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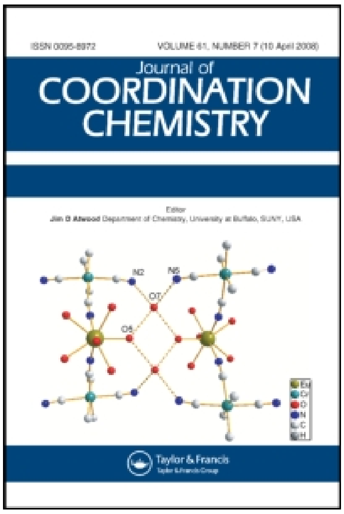

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FORMATION OF IRON(III) CLUSTER COMPLEXES WITH A NEW (N_2O_2) SCHIFF BASE

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Two new series of Fe(III) Schiff-base complexes have been prepared and characterized by elemental and thermogravimetric analyses, IR, electronic, ESR and Mössbauer spectra. The Fe(III) complexes possess octahedral, pseudo-octahedral or pseudo-tetrahedral geometries around Fe(III), depending on the nature of the Schiff-base ligand used.

Keywords: Fe(II) cluster complexes; Normal Fe(II) complexes; Schiff-base complexes

INTRODUCTION

Fe(III) Schiff-base complexes have been the subject of numerous investigations owing to their important biological and technical applications [1–7]. We have prepared two new aldehydes, 3-formyl-2-hydroxy acetophenone (FHA), and 3,5-diformyl-4-hydroxyacetophenone (DFHA). From these two aldehydes we were able to prepare new Schiff-base ligands with 1,2-ethylenediamine or 1,3-propylenediamine, which were used to prepare and characterize a number of new Fe(III) Schiff-base complexes.

An investigation of the effect of varying the nature of the Schiff-base ligands on the structure and properties of Fe(III) complexes was also attempted in order to elucidate their structures and geometry.

EXPERIMENTAL

Preparation of ligands

Formylation of *o*- and *p*-hydroxyacetophenone was carried out according to the procedures of sen and Ray [8]. *o*-Hydroxyacetophenone (1.36 g, 0.01 mol) was dissolved in chloroform (8.5 cm^3, 0.1 mol) and 90 cm^3 of 15% NaOH. The reaction mixture was heated under reflux for 4 h, on a water bath, during which the color of the solution

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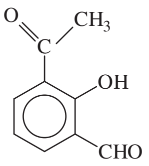
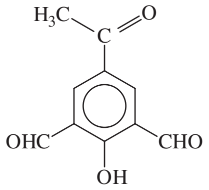
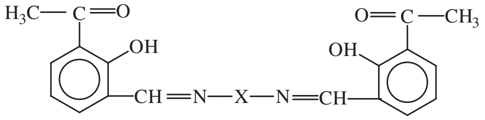
changed to red. After cooling, the pH of the solution was adjusted to 4–5. The oily product obtained solidified on addition of 15 cm^3 of methanol. The precipitate formed was filtered off, and washed with water to remove any untreated *o*-hydroxyacetophenone. Formylation of *o*-hydroxyacetophenone leads to 3-formyl-2-hydroxy acetophenone (FHA) whereas formylation of *p*-hydroxyacetophenone gives 3,5-diformyl-4-hydroxyacetophenone (DFHA). The solids separated were purified by repeated crystallization from ethanol to constant melting point. The formylated compounds involved in the present study have the following structures:



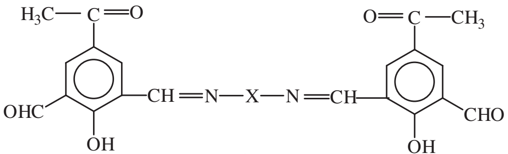


	(FHA)	(DFHA)
Color	Yellow	Light brown
m.p. (°C)	260	290
% yield	65–70	60–65

The new Schiff-base ligands were prepared by condensation of FHA or DFHA with ethylene or propylenediamine according to the procedures of Diehl and Hach [9]. The purities of FHA, DFHA and the Schiff-base ligands under investigation were tested by elemental analysis, IR, ^1H NMR, UV–Vis and mass spectra as described elsewhere [7]. The Schiff bases included in the present study have the following general structural formulae:



(I)



(II)

where

X	Ligand abbreviation	
$(CH_2)_2$	BHMAE (I)	BFHMAE (II)
$(CH_2)_3$	BHMAP (I)	BFHMAP (II)

Preparation of Complexes

0.001735 mol of KOH dissolved in the least amount of water (~2 cm^3) was added to 0.001 mol of the ligand and dissolved in 50 cm^3 of ethanol to convert it to an ionic form. The mixture was stirred for 30 min, after which 0.001 mol of $FeSO_4 \cdot 6H_2O$ dissolved in doubly distilled water (~5 cm^3) was added to the mixture. The reaction mixture was stirred for about 40 h over three days. The precipitated complex was then filtered, washed several times with doubly distilled water to eliminate the salt, then with a small amount of ethanol to remove any traces of free ligand and finally with diethylether. It was then dried *in vacuo*.

Preparation of Polynuclear (Cluster) Complexes

The procedures described above were followed but in this case 0.005 mol of $Fe_2(SO_4)_3 \cdot H_2O$ was used. The complexes are partially soluble in DMF, EtOH, $CHCl_3$ and insoluble in most common organic solvents viz., benzene, toluene. The complexes are insoluble in inorganic acids even with boiling so X-ray fluorescence (XRF) was used to determine the metal and sulfur contents for each complex under investigation.

Physical measurements

Quantitative analyses of metal, sulfur and chloride

These were carried out using a tube excited X-ray fluorescence analyzer (TEFA) Model 6111.

Electron spin resonance (ESR)

ESR spectra were recorded on a JEOL Microwave unit, JES-FE_2XG spectrometer at the central laboratories of Tanta University. The magnetic field was calibrated with 2,2-diphenyl-1-picrylhydrazyl purchased from Aldrich.

Mössbauer spectra

The Mössbauer spectra were obtained on a Mössbauer spectrometer Ms-900 ranges using ^{57}Co(Rh) source at the central laboratories of Tanta University. The calibration of the spectrometer was done with a standard αFe_2O_3absorber. The measurements were performed using a velocity drive in constant acceleration mode. Data analyses were done by computer using the MM/Sirius program.

Thermo-gravimetric analysis (TGA)

TGA curves were obtained using a NETZSCH Gerateban Bestell Nr 348472 C instrument equipped with a thermobalance. Samples ($\sim$50 mg) were heated at a programmed rate of 5° min^{-1} in a dynamic N_2 atmosphere. The sample was contained in a boat-shaped platinum pan suspended in the center of a furnace.

The other physical measurements were carried out as previously described [10,11].

RESULTS AND DISCUSSION

Two types of Fe(III) Schiff-base complexes were isolated, Complexes **1**–**4** and cluster complexes **5**–**8** as indicated by the results of elemental analysis (Table I). Addition of Fe(II) sulfate to the ligands gave normal Fe(III) complexes whereas

TABLE I Microanalysis results and ESR g_{eff} values of normal and cluster Fe(III) Schiff's base complexes

Complex	*Formula*	*Color*	*m.p (°C)*	*Analysis (%)*		*(Calcd.) Found*		g_{eff}
				C	*H*	*S*	*M*	
1	$[Fe_2(BHMAE)(O)(OH)_2(H_2O)_3] \cdot \frac{1}{2}H_2O$	Red brown	320	(42.54)	(4.05)	–	(18.4)	1.992
				41.74	4.69		19.4	
2	$[Fe_2(BHMAP)_2(OH)_2] \cdot H_2O$	Red brown	270	(56.51)	(4.53)	–	(11.9)	2.0008
				56.5	4.93		12.6	
3	$[Fe(BFHMAE)(OH)(H_2O)] \cdot 4\frac{1}{2}H_2O$	Light brown	310	(45.70)	(5.00)	–	(8.72)	2.0857
				45.67	5.54		9.69	
4	$[Fe_2(BFHMAP)O_2] \cdot EtOH$	Light brown	320	(49.50)	(4.9)	–	(17.33)	2.055
				49.18	4.26		18.36	
5	$[Fe_8(BHMAP)_5(O)_6(SO_4)(H_2O)_5]$	Light brown	> 360	(49.37)	(4.23)	(1.05)	(17.52)	2.0023
				49.41	4.31	1.25	17.57	
6	$[Fe_8(BHMAE)_5(O)_6(SO_4)(H_2O)_5]$	Light brown	325	(48.33)	(4.42)	(1.27)	(17.55)	2.0083
				48.39	4.03	1.29	18.06	
7	$[Fe_8(BFHMAP)_5(O)_6(SO_4)(H_2O)_{11}] \cdot 4EtOH$	Light brown	230	(47.20)	(5.2)	(0.316)	(14.38)	2.0023
				48.28	4.68	1.02	14.35	
8	$[Fe_5(BFHMAE)_6(OH)(H_2O)_3(SO_4)] \cdot 3H_2O$	Light brown	300	(53.84)	(4.23)	(0.64)	(9.63)	1.9695
				53.93	4.26	1.09	9.53	

% Microanalysis result (calculated) Found.

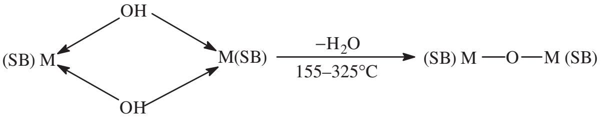
addition of Fe(III) sulfate gave Fe(III) clusters. This behavior is in line with the preparation of different Fe(III) complexes and Fe(III) cluster complexes as indicated elsewhere [12–14]. Most of the prepared complexes have one or more water or EtOH molecules associated with the complex, which are not removed by static vacuum for 3 h at room temperature. The cluster Fe(III) Schiff-base complexes gave no white precipitate with $BaCl_2$ solution, indicating that SO_4^{2-} is coordinated in these complexes.

Thermogravimetric analysis of the complexes under investigation indicated the following:

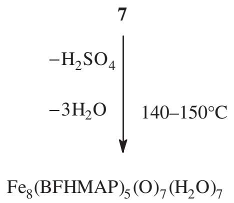
(a) Lattice water molecules associated with complex formation are removed at 60–85°C whereas coordinated water and/or ethanol molecules are volatilized within the temperature range 130–165°C.

(b) Decomposition of the complexes to metal oxides takes place in the temperature range 160–460°C. The decomposition occurs in more than one step for complex **2** but takes place in one step with the other complexes.

(c) For complex **2** the removal of bis μ-hydroxo can be formulated as



(d) Coordinated SO_4^{2-} is volatilized for complex **7** at 146–150°C as follows:



IR spectral data of the free ligands are given in Table II, and those of the solid complexes of the ligands BHMAE, BHMAP, BFHMAE and BFHMAP with Fe^{3+} in Table III. The following points arise from a comparison of the two set of data.

(a) The spectra of most complexes exhibit a broad band around 3422–3387 cm^{-1} which could be assigned to ν_{OH} of water or ethanol molecules associated with the complex. Bands occurring in the region 989–933 and 677–600 cm^{-1} which are absent in the spectra of free ligands, are attributed to $\rho(H_2O)$ and $\rho\omega(H_2O)$, respectively, of the coordinated water.

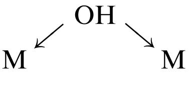
(b) The ketonic $\nu_{C=O}$ located at 1798–1766 cm^{-1} in the IR spectra of all the ligands and also $\nu_{H-C=O}$ in the IR spectra of BFHMAP and BFHMAE ligands at 1740–1733 cm^{-1} are present at the same positions in the IR spectra of the metal complexes, indicating that neither ketonic nor aldehydic C=O groups participate in complex formation.

(c) The IR spectra of the dehydrated iron(III) complexes with the ligands show the disappearance of ν_{OH} phenolic, δ(OH) and ν_{C-OH} bands 3730–3400, 1537–1430 and 1294–1175 cm^{-1}, respectively, in the IR spectra of the free ligands indicating proton displacement from the phenolic OH groups through metalation. Thus, bonding of metal ions to the ligands takes place through two covalent links with the oxygen of the phenolic groups. The bands at 1695–1675 cm^{-1}, corresponding to $\nu_{C=N}$ of the free ligands, shift to lower frequency on complex formation by 73–55 cm^{-1}, indicating that the azomethine nitrogen atom also contributes to the bond in all the metal complexes. This shift is due to coordination of the azomethine nitrogen to the metal atom, which reduces the electron density on the azomethine linkage. This finds support in two new bands in the IR spectra of all metal chelates, which are absent in the IR spectra of the free ligands, at 590–444 and 489–366 cm^{-1}, which could be assigned to ν_{M-O} and ν_{M-N}, respectively.

(d) The new band observed in the IR spectra of the $[Fe(BFHMAE)(OH)(H_2O)]\cdot 4\frac{1}{2}H_2O$ and $[Fe_2(BHMAE)(O)(OH)_2(H_2O)_3]\cdot\frac{1}{2}H_2O$ complexes at 1144–1044 cm^{-1}, which is absent in the IR spectra of the free ligands, could be assigned to M–OH.

(e) The IR spectra of $[Fe_8(BHMAP)_5O_6(SO_4)(H_2O)_5]$, $[Fe_8(BHMAE)_5O_6(SO_4)(H_2O)_5]$, $[Fe_8(BFHMAP)_5O_6(SO_4)(H_2O)_4]\cdot 4EtOH$ and $[Fe_5(BFHMAE)_6(OH)(H_2O)_3\ SO_4]\cdot 3H_2O$ show the SO_4^{2-} bands at ν_1 910–940, ν_2 438–470, ν_3 1188–1199 and ν_4 620–633 cm^{-1}. The position of SO_4^{-2} bands show chelating bidentate sulfate ions coordinated to the central Fe(III) ion by bridging through two oxygens [15,16]. This is in line with earlier studies on sulfato complexes, where SO_4^- can coordinate through two oxygen atoms as a bridging bidentate donor.

(f) The appearance of a new band located at 956–900 cm^{-1} in the IR spectra of the $[Fe_2(BHMAP)_2(OH)_2]H_2O$, $[Fe_2(BHMAE)(O)(HO)_2(H_2O)_3]\cdot\frac{1}{2}H_2O$ and $[Fe_5(BFHMAE)_6(OH)(H_2O)_2(SO_4)]\cdot 4H_2O$ which is absent in the IR spectra of the free ligands, leads to the assumption that this band can be assigned to the stretching mode of a bridging M–OH in the structure, *i.e.*,



$$M \swarrow \overset{OH}{} \searrow M$$

(g) IR spectra of $[Fe_8(BFHMAP)_5(O)_6(SO_4)(H_2O)_{11}]\cdot 4EtOH$, $[Fe_2(BFHMAP)(O)_2]\cdot EtOH$, $[Fe_8(BHMAP)_5(O)_6(SO_4)(H_2O)_5]$, $[Fe_2(BHMAE)(O)(OH)_2(H_2O)_3]\cdot 2H_2O$

TABLE II IR spectral data for the Schiff base and related compounds

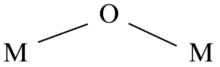
Compound	*IR (cm^{-1})*								
	ν_{OH}		ν_{CH_3}	$\nu_{C=O}$		$\nu_{C=N}$		ν_{C-OH}	ν_{C-N}
	free	*bonded*		*free keto*	*bonded keto*	*free*	*bonded*		
3-formyl-2-hydroxy-acetophenone (FHA)*	3730–3680	3520–3440	2920	1730	–	–	–	1220	–
3,5-diformyl-1-4-hydroxyacetophenone (DFHA)**	3400–3480	3160–3240	2960	1710	–	–	–	1215	–
bis(2-hydroxy-3-methylidinylacetophenone)-3-ethylenediamine (BHMAE)	3693	3662	2922	1798	1695	1680	1692	1294	1212
bis(2-hydroxy-3-methylidinyl-acetophenone)-3-(1,3-propylenediimine) (BHMAP)	3713	3703	2922	1798	1685	1675	1655	1210	1067
bis(5-formyl-4-hydroxy-3-methylidinylacetophenone)-3-ethylenediimine (BFHMAE)	3436	3389	2925	1778	1680	1685	1660	1175	1117
bis(5-formyl-4-hydroxy-3-methylidinylacetophenone)-3-(1,3-propylenediimine) (BFHMAP)	3682	3662	2929	1768	1690	1680	1713	1222	1117

*,**$\nu_{C=O}$ free aldehydes of FHA = 1690; free and bonded aldehydes of DFHA = 1685 and 1660 respectively.

TABLE III IR spectral data for the Schiff-base complexes of ligands BHMAP and BHMAE

Complex	*Formula*	*IR (cm^{-1})*														
		ν_{OH}	$\nu_{C=O}$	ν_{CHO}	$\nu_{C=N}$	$\nu 1_{S-O}$	$\nu 2_{SO_4}$	$\nu 3_{S=O}$	$\nu 4_{SO_4}$	σ_{M-OH}	$\rho(H_2O)$	σ_{M-OH-M}	σwH_2O	ν_{M-O-M}	ν_{M-O}	ν_{M-N}
1	$[Fe_2(BHMAE)(O)(OH)_2(H]_2O)_3]\cdot\frac{1}{2}H_2O$	3404	1798	–	1633	–	–	–	–	1133	978	933	655	533	455	377
2	$[Fe_2(BHMAP)_2(OH)_2]\cdot H_2O$	3416	1798	–	1640	–	–	–	–	–	989	922	633	–	550	444
3	$[Fe(BFHMAE)(OH)(H_2O)]\cdot 4\frac{1}{2}H_2O$	3399	1766	1733	1640	–	–	–	–	1044	989	–	677	–	588	478
4	$[Fe_2(BFHMAP)O_2]\cdot EtOH$	3397	1768	1740	1633	–	–	–	–	–	–	–	–	633	544	366
5	$[Fe_8(BHMAP)_5(O)_6(SO_4)(H_2O)_5]$	3388	1797	–	1622	940	438	1189	625	–	945	–	622	511	466	389
6	$[Fe_8(BHMAE)_5(O)_6(SO_4)(H_2O)_5]$	3388	1797	–	1622	937	450	1199	630	–	945	–	622	511	466	389
7	$[Fe_8(BFHMAP)_5(O)_6(SO_4)(H_2O)_{11}]\cdot 4EtOH$	3388	1767	1740	1633	910	470	1199	635	–	944	–	633	559	511	380
8	$[Fe_5(BFHMAE)_6(OH)(H2O)_3(SO_4)]\cdot 3H_2O$	3387	1778	1733	1640	940	438	1188	620	–	977	911	633	–	522	477

and $[Fe_8(BHMAP)_5(O)_6(SO_4)\ (H_2O)_5]$ show a new band at 650–511 cm^{-1} which is not present in the spectra of the other metal chelates or in the IR spectra of the free ligands. This new band can be assigned to μ-oxo [17–20] *i.e.*,



The electronic absorption spectra of Schiff-base ligands in Nujol mull and different organic solvents exhibit five absorption bands. The positions of the bands and their electronic transitions are summarized in Table IV. The electronic absorption spectra of the complexes (Table V) were studied in DMF solution and in Nujol mull. The spectra of Fe(III) Complexes **1**–**3** and **5**–**8** exhibit three absorption bands with λ_{max} located at 450–420, 490–470 and 530–510 nm either in Nujol mull or DMF solution. The first two bands are assigned to charge-transfer transitions within the C=O and C=N groups, respectively, as a result of complex formation. The third band can be assigned to the $^6A_{1g} \rightarrow ^4 T_{1g}(G)$ electronic transition of the Fe^{3+} ion. The spectral patterns indicate an octahedral arrangement around the central Fe(III) ion in DMF solution. Complex **4** has three absorption bands situated at λ_{max} 420–440, 480 and 640 nm in Nujol mull. The first two bands are assigned to charge-transfer transitions within the C=O and C=N groups, respectively, whereas the third band can be assigned to the $^6T_{1g} \rightarrow {}^4T_{2g}$ (G) electronic transition of Fe(III). The shape of the bands and the position of λ_{max} indicate tetrahedral geometry around Fe(III). The electronic spectra of the complexes in DMF solutions were compared with those in Nujol mull and it is found that:

(a) The position of the bands in Complexes **1**, **2**, **3**, **7** and **8** are unchanged. This indicates that no structural changes are observed on going from the solid state to DMF solution, *i.e.*, these complexes have octahedral geometry around Fe(III) ions.

(b) The positions of the bands in the spectra of Complexes **4**, **5** and **6** in Nujol mull exhibit some shift to lower or higher wavelengths in DMF. These indicate that the first complexes has an octahedral and the other a pseudo-octahedral arrangement around the Fe(III) ion in the solid state.

X-band ESR spectra of the complexes under investigation at room temperature (298 K) are shown in Fig. 1. The g_{eff} values of the complexes are given in Table I. For Fe(III) complexes a broad signal is observed which splits into six lines as a result of interaction between the ^{55}Fe nuclei. In case of the cluster complexes a sharp signal is observed with no obvious hyperfine structure. The relations between the Lande g effective factor (g_{eff}) and the Hammet constant, (σ_x) are plotted using the least square method, giving a satisfactory linear relationship which indicates that the g_{eff} values of the Fe(III) complexes are governed by the electron density on the Schiff-base ligands. The shape of the ESR signal together with the g_{eff} values indicate octahedral geometry for all complexes except Complex **4**, which has a pseudo-tetrahedral arrangement around the Fe (III) ion.

Mössbauer spectra of Fe(III) and Fe(III) cluster complexes exhibit two quadrupole splitting doublets except for the three Complexes **1**, **2** and **3** as shown in Fig. 2. The hyperfine parameters, isomer shift (IS), quadrupolar splitting (QS) and line width (LW), obtained from computer analysis of the spectra are collected in Table VI. Analysis of the Mössbauer spectra of Complexes **1**, **2** and **3** revealed the presence of

TABLE IV Electronic absorption spectra for the Schiff-base compound in Nujol mull and in different organic solvents*

Compound	λ_{max} (*nm*)(*Nujol mull*)					*Solvent*	λ_{max} (*nm*)(*solution*)^{a,b}				
	$1_{L_a} - 1_{A_A}$	$1_{L_b} - 1_A$	$C{=}O$ $\pi - \pi^*$	$C{=}N$ $\pi - \pi^*$	*CT*		$1_{L_a} - 1_{A_A}$	$1_{L_b} - 1_A$	$C{=}O$ $\pi - \pi^*$	$C{=}N$ $\pi - \pi^*$	*CT*
bis(2-Hydroxy-3-methylidinylacetophenone)-3-ethylenediamine (BHMAE)	220	260	290	390	480, 455	$CHCl_3$	240	265	320	385	485, 446
						EtOH	220	–	275	315	481, 450
						DMF	260	310	370	385	476, 449
bis(2-Hydroxy-3-methylidinylacetophenone)-3-(1,3-propylenediimine) (BHMAP)	235	260	285	320	480, 450	$CHCl_3$	235	270	310sh	385sh	483, 451
						EtOH	225	275	295	315sh	478, 446
						DMF	260	315	375sh	385sh	478, 450
bis(5-Formyl-4-hydroxy-3-methylidinylacetophenone)-3-ethylenediimine (BFHMAE)	240	280	315	340	485, 445	$CHCl_3$	235	–	270sh	315sh	485, 450
						EtOH	215	230	275sh	360sh	477, 450
						DMF	265	345sh	375sh	385	475, 440
bis(5-Formyl-4-hydroxy-3methylidinylacetophenone)-3-(1,3-propylenediimine) (BFHMAP)	235	270	350	390	495, 465	$CHCl_3$	230	–	275sh	310sh	487, 448
						EtOH	225	–	275sh	315sh	482, 452
						DMF	260	340	375sh	385sh	478, 448

[a] sh = weak band-shoulder. [b],*Saturated solutions were used.

TABLE V Electronic spectral data of normal and cluster Fe(III) Schiff-base complexes

Complex	*Formula*	*CT (C=O) DMF (Nujol)*	*CT (C=N) DMF (Nujol)*	*Band assignment due to d–d transition DMF (Nujol mull)*
1	$[Fe_2(BHMAE)(O)(OH)_2(H_2O)_3]\cdot\frac{1}{2}H_2O$	440 (450)	480 (480)	530 (520) $[^6A_{1g}-^4T_{1g}(G)]$
2	$[Fe_2(BHMAP)_2(OH)_2]\cdot H_2O$	450 (440)	480 (470)	590 (560) $[^6A_{1g}-^4T_{1g}(G)]$
3	$[Fe(BFHMAE)(OH)(H_2O)]\cdot 4\frac{1}{2}H_2O$	420 (440)	480 (470)	520 (530) $[^6A_{1g}-^4T_{1g}(G)]$
4	$[Fe_2(BFHMAP)O_2]\cdot EtOH$	420 (440)	480 (480)	640 (510) $[^6T_{1g}\rightarrow{}^4T_{2g}]$
5	$[Fe_8(BHMAP)_5(O)_6(SO_4)(H_2O)_5]$	450 (450)	480 (480)	500 (520) $[^6A_{1g}-^4T_{1g}(G)]$
6	$[Fe_8(BHMAE)_5(O)_6(SO_4)(H_2O)_5]$	450 (450)	480 (480)	550 (520) $[^6A_{1g}-^4T_{1g}(G)]$
7	$[Fe_8(BFHMAP)_5(O)_6(SO_4)(H_2O)_{11}]\cdot 4EtOH$	450 (450)	490 (480)	520 (510) $[^6A_{1g}-^4T_{1g}(G)]$
8	$[Fe_5(BFHMAE)_6(OH)(H_2O)_3(SO_4)]\cdot 3H_2O$	450 (450)	490 (480)	530 (530) $[^6A_{1g}-^4T_{1g}(G)]$

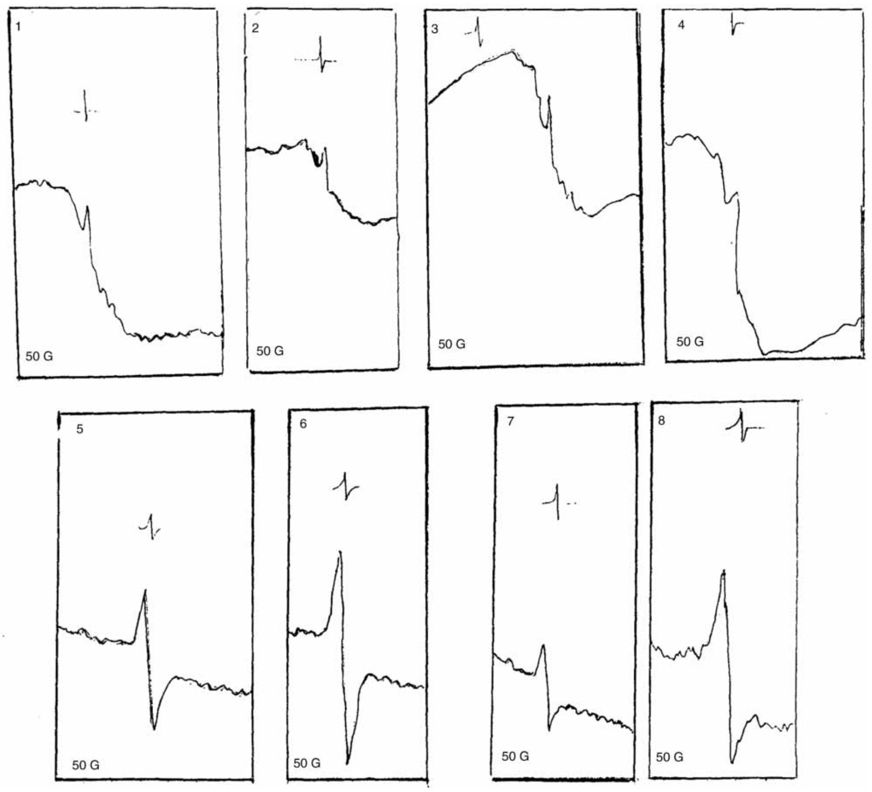


FIGURE 1 ESR of normal Fe(III) Schiff-base complexes (top) and cluster Fe(III) Schiff-base complexes (bottom).

Fe^{3+} as one site while the spectra of Complexes **4**, **5**, **6**, **7** and **8** showed the presence of the iron as Fe^{3+} in two different sites. From the QS values of site (II) the ferric ions are distorted octahedral. The distortion in Complex **4** is higher than in the other samples, indicating a different geometry from the other two types [21,22].

If the Hammett equation is applied to isomer shift (IS) and quadrupolar splitting (QS), a satisfactory linear relation is observed for Fe(III) complexes and a non-linear relation is observed for Fe(III) cluster complexes, Fig. 3. Deviation from linearity

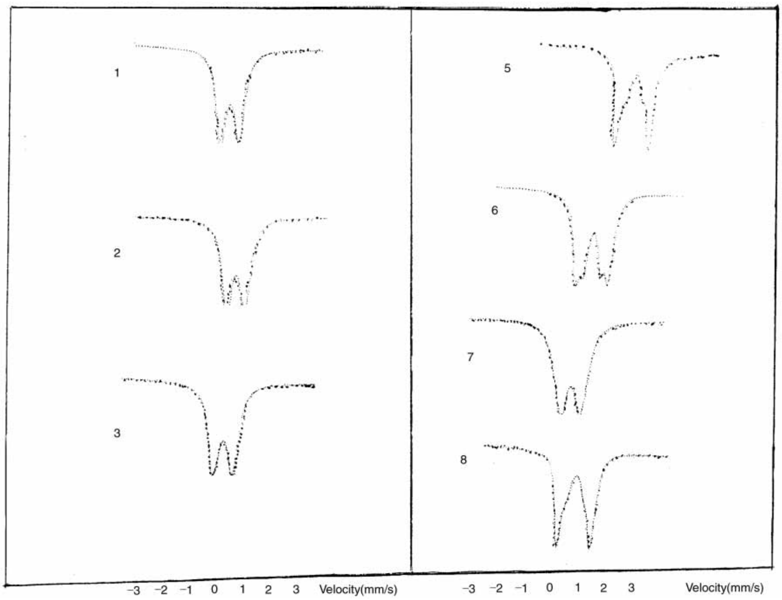


FIGURE 2 Mössabauer spectra of normal (left) and cluster (right) Fe(III) Schiff-base complexes.

TABLE VI Isomeric shift (IS) quadrupole splitting (QS) and line width (LW) of Fe(III) Schiff-Base complexes

Complex	*Formula*	*Site 1*		*Site II*		*LW (mm/s)*
		IS (mm/s)	*Qs (mm/s)*	*IS(mm/s)*	*QS(mm/s)*	
1	$[Fe_2(BHMAE)(O)(OH)_2(H_2O)_3]\cdot\frac{1}{2}H_2O$	0.3174	0.6566	–	–	0.4569
2	$[Fe_2(BHMAP)_2(OH)_2]\cdot H_2O$	0.3199	0.6821	–	–	0.4377
3	$[Fe(BFHMAE)(OH)(H_2O)]\cdot 4\frac{1}{2}H_2O$	0.3467	0.7015	–	–	0.5112
4	$[Fe_2(BFHMAP)O_2]\cdot EtOH$	0.3458	0.7335	0.2498	1.4555	0.6100
5	$[Fe_8(BHMAP)_5(O)_6(SO_4)(H_2O)_5]$	0.3729	0.6321	0.3808	1.3292	0.3281
6	$[Fe_8(BHMAE)_5(O)_6(SO_4)(H_2O)_5]$	0.3728	0.6706	0.3824	1.3154	0.3855
7	$[Fe_8(BFHMAP)_5(O)_6(SO_4)(H_2O)_{11}]\cdot 4EtOH$	0.3354	0.6687	0.3548	1.1858	0.5536
8	$[Fe_5(BFHMAE)_6(OH)(H_2O)_3(SO_4)]\cdot 3H_2O$	0.3807	0.6627	0.3845	1.3331	0.3680

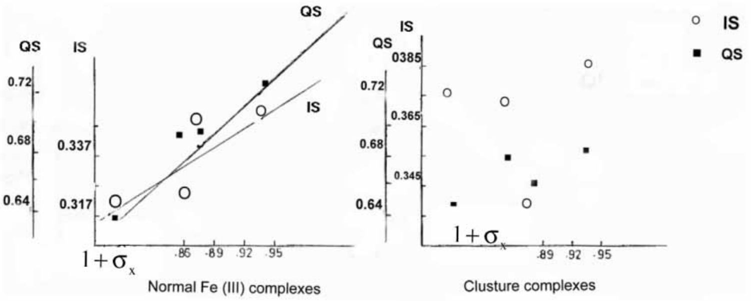
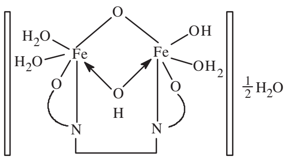


FIGURE 3 Relation between Hamett constant σ_x and IS or QS. In normal Fe(III) Schiff-base complexes $g=2.120602$, standard deviation $(s)=0.025249$. Correlation coefficient $(R)=0.8871201$ and slope $(p)=0.645929$. In cluster Fe(III) Schiff-base complex $g=1.960834$, standard deviation $(s)=0.89443$, correlation coefficient $(R)=0.89443$, and slope $(p)=0.25752$.

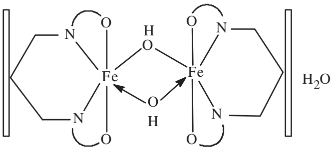
may be attributed to steric effects, strength of hydrogen bonds and keto–enol tautomerism, which plays an important role in electron density within the molecule in addition to the mesomeric effect.

Based on the results gained from elemental and thermogravimetric analyses, IR, electronic, ESR and Mössbauer spectra, the structures of Fe(III) complexes with Schiff-base ligands can be formulated as follows:



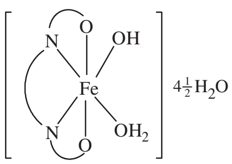
$[Fe_2(BHMAE)(O)(OH)_2(H_2O)_3]\,\frac{1}{2}H_2O$

(1)



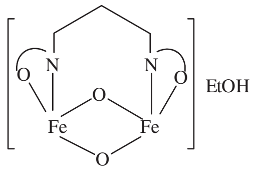
$[Fe_2(BHMAP)_2(OH)_2]\cdot H_2O$

(2)



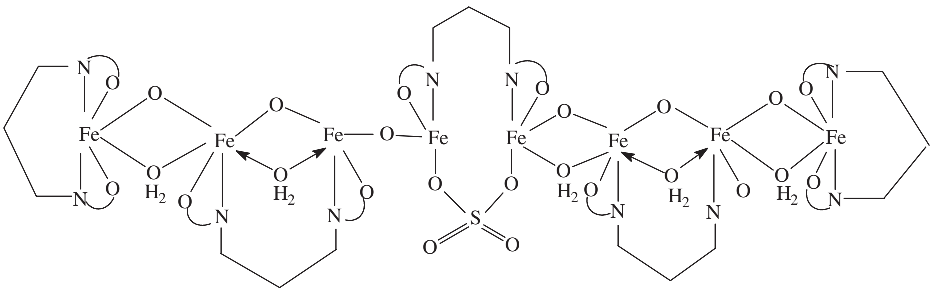
$[Fe(BFHMAE)(OH)(H_2O)]\;4\frac{1}{2}H_2O$

(3)



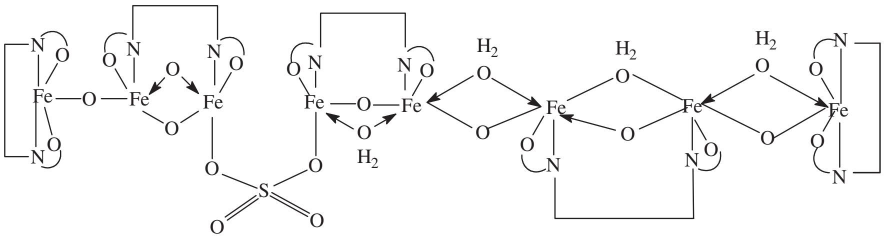
$[Fe_2(BFHMAP)O_2]\cdot EtOH$

(4)



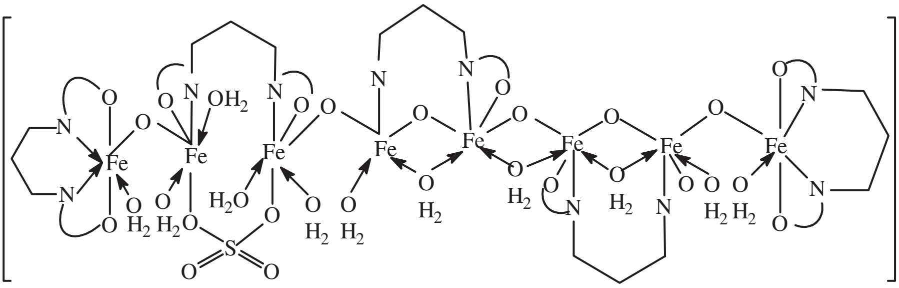
$[Fe_8(BHMAP)_5(O)(SO_4)(H_2O)_5]$

(5)



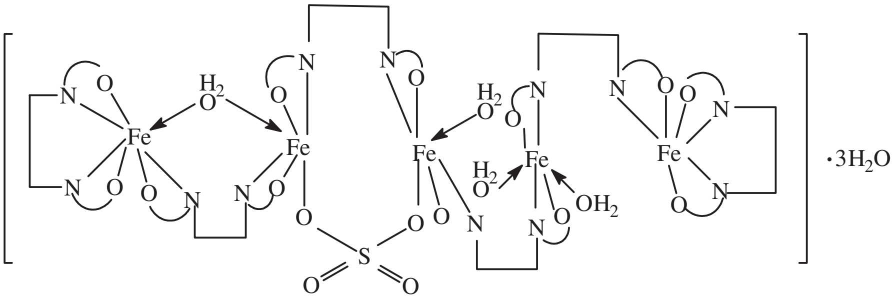
$[Fe_8(BHMAE)_5(O)_6(SO_4)(H_2O)_{11}]\cdot 4EtOH$

(6)



$[Fe_8(BFHMAP)_5(O)_6(H2O)_{11}]\cdot 4EtOH$

(7)



$[Fe_5(BFHMAE)_6(OH)(H_2O)_3(SO_4)]\cdot 3H_2O$

(8)

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