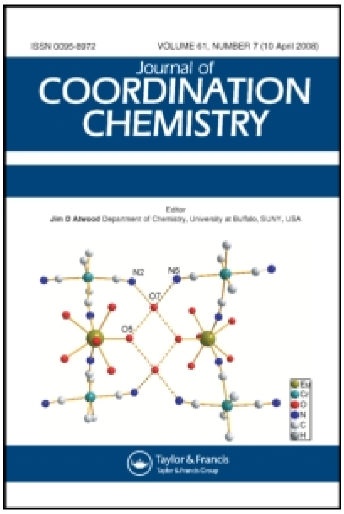

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Mono- and Bi-Nuclear Metal Complexes of Schiff-Base Hydrazone (ONN) Derived from *o*-Hydroxyacetophenone and 2-Amino-4-Hydrazino-6-Methyl Pyrimidine

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MONO- AND BI-NUCLEAR METAL COMPLEXES OF SCHIFF-BASE HYDRAZONE (ONN) DERIVED FROM *o*-HYDROXYACETOPHENONE AND 2-AMINO-4-HYDRAZINO-6-METHYL PYRIMIDINE

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A tridentate ONN donor Schiff-base hydrazone ligand, H_2L, was synthesized by the condensation of 2-amino-4-hydrazino-6-methyl pyrimidine with *o*-hydroxyacetophenone. The structure of the ligand was elucidated by IR and ^{1}H NMR spectra which indicated the presence of three different coordinating groups, the oxygen atom of the phenolic OH group, the nitrogen atom of the azomethine, C=N, group and one of the nitrogen atoms of the heterocyclic ring. The ligand behaves either as a tridentate (N_2O sites) neutral, mono- or di-basic ligand or as a bidentate (NO sites) monobasic ligand depending on the pH of the reaction medium and the metal ion. The mass spectrum of the ligand showed the presence of the molecular ion peak. Different types of metal complexes, mononuclear such as $[(HL)M(OAc)]\cdot xH_2O$ (M = Cu or Zn), $[(HL)M(OAc)H_2O]\cdot xH_2O$ (M = Ni or UO_2), $[(HL)Co(OH_2)Cl]\cdot 2H_2O$, $[(H_2L)FeCl_3]\cdot 3\frac{1}{2}H_2O$, $[(L)FeCl(H_2O)_2]\cdot 2\frac{1}{4}H_2O$, $[(HL)L'FeCl(H_2O)]\cdot H_2O$ (L′ = 8-hydroxyquinoline, 8-HQ), $[(HL)L'FeCl]Cl\cdot xH_2O$ (L′ = 1,10-phenanthroline, phen, or 2,2′-bipyridyl, bpy) and $[(HL)L'Cu]\cdot ClO_4$ (L′ = phen). Also, binuclear complexes with oxalic acid of the type [(HL)ClFe(ox)FeCl(HL)], [(HL)Cu(ox)Cu(HL)] were obtained. The IR spectra of the binuclear complexes indicated that the oxalate anion acts as a bridging tetradentate ligand. Elemental analyses, IR, electronic and ESR spectra as well as conductivity and magnetic susceptibility measurements were used to elucidate the structures of the newly prepared metal complexes. Square-planar geometry is suggested for the Cu(II) complex, octahedral geometry for the Fe(III), Ni(II) complexes, tetrahedral geometry for the Co(II) and Zn(II) complexes and pentagonal-bipyramidal geometry for the UO_2(VI) complex.

Keywords: Macroacyclic Schiff-base hydrazone complexes; Mono- and binuclear transition metal complexes

INTRODUCTION

Heterocyclic diazines, such as pyrazine, pyrimidine and pyridazine, are known to act as bidentate ligands when coordinated to metal ions [1,2]. Diazine ligands such as pyrazole can form binuclear complexes; the bridges between the metallic ions may be two diazine molecules [3–7] or only one diazine molecule [8,9].

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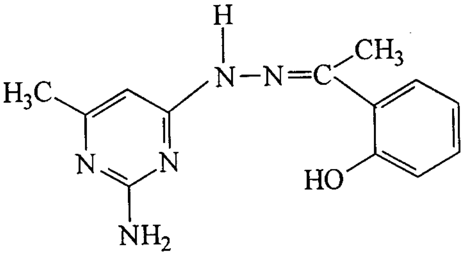


FIGURE 1 A tridentate Schiff-base hydrazone ligand, H_2L.

Transition metal complexes containing an imidazole or pyrimidine ligand are commonly found in biological media and play important roles in processes such as catalysis of drug interaction with biomolecules [10,11].

The aim of this work is preparation and characterization of complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and UO_2(VI) of a new Schiff-base hydrazone ligand derived from the pyrimidine nucleus, Fig. 1. The complexes were characterized by elemental analysis, IR, UV-Visible and ESR spectra, conductivity and magnetic susceptibility measurements at room temperature as well as thermal analysis. The present study is a continuation of our work on quinolone and 1,8-naphthpyridine nuclei which have been previously prepared [12–15].

EXPERIMENTAL

Materials

Cu(II), Ni(II), Zn(II) and UO_2(VI) acetates, Co(II) and Fe(III) chlorides, $Cu(ClO_4)_2 \cdot 6H_2O$, hydrazine hydrate, *o*-hydroxyacetophenone and DMF were obtained from Merck. Organic solvents were reagent grade. 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and 8-hydroxyquinoline (8-HQ) were purchased from Aldrich.

Measurements

FT-IR spectra were recorded on a Monson FT-IR 4000 spectrometer (4000–400 cm^{-1}) using KBr pellets. Visible spectra of the metal complexes as DMF solutions (10^{-3} M) and in certain cases concentrated solutions, more than 10^{-3} M, were recorded on a Jasco 550 spectrophotometer. Reflectance spectra of some of the complexes were carried out using $BaSO_4$ discs on a Shimadzu 1601 PC spectrophotometer. The ^{1}H NMR spectra of the ligand and the Zn(II) and UO_2(VI) complexes, as a solution in DMSO-d_6, were recorded on a Bruker WP 200 SY spectrometer at room temperature using TMS as an internal standard. Mass spectra were recorded at 290°C and 70 eV on a Hewlett-Packard mass spectrometer model MS-5988. TGA-DTG measurements were carried out on a Shimadzu-50 thermal analyzer. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey, Alfa Products, Model MKI magnetic susceptibility balance. The 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. ESR spectra of the Cu(II) complexes were recorded on a JEOL microwave unit, JES-FE_2XG spectrometer at the Central Laboratories, Tanta University, Tanta, Egypt. The magnetic field was calibrated with a 2,2-diphenyl-1-picryl-hydrazyl sample purchased from Aldrich. Molar conductances of 10^{-3} M solutions of the complexes in DMF were measured on the Corning conductivity meter NY 14831 model 441 (USA).

Microanalyses of carbon, hydrogen, nitrogen and chlorine were carried out at the Microanalysis Center, Cairo University, Giza, Egypt. Analyses of the metals followed the dissolution of the solid complex in concentrated HNO_3 acid, neutralizing the diluted aqueous solutions with ammonia and titrating the metal solutions with Na_2EDTA.

Preparation of the 2-Amino-4-Hydrazino-6-Methyl Pyrimidine

This preparation was performed as cited in the literature [16,17].

Preparation of the Schiff-base hydrazone Ligand, H_2L

The Schiff-base hydrazone ligand, Fig. 1, was prepared by refluxing 2-amino-4-hydrazino-6-methyl pyrimidine (10 g, 72.0 mmol) and *o*-hydroxyacetophenone (9.8 g, 72.0 mmol) in ethanol (100 mL) for 4 h. The yellowish orange color of the solution changed to pale yellow and a yellow precipitate was obtained on cooling. The precipitate was filtered, washed with ethanol, air-dried and recrystallized from ethanol. The crystals were dried in a desiccator over calcium chloride. The chemical analysis of the ligand, its yield and melting point are shown in Table I. The molecular ion peak was observed at 257.1 a.m.u. in the mass spectrum confirming the molecular weight of the prepared ligand.

Preparation of the Metal Complexes

Ethanolic solutions of the metal salt and the ligand were mixed in a 1 : 1 molar ratio and stirred for 2 h. The uranyl complex was prepared in methanol as uranyl acetate is more soluble in this solvent. The resulting precipitates were filtered, washed with ethanol then ether and finally air-dried. All complexes were soluble in DMF and complexes **6**, **7** and **11** were insoluble in all common solvents. The following detailed preparations are given as examples; the other complexes were obtained similarly.

Preparation of the $[(H_2LFeCl_3(OH_2)] \cdot 3\frac{1}{2}H_2O$, Complex (2)

An ethanolic solution (30 mL) of $FeCl_3 \cdot 6H_2O$ (0.526 g, 1.95 mmol) was added gradually to an ethanolic solution (40 mL) of the ligand (0.5 g, 1.95 mmol). The solution was stirred for 4 h and a dark brown complex was precipitated. The precipitate was filtered, washed with ethanol, then diethyl ether, and finally air-dried. Yield, 0.6 g (44%).

Preparation of the [(HL)ClFe(ox)FeCl(HL)], Complex (3)

An aqueous solution (10 mL) of oxalic acid (0.126 g, 1.0 mmol) was added gradually to an ethanolic solution (10 mL) of $FeCl_3 \cdot 6H_2O$ (0.541 g, 2.0 mmol). The solution was

TABLE I Analytical and physical data for the metal complex

No.	*Reactions*	*Complexes M. F. [F. Wt]*	*Color*	*Yield* (%)	*M.P* (°C)	*Elemental Analysis,* (%) *Found*/(*Calc.*)				
						C	*H*	*N*	*M*	*Cl*/*S*
(1)	H_2L	$C_{13}H_{15}N_5O$ [257.3]	Yellow	74.0	205	60.7 (60.7)	5.8 (5.9)	27.1 (27.2)	–	–
(2)	$H_2L + FeCl_3 \cdot 6H_2O$	$[(H_2L) + FeCl_3] \cdot 3\frac{1}{2}H_2O$ $C_{13}H_{22}N_5O_4^{\frac{1}{2}}FeCl_3$ [482.6]	Dark green	44.0	238	32.4 (32.4)	4.2 (4.6)	14.7 (14.5)	11.6 (11.6)	21.7 (22.0)
(3)	$H_2L + FeCl_3 \cdot 6H_2O +$ Oxalic acid	[(HL)ClFe(ox)FeClHL] $C_{28}H_{28}N_{10}O_6Fe_2Cl_2$ [783.2]	Pale brown	46.0	227	43.1 (42.9)	3.8 (3.6)	17.5 (17.8)	14.1 (14.3)	9.3 (9.1)
(4)	$H_2L + FeCl_3 \cdot 6H_2O +$ 8-Hydroxyquinoline (8-HQ)	$[(HL)FeCl(8\text{-}HQ)] \cdot H_2O$ $C_{22}H_{22}N_6O_3FeCl$ [509.8]	Grey	60.0	242	51.8 (51.8)	4.5 (4.4)	16.7 (16.5)	10.7 (11.0)	7.4 (7.0)
(5)	$H_2L + FeCl_3 \cdot 6H_2O +$ 1,10-Phenanthroline (phen.)	$[(HL)Fe(phen)Cl]Cl \cdot 3\frac{1}{2}H_2O$ $(C_{25}H_{29}N_7O_{4.5}FeCl_2)$ [626.3]	Red	49.0	232	47.9 (47.9)	4.5 (4.7)	15.4 (15.7)	8.8 (8.9)	11.6 (11.3)
(6)	$H_2L + FeCl_3 \cdot 6H_2O +$ 2,2′-bipyridine (bpy)	[(HL)Fe(bpy)Cl]Cl $(C_{23}H_{22}N_7Ocl_2Fe)$ [539.3]	Red	53.6	222	53.3 (53.2)	4.1 (4.1)	17.8 (18.2)	10.00 (10.4)	13.3 (13.2)
(7)	$H_2L + FeCl_3 \cdot 6H_2O$ in NH_3 solution	$[(L)Fe(H_2O)_2Cl] \cdot 2\frac{1}{4}H_2O$ $(C_{13}H_{22.5}N_5O_{5\frac{1}{4}}FeCl)$ [424.2]	Brown	47.0	245	36.7 (36.8)	5.4 (5.4)	16.2 (16.5)	12.8 (13.2)	8.4 (8.4)
(8)	$H_2L + CoCl \cdot 6H_2O$	$[(HL)Co(H_2O)Cl] \cdot 2H_2O$ $(C_{13}H_{20}O_4N_5CoCl)$ [404.7]	Olive-Green	97.0	> 360	38.4 (38.6)	4.7 (5.0)	16.9 (17.3)	14.5 (14.6)	8.5 (8.8)
(9)	$H_2L + Ni(OAc)_2 \cdot 4H_2O$	$[(HL)Ni(OAc)(H_2O)] \cdot H_2O$ $(C_{15}H_{21}N_5O_5Ni)$ [410.1]	Brownish-Yellow	40.0	> 360	44.0 (43.9)	5.2 (5.2)	16.8 (17.1)	14.3 (14.3)	–
(10)	$H_2L + Cu(OAc)_2 \cdot H_2O$	$[(HL)Cu(OAc)] \cdot \frac{1}{4}H_2O$ $(C_{15}H_{17.5}N_5O_{3\frac{1}{4}}Cu)$ [383.4]	Olive-Green	72.0	268	47.0 (47.0)	4.6 (4.6)	18.2 (18.3)	16.4 (16.6)	–
(11)	$H_2L + Cu(OAc)_2 \cdot H_2O +$ Oxalic acid	[(HL)Cu(ox)CuHL] $(C_{28}H_{28}N_{10}O_6Cu_2)$ [727.7]	Olive-Green	41.0	> 360	45.9 (46.2)	4.3 (3.9)	19.1 (19.3)	17.2 (17.5)	–
(12)	$H_2L + Cu(ClO_4)_2 \cdot 6H_2O +$ 1,10-Phenanthroline	$[(HL)Cu(phen)]ClO_4$ $(C_{25}H_{22}N_7O_{1.5}Cu)$ [598.5]	Green	65.8	240	50.1 (50.2)	4.0 (4.4)	16.5 (16.4)	10.4 (10.6)	–
(13)	$H_2L + Zn(OAc)_2$	[(HL)Zn(OAc)] $(C_{15}H_{17}N_5O_3Zn)$ [380.7]	Pale yellow	66.0	294	47.1 (47.3)	3.8 (3.5)	18.2 (18.4)	17.1 (17.2)	–
(14)	$H_2L + UO_2(OAc)_2 \cdot 2H_2O$	$[(HL)(UO_2)(Oac)H_2O] \cdot \frac{1}{2}H_2O$ $(C_{15}H_{20}O_{6.5}N_5U)$ [612.4]	Red	45.0	> 360	29.3 (29.4)	3.7 (3.3)	11.6 (11.4)	– (38.9)	– –

stirred for 1 h, then an ethanolic solution (30 mL) of the ligand (0.514 g, 2.0 mmol) was added gradually and the solution stirred for 6 h during which the solid complex precipitated. The product was filtered off, washed with ethanol then diethyl ether and finally air-dried. Yield, 0.69 g (46.0%).

The complex **11**, [(HL)Cu(ox)Cu(HL)], was prepared by a similar method.

Preparation of Mixed Ligand Complexes of Fe(III) and Cu(II), 4,5,6 and 12

An ethanolic solution (30 mL) of $FeCl_3 \cdot 6H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$ was added gradually to an ethanolic solution of the ligand (40 mL) in the molar ratio 1 : 1. The solution was stirred for 0.5 h; then an ethanolic solution of 8-HQ, phen or bpy was added to the previous solution in the molar ratio 1 : 1. The solution was continuously stirred for 5 h where the solid complexes were precipitated. The precipitates were filtered, washed with ethanol then diethyl ether and finally air-dried. In the case of Cu(II) only phen was tried.

Preparation of the $[LFeCl(OH_2)_2] \cdot 2\frac{1}{4}H_2O$, Complex (7)

An ethanolic solution (30 mL) of $FeCl_3 \cdot 6H_2O$ (0.526 g, 1.95 mmol) was added gradually to an ethanolic solution (40 mL) of the ligand (0.5 g, 1.95 mmol). The solution was refluxed for 0.5 h; then a mixture of ammonia solution, 26% NH_3 solution, and ethanol (1 : 2 by volume) was added dropwise to the stirred hot mixture until it became alkaline. The solution was then stirred for 5 h to precipitate the solid complex. The brown product was filtered off, washed with cold ethanol, then diethyl ether and finally dried in a vacuum desiccator over anhydrous calcium chloride. Yield, 0.4 g (47%).

Preparation of the $[HLCoCl(H_2O)] \cdot 2H_2O$, Complex (8)

An aqueous solution (10 mL) of KOH (0.28 g, 5.0 mmol) was added to an ethanolic solution (40 mL) of the ligand (0.64g, 2.5 mmol). The solution was stirred for 0.5 h, then an aqueous solution (15 mL) of $CoCl_2 \cdot 6H_2O$ (0.595 g, 2.5 mmol) was added and the solution stirred for 5 h during which the solid complex precipitated. The product was filtered off, washed with cold ethanol, then with diethyl ether and finally dried in a vacuum desiccator over anhydrous calcium chloride. Yield, 0.762 (97%).

Table I shows chemical analyses and other data of the ligand and its metal complexes. Table II shows their characteristic IR bands; Table III shows their electronic spectra, magnetic moments and molar conductance and Table IV shows characteristic ^1H NMR signals of the ligand and its Zn(II) and UO_2(VI) complexes.

RESULTS AND DISCUSSION

The Ligand

The molecular ion peak of the ligand was observed at 257.1 a.m.u. in its mass spectrum confirming its formula weight (F.W.257.3). The ^1H NMR spectrum of the ligand in DMSO-d_6 showed signals, Table IV, that support its suggested structure. The Schiff-base hydrazone acts as a tridentate (N_2O) neutral, mono-, or dibasic ligand or

TABLE II IR spectral data of the ligand and its metal complexes

No.	*Complexes*	*IR Spectra* (cm^{-1})[a]										
		νOH *(phenolic + H_2O)*	νNH_2	νNH	νCOO *(OAc or ox)*	δOH *(H_2O)*	$\nu C{=}N$	$\nu C{=}N$	$\delta C{-}O$ *phenolic*	$\nu M{-}O$	$\nu M{-}N$	*Other Bands*
1	H_2L	3578, m, br	3472,m 3372,vs	3200, m, br	–	–	1600, vs	–	1252, s	–	–	1314, s, δOH (phenolic)
2	$[H_2LFeCl_3] \cdot 3\frac{1}{2}H_2O$	3470, s, br	3364, s, br	3162, m, br	–	1650, vs	1591, m		1243, m	562, w	435, w	1326, m, δOH (phenolic)
3	[HLClFe(ox)FeClHL]	3497, s	3428, s	3195, m. br	1651, vs	–	1580, m	1563, m	1236, w	562, w	435, w	–
4	$[(HL)FeCl(8\text{-}HQ)] \cdot H_2O$	3431, vs, br		3165, w	–	1651, m	1582, m	1569, w	1236, w	562, w	460, w	–
5	$[(HL)Fe(phen)Cl]Cl \cdot 3\frac{1}{2}H_2O$	3431, vs, br		3165, w	–	1652, s	1590, s	1569, w	1243, w	564, w	440, w	–
6	[(HL)Fe(bpy)Cl]Cl	3423, s, br		3205, w	–	–	1590, vs	1560, m	1245, s	547, w	455, w	–
7	$[Lfe(H_2O)_2Cl] \cdot 2\frac{1}{4}H_2O$	3520, s	3429, vs 3354, vs	–	–	1655, vs	1593, m	–	–	564, w	450, w	–
8	$[(HL)Co(H_2O)Cl] \cdot 2H_2O$	3460, vs, br		3200, sh	–	1655, sh	1601, s	–	1244, w	524, w	446, w	–
9	$[(HL)Ni(OAc)(H_2O)] \cdot H_2O$	3428, vs, br	3330, sh	3222, m, br	1660, sh	1620, m	1580, s	1512, m	1248, m	567, m	429, w	–
10	$[(HL)Cu(OAc)] \cdot \frac{1}{4}H_2O$	3396, vs, br		3212, m, br	1675, m	–	1586, s	1544, s	1239, m	567, w	437, w	–
11	[(HL)Cu(ox)CuHL]	3470, sh	3382, vs, br	3231, w, br	1677, vs	–	1605, m	1569, m	1237, m	562, w	436, w	–
12	$[(HL)Cu(phen)]ClO_4$	3432, vs, br		3185, sh	–	–	1603, s	1571, m	1228, m	565, w	438, w	1088, s, br, νClO_4
13	[(HL)Zn(OAc)]	3426, vs, br		3205, m	1643, vs	–	1607, sh	1575, m	1244, m	549, m	413, w	–
14	$[(HL)(UO_2)(OAc)H_2O] \cdot \frac{1}{2}H_2O$	3430, vs, br		3202, sh	1665,	–	1600, s	1512, m	1242, m	557, w	450, w	897, s ν_3OU=O

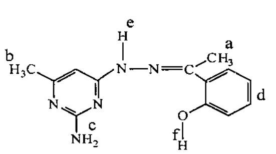
[a] s = strong, m = medium, w = weak, v = very and b = broad.

TABLE III Electronic spectra, magnetic moments and molar conductivity data of metal complexes

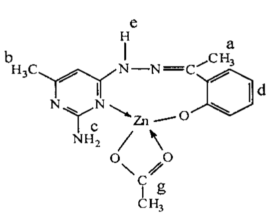
No	*Complexes*	*Electronic Spectral bands* (nm)	μ_{eff}[a] B.M.	μ_{compl}[b] B.M.	*Conductance*[c] Ohm^{-1} cm^2 mol^{-1}
1	H_2L	225,304,333,384	–	–	–
2	$[(H_2L)FeCl_3]\cdot 3½H_2O$	525,591	5.92	–	29.0
3	[(HL)ClFe(ox)FeClHL]	577	1.78	2.51	38.0
4	$[(HL)FeCl(8-HQ)]\cdot H_2O$	448,527,578,587	4.43	–	24.0
5	$[(HL)Fe(phen)Cl]Cl\cdot 3½H_2O$	508,517,530,539,548,560,655	1.80	–	44.0
6	[(HL)Fe(bpy)Cl]Cl	499,513,548,556	1.65	–	Insoluble
7	$[(L)Fe(H_2O)_2Cl]\cdot 2¼H_2O$	539	3.3	–	Insoluble
8	$[(HL)Co(H_2O)Cl]\cdot 2H_2O$	628–700	3.55	–	30.0
9	$[(HL)Ni(OAc)(H_2O)]\cdot H_2O$	421,427,438 & (438,558,800)[d]	3.0	–	6.8
10	$[(HL)Cu(Oac)]\cdot ¼H_2O$	(401,667)[d]	1.76	–	6.0
11	[(HL)Cu(ox)CuHL]	480,491,499 & (595,632,865)[d]	1.70	2.42	Insoluble
12	$[(HL)Cu(phen)]ClO_4$	636	1.50	–	36.0
13	[(HL)Zn(Oac)]	425	–	–	4.0
14	$[(HL)(UO_2)(OAc)H_2O]\cdot ½H_2O$	435	–	–	4.0

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

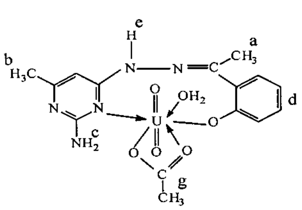
TABLE IV The ^1H NMR data of the free ligand H_2L (A) and its Zn(II) (B) and UO_2(VI) (C) complexes



(A)
A tridentate ligand (H_2L)



(B)
[(HL)Zn(OAc)]



(C)
$[(HL)UO_2(OAc)H_2O].1/2H_2O$

	$\delta_H(ppm)$						
	H^a	H^b	H^c	$H^d_{ar\cdot\&heterocyclic}$	H^e	H^f	H^g
(A) H_2L	2.15 (s)* (3H)	2.4 (s) (3H)	5.90 (s) (2H)	6.65–7.65 (m) (5H)	9.9 (s, br) (1H)	12.58 (s, br) (1H)	–
(B) [(HL)Zn(Oac)]	1.8 (s) (3H)	2.32 (s) (3H)	5.73 (s) (2H)	6.25–7.60 (m) (5H)	–	–	2.05 (s) (3H)
(C) $[(HL)UO_2(OAc)H_2O]\cdot ½H_2O$	2.15 (s) (3H)	2.35 (s) (3H)	5.87(s) (2H)	6.45–7.47 (m) (5H)	–	–	2.05 (s) (3H)

*s = singlet, m = multiplet and br = broad.

a bidentate (NO) monobasic ligand. The IR spectrum of the ligand, Table II, showed a broad band at 3200 cm^{-1} due to the overlap of the stretching vibrational modes of the heterocyclic (NH) group and the enolic (NH) group originating through resonance between the (C=N) and the (OH) groups as indicated in Fig. 2. The low value of ν(C=N), at 1600 cm^{-1}, is due to the resonance between the enol and keto tautomers, Fig. 2. The stretching vibration of the phenolic (OH) group appears at 3578 cm^{-1}.

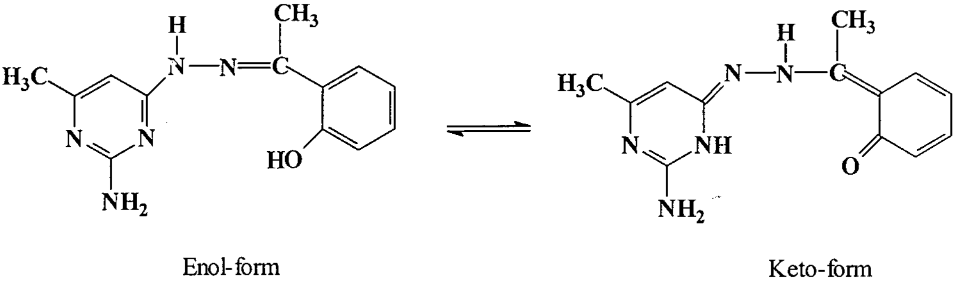


FIGURE 2 Keto-enol tautomers of the Schiff-base hydrazone ligand.

In addition, the IR spectrum showed two bands at 3372 and 3472 cm^{-1} which are assigned to ν_s and ν_{as} of the amino group.

The UV spectrum of the free ligand (8×10^{-5} M) in ethanol, Table III, showed bands at 225 nm ($\varepsilon = 19555$) assigned to a π–π* transition of the aromatic and heterocyclic rings. The bands at 304 nm ($\varepsilon = 17500$) and 333 nm ($\varepsilon = 18250$) are due to n–π* transition within the azomethine, C=N, group. The band at 384 nm ($\varepsilon = 15500$) is due to a charge transfer within the whole molecule originating from the heterocyclic ring to the azomethine linkage.

The Metal Complexes

The reaction of Schiff-base hydrazone ligands with transition metal ions can proceed according to two pathways attaining either the ketonic or the phenolic structure. These reactions produced new mono- and binuclear metal complexes of the types $[(HL)M(OAc)]\cdot xH_2O$ (M = Cu or Zn), $[(HL)M(OAc)H_2O]\cdot xH_2O$ (M = Ni or UO_2), $[(HL)Co(OH_2)Cl]\cdot 2H_2O$, $[(H_2L)FeCl_3]\cdot 3\frac{1}{2}H_2O$, $[LFeCl(H_2O)_2]\cdot 2\frac{1}{4}H_2O$, $[(HL)L'FeCl(H_2O)]\cdot H_2O$ (L′ = 8-HQ), $[(HL)L'FeCl]Cl\cdot xH_2O$ (L′ = phen, or bpy) and $[(HL)L'Cu]\cdot ClO_4$ (L′ = phen). Also, binuclear complexes with oxalic acid of the type [(HL)ClFe(ox)FeCl(HL)], [(HL)Cu(ox)Cu(HL)] (ox = oxalate) were obtained.

IR Spectra of Metal Complexes

The IR spectra of the solid complexes, Table II, showed a shift of the absorbance of the ν(C=N) to lower frequencies, in the range 1580–1591 cm^{-1}, except the complexes **8**, **11**, **12**, **13** and **14** which showed their band at the same or higher value than that of the H_2L ligand. The bands due to the NH_2 group remained unaltered in the IR spectra of the complexes or were overlapped by ν(OH) bands of hydrated and/or coordinated water molecules in the range 3420–3500 cm^{-1}. The disappearance of δ(OH) of the phenolic group and the shift of ν(C–O) by 7–24 cm^{-1} to lower frequencies indicate the replacement of the phenolic proton by metal cations. These bands were observed in the IR spectrum of the ligand at 1314 and 1252 cm^{-1}, respectively. The IR spectra of the complexes also showed new bands between 524–567 and 413–460 cm^{-1} assigned to ν(M–O) and ν(M–N), respectively, supporting the view that bonding of the metal ions to the ligand is achieved through the phenolic oxygen atom and one of the nitrogen atoms of the heterocyclic ring and/or the nitrogen atom of the azomethine group. The IR spectra of the complexes containing the ligand L′, phen, showed additional characteristic bands at 719–725, 843–845 and 1520 cm^{-1} which confirm that the metal ion is coordinated to this ligand [18,19].

UV-VISIBLE AND ESR SPECTRA, MAGNETIC MOMENTS, ELECTRIC CONDUCTANCE AND THERMAL ANALYSES OF THE METAL COMPLEXES

The Ni(II) Complex (9)

The electronic spectrum of the nickel(II) complex was measured in the solid state and DMF solution. The reflectance spectrum of the complex showed two bands at 800 and 438 nm. These bands could be assigned to the $^3A_2g \rightarrow T_1g$ and $^3A_2g \rightarrow {}^3T_1g(P)$ electronic transitions, respectively, consistent with an octahedral geometry of the complex [20]. The solution spectrum of the nickel(II) complex also showed bands at 438, 427 and 421 nm. The magnetic moment of the complex is 3.0 B.M. which indicates the presence of two unpaired electrons per the Ni(II) ion, also confirming its octahedral geometry [21,22]. The octahedral geometry was completed through a bidentate acetate group and a water molecule. The IR spectrum of the complex showed a new band at 1660 cm^{-1} attributed to the bidentate acetate group. Also, the IR spectrum showed bands at 950 and 740 cm^{-1} due to rocking and wagging vibrations of the coordinated water molecule [23]. This coordination was also supported by a TGA study. The thermogram of the complex was recorded in the temperature range 21–798.5°C. It shows two inflections, due to the presence of one hydrated and one coordinated water molecules, in the DTG curve at 50 and 150°C. Another inflection point is observed at 370°C and a weight loss 16.5% corresponding to the elimination of an acetate group. The molar conductance of the complex in DMF solution (10^{-3} M) is 6.8 $Ohm^{-1} cm^2 mol^{-1}$ (Table III) indicates that the complex is a non-electrolyte. Thus, on the basis of the basis of elemental analyses (Table I), molar conductance, IR and visible spectra, magnetic moment and thermal analyses, the geometry of the Ni(II) complex is octahedral, as shown in Fig. 3.

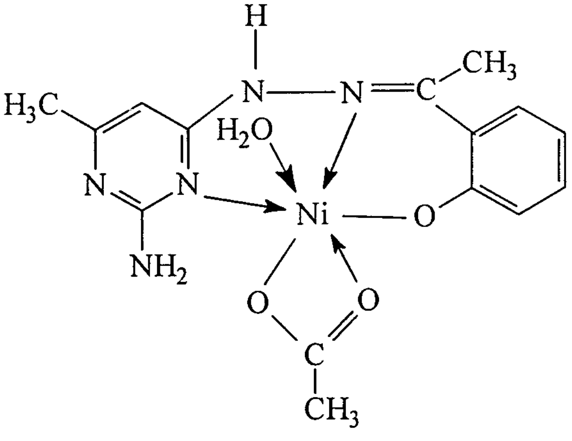


FIGURE 3 The proposed structure of the Ni(II) complex (9).

The Co(II) Complex (8)

The reaction of $CoCl_2 \cdot 6H_2O$ with the ligand H_2L in the presence of KOH yielded an olive green complex. The visible spectrum of Co(II) complex (**8**) showed a split band at 628–700 nm characteristic of the Co(II) ion in tetrahedral geometry. It is well known that the electronic spectra of Co(II) in its octahedral complexes, which are usually high spin, lead to a weak band ($\varepsilon < 10$) near 500 nm while for tetrahedral complexes a much stronger band ($\varepsilon > 100$) at 600–700 nm is expected [24]. The magnetic moment of the complex is 3.55 B.M. while the expected value for tetrahedral complexes is 4.4–4.8 B.M. The low value of the magnetic moment of the complex would point to a not purely tetrahedral geometry of Co(II) and a tendency towards square-planar; the latter geometry is characterized by lower magnetic moments (2.1–2.8 B.M.) [25]. This result was supported by TG analysis and its IR spectrum. TGA of the complex indicated that two hydrated water molecules were lost at 103°C and a coordinated water molecule was lost at 165°C. IR spectrum of the complex showed a band at $1601\,cm^{-1}$, due to $\nu C{=}N$, similar to that observed for the ligand which indicates that this group was not involved in chelating the Co(II) ion. The data thus indicate that the Co(II) cation is tetracoordinate, Fig. 4. The molar conductance of the complex in DMF solution (10^{-1} M) is $30.0\,Ohm^{-1}\,cm^2\,mol^{-1}$ which indicates that it is a non-electrolyte, however, the observed value may be due to the strong donor capacity of DMF which leads to the partial displacement of the coordinated chloride ion.

Fe(III) Complexes

Five new Fe(III) complexes were obtained which have different formulas. The reaction of $FeCl_3 \cdot 6H^2O$ with the ligand H_2L in an acidic medium (pH = 1.77) yielded the complex $[H_2LFeCl_3] \cdot 3\tfrac{1}{2}H_2O$ (**2**), Fig. 5, while in basic medium produced the complex $[LFeCl(H_2O)_2] \cdot 2\tfrac{1}{4}H_2O$ (**7**), Fig. 5. The IR spectrum of complex (**7**) does not show the characteristic ν(N–H) band which was observed in the free ligand at $3200\,cm^{-1}$ lending further support to the suggestion that the ligand tauterizes to the ketonic form during coordination with the Fe(III) ion in basic solution. The $\nu C{=}O$ band was overlapped by δOH of the hydrated and coordinated water molecules. The disappearance of $\nu C{=}O$ of the phenolic group also supports this conclusion. Complex (**7**) was prepared in an alkaline solution and it was expected to contain either hydroxo- or oxo- bridges between Fe(III) ions in dimeric or oligomeric structures, however, its

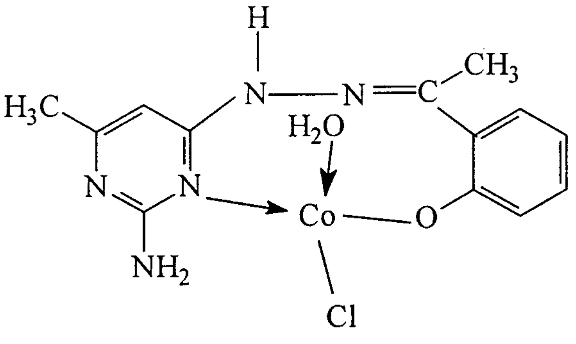
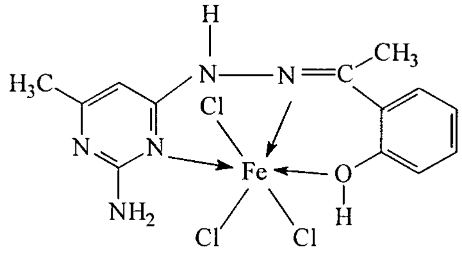
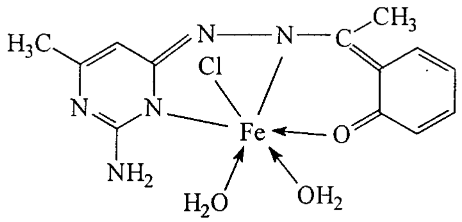


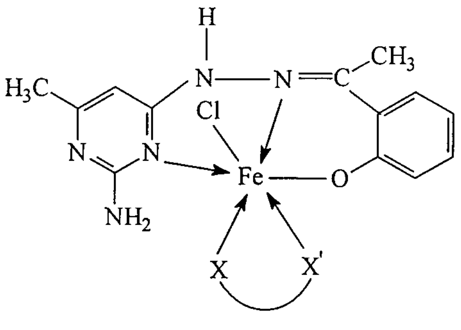
FIGURE 4 The proposed structure of the Co(II) complex (**8**).



Complex (**2**)



Complex (**7**)



X = N, X' = O, 8-HQ (**4**)
X = X' = N, phen (**5**) or bpy (**6**)

FIGURE 5 The proposed structures of the mononuclear Fe(III) complexes.

IR spectrum did not show the bands characteristic of these bridges [26,27]. TGA showed two inflections, due to the presence of 2¼ hydrated water at 103°C and two coordinated water molecules at 163°C. Complex (**2**) showed low value of the molar conductance, 29 $\mathrm{Ohm^{-1}\,cm^{2}\,mol^{-1}}$ indicating that it is a non-electrolyte and the observed low value may be due to exchange between solvents molecules and chloride ions. Complex (**7**) was insoluble in all common solvents which hindered the determination of its conductivity.

The reaction of $FeCl_3 \cdot 6H_2O$ with the H_2L ligand and another chelating agent such as phen, bpy or 8-HQ resulted in the isolation of the complexes listed in Table (I), [(HL)(8-HQ)FeCl]·H_2O (**4**), [(HL)L′FeCl]Cl, (L′ = phen or bpy) (**5**) and (**6**). Complexes (**4**) and (**5**) are only soluble in DMSO and DMF and sparingly soluble in methanol. Complex (**4**) showed a low value for molar conductance which indicates that it is a non-electrolyte and the observed value may be due to displacement of part of the coordinated chloride ions by DMF solvent molecules. It has been reported that DMF is a good donor solvent and can replace NO_3^- or Cl^- from the coordination sphere of metal complexes [28,29]. The molar conductance of complex (**5**) in DMF solution, 10^{-3} M, is 44.0 $Ohm^{-1} cm^2 mol^{-1}$ (Table III) lower than expected for 1 : 1 electrolytes (70–110 $Ohm^{-1} cm^2 mol^{-1}$) and may be due to the low mobility of its bulky cation. Complex (**6**) was insoluble in all common solvents, thus its conductance was not determined.

The value of the magnetic moment of complex (**2**), 5.92 B.M., Table III, is consistent with the presence of five unpaired electrons in the Fe(III) ions in octahedral geometry [25]. However the values of the magnetic moments of complexes (**5**) and (**6**) are in the range 1.65–1.80 B.M. which may be due to the effect of the strong fields of the additional ligands, e.g. bpy, phen. This would lead to spin-pairing of the electrons; low-spin magnetic moments of Fe(III) ion are in the range 2.1–2.5 B.M. [21], and/or antiferromagnetic interactions between Fe(III) ions in neighboring molecules. The magnetic moment of complexes (**4**) and (**7**) are 4.43 and 3.30 B.M., respectively, lower than expected, perhaps due to antiferromagnetic interactions between Fe(III) ions in neighboring molecules.

The electronic spectra of the Fe(III) complexes show two absorption bands at 448–539 and 548–655 nm corresponding to $^6A_1 \rightarrow ^4A_1$, $^4E(G)$ and to $^6A_1 \rightarrow ^4T_2$ electronic transitions [25], respectively, suggesting an octahedral field around the Fe(III) ion. The octahedral geometry of the iron(III) is achieved by the coordinated ligand, chloride ions or bidentate ligands such as 8-HQ, bpy or phen and/or water molecules.

Cu(II) Complexes

Two different types of Cu(II) complexes were obtained, a mononuclear complex [(HL)-Cu(OAc)]·¼H_2O (**10**) from the reaction of the H_2L ligand with $Cu(OAc)_2 \cdot H_2O$ in the molar ratio 1 : 1 and a mixed ligand complex [HLCu(phen)]ClO_4 (**12**) from the reaction of the H_2L ligand, $Cu(ClO_4)_2 \cdot 6H_2O$ and phenanthroline in the molar ratio 1 : 1 : 1. The molar conductances of the complexes in DMF solutions were 6.0 and 36.0 $Ohm^{-1} cm^2 mol^{-1}$, respectively, indicating that the former complex was a non-electrolyte while the latter one was 1 : 1 electrolyte. The low value of the molar conductance of the latter complex would be due to the low mobilities of both the bulky cation and anion.

The reflectance spectrum of the complex [HLCu(OAc)]·¼H_2O (**10**) shows two bands at 667 and 401 nm while the visible spectrum of concentrated solution of the complex [HLCu(phen)]ClO_4 (**12**) in DMF solvent shows only one band at 636 nm. The low-energy bands at 636 and 667 nm for the two complexes correspond to the $^2B_{1g} \rightarrow ^2A_{1g}$ transition in square-planar geometry [30–32]. The strong high-energy band at 401 nm of the former complex is assigned to charge transfer transition metal → ligand or vice versa. In addition, the magnetic moments of the complexes are 1.76 and 1.50 B.M., respectively, which are consistent with the proposed square-planar structure [21] of the complexes, Figs. 6 and 7.

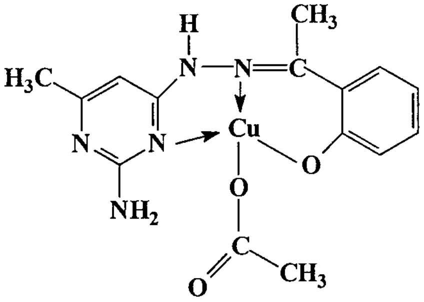


FIGURE 6 Proposed structure of the copper(II) complex (**10**).

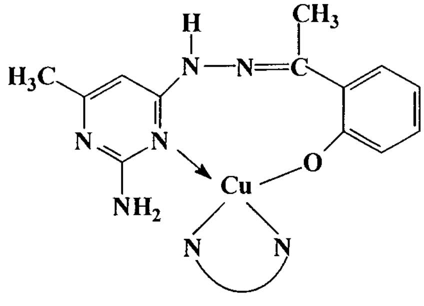


FIGURE 7 Proposed structure of the copper(II) complex (**12**).

The ESR spectra of the crystalline mononuclear copper complexes [HLCu-(OAc)] · ¼H_2O and [(HL)Cu(phen)]ClO_4 in the powder form and at room temperature, Fig. 8, show one broad signal at $g_{\mathrm{eff}} = 1.822$ for the former complex and two signals at $g_{\perp} = 1.861$ and $g_{\parallel} = 1.828$ for the latter complex consistent with square-planar geometry for the former complex and square-planar distorted towards tetrahedral for the latter one.

Zn(II) and UO_2(VI) Complexes

The reactions of the ligand with both Zn(II) and UO(VI) cations yielded mononuclear complexes [(HL)Zn(OAc)] (**13**) and [(HL)UO_2(OAc)H_2O] · ½H_2O (**14**), respectively. Table I. Their IR specta, Table II, indicated that the acetate group is coordinated as a bidentate ligand [33], and also showed a slight shift of the νC=N band compared to that of the free ligand. Uranyl ion is reported to exhibit three characteristic bands ν_1 sym. at 860 cm^{-1}, ν_3 asym. at 930 cm^{-1} and ν_2 bending at 210 cm^{-1}. If the UO_2(VI) is not linear, all three frequencies should be IR active. If the cation is linear ν_2 and ν_3 should be IR active. The IR spectra of the UO_2(VI) complex (**13**) shows only one strong absorption band at 897 cm^{-1} which is assigned to the antisymmetric ν_3(O=U=O) vibration [33] indicating that the uranyl ion is linear.

^1H NMR spectra of the Zn(II) and UO_2(VI) complexes were recorded in DMSO-d_6 solutions; the data and assignments are included in Table (IV). The signal due to the

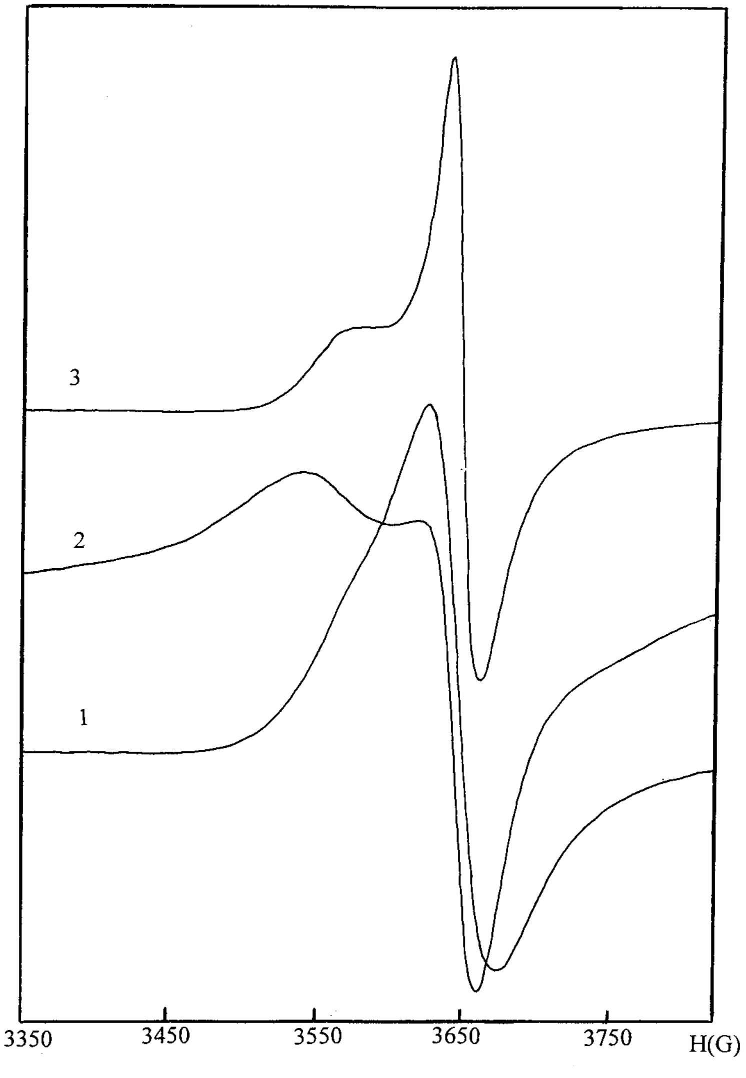


FIGURE 8 ESR spectra of the complexes 1 : [(HL)Cu(OAc)] · ¼H_2O (**10**), 2 : [(HL)Cu(phen)]ClO_4 (12) and 3: [(HL)Cu(ox)Cu(HL) (**11**).

proton of the phenolic OH group in the parent ligand disappeared in the spectra of the complexes indicating deprotonation during complex formation. Unfortunately, although the νNH band was observed in the IR spectra of both Zn(II) and UO_2(VI) complexes, the signal due to the NH group in the ^1H NMR spectra was not observed, perhaps due to H-bonding with other neighboring groups in their complexes. Also, a new signal appeared in the spectra of the complexes at δ 2.05 ppm for the protons of the CH_3 group of the acetate group indicating the involvement of this group in the coordination.

Thermal analysis of the Zn(II) complex indicated its stability to 138°C and no weight loss indicating that the complex does not contain water or solvent molecules in the coordination sphere. Also, the complex shows a weight loss at 277°C due to elimination of the acetate group. The UO_2(VI) complex shows weight loss at 69 and 144°C due to elimination of hydrated and coordinated water molecules, respectively.

The IR and ^{1}H NMR spectra and the thermal data thus indicate that the UO_2(VI) cation is heptacoordinate while the Zn(II) cation is tetracoordinate, Fig. 9, and may be tetrahedral as was the Co(II) complex (**8**).

The electronic spectra of the Zn(II) and UO_2(VI) complexes exhibit one absorption band at 425 and 435 nm, respectively, which are attributed to charge transfer transitions from the ligand to the Zn(II) and uranium(VI) ions or vice versa.

Binuclear Complexes

Two new μ-oxalato binuclear Fe(III) and Cu(II) complexes, [HLClFe(ox)FeClHL] (**3**) and [HLCu(ox)CuHL] (**11**), have been synthesized by reaction of $FeCl_3 \cdot 6H_2O$ or $Cu(OAc)_2 \cdot H_2O$ with oxalic acid and the Schiff-base hydrazone ligand, H_2L, in the molar ratio 2 : 1 : 2, respectively. The complexes have been characterized by FT-IR, electronic, ESR and mass spectra as well as thermal analysis and magnetic moments.

IR spectra of the complexes showed bands at 1677–1651 cm^{-1}due to the ν_{as} and ν_s of the oxalate group and another band at 1304–1324 cm^{-1} due to its bending vibration. These values are consistent with known absorptions of tetradentate oxalate groups [34,35]. Also, the IR spectrum of the binuclear Fe(III) complex, Table II, showed a shift of the νC=N to a lower frequency, 20 cm^{-1}, while the binuclear Cu(II) complex do not show any change indicating that the C=N group is involved only in the chelation of the Fe(III) complex.

The thermal behavior of the complexes have been deduced from their TGA and DTG curves. The binuclear Fe(III) complex showed weight loss at 139 and 223°C due to the elimination of two chlorine atoms; after 225°C, the thermogram shows stepwise decomposition. The thermogram of the Cu(II) complex shows that it is stable up to 350°C; no weight loss indicating that the complex does not contain water or solvent molecules in its coordination sphere.

The results of the IR spectra and thermal analysis thus indicate that the coordination geometries of the Cu(II) and Fe(III) complexes are square-planar and octahedral, respectively, Fig. 10.

The reflectance spectrum of the binuclear Cu(II) complex [HLCu(ox)CuHL] showed bands at 595, 632 and 865 nm which are assigned to a square-planar complex distorted towards tetrahedral geometry. The magnetic moment of the complex (1.7 B.M. per one Cu(II) ion) thus supports its geometry. Each Cu(II) atom is coordinated to the bidentate (NO) sites of the Schiff-base hydrazone monobasic ligand anion (HL^-) and two oxygen atoms from an oxalate ion which acts as a bridge between two Cu(II) ions.

The powder ESR spectrum of the binuclear copper complex [HLCu(ox)CuHL], Fig. 8, has been recorded at room temperature and exhibits two signals with two g-values, $g_{\parallel}$ at 1.828 and $g_{\perp}$ at 1.861.

The electronic spectrum of the binuclear Fe(III) complex, [HLClFe(ox)FeClHL] shows an absorption band at 577 nm corresponding to the $^6A \rightarrow {}^4T_2$ electronic transition suggesting an octahedral geometry around the Fe(III) [36]. Each iron(III) ion is coordinated to the tridentate monobasic Schiff-base hydrazone ligand anion, (HL^-), two oxygen atoms from an oxalate ion, which acts as a bridge between two

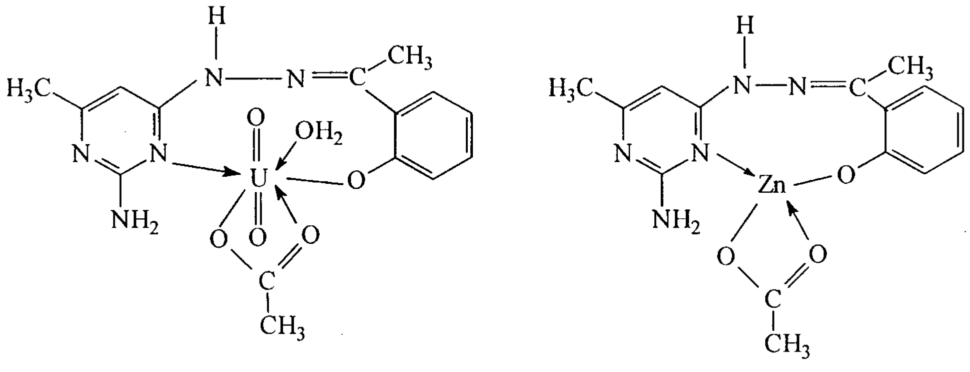
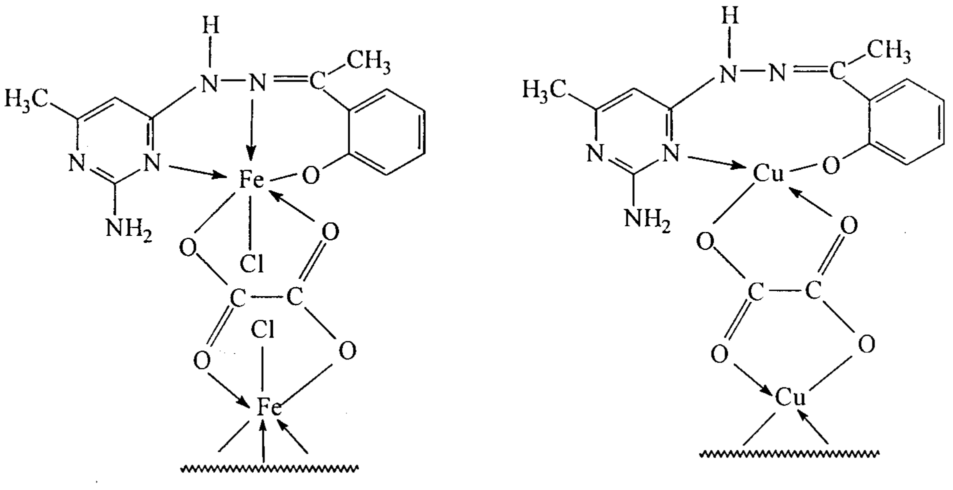


FIGURE 9 Proposed structures of the UO_2(VI) (**14**) and Zn(II) (**13**) complexes.



Complex (**3**) Complex (**11**)

FIGURE 10 The proposed structures of the binuclear complexes (only half of the complex molecule is shown and the bridging oxalate group).

Fe(III) ions, and a chloride ion. The magnetic moment of the complex is 1.78 B.M./ Fe(III) in agreement with its low-spin configuration.

Mass Spectra of the Metal Complexes

The mass spectra of the complexes provide good evidence for the molecular formulas of these complexes. The complexes **4**, **14**, **3** and **11**, [HLFe(8-HQ)Cl] · H_2O (F.W.509.8), [$HLUO_2(OAc)H_2O$] · ½H_2O, (F.W. 612.4), [HLClFe(ox)FeClHL] (F.W. 783.2) and [HLCu(ox)CuHL] (F.W. 727.7) were selected as representative complexes. The mass spectra of these complexes showed that the highest mass peaks agree with the formula weights of the anhydrous complexes [HLFe(8-HQ)Cl] (F.W.495), [$HLUO_2(OAc)$]

(F.W. 581), [HLClFe(ox)FeClHL] (F.W. 786) and [HLCu(ox)CuHL] (F.W. 730). The fragmentation patterns of the complexes show a fragment at 257 due to the Schiff-base hydrazone ligand, (H_2L-1).

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