CHAPTER 5: CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORKS

5.1 Conclusions

Complexes of copper(II) and iron(II) alkylcarboxylates and \( p \)-alkyloxybenzoates with 2,2'-bipyridine as ligand were successfully synthesized and characterized. Their structural formulae are shown in Table 5.1 and Table 5.2.

Table 5.1 Structural formulae of copper(II) and iron(II) alkylcarboxylates with bpy as ligand

<table>
<thead>
<tr>
<th>Copper(II) complexes</th>
<th>Iron(II) complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(_2)(CH(_3))(CH(_2))(COO)(_4)(bpy)(_2)] (1)</td>
<td></td>
</tr>
<tr>
<td>[Cu(_2)(CH(_3))(CH(_2))(COO)(_4)(bpy)(_2)] (2)</td>
<td>[Fe(_2)(CH(_3))(CH(_2))(COO)(_4)(bpy)(H(_2)O)(_2)] (6)</td>
</tr>
<tr>
<td>[Cu(_2)(CH(_3))(CH(_2))(COO)(_4)(bpy)(_2)] (3)</td>
<td>[Fe(_2)(CH(_3))(CH(_2))(COO)(_4)(bpy)(H(_2)O)(_2)].2H(_2)O (7)</td>
</tr>
<tr>
<td>[Cu(_2)(CH(_3))(CH(_2))(COO)(_4)(bpy)(_2)] (4)</td>
<td>[Fe(_2)(CH(_3))(CH(_2))(COO)(_4)(bpy)(H(_2)O)(_2)] (8)</td>
</tr>
<tr>
<td>[Cu(_2)(CH(_3))(CH(_2))(COO)(_4)(bpy)(_2)] (5)</td>
<td>[Fe(_2)(CH(_3))(CH(_2))(COO)(_4)(bpy)(H(_2)O)(_2)] (9)</td>
</tr>
</tbody>
</table>

Table 5.2 Structural formulae of copper(II) and iron(II) \( p \)-alkyloxybenzoates with bpy as ligand

<table>
<thead>
<tr>
<th>Copper(II) complexes</th>
<th>Iron(II) complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(_2)(R1COO)(_4)(bpy)(_2)] .2H(_2)O (10)</td>
<td>[Fe(_2)(μ-R1COO)(_2)(R1COO)(_2)(bpy)] (14)</td>
</tr>
<tr>
<td>[Cu(_2)(R2COO)(_4)(bpy)(_2)] (11)</td>
<td>[Fe(_2)(μ-R2COO)(_2)(R2COO)(_2)(bpy)] (15)</td>
</tr>
<tr>
<td>[Cu(_2)(R3COO)(_4)(bpy)(_2)] (12)</td>
<td>[Fe(R3COO)(_2)(bpy)] (16)</td>
</tr>
<tr>
<td>[Cu(_2)(R4COO)(_4)(bpy)(_2)] (13)</td>
<td>[Fe(R4COO)(_2)(bpy)] (17)</td>
</tr>
</tbody>
</table>

R1 = \( p \)-CH\(_3\)(CH\(_2\))\(_9\)OC\(_6\)H\(_4\); R2 = \( p \)-CH\(_3\)(CH\(_2\))\(_11\)OC\(_6\)H\(_4\); R3 = \( p \)-CH\(_3\)(CH\(_2\))\(_13\)OC\(_6\)H\(_4\); R4 = \( p \)-CH\(_3\)(CH\(_2\))\(_15\)OC\(_6\)H\(_4\)

All copper(II) complexes were dinuclear with square pyramidal copper(II) atoms, monodentate nonbridging and \( \text{syn-anti} \) monodentate bridging carboxylato and chelating bpy ligands. Complexes 1, 2, 3 and 5 were crystals in the triclinic systems. Complex 1 showed negligible magnetic interactions between two copper(II) centres, while the other complexes showed ferromagnetic interactions when their effective magnetic moments were compared with the calculated value using the equation for two non-interacting copper(II) atoms with \( g = 2 \). However, the magneto-structural correlation studies using the Cu-O-Cu bonds from the X-ray data for the crystalline
complexes and the calculated $2J$ values showed strong antiferromagnetic interactions between the two copper(II) atoms. The latter results was supported by the results of molecular modeling for 1, which showed good agreement between the experimental and calculated structures. Their decomposition temperatures were in the range of 161 – 240 °C, and in general, showed a gradually decreasing trend with increasing number of carbon atoms in the alkyl(oxy) chains. Complexes 1 – 5, 10 and 11 behaved as thermotropic liquid crystals, while 12 and 13 were not mesomorphic.

All iron(II) complexes with alkylcarboxylato were dinuclear with chelating carboxylato and bridging bpy ligands. On the other hand, complexes with $p$-alkyloxybenzoato ligands were dinuclear involving bridging and chelating carboxylato and bridging bpy ligands for 14 and 15, and mononuclear involving chelating carboxylato and bpy ligands 16 and 17. Molecular modelling performed for 6 and 16 showed good agreement between the experimental and simulated FTIR spectra, supporting the proposed structure formulae for these complexes. All dinuclear complexes were made up of both HS and LS iron(II) atoms at room temperature with higher percentage of LS iron(II) atoms, while all mononuclear complexes have 100% LS iron(II) atoms at room temperature. The complexes were thermally stable in the temperature range of 121 °C to 172 °C. Their decomposition temperatures decreased with increasing number of carbon atoms in the alkyl chain, as similarly observed for copper(II) complexes. All complexes with the alkylcarboxylato ligands have higher percentages of HS Fe(II) on heating, due to dissociation of \([\text{Fe}_2(\text{R})_n(\text{bpy})(\text{H}_2\text{O})_2]\) to \([\text{Fe}(\text{R})_2(\text{bpy})]\) and \([\text{Fe}(\text{R})_2(\text{H}_2\text{O})_2]\). Complexes 6, 8 and 9 were not mesomorphic while all other complexes behaved as thermotropic liquid crystals. On heating, it is proposed that the bridging bpy ligands in 14 and 15 dissociated and the molecules formed \([\text{Fe}_2(\text{RCOO})_4]\) with the paddle-wheel structure.
5.2 Suggestions for Future Works

Variable-temperature small and wide angles X-ray scattering (SWAXS) experiments for the mesomorphic complexes are needed to confirm their mesophases.

In designing novel functional metallomesogens with more challenging requirements and for high-technology applications, combination of spin crossover and liquid crystalline behavior may lead to a number of advantages. For example, convenient processing SCO materials in the form of thin films, enhancement of spin transition signals, switching and sensing in different temperature regimes, or achievement of photo- and thermochromism in Fe(II) containing liquid crystals [89-94]. Hence, to gain further insight about the SCO, Superconducting Quantum Interfering Device (SQUID) is an important tool to use as it measures the molar magnetic susceptibility as a function of temperature. From the SQUID data, important data, such as the SCO temperature ($T_{1/2}$) and thermal hysteresis ($\Delta T$) can be determined for the iron(II) complexes.

The SCO studies may also be extended to complexes of manganese(II) (valence electronic configuration $d^5$) and cobalt(II) (valence electronic configuration $d^7$).

Other potential uses of the copper(II) complexes, such as in medical applications, and of the iron(II) complexes, such as in dye-sensitised solar cells [95-97] and thermoelectricity, which converts heat energy directly to electricity [62,98], may be explored.

Finally, this research may be extended for complexes with carboxylato ligands with odd number of carbon atoms and branched chains, and with alkyl(oxy) substituted 2,2’-bipyridine in order to reduce their melting temperatures, and hence minimised decomposition and structural changes on heating.