

# Synthesis and Characterisation of Dinuclear Iron(III) of Mannich Base Ligands

G.Ananthakrishnan\*, S.Sujatha, K. Balasubramanian

Post Graduate and Research, Department of Physics, Saranathan College of Engineering, Tiruchirappalli 621 105, India.

**Abstract:** - Binuclear Fe (III) complex of Mannich base ligands have intervalence charge transfer transition which is a characteristics of mixed valence complexes and was prepared through the thermal transformation of its mononuclear complex to the binuclear one. All complexes and the corresponding thermal products were isolated and their structures were elucidated by elemental analyses, conductance, IR and electronic absorption spectra, magnetic moments,  $^1\text{H}$  NMR and EPR.

## I. INTRODUCTION

The chemistry of binucleating ligands, that provide chemically distinct donor sets, is of current interest to bioinorganic chemists<sup>1-5</sup>. This observation led to the suggestion that unsymmetrical dinucleating ligands are beacons for modeling the active site structure of binuclear metallo bio sites existing in biological systems.

Dinuclear iron complexes continue to attract attention largely because of their use as models for iron-oxo proteins<sup>6,7</sup> and catalysts for the oxidation of hydrocarbons<sup>8</sup> but also because of attempts to correlate the geometries of the bridging moieties in crystalline species with the size and sign of the magnetic exchange  $j$  parameter<sup>8,9-10</sup>. The current state of Fe...Fe magnetostructural correlations has recently been summarized by Holm *et al.*<sup>9</sup> in order to make comparisons with the unexpected ferromagnetic coupling found in some di- $m$ -alkoxo bridged  $fe$ -hydrosalicylamide complexes, a group of compounds which we had also studied some years ago<sup>11</sup>. Some excellent synthetic models of types  $LFe(O)(OAc)_2FeL$  and  $L'Fe(O)(OAc)FeL'$  have recently been developed to mimic the  $m$ -oxo- $m$ -carboxylato-bridge centers in the oxidized forms of the proteins hamerythrin (Hr)<sup>12</sup>, ribonucleotide reductase (RRB2)<sup>13</sup> and methane monooxygenase (MMO).

## II. EXPERIMENTAL

### Preparation of Mannich base precursors

**4-Methoxy-6-[(*N*-methylpiperazin-1-yl)methyl]phenol (MMP) (PC<sub>1</sub>)**

*p*-Methoxy (0.5g, 1mmol) in ethanol (75 ml) was mixed with *N*-methyl piperazine (0.45ml, 1mmol) and cooled in ice. Formaldehyde solution (7 ml, 1mmol) was then added dropwise with stirring. The mixture was stirred at room temperature for half-an-hour and gently heated in a

microwave oven at 40°C. for two minutes .A white powder was isolated. It was recrystallised from ethanol.

Yield: 90%

$C_{13}H_{20}N_2O_2$  (236.31), M.pt = 110-112°C

$^1\text{H}$ NMR in  $CdCl_2$   $\delta$  ppm: 1.3-1.5 (s, 3H, OCH<sub>3</sub>); 2.2-2.3 (s, 3H, N-CH<sub>3</sub>); 2.4-2.7 (s, 8H, N-CH<sub>2</sub>); 3.2-3.5 (s, 2H, CH<sub>2</sub>-Ph); 6.5-6.7 (m, 3H, ArH). The NMR spectrum of the precursor [PC<sub>1</sub>] is shown in Fig. 5.1 and Scheme 5.1. These precursors (PC<sub>2</sub>), (PC<sub>3</sub>), (PC<sub>4</sub>), (PC<sub>5</sub>) and (PC<sub>6</sub>) were synthesized by the same synthetic procedure as (PC<sub>1</sub>).

**4-Methoxy-6-[(*N*-phenylpiperazin-1-yl)methyl]phenol (MPP) (PC<sub>2</sub>)**

Yield: 95%

$C_{18}H_{22}N_2O_2$  (298.37), M.pt = 105-108°C,

$^1\text{H}$ NMR in  $CdCl_2$   $\delta$  ppm: 1.3-1.5 (s, 3H, OCH<sub>3</sub>); 2.4-2.6 (s, 8H, N-CH<sub>2</sub>); 3.5-3.6 (s, 2H, CH<sub>2</sub>-Ph); 6.5-6.9 (m, 8H, ArH).

**4-Chloro-3-methyl-6-[(*N*-methylpiperazin-1-yl)methyl]phenol (CMMP) (PC<sub>3</sub>)**

Yield: 92%

$C_{13}H_{19}ClN_2O$  (254.76), M.pt = 125-127°C

$^1\text{H}$ NMR in  $CdCl_2$   $\delta$  ppm: 1.3 (s, 3H, Ar-CH<sub>3</sub>); 2.5 (s, 3H, -CH<sub>3</sub>); 2.6-3.5 (s, 8H, N-CH<sub>2</sub>); 3.69 (s, 2H, benzylic CH<sub>2</sub>); 6.3-6.5 (m, 2H, aromatic).

**4-Chloro-3-methyl-6-[(*N*-phenylpiperazin-1-yl)methyl]phenol (CMPP) (PC<sub>4</sub>)**

Yield: 94%

$C_{18}H_{21}ClN_2O$  (316.83), M.pt = 135-137°C

$^1\text{H}$ NMR in  $CDCl_3$   $\delta$  ppm: 1.2 (s, 3H, Ar-CH<sub>3</sub>); 2.6-2.7 (s, 4H, N-CH<sub>2</sub>); 3.2-3.5 (s, 4H, N-CH<sub>2</sub>); 3.7-3.8 (s, 2H, benzylic CH<sub>2</sub>); 6.6-7.4 (m, 7H, aromatic).

**4-chloro-6-[(*N*-methylpiperazin-1-yl)methyl]phenol (CMP) (PC<sub>5</sub>)**

Yield: 89%

$C_{12}H_{17}ClN_2O$  (240.72), M.pt = 115-117°C

$^1\text{H NMR}$  in  $\text{CDCl}_3$   $\delta$  ppm: 2.2-2.4 (s, 3H, N- $\text{CH}_3$ ); 2.4-2.5 (s, 8H, N- $\text{CH}_2$ ); 3.6-3.7 (s, 2H, benzylic  $\text{CH}_2$ ); 6.6-6.9 (m, 3H, ArH).

*4-chloro-6-[(N-phenylpiperazin-1-yl)methyl]phenol (CPP)* ( $\text{PC}_6$ )

Yield: 86%

$\text{C}_{17}\text{H}_{19}\text{ClN}_2\text{O}$  (302.79), M.pt = 117-120°C

$^1\text{H NMR}$  in  $\text{CDCl}_3$   $\delta$  ppm: 2.7-2.8 (s, 8H, N- $\text{CH}_2$ ); 3.5-3.6 (s, 2H, benzylic  $\text{CH}_2$ ); 6.5-7.5 (m, 8H, aromatic).

### III. PREPARATION OF MANNICH BASE LIGANDS

**Synthesis of 4-methoxy-2-[(prolin-1-yl)methyl]-6-[(N-methylpiperazin-1-yl)methyl]phenol (MPMP) ( $\text{L}_1$ )**

*4-Methoxy-6-[(N-methylpiperazin-1-yl)methyl]phenol* (1.0g, 0.02mol) was mixed with L-proline (0.487, 0.02mol) and cooled in ice. Formaldehyde solution (14ml, 0.02mol) was then added drop wise with stirring. The mixture was stirred at room temperature for half-an-hour and gently heated in a microwave oven at 50°C for two minutes. The resulting white powder was washed with saturated sodium carbonate solution, dried with anhydrous magnesium sulphate and filtered before recovery.

Yield: 85%

$\text{C}_{19}\text{H}_{29}\text{N}_3\text{O}_4$  (363.51), M.pt = 225-227°C

$^1\text{H NMR}$  in  $\text{CDCl}_3$   $\delta$  ppm: 1.5-2.0 (s, 3H,  $\text{OCH}_3$ ); 2.3-2.4 (m, 12H); 2.5-2.7 (3H, N- $\text{CH}_3$ ); 3.2-3.5 (s, 4H, benzylic  $\text{CH}_2$ ); 4.5 (m, 2H Pro); 4.8 (t, N-CH Pro); 6.4-7.0 (m, 2H, ArH). The NMR spectrum of the ligand ( $\text{L}_{16}$ ) is shown in Fig. 5.2. These ligands ( $\text{L}_2$ ), ( $\text{L}_3$ ), ( $\text{L}_4$ ), ( $\text{L}_5$ ) and ( $\text{L}_6$ ) were synthesized by the same synthetic procedure as ( $\text{L}_1$ ).

*Synthesis of 4-methoxy-2-[(prolin-1-yl)methyl]-6-[(N-phenylpiperazin-1-yl)methyl]phenol (MPPP) ( $\text{L}_2$ )*

Yield: 83%

$\text{C}_{24}\text{H}_{31}\text{N}_3\text{O}_4$  (425.52), M.pt = 252-253°C

$^1\text{H NMR}$  in  $\text{CDCl}_3$   $\delta$  ppm: 1.5-1.6 (s, 3H,  $\text{OCH}_3$ ); 2.3-2.4 (m, 12H); 3.2-3.6 (s, 4H, benzylic  $\text{CH}_2$ ); 4.2-4.5 (m, 2H Pro); 4.6-4.8 (t, N-CH Pro); 6.4-6.6 (m, 5H); 7.2 (s, 2H, ArH).

*Synthesis of 4-chloro-3-methyl-2-[(prolin-1-yl)methyl]-6-[(N-methylpiperazin-1-yl)methyl]phenol (CMPMP) ( $\text{L}_3$ )*

Yield: 80%

$\text{C}_{19}\text{H}_{28}\text{N}_3\text{O}_3\text{Cl}$  (381.89), M.pt = 297-298°C

$^1\text{H NMR}$  in  $\text{CDCl}_3$   $\delta$  ppm: 1.5-2.0 (s, 3H,  $\text{CH}_3$ ); 2.3-2.5 (m, 12H); 2.7-2.8 (s, 3H, N- $\text{CH}_3$ ); 3.2-3.5 (m, 4H, benzylic  $\text{CH}_2$ ); 4.4-4.6 (m, 2H, Pro); 4.7-4.8 (t, N-CH); 6.4-6.6 (m, 1H, ArH).

*Synthesis of 4-Chloro-3-methyl-2-[(prolin-1-yl)methyl]-6-[(N-phenylpiperazin-1-yl)methyl]phenol (CMPPP) ( $\text{L}_4$ )*

Yield: 89%,

$\text{C}_{24}\text{H}_{30}\text{ClN}_3\text{O}_3$  (443.96), M.pt = 302-303°C

$^1\text{H NMR}$  in  $\text{CDCl}_3$   $\delta$  ppm: (1.6-3.3, m, 12H); 2.2-2.4 (s, 3H,  $\text{CH}_3$ ); 3.6-3.8 (m, 4H, benzylic  $\text{CH}_2$ ); 4.1-4.3 (m, 2H, N $\text{CH}_2$ -Pro); 4.5-4.8 (t, 1H, NCH-Pro); 6.7-7.2 (m, 6H, ArH).

*Synthesis of 4-Chloro-2-[(prolin-1-yl)methyl]-6-[(N-methylpiperazin-1-yl)methyl]phenol (CPMP) ( $\text{L}_5$ )*

Yield: 86 %

$\text{C}_{18}\text{H}_{26}\text{ClN}_3\text{O}_3$  (367.87), M.pt = 265-267°C

$^1\text{H NMR}$  in  $\text{CDCl}_3$   $\delta$  ppm: 1.5-3.2 (m, 12H); 2.5-2.7 (3H, N- $\text{CH}_3$ ); 3.3-3.7 (m, 4H benzylic); 4.2-4.3 (m, 2H Pro); 4.5-4.7 (t, N-CH); 6.8-7.4 (m, 2H aromatic).

*Synthesis of 4-Chloro-2-[(prolin-1-yl)methyl]-6-[(N-phenylpiperazin-1-yl)methyl]phenol (CPPP) ( $\text{L}_6$ )*

Yield: 92%

$\text{C}_{23}\text{H}_{28}\text{ClN}_3\text{O}_3$  (429.94), M.pt = 270-271°C

$^1\text{H NMR}$  in  $\text{CDCl}_3$   $\delta$  ppm: 1.5-3.2 (m, 12H); 3.3-3.7 (m, 4H benzylic); 4.3-4.4 (m, 2H Pro); 4.5-4.6 (t, N-CH); 6.8-7.4 (m, 7H aromatic).

### IV. SYNTHESIS OF THE DI-IRON COMPLEXES

(a) *Hydroxo bridged complexes*

**$[\text{Fe}_2(\text{L}_1)(\text{OH})\text{ClO}_4 \cdot \text{H}_2\text{O}$  ( $\text{C}_1$ )**: Sodium hydroxide (0.001mol) was added to the methanolic solution of the ligand ( $\text{L}_{16}$ ) (0.001mol), followed by a solution of iron(III) perchlorate hexahydrate (0.002mol) dissolved in methanol. The obtained solution was refluxed for 4 hours and then filtered. On evaporation of the solution at room temperature for several days dark green precipitate was obtained. The complex was recrystallized from aqueous methanol. These complexes ( $\text{C}_2$ ), ( $\text{C}_3$ ), ( $\text{C}_4$ ), ( $\text{C}_5$ ) and ( $\text{C}_6$ ) were synthesized by the same synthetic procedure as ( $\text{C}_1$ ) using the ligands ( $\text{L}_2$ ), ( $\text{L}_3$ ), ( $\text{L}_4$ ), ( $\text{L}_5$ ), ( $\text{L}_6$ ) in place of ( $\text{L}_1$ ).

Data for  **$[\text{Fe}_2(\text{L}_1)(\text{OH})\text{ClO}_4 \cdot \text{H}_2\text{O}$  ( $\text{C}_1$ )**

Yield-81% ESI-MS:  $m/z = 488(100\%)$   $[\text{Fe}_2(\text{L}_1)(\text{OH})]^+$  FT-IR(KBr,  $\text{v}/\text{cm}^{-1}$ ): 3550, 1623, 1580, 1472, 1385, 1238, 1182, 1088, 926, 842, 647, 565, 411.

Data for  **$[\text{Fe}_2(\text{L}_2)(\text{OH})\text{ClO}_4 \cdot \text{H}_2\text{O}$  ( $\text{C}_2$ )**

Yield-74% ESI-MS:  $m/z = 552(100\%)$   $[\text{Fe}_2(\text{L}_2)(\text{OH})]^+$  FT-IR(KBr,  $\text{v}/\text{cm}^{-1}$ ): 3420, 1549, 1465, 1446, 1319, 1245, 1150, 1024, 836, 625, 525.

Data for  **$[\text{Fe}_2(\text{L}_3)(\text{OH})\text{ClO}_4 \cdot \text{H}_2\text{O}$  ( $\text{C}_3$ )**

Yield-79% ESI-MS:  $m/z = 508(100\%)$   $[\text{Fe}_2(\text{L}_3)(\text{OH})]^+$  FT-IR(KBr,  $\text{v}/\text{cm}^{-1}$ ): 3520, 1594, 1472, 1382, 1304, 1252, 1150, 1034, 842, 805, 747, 626, 527, 405.

Data for  **$[\text{Fe}_2(\text{L}_4)(\text{OH})\text{ClO}_4 \cdot \text{H}_2\text{O}$  ( $\text{C}_4$ )**

Yield-86% ESI-MS:  $m/z = 570(100\%)$   $[\text{Fe}_2(\text{L}_4)(\text{OH})]^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3480, 1560, 1474, 1446, 1388, 1240, 1147, 1090, 931, 802, 630, 523.

Data for  $[\text{Fe}_2(\text{L}_5)(\text{OH})]\text{ClO}_4 \cdot \text{H}_2\text{O}$  (**C**<sub>5</sub>)

Yield-75% ESI-MS:  $m/z = 494(100\%)$   $[\text{Fe}_2(\text{L}_5)(\text{OH})]^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3410, 1650, 1580, 1472, 1392, 1380, 1238, 1125, 1088, 926, 868, 830, 652, 545.

Data for  $[\text{Fe}_2(\text{L}_6)(\text{OH})]\text{ClO}_4 \cdot \text{H}_2\text{O}$  (**C**<sub>6</sub>)

Yield-81% ESI-MS:  $m/z = 556(100\%)$   $[\text{Fe}_2(\text{L}_6)(\text{OH})]^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3530, 1604, 1472, 1406, 1386, 1306, 1254, 1172, 1030, 931, 842, 622, 520, 456.

#### (b) Bis-Acetato bridged complexes

**$[\text{Fe}_2(\text{L}_1)(\text{OAc})_2] \cdot \text{ClO}_4 \cdot \text{H}_2\text{O}$  (**C**<sub>7</sub>):** Ferric(III) acetate monohydrate (0.002mol) was dissolved in warm aqueous methanol (75ml). Addition of methanolic solution of the ligand (**L**<sub>16</sub>) (0.001mol) and  $\text{LiClO}_4$  (0.002mol) are added to it led to the formation of a dark-violet solution. The mixture was then refluxed for four hours and filtered. Upon concentration, amorphous violet powder was obtained. These complexes (**C**<sub>8</sub>), (**C**<sub>9</sub>), (**C**<sub>10</sub>), (**C**<sub>11</sub>) and (**C**<sub>12</sub>) were synthesized by the same synthetic procedure as (**C**<sub>7</sub>) using the ligands (**L**<sub>2</sub>), (**L**<sub>3</sub>), (**L**<sub>4</sub>), (**L**<sub>5</sub>), (**L**<sub>6</sub>) in place of (**L**<sub>1</sub>).

Data for  $[\text{Fe}_2(\text{L}_1)(\text{OAc})_2] \cdot \text{ClO}_4 \cdot \text{H}_2\text{O}$  (**C**<sub>7</sub>)

Yield-81% ESI-MS:  $m/z = 586(96.5\%)$   $[\text{Fe}_2(\text{L}_1)(\text{CH}_3\text{COO})_2]^+ - 3\text{H}^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3424, 1637, 1544, 1519, 1435, 1385, 1240, 1124, 1091, 935, 736, 625, 545, 421.

Data for  $[\text{Fe}_2(\text{L}_2)(\text{OAc})_2] \cdot \text{ClO}_4 \cdot \text{H}_2\text{O}$  (**C**<sub>8</sub>) Yield-85% ESI-MS:  $m/z = 650(97\%)$   $[\text{Fe}_2(\text{L}_2)(\text{CH}_3\text{COO})_2]^+ - 3\text{H}^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3419, 1613, 1597, 1491, 1413, 1387, 1250, 1166, 1117, 1081, 830, 724, 552, 476.

Data for  $[\text{Fe}_2(\text{L}_3)(\text{OAc})_2] \cdot \text{ClO}_4 \cdot \text{H}_2\text{O}$  (**C**<sub>9</sub>)

Yield-74% ESI-MS:  $m/z = 606(95\%)$   $[\text{Fe}_2(\text{L}_3)(\text{CH}_3\text{COO})_2]^+ - 3\text{H}^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3460, 1604, 1500, 1494, 1386, 1306, 1254, 1172, 1030, 931, 842, 622, 548.

Data for  $[\text{Fe}_2(\text{L}_4)(\text{OAc})_2] \cdot \text{ClO}_4 \cdot \text{H}_2\text{O}$  (**C**<sub>10</sub>)

Yield-69% ESI-MS:  $m/z = 668(98\%)$   $[\text{Fe}_2(\text{L}_4)(\text{CH}_3\text{COO})_2]^+ - 3\text{H}^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3470, 1637, 1550, 1519, 1481, 1380, 1240, 1124, 1091, 935, 736, 625, 547, 405.

Data for  $[\text{Fe}_2(\text{L}_5)(\text{OAc})_2] \cdot \text{ClO}_4 \cdot \text{H}_2\text{O}$  (**C**<sub>11</sub>)

Yield-73% ESI-MS:  $m/z = 592(98\%)$   $[\text{Fe}_2(\text{L}_5)(\text{CH}_3\text{COO})_2]^+ - 3\text{H}^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3534, 1637, 1595, 1519, 1484, 1383, 1240, 1124, 1091, 935, 736, 625, 575.

Data for  $[\text{Fe}_2(\text{L}_6)(\text{OAc})_2] \cdot \text{ClO}_4 \cdot \text{H}_2\text{O}$  (**C**<sub>12</sub>)

Yield-65% ESI-MS:  $m/z = 654(98\%)$   $[\text{Fe}_2(\text{L}_6)(\text{CH}_3\text{COO})_2]^+ - 3\text{H}^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3500, 1613, 1525, 1493, 1413, 1367, 1250, 1166, 1117, 1081, 830, 724, 525, 447.

#### (c) Bis nitrito complexes

**$[\text{Fe}_2(\text{L}_1)(\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (**C**<sub>13</sub>):** To a methanolic solution containing the ligand (**L**<sub>16</sub>) (0.001mol) and iron(III) perchlorate hexahydrate (0.002mol), a solution of sodium nitrite (0.003mol) dissolved in methanol (75ml) was added. The resulting dark violet solution was refluxed for 4 hours and filtered. Concentration of this solution yielded blackish violet amorphous powder, which was recrystallized from aqueous methanol. These complexes (**C**<sub>14</sub>), (**C**<sub>15</sub>), (**C**<sub>16</sub>), (**C**<sub>17</sub>) and (**C**<sub>18</sub>) were synthesized by the same synthetic procedure as (**C**<sub>13</sub>) using the ligands (**L**<sub>2</sub>), (**L**<sub>3</sub>), (**L**<sub>4</sub>), (**L**<sub>5</sub>), (**L**<sub>6</sub>) in place of (**L**<sub>1</sub>).

Data for  $[\text{Fe}_2(\text{L}_1)(\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (**C**<sub>13</sub>)

Yield-72% ESI-MS:  $m/z = 662(58\%)$   $[\text{Fe}_2(\text{L}_1)(\text{NO}_2)_2(\text{ClO}_4)]^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3500, 2958, 1610, 1580, 1542, 1479, 1458, 1431, 1382, 1361, 1328, 1265, 1203, 1182, 835, 806, 771, 750, 647, 555.

Data for  $[\text{Fe}_2(\text{L}_2)(\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (**C**<sub>14</sub>)

Yield-85% ESI-MS:  $m/z = 726(60\%)$   $[\text{Fe}_2(\text{L}_2)(\text{NO}_2)_2(\text{ClO}_4)]^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3439, 2938, 1610, 1570, 1540, 1479, 1487, 1444, 1380, 1357, 1318, 1260, 1220, 1175, 845, 816, 747, 620, 505.

Data for  $[\text{Fe}_2(\text{L}_3)(\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (**C**<sub>15</sub>)

Yield-74% ESI-MS:  $m/z = 683(58\%)$   $[\text{Fe}_2(\text{L}_3)(\text{NO}_2)_2(\text{ClO}_4)]^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3520, 2940, 1650, 1565, 1538, 1475, 1458, 1428, 1386, 1360, 1318, 1260, 1213, 1157, 868, 820, 625, 576, 420.

Data for  $[\text{Fe}_2(\text{L}_4)(\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (**C**<sub>16</sub>)

Yield-78% ESI-MS:  $m/z = 745(52\%)$   $[\text{Fe}_2(\text{L}_4)(\text{NO}_2)_2(\text{ClO}_4)]^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3480, 1633, 1562, 1472, 1693, 1378, 1252, 1199, 1150, 1042, 990, 864, 823, 630, 586.

Data for  $[\text{Fe}_2(\text{L}_5)(\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (**C**<sub>17</sub>)

Yield-84% ESI-MS:  $m/z = 669(52\%)$   $[\text{Fe}_2(\text{L}_5)(\text{NO}_2)_2(\text{ClO}_4)]^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3489, 2958, 1614, 1571, 1492, 1440, 1363, 1312, 1268, 1250, 1125, 1026, 978, 880, 751, 652, 580, 431.

Data for  $[\text{Fe}_2(\text{L}_6)(\text{NO}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  (**C**<sub>18</sub>)

Yield-70% ESI-MS:  $m/z = 731(52\%)$   $[\text{Fe}_2(\text{L}_6)(\text{NO}_2)_2(\text{ClO}_4)]^+$  FT-IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3530, 1593, 1471, 1452, 1350, 1306, 1240, 1100, 1091, 931, 733, 635, 542.

## V. ANALYSIS AND PHYSIOCHEMICAL STUDIES OF THE COMPLEXES

All the complexes were analysed for the metal percentage. The anions present in the complexes were also estimated. The molar conductivities of the complexes DMF ( $\sim 10^{-3}$  M solutions) were measured at room temperature ( $28 \pm 2^\circ\text{C}$ ). Elemental analysis was performed on a Perkin Elmer series II CHN ANALYSER 2400. Electronic spectra of complexes were recorded using Varian model: 5000 UV-VIS-NIR spectrophotometer. IR spectra were recorded on FT-IR

spectrophotometer using ThermoNicolet model: 6700 FT-IR spectrophotometer. EPR spectra of powdered samples were measured at room temperature on a JEOL JES-TE100 EPR spectrometer operating at X-band frequencies, and having a 100 kHz phase modulation to obtain the first derivative EPR spectrum. DPPH with a  $g$  value of 2.0036 was used as an internal field marker. Mass spectra were performed on a Thermo Finigan LCQ 6000 Advantage Max and Q-TOF ESI-MS instrument. Magnetic measurements of the complexes at room temperature were carried out by using a Guoy magnetic balance.

## VI. RESULTS AND DISCUSSION

### *Elemental Analysis*

The molecular weight of the ligands and the metal complexes are presented in Tables 1-4.

### *IR Spectroscopy*

IR spectra of all the ligands exhibit higher higher energy absorptions in the region of 3450-3500  $\text{cm}^{-1}$  which can be correlated with the -OH group. The band at 740  $\text{cm}^{-1}$  is due to  $\text{Cl}^-$  group and the band at 1380  $\text{cm}^{-1}$  is due to N- $\text{CH}_3$  and N- $\text{C}_6\text{H}_5$  stretching vibration. A band around 3480-3600 can be attributed to the coordinated water molecule. All the hydroxy bridged complexes exhibit a sharp band in the region 3480-3600  $\text{cm}^{-1}$  which is assigned to the -OH stretch on the basis of previous reports<sup>14, 15</sup>. The bis acetate complexes exhibit<sup>16</sup> strong COO bands around 1472  $\text{cm}^{-1}$  and 1594  $\text{cm}^{-1}$ . The nitrito complexes around 1450  $\text{cm}^{-1}$  and 1220  $\text{cm}^{-1}$ ,<sup>17</sup> which would suggest a monodentate O-bonded mode for the nitrite groups. The peak at 1365  $\text{cm}^{-1}$  and the shoulder at 1475  $\text{cm}^{-1}$  are assigned to symmetric C-H bend of the methyl group, which are not much affected in the complexes. The peak at 1300  $\text{cm}^{-1}$  which is C-O or O-H deformation of the acid group is shifted lower to 1285  $\text{cm}^{-1}$  in the complexes. The peak at 1215  $\text{cm}^{-1}$  and 1182  $\text{cm}^{-1}$  of the ligand which are due to C-O or C-O-C of the acetate group are shifted higher lower to 1240  $\text{cm}^{-1}$  and 1200  $\text{cm}^{-1}$  in the spectra of the complexes.  $\Delta\text{OCO}$  and C-H out of plane aromatic ring, found at 915  $\text{cm}^{-1}$  and 840  $\text{cm}^{-1}$  are shifted to 880  $\text{cm}^{-1}$  and 850  $\text{cm}^{-1}$  in the spectra of the complexes. The absence of asymmetric and symmetric C-O stretching frequency and presence of anion ( $\text{Cl}^-$  or  $\text{ClO}_4^-$ ) indicate that the carbonyl (C=O) of the carboxylic acid is coordinated to the metal atom and the acid group is not ionized.

Nearly 840  $\text{cm}^{-1}$  in IR spectroscopy which has been previously attributed to the asymmetric stretch of the Fe-O-Fe bridge<sup>18-21</sup>. The band at 465  $\text{cm}^{-1}$  and 535  $\text{cm}^{-1}$  of the complexes which are absent in the spectra of the ligand may be due to M-O and M-N<sup>22</sup> stretching frequency as shown in Fig.1 The complexes exhibits a broad band at 1363-1370nm in the near region, it can be assigned to the intervalence charge transfer transition which is a characteristics of mixed valence complexes<sup>23</sup> exhibited in Fig.1

### *UV-Visible Spectroscopy*

The hydroxo bridged complexes exhibit three absorption bands around 220-250 nm are probability for charge transfer band involving other ligands atoms. The band observed at 303-313 nm and 386-402 nm are due to internal ligand transition (C=N-and phenolate chromophores), while the band at 586nm is due to phenolate  $\rightarrow$  iron(III) charge transfer transition. In the acetate bridged complexes the first two bands are blue-shifted to 261-270 nm, 333-378 nm, while the absorption due to phenolate  $\rightarrow$  iron(III) charge transfer transition appears as weak band occurring around 650-680 nm. The nitro bridged exhibits three absorption bands at 257 nm - 263 nm, 412 nm - 450 nm and shows a broad shoulder at about 580-600 nm<sup>24</sup>. The oxo-bridged di-iron(III) complexes are known to exhibit several symmetry related to oxo-  $\rightarrow$  iron(III) charge transfer transition whose energy depend on Fe-O-Fe bridge angle<sup>25</sup>. Fe-O-Fe bridges have been reported to exhibit UV/Vis absorbances at 360-380 nm which have been attributed to charge transfer states<sup>26,27-30</sup>. The important UV-Vis, IR spectra data of the di-iron were explained in (Fig.2) and Tables (5-7).

### *EPR Spectroscopy*

EPR spectroscopy has been very useful for characterizing the electronic and magnetic properties of the di-iron(II,III) centers in the dinuclear metal complexes and proteins<sup>31</sup>. When the high-spin  $\text{Fe}^{\text{II}}$  ( $S_1 = 2$ ) and  $\text{Fe}^{\text{III}}$  ( $S_2 = 5/2$ ) centers are antiferromagnetically coupled, they exhibit characteristic signals at  $g(\text{avg}) < 2.0$  resulting from a ground state ( $S_{\text{total}} = 1/2$ )<sup>32</sup>. All the diiron, complex exhibits the intense EPR signals at  $g = (8.5-8.0), (5.4-5.0), (4.3-4.1)$  with a very weak signals in the region of  $g < 2.0$  Fig.3 & Fig. 4. These intense signals are originated from the mononuclear high-spin  $\text{Fe}^{\text{III}}$  ( $S = 5/2$ ) center with almost axial symmetry ( $g = 8.56, 5.45$ ) and rhombic symmetry ( $g = 4.30$ ). Thus, we can suggest that complexes has a very weakly antiferromagnetic coupling between the  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  center.

### *Conductance Measurements*

The electrical conductance's of the di-iron complexes have been studied using DMF as solvent. The type of 1:1 electrolyte is for acetate and nitrito bridged di-iron complexes and 1:2 for hydroxo bridged complexes<sup>33</sup>. The conductance data are given in Tables 5,6&7.

### *ESI-MS Studies*

The ESI-MS of all the ligands and the complexes showing a prominent peak corresponding Diiron complexes datas are discussed in detail in Table.8 and shown in Figs.5-10. Moreover these complexes show peaks indicative of their binuclear nature along with peaks derived from fragmentations to the mononuclear species<sup>34</sup>.

### *Magnetic Studies*

For all the di-iron complexes, the observed effective magnetic moment ( $\mu_{\text{eff}} = 6.05 \text{ BM}$ ) is slightly smaller than the value of the magnetically uncoupled high-spin  $\text{Fe}^{\text{II}}$  and

Fe<sup>III</sup> system (spin only value:  $\mu_{\text{eff}} = [g(S_1(S_1 + 1) + S_2(S_2 + 1))]^{1/2} = 7.68 \text{ B.M.}$ )<sup>35</sup>. Thus, di-iron complex has a very weak antiferromagnetic coupling that is consistent with EPR data. This unusual magnetic behaviour is due to the electron-withdrawing effect of the chloro group in the bridging phenolate moiety. Therefore, we can suggest that the major magnetic exchange interaction action between the iron centers. Therefore, the dependence of the physical properties on the bridging and terminal ligand environment in the model complexes can provide important insights into the electronic and magnetic interaction of such dinuclear iron centers surrounded with hydrophobic pocket amino acid residues in biological systems pathway between the iron centers is the oxygen atom of the bridged phenolate ligand.

## VII. SUMMARY

The IR, Elemental Analysis, UV, EPR, Magnetic moment ESI-MS studies, conductance measurements are discussed for the diiron complexes. ESI-MS studies explains about the EPR signals with almost axial symmetry  $g$  value = (8.5-8.0), (5.4-5.0) and rhombic symmetry  $g$  value = (4.3-4.1), with a very weak signals in the region of  $g < 2.0$  and effective magnetic moment ( $\mu_{\text{eff}} = 6.05 \text{ B.M.}$ ) is slightly smaller than the value of the magnetically uncoupled high-spin Fe<sup>II</sup> and Fe<sup>III</sup> system (spin only value:  $\mu_{\text{eff}} = [g(S_1(S_1 + 1) + S_2(S_2 + 1))]^{1/2} = 7.68 \text{ B.M.}$ ). Thus, di-iron complexes have a very weak antiferromagnetic coupling that is consistent with EPR data. This confirms a weak anti ferromagnetic coupling. The ESI-MS of all the complexes show peaks, indicative of their binuclear nature.

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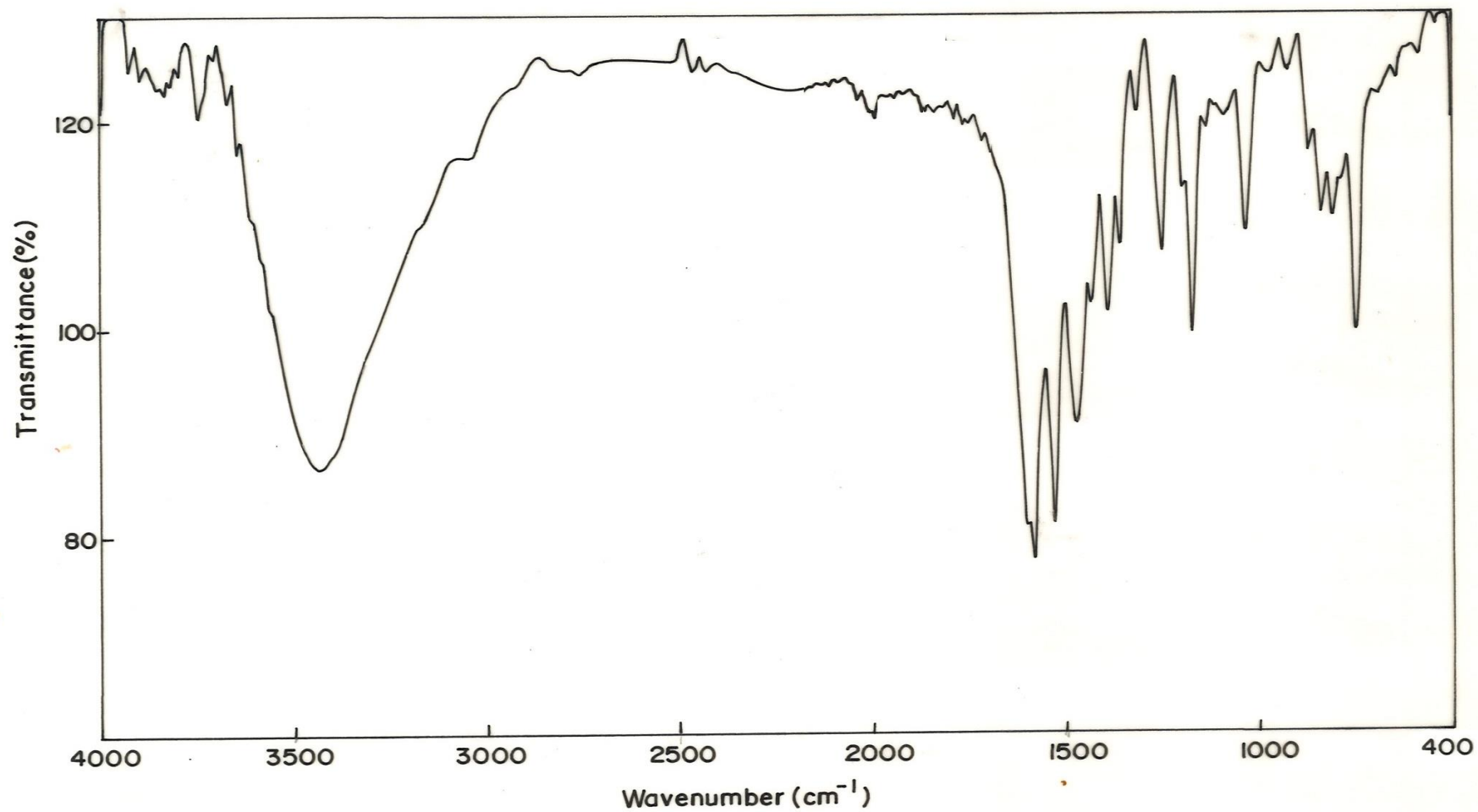


Fig. 1: Infrared spectrum of  $\text{Fe}_2(\text{L}_5)(\text{NO}_2)_2(\text{H}_2\text{O})(\text{ClO}_4)$

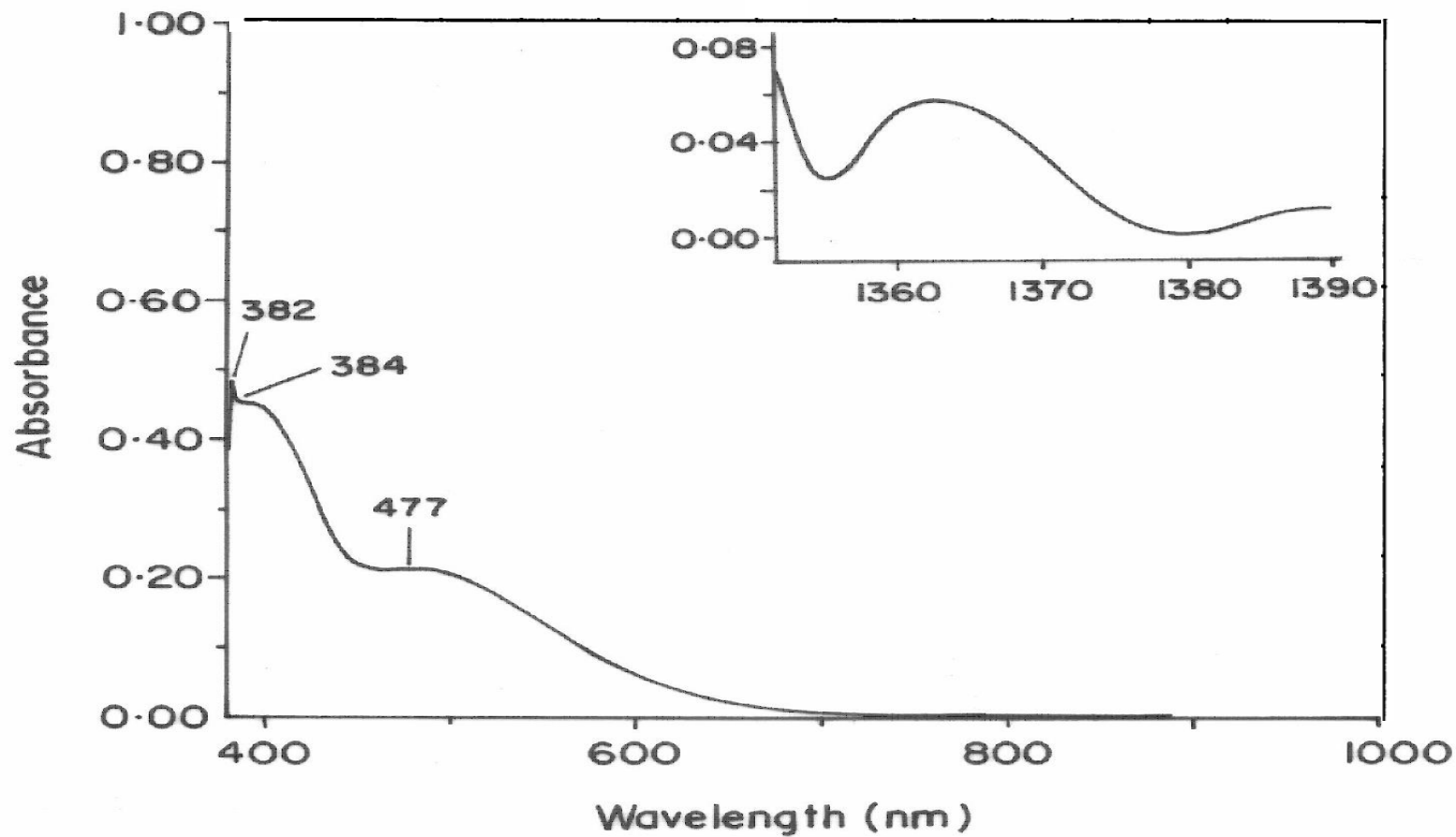


Fig. 2: UV-Vis absorption spectra of Complexes  $Fe_2(L_3)(OAc)_2$  in DMF at 298K and inserted near IR spectrum of the same complex in DMF

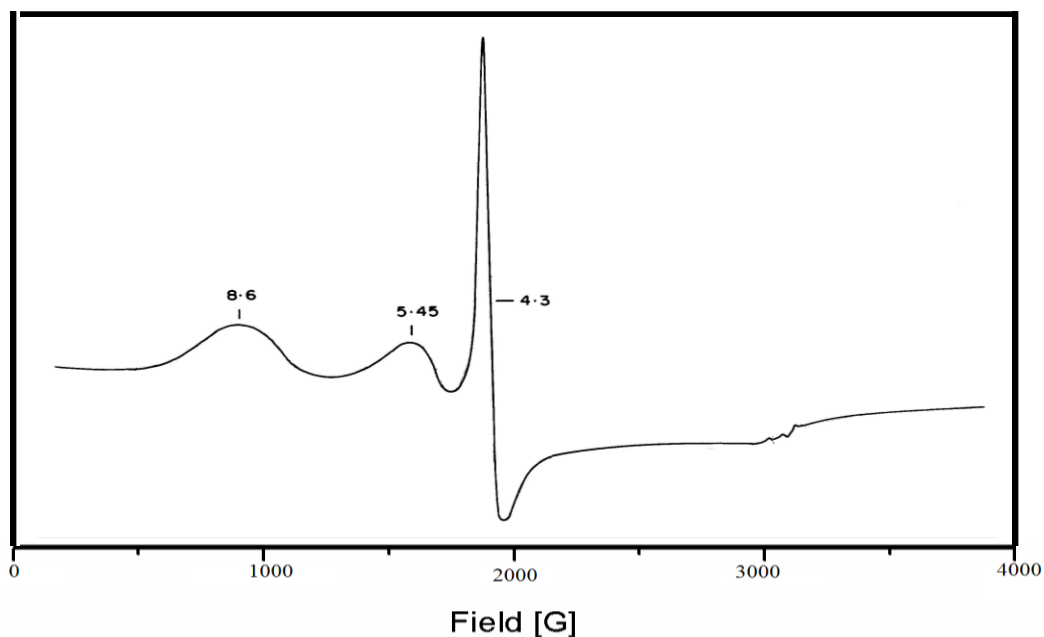


Fig. 3: EPR spectrum of a frozen solution of  $\text{Fe}_2(\text{L}_1)$  hydroxyl bridged complex in  $\text{CH}_3\text{CN}$  at 4 K. Instrumental parameters: microwave frequency, 9.42 GHz; power, 5 mW; modulation frequency, 100 kHz; modulation amplitude, 5.08; gain,  $2.5 \times 10^4$

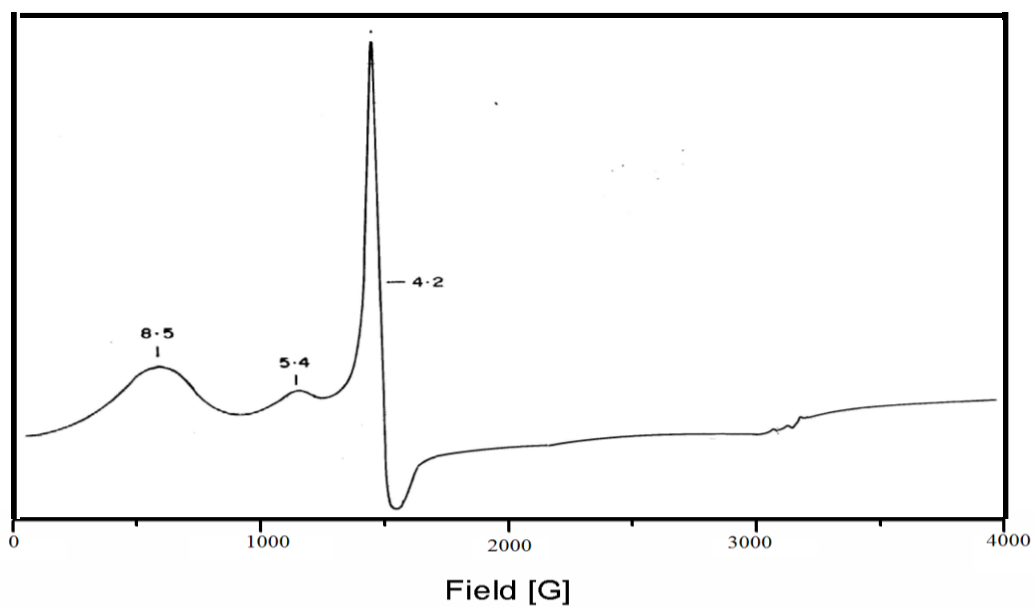


Fig. 4: EPR spectrum of a frozen solution of  $\text{Fe}_2(\text{L}_4)$  Acetate bridged complex of in  $\text{CH}_3\text{CN}$  at 4 K. Instrumental parameters: microwave frequency, 9.42 GHz; power, 5 mW; modulation frequency, 100 kHz; modulation amplitude, 5.08; gain,  $2.5 \times 10^4$



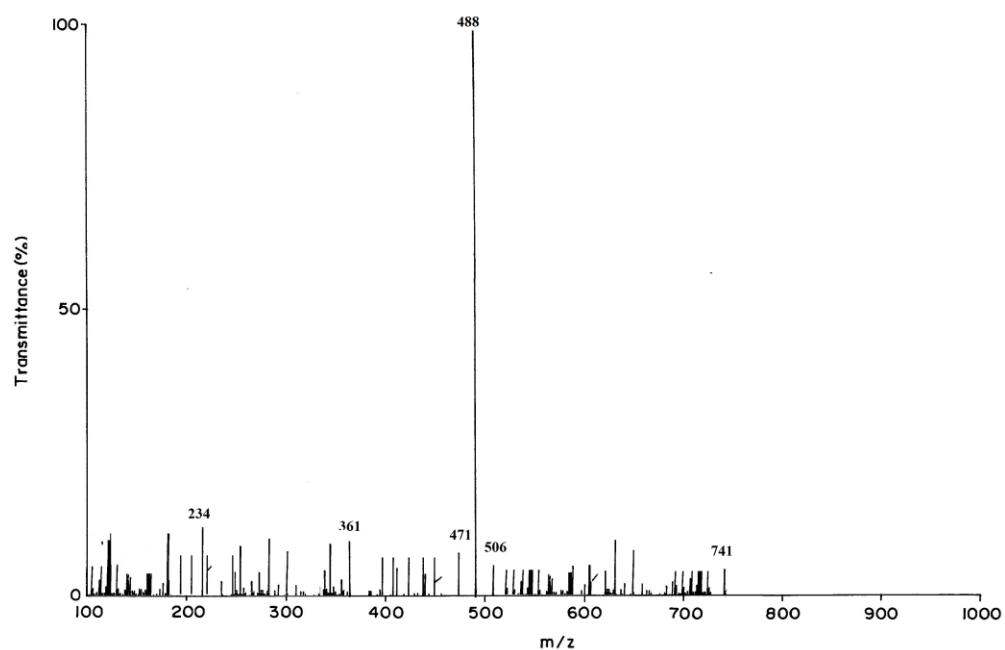


Fig. 5: Electrospray mass spectrum of  $\text{Fe}_2(\text{L}_1)\text{OH}(\text{H}_2\text{O})_5(\text{ClO}_4)_2$

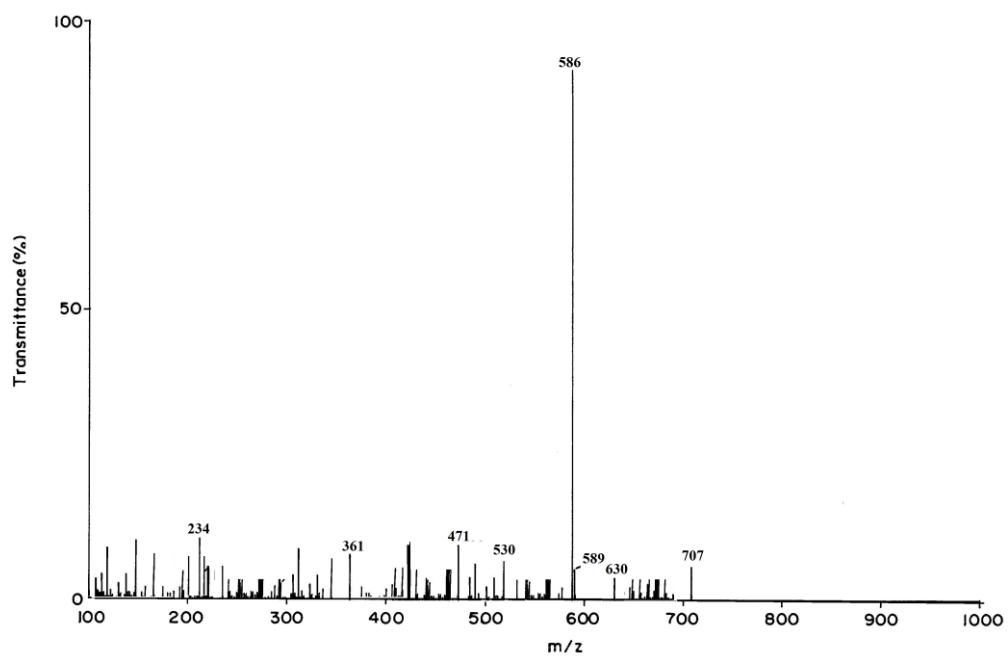


Fig. 6: Electrospray mass spectrum of  $\text{Fe}_2(\text{L}_1)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})(\text{ClO}_4)$

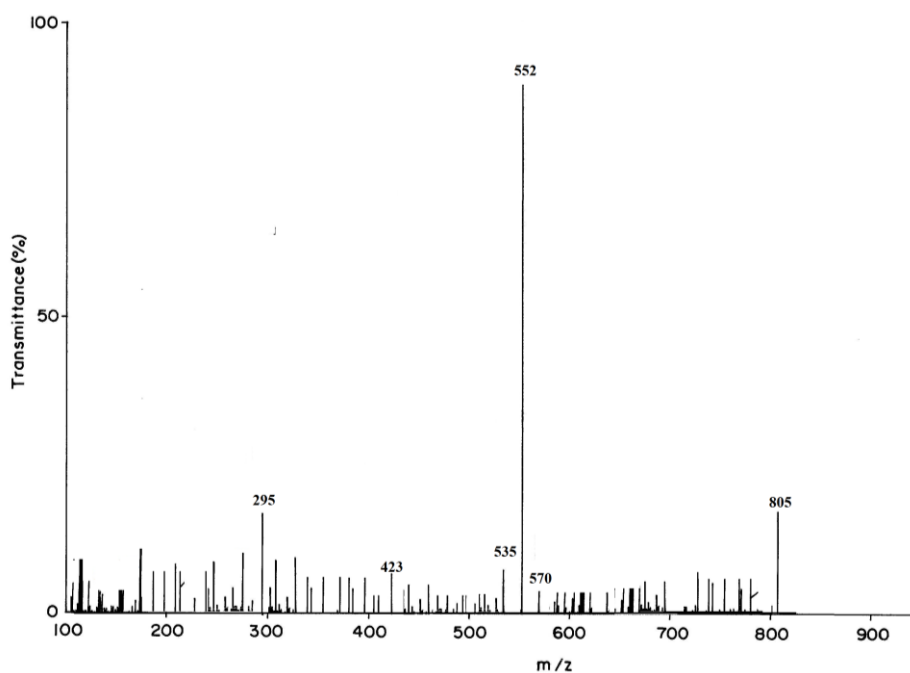


Fig. 7: Electrospray mass spectrum of  $\text{Fe}_2(\text{L}_2)\text{OH}(\text{H}_2\text{O})_3(\text{ClO}_4)_2$

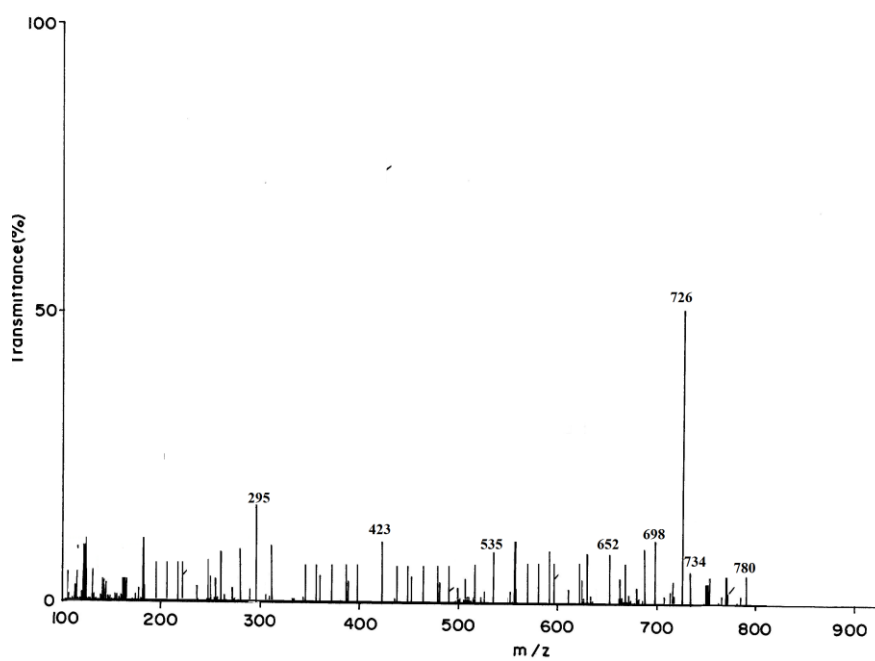


Fig. 8: Electrospray mass spectrum of  $\text{Fe}_2(\text{L}_2)(\text{NO}_2)_2(\text{H}_2\text{O})(\text{ClO}_4)$

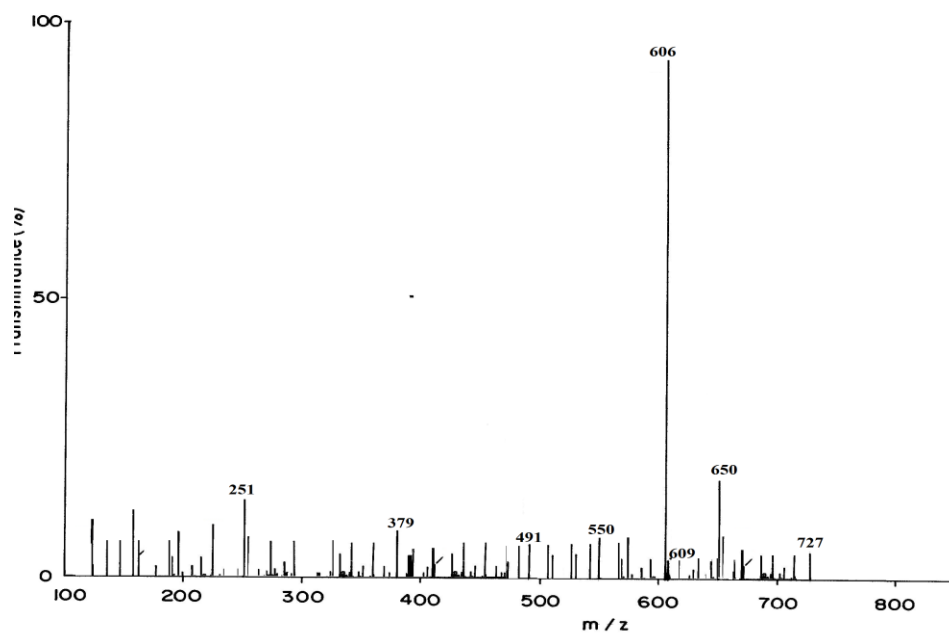


Fig. 9: Electrospray mass spectrum of  $\text{Fe}_2(\text{L}_3)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})(\text{ClO}_4)$

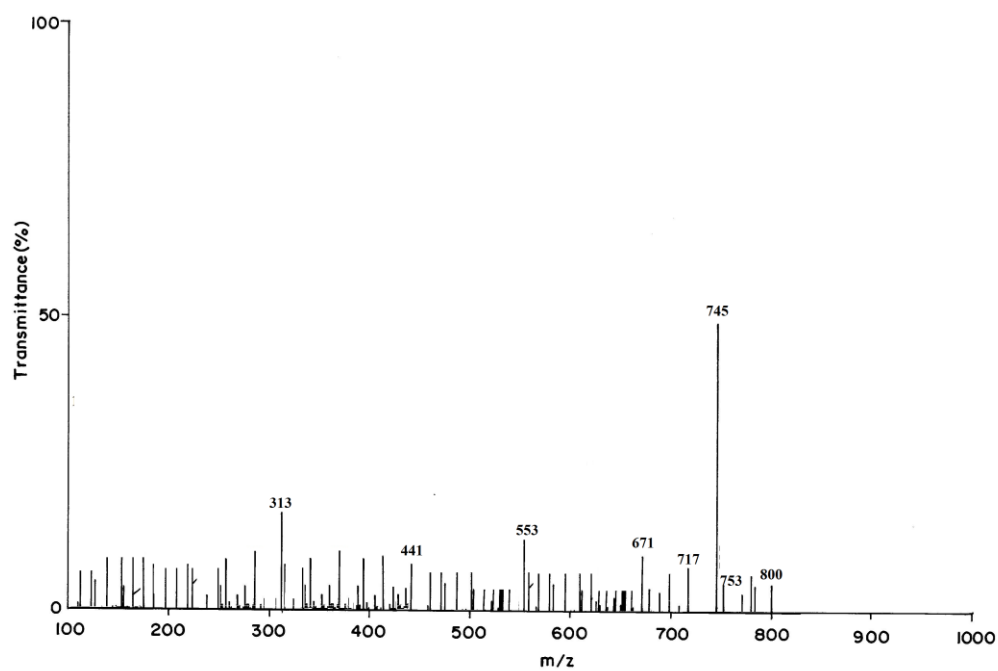


Fig. 10 Electrospray mass spectrum of  $\text{Fe}_2(\text{L}_4)(\text{NO}_2)_2(\text{H}_2\text{O})(\text{ClO}_4)$

Table.1: Molecular weight and elemental analysis of the ligands (L<sub>1</sub>) - (L<sub>6</sub>)

Ligand	Molecular formula	Colour	UV DATA(nm)	Formula weight (Calculated)	Yield %	Observed(calculated)%				
						C	H	N	O	Cl
(L <sub>1</sub> )	C <sub>19</sub> H <sub>29</sub> N <sub>3</sub> O <sub>4</sub>	White powder	225, 265, 349	363.51	85	62.79 (63.25)	8.04 (8.98)	11.56 (11.08)	17.61 (17.02)	
(L <sub>2</sub> )	C <sub>24</sub> H <sub>31</sub> N <sub>3</sub> O <sub>4</sub>	White powder	206, 257, 339	425.52	83	67.74 (68.52)	7.34 (7.58)	9.87 (9.56)	15.04 (15.95)	---
(L <sub>3</sub> )	C <sub>19</sub> H <sub>28</sub> ClN <sub>3</sub> O <sub>3</sub>	Dirty white powder	290, 323, 381	381.89	80	59.76 (58.85)	7.39 (7.80)	11.00 (12.00)	12.57 (12.35)	9.28 (9.78)
(L <sub>4</sub> )	C <sub>24</sub> H <sub>30</sub> ClN <sub>3</sub> O <sub>3</sub>	Dirty white powder	251, 324, 363	443.96	89	66.15 (67.21)	5.55 (4.95)	11.02 (10.95)	6.29 (6.18)	10.98 (11.08)
(L <sub>5</sub> )	C <sub>18</sub> H <sub>26</sub> ClN <sub>3</sub> O <sub>3</sub>	White powder	236, 343, 385	367.87	86	58.77 (58.48)	7.12 (6.56)	11.42 (12.00)	13.05 (13.87)	9.64 (9.52)
(L <sub>6</sub> )	C <sub>23</sub> H <sub>28</sub> ClN <sub>3</sub> O <sub>3</sub>	White powder	261, 333, 389	429.94	92	64.49 (64.52)	7.34 (7.58)	9.87 (9.56)	15.04 (15.95)	---

Table. 2: Analytical and effective moment value for Hydroxo bridged di-iron complexes of (L<sub>1</sub>) - (L<sub>6</sub>)

Hydroxy bridged Complex	Molecular formula	Color & ( $\mu_{\text{eff}}$ B.M)	Formula weight	Yield %	(Calculated)%Found					
					C	H	N	O	Fe	Cl
Fe <sub>2</sub> (L <sub>1</sub> )(OH)	C <sub>19</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>14</sub> Fe <sub>2</sub>	Dark Green (6.10)	707.05	80	32.27 (32.25)	3.16 (3.98)	5.94 (5.08)	31.66 (31.02)	15.79 (15.52)	10.02 (10.20)
Fe <sub>2</sub> (L <sub>2</sub> )(OH)	C <sub>24</sub> H <sub>32</sub> N <sub>3</sub> Cl <sub>2</sub> O <sub>14</sub> Fe <sub>2</sub>	Dark Green (6.25)	769.12	75	37.47 (37.30)	4.19 (4.58)	5.46 (5.56)	29.10 (28.95)	14.52 (14.45)	9.21 (9.50)
Fe <sub>2</sub> (L <sub>3</sub> )(OH)	C <sub>19</sub> H <sub>29</sub> N <sub>3</sub> Cl <sub>3</sub> O <sub>13</sub> Fe <sub>2</sub>	Dark Green (5.80)	725.49	80	31.45 (30.45)	4.02 (4.66)	5.79 (5.40)	28.65 (27.47)	15.39 (15.78)	14.65 (14.78)
Fe <sub>2</sub> (L <sub>4</sub> )(OH)	C <sub>24</sub> H <sub>31</sub> N <sub>3</sub> Cl <sub>3</sub> O <sub>13</sub> Fe <sub>2</sub>	Dark Green (6.05)	787.56	60	36.60 (35.90)	3.96 (3.25)	5.33 (5.66)	26.39 (27.02)	14.18 (14.95)	13.50 (13.56)
Fe <sub>2</sub> (L <sub>5</sub> )(OH)	C <sub>18</sub> H <sub>27</sub> N <sub>3</sub> Cl <sub>3</sub> O <sub>13</sub> Fe <sub>2</sub>	Dark Green (5.98)	711.47	70	30.38 (31.48)	3.82 (4.56)	5.90 (6.00)	29.21 (28.87)	15.58 (14.97)	14.94 (14.00)
Fe <sub>2</sub> (L <sub>6</sub> )(OH)	C <sub>23</sub> H <sub>29</sub> N <sub>3</sub> Cl <sub>3</sub> O <sub>13</sub> Fe <sub>2</sub>	Dark Green (5.85)	773.54	75	35.71 (35.52)	3.77 (3.56)	5.43 (5.25)	26.87 (26.78)	14.44 (15.08)	13.74 (13.50)

Table.3 Analytical and effective moment value for Acetate bridged di-iron complexes of (L<sub>1</sub>) - (L<sub>6</sub>)

Acetate bridged Complex	Molecular formula	Colour & $\mu_{\text{eff}}$ (B.M)	Formula weight	Yield %	Observed(calculated)%					
					C	H	N	O	Fe	Cl
Fe <sub>2</sub> (L <sub>1</sub> )(OAc) <sub>2</sub>	C <sub>23</sub> H <sub>35</sub> ClN <sub>3</sub> O <sub>13</sub> Fe <sub>2</sub>	Purple (6.58)	708.77	65	38.97 (37.85)	4.97 (5.95)	5.92 (5.15)	29.32 (29.02)	15.75 (15.52)	5.00 (4.73)
Fe <sub>2</sub> (L <sub>2</sub> )(OAc) <sub>2</sub>	C <sub>28</sub> H <sub>37</sub> ClN <sub>3</sub> O <sub>13</sub> Fe <sub>2</sub>	Purple (6.53)	770.73	70	43.63 (43.30)	4.83 (4.98)	5.45 (5.26)	26.97 (26.05)	14.49 (14.04)	4.59 (4.50)
Fe <sub>2</sub> (L <sub>3</sub> )(OAc) <sub>2</sub>	C <sub>23</sub> H <sub>34</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>12</sub> Fe <sub>2</sub>	Purple (6.07)	727.08	70	37.99 (36.95)	4.71 (4.28)	5.77 (5.40)	26.39 (25.77)	15.36 (15.30)	9.75 (9.65)
Fe <sub>2</sub> (L <sub>4</sub> )(OAc) <sub>2</sub>	C <sub>28</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>12</sub> Fe <sub>2</sub>	Purple (6.21)	789.18	80	42.61 (49.50)	4.59 (5.20)	5.32 (6.20)	24.31 (24.31)	14.15 (14.35)	8.98 (8.15)
Fe <sub>2</sub> (L <sub>5</sub> )(OAc) <sub>2</sub>	C <sub>22</sub> H <sub>32</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>12</sub> Fe <sub>2</sub>	Purple (6.26)	713.08	75	37.05 (37.55)	4.52 (4.56)	5.89 (5.08)	26.90 (26.87)	15.66 (15.75)	9.94 (9.73)
Fe <sub>2</sub> (L <sub>6</sub> )(OAc) <sub>2</sub>	C <sub>27</sub> H <sub>34</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>12</sub> Fe <sub>2</sub>	Purple (6.05)	777.15	75	41.79 (41.48)	4.38 (4.56)	5.41 (5.05)	24.76 (24.89)	14.10 (15.08)	9.14 (9.50)

Table .4

Analytical and effective moment value for Nitrito-bridged di-iron Complexes of (L<sub>1</sub>) - (L<sub>6</sub>)

Nitrito bridged Complex	Molecular formula	Colour & $\mu_{\text{eff}}$ (B.M)	Formula weight	Yield %	Observed(calculated)%					
					C	H	N	O	Fe	Cl
Fe <sub>2</sub> (L <sub>1</sub> )(NO <sub>2</sub> ) <sub>2</sub>	C <sub>19</sub> H <sub>33</sub> ClN <sub>5</sub> O <sub>15</sub> Fe <sub>2</sub>	Violet (6.98)	718.63	70	31.75 (31.65)	4.62 (4.95)	9.76 (10.65)	33.37 (32.42)	15.54 (15.52)	4.93 (4.73)
Fe <sub>2</sub> (L <sub>2</sub> )(NO <sub>2</sub> ) <sub>2</sub>	C <sub>24</sub> H <sub>35</sub> ClN <sub>5</sub> O <sub>15</sub> Fe <sub>2</sub>	Violet (6.66)	780.70	75	36.92 (36.02)	4.51 (4.98)	8.98 (8.76)	30.72 (30.05)	14.30 (14.45)	9.08 (9.50)
Fe <sub>2</sub> (L <sub>3</sub> )(NO <sub>2</sub> ) <sub>2</sub>	C <sub>19</sub> H <sub>32</sub> N <sub>5</sub> Cl <sub>2</sub> O <sub>14</sub> Fe <sub>2</sub>	Violet (6.75)	737.08	75	30.96 (30.25)	4.37 (3.66)	9.49 (9.40)	30.37 (29.77)	15.15 (15.00)	9.61 (9.56)
Fe <sub>2</sub> (L <sub>4</sub> )(NO <sub>2</sub> ) <sub>2</sub>	C <sub>24</sub> H <sub>34</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>14</sub> Fe <sub>2</sub>	Violet (6.59)	799.15	70	36.07 (44.50)	4.28 (4.25)	8.77 (8.95)	28.01 (27.98)	13.97 (14.35)	8.87 (8.56)
Fe <sub>2</sub> (L <sub>5</sub> )(NO <sub>2</sub> ) <sub>2</sub>	C <sub>18</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>14</sub> Fe <sub>2</sub>	Violet (6.51)	723.05	80	29.90 (29.65)	4.18 (4.56)	9.68 (9.98)	30.96 (31.05)	15.44 (16.05)	9.80 (9.73)
Fe <sub>2</sub> (L <sub>6</sub> )(NO <sub>2</sub> ) <sub>2</sub>	C <sub>23</sub> H <sub>32</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>14</sub> Fe <sub>2</sub>	Violet (6.50)	785.12	80	35.18 (43.48)	4.10 (4.56)	8.93 (8.25)	28.51 (28.78)	14.22 (14.08)	9.03 (9.50)

Table .5

UV-Vis absorption spectra, Infrared Spectral data, conductance values for the hydroxo bridged di-iron complexes of ((L<sub>1</sub>) - (L<sub>6</sub>))

Hydroxo bridged Complex	Molecular formula	UV(data)nm	IR spectral data (cm <sup>-1</sup> )				$\Lambda_M$ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
			$\nu_{\text{H}_2\text{O}}$	$\nu_{\text{ClO}_4}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	
Fe <sub>2</sub> (L <sub>1</sub> )(OH)	C <sub>19</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>14</sub> Fe <sub>2</sub>	380, 430, 590, 1320	3550	1182,647	565	411	140.5
Fe <sub>2</sub> (L <sub>2</sub> )(OH)	C <sub>24</sub> H <sub>32</sub> N <sub>5</sub> Cl <sub>2</sub> O <sub>14</sub> Fe <sub>2</sub>	323(sh), 360, 581, 1325	3420	1150,625	525	-----	161.5
Fe <sub>2</sub> (L <sub>3</sub> )(OH)	C <sub>19</sub> H <sub>29</sub> N <sub>5</sub> Cl <sub>3</sub> O <sub>13</sub> Fe <sub>2</sub>	387, 448, 601, 1350	3439	1150,626	527	405	135.6
Fe <sub>2</sub> (L <sub>4</sub> )(OH)	C <sub>24</sub> H <sub>31</sub> N <sub>5</sub> Cl <sub>3</sub> O <sub>13</sub> Fe <sub>2</sub>	385, 490, 580, 1370	3480	1147,630	523	---	140.4
Fe <sub>2</sub> (L <sub>5</sub> )(OH)	C <sub>18</sub> H <sub>27</sub> N <sub>5</sub> Cl <sub>3</sub> O <sub>13</sub> Fe <sub>2</sub>	324(sh), 378(sh), 643, 1346	3410	1125,652	545	-----	155.7
Fe <sub>2</sub> (L <sub>6</sub> )(OH)	C <sub>23</sub> H <sub>29</sub> N <sub>5</sub> Cl <sub>3</sub> O <sub>13</sub> Fe <sub>2</sub>	363, 403, 655, 1335	3530	1100,635	520	456	167.4

Table.6

UV-Vis absorption spectra, Infrared Spectral data conductance values for the Acetato bridged di-iron complexes of (L<sub>1</sub>) - (L<sub>6</sub>)

Acetate bridged Complex	Molecular formula	UV(data)nm	IR spectral data (cm <sup>-1</sup> )				$\Lambda_M$ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
			$\nu_{\text{H}_2\text{O}}$	$\nu_{\text{COO}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	
Fe <sub>2</sub> (L <sub>1</sub> )(OAc) <sub>2</sub>	C <sub>23</sub> H <sub>35</sub> ClN <sub>5</sub> O <sub>13</sub> Fe <sub>2</sub>	207,435,592,1365	3424	1544,1435	545	421	89.5
Fe <sub>2</sub> (L <sub>2</sub> )(OAc) <sub>2</sub>	C <sub>28</sub> H <sub>37</sub> ClN <sub>5</sub> O <sub>13</sub> Fe <sub>2</sub>	245,445, 571,1380	3418	1597,1491	552	475	70.5
Fe <sub>2</sub> (L <sub>3</sub> )(OAc) <sub>2</sub>	C <sub>23</sub> H <sub>34</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>12</sub> Fe <sub>2</sub>	225,485, 550,1390	3460	1500,1494	548	415	65.6
Fe <sub>2</sub> (L <sub>4</sub> )(OAc) <sub>2</sub>	C <sub>28</sub> H <sub>36</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>12</sub> Fe <sub>2</sub>	270,379, 582,1365	3470	1544,1520	547	405	72.6
Fe <sub>2</sub> (L <sub>5</sub> )(OAc) <sub>2</sub>	C <sub>22</sub> H <sub>32</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>12</sub> Fe <sub>2</sub>	265,372, 579,1358	3534	1484,1595	554	-----	85.9
Fe <sub>2</sub> (L <sub>6</sub> )(OAc) <sub>2</sub>	C <sub>27</sub> H <sub>34</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>12</sub> Fe <sub>2</sub>	256,357, 543,1360	3500	1493,1525	525	447	75.8

Table .7

UV-Vis absorption spectra, Infrared Spectral data, Conductance values for the Nitrito bridged di-iron complexes of (L<sub>1</sub>) - (L<sub>6</sub>)

Nitrito bridged Complex	Molecular formula	UV(data)nm	IR spectral data (cm <sup>-1</sup> )				$\Lambda_M$ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
			$\nu_{H_2O}$	$\nu_{ClO_4}$	$\nu_{M-N}$	$\nu_{M-O}$	
Fe <sub>2</sub> (L <sub>1</sub> )(NO <sub>2</sub> ) <sub>2</sub>	C <sub>19</sub> H <sub>33</sub> ClN <sub>5</sub> O <sub>15</sub> Fe <sub>2</sub>	228,441,585	3550	1182,647	555	---	73.6
Fe <sub>2</sub> (L <sub>2</sub> )(NO <sub>2</sub> ) <sub>2</sub>	C <sub>24</sub> H <sub>35</sub> ClN <sub>5</sub> O <sub>15</sub> Fe <sub>2</sub>	287,460,571	3439	1175,620	505	---	62.6
Fe <sub>2</sub> (L <sub>3</sub> )(NO <sub>2</sub> ) <sub>2</sub>	C <sub>19</sub> H <sub>26</sub> N <sub>5</sub> Cl <sub>2</sub> O <sub>14</sub> Fe <sub>2</sub>	251,481,651	3520	1150,625	576	420	75.9
Fe <sub>2</sub> (L <sub>4</sub> )(NO <sub>2</sub> ) <sub>2</sub>	C <sub>24</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>14</sub> Fe <sub>2</sub>	290,390,623	3480	1150,630	586	---	80.8
Fe <sub>2</sub> (L <sub>5</sub> )(NO <sub>2</sub> ) <sub>2</sub>	C <sub>18</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>14</sub> Fe <sub>2</sub>	225,387,625	3489	1125,652	580	430	87.5
Fe <sub>2</sub> (L <sub>6</sub> )(NO <sub>2</sub> ) <sub>2</sub>	C <sub>23</sub> H <sub>32</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>14</sub> Fe <sub>2</sub>	250,360,615	3530	1100,635	542	---	69.8

Table .8

ESI-MS Analysis for the hydroxo, acetato and nitrito bridged complexes of Fe<sub>2</sub>(L<sub>1</sub>)

Complex	Peak assignment(m/z)
<b>HYDROXO BRIDGED COMPLEX</b>	[C <sub>13</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> ] <sup>+</sup> (234) [C <sub>19</sub> H <sub>27</sub> N <sub>3</sub> O <sub>4</sub> ] <sup>+</sup> (361) [Fe <sub>2</sub> (L <sub>1</sub> )] <sup>+</sup> (471) [Fe <sub>2</sub> (L <sub>1</sub> )(OH)] <sup>+</sup> (488) [Fe <sub>2</sub> (L <sub>1</sub> )(OH)(H <sub>2</sub> O)] <sup>+</sup> (506) [Fe <sub>2</sub> (L <sub>1</sub> )(OH)(H <sub>2</sub> O) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub> ] <sup>3+</sup> (741)
<b>ACETATO BRIDGED COMPLEX</b>	[C <sub>13</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> ] <sup>+</sup> (234) [C <sub>19</sub> H <sub>27</sub> N <sub>3</sub> O <sub>4</sub> ] <sup>+</sup> (361) [Fe <sub>2</sub> (L <sub>1</sub> )] <sup>+</sup> (471) [Fe <sub>2</sub> (L <sub>1</sub> )(CH <sub>3</sub> COO)] <sup>+</sup> (530) [Fe <sub>2</sub> (L <sub>1</sub> )(CH <sub>3</sub> COO) <sub>2</sub> ] <sup>+</sup> -3H <sup>+</sup> (586) [Fe <sub>2</sub> (L <sub>1</sub> )(CH <sub>3</sub> COO) <sub>2</sub> ] <sup>+</sup> (589) [Fe <sub>2</sub> (L <sub>1</sub> )(CH <sub>3</sub> COO)(ClO <sub>4</sub> )] <sup>+</sup> (629) [Fe <sub>2</sub> (L <sub>1</sub> )(OAc) <sub>2</sub> (ClO <sub>4</sub> )(H <sub>2</sub> O)] <sup>3+</sup> (706)
<b>NITRITO BRIDGED COMPLEX</b>	[C <sub>13</sub> H <sub>17</sub> N <sub>2</sub> O <sub>2</sub> ] <sup>+</sup> (234) [C <sub>19</sub> H <sub>27</sub> N <sub>3</sub> O <sub>4</sub> ] <sup>+</sup> (361) [Fe <sub>2</sub> (L <sub>1</sub> )] <sup>+</sup> (471) [Fe <sub>2</sub> (L <sub>1</sub> )(ClO <sub>4</sub> )(H <sub>2</sub> O)] <sup>+</sup> (588) [Fe <sub>2</sub> (L <sub>1</sub> )(NO <sub>2</sub> )(ClO <sub>4</sub> )(H <sub>2</sub> O)] <sup>+</sup> (634) [Fe <sub>2</sub> (L <sub>1</sub> )(NO <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> )] <sup>+</sup> (662.) [Fe <sub>2</sub> (L <sub>1</sub> )(NO <sub>2</sub> )(ClO <sub>4</sub> )(H <sub>2</sub> O) <sub>3</sub> ] <sup>+</sup> (670) [Fe <sub>2</sub> (L <sub>1</sub> )(NO <sub>2</sub> ) <sub>2</sub> (ClO <sub>4</sub> )(H <sub>2</sub> O) <sub>3</sub> ] <sup>3+</sup> (716)