CHAPTER 5 CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORKS

5.1 Conclusions

Nine Co(II) and five Fe(II) Schiff base complexes were successfully obtained by one-pot syntheses and their structures, thermal, mesomorphic, and spin crossover properties determined. The chemical formulae of these complexes are shown in **Table 5.1** and **Table 5.2**.

Table 5.1 Chemical formulae of Co(II) complexes

Complex	Chemical Formula
1	$Co[C_5H_3N(CHN(CH_2)_5CH_3)_2]_2(BF_4)_2$
2	$Co[C_5H_3N(CHN(CH_2)_7CH_3)_2]_2(BF_4)_2.H_2O$
3	$Co[C_5H_3N(CHN(CH_2)_9CH_3)_2]_2(BF_4)_2$
4	$Co[C_5H_3N(CHN(CH_2)_{11}CH_3)_2]_2(BF_4)_2$
5	$Co[C_5H_3N(CHN(CH_2)_{13}CH_3)_2]_2(BF_4)_2.H_2O$
6	$Co[C_5H_3N(CHN(CH_2)_{15}CH_3)_2]_2(BF_4)_2.H_2O$
7	$Co[C_5H_3N(CHN(CH_2)_{11}CH_3)_2]_2(ClO_4)_2$
8	$Co[C_5H_3N(CHN(CH_2)_{15}CH_3)_2]_2(ClO_4)_2$
9	$Co[C_5H_3N(CHN(CH_2)_5CH_3)_2]_2(PF_6)_2$

Table 5.2 Chemical formulae of Fe(II) complexes

Complex	Chemical Formula
10	$Fe[C_5H_3N(CHN(CH_2)_5CH_3)_2]_2(BF_4)_2$
11	$Fe[C_5H_3N(CHN(CH_2)_{11}CH_3)_2]_2(BF_4)_2.H_2O$
12	$Fe[C_5H_3N(CHN(CH_2)_{15}CH_3)_2]_2(BF_4)_2$
13	$Fe[C_5H_3N(CHN(CH_2)_{15}CH_3)_2]_2(ClO_4)_2$
14	$Fe([C_5H_3N(CHN(CH_2)_5CH_3)_2]_2(PF_6)_2$

All complexes with BF_4^- and PF_6^- ions were obtained in good yields (76 – 93%) while complexes with ClO_4^- ion were obtained in low to medium yields (27 – 52%). Complexes with the shorter alkyl chain lengths (C_6-C_{10}) readily absorb atmospheric moisture.

The structures of **Complexes 4** and **13** were confirmed by single x-ray crystallography. All complexes were octahedral, mononuclear, and thermally stable (T_{dec}>373 K). These features were independent of anionic sizes. High spin (HS) complexes were preferentially formed from ligands with long alkyl chains and in the absence of H_2O.

The mesogenic properties were only shown by complexes with long alkyl chains (C_{12}-C_{16}) and with the smallest counter anion (BF_4^-). The mesophase was columnar (*Col*) at temperatures higher than 373 K.

Co(II) complexes with shorter alkyl chain length (C_6-C_{10}) were made up of low spin (LS) and HS Co(II) at room temperature, while complexes with longer alkyl chain length (C_{12}-C_{16}) preferred HS state at room temperature. The HS Co(II) complexes (C_{12} and C_{16}) showed normal SCO behaviour in the solid state at room temperature, with $T_{½}$ at almost near room temperature (337 and 335 K, respectively). The percentage HS Co(II) were lower in complexes with larger anions.

In contrast, all Fe(II) complexes were mostly LS (89 – 99%) at room temperature. There was no correlation between anionic sizes and percentage of LS in these complexes.

5.2 Suggestion for Future Work

The complexes in this research were prepared by one-pot syntheses. It would be interesting to compare if similar complexes may be formed by step-wise syntheses, and also to compare their yields. It would also be interesting to study complexes with odd number of carbon atoms in the alkyl chain length, branch alkyl chains (to lower the melting temperature and minimise decomposition), and other anions, especially coordinating ones such as acetate and benzoate (to increase the nuclearity of complexes and hence the effect on SCO behaviour).

The mesomorphisms of complexes prepared in this research may be further ascertained by low angle variable-temperature PXRD [1], while the SCO properties should be ascertained using the SQUID and UV-visible variable temperature in wider temperature range [2]. Other techniques for SCO, such as vibrational spectra, heat capacity measurements, X-ray structural studies, synchrotron radiation studies and magnetic resonance studies may be applied to further explore the SCO response from other stimuli other than temperature, namely pressure, light induced excited spin state trapping (LIESST) and magnetic field [3].

In addition, other potential applications of these complexes may be studied, such as in dye-sensitised solar cells (DSSC), thermoelectricity (a phenomena in which a temperature difference create an electric potential or an electric potential creates a temperature difference) [4,5]. This may lead to numerous electric and electrical applications such as thermoelectric cooling of microelectronic products, thermoelectric converter for energy conservation, wireless sensor, photon sensing devices and in waste-heat recovery [5].

References

[1] S. Hayami, Y. Kojima, D. Urakami, K. Ohta, and K. Inoue, *Polyhedron*, vol. 28, pp. 2053-2057, 6/22/ (2009).

[2] M. Tafili-Kryeziu, M. Weil, T. Muranaka, A. Bousseksou, M. Hasegawa, A. Jun,W. Linert, *Dalton Trans.*, vol. 42, pp. 15796-15804 (2013).

[3] P. Gütlich and H. A. Goodwin, "Spin Crossover—An Overall Perspective," vol. 233, pp. 1-47 (2004).

[4] D. Wei, *Int. J. Mol. Sci.*, vol. 11, pp. 1103-13 (2010).

[5] T. M. Tritt, "Thermoelectric Phenomena, Materials, and Applications," in *Annual Review of Materials Research, Vol 41*. vol. 41, D. R. Clarke and P. Fratzl, Eds., ed Palo Alto: Annual Reviews (2011), pp. 433-448.