Asian Journal of Chemistry Vol. 10, No. 1 (1998), 175–179

Schiff Base Complexes of Iron(II) and Their Spectral Properties

B.H. MEHTA* and KEDAR V. PURANDARE
Department of Chemistry
University of Mumbai, Vidyanagari, Kalina,
Santacruz (E), Mumbai-400 098, India

A series of mononuclear Fe(II) complexes with a commercially important Schiff base has been synthesized. The mononuclear Fe(II) complexes have been obtained by the reaction of the ligand Schiff base which was derived from condensation of 2-hydroxy-1-naphthaldehyde with anthranilic acid, *o*-toluidine, *p*-toludine and aniline The recrystallised metal complexes were analysed for their elemental analysis and other analytical parameters. The structural diagnosis was inferred from various spectral measurements. The data was well supported by magnetic susceptibility measurements at room temperature.

INTRODUCTION

The synthesis and coordiantion ability of compartmental ligands have been the goal of much research in recent years owing to the specific properties of Schiff bases and their transition metal complexes, which have been applied in bioinorganic chemistry, material sciences, catalysis and incapsulation services.[1–4] Schiff bases have been investigated because of the easy synthesis and remarkable versatility towards coordinating ability with transition metals.[5–7] Many Fe(II) complexes are reported which generally crystallise with octahedral orientation of the ligands. It is also possible to isolate 1 : 6 complexes with monodentate Schiff base ligand. The periphery of such compounds exhibits an excess organic material. Such species are of vital importance in the production of metal containing phrmaceutical products and in the formulation of selective metal ion extractant.

Most recently, iron(II) complexes with certain hexadentate ligands have aroused interest because of their anomalous magnetic behaviour. The equilibrium between high and low spin states in the solid state and in the solution have been studied by variable temperature, magnetic moment and few spectroscopic measurements.[8–10] Many laboratories are currently directed towards the elucidation of the geometric and electronic structure of binuclear bridge and oxygen bridge Fe clusters of proteins.[11]

In view of possible future applications as fast optical switching devices, thin-layer systems exhibiting thermal spin-crossover appears to be preferable for the crystalline material. It would be of value to diagnose structurally and quantify the magnetic interaction of iron complexes with Schiff base chelating systems. The chelating systems of the Schiff bases were synthesized by condensing 2-hydroxy-1-naphthaldehyde with anthranilic acid, *o*-toluidine, *p*-toluidine and aniline. All these chelates were characterized for their analytical parameters prior to chelation with iron(II) salts. During the proceeding of these studies the ferrous complexes were characterized using several spectroscopic methods. It was expected that these iron(II) complexes may give novel structural details which is probably an important information towards the utilization of these complexes as versatile bio-inorganic molecules.

EXPERIMENTAL

2-Hydroxy-1-naphthaldehyde, anthranilic acid, *o*-toluidine, *p*-toluidine, aniline, various solvents and salts were of commercial grade and were used without purification.

Preparation of ligands: A methanolic solution of an appropriate amine (millimole) was added to 2-hydroxy-1-naphthaldehyde in methanol. The mixture was refluxed for 4 h on a water bath. The orange to yellow colour compounds so obtained were collected by filtration, washed with methanol and dried in vacuum.

Iron complexes: A methanolic solution of ligand was added to iron(II) salt solution and the resulting mixture was refluxed for 4 h on a boiling water bath. The precipitate obtained by refluxation was filtered and washed with methanol and dried in vacuum.

The elemental analyses of ligands and their Fe(II) complexes are reported in Table-1

TABLE-1
ANALYTICAL RESULTS OF LIGANDS AND COMPLEXES

Ligands and metal complexes	m.w.	Colour	Analysis %, found (calcd.)				μ_{eff} B.M.
			C	H	N	Fe	
L_1—$C_{18}H_{13}NO_3$	291	Orange	73.04	5.80	4.67	—	Diamag.
			(74.22)	(4.46)	(4.81)		
$Fe(C_{18}H_{12}NO_3)_6$	1790	Brown	72.98	4.44	4.10	3.57	3.41
			(72.36)	(4.05)	(4.69)	(3.11)	
L_2—$C_{18}H_{15}NO$	261	Pale yellow	81.11	5.97	6.40	—	Diamag.
			(82.75)	(5.19)	(5.36)		
$Fe(C_{18}H_{14}NO)_6$	1610	Yellow	81.47	6.64	5.09	3.57	2.06
			(80.45)	(5.25)	(5.21)	(3.46)	
L_3—$C_{18}H_{15}NO$	261	Pale yellow	83.22	6.06	5.02	—	Diamag.
			(82.75)	(5.79)	(5.36)		
$Fe(C_{18}H_{14}NO)_6$	1610	yellow	81.23	6.31	4.79	3.57	2.19
			(80.45)	(5.25)	(5.21)	(3.46)	
L_4—$C_{17}H_{13}NO$	247	Yellow	76.89	5.67	5.30	—	Diamag.
			(82.55)	(5.30)	(5.60)		
$Fe(C_{17}H_{12}NO)_6$	1527	Brown	80.34	4.99	7.64	3.57	1.53
			(80.13)	(4.75)	(5.49)	(3.65)	

TABLE-2

SALIENT FEATURES OF UV-VISIBLE, IR AND SPECTRAL DATA

Schiff base metal complexes	Electron absorption spectral data λ_{max} in cm^{-1}			Key IR bands (cm^{-1})				
	UV	Visible	Reflectance	ν(OH)	ν(C=N)	ν(CO)	ν(Fe—N)	ν(Fe—O)
L_1—$C_{18}H_{13}NO_3$	49019 (18.31) 51020 (19.00)	21528 (32.00)	—	3400 (w, b)	1620 (s)	1290 (m)	—	—
$Fe(C_{18}H_{12}NO_3)_6$	49382 (29.50)	21598 (43.71) 22547 (45.50)	20964	3400 (w, b)	1610 (s)	1365 (m)	500 (m)	460 (m)
L_2—$C_{18}H_{15}NO$	—	21668 (37.90) 22701 (38.90)	—	3400 (w)	1620 (s)	1280 (m)	—	—
$Fe(C_{18}H_{14}NO)_6$	—	21645 (37.87) 22701 (38.90)	21008 22547	—	1620 (m)	1325 (m)	470 (m)	450 (w)
L_3—$C_{18}H_{15}NO$	48426 (20)	21645 (39.90) 22624 (41.66)	—	3400 (b)	1620 (s)	1320 (m)	—	—
$Fe(C_{18}H_{14}NO)_6$	—	21691 (18.81) 22701 (19.50)	21253	—	1620 (s)	1325 (m)	500 (w)	470 (w)
L_4—$C_{17}H_{13}NO$	—	21786 (39.30) 22805 (40.60)	—	3400 (b)	1620 (s)	1330 (m)	—	—
$Fe(C_{17}H_{12}NO)_6$	—	21786 (49.90) 22779	21276 22650	—	1620 (s)	1320 (w, b)	480 (m)	430 (m)

Physico-chemical measurements: IR spectra were recorded as KBr pellets using Shimadzu FTIR-4200 spectrophotometer. Magnetic susceptibilities at room temperature were determined by the Gouy's balance method. The instruments were calibrated using mercury cobalt tetrathiocynate [$HgCo(CNS)_4$].[12] The electronic absorption spectra were recorded on Shimadzu UV-2100 spectrophotometer using DMSO as a solvent. The diffused reflectance pattern of the Schiff bases as well as their iron complexes were recorded using perfectly white barium sulphate powder which also acts as a diluent. The results of all these findings are tabulated in Table-2.

RESULTS AND DISCUSSION

A broad band in the region 3500 to 3200 cm^{-1} for free ligands may be attributed to ν(OH).[14] These bands are absent in the corresponding spectra of iron(II) complexes. However, in case of the ligand L_1, it is observed in the respective complexes due to the presence of carboxylic acid group. The IR spectra rule out the presence of acetate group as a counter anion in the mononuclear complexes derived from ligand L_1, because of the absence of the characteristic IR absorption bands due to the carboxylate groups.

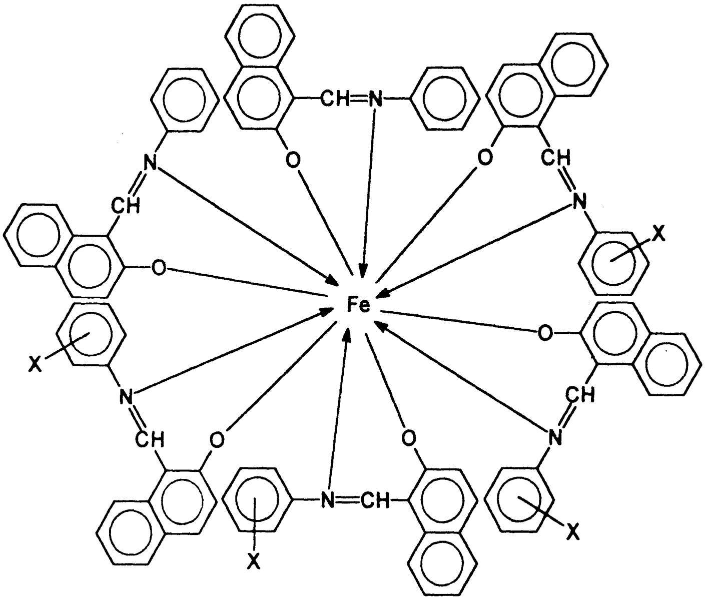
The comparison of IR spectra of these ligands and of the complexes show that ν(C=N) is present as a very strong band in the range 1650–1590 cm^{-1}. The position of these absorption bands also suggests that it is not significantly affected by the coordination of metal ion. However, in few complexes remarkable shift is observed on going from the free ligand to the mononuclear complexes. The lowering of a ν(C=N) mode by 5 to 15 cm^{-1} in the complexes indicates the coordination of azomethane nitrogen atom to the metal centre.[14] Appearance of a strong band centred in the range of 510 cm^{-1} to 420 cm^{-1} is assignable to ν(Fe—N) bond which is absent in the respective spectra of the ligand.

ν(CO) of aromatic carbon and phenolic oxygen is observed in the range 1390 cm^{-1} to 1280 cm^{-1} for free ligand. The ν(CO) mode is shifted by 20 to 30 cm^{-1} in the higher region in the complexes suggesting thereby Fe—O linkage. The assignment to these bands is further supported by the new band appearing in the range of 500 to 400 cm^{-1} assignable to ν(Fe—O).

Electronic absorption spectral data for the complexes are given in Table-2. It can be seen that the bands appearing in the range 17,000–16,000 cm^{-1} are assignable to $A_{1g} \rightarrow T_{2g}(G)$ transitions. The d–d transitions are given for octahedrally oriented high spin iron(II) complexes. However, such absorption spectra for low spin iron(II) complexes are not being adequately characterised due to a strong charge transfer transition. The charge transfer transition generally dominates in the visible portion. The d-π metal to ligand transition usually appears[15] in the range 22,000 cm^{-1}–15,000 cm^{-1}. The bands below 15,000 cm^{-1} which are assignable to d–d transitions of the pair cations could not be detected due to poor resolution.

The electrical conductivity measurements are in conformity with the non-electrolytic nature of these complexes. A very low value [170 mhos/m to 10 mhos/m] suggests that the total charge neutrality exists with these complexes. The magnetic moment value at room temperature of the complexes is a low spin with a value in the range 1.531–3.410 B.M. The observed magnetic moment may be rationalised as an average contribution from low spin Fe(II) site.

Conclusively, all the ferrous complexes of the newly prepared Schiff bases are crystallised with octahedral geometry having metal : ligand stoichiometry as 1:6. Following structure can be assigned to all the complexes.



Structure of iron complexes

L_1—X = -COOH, L_2—X = o-CH_3, L_3—X = p-CH_3, L_4—X = H

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(*Received:* 23 August 1997; *Accepted:* 22 September 1997) AJC-1353