-3-(1-aminopropan-2-ylimino)-1-(2-hydroxyphenyl)butan-1-one dissolved in $CHCl_3$ with 2-hydroxy-5-nitrobenzaldehyde. A yellow solid product is formed upon cooling the solution slowly to room temperature and the precipitate was filtered off, washed with chloroform then diethyl ether and finally air-dried. The analytical and physical data for the ligand and its metal complexes are listed in Table 1. Scheme 1 represents the synthetic outline of the asymmetric Schiff base ligand.

2.3. Syntheses of the metal complexes

A general method has been used for the preparation of all complexes. A hot 20 mL ethanolic solution of the metal salt of VO^{2+}, Fe(III), Co(II), Ni(II), Cu(II) and UO_2^{2+} was gradually added to a chloroform solution of the ligand (30 mL) in 1:1 or 1:2 molar ratio and the solution was heated under reflux for 3 h on a water bath during which the solid complex precipitated. The precipitate was filtered off, washed with ethanol then diethyl ether and finally air-dried. In case of VO^{2+} complex, water was added to ensure complete dissolution of $VOSO_4{\cdot}H_2O$. The uranyl complex was prepared in methanol. The following detailed preparations are given as examples and the other complexes were obtained similarly.

2.3.1. [Co(HL)], ***6***

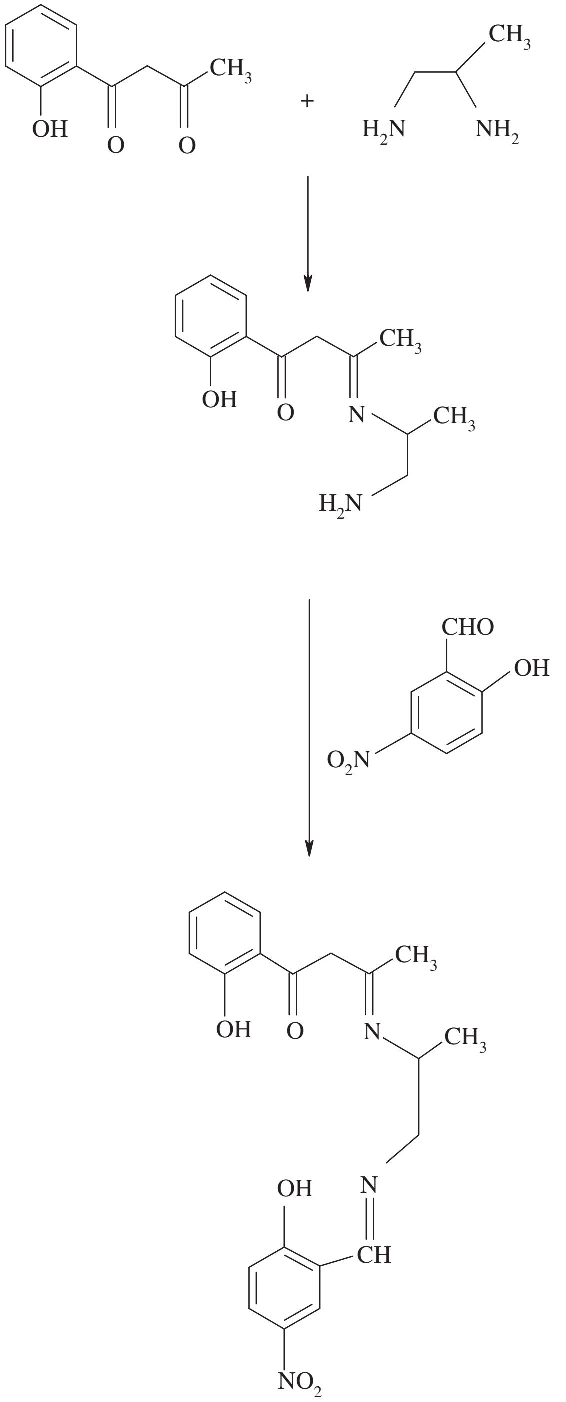
Cobalt(II) acetate tetrahydrate, $Co(OAc)_2{\cdot}4H_2O$ (0.39 g, 1.57 mmol) in ethanol (20 mL) was added gradually with constant stirring to the solution of the ligand, H_3L, (0.6 g, 1.57 mmol) in chloroform (25 mL). The reaction mixture was heated under reflux for 3 h. The precipitate was filtered off, washed with ethanol then ether and finally air-dried. Yield: 0.5 g (72.5%).

2.3.2. $[Fe_2(H_2L)(ox)Cl_3(H_2O)_2]{\cdot}5H_2O$, ***5***

Lithium hydroxide monohydrate, $LiOH{\cdot}H_2O$ (0.197 g, 4.7 mmol) in methanol (10 mL) was added gradually with constant stirring to the solution of the ligand, H_3L, (0.6 g, 1.57 mmol) in chloroform (25 mL). Oxalic acid (0.197 g, 1.57 mmol) in ethanol (15 mL) was added gradually to the above mixture then iron(III) chloride hexahydrate, $FeCl_3{\cdot}6H_2O$ (0.85 g, 3.15 mmol) in ethanol (20 mL) was added and the reaction mixture was heated under reflux for 3 h.

Table 1
Analytical and physical data for the Schiff base, H_3L, ligand and its metal complexes.

No.	Reactions	Complexes M.F. [F.W.]	Color	Yield (%)	M.P. (°C)	Elemental analysis, % Found/(Calc.)				
						C	H	N	Cl (S)	M
1	H.U.	$[C_{13}H_{18}N_2O_2]$ [234.30]	Yellow	83.8	78	66.7 (66.64)	7.5 (7.74)	12.1 (11.96)	–	–
2	H_3L	$[C_{20}H_{21}N_3O_5]$ [383.41]	Yellow	77.0	137	62.7 (62.65)	5.5 (5.52)	11.1 (10.96)	–	–
3	$H_3L + VOSO_4{\cdot}H_2O$	$[VO(H_3L)(SO_4)(H_2O)]{\cdot}H_2O$ $[C_{20}H_{25}N_3O_{12}SV]$ [582.44]	Pale brown	60.0	>342	41.0 (41.24)	4.1 (4.33)	7.3 (7.21)	5.5 (5.51)	8.7 (8.75)
4	$H_3L + FeCl_3{\cdot}6H_2O$	$[Fe(H_2L)Cl_2(H_2O)]{\cdot}2\frac{1}{2}H_2O$ $[C_{20}H_{27}N_3O_{8\frac{1}{2}}Cl_2Fe]$ [572.21]	Deep brown	77.0	>342	42.1 (41.98)	4.6 (4.76)	7.3 (7.34)	12.5 (12.39)	9.7 (9.76)
5	H_3L + Oxalic acid + $LiOH{\cdot}H_2O + FeCl_3{\cdot}6H_2O$	$[Fe_2(HL)(ox)Cl_3(H_2O)_2]{\cdot}5H_2O$ $[C_{22}H_{34}N_3O_{16}Cl_3Fe_2]$ [814.58]	Reddish brown	51.7	>342	32.2 (32.44)	4.0 (4.21)	5.3 (5.16)	12.8 (13.06)	13.7 (13.71)
6	$H_3L + Co(OAc)_2{\cdot}4H_2O$	$[Co(HL)]$ $[C_{20}H_{19}N_3O_5Co]$ [440.32]	Bick red	72.5	>342	54.5 (54.56)	4.4 (4.35)	9.5 (9.54)	–	13.3 (13.38)
7	$H_3L + Ni(OAc)_2{\cdot}4H_2O$	$[Ni(HL)]$ $[C_{20}H_{19}N_3O_5Ni]$ [440.10]	Red	70.0	308	54.5 (54.58)	4.3 (4.35)	9.3 (9.55)	–	13.4 (13.34)
8	$H_3L + Cu(OAc)_2{\cdot}H_2O$	$[Cu(HL)]$ $[C_{20}H_{19}N_3O_5Cu]$ [444.94]	Pale violet	83.5	>342	53.8 (53.99)	4.4 (4.30)	9.3 (9.44)	–	14.2 (14.28)
9	$H_3L + CoCl_2{\cdot}6H_2O + LiOH{\cdot}H_2O$	$[Co_2(L)Cl(H_2O)_2]{\cdot}\frac{1}{2}H_2O$ $[C_{20}H_{23}N_3O_{7\frac{1}{2}}ClCo_2]$ [578.74]	Brown	66.7	>342	41.5 (41.51)	4.2 (4.01)	7.2 (7.26)	6.2 (6.13)	20.5 (20.37)
10	$H_3L + NiCl_2{\cdot}6H_2O + LiOH{\cdot}H_2O$	$[Ni_2(L)Cl(H_2O)_2]{\cdot}\frac{1}{2}H_2O$ $[C_{20}H_{23}N_3O_{7\frac{1}{2}}ClNi_2]$ [578.29]	Pale brown	80.0	>342	41.3 (41.54)	3.9 (4.01)	7.4 (7.27)	6.3 (6.13)	20.3 (20.30)
11	$H_3L + CuCl_2{\cdot}2H_2O + LiOH{\cdot}H_2O$	$[Cu(H_2L)Cl]$ $[C_{20}H_{20}N_3O_5ClCu]$ [481.40]	Brown	75.0	>342	49.8 (49.90)	4.3 (4.19)	8.7 (8.73)	7.4 (7.36)	13.0 (13.20)
12	$[Ni(HL)] + FeCl_3{\cdot}6H_2O + LiOH{\cdot}H_2O$	$[Ni_2(L)_2FeCl(H_2O)]{\cdot}H_2O$ $[C_{40}H_{40}N_6O_{12}ClNi_2Fe]$ [1005.52]	Brownish red	82.0	>342	47.5 (47.78)	4.0 (4.01)	8.4 (8.36)	3.6 (3.53)	Ni;11.5 (11.68), Fe; 5.4 (5.55)
13	$[Ni(HL)] + CoCl_2{\cdot}6H_2O + LiOH{\cdot}H_2O$	$[Ni_2(HL)_2CoCl_2]$ $[C_{40}H_{38}N_6O_{10}Cl_2Ni_2Co]$ [1010.04]	Reddish brown	69.5	>342	47.5 (47.57)	3.8 (3.79)	8.4 (8.32)	6.8 (7.02)	Ni;11.7 (11.63), Co; 5.6 (5.83)
14	$[Ni(HL)] + NiCl_2{\cdot}6H_2O + LiOH{\cdot}H_2O$	$[Ni_2(L)Cl(H_2O)_2]$ $[C_{20}H_{22}N_3O_7ClNi_2]$ [569.29]	Brown	71.0	>342	42.3 (42.20)	3.7 (3.90)	7.4 (7.38)	6.2 (6.23)	20.5 (20.63)
15	$H_3L + UO_2(OAc)_2{\cdot}2H_2O$	$[UO_2(H_2L)(OAc)(H_2O)_2]$ $[C_{22}H_{27}N_3O_{11}U]$ [747.50]	Orange	81.0	144	35.1 (35.35)	3.5 (3.64)	5.8 (5.62)	–	31.4 (31.84)



Scheme 1. Synthetic outline of the asymmetric Schiff base, H_3L, ligand.

The precipitate was filtered off, washed with ethanol then ether and finally air-dried. Yield: 0.66 g (51.7%).

2.3.3. Heterotrinuclear complex $[Ni_2(HL)_2CoCl_2]$, 13

Cobalt(II) chloride hexahydrate, $CoCl_2 \cdot 6H_2O$ (0.27 g, 1.13 mmol) in ethanol (20 mL) was added gradually with constant stirring to the hot mixture of the mononuclear Ni(II) complex, $[Ni(HL)] \cdot H_2O$, (0.5 g, 1.13 mmol) in chloroform (30 mL) and LiOH (0.048 g, 1.13 mmol) in methanol (5 mL). The reaction mixture was heated under reflux for 10 h. The reddish brown precipitate was filtered off, washed several times with ethanol then ether and finally air-dried. Yield was 0.8 g (69.5%). The complex $[Ni_2(L)_2FeCl(H_2O)] \cdot H_2O$ was prepared by a similar method.

2.4. Analytical and physical measurements

Electronic spectra were recorded as solutions in DMF on a Jasco UV–Vis spectrophotometer model V-550 UV–Vis. IR spectra were recorded using KBr disks on a FT-IR 1650 Shimadzu Spectrometer. ^1H and ^{13}C NMR spectra were carried out in DMSO-d_6 at room temperature using TMS as internal standard on a Brucker 400 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. Effective magnetic moments were calculated using the relation $\mu_{eff.} = 2.828(\chi_m T)^{1/2}$ B.M. where χ_m is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds. Molar conductivities of 10^{-3} M solutions of the solid complexes in DMF were measured on the Corning conductivity meter NY 14831 model 441. The TG–DTG measurements were carried out on a Shimadzu thermogravimetric analyzer in dry nitrogen atmosphere and a heating rate of 20 °C/min using the TA-50 WS1 program. Mass spectra were recorded at 70 eV and 300 °C on a GC MS-QP 100 Ex 5988 mass spectrometer. Analyses of the metals followed decomposition of their complexes with concentrated nitric acid. The resultant solution was diluted with bidistilled water and filtered. The solution was then neutralized with aqueous ammonia solution and the metal ions titrated with EDTA. The uranium content of the UO_2^{2+} complex was determined by igniting a definite quantity of the complex at ≈1000 °C and weighing the residue as U_2O_3. Microanalyses of carbon, hydrogen, nitrogen, chlorine and sulfur were carried out at the Microanalytical Center, Cairo University, Giza, Egypt. The antimicrobial activity was studied using the disk diffusion method [25] at the Microanalytical Center, Cairo University, Giza, Egypt.

2.5. Antimicrobial activity

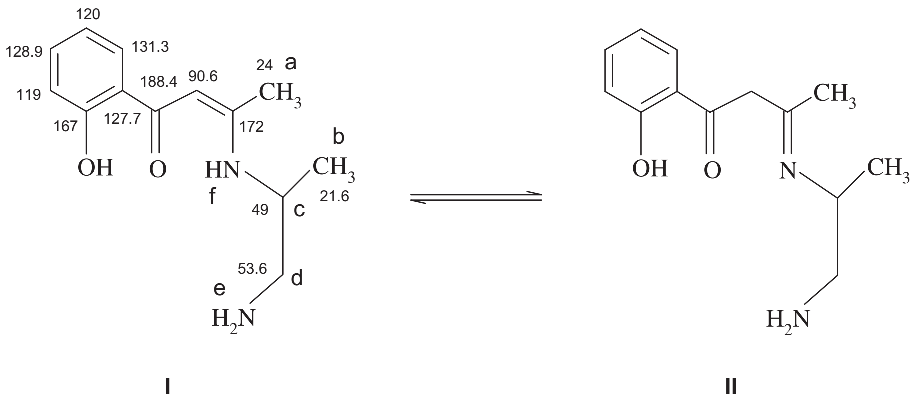
The standardized disk–agar diffusion method [25] was followed to determine the activity of the synthesized compounds against the sensitive organisms *Staphylococcus aureus* as Gram positive bacteria, *Escherichia coli* as Gram negative bacteria and the fungi *Candida albicans* and *Aspergillus flavus*. Tetracycline was used as a standard reference in the case of bacteria while Amphotricine B was used as a standard antifungal reference.

The tested compounds were dissolved in dimethylsulfoxide [(DMSO) which has no inhibition activity] to get concentration of 2 mg/mL. The test was performed on medium potato dextrose agar (PDA) which contains infusion of 200 g potatoes, 6 g dextrose and 15 g agar [26]. 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 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.

3. Results and discussion

3.1. The ligand

The 1:1 condensation of *o*-acetoacetylphenol and 1,2-diaminopropane yielded (*E*)-3-(1-aminopropan-2-ylimino)-1-(2-hydroxyphenyl)butan-1-one (H.U.). Condensation of the formed compound with 2-hydroxy-5-nitrobenzaldehyde yielded the new Schiff base ligand, H_3L. The IR spectrum of (H.U.) showed bands at 3382 and 3305 cm^{-1} that may be assigned to ν_{asym} and ν_{sym} of the —NH_2 group, respectively. The two bands observed at 1600



Scheme 2. Tautomeric structures of (H.U.).

Table 2
Characteristic IR spectral data (cm^{-1})[a] of the Schiff base, H_3L, ligand and its metal complexes.

No.	Compound	IR spectra (cm^{-1})						
		νOH (Phenolic + H_2O)	νC=N	ν C⎓O + ν C⎓C	νC⎓N	νC—O, phenolic	νH_2O, coordinate	Other bands
1	H.U.	3420 m, b	1600 s	1543 m	1519 s	1330 m	–	3382 m, 3305 m, sharp; νNH_2 (amino group)
2	H_3L	3450 m, b	1627 s	1562 m	1519 s	1338 m	–	
3	$[VO(H_3L)(SO_4)(H_2O)]\cdot H_2O$	3450 m, b	1645 s	1554 m	1500 m	1311 m	802 m, 756 m	1107 s, 1060 b; νSO_4, 984 m; νV=O
4	$[Fe(H_2L)Cl_2(H_2O)]\cdot 2½H_2O$	3440 m, b	1627 s	1554 m	1508 s	1303 m	806 s, 756 m	
5	$[Fe_2(HL)(ox)Cl_3(H_2O)_2]\cdot 5H_2O$	3449 m, b	1635 s	1558 m	1504 s	1303 s	802 m, 756 w	1670 m; νCOO, oxalate
6	[Co(HL)]	3444 w	1600 m	1558 m	1496 s	1319 s		
7	[Ni(HL)]	3445 w	1600 s	1554 m	1473 s	1319 m		
8	[Cu(HL)]	3450 m, b	1619 s	1550 s	1508 s	1303 m		
9	$[Co_2(L)Cl(H_2O)_2]\cdot ½H_2O$	3452 s, b	1604 s	1550 s	1496 s	1319 s	803 m, 752 w	
10	$[Ni_2(L)Cl(H_2O)_2]\cdot ½H_2O$	3421 m, b	1604 m	1550 m	1508 s	1315 s	804 m, 752 w	
11	$[Cu(H_2L)Cl]$	3463 m, b	1643 s	1554 m	1508 s	1315 s		3290 w; νNH
12	$[Ni_2(L)_2FeCl(H_2O)]\cdot H_2O$	3440 s, b	1601 s	1554 m	1508 s	1315 s	833 m, 748 w	
13	$[Ni_2(HL)_2CoCl_2]$	3444 m, b	1600 m	1554 w	1508 m	1315 s		
14	$[Ni_2(L)Cl(H_2O)_2]$	3444 s, b	1600 s	1554 m	1508 m	1315 s	833 m, 748 m	
15	$[UO_2(H_2L)(OAc)(H_2O)_2]$	3440 vs, b	1627 s	1554 s	1485 s	1315 s	802 m, 759 m	1535 s, 1400 m; νCOO, acetate, 906 vs; νO=U=O

[a] vs: very strong; s: strong; m: medium; w: weak; b: broad.

and 1330 cm^{-1} can be assigned to ν(C=N) (tautomer II, Scheme 2) and ν(C—O) phenolic, respectively. Comparison of the IR spectral data of the Schiff base ligand with that of (H.U.) (Table 2) showed the disappearance of $\nu(NH_2)$, confirming the formation of the Schiff base ligand. The IR spectrum of the Schiff base ligand showed bands at 1627 and 1338 cm^{-1} that may be assigned to ν(C=N) and ν(C—O) phenolic, respectively. Finally, the IR spectra of (H.U.) and the ligand displayed bands in the ranges of 3420–3450 and 1543–1562 cm^{-1} that may be due to ν(O—H) phenolic and ν(C⎓O) + ν(C⎓C) groups, respectively.

The ^1H NMR spectrum of (H.U.), Fig. S1 (Supplementary material) showed a singlet peak at 10.9 ppm which may be assigned to the proton of the —NH group (f), Scheme 2. The triplet peak appeared at 5.8 ppm may be assigned to $—NH_2$ protons (e). The multiplet peak at 2.1 ppm corresponding to the protons, c and d, Scheme 2. The peaks at 1.0 and 1.8 ppm may be assigned to the protons of methyl groups (a and b). The observed signals at 7.2–7.8 ppm may be attributed to the aromatic protons (m, 4Ar—H). ^{13}C NMR spectrum of (H.U.), Fig. S1 (Supplementary material) exhibited signals at 188.4, 172 and 167 ppm corresponding to the carbon of ketonic (C=O), (=C—NH) and phenolic (C—OH) groups, respectively. Also, the spectrum showed peaks at 131–119 ppm corresponding to carbons of the phenyl ring.

^1H NMR spectral data of H_3L dissolved in DMSO-d_6, Fig. 1, exhibited two peaks at 14.3 and 13.5 ppm, which are due to hydrogen-bonded phenolic protons. Signals for the methine protons of the azomethine group, —N=C(H)—, and NH protons were observed at 7.3 and 10.95 ppm, respectively. The aromatic protons were observed in the range of 7.6–6.8 ppm. Assignment of the ^{13}C NMR spectral data of the H_3L ligand, Fig. 2, is based on ^{13}C shifts in similar Schiff base ligands [27]. The chemical shifts for carbons of $—N—CH_2CH_2—N—$ were recorded between 48.3 and 61.2 ppm while carbons of (=C—NH) and (—N=C(H)—) groups were observed between 165.6 and 161.4 ppm. The signals observed at 188.7, 167.2 and 173.2 ppm are assigned to (C=O) and the two (C—O) phenolic carbons, respectively. Methyl groups were observed between 19.4 and 18.5 ppm. Based on IR and NMR spectral data, it was concluded that the half-unit (H.U.) and H_3L ligands exist as tautomer II in solid state and tautomer I in solutions.

Mass spectra of (H.U.) and Schiff base ligand (Fig. 3) showed the molecular ion peaks at m/e 234 and 383, confirming their formula weights (F.W. 234.30 and 383.41), respectively.

3.2. Metal complexes

The Schiff base ligand, H_3L, possesses two compartments and thus able to bind more than one cation because the bridging ability of their oxygen atoms and their conformational flexibility. Reactions of the ligand with VO^{2+}, Fe(III), Co(II), Ni(II), Cu(II) and UO_2^{2+}, in the molar ratio 1:1 or 1:2 (L:M) in presence and absence

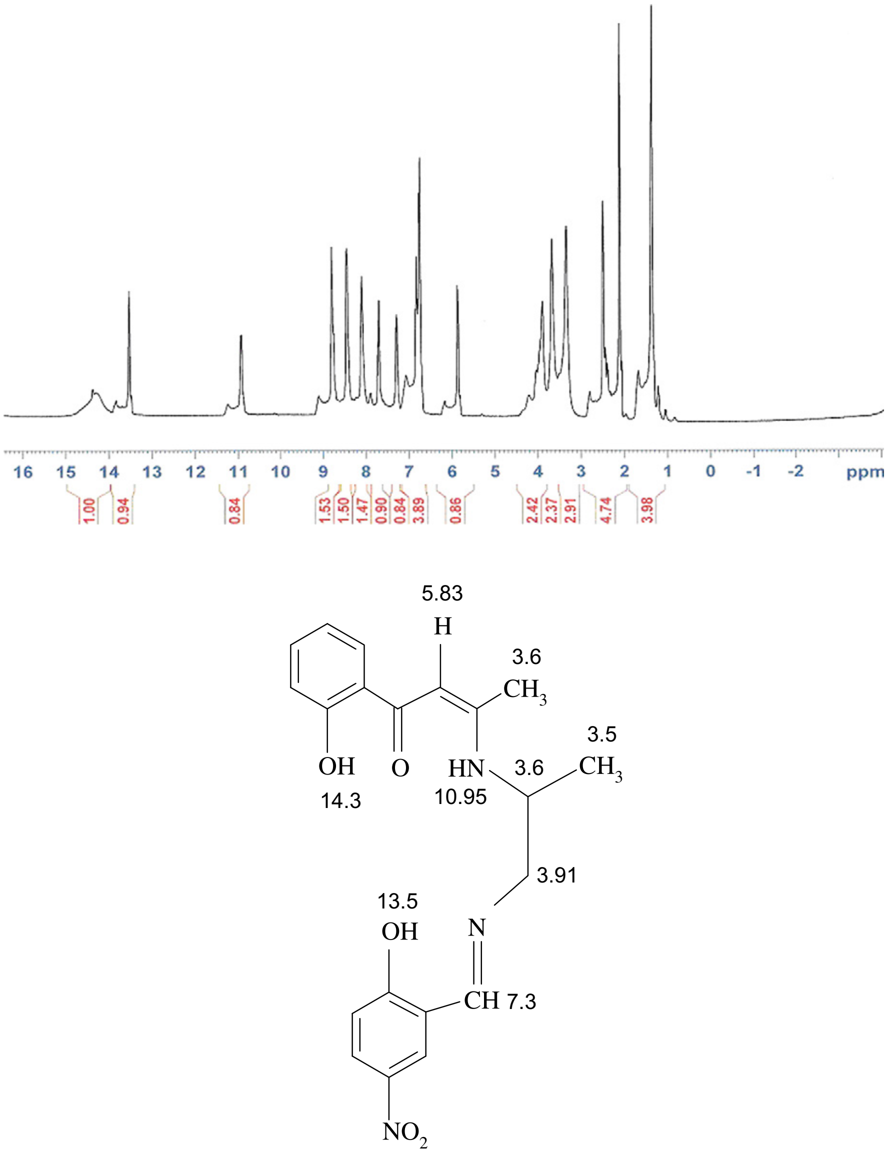


Fig. 1. ^{1}H NMR spectrum of the Schiff base ligand and its assignment.

of LiOH·H_2O as a deprotonating agent yielded mono- and bi-nuclear complexes. Also, the mononuclear Ni(II) complex, [Ni(HL)], has been used as a further ligand towards Fe(III), Co(II) and Ni(II) ions to produce homo- and hetero-bi- and tri-nuclear complexes.

3.2.1. IR spectra

The IR spectral data of the metal complexes are listed in Table 2. Comparison of the IR spectra of the metal complexes with that of the free ligand revealed that all complexes showed broad bands in the range 3421–3463 cm^{-1} which can be assigned to the stretching frequency of the phenolic —OH groups of the ligand, ν(OH), coordinated or uncoordinated water molecules associated with the complexes which are confirmed by elemental and thermal analyses. Also, the presence of coordinated water molecules in the complexes is supported by the two bands in the ranges 802–833 and 748–759 cm^{-1} which are due to (H_2O) rocking and wagging mode of vibrations, respectively [28]. The ν(C—O) phenolic of the free ligand at 1338 cm^{-1} was shifted to lower frequencies in all complexes, suggesting its participation in chelation [29–31]. The strong band at 1627 cm^{-1} assigned to ν(C=N) in the free ligand was shifted to lower frequencies in case of complexes **6**–**10** and **12**–**14**, indicating the participation of the azomethine group in chelation [32,33]. However, in complexes **3**–**5**, **11** and **15**, no shift of the ν(C=N) band was observed where metal ions are coordinated to the outer O_2O compartment of the ligand. The band assigned to ν(C$\overset{...}{=}$O) + ν(C$\overset{...}{=}$C) was shifted to lower frequencies in all complexes, suggesting the participation of the carbonyl oxygen in chelation. The VO^{2+} complex **3** showed new bands at 1107 and 1060 cm^{-1} which may be assigned to the coordinated sulphate group in a monodentate fashion [34]. Also, the complex displayed a strong band at 984 cm^{-1}, assignable to ν(V=O) moiety [35,36], consistent with a six-coordination geometry which is completed by coordinating sulphate and water molecules, Fig. 4. Also, complex **5** showed a new band at 1670 cm^{-1} that can be assigned to the bidentate oxalate group. Finally, complex **15** showed new bands characteristic for $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ of acetate ion at 1535 and 1400 cm^{-1}. The higher difference (135 cm^{-1}) between the two bands indicates the monodentate nature of the acetate group [37,38]. Also, the complex displayed a new band at 906 cm^{-1}, which may be assigned to the $\nu_3(UO_2)$, suggesting that the uranyl ion is linear [28].

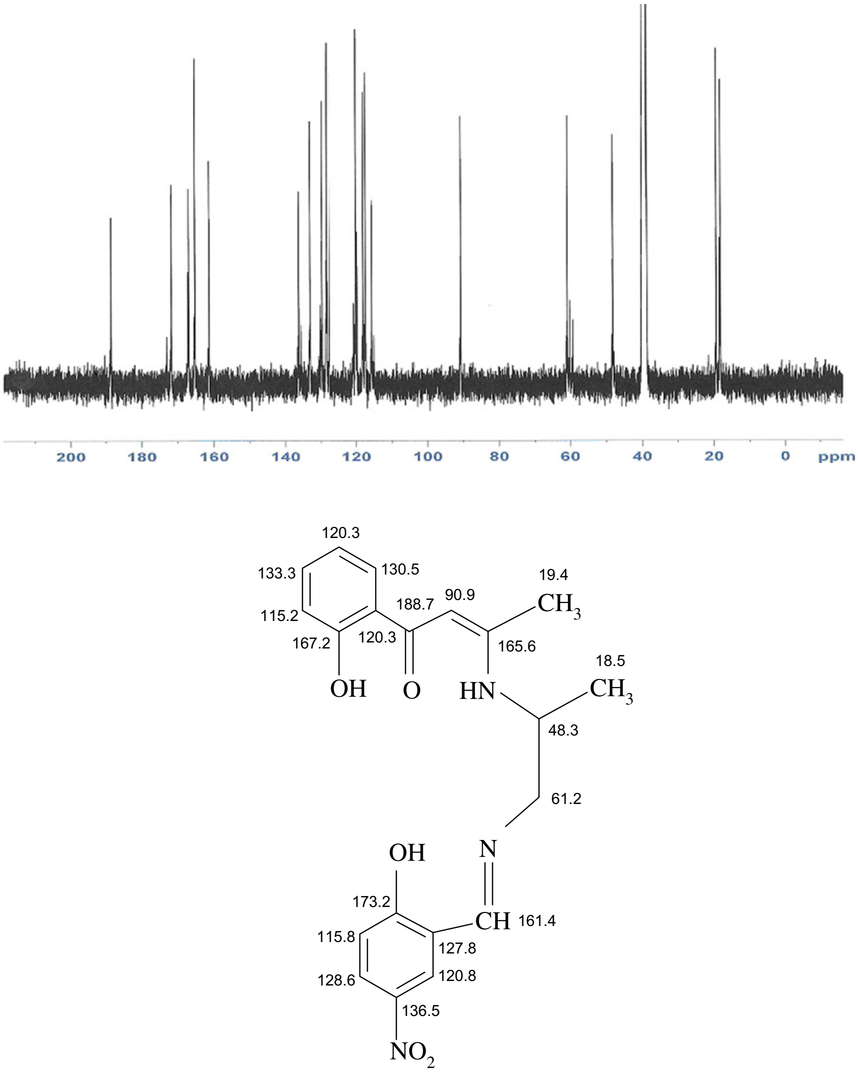


Fig. 2. ^{13}C NMR spectrum of the Schiff base ligand and its assignment.

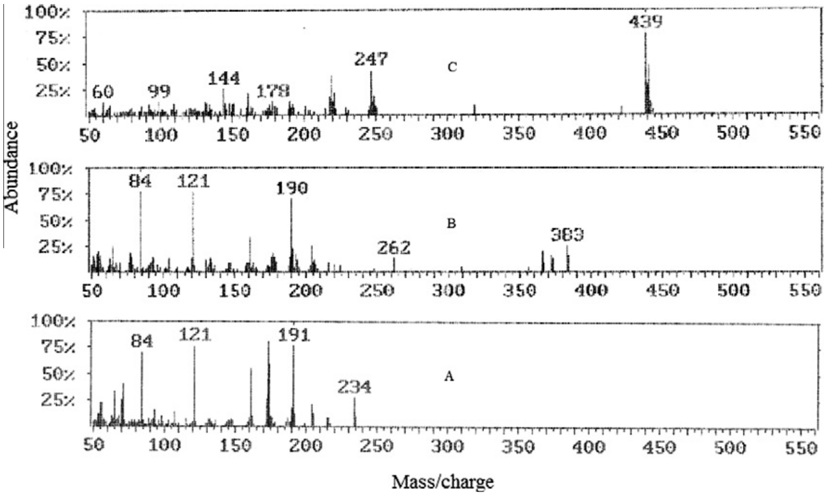
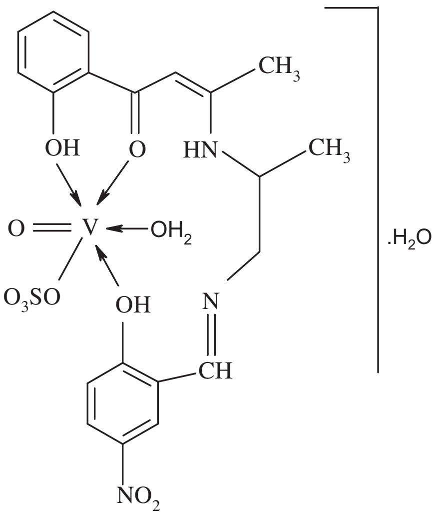


Fig. 3. Mass spectra of (H.U.) (A), H_3L ligand (B) and complex **7** (C).

3.2.2. Conductivity measurements

The molar conductance values of the complexes in DMF (10^{-3} M solutions) were measured at room temperature and the results are listed in Table 3. The values show that all complexes have non-electrolytic nature. The relatively high molar conductance values of some complexes (**4**, **5**, **12** and **13**) may be due to the replacement



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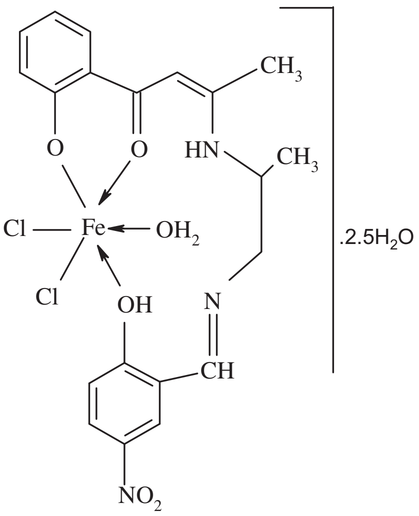

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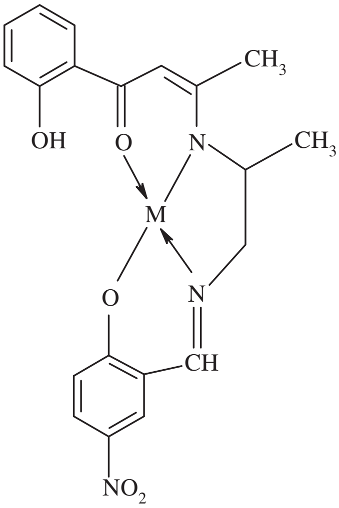
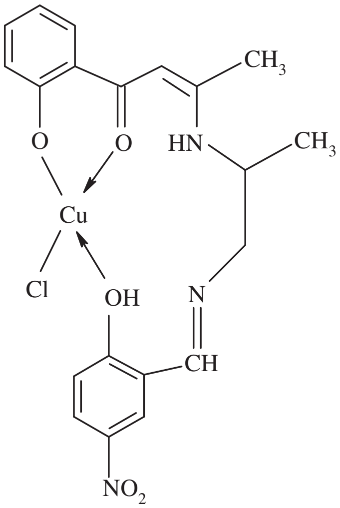


M	Complex
Co	**6**
Ni	**7**
Cu	**8**



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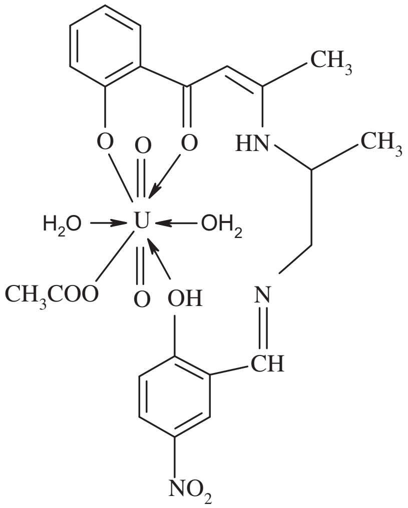

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Fig. 4. Suggested structures of the mononuclear complexes.

of the coordinated chloride ions by solvent molecules, a phenomenon usually encountered in complexes containing chloride ions [39].

3.2.3. Electronic, mass, ^1H and ^{13}C NMR spectra and magnetic measurements

3.2.3.1. Mono- and bi-nuclear complexes. Most of the mononuclear VO^{2+} complexes with square-pyramidal coordination are green while the polynuclear linear chain octahedral structures (V=O—V=O—) are usually orange [40].

The electronic spectrum of the VO^{2+} complex **3** showed absorption bands at 580 nm (Table 3) that can be assigned to the $^2B_2 \rightarrow {}^2B_1$ (ν_2) transition in an octahedral geometry [41] (Fig. 4). Its magnetic moment ($\mu_{\text{eff.}}$) is 1.8 B.M., which is in the range of the spin only value for VO^{2+} complexes when the orbital contribution is quenched.

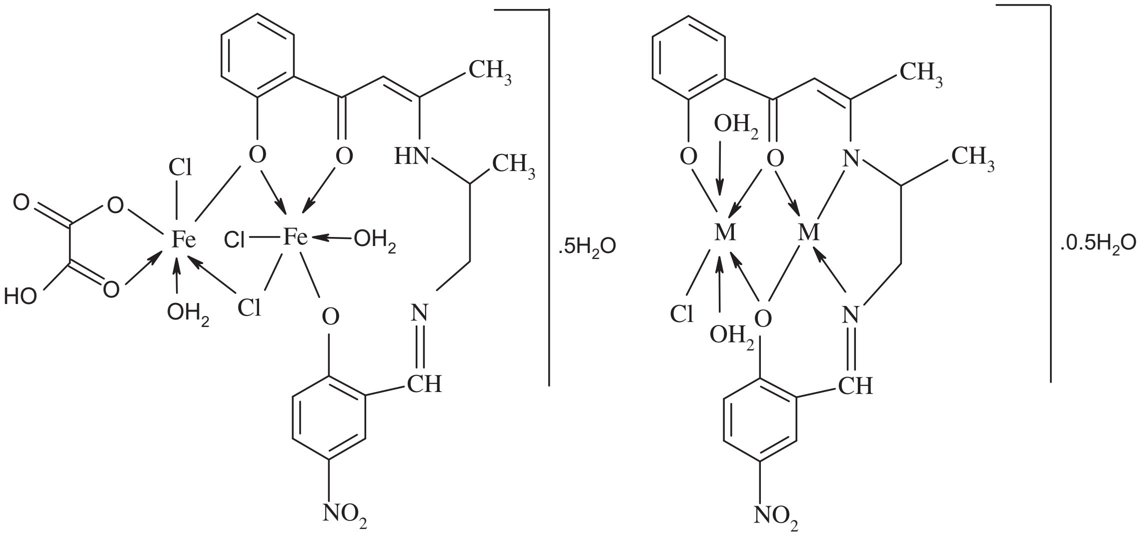
The electronic spectra of the Fe(III) complexes, **4** and **5** showed bands in the range of 495–510 nm, within the range reported for octahedral complexes [42]. The magnetic moments of the complexes (Table 3) are compatible with those reported for octahedral iron(III) complexes [43,44]. The octahedral geometry of the iron(III) complexes is achieved by chloride, oxalate ions and water molecules (Figs. 4 and 5) as evidenced by elemental analyses, IR and conductivity measurements.

The electronic spectrum of the Co(II) complex **6**, [Co(HL)], showed two bands at 575 and 450 nm which may be assigned to $^2A_1g \rightarrow {}^2B_2g$ and $^2A_1g \rightarrow {}^2Eg$ transitions, respectively, for Co(II) in a square-planar geometry [45,46] (Fig. 4). This is supported by

Table 3
Electronic spectra, magnetic moments and molar conductivity data of the metal complexes of the Schiff base, H_3L, ligand.

No.	Compounds	Electronic spectral bands[a] (nm)	Magnetic moments (B.M.)		Conductance[d] $Ohm^{-1}\ cm^2\ mol^{-1}$
			$\mu_{compl.}$[b]	$\mu_{eff.}$[c]	
3	$[VO(H_3L)(SO_4)(H_2O)]\cdot H_2O$	580 (0.13)	–	1.80	8
4	$[Fe(H_2L)Cl_2(H_2O)]\cdot 2\tfrac{1}{2}H_2O$	510 (0.15)	–	5.85	37
5	$[Fe_2(HL)(ox)Cl_3(H_2O)_2]\cdot 5H_2O$	495 (0.17)	7.93	5.60	40
6	$[Co(HL)]$	575 (0.02), 450 (0.03)	–	2.55	5
7	$[Ni(HL)]$	528 (0.08), 440 (0.1)	–	Diamagnetic	7
8	$[Cu(HL)]$	577 (0.12)	–	1.8	8
9	$[Co_2(L)Cl(H_2O)_2]\cdot \tfrac{1}{2}H_2O$	650 (0.03), 550 (0.02)	5.2	3.70	20
10	$[Ni_2(L)Cl(H_2O)_2]\cdot \tfrac{1}{2}H_2O$	548 (0.07)	3.2	–	21
11	$[Cu(H_2L)Cl]$	572 (0.14)	–	2.04	22
12	$[Ni_2(L)_2FeCl(H_2O)]\cdot H_2O$	565 (0.12), 520 (0.09)	5.95	–	33
13	$[Ni_2(HL)_2CoCl_2]$	585 (0.08), 525 (0.1)	5.50	–	30
14	$[Ni_2(L)Cl(H_2O)_2]$	620 (0.14), 515 (0.12)	2.90	–	12
15	$[UO_2(H_2L)(OAc)(H_2O)_2]$	510 (0.32), 440 (0.34)	–	–	9

[a] Values of ε_{max} are in parentheses and multiplied by 10^{-4} ($L\ mol^{-1}cm^{-1}$).
[b] $\mu_{compl.}$ is the magnetic moment of all cations in the complex.
[c] $\mu_{eff.}$ is the magnetic moment of the complex.
[d] Solutions in DMF (10^{-3} M).



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M	Complex
Co	**9**
Ni	**10**

Fig. 5. Suggested structures of the binuclear complexes.

the magnetic moment ($\mu_{eff.}$) of the complex (2.55 B.M.) which indicates a square-planar configuration. On the other hand, the electronic spectrum of the Co(II) complex **9**, $[Co_2(L)Cl(H_2O)_2]\cdot \tfrac{1}{2}H_2O$, (Table 3) showed two bands at 550 and 650 nm that may be assigned to the $^4T_1g(F) \rightarrow {}^4T_1g(P)$ and $^4T_1g(F) \rightarrow {}^4A_2g(F)$ transitions, respectively, of the octahedral geometry [47]. The lower magnetic moment of the complex (3.70 B.M.) suggests the presence of both square-planar and octahedral geometries around the Co(II) ions [48,49] (Fig. 5).

The electronic spectrum of the Ni(II) complex **7** showed a band at 528 nm that may be assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, indicating a square-planar environment around the nickel(II) ion [50] (Fig. 4) which is confirmed by the diamagnetic properties of the complex. The mass spectrum of the nickel(II) complex **7** (Fig. 3), showed the first mass peak at m/e 439 which agrees well with the molecular ion peak for [Ni(HL)], confirming its structure. On the other hand, the electronic spectrum of the Ni(II) complex **10** showed a band at 548 nm, which can be assigned to the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition indicating an octahedral nickel(II) complex [51]. The magnetic moment of complex **10** is 3.2 B.M., which suggests the presence of octahedral and diamagnetic square-planar geometries together [52,53] (Fig. 5).

The electronic spectra of the Cu(II) complexes **8** and **11** showed bands in the range 572–577 nm that may be assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition in a square-planar geometry [54] (Fig. 4). The magnetic moment ($\mu_{eff.}$) for complexes **8** and **11** are 1.80 and 2.04 B.M., respectively which is consistent with one unpaired electron (d^9) [55]. The higher $\mu_{eff.}$ value of complex **11** indicates that

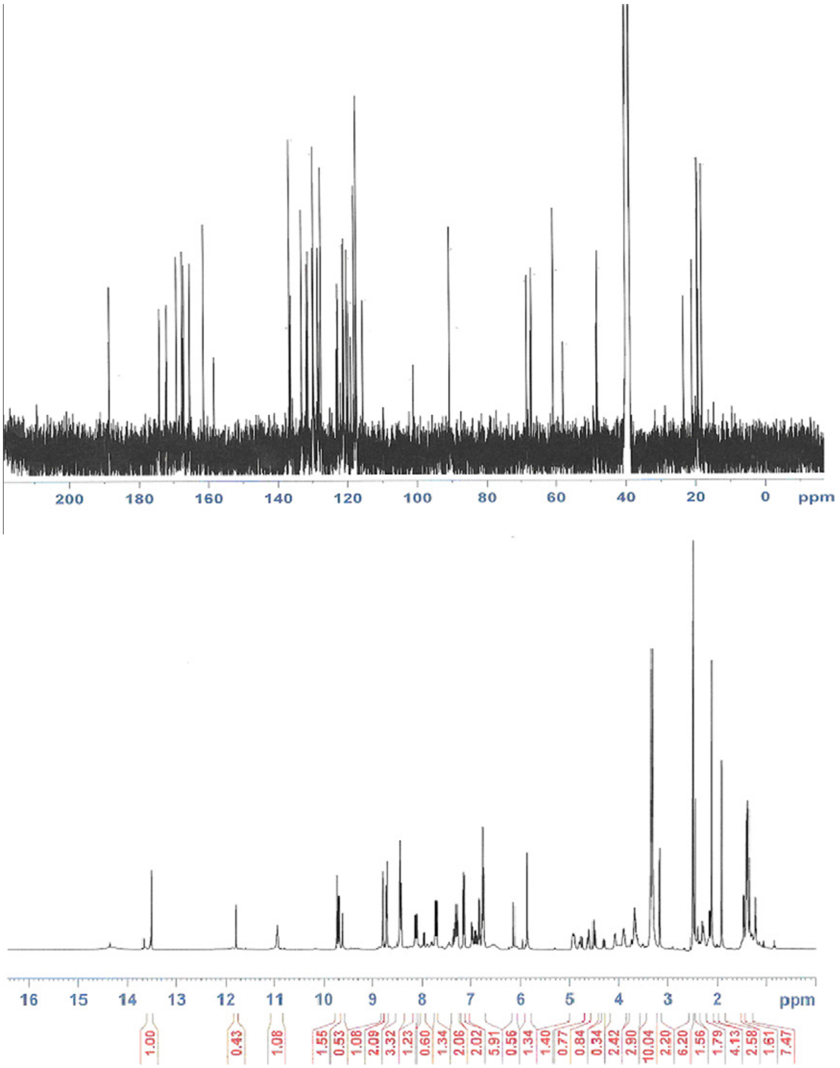


Fig. 6. ^1H and ^{13}C NMR spectra of the UO_2^{2+} complex (**15**).

the complex is slightly distorted towards tetrahedral symmetry [56].

The electronic spectrum of the uranyl complex **15** showed two bands at 440 and 510 nm. The higher energy band is attributed to electronic transitions from apical oxygen atoms to *f* orbitals of the uranium(VI) ion and the lower energy band is due to charge transfer transition from equatorial ligand to the uranium(VI) ion [57].

Comparing of the ^1H NMR spectrum of the uranyl complex, $[UO_2(H_2L)(OAc)(H_2O)_2]$, Fig. 6, with that of the free ligand revealed the following:

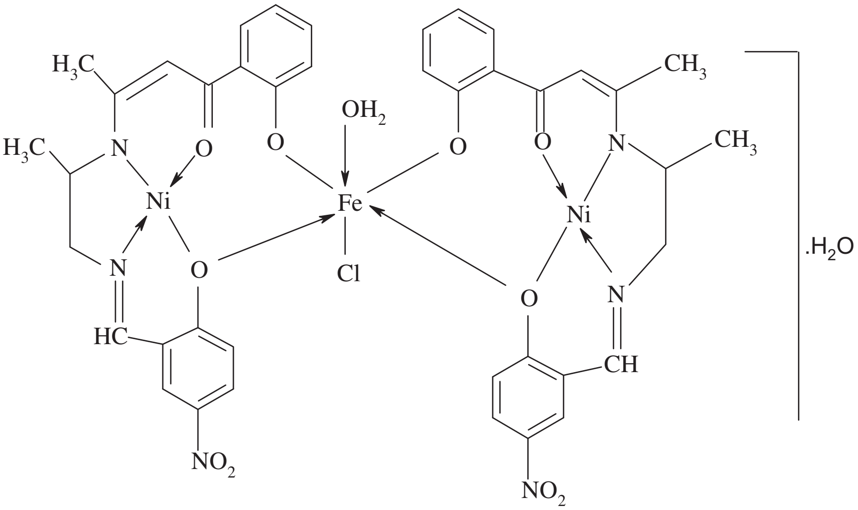
1. The disappearance of one signal of the phenolic OH group ($\delta = 14.3$) referring to its involvement in coordinating with uranyl cation after deprotonation [58–60], while the signal of the other phenolic OH ($\delta = 13.5$ ppm) and NH ($\delta = 10.95$ ppm) groups are unchanged, confirming the suggested structure of the complex (Fig. 4).
2. The signals due to the aromatic ring showed fine structure and appear as four separate signals at $\delta = 6.53$, 6.67, 7.14 and 7.6 ppm. The absence of OH protons (coordinated H_2O) may be due to their replacement by DMSO-d_6 molecules [61].

Also, the comparison of the ^{13}C NMR spectrum of the UO_2^{2+} complex, Fig. 6, and its ligand leads to a similar conclusion and indicates changes in the charge redistribution in the whole molecule induced by the complexation. The spectrum exhibited a sharp signal corresponding to the azomethine carbon (C═N) at 161.4 ppm as observed in the ligand, indicating the non-participation of the group in complexation which is consistent with the IR spectral data (Table 2).

3.2.3.2. Heteronuclear complexes. Since the complex [Ni(HL)] (**7**) has di-μ-phenoxy oxygen bridges which act as O_2O coordinating sites, it can be used as a chelating agent towards metal cations [Fe(III), Co(II) and Ni(II)]. Also, the complex ligand (**7**) has diamagnetic properties, so any magnetic moments of the homo- and hetero-nuclear complexes were altered by the introduction of metal cations.

The reactions of the complex ligand [Ni(HL)], **7**, with $FeCl_3{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$ and $NiCl_2{\cdot}6H_2O$ in the molar ratio 1:1 in the presence of $LiOH{\cdot}H_2O$ yielded trinuclear complexes, $[Ni_2(L)_2FeCl(H_2O)]{\cdot}H_2O$, **12** and $[Ni_2(HL)_2CoCl_2]$, **13** and binuclear Ni(II) complex, $[Ni_2(L)Cl(H_2O)_2]$, **14**, Fig. 7. It was found that Ni(II) complex, **14**, is similar to **10**.

The electronic spectrum of the homobinuclear complex $[Ni_2(L)Cl(H_2O)_2]$, **14** showed two absorption bands at 620 and 515 nm. The band at 620 nm is due to the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition, indicating an octahedral nickel(II) of O_2O sites while the band at 515 nm is assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, indicating a



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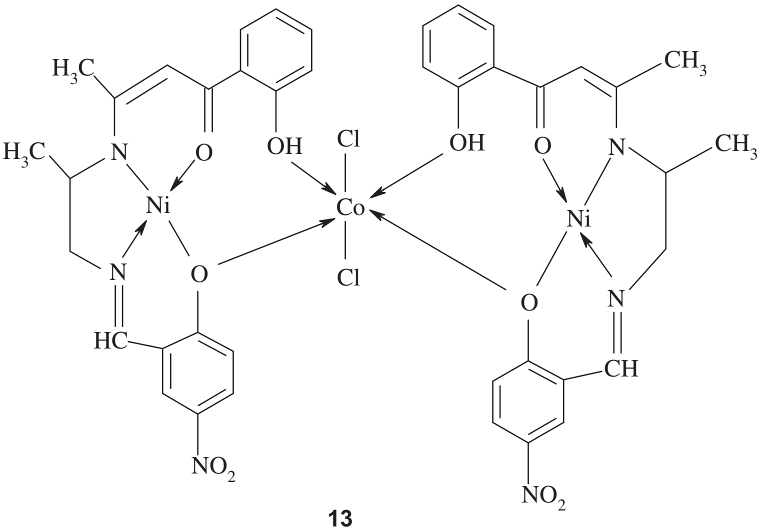

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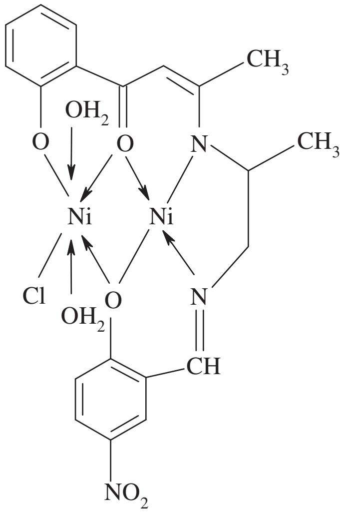

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Fig. 7. Suggested structures of the hetero- and homo-nuclear complexes.

square-planar environment around the inner nickel(II) ion of N_2O_2 sites. The magnetic moment of complex **14** is 2.9 B.M. which is in good agreement with the presence of the outer Ni(II) ion in octahedral geometry.

Table 4
Antimicrobial activity of the Schiff base ligand and its metal complexes.

No.	Sample	Mean[a] of zone diameter, nearest whole mm			
		Escherichia coli	*Staphylococcus aureus*	*Candida albicans*	*Aspergillus flavus*
	Control DMSO	0.0	0.0	0.0	0.0
	Tetracycline (Antibacterial agent)	32	34	–	–
	Amphotricine B (Antifungal agent)	–	–	21	17
1	H.U.	14	14	0	15
2	H_3L	21	23	12	20
3	$[VO(H_3L)SO_4(H_2O)]\cdot H_2O$	12	18	0.0	0.0
4	$[Fe(H_2L)Cl_2(H_2O)]\cdot 2\frac{1}{2}H_2O$	14	16	0.0	0.0
5	$[Fe_2(HL)(ox)Cl_3(H_2O)_2]\cdot 5H_2O$	13	20	0.0	0.0
6	$[Co(HL)]$	20	20	0.0	0.0
7	$[Ni(HL)]$	0.0	14	0.0	0.0
8	$[Cu(HL)]$	0.0	0.0	0.0	0.0
9	$[Co_2(L)Cl(H_2O)_2]\cdot \frac{1}{2}H_2O$	14	23	16	13
10	$[Ni_2(L)Cl(H_2O)_2]\cdot \frac{1}{2}H_2O$	18	18	0.0	14
11	$[Cu(H_2L)Cl]$	17	21	0.0	0.0
12	$[Ni_2(L)_2FeCl(H_2O)]\cdot H_2O$	11	13	0.0	0.0
13	$[Ni_2(HL)_2CoCl_2]$	20	21	16	14
14	$[Ni_2(L)Cl(H_2O)_2]$	15	20	0.0	15
15	$[UO_2(H_2L)(OAc)(H_2O)_2]$	14	15	0.0	0.0

[a] Calculated from three values.

The electronic spectra of the heterotrinuclear complexes **12** and **13** (Table 3) showed two bands in the ranges of 565–585 and 520–525 nm. The first band of each complex is attributed to a *d*–*d* transition of both Fe(III) and Co(II) ions in octahedral geometries [30,44]. The second band is due to a *d*–*d* transition of Ni(II) in square-planar geometry and similar to that of the complex ligand [Ni(HL)]. The magnetic moments of the heterotrinuclear complexes $[Ni_2(L)_2FeCl(H_2O)]\cdot H_2O$, **12** and $[Ni_2(HL)_2CoCl_2]$, **13** are 5.95 and 5.5 B.M., respectively, which is consistent with the presence of both Fe(III) and Co(II) ions in high spin octahedral geometries.

3.2.4. Thermal analysis

Thermal gravimetric analyses for some selected complexes were obtained to give information concerning the thermal stability of the complex and decide whether the water molecules are in the inner or outer coordination sphere of the central metal ion. The results of thermal analyses showed good agreement with the theoretical formula as suggested from the elemental analyses.

The TG and DTG curves of [Co(HL)], [Ni(HL)], [Cu(HL)] and $[Cu(H_2L)Cl]$ showed the absence of hydrated or coordinated water molecules. Thermal decomposition of the anhydrous products takes place at different temperatures, 338.3, 357.6, 348.4 and 340 °C, respectively. The thermogram of the UO_2^{2+} complex (**15**), represents four decomposition steps. The first step of decomposition at 167.5 °C corresponds to the loss of two coordinated water and acetate molecules with a weight loss of 12.2% (calcd. 12.7%), confirming the suggested formula of the complex. The remaining steps of decomposition within the temperature range 168–600 °C correspond to the removal of H_3L ligand as gases. The overall weight losses amount to 66.59% (calcd. 64%). The percentage of uranium can be determined as U_2O_3 and was 30% (calcd. 31.8%).

3.3. Antimicrobial activity

The Schiff base ligand and its metal complexes were evaluated for antimicrobial activity against Gram positive bacteria (*S. aureus*), Gram negative bacteria (*E. coli*) and fungi (*C. albicans* and *A. flavus*) and the results are summarized in Table 4.

The Schiff base ligand was found to be biologically active and its metal complexes showed some antimicrobial activity. The remarkable result is that the complexes showed lower inhibition against *E. coli* and *S. aureus* as compared with its ligand. Complexes **6** and **13** had the highest inhibition against *E. coli* while complexes **9** and **13** had the highest inhibition against *S. aureus*. Some of the metal complexes had inhibition against *C. albicans* and *A. flavus.* Complexes **9** and **13** had inhibition against *C. albicans* higher than its ligand. Also, complexes **9**, **10**, **13** and **14** had inhibition against *A. flavus*. Generally, it was found that the highest antimicrobial activity is obtained in Co(II)-containing complexes regardless of their structures (mono-, bi- or tri-nuclear complexes).

4. Conclusion

In this work, the synthesis and characterization of a new asymmetric Schiff base ligand were reported. Mono-, homo- and hetero-bi- and tri-nuclear complexes were synthesized and characterized using spectroscopic methods, molar conductivity, magnetic measurements and thermal analysis. The Schiff base ligand behaved as versatile chelating agent exhibiting variable denticity towards metal ions depending on the pH of the reaction medium and the metal ion. The Schiff base ligand and its complexes showed antimicrobial activity against selected kinds of bacteria and fungi.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.06.034.

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