

SYNTHESIS, SPECTRAL AND BIOLOGICAL STUDIES OF IRON(III) COMPLEXES

5.1. Introduction

Iron is the second most abundant metal after Al and the fourth most abundant element in the earth's crust. The name 'iron' is Anglo-Saxon in origin (*iren*) and the symbol Fe and words such as ferrous and ferric are derived from the Latin *ferrum*, *iron*. Iron is the most important transition element involved in living systems, being vital to both plants and animals. Iron plays crucial role in the transport and storage of oxygen and also in electron transport [1].

The main oxidation states of iron are II (d^6) and III (d^5). Most iron(II) complexes are octahedral, tetrahedral, square planar and trigonal bipyramidal, though dodecahedral iron(II) complexes also are known to exist. Iron(III) complexes may be high spin or low spin, and an octahedral stereochemistry is most common. A number of other geometries also are found.

There have been several reports on iron(III) complexes of 2-acetylpyridine thiosemicarbazone, 2-formylpyridine thiosemicarbazone, substituted 2-acetylpyridine thiosemicarbazones etc [2, 3, 4]. Spingam and Sartorelli [5] have synthesized several thiosemicarbazones of 2-pyrazine carboxaldehyde thiosemicarbazone and related compounds to remove iron from the model systems designed to mimic particular aspects of chronic transfusional iron overload. The 2-pyrazine carboxaldehyde thiosemicarbazone has been found to be more effective in reducing tissue iron levels than the deferoxamine, which is used for removing the excess iron accumulated in the tissues of patients with Cooley's anemia [6, 7]. This Chapter contains the synthesis of four iron(III) complexes using the ligands HL¹ and HL² and their spectral, magnetic and biological studies.

5.2. Experimental

5.2.1. Materials

The details regarding the synthesis and characterization of HL¹ and HL² are given in Chapter 2. All the iron(III) salts were used as received. The solvents were purified by the usual methods.

5.2.2. Synthesis of complexes

$[Fe(L^1)_2NO_3] \cdot C_2H_5OH$ (13)

Ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$ (1 mmol, 0.404 g) in 20 ml ethanol and HL¹ (2 mmol, 0.676 g) in 50 ml hot ethanol were mixed and refluxed for 8 hrs. On keeping for 2 days the brown shining solids that separated, were filtered, washed with hot water, hot ethanol and ether and dried over P_4O_{10} *in vacuo*.

$[Fe(L^2)_2NO_3] \cdot 2H_2O$ (14)

Ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$ (1 mmol, 0.404 g) in 20 ml methanol and HL² (2 mmol, 0.664 g) in 40 ml hot methanol were mixed and refluxed for 6 hrs. On cooling, the brown shining solids that separated, were filtered, washed with hot water, hot ethanol and ether and dried over P_4O_{10} *in vacuo*.

$[Fe(L^2)_2Cl]$ (15)

Ferric chloride anhydrous $FeCl_3$ (1 mmol, 0.162 g) dissolved in 20 ml hot methanol and HL² (2 mmol, 0.664 g) dissolved in 40 ml hot methanol were mixed and refluxed for 6 hrs. The blue colored solids that separated while heating, were filtered, washed with hot water, hot methanol and ether. The compound was dried over P_4O_{10} *in vacuo*.

[Fe(L²)₂NCS] (16)

Ferric chloride, FeCl₃ (1 mmol, 0.162 g) dissolved in 20 ml hot methanol and HL² (2 mmol, 0.664 g) dissolved in 40 ml hot methanol were refluxed for 2 hrs. To the refluxing solution, potassium thiocyanate (1 mmol, 0.097 g) in 10 ml methanol was added and again refluxed for 4 hrs. The black crystals that separated, on keeping overnight, were filtered, washed with hot water, hot methanol and ether and dried over P₄O₁₀ *in vacuo*.

5.2.3. Analytical methods

Details regarding the various analytical methods such as elemental analysis, magnetic susceptibility measurements, molar conductivity measurements, electronic, infrared, and EPR spectral analyses were discussed in Chapter 2.

5.3. Results and discussion***5.3.1. Analytical measurements***

The colors, stoichiometries, elemental analyses, and magnetic moments of the Fe(III) complexes are given in Table 5.1. The analytical data calculated for the four iron(III) complexes reveal the 1:2:1 stoichiometry for iron, thiosemicarbazone and gegenion. All the iron(III) complexes are found to be insoluble in methanol, ethanol, acetone and chloroform, but soluble in dimethylformamide and in dimethyl sulphoxide.

The molar conductivity measurements of all the complexes in DMF (10⁻³ M solution) have values in the range 30-50 ohm⁻¹cm² mole⁻¹, which are consistent with their non-electrolytic nature [8]. This indicates that the anions are associated in the first coordination sphere of Fe(III).

Table 5.1 Analytical data, color and magnetic moments of Fe(III) complexes

Compound	Empirical formula	Color	Analytical data. Found (Calculated)%			μ (B.M.) at 300K	Λ^*_M (in DMF)
			C	H	N		
[Fe(L ¹) ₂ NO ₃].C ₂ H ₅ OH (13)	C ₄₀ H ₄₈ N ₉ S ₂ O ₄ Fe	Brown	56.95 (57.29)	5.62 (5.73)	15.16 (15.04)	2.0	49.9
[Fe(L ²) ₂ NO ₃].2H ₂ O (14)	C ₃₈ H ₃₄ N ₉ S ₂ O ₅ Fe	Brown	56.57 (55.89)	4.41 (4.16)	15.07 (15.44)	2.2	35.6
[Fe(L ³) ₂ Cl]	(15) C ₃₈ H ₃₀ N ₈ S ₂ ClFe	Blue	60.91 (60.53)	4.11 (3.98)	14.60 (14.86)	2.49	31.2
[Fe(L ²) ₂ NCS]	(16) C ₃₉ H ₃₀ N ₉ S ₃ Fe	Black	60.01 (60.32)	4.09 (3.87)	16.04 (16.24)	1.98	42.6

*Molar conductivity in ohm⁻¹cm²mol⁻¹ at 298 K using 10⁻³ M solution

5.3.2. Magnetic susceptibilities

High spin Fe(III) complexes in general, have magnetic moments at room temperature very close to the spin only value of 5.9 B.M. because the ground state (derived from the 6S state of free ion) has no orbital angular momentum and there is no effective mechanism for introducing any coupling with the excited state. The low-spin complexes with t_{2g}^5 configurations, usually have considerable orbital contribution to their magnetic moments and at room temperature the magnetic moment value is ~ 2.3 B.M. [9]. The magnetic moments of the synthesized iron(III) complexes in the polycrystalline state at room temperature are found to be in the range of 1.95-2.46. These μ_{eff} values fall in the range of those of low-spin iron(III) complexes [4].

5.3.3. Infrared spectra

The tentative infrared spectral assignments of the ligands HL¹ and HL² and their Fe(III) complexes are given in Table 5.2. The $\nu(C=N)$ bands of the thiosemicarbazones are found at 1582 and 1591 cm^{-1} respectively. These strong bands are shifted after coordination towards lower energies by *ca.* 30 cm^{-1} , indicating coordination *via* azomethine nitrogen [10]. The $\nu(N-N)$ bands of the thiosemicarbazones are found at 1118 and 1102 cm^{-1} . The increase in the frequency of this band in the spectra of the complexes is an evidence for the enolisation of the ligand and the coordination *via* the azomethine nitrogen.

The bands observed at 833 and 835 cm^{-1} for HL¹ and HL² respectively are assigned to $\nu(C=S)$. These bands are found to be shifted to low energy in the spectra of the complexes, indicating coordination *via* the thiolate sulfur. The out-of-plane pyridine ring deformation modes of the free ligands at 607 and 622 cm^{-1}

are found to be shifted to higher energies in the spectra of the complexes indicating coordination *via* the nitrogen atom of the pyridine ring [11].

The coordination positions of the thiosemicarbazones in the iron(III) complexes are confirmed by assigning the strong bands observed in the far IR spectra of the complexes as suggested by Nakamoto [12]. The strong bands observed at 363-370 cm^{-1} are assigned to $\nu(\text{Fe-N})$ of the pyridine ring. Another $\nu(\text{Fe-N})$ band is observed at 482-495 in the spectra of the Fe(III) complexes indicating $\nu(\text{Fe-N})$ of the azomethine group. Again the strong bands observed in the region 442-455 are assigned to the $\nu(\text{Fe-S})$ bond. The iron-chlorine stretching band is normally observed between 300-200 cm^{-1} [13]. A strong band at 255 cm^{-1} in the chloro complex confirms the coordination of the chloride ion to Fe(III).

The IR spectrum of $[\text{Fe}(\text{L}^1)_2\text{NO}_3]\cdot\text{C}_2\text{H}_5\text{OH}$ which exhibits two bands at 1492 and 1384 cm^{-1} corresponds to the NO stretching bands of the nitrate ion. The separation of these bands by 108 cm^{-1} indicates the unidentate nature of the nitrate ion in the complex [14].

Similarly the bands at 1439 and 1319 cm^{-1} in the spectrum of $[\text{Fe}(\text{L}^2)_2\text{NO}_3]\cdot 2\text{H}_2\text{O}$ confirm the terminal unidentate coordination of the nitrate ion to Fe(III) in the complex. According to Stefov et al [15] coordinated water should exhibit frequencies at 825, 575 and 500 cm^{-1} . The absence of spectral bands in these regions in the spectrum of this complex indicates that the water molecules in $[\text{Fe}(\text{L}^2)_2\text{NO}_3]\cdot 2\text{H}_2\text{O}$ are not coordinated, but exist as lattice water.

Table 5.2 I.R. spectral assignments (cm^{-1}) of HL^1 and HL^2 and its Fe(III) complexes

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{C}-\text{S})$	$\rho(\text{py})$	$\nu(\text{Fe}-\text{N})$	$\nu(\text{Fe}-\text{N})_{\text{py}}$	$\nu(\text{Fe}-\text{S})$	$\nu(\text{Fe}-\text{X})$
HL^1	1582w	1118s	833m	607m	--	--	--	--
$[\text{Fe}(\text{L}^1)_2\text{NO}_3] \cdot \text{C}_2\text{H}_5\text{OH}^{\text{a}}$ (13)	1546s	1153m	744m	641w	482s	368s	454s	--
HL^2	1591s	1102s	835	622m	--	--	--	--
$[\text{Fe}(\text{L}^2)_2\text{NO}_3] \cdot 2\text{H}_2\text{O}^{\text{b}}$ (14)	1546s	1125m	752m	665m	492s	363s	442s	--
$[\text{Fe}(\text{L}^2)_2\text{Cl}]$ (15)	1566s	1123s	756s	659m	491s	368s	455s	255s
$[\text{Fe}(\text{L}^2)_2\text{NCS}]$ (16)	1562 s	1118m	766s	638w	495s	370s	451s	--

^a $\nu(\text{NO}_3)$ -1492 cm^{-1} , 1384 cm^{-1} : ^b $\nu(\text{NO}_3)$ -1439 cm^{-1} , 1319 cm^{-1}

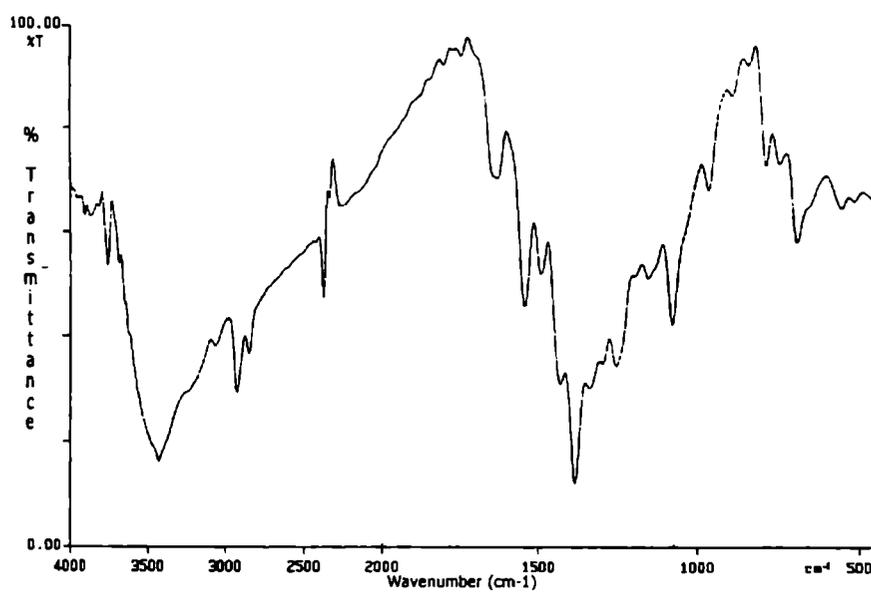


Fig.5.1. IR Spectrum of compound 13

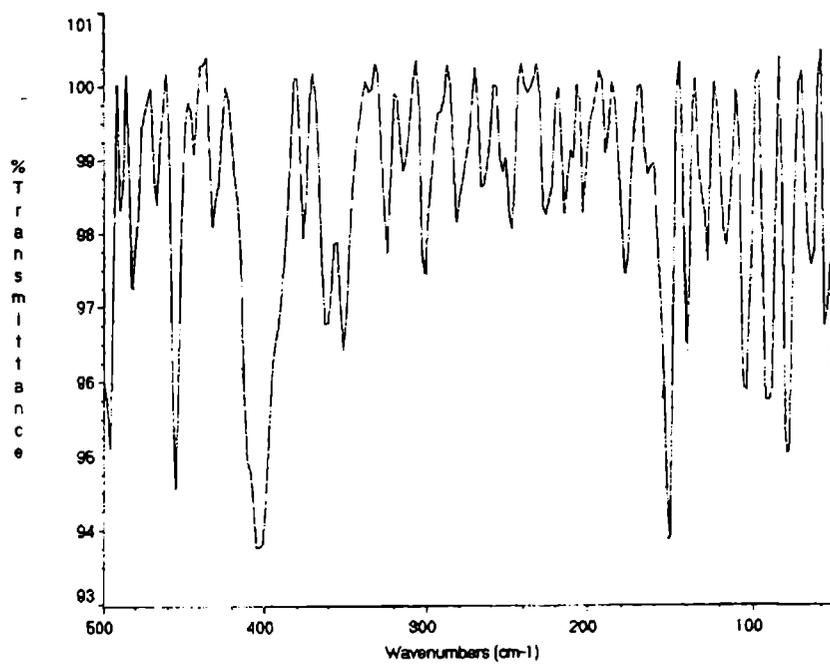


Fig. 5.2. Far IR spectrum of compound 13

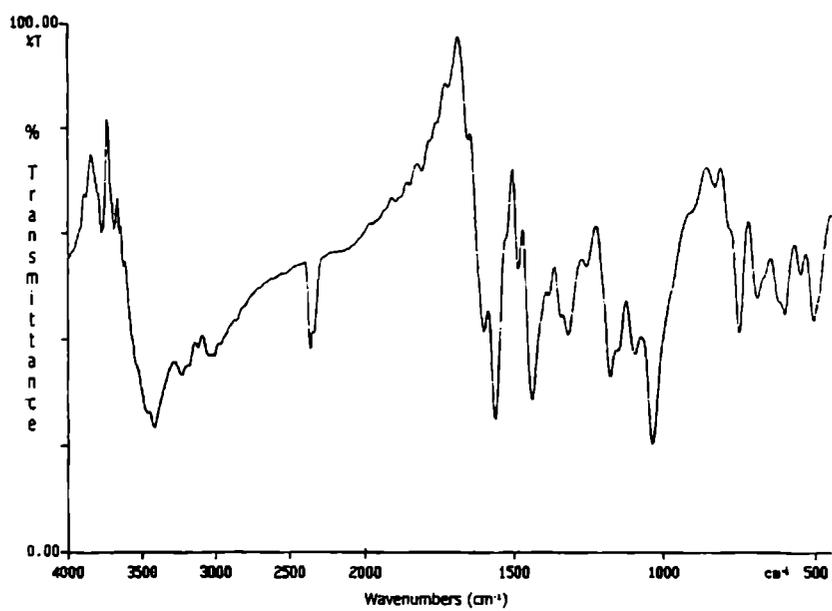


Fig.5.3. IR Spectrum of compound 14

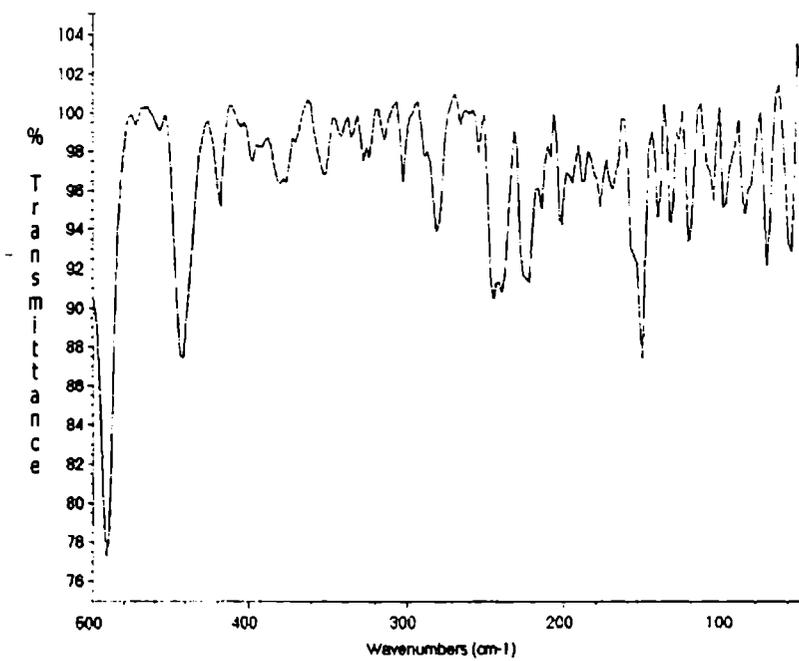


Fig. 5.4. Far IR spectrum of compound 14

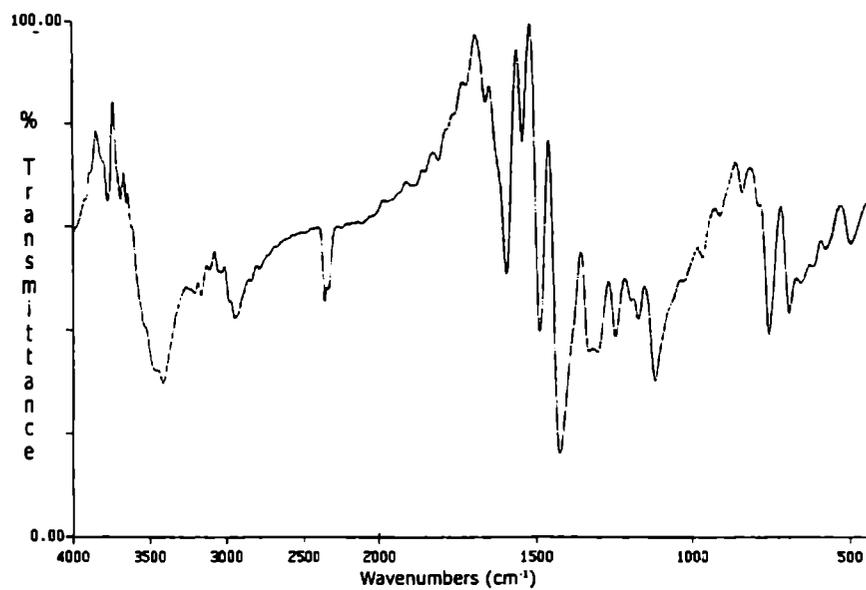


Fig.5.5. IR spectrum of compound 15

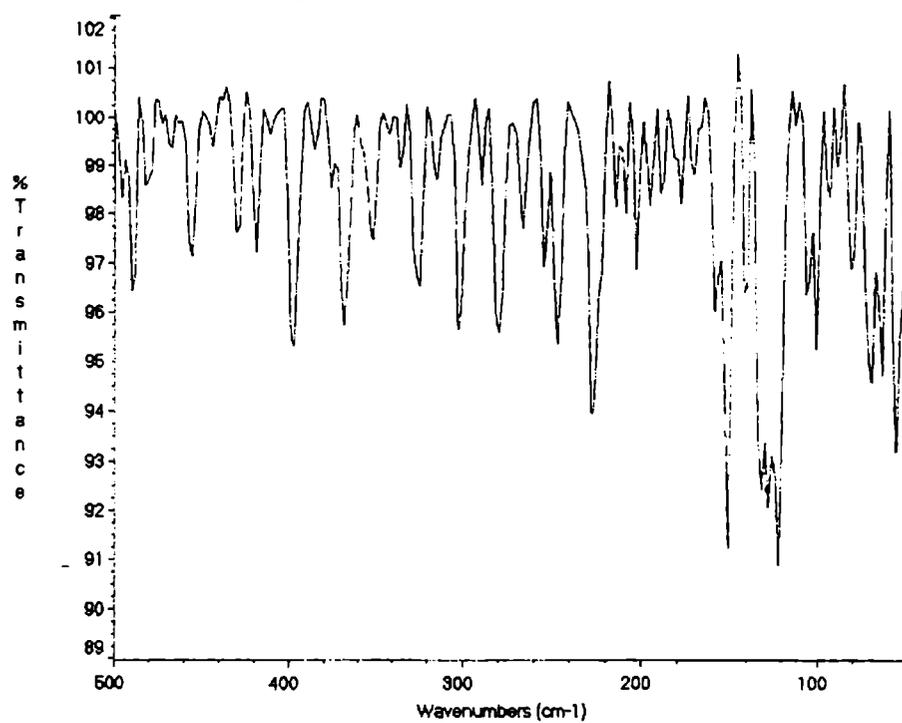


Fig.5.6. Far IR spectrum of compound 15

5.3.4. Electronic spectra

The electronic absorption bands recorded in the polycrystalline state of the iron(III) complexes are given in Table 5.3. The bands observed at *ca.* 277 and 335 nm can be assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the ligand. Usually $n \rightarrow \pi^*$ transitions occur at a lower energy than $\pi \rightarrow \pi^*$ transitions. Two broad absorption bands are present in the region 656–400 nm. They are charge transfer transitions [16] due to $d \rightarrow \pi^*$ metal-to-ligand and $S \rightarrow Fe(III)$ electronic transitions [17].

Because of the greater oxidizing power of Fe(III), ligand to metal charge transfer bands often obscure the very low intensity, spin forbidden, $d-d$ absorption bands [18]. In the spectra of iron(III) complexes, the shoulders that appeared at *ca.* 890 nm are due to $d \rightarrow d$ transitions [11].

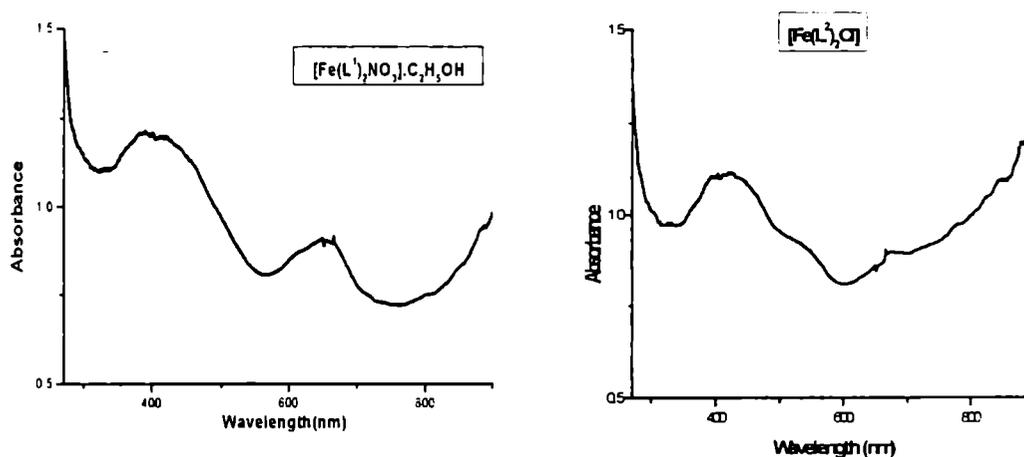


Fig.5.7. Electronic spectra of compounds 13 and 14

Table 5.3 Electronic spectral data (nm) of Iron(III) complexes

Compound	<i>d-d</i>	Charge transfer	<i>n</i> → <i>π</i> *	<i>π</i> → <i>π</i> *
Fe(L ¹) ₂ NO ₃ ·C ₂ H ₅ OH (13)	890sh	650, 402	335	276
[Fe(L ²) ₂ NO ₃]·2H ₂ O (14)	875sh	656, 419	332	278
[Fe(L ²) ₂ Cl] (15)	887sh	655, 417	337	278
[Fe(L ²) ₂ NCS (16)	884sh	652, 408	330	280

5.3.5. Electron paramagnetic resonance spectra

The EPR spectra of the iron(III) complexes in the polycrystalline state were recorded at 298 and 110 K and in DMF solution at 110 and 77 K and the EPR parameters are given in Table 5.4. The EPR spectrum of the *d*⁵ iron(III) is expressed by the spin Hamiltonian [19, 20]:

$$\hat{H} = \beta[g_x H_x \cdot S_x + g_y H_y \cdot S_y + g_z H_z \cdot S_z] \quad \text{with } S = 1/2 \text{ and } g = 2.00$$

The spectra of all the complexes in the polycrystalline state and in DMF solution at different temperatures, show three *g* values, indicating that these complexes have rhombic distortion. There is little difference in the spectra obtained in frozen DMF and in the solid state indicating that the iron(III) centres do not undergo alteration in solution.

The observed anisotropic character with three *g* values due to rhombic distortion is common for spin-paired iron(III) complexes [21]. The *g* values confirm the low-spin character of iron(III) as obtained from the magnetic moment. The anisotropic character with the three *g* values due to rhombic distortion is not uncommon for spin paired iron(III) since this behavior has been reported for Schiff base as well as porphyrin Fe(III) complexes. The small deviation of the anisotropic

g value from 2.0 suggests that the electronic structure of the ground state is $(d_{xz})^2$, $(d_{yz})^2$, $(d_{xy})^1$ [22,23].

At 77 and 110 K, all the iron(III) complexes in DMF solution have similar anisotropic spectra with almost the same g_{av} values, indicating that the bonding in all the complexes is similar and is unaffected by the coordination of the anion.

Based on the physicochemical studies, the iron(III) complexes with nitrate, chloro, thiocyanato as counter-ions are assigned either a capped octahedral or a pentagonal bipyramidal geometry [24]. EPR data also suggest that the iron(III) complexes are low spin with the association of anions in the first coordination sphere of iron(III) in the solid state. In the capped octahedral structure two molecules of the ligand L^2 or L^1 can occupy the six corners of an octahedron and an additional position is occupied by an anion at one triangular face of this octahedron. In an alternate pentagonal bipyramidal structure [25], two molecules of the L^2 or L^1 can occupy two axial positions and four positions in the equatorial position plane, an additional fifth position in the equatorial plane being occupied by the anion. The structure suggested for the complexes is shown in Fig. 5.18.

Table 5.4 EPR spectral parameters of iron(III) complexes

Compound	State	Temperature (K)	g_1	g_2	g_3
[Fe(L ¹) ₂ NO ₃]-C ₂ H ₅ OH (13)	Powder	298	2.080	2.2940	2.3344
	Powder	110	2.0176	2.1731	2.2098
	DMF	110	2.0199	2.1594	2.2046
	DMF	77	2.0695	2.1484	2.1809
[Fe(L ²) ₂ NO ₃]-2H ₂ O (14)	Powder	298	2.0446	2.1282	2.1796
	Powder	110	2.0270	2.1414	2.1837
	DMF	110	2.0218	2.1564	2.2029
	DMF	77	2.0042	2.1292	2.1796
[Fe(L ³) ₂ Cl (15)	Powder	298	2.0085	2.1301	2.1547
	Powder	110	2.0228	2.1496	2.1838
	DMF	110	2.0254	2.1472	2.1847
	DMF	77	2.1128	2.1266	2.1584
[Fe(L ³) ₂ NCS (16)	Powder	298	2.0084	2.1340	2.1697
	DMF	77	2.0053	2.1272	2.1663

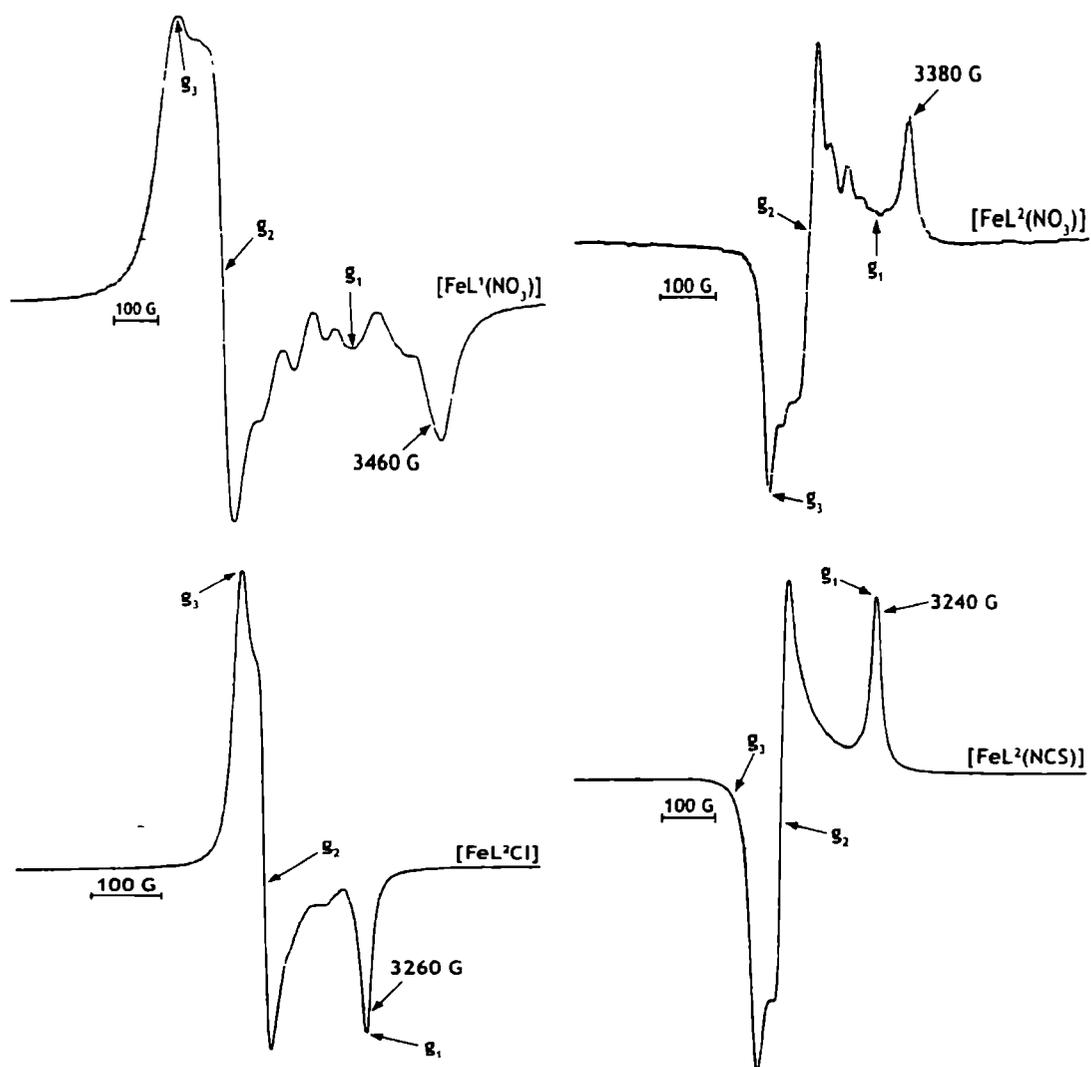


Fig 5.8. EPR spectra of compounds 13, 14, 15 and 16 in the polycrystalline state at 298 K

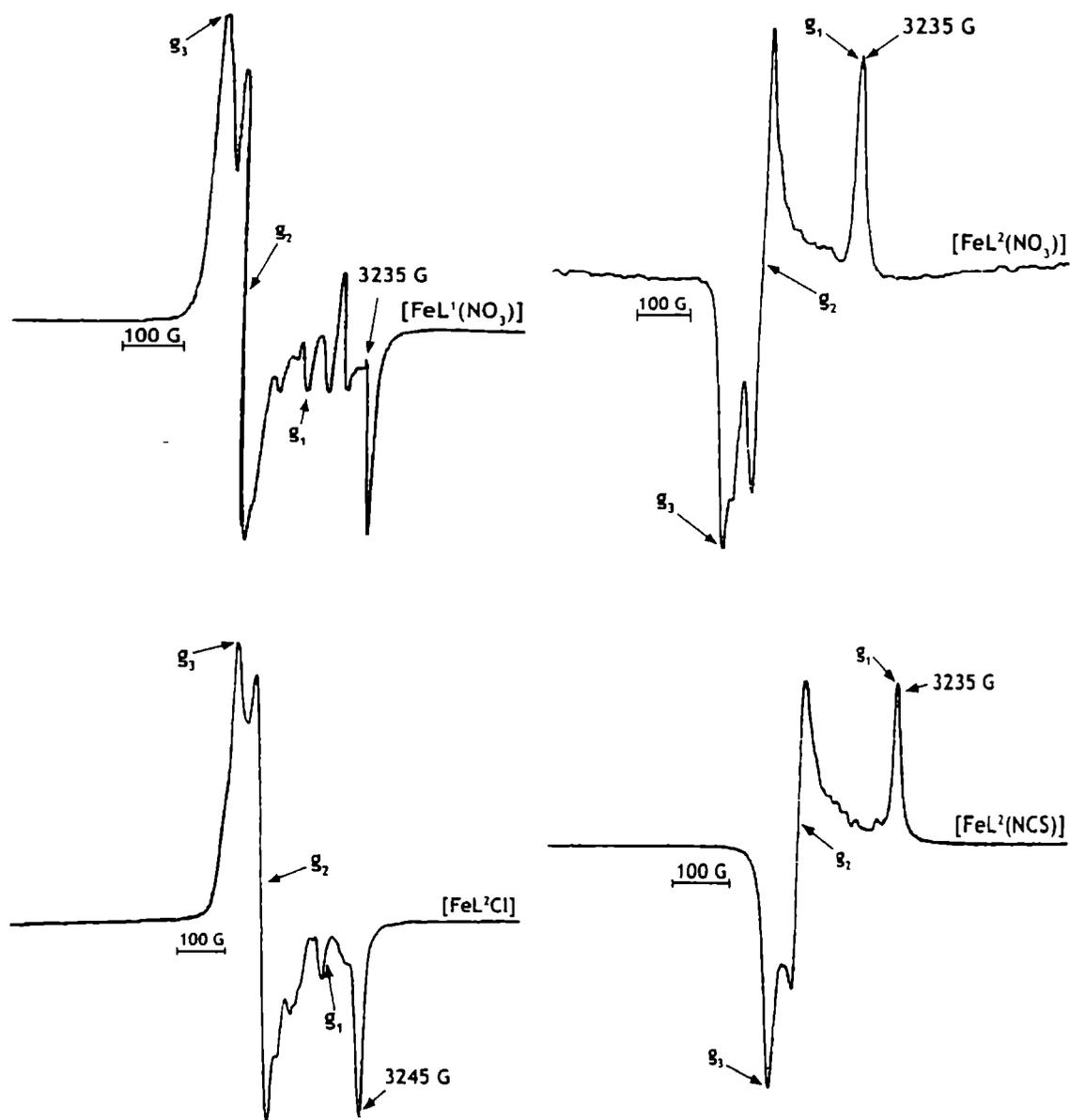


Fig 5.9. EPR spectra of compounds 13, 14, 15 and 16 in DMF at 77 K

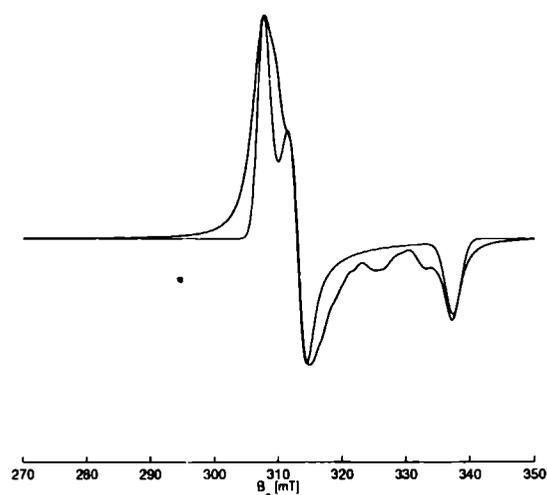


Fig.5.10. EPR spectrum of compound **13** in the polycrystalline state at 298 K

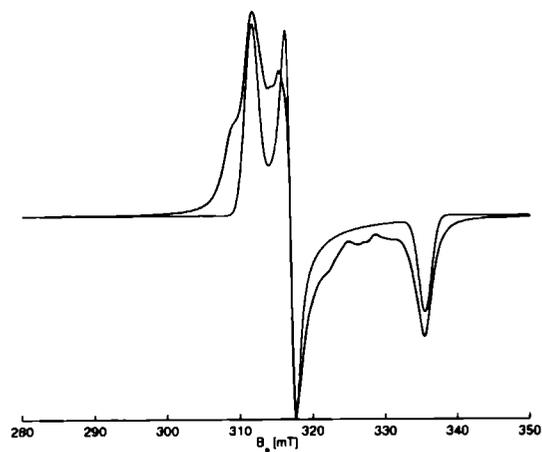


Fig.5.11. EPR spectrum of compound **14** in the polycrystalline state at 298 K

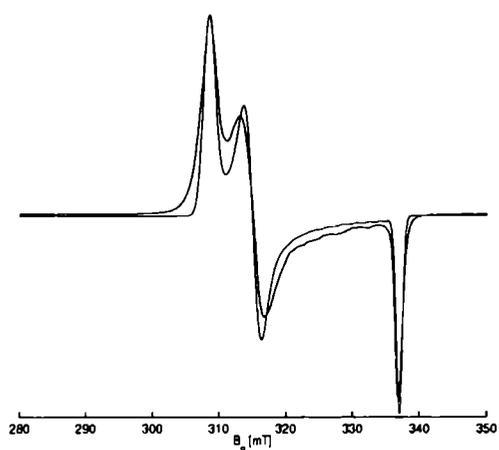


Fig.5.12. EPR spectrum of compound **13** in DMF at 110 K

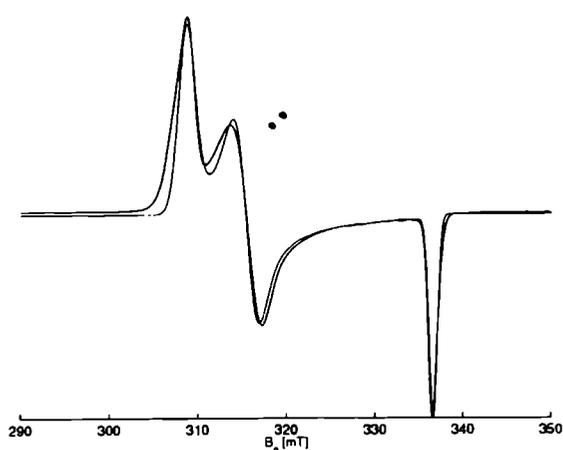


Fig.5.13. EPR spectrum of compound **14** in DMF at 110 K

Red-simulated; Blue-experimental

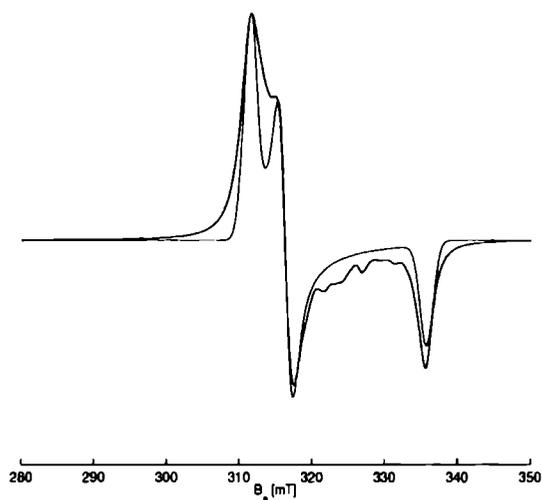


Fig.5.14. EPR spectrum of compound 15 in the polycrystalline state at 298 K

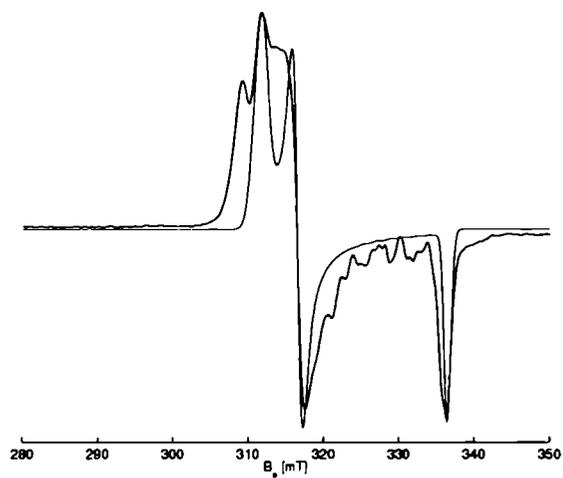


Fig.5.15. EPR spectrum of compound 15 in DMF at 110 K

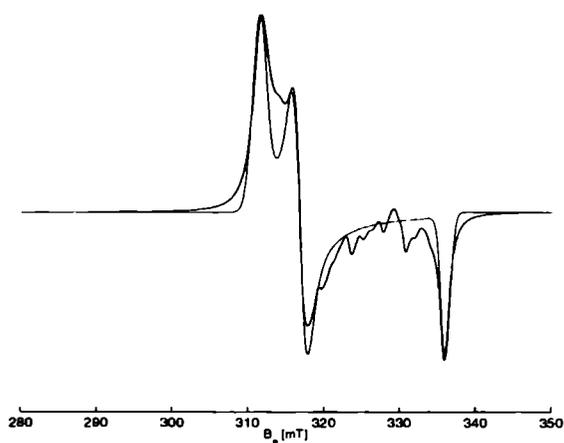


Fig.5.16. EPR spectrum of compound 13 in the polycrystalline state at 110 K

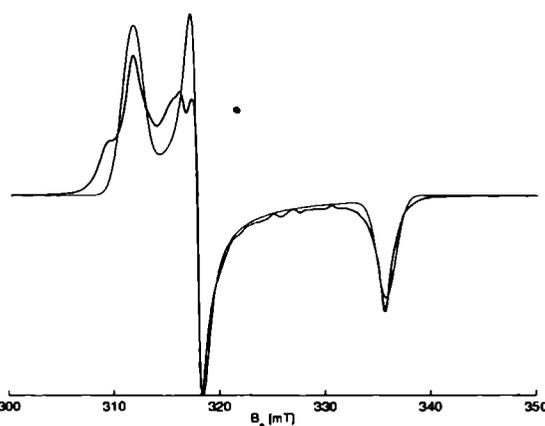


Fig.5.17. EPR spectrum of compound 14 in the polycrystalline state at 110 K

Red-simulated; Blue- experimental

5.4. Antimicrobial activity

The four Fe(III) complexes are screened for antimicrobial activity using the Disc diffusion method against the five types of bacteria: 1. *Staphylococcus aureus*, 2. *Bacillus* sp (Gram Positive) 3. *Escherichia coli* 4. *Salmonella paratyphi* 5. *Vibrio cholerae* O1 (Gram Negative). All the complexes are found to be microbial inactive.

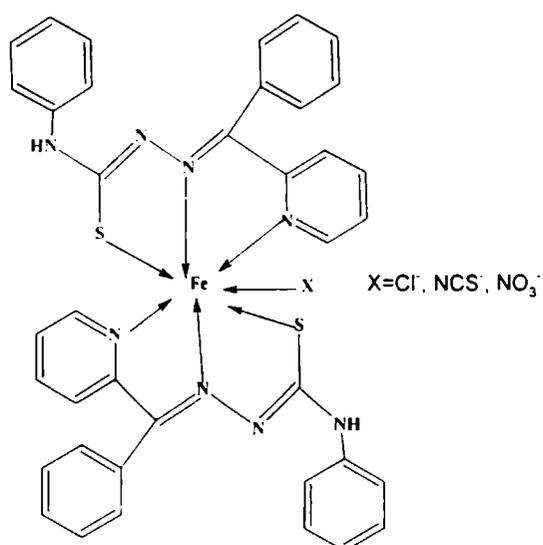


Fig.5.18. Tentative structure for [Fe(L²)₂X]

References

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