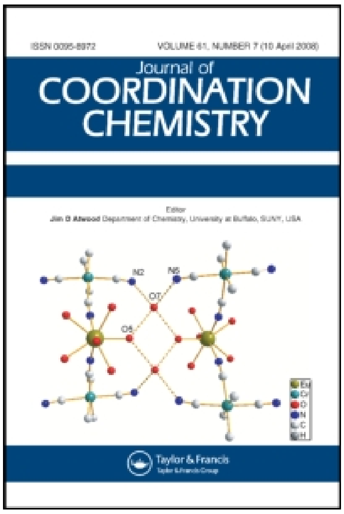

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and biological activities of mononuclear and binuclear Fe(III) complexes with some symmetric and unsymmetric Schiff-base ligands

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To cite this Article Ismail, Tarek M. A.(2006) 'Synthesis, characterization and biological activities of mononuclear and binuclear Fe(III) complexes with some symmetric and unsymmetric Schiff-base ligands', Journal of Coordination Chemistry, 59: 3, 255 — 270

To link to this Article: DOI: 10.1080/00958970500095563

URL: http://dx.doi.org/10.1080/00958970500095563

Journal of Coordination Chemistry
Vol. 59, No. 3, 15 February 2006, 255–270

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Synthesis, characterization and biological activities of mononuclear and binuclear Fe(III) complexes with some symmetric and unsymmetric Schiff-base ligands

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(*Received 16 June 2004; revised 13 September 2004; in final form 28 February 2005*)

A series of mononuclear and binuclear Fe(III) complexes of some new symmetrical and unsymmetrical Schiff bases containing quinoline derivatives were synthesized and characterized by elemental and thermal analysis, conductance measurements and IR spectra. In mononuclear complexes, the unsymmetric Schiff bases are monobasic tetradentate towards the Fe(III) ion. However, in binuclear complexes, the symmetric Schiff-base ligands behave as monobasic bidentate towards each Fe(III) ion. The structure of the solid complexes are discussed and based on magnetic susceptibility measurements, electronic and ESR spectral studies. The biological activities of the ligands and their complexes are reported.

Keywords: Iron(III); Schiff-base; Macrocycle; Biological activity; Binuclear

1. Introduction

Extensive research has been carried out on Schiff bases and their metal complexes due to their biological applications and pharmaceutical activities [1–4]. The biological activity of Schiff-base compounds is related to coordination of metal ions; the combination of ligands and metal ions increases their antibiotic activity [5]. Iron has some importance in pharmaceutical preparations in connection with the mode of action of drugs in the human body [6]. Iron-containing pharmaceutical formulations are commonly used in the treatment or prophylaxis of iron-deficiency anemias [7]. It has been observed that iron Schiff-base complexes exhibit wide applications in biological systems [8, 9]. Also, the chemistry of quinoline and its derivatives has

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500095563

attracted special interest due to their therapeutic properties [10]. These compounds have been used in the treatment of cancer [11], diabetes [12], malaria [13] and convulsion [14]. The present study deals with the preparation and characterization of some Fe(III) complexes involving bioactive Schiff-base ligands derived from 7-formyl-8-hydroxyquinoline or 4-chloro-7-formyl-8-hydroxyquinoline with some aliphatic and aromatic diamines and β-diketones. Some of the Schiff-base ligands reported here are known compounds [15, 16]. The other Schiff-base compounds, L^4, L^5, L^{12} and L^{13} are new. Also, the iron(III) complexes of these ligands have not been studied previously. The preparation of these compounds and their characterization by various spectroscopic methods are reported. Biological activities of the ligands and their iron complexes were also studied.

2. Experimental

All compounds used in the present study were pure grade BDH or Prolabo chemicals. Organic solvents used were reagent grade.

2.1. *Apparatus and working procedures*

Electronic spectra of solutions of the complexes in DMF were recorded on a Jasco model V.550 UV-Vis spectrophotometer. IR spectra of the ligands were recorded as KBr discs using the IR Shimadzo model 470 (400–4000 cm^{-1}). Also the IR spectra of the complexes were obtained as KI discs, on a Perkin-Elmer 598 Infrared Spectrophotometer in the range 200–4000 cm^{-1}. The ^{1}H NMR spectra were obtained using the JEOL-D_{60} spectrophotometer at 200 MHz at the central laboratories of Tanta University, Tanta, Egypt, using (DMSO, d_6) which was obtained from Aldrich Chemical Company. The mass spectra of the ligands were recorded on a MS 5988 Hewlett-Packard mass spectrometer, the fragmentation was carried out at 300°C and 70 eV. EPR spectra of the metal complexes were recorded on the Jeol microwave unit JES-FE2XG spectrophotometer at the central laboratories of Tanta University, Tanta, Egypt, the magnetic field was calibrated with 2,2-diphenyl-1-picrylhydrazine purchased from Aldrich. TGA measurements were carried out on a SHIMADZU thermogravimetric analyzer in dry nitrogen with a heating rate of $10^\circ\,\mathrm{min}^{-1}$ using the TA – 50 WSI program. Microanalyses of carbon, hydrogen and nitrogen were carried out at the Microanalytical Center, Cairo University, Giza, Egypt. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey Alfa, Model No. MKI, magnetic susceptibility balance with $Hg[Co(CNS)_4]$ as calibrant. Conductivities were measured for solutions of the complexes in DMF (1×10^{-3} M) using a Model LBR 40A, conductivity meter (Wissenschaftlich–Techmische Werkstatten, D8120 Weilheim, Germany). Also, the conductometric titrations used for the determination of composition of complexes were carried out by titrating a certain volume of 10^{-3} M Fe(III) ion in 50% DMF/water mixture with 10^{-2} M Schiff base. The corrected conductivity values were plotted *versus* the molar ratio (Fe(III) : L). The plots gave straight lines intersecting at the molar ratio of the formed chelates. Melting points of the compounds were determined using a Gallen Kamp, England, electric melting point apparatus.

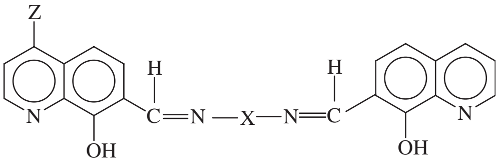
Screening of the investigated compounds for algicidal activities was performed via Czpeck's agar medium, using the disc diffusion method as follows:

Filter paper discs (5 mm in diameter) were impregnated with 100 ppm of each compound in DMF, which was used as a control. Individual discs were placed aseptically on the surface of Czapeck's agar medium seeded with the alga *Chloerella* sp at 30°C for 7 days. The diameter of the inhibition zone was measured and the percentage inhibition was calculated.

The other physical measurements and analyses are the same as previously described [17, 18].

2.2. *Preparation of ligands*

2.2.1. Symmetrical Schiff bases. Schiff bases were prepared according to the known procedures of Diehl and Hach [19] by condensation of (0.01 mol) aliphatic or aromatic diamines with (0.02 mol) 7-formyl-8-hydroxyquinoline or 4-chloro-7-formyl-8-hydroxyquinoline in absolute ethanol. The solids were separated and purified by repeated crystallization from 80% aqueous ethanol. % yield of the ligands and m.p. (°C) values are collected in table 1. On the basis of elemental analyses (table 1), IR spectra (table 2), ^{1}H NMR spectra (table 2) and mass spectra (figure 1), the symmetric Schiff bases have the following formula:



Compounds	X	Z
L^1	$(CH_2)_2$	H
L^2	$(CH_2)_3$	H
L^3	O-ph	H
L^4	$(CH_2)_2$	Cl
L^5	$(CH_2)_3$	Cl

2.2.2. Unsymmetric Schiff base. The unsymmetric Schiff-base ligands in the present investigation were prepared as follows:

(i) Condensation of (0.01 mol) of acetylacetone or benzoylacetone with (0.01 mol) aliphatic and aromatic diamines was carried out in absolute ethanol. The ethanolic solutions were refluxed for about 4 h; yellow products were separated, filtered off and washed several times with ethanol and then dried *in vacuo*.

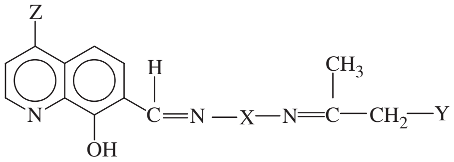
(ii) The second step involved refluxing (0.01 mol) of the above products with (0.01 mol) 7-formyl-8-hydroxyquinoline or 4-chloro-7-formyl-8-hydroxyquinoline in absolute ethanol for 6 h on a water bath. After cooling, the solids obtained were filtered off

Table 1. Results of microanalysis of the Schiff-base ligands under investigation.

Ligands	Colours	% Yield[a]	m.p. (°C)	Elemental analysis Found (Calculated) %		
				% C	% H	% N
L^1	Pale brown	78	172	71.30 (71.35)	5.1 (4.86)	15.60 (15.14)
L^2	Brown	76	190	72.20 (71.87)	5.7 (5.20)	14.60 (14.58)
L^3	Buff	72	195	75.00 (74.64)	4.43 (4.31)	13.73 (13.39)
L^4	Pale brown	75	201	59.81 (60.14)	3.70 (3.64)	12.52 (12.76)
L^5	Reddish brown	76	211	61.01 (60.93)	4.23 (3.97)	12.80 (12.36)
L^6	Brown	70	198	69.27 (68.70)	6.08 (6.40)	14.08 (14.14)
L^7	Reddish brown	68	205	68.91 (69.45)	6.84 (6.75)	13.21 (13.50)
L^8	Brown	65	260	73.05 (73.04)	5.34 (5.51)	11.81 (12.17)
L^9	Reddish brown	68	180	72.91 (73.50)	5.80 (5.85)	11.31 (11.64)
L^{10}	Reddish brown	66	210	74.03 (74.00)	6.49 (6.46)	10.76 (11.26)
L^{11}	Brown	70	165	77.00 (76.70)	5.51 (5.16)	10.60 (10.34)
L^{12}	Brown	65	217	61.32 (61.54)	5.23 (5.43)	13.11 (12.67)
L^{13}	Brown	67	228	63.91 (64.20)	5.71 (5.94)	12.40 (12.48)

[a] % Yield of the ligands have been calculated from 7-formyl-8-hydroxquinoline or 4-chloro-7-formyl-8-hydroxyquinoline.

and purified by repeated crystallization from 80% aqueous ethanol, % yield and m.p. (°C) values are listed in table 1. The purity of the ligands were examined by elemental analyses (table 1), IR (table 2), ^{1}H NMR (table 2) and mass spectra (figure 2). The unsymmetric Schiff bases can be formulated as follows:



Compounds	X	Y	Z
L^6	$(CH_2)_2$	CH_3CO	H
L^7	$(CH_2)_3$	CH_3CO	H
L^8	o-ph	CH_3CO	H
L^9	$(CH_2)_2$	C_6H_5CO	H
L^{10}	$(CH_2)_3$	C_6H_5CO	H
L^{11}	o-ph	C_6H_5CO	H
L^{12}	$(CH_2)_2$	CH_3CO	Cl
L^{13}	$(CH_2)_3$	CH_3CO	Cl

The most important and characteristic bands of the IR spectra of symmetric and unsymmetric Schiff bases under investigation have been assigned. The data are shown in table 2.

The ^{1}H NMR spectra of the symmetrical Schiff bases (**1**, **2**, **4**) and unsymmetrical Schiff bases (**6**, **7**, **9**, **10**, **12**) (table 2) were recorded in deuterated DMSO (d_6) as

Table 2. IR spectral data of free ligands and their Fe(III) complexes. ^{1}H NMR signals of some selected ligands are included.

	IR spectra								^{1}H NMR spectra							
Compounds	ν_{H_2O} water	ν OH phenolic	$\nu_{C=O}$	ν C=N aliphatic	ν C=N aromatic	ν_{M-O}	ν_{M-N}	ν_{M-Cl}	δ CH$_3$	δ CH$_2$N	δ CH$_2$	δ CH=N	δ CH arom.	δ CH hetero.	δ OH ph.	H-bond
L^1		3200		1635	1580				–	3.10	–	5.90	7.45	8.1	8.7	10.3
FeIII, L^1	3340			1615	1580	500	455	375								
L^2		3230		1625	1580				–	2.55	3.95	6.15	7.25	8.2	8.8	11.00
FeIII, L^2	3340			1610	1850	505	465	380								
L^3		3200		1625	1580											
FeIII, L^3	3350			1615	1578	510	450	360								
L^4		3200		1635	1575				–	3.35	–	5.9	7.4	8.0	8.65	10.75
FeIII, L^4	3350			1620	1575	500	460	365								
L^5		3215		1625	1575											
FeIII, L^5	3350			1615	1575	520	470	375								
L^6		3200	1690	1630	1585				2.1	3.5	3.6	5.8	7.4	7.8	8.4	11.3
FeIII, L^6	3350		1670	1620	1583	515	470	370								
L^7		3210	1695	1625	1585				2.15	3.40	3.60	5.85	7.55	7.9	8.4	11.55
FeIII, L^7	3340		1675	1615	1580	515	475	370								
L^8		3250	1695	1630	1580											
FeIII, L^8	3335		1675	1615	1580	520	480	380								
L^9		3250	1690	1630	1580				2.15	3.45	3.60	5.75	7.35	7.8	8.7	11.30
FeIII, L^9	3320		1675	1620	1580	505	480	365								
L^{10}		3230	1680	1635	1590				2.10	3.55	3.65	5.80	7.25	8.1	8.75	11.5
FeIII, L^{10}	3300		1665	1625	1590	500	470	370								
L^{11}		3220	1680	1625	1590											
FeIII, L^{11}	3310		1665	1615	1590	510	455	365								
L^{12}		3220	1685	1622	1580				2.3	3.6	3.8	5.95	7.35	8.25	8.95	11.35
FeIII, L^{12}	3333		1670	1610	1583	505	455	365								
L^{13}		3210	1680	1620	1582											
FeIII, L^{13}	3330		1665	1610	1580	505	450	360								

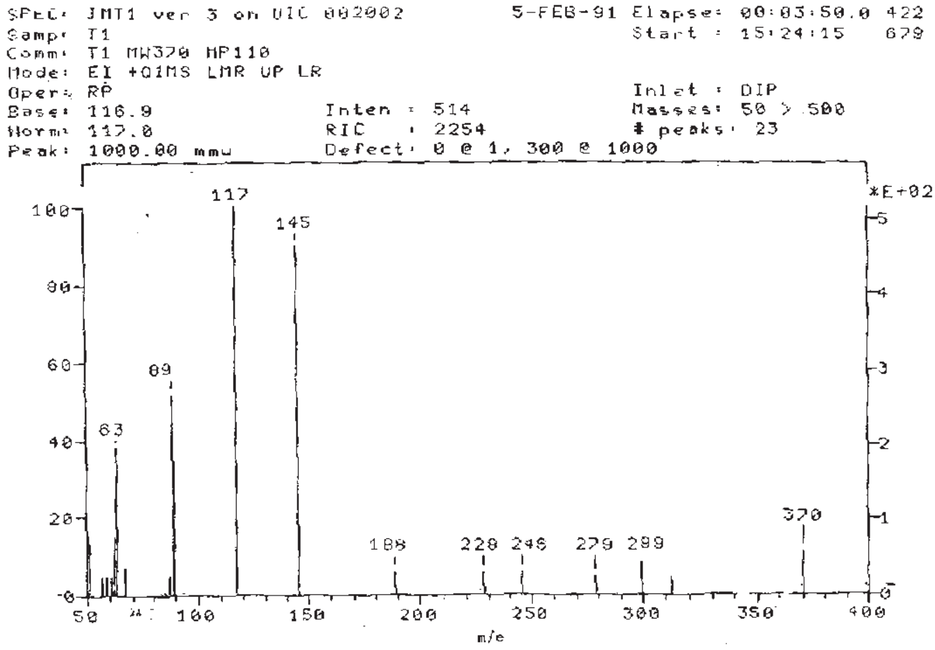


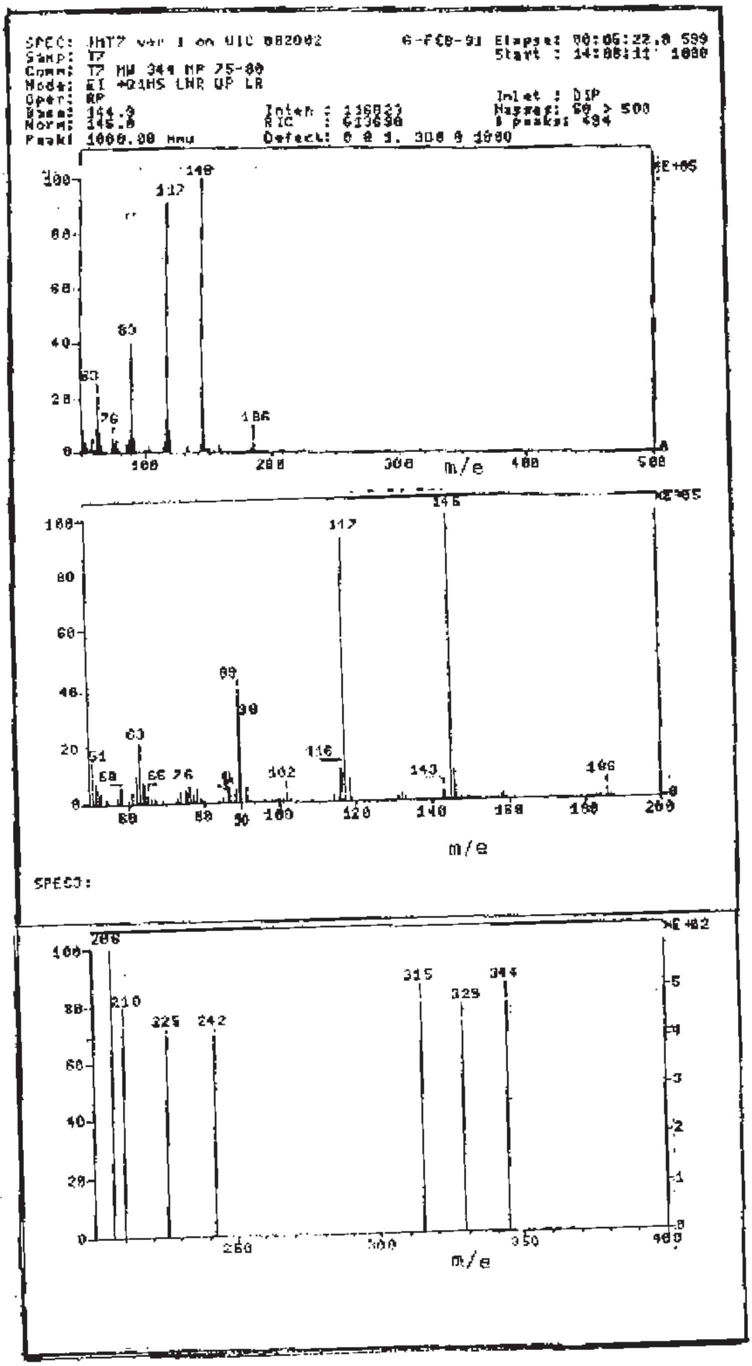
Figure 1. Mass spectra of (L^1) compound.

a solvent with TMS as internal standard. All compounds show a signal at 8.40–8.95 ppm which can be assigned to the phenolic OH group with integration equivalent to one proton. All compounds show a group of multiplets corresponding to the aromatic and hetero aromatic protons at 7.25–7.55 and 7.8–8.25 ppm, respectively. The ligands under investigation show a broad diffuse signal at 10.3–11.55 ppm which may be attributed to intramolecular hydrogen bonds between the phenolic OH group and the quinoline ring or the azomethine group [15]. The spectra of compounds **1**, **2** and **4** contain one signal at 2.55 and 3.35 ppm with integration equivalent to 4H ($I \equiv 4H$). This is due to CH_2N. Ligand **2** shows a band at 3.95, which may be assigned to δ CH_2–. For compounds **6**, **7**, **9**, **10** and **12** two signals are observed with integration equivalent to 4H and can be assigned to δ CH_2N and δ CH_2 methylene. the unsymmetric Schiff bases **6**, **7**, **9**, **10** and **12** show signals at 2.1–2.3 ppm, absent in the ^{1}H NMR spectra of symmetric Schiff bases **1**, **2** and **4**. Therefore, these signals can be assigned to δ CH_3 [16]. The signals at 5.8–6.15 ppm for all ligands under investigation may be assigned to CH=N.

The mass spectra of the symmetric Schiff base ligand **1** and unsymmetric Schiff base ligand **8** are shown in figures 1 and 2. The mass spectrum of each compound corresponds to its molecular weight (*m*/*e*).

2.3. *Preparation of metal complexes*

Ethanolic solutions of the Schiff bases (1 mmol) were added with constant stirring to an ethanolic solution of ferric chloride hexahydrate, $FeCl_3 \cdot 6H_2O$ (1 mmol or 2 mmol).



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Mode: EI +Q1MS LMR UP LR
Oper: RP                                         Inlet  : DIP
Base: 144.9              Inten : 136823          Masses: 50 > 500
Norm: 145.0              RIC   : 613690          # peaks: 494
Peak: 1000.00 mmu        Defect: 0 @ 1. 300 @ 1000
```

Figure 2. Mass spectra of (L^8) compound.

The mixture was refluxed for 2 h on a water bath, during which the solid complex precipitated. The precipitate was filtered off, washed several times with ethanol to remove any traces of metal ion or free ligand, and finally washed with diethyl ether and then dried *in vacuo*, yield 62–75%. All the solid complexes are soluble in DMF but insoluble in common organic solvents.

3. Results and discussion

The stoichiometries of the complexes formed between Fe(III) and symmetric and unsymmetric Schiff-base ligands determined by conductometric titrations in solution. The conductance molar ratio curves of Fe(III) with unsymmetric Schiff bases (**6**–**13**) have breaks denoting the formation of (1 : 1) (Fe(III) : L) mononuclear complexes. Symmetric ligands (**1**–**5**) display a break at a mole ratio 2 : 1 (Fe(III) : L) due to formation of binuclear complexes. The curves exhibit a gradual increase in conductance with increasing volume of the ligand added, reflecting the displacement of H^+ from the ligand by Fe(III), through complexation [20].

3.1. *Elemental analysis and conductance measurements*

The analytical data, table 3, support the stoichiometric ratio of the complexes formed in the solid state 1 : 1 and 2 : 1 (Fe(III) : L). The elemental analyses of Fe(III) complexes of the symmetric Schiff-base ligands (table 3), indicate that the stoichiometry of the complexes is 2 : 1 (Fe(III) : L), denoting binuclear complexes in which the Schiff bases bind to two metal ions. The elemental analyses values of the Fe(III) complexes of unsymmetric Schiff bases (table 3), indicate a 1 : 1 (Fe(III) : L) stoichiometry.

Molar electrical conductance values in DMF of Fe(III) complexes are shown in table 3. The low conductance values for all the complexes indicate the non-ionic character of the complexes prepared and also that the chloride ion is coordinated to Fe(III) [21].

3.2. *Thermogravimetric analysis*

The TGA data for complex (**1**), $[Fe_2L^1Cl_4(H_2O)_4]H_2O$ and complex (**6**), $[FeL^6Cl_2]2H_2O$ lead to the following conclusions:

(a) The weight loss within the temperature range 70–105°C could be correlated with the removal of lattice water for both complexes **1** and **6**. The four coordinated water molecules in complex **1** were eliminated between 120 and 270°C in one step. The number of water molecules determined from the thermograms confirms the data obtained by elemental analysis.
(b) The Cl^- ion was lost as HCl [22] in the temperature range 290–395°C.
(c) The decomposition temperature for the Fe(III) complex of the symmetric Schiff base, complex **1** is higher than for the Fe(III) complex of the unsymmetric Schiff base, complex **6**, i.e., the binuclear complex is more stable than the mononuclear one.

The results of TGA for the complexes **1** and **6** indicates the following:

$$\boxed{[Fe_2L^1Cl_4(H_2O)_4]H_2O}$$

$$\Big\downarrow \; -H_2O \quad 70\text{–}95^{\circ}C$$

$$[Fe_2L^1Cl_4(H_2O)_4]$$

% found 4.65 | % calculated 4.86

$$\Big\downarrow \; -4H_2O \quad 120\text{–}270^{\circ}C$$

$$[Fe_2L^1Cl_4]$$

% found 12.65 | % calculated 12.61

$$\Big\downarrow \; -4Cl^- \quad 310\text{–}395^{\circ}C$$

$$[Fe_2L^1]$$

% found 32.75 | % calculated 32.50

$$\Big\downarrow \; 495^{\circ}C \quad \text{decomposition}$$

$$2Fe_2O_3$$

$$\boxed{[FeL^6Cl_2]2H_2O}$$

$$\Big\downarrow \; -2H_2O \quad 80\text{–}105^{\circ}C$$

$$[FeL^6Cl_2]$$

% found 7.55 | % calculated 7.83

$$\Big\downarrow \; -2Cl^- \quad 290\text{–}370^{\circ}C$$

$$[FeL^6]$$

% found 23.10 | % calculated 23.26

$$\Big\downarrow \; 440^{\circ}C \quad \text{decomposition}$$

$$Fe_2O_3$$

Table 3. Microanalytical results and conductance measurements for some Fe(III) complexes of Schiff bases.

No	Complexes	Colour	Microanalytical results (Found) Calculated %C	%H	%N	$\%Fe^{3+}$	Λ (Ω^{-1} cm^2 mol^{-1})
1	$[Fe_2L^1Cl_4(H_2O)_4]H_2O$	Brown	(36.90) 37.08	(3.40) 3.65	(7.51) 7.87	(16.11) 15.73	20
2	$[Fe_2L^2Cl_4(H_2O)_4]H_2O$	Brown	(38.31) 38.02	(3.72) 3.86	(7.20) 7.71	(15.64) 15.43	21
3	$[Fe_2L^3Cl_4(H_2O)_4]2H_2O$	Brown	(40.21) 40.01	(3.91) 3.60	(7.31) 7.20	(14.81) 14.40	22
4	$[Fe_2L^4Cl_4(H_2O)_4]H_2O$	Reddish brown	(33.50) 33.80	(3.15) 3.07	(6.81) 7.17	(14.70) 14.34	18
5	$[Fe_2L^5Cl_4(H_2O)_4]H_2O$	Reddish brown	(34.55) 34.72	(3.41) 3.27	(7.30) 7.04	(13.80) 14.09	19
6	$[FeL^6Cl_2]2H_2O$	Dark red	(44.40) 44.44	(4.63) 4.79	(8.83) 9.15	(12.00) 12.20	10
7	$[FeL^7Cl_2]H_2O$	Brown	(47.62) 47.47	(4.55) 4.84	(9.11) 9.23	(12.60) 12.31	12
8	$[FeL^8Cl_2]H_2O$	Reddish brown	(51.34) 51.53	(3.90) 4.19	(8.80) 8.59	(11.11) 11.45	18
9	$[FeL^9Cl_2]EtOH \cdot H_2O$	Brown	(48.41) 48.09	(4.81) 5.10	(7.25) 7.65	(9.81) 10.20	15
10	$[FeL^{10}Cl_2]2H_2O$	Reddish brown	(51.70) 51.59	(4.60) 4.86	(8.30) 7.85	(10.30) 10.47	11
11	$[FeL^{11}Cl_2]H_2O$	Dark red	(56.93) 56.62	(4.25) 3.99	(7.91) 7.62	(10.21) 10.16	10
12	$[FeL^{12}Cl_2]H_2O$	Brown	(43.15) 42.90	(4.10) 3.99	(9.30) 8.83	(11.70) 11.78	13
13	$[FeL^{13}Cl_2]H_2O$	Brown	(44.50) 44.13	(4.21) 4.24	(8.83) 8.58	(11.21) 11.44	12

3.3. *Infrared spectra*

The IR spectral data of the ligands and their Fe(III) complexes are listed in table 2. Comparing the IR spectra of the Fe(III) solid complexes with those of the free ligands, one may conclude the following:

(a) The IR spectra of each complex under investigation exhibits a broad band around 3300–3350 cm^{-1} attributed to νOH of water and/or ethanol molecules associated with the complex formation.
(b) The ligands show a broad band at 3200–3250 cm^{-1} due to the phenolic OH group of the conjugate chelate ring involving the $\mathrm{OH}\cdots\mathrm{N{=}C}$ hydrogen bond [23]. This band disappears on complex formation indicating deprotonation of the phenolic OH group and coordination of the metal ion to the phenolic oxygen [24].
(c) The IR spectra of the unsymmetric Schiff bases exhibit a band at 1680–1690 cm^{-1} corresponding to ν(C=O) of the free ligand. These bands shift to lower frequency on complex formation (1665–1675) cm^{-1} by (15–20) cm^{-1}, hence the oxygen atom of the keto form of β-diketone should bond with the Fe(III).
(d) Bands due to ν(C=N) of the quinoline moiety at 580–1590 cm^{-1} in the IR spectra of all ligands, remain at the same position in the metal complexes, indicating that the N-atom of the aromatic ring does not participate in complex formation [25, 26].
(e) The bands at 1635–1660 cm^{-1} corresponding to the azomethine ν(C=N) of the free ligands shift to lower frequency on complex formation by 10–20 cm^{-1}, hence the nitrogen atom of the azomethine group coordinates to Fe(III) in all complexes. All complexes show new bands at 500–520, 450–480 and 360–380 cm^{-1}, which could be assigned to ν(M–O), (M–N) and (M–Cl) [27], respectively.

3.4. *Electronic spectra*

Electronic spectra of the Fe(III) complexes were obtained in DMF solutions; the $\lambda_{\max}$ values and the molar absorptivity $\varepsilon_{\max}$ are listed in table 4. Transitions due to the

Table 4. Electronic spectra of Fe(III) Schiff bases in DMF, g_{eff} values and magnetic data.

		$\lambda_{\max}$(nm) in DMF ($\varepsilon \times 10^4\ \mathrm{L\,mol^{-1}cm^{-1}}$)						
No	Complexes	π–π* aromatic	π–π* C=O	π–π* C=N	CT L → M	d–d transition $^6A_{1g}$–$^4T_{1g}$ assignment	g_{eff}	μ_{eff} BM/M
1	Fe(III), L^1	285 (0.16)		400 (0.49)	470 (0.55)	595 (0.09)	2.11	4.50
2	Fe(III), L^2	290 (0.19)		400 (0.52)	480 (0.58)	605 (0.11)		4.70
3	Fe(III), L^3	280 (0.18)		405 (0.51)	475 (0.60)	590 (0.10)		4.35
4	Fe(III), L^4	280 (0.20)		400 (0.55)	480 (0.60)	600 (0.11)		4.65
5	Fe(III), L^5	285 (0.18)		405 (0.48)	480 (0.54)	600 (0.08)		4.73
6	Fe(III), L^6	300 (0.13)	365 (0.30)	410 (0.40)	490 (0.49)	610 (0.06)	2.09	5.95
7	Fe(III), L^7	280 (0.14)	370 (0.34)	415 (0.41)	490 (0.50)	620 (0.07)		5.87
8	Fe(III), L^8	285 (0.13)	370 (0.28)	415 (0.38)	490 (0.45)	610 (0.06)		5.90
9	Fe(III), L^9	285 (0.11)	365 (0.33)	415 (0.37)	490 (0.43)	630 (0.07)		5.92
10	Fe(III), L^{10}	290 (0.09)	380 (0.28)	405 (0.35)	485 (0.43)	615 (0.055)		5.83
11	Fe(III), L^{11}	290 (0.12)	380 (0.31)	410 (0.40)	485 (0.64)	625 (0.05)		5.81
12	Fe(III), L^{12}	285 (0.13)	385 (0.30)	405 (0.41)	480 (0.47)	615 (0.06)		5.63
13	Fe(III), L^{13}	290 (0.1)	385 (0.28)	405 (0.36)	480 (0.46)	615 (0.05)		5.52

ligands are characterized by their higher ε_{max} values, while those due to d–d transitions of the central transition metal ions are lower. Binuclear complexes have higher ε_{max} values than mononuclear complexes. The electronic spectra of all Fe(III) complexes of the symmetric Schiff bases have three bands with λ_{max} in the region 280–300, 400–415 and 470–490 nm assigned to π–π^* transition within the organic molecules, π–π^* of the C=N group and a ligand to metal ion charge transfer (LMCT) (L→Fe(III)), respectively, as a result of complex formation. The Fe(III) complexes of unsymmetric Schiff bases have, in general, four bands in the ranges 280–290, 365–385, 405–415 and 475–485 nm. The first band can be assigned to a π–π^* transition within the organic molecule. The second and the third bands can be assigned to π–π^* transitions of C=O and C=N groups, respectively. The last band can be assigned to a charge transfer band L → Fe(III). The electronic spectra of all complexes under investigation also exhibit one band at 590–630 nm, assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$ characteristic of octahedral structure [28, 29].

3.5. *Magnetic properties*

Iron (III) has a $3d^5$ configuration and its complexes may be either high-spin ($S = 5/2$, HS), intermediate-spin ($S = 3/2$, IS), or low-spin ($S = 1/2$, LS). The majority of iron (III) compounds are HS or LS [30].

A relatively small number of six-coordinate iron (III) compounds can exhibit both the HS and LS configurations. A spin transition (LS→HS) occurs from coupling between the intraionic electron transfer $e_g \leftrightarrow t_{2g}$, changes in the metal–ligand bond distance and the crystal lattice vibrations [31].

Values of the magnetic moment for all complexes under investigation are summarized in table 4. Magnetic susceptibility measurements for the mononuclear complexes at room temperature, 300 K, are indicative of five unpaired electrons per Fe(III), $\mu_{eff} = 5.52$–5.95 revealing high spin octahedral geometry [32]. The magnetic moment values for the binuclear complexes were lower than the value corresponding to five unpaired electrons perhaps due to antiferromagnetic exchange interaction between the iron atoms [23, 33], suggesting the possibility of spin-coupling [28, 34]. Another possibility is that the reduced moment represents a solid state intermolecular interaction, rather than an intramolecular coupling.

3.6. *EPR spectra*

Solid state EPR spectra (figure 3) of complex **1** and complex **6** were measured in the solid state at room temperature.

(1) The EPR spectra of both mononuclear and binuclear complexes exhibit a broad signal with no obvious hyperfine structure.
(2) The values of g_{eff} (table 4) for both binuclear or mononuclear complexes and line broadening together with width of the signals may suggest octahedral structure around the Fe(III) ion [35], with two Cl^- ions occupying equatorial position.
(3) Both mononuclear and binuclear Fe(III) complexes show positive deviation in the g_{eff} value of free electron, 2.0023, due high covalent character in the bonding between the ligand and Fe(III) [36].

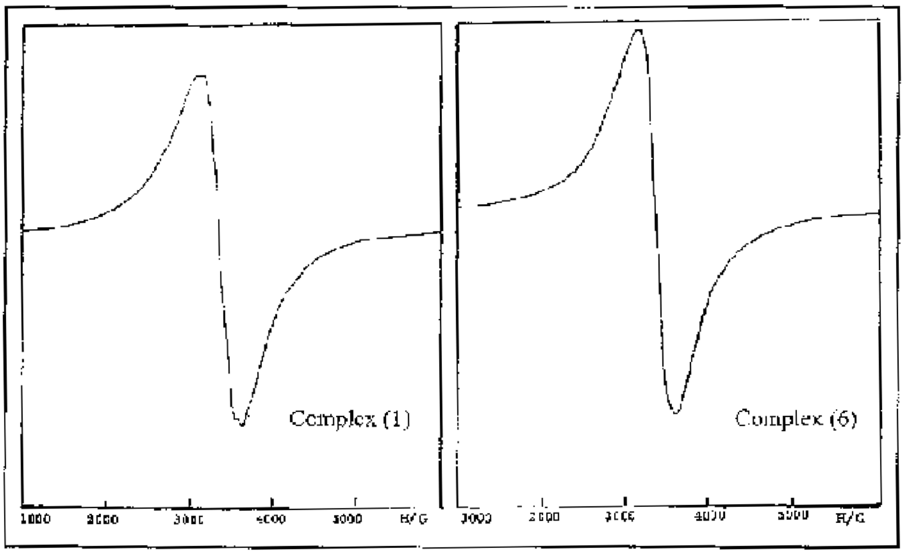


Figure 3. X-Band and ESR spectra of iron (III) complexes (**1** and **6**) at 300 K.

Table 5. Biological activities of the Schiff-base ligands and their iron (III) complexes.

Compound	Clear zone (cm)	% Inhibition*
L^1	2.54	28.30 ± 0.21
L^2	2.55	28.81 ± 0.14
L^4	2.76	30.84 ± 0.17
L^5	2.89	$32.01 + 0.11$
$Fe^{3+} : L^1$	3.07	33.37 ± 0.14
$Fe^{3+} : L^2$	3.00	33.33 ± 0.18
$Fe^{3+} : L^4$	3.44	38.26 ± 0.16
$Fe^{3+} : L^5$	4.23	46.93 ± 0.22
L^6	3.38	38.12 ± 0.21
L^7	3.20	35.56 ± 0.33
L^{12}	3.45	38.29 ± 0.28
L^{13}	3.61	39.71 ± 0.31
$Fe^{3+} : L^6$	4.55	50.61 ± 0.32
$Fe^{3+} : L^7$	4.33	48.15 ± 0.39
$Fe^{3+} : L^{12}$	4.55	49.99 ± 0.41
$Fe^{3+} : L^{13}$	5.11	56.77 ± 0.31

* Values are the mean of three experiments and (±) means the standard deviation.

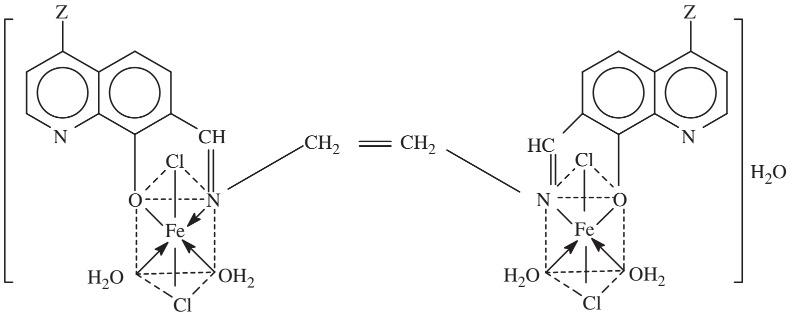
3.7. ***Biological activities***

The results of the biological activity tests of the ligands and their iron complexes are presented in table 5. The compounds show variable degrees of inhibition. The algalcidal studies show that the unsymmetric Schiff base ligands were more toxic than symmetric Schiff-base ligands. Fe(III) binuclear complexes were less toxic than Fe(III) mononuclear complexes. Schiff bases containing chloro groups were found to be more toxic than those without a chloro group [8, 37]. Generally, the order of toxicity observed takes place as follows:

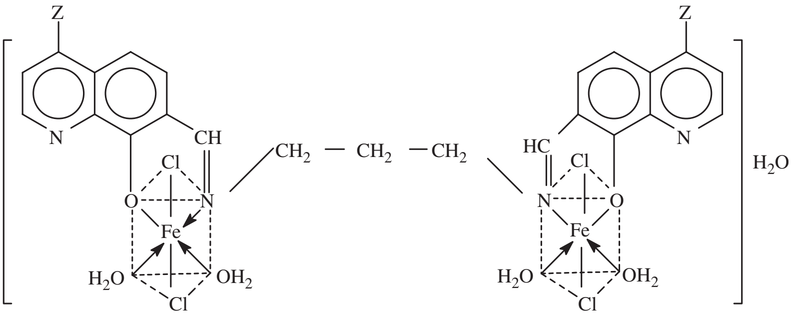
Fe(III) mononuclear complex > Fe(III) binuclear complex > unsymmetric Schiff-base ligand > symmetric Schiff-base ligand.

4. Conclusions

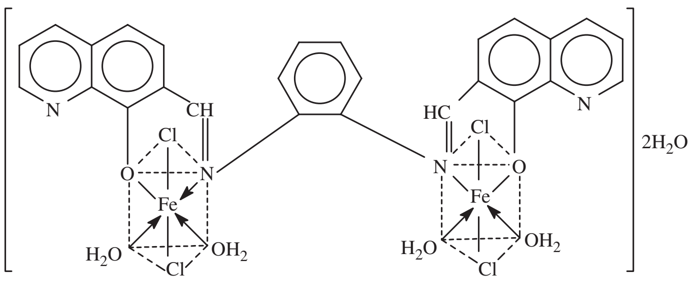
Based on the above results, the bonding of Fe(III) to the symmetric and unsymmetric Schiff bases takes place as follows:



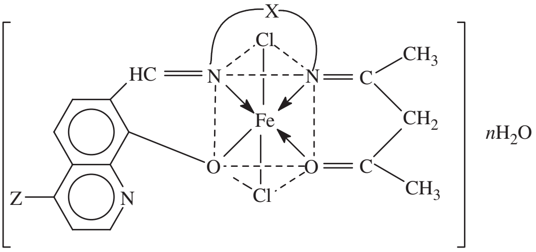
Complexes **1** (Z = H) and **4** (Z = Cl)



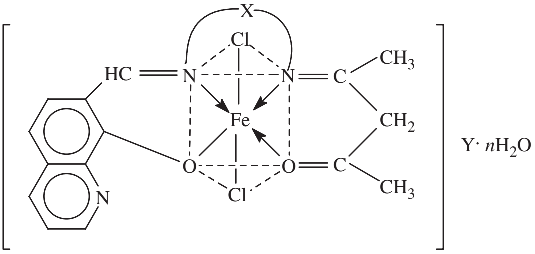
Complexes **2** (Z = H) and **5** (Z = Cl)



Complex **3**



Complex **6** (X = $(CH_2)_2$, Z = H, *n* = 2),
7 (X = $(CH_2)_3$, Z = H, *n* = 1),
8 (X = o-ph, Z = H, *n* = 1),
12 (X = $(CH_2)_2$, Z = Cl, *n* = 1) and
13 (X = $(CH_2)_3$, Z = Cl, *n* = 1)



Complex **9** (X = $(CH_2)_2$, Y = EtOH , *n* = 1),
10 (X = $(CH_2)_3$, Y = O, *n* = 2) and
11 (X = o-ph, Y = O, *n* = 1)

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