CHAPTER I

INTRODUCTION

1.1 Background

Spin-crossover (SCO) complexes, also known as spin-transition (ST) complexes, represent a fascinating class of switchable molecules. Their switching process can be triggered by external stimuli such as changes in temperature, pressure, magnetic field, or exposure to light (Hauser, 2013) as shown in Figure 1.1. In iron(III) systems with d^5 electron configuration, this transition involves a shift from a high-spin state ($^6A_1$, S = 5/2) to a low spin state ($^2T_2$, S = 1/2), with both states exhibiting paramagnetic behavior (van Koningsbruggen et al., 2004), (Nihei et al., 2007). SCO materials are attractive candidates for molecular magnetic devices and sensors, because switching can occur at or near ambient temperature. Compared to the more commonly studied Fe(II) systems, Fe(III) compounds offer greater air stability, making them promising candidates for future device applications. For practical use, it is also essential that the spin crossover (SCO) occurs sharply and exhibits a hysteresis of at least 40 K. In SCO complexes, hysteresis arises from strong interactions between SCO centers, which facilitate rapid propagation of the transition throughout the material. This connectivity can be achieved via coordination bonds or, more frequently, through supramolecular interactions. Consequently, effective SCO material design relies on the principles of crystal engineering (Harding et al., 2016).

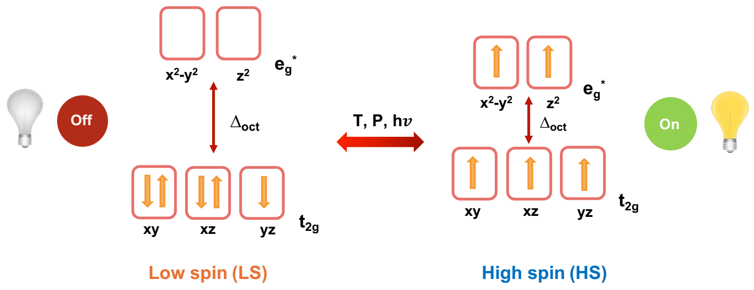

Figure 1.1 Illustration of the spin crossover phenomenon in iron(III) complexes.

1.2 Research objectives

The broad objective of this thesis is to explore the molecular magnetism of simple iron complexes and develop a better understanding of the structure:function relationships that exist in these systems. Specifically, we aim to:

1.2.1 To synthesize new Schiff base ligands with N_2O donor set.

1.2.2 To synthesize and characterize [Fe(salBzen-5-OMe)$_2$]A and [Fe(salPren-5-OMe)$_2$]A where A = Cl^-, Br^-, I^-, NO_3^-, and ClO_4^- complexes using FT-IR, UV-Vis spectroscopy, elemental analysis, mass spectrometry, and Powder X-ray diffraction.

1.2.3 To study the structures of the iron(III) salRen complexes using single crystal X-ray crystallography.

1.2.4 To investigate the magnetic properties of the iron(III) salRen complexes using SQUID magnetometry.

1.2.5 To explore the electron transfer processes in [Fe(salBzen-5-OMe)$_2$]A and [Fe(salPren-5-OMe)$_2$]A complexes with cyclic voltammetry.

1.2.6 To study the impact of the anion and the ligand substituent position on the interaction and magnetic performance as an aid to understanding the structure:function relationships in this novel series of Fe(III) spin crossover systems.

1.3 Scope and limitation of the study

This research aims to synthesize [Fe(salRen-5-OMe)$_2$]A complexes with different counter ions (A = Cl^-, Br^-, I^-, NO_3^-, and ClO_4^-) and substituent groups on the ligands (R = salBzen-5-OMe, salPren-5-OMe) and characterize both series by infrared (IR), UV-Visible spectroscopy, elemental analysis, mass spectrometry, Powder X-ray diffraction, X-ray crystallography, cyclic voltammetry, and SQUID magnetometry.

1.4 References

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