

## Novel Fe(II) Complexes of Schiff base Ligands: Synthesis, Characterization, Antimicrobial Studies

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### Abstract

The synthesis of some Fe(II) complexes with acid Schiff bases are reported here. These Schiff bases were derived by condensing carbonyl oximes and amines like sulphanic acid. The characterization of the complexes was done on the basis of elemental analysis, molar conductivity, spectral studies like IR and Electronic and Anti-bacterial activity. On the basis of these analysis it was concluded that Fe(II) complexes exhibit Octahedral binuclear geometry with  $M_2L_2SO_4 \cdot 4H_2O$  stoichiometry. The molar conductivity data indicate that the complexes are non-electrolytic in nature. The metal complexes have been screened for their antibacterial activity.

**KEYWORDS:** Fe(II) complexes, Schiff bases, Structural analysis, Antimicrobial studies.

### 1. INTRODUCTION

Schiff bases and their coordination compounds have gained importance recently because of their application as models in biological, biochemical, and analytical, antimicrobial system, anticancer, antibacterial and antifungal activities. Studies of new kinds of chemotherapeutic Schiff bases are now attracting the attention of biochemists<sup>[1-2]</sup> Schiff bases contain azomethine ( $>C=N$ ) group as functional group and hence act as an effective ligand. In addition the presence of nitrogen and oxygen donor atoms in the complexes act as stereospecific catalyst for many reactions like oxidation<sup>3</sup>, reduction<sup>4</sup>, hydrolysis<sup>5</sup> and possess antibacterial<sup>6</sup> activity. In this paper, the synthesis, characterization of some Fe(II) complexes with polydentate Schiff base ligands are reported.

### 2. Materials and Methods

All chemicals used were of A. R. grade purchased from S. D. Fine chemicals (Mumbai) & used without further purification. Distilled solvents were used throughout the experiments. Metal content was determined in the laboratory by the reported methods<sup>[7]</sup>. C, H and N analysis were performed at the IIT Mumbai. The infra-red spectra of the ligands and of their metal complexes were recorded in KBr pellets in the 4000-400  $cm^{-1}$  region using a FTIR spectrum one supplied by Perkin Elmer instrument. The electronic spectra were recorded on Beckman Spectrophotometer the diffuse reflectance spectra of solid complexes taken on Carl-Zeiss VSU -2P spectrophotometer. The  $^1H$  NMR spectra were recorded on a VXR-300s Varian Super Nuclear Magnetic Resonance spectrophotometer using TMS as an internal standard. TGA analysis was carried out using a Shimadzu DT-30 recording thermal analysis in an inert atmosphere of nitrogen, from room temperature to 900<sup>o</sup>c.

Antimicrobial studies: The *in-vitro* biological screening effects of the investigated compounds were tested against the bacteria *Escherichia coli*, *Staphylococcus*, *B.cereus*, *Bacillus subtilis* were studied on laboratory grown cultures. Stock solutions were prepared by dissolving the compounds in DMSO and serial dilutions of the compounds were prepared in sterile distilled water to determine the minimum inhibition concentration (MIC). The nutrient agar medium was poured into Petri plates. A suspension of the tested microorganism (0.5 ml) was spread over the solid nutrient agar plates with the help of a spreader. Different dilutions of the stock solutions were applied on the 10 mm diameter sterile disc. After evaporating the solvent, the discs were placed on the inoculated plates. The Petri plates were placed at low temperature for two hours to allow the diffusion of the chemical and then incubated at a suitable optimum temperature for 30-36 hrs. The diameter of the inhibition zones was measured in millimetres.

### 2.1 Synthesis of Fe complexes

The Metal complexes of Schiff base were synthesized *in situ* condensing ethanolic solution of 0.01 mol of carbonyl oximes, namely-isonitrosoacetophenone (HINAP)<sup>[8]</sup>,  $\alpha$ -benzyl monoxime (HBMO)<sup>[8]</sup>, isonitroso acetyl acetone(HINAA)<sup>[8]</sup> with 0.01 mol of aqueous solution of sulphanilic acid and metal salt in 1:1:1 stoichiometric ratio. Metal complexes of Schiff base were synthesized *in situ* condensing ethanolic solution of 0.01 mol of carbonyl oximes, namely HINAP, HBMO, HINAA with 0.01 mol of aqueous solution of sulphanilic acid and FeSO<sub>4</sub>.7H<sub>2</sub>O (equimolar in minimum quantity of water was prepared. To avoid the oxidation Fe(II) to Fe(III) sodium thiosulphate was added to the Fe(II) and filtered solution was added to the reaction mixture in 1:1:1 stoichiometric ratio. pH of the solution was raised to ~8 with 0.1 N NaOH solution, when 1-phenyl 1-hydroimino ethylideneiminobenzene 4-sulphonic acid L<sub>1</sub> (HPEIBSA), 1,2-diphenyl 1-hydroxyimino ethylideneiminobenzene 4-sulphonic acid L<sub>2</sub> (HBEIBSA), and 1-acetyl 2-methyl 1-hydroiminoethylideneiminobenzene 4-sulphonic acid L<sub>3</sub> HAMEIBSA were respectively obtained and were then digested on water bath for about half an hour. The solid precipitated was filtered off, washed repeatedly with hot water followed by 50% alcohol and dried in vacuum.

## 3. RESULTS AND DISCUSSION

All the metal complexes are intensely coloured. They are thermally quite stable, as shown by their high decomposition temperatures, which indicate strong metal to ligand bonding solids. The complexes are insoluble in water, ethanol, methanol, chloroform, carbon tetrachloride etc. but soluble in DMF and DMSO. The complexes dissolve in alkali like sodium hydroxide giving colour, indicating the presence of a free oxime group, suggesting oximino proton is not replaced during complexation. The elemental analysis show 1:1 ligand metal stoichiometry for all the complexes. The analytical data along with some physical properties of the ligand and metal complexes are reported in Table 1. The molar conductivities of  $1 \times 10^{-3}$  mhos cm<sup>2</sup> mol<sup>-1</sup> solutions of the complexes in nitro benzene indicate their non-electrolytic nature<sup>[9]</sup>. The elemental analysis suggest 1:1 (metal: ligand) stoichiometry for all the metal complexes. They are formulated as M<sub>2</sub>L<sub>2</sub>SO<sub>4</sub> 4H<sub>2</sub>O. Here L represents HPEIBSA, HBEIBSA and HAMEIBSA.

### 3.1 The infrared spectra

The infrared spectra of the free carbonyl oximes were compared with those of their Fe(II) complexes to determine the bonding mode of the ligands to the metal in the complexes. The strong C=O stretching vibrations, in HINAP is absent in the spectra of the metal complexes corresponding ligands. The observations confirm the successful replacement of carbonyl oxygen by imino nitrogen during Schiff base formation prior to the *in situ* formation of the complexes.

The N-O vibrations in the spectra of the present complexes are observed in the range 883-1024  $\text{cm}^{-1}$  indicating a shift in the positions of  $\nu_{\text{N-O}}$  frequency as compared to that in the free carbonyl oximes concomitant to the bonding through the nitrogen atom without the deprotonation of the free oxime (=NOH) group complexes. The infrared spectra of the free carbonyl oximes were compared with those of their Fe(II) complexes to determine the bonding mode of the ligands to the metal in the complexes. The strong C=O stretching vibrations, in HINAP<sup>[10]</sup> is absent in the spectra of the metal complexes corresponding ligands. The observations confirm the successful replacement of carbonyl oxygen by imino nitrogen during Schiff base formation prior to the *in situ* formation of the complexes. The spectra of the parent carbonyl oximes shows strong and broad absorption band in the region 3300  $\text{cm}^{-1}$ , which is due to  $\nu_{\text{O-H}}$  band due to =NOH. The FT-IR spectra of the metal complexes reveal a band in the region 3246-3398 attributed to O-H stretching vibrations of free =NOH group. It is also corroborated by PMR spectra of complexes. It may be concluded that sulphonic group is deprotonated on the basis of Pka values of  $-\text{SO}_3$  group. The region around 3500-3600  $\text{cm}^{-1}$  is characterised by the presence of water molecule which is further confirmed by TGA analysis. The coordination of azomethine nitrogen is confirmed by the presence of bands in the 1590-1598  $\text{cm}^{-1}$  region in the ligand which underwent a shift to a lower frequency after complexation<sup>[11]</sup>. All complexes show extra bands in the 515-618  $\text{cm}^{-1}$  and 413-492  $\text{cm}^{-1}$  region assigned to  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$ <sup>[12]</sup> stretching vibrations. The presence of strong band at 1200  $\text{cm}^{-1}$  and 1059  $\text{cm}^{-1}$  (split) together with the band of medium intensity around 880-890  $\text{cm}^{-1}$  indicate a bridging behaviour of  $\text{SO}_4^{2-}$ <sup>[13]</sup>. Thus these Schiff bases behave as multi-dentate ligand coordinating through the deprotonated sulphonic group and azomethine, nitrogen azomethine the presence of an ionised  $-\text{SO}_3$  is indicated by 1120-1160  $\text{cm}^{-1}$ . Selected IR bands for the ligands and their metal complexes are represented in Fig.a.

The observations on the infrared spectra of the metal complexes as discussed above indicate bonding through the sulphonic acid and coordinating through azomethine and oximino nitrogen donor atoms. On the basis of elemental analysis, electrical conductance measurements and spectral studies, thus the Fe(II) complexes are the compounds polymers in which monomers are linked by  $\text{SO}_4^{2-}$  ion bridging the two metal centres<sup>[14]</sup>. The possible structure of the Fe(II) complexes may tentatively be represented as shown in the proposed structure. The presence of co-ordinated water in the Fe complexes is confirmed by the presence of bands around 890 – 928  $\text{cm}^{-1}$ <sup>[14]</sup>.

### 3.2 The Magnetic Moment

The magnetic moments of the complexes exhibit paramagnetic in the range 5.07-5.26 B.M. at room temperature. Most of the octahedral ferrous complexes are found to

show either diamagnetism or paramagnetism corresponding to the presence of four unpaired electrons in strong or weak ligand field respectively. The observed magnetic moments are in the range for spin free octahedral environment of the ligand around Fe(II), a  $d^6$  ion.

### 3.3 The PMR spectra

The pmr spectra of the complexes indicate that oximino proton of HINAP observed at  $11.4\delta$  in dioxan or at  $9.06\delta$  in  $CDCl_3$  is shifted to  $12-12.6\delta$  this positive shift indicates the proton of the =NOH is not replaced.

### 3.4 Electronic absorptions spectra

The electronic spectra of the complexes show transition in ultra violet region in the range  $35,480-49,400$  ( $cm^{-1}$ ). The transition observed  $37,740-43,400$  ( $cm^{-1}$ ) are attributed to  $\pi-\pi^*$  transition the intense band observe with energy higher than  $43,400$   $cm^{-1}$  in several cases is due to an intra ligand transition.

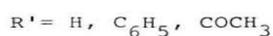
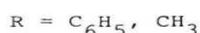
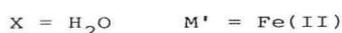
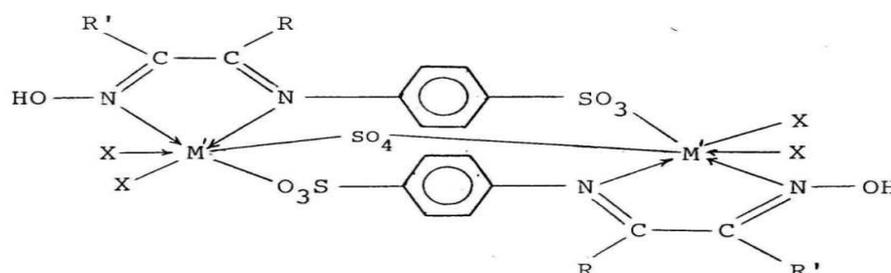
### 3.5 Thermal studies

The thermal studies of the complexes show that they are thermally stable to varying degree. The complexes show loss in weight up to about  $100 - 110^\circ C$ . This observation suggests (1-1.5%) the absence of any lattice water or water of crystallization. It clearly indicates the nature of water molecules present as being coordinated to the central metal ion by loss of coordinated water in the temperature range  $120-220^\circ C$ . With further increase in temperature the complexes show decomposition by fragmentation and thermal degradation of the organic part of the metal complexes, finally resulting into corresponding metal oxide.

### 3.6 Antimicrobial studies

The result of the preliminary study on antimicrobial activity of Fe(II) complexes screened against *B.subtilis*, *B.cereus*, *E.coli* and *S.aureus* are tabulated in table 5. The test for complexes carried out in DMF solution using the agar cup method with DMF as blank control. They show resistance to most of the complexes. *S.aureus* and *E.coli* are fair to moderately sensitive to Fe(II) complexes<sup>[19]</sup>. They show varying action towards these bacteria.

The possible structure of the Fe(II) complexes may tentatively be represented as follows



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Table-1 Physical and Analytical Data of the metal complexes

Complex	Colour	Temp 'C M.P.	M	C	H	N	S	$\mu^M$ [S cm <sup>2</sup> mol <sup>-1</sup> ]	$\mu$ eff
Fe <sub>2</sub> (L <sub>1</sub> ) <sub>2</sub> SO <sub>4</sub> 4H <sub>2</sub> O	Blue	170	12.0	36.2	3.2	6.2	5.59	0.847	5.26
			(12.54)	(37.96)	(3.38)	(6.32)	(7.9)		
Fe <sub>2</sub> (L <sub>2</sub> ) <sub>2</sub> SO <sub>4</sub> 4H <sub>2</sub> O	Green	172	10.6	46.6	3.2	5.0	8.9	0.920	5.19
			(10,76)	(46.25)	(3.67)	(5.39)	(9.25)		
Fe <sub>2</sub> (L <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> 4H <sub>2</sub> O	Brown	173	13.0	30.8	3.2	5.9.2	10.9	0.942	5.07
			(13.13)	(31.24)	(3.5)	(6.62)	(11.36)		

Table-2 I.R. Spectral data of Fe(II) complexes (cm<sup>-1</sup>)

Complex	$\nu$ O-H	$\nu$ C=N azomethine	$\nu$ C=N oximino	$\nu$ N-O	$\nu$ M-N	$\nu$ M-O
Fe <sub>2</sub> (L <sub>1</sub> ) <sub>2</sub> SO <sub>4</sub> 4H <sub>2</sub> O	3580 3390	1596	1596	889	524	443
Fe <sub>2</sub> (L <sub>2</sub> ) <sub>2</sub> SO <sub>4</sub> 4H <sub>2</sub> O	3567 3382	1596	1551	883	542	490
Fe <sub>2</sub> (L <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> 4H <sub>2</sub> O	3578 3380	1590	1550	1020	500	431

Table-3 U.V.Spectral Data for the Fe(II) complexes

Complexes	Band Position (cm-1)		
Fe <sub>2</sub> (L <sub>1</sub> ) <sub>2</sub> SO <sub>4</sub> 4H <sub>2</sub> O	48,070	39,680	28,250
Fe <sub>2</sub> (L <sub>2</sub> ) <sub>2</sub> SO <sub>4</sub> 4HO	47,620	40,000	

Table-4 Diffuse Reflectance Spectral data of Fe(II) complexes (cm<sup>-1</sup>)

Complex	Band position In cm <sup>-1</sup>	Tentative assignment
Fe <sub>2</sub> (L <sub>1</sub> ) <sub>2</sub> SO <sub>4</sub> 4H <sub>2</sub> O	9520	d-d transition MECT and MACT Transition
	15,384	
	27,770	
Fe <sub>2</sub> (L <sub>2</sub> ) <sub>2</sub> SO <sub>4</sub> 4HO	10,000	d-d transition MECT and MACT transition
	14,700	
	13,150	
Fe <sub>2</sub> (L) <sub>2</sub> SO <sub>4</sub> 4H <sub>2</sub> O	10,520	d-d transition MACT and MACT transition
	13,150	
	18,510	
	25,640	

Table-5 Agar cup method for the antibacterial activity of the Fe(II) complexes in (DMF)

COMPOUND	B.subtilis(mm)	B.cereus(mm)	S.aureus(mm)	E.coli(mm)
Fe <sub>2</sub> (L <sub>2</sub> ) <sub>2</sub> SO <sub>4</sub> 4HO	18	16	14	13
Fe <sub>2</sub> (L <sub>3</sub> ) <sub>2</sub> SO <sub>4</sub> 4H <sub>2</sub> O	14	15	13	17

Fig.a Infrared absorption Spectrum of Fe<sub>2</sub>(L<sub>1</sub>)<sub>2</sub>SO<sub>4</sub>4H<sub>2</sub>O

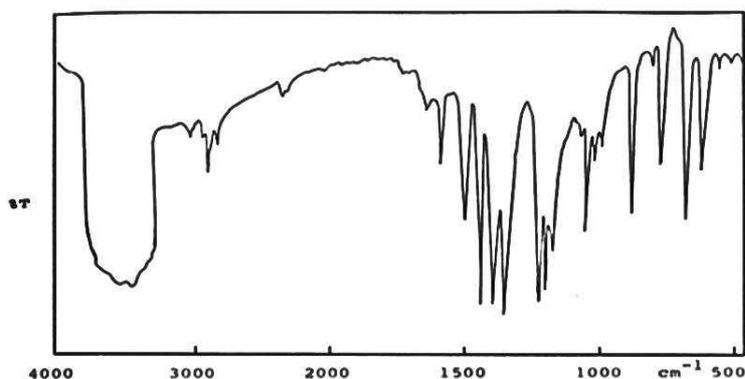


Fig b Electronic Absorption Spectrum of  $\text{Fe}_2(\text{L}_1)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$

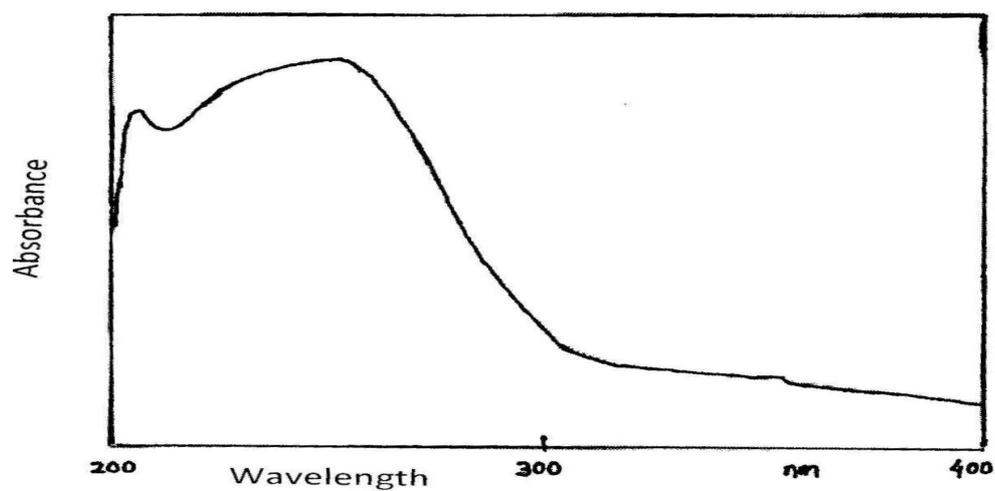


Figure c. Diffuse reflectance spectrum of  $\text{Fe}_2(\text{L}_1)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$

