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**Magneto-structural correlations of
Iron-salicylaldoxime clusters.**

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ABSTRACT

The syntheses and characterisation of polynuclear metal clusters using a series of derivatised salicylaldoxime ligands are described in this thesis. The polynuclear iron clusters contain metallic cores consisting of oxo-centred triangles. It was found that slight modifications of the phenolic oxime ligands can lead to metal clusters with different nuclearities, thus producing a variety of magnetic properties within the materials. The predominant building block in the complexes is a triangular $[\text{Fe}_3\text{O}(\text{R-sao})_3]^+$ (R = alkyl derivative, sao = salicylaldoxime) unit which can self-assemble into more complicated arrays depending on reaction conditions.

A number of ligands containing a single phenolic oxime unit has been synthesised. These ligands have been used to form di-iron (**C1**), hexairon (**C2**), and heptairon (**C3**) complexes.

A second series of ligands containing two double-headed phenolic oxime units linked by diamine straps has been synthesised and fully characterised. Two copper complexes **C5** and **C7** were crystallised and pyridine also took part in coordination to the copper centres. Three of the iron complexes formed with double-headed oxime ligands are heptairon compounds. The heptairon compounds were all analogous in their iron coordination environment. The hexairon complex (**C8**) formed from a double-headed oxime was analogous to the complex **C2** formed from a single-headed oxime ligand in its iron coordination environment. The tri-iron complex (**C10**) also contains a metaborate ion. In each case of the heptairon complexes and the hexairon complex, the metallic skeleton of the cluster was based on a trigonal prism in which two $[\text{Fe}_3^{\text{III}}\text{O}]$ triangles are fastened together via three helically twisted double-headed oxime ligands. Each of these ligands is present as (**L-2H**) where the oximic and phenolic O-atoms are deprotonated and the amino N-atoms protonated, with the oxime moieties bridging across the edges of the metal triangles. The identity of the metal ion has a major impact on the nuclearity and topology of the resultant cluster.

The magnetic susceptibility measurements of these iron complexes suggest the presence of strong antiferromagnetic interactions between the metal centres and the Mössbauer analyses confirm the oxidation state of all the iron centres is 3+. The CHN analyses and

other general characterisation allowed verifying and / or modifying the formulae generated by the X-ray analyses.

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DECLARATION BY THE CANDIDATE

I do hereby declare that the work described in this thesis was carried out by me under the supervision of Associate Professor Paul Plieger and Professor David Harding and a report on this has not been submitted in whole or part to any university or any other institution for another Degree or Diploma. To the best of my knowledge it does not contain any material published or written by another person, except as acknowledged in the text.

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DECLARATION BY THE SUPERVISORS

This is to certify that this dissertation is based on the work carried by Ms D.N.T. De Silva under our supervision. The dissertation has been prepared according to the format stipulated and is of acceptable standard.

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CONTENTS

ABSTRACT.....	I
ACKNOWLEDGEMENTS.....	III
PUBLICATIONS AND CONFERENCES ATTENDED.....	V
DECLARATION.....	VI
CONTENTS.....	VII
LIST OF FIGURES.....	XI
LIST OF TABLES.....	XX
ABBREVIATIONS.....	XXIII
CHAPTER 1: INTRODUCTION.....	1
1.1 Objectives.....	1
1.2 Magnetism.....	1
1.2.1 Magnetisation (M) / A m ⁻¹	2
1.2.2 Exchange interactions occur in polynuclear clusters.....	9
1.3 Single molecule magnets (SMMs).....	11
1.3.1 Magnetic properties of iron.....	14
1.4 Salicylaldoxime-metal clusters.....	15
1.4.1 Iron complexes.....	15
1.4.2 Manganese complexes.....	23
1.5 Phenolic oxime ligands.....	29
1.5.1 Derivatised salicylaldoximes.....	31
1.6 Basic techniques.....	33
1.6.1 X-ray diffraction (<i>XRD</i>).....	33
1.6.2 Magnetic measurements.....	34
1.6.3 Mössbauer spectroscopy.....	37
1.6.3.1 Theory.....	38
References.....	41
CHAPTER 2: IRON COMPLEXES OF SINGLE-HEADED	
SALICYLALDOXIMES.....	49
2.1 Salicylaldoximes.....	49
2.2 Single-headed salicylaldoximes.....	51
2.2.1 Synthesis of the ligands.....	52
2.2.2 NMR interpretation of the oximes and their precursor	

aldehydes.....	53
2.3 Complexation reactions and crystallisation.....	59
2.3.1 Crystal structure of L2.....	61
2.4 IR spectral analyses of the Fe complexes.....	62
2.4.1 Complex $[\text{Fe}_2\text{B}_2(\text{L1-H})_4(\text{F})_2(\text{O})_2](\text{BF}_4)_2(\text{MeOH})_4$, C1 ·4MeOH.....	63
2.4.2 Complex $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})](\text{BF}_4)_2$ (MeOH) ₅ , C2 ·5MeOH.....	70
2.4.3 Complex $\text{Na}[\text{Fe}_7(\text{OH})_8(\text{L11-2H})_6\text{Py}_6]$ $(\text{BF}_4)_2(\text{H}_2\text{O})_6(\text{Py})_3$, C3 ·6H ₂ O·3Py.....	79
2.5 Results and discussion.....	84
2.6 Magnetism.....	86
2.6.1 Magnetic measurements of the complex C1	86
2.6.2 Magnetic measurements of the complex C2	89
2.6.3 Magnetic measurements of the complex C3	91
2.7 Mössbauer spectroscopy.....	93
2.7.1 Results and discussion.....	93
2.8 Conclusion.....	97
References.....	98
CHAPTER 3: METAL COMPLEXES OF DOUBLE-HEADED	
SALICYLALDOXIMES.....	101
3.1 Double-headed salicylaldoximes.....	101
3.2 Copper complexes of double-headed salicylaldoximes.....	101
3.2.1 Complex $[\text{Cu}_3(\text{L5-H})_3(\text{Py})_3](\text{BF}_4)_2\text{PF}_6(\text{H}_2\text{O})_3(\text{MeOH})_3$, C5 ·3H ₂ O·3MeOH.....	104
3.2.2 Complex $[\text{Cu}_4(\text{L8-3H})_2\text{Py}_2](\text{BF}_4)_2(\text{MeOH})(\text{Py})$, C7 ·MeOH·Py.....	108
3.3 Iron complexes of double-headed salicylaldoximes.....	112
3.3.1 Complex $[\text{Fe}_3\text{BO}_2(\text{L9-2H})_2(\text{OH})_2(\text{Py})_2]$ $(\text{BF}_4)_2(\text{H}_2\text{O})_2(\text{MeOH})(\text{Py})$, C10 ·2H ₂ O·MeOH·Py.....	112
3.3.1.1 Magnetic measurements of the complex C10	117
3.3.2 Complex $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L7-2H})_3](\text{BF}_4)_3(\text{H}_2\text{O})_7\text{Py}$, C8 ·7H ₂ O·Py.....	120

3.3.2.1 Magnetic measurements of the complex, C8 ·7H ₂ O·Py.....	124
3.3.3 Complex [Fe ₇ O ₂ (OH) ₆ (L5 -2H) ₃ Py ₆](BF ₄) ₄ PF ₆ (H ₂ O) ₇ Py ₃ , C4 ·7H ₂ O·3Py.....	126
3.3.3.1 Magnetic measurements of the complex, C4	131
3.3.4 Complex [Fe ₇ O ₂ (L6 -2H) ₃ (OH) ₆ (Py) ₆](PF ₆) ₅ (H ₂ O) ₂ , C6 ·5PF ₆ ·2H ₂ O.....	132
3.3.4.1 Magnetic measurements of the complex C6	136
3.3.5 Complex [Fe ₇ O ₂ (L10 -2H) ₃ (OH) ₆ (Py) ₆](BF ₄) ₃ (PF ₆) ₂ (H ₂ O) ₃ (Py) ₂ , C9 ·3BF ₄ ·PF ₆ ·3H ₂ O·2Py.....	138
3.3.5.1 Magnetic measurements of the complex C9	142
3.4 Results and discussion of the crystal structures.....	143
3.5 Mössbauer results and discussion of the iron complexes.....	147
3.6 Conclusion.....	152
References.....	153
CHAPTER 4: CONCLUSIONS AND FUTURE APPROACH.....	155
4.1 Single- and Double-headed Derivatised Salicylaloximes.....	155
4.2 Dinuclear and Trinuclear iron complexes.....	156
4.3 High nuclearity complexes.....	158
4.3.1 The hexairon complexes.....	158
4.3.2 The heptairon complexes.....	160
4.4 Conclusion.....	163
References.....	165
APPENDIX A: EXPERIMENTAL.....	166
A.1 General Experimental.....	166
A.1.1 Reagents and solvents.....	166
A.1.2 Synthetic methods.....	166
A.1.3 Chromatography.....	166
A.1.4 Synthesis and characterisation.....	167
A.2 Experimental.....	171
A.2.1 Synthesis of single-headed oxime ligands.....	171
A.2.2 Synthesis of double-headed oxime ligands.....	204
A.2.3 Synthesis of metal clusters.....	253

References..... 260

LIST OF FIGURES

1.1: left: Variation of magnetisation (M) with external magnetic field (H), right: Variation of magnetic susceptibility (χ) with temperature (T) of diamagnets.....	2
1.2: left: Variation of magnetisation (M) with external magnetic field (H), right: Variation of magnetic susceptibility (χ) with temperature (T) of paramagnets.....	3
1.3: Applied magnetic field (H) vs magnetisation (M) in ferromagnetic materials.....	4
1.4: Switch from paramagnetism to ferromagnetism.....	4
1.5: Hysteresis loop that exhibits the history dependent nature of magnetisation of ferromagnetic materials.....	5
1.6: Paramagnetism-antiferromagnetism transition.....	6
1.7: Illustration of Curie-Weiss law in (a) antiferromagnetic and (b) ferromagnetic materials.....	8
1.8: Curie temperatures.....	8
1.9: Antiferromagnetic superexchange.....	10
1.10: Ferromagnetic superexchange.....	10
1.11: Energy diagram exhibiting the relative positions of the ZFS, M_S levels of an $S = 10$ system (blue arrow indicates the energy barrier and the red arrows indicate the thermal pathway to reorientate from $-M_S$ to $+M_S$), and the barrier between the $M_S + 10$ and -10 states).....	12
1.12: Change in potential energy of an SMM as the magnetic field is changed from $H = 0$ to $H = nD/g\mu_B$	13
1.13: Structure of $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]$ (I) (codes for atoms: large grey; Mn, medium black; O, rest; C, and H atoms are omitted for clarity).....	14
1.14: Hysteresis loop of magnetisation for Mn_{12}Ac	14
1.15: Schematic diagram of spin alignment of μ_3 -oxo bridge (Fe = light green; O = red).....	15

1.16: Structural formulae of salicylaldoxime ligands discussed in the text.....	16
1.17: Metallic core of the complex $[\text{Fe}_6\text{O}_2\text{H}(\text{sao})_6(\text{CH}_3\text{O})_3(\text{OH})_3]^{3-}$ (VI) (all the H-atoms are omitted for clarity except the proton between the $[\text{Fe}_3\text{O}]$ triangles and the symmetry-independent part is labelled).....	17
1.18: The molecular structure of the anion of $[\text{HET}_3\text{N}][\text{Fe}_2(\text{OMe})(\text{Ph-sao})_2(\text{Ph-saoH})_2] \cdot 5\text{MeOH}$ (VII).....	17
1.19: Fe-O core of $[\text{HET}_3\text{N}]_2[\text{Fe}_6\text{O}_2(\text{Me-sao})_4(\text{SO}_4)_2(\text{OMe})_4(\text{MeOH})_2]$ (VIII).....	18
1.20: Fe-O core of $[\text{Fe}_8\text{O}_3(\text{R1-sao})_3(\text{tea})(\text{teaH})_3(\text{O}_2\text{CMe})_3] \cdot x\text{MeOH}$ (XI).....	19
1.21: The molecular structure of $[\text{Fe}_8\text{O}_2(\text{OMe})_4(\text{Me-sao})_6\text{Br}_4(\text{py})_4]$ (XII) (Fe-olive green, O-red, N-dark blue, C-gold, Br-light blue).....	20
1.22: The molecular structure of $[\text{Fe}_6\text{O}_2(\text{OMe})_4\text{Cl}_2(\text{O}_2\text{CPh-4-NO}_2)_4(\text{Me-sao})_2\text{Cl}_2(\text{py})_2]$ (XIV) (Fe-olive green, O-red, N-dark blue, C-gold, Cl-bright green).....	21
1.23: The most successful co-ligands in synthesis of Fe(III) clusters.....	21
1.24: Crystal structure of the cation $[\text{Mn}^{\text{III}}_3\text{-O}(\text{MeCO}_2)_3(\text{mpko})_3]^+$, Mn-brown, O-blue, N-green, C-gray.....	24
1.25: (a) The structure of $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{O}_2\text{CH})_2(\text{sao})_6(\text{MeOH})_4]$ (b) its magnetic core (MnIII = purple; O = red; N = blue; C = black. H-atoms are omitted for clarity).....	25
1.26: The structure of $[\text{Mn}_3\text{O}(\text{sao})_3(\text{O}_2\text{CCH}_3)(\text{py})_3\text{-}(\text{H}_2\text{O})]$ cluster.....	25
1.27: Schematic representation showing the three straps and the interplane $(\mu_3\text{-O}) \cdots \text{H} \cdots (\mu_3\text{-O})$ hydrogen bond.....	26
1.28: Molecular structures of (a) $[\text{Mn}^{\text{III}}_3\text{O}(\text{Et-sao})_3(\text{HCO}_2)(\text{MeOH})_5]$ and (b) $[\text{Mn}^{\text{III}}_3\text{O}(\text{Me-sao})_3(\text{Me-OH})_5]\text{Cl}$	27
1.29: (a) Mn_6 cluster (b) coordination chain of Mn_6 (c) their assembly into 2D through coordination of Na ions by some of the carboxylic groups, phenyl ring of sao^{2-} ligands and hydrogen atoms have been omitted for clarity (Mn-purple, N-blue, O-red, Na^+ -green, C-gray).....	28
1.30: General molecular structure of salicylaldoxime.....	29
1.31: <i>pseudo</i> -Macrocyclic arrangement of singly deprotonated salicylaldoxime.....	29
1.32: $[\text{M}_3\text{O}(\text{oximate})_3]^+$ moiety.....	30

1.33: General structure of derivatised salicylaldoximes.....	31
1.34: General X-ray experimental set up.....	33
1.35: Superconducting detection coil.....	36
1.36: Typical output from the SQUID.....	37
1.37: Nuclear decay scheme of ^{57}Co exhibiting the transition giving a 14.4 ke V Mössbauer gamma ray.....	39
1.38: Energy level diagram showing the isomer shift (δ) and quadrupole splitting (ΔE_Q) for the $3/2$ to $1/2$ transition in ^{57}Fe	40
1.39: Energy level diagram illustrating magnetic splitting in ^{57}Fe	40
2.1: General structure of salicylaldoxime.....	49
2.2: Coordination and bridging modes of salicylaldoximes.....	50
2.3: The most common building block for polynuclear complexes of salicylaldoximes, the $[\text{M}_3\text{O}(\text{oximate})_3]^+$ moiety, where $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{R}_3 = \text{alkyl groups}$	51
2.4: Examples for single-headed oximes utilised in this project.....	52
2.5: The common numbering for the aldehydes and the oximes, $\text{R}_y = \text{rest of the ligand}$	53
2.6: The ^1H NMR spectrum of L1a	54
2.7: The ^1H NMR spectrum of L1	54
2.8: The ^{13}C NMR spectrum of L1a	55
2.9: The ^{13}C NMR spectrum of L1	56
2.10: The HMQC spectrum of L1	56
2.11: General structure of derivatised salicylaldoximes.....	57
2.12: General synthetic scheme of the salicylaldoxime ligands.....	58
2.13: (a) Crystal structure of HL2 $^+\cdot\text{NO}_3^-$ (b) H-bonds present within the lattice (C-brown, N-blue, O-red, H-white, H-bonds are illustrated in brown dotted lines); ORTEP view at 30% probability level.....	62
2.14: Asymmetric components of the crystal structure C1 $\cdot 4\text{MeOH}$, $[\text{FeB}(\text{L1-H})_2\text{F}(\text{O})](\text{BF}_4)(\text{MeOH})_2$ (Fe-cyan, B-orange, N-blue, O-red, F-green, C-brown H-white and all H-atoms are omitted for clarity except the ones bound to tertiary nitrogen atoms); ORTEP view at 50% probability level.....	65
2.15: Crystal structure of $[\text{Fe}_2\text{B}_2(\text{L1-H})_4\text{F}_2(\text{O})_2]^{2+}$ ion of the complex C1	

(Fe-cyan, F-green, B-orange, N-blue, O-red, C-brown, and H-white and all the H-atoms are omitted for clarity except the ones bound to tertiary nitrogen atoms); ORTEP view at 50% probability level.....	66
2.16: Metallic core of the structure (see the plane of Fe1-O13 -Fe1-O13a) of the complex C1 ; ORTEP view at 50% probability level.....	66
2.17: Selected H-bond contacts drawn in brown dotted lines within the complex, $[\text{Fe}_2\text{B}_2(\text{L1-H})_4\text{F}_2(\text{O})_2]^{2+}$ (Fe-cyan, F-green, N-blue, O-red, C-brown, B-orange, H-white and all the non H-bonding H-atoms are omitted for clarity except the ones bound to tertiary nitrogen atoms); ORTEP view at 50% probability level.....	67
2.18: (a) The core of the complex C1 , (b) Compound (I), $[\text{Fe}_2(\text{C}_{30}\text{H}_{29}\text{B}_2\text{N}_6\text{O}_6)\text{Cl}_2(\text{CH}_3\text{O})]$	69
2.19: (a) Linear tetranuclear complex containing a $\text{B}^{\text{III}}\text{Mn}^{\text{II}}\text{Mn}^{\text{II}}\text{B}^{\text{III}}$ unit, (b) 2-6-diformyl-4-methylphenol oxime (H_3dfmp).....	70
2.20: Asymmetric components of the crystal structure of $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})]^{2+}$ (Fe-cyan, N-blue, O-red, C-brown, and all the H atoms are omitted for clarity except the ones bound to tertiary amine N-atoms); ORTEP view at 50% probability level	71
2.21: The crystal structure of the first independent complex $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})]^{2+}$ (Fe-cyan, N-blue, O-red, C-brown, and all the H atoms are omitted for clarity except the ones bound to tertiary amine N-atoms); ORTEP view at 15% probability level	74
2.22: The metallic core of the crystal structure $[\text{Fe}_6\text{O}_2(\text{OH})_6(\text{L1-H})_5(\text{L1-2H})]^{2+}$ (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level.....	75
2.23: The crystal structure of the second independent complex $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})]^{2+}$ (Fe-cyan, N-blue, O-red, C-brown, and all the H atoms are omitted for clarity except the ones bound to tertiary amine N-atoms); ORTEP view at 15% probability level	75
2.24: The metallic core of the crystal structure of the second independent complex $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})]^{2+}$ (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level.....	76

2.25: Selected H-bond contacts within asymmetric unit of the complex, C2 drawn in brown dotted lines (Fe-cyan, N-blue, O-red, C-brown, all the H-atoms involved in forming H-bonds are illustrated in white); ORTEP view at 50% probability level	76
2.26: Asymmetric components of the crystal structure, C3 {Na _{0.167} [Fe _{1.66} (OH) _{1.333} (L11-H)Py](BF ₄) _{0.333} (H ₂ O)Py _{0.500} } (Fe-cyan, B-orange, N-blue, O-red, F-green, C-brown, Na-yellow, and all the H atoms are omitted for clarity except the ones bound to the tertiary amine nitrogen atoms of the ligand); ORTEP view at 50% probability level.....	80
2.27: Parallel view of Na[Fe ₇ (OH) ₈ (L11-2H) ₆ Py ₆] ²⁺ (C3) (Fe-cyan, N-blue, O-red, C-brown, and all the H atoms (white) are omitted for clarity. All the atoms involved in forming hydrogen bonding are labelled); ORTEP view at 25% probability level	81
2.28: Magnetic core of Na[Fe ₇ (OH) ₈ (L11-2H) ₆ Py ₆] ²⁺ (C3) (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level.....	83
2.29: Plot of $\chi_M T$ vs T for the complex C1	87
2.30: Plot of $\chi_M T$ vs T for the complex C1 with fitted data with 15% impurity removed from the raw data (fitted data best drawn as a line in red colour).....	88
2.31: M vs. H/T plot for C1	89
2.32: Plot of $\chi_M T$ vs T for the complex C2	90
2.33: M vs. H/T plot for C2	90
2.34: Plot of $\chi_M T$ vs T for the complex C3	91
2.35: M vs. H/T plot for C3	92
2.36: ⁵⁷ Fe Mössbauer spectra of the complex C1 (raw data with error bar lines – spikey lines, simulated – continuous lines) at high and low temperature.....	94
2.37: ⁵⁷ Fe Mössbauer spectra of the complex C2 [raw data with error bar lines – spikey lines, simulated – continuous lines (red and blue lines - different species, black line – the overall fit] at high and low temperature.....	96
2.38: ⁵⁷ Fe Mössbauer spectra of the complex C3 [raw data with error bar lines	

– spikey lines, simulated – continuous lines (red and blue lines - different species, black line – the overall fit] at high and low temperature.....	96
2.39: The relationship between the isomer shift and quadrupole splitting of the iron compounds (figure adapted from a presentation titled ‘ ⁵⁷ Fe Mössbauer Spectroscopy: a Tool for the Remote Characterisation of Phyllosilicates’ by Enver Murad.).....	96
3.1: (a) Double-headed oxime, where R ₁ = - <i>tert</i> -Bu, -CH ₃ , R ₂ = linkers (see Figure 3.2), and R ₃ = -CH ₃ , -CH ₂ -Ar (see Figure 3.2). (b) The planar [M ₃ O(oximate) ₃] ⁺ with 3-fold symmetry, where X = rest of the ligand.....	102
3.2: The R ₂ linkers used in this chapter with R ₃ modes (R ₃ = -CH ₃ , -CH ₂ -Ar) shown.....	103
3.3: Crystal structure of the cation [Cu ₃ (L5 -H) ₃ (Py ₃)] ³⁺ (Cu-dark green, N-blue, O-red, C-brown, and H atoms except H-atoms on the straps are omitted for clarity); ORTEP view at 50% probability level....	104
3.4: Selected H-bond contacts drawn in brown dotted lines (Cu-dark green, N-blue, O-red, C-brown, H-white, and all the H-atoms are omitted for clarity except the ones involved in forming H-bonds and the ones on amine N-atoms); ORTEP view at 30% probability level	107
3.5: Cation, [Cu ₄ (L8 -3H) ₂ Py ₂] ²⁺ of the complex [Cu ₄ (L8 -3H) ₂ Py ₂](BF ₄) ₂ (MeOH)Py (C7 ·MeOH·Py) [Cu-green, N-blue, O-red, C-brown, (C-atoms of the pyridine molecules are omitted for clarity) and H atoms are omitted for clarity except the oximic H-atoms]; ORTEP view at 50% probability level.....	109
3.6: Crystal structure of the cation [Fe ₃ BO ₂ (L9 -2H) ₂ (OH) ₂ (Py) ₂] ²⁺ of the complex C10 (Fe-cyan, B-orange, N-blue, O-red, C-brown) H atoms are omitted for clarity except the protons on the tertiary amines, counterions and solvent molecules have also been removed for clarity; ORTEP view at 50% probability level.....	113
3.7: Metallic core of the structure C10	

(see the plane of Fe1- O5 - B1- O5a- Fe1); ORTEP view at 50% probability level	115
3.8: Hydrogen bonding present within the complex C10 ; ORTEP view at 50% probability level.....	116
3.9: Plot of $\chi_M T$ vs T for the complex C10 with fitted data (fitted data illustrated in red colour).....	117
3.10: Schematic J model for the complex C10	118
3.11: Plot of energy vs total spin of the complex C10	118
3.12: M vs. H/T plot for C10	119
3.13: Crystal structure of the cation of the complex C8 $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L7-2H})_3]^{3+}$ (Fe-cyan, N-blue, O-red, C-brown). The H atoms are omitted for clarity except the ones bound to tertiary nitrogen atoms; ORTEP view at 50% probability level.....	121
3.14: Metallic core of $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L5-2H})_3]^{3+}$ of the complex C5 emphasising the hydrogen bond contact (dark green dotted line) between the central oxygen atoms (O10 & O11) of the lower and upper triangles and the internal hexagon (O15 through O20, shown in dotted light green line) (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level.....	123
3.15: Plot of $\chi_M T$ product vs T for the complex C8 ·7H ₂ O·Py with fitted data (fitted data illustrated in red colour).....	124
3.16: Plot of energy vs total spin for the complex C8 ·7H ₂ O·Py.....	125
3.17: Schematic J model for the complex C8 ·7H ₂ O·Py.....	126
3.18: Crystal structure of the cation of the complex, C4 $[\text{Fe}_7\text{O}_2(\text{OH})_6(\text{L5-2H})_3]^{5+}$ (Fe-cyan, N-blue, O-red, C-brown, all the H atoms except the ones bound to tertiary nitrogen atoms and all the axial pyridine molecules are omitted for clarity); ORTEP view at 50% probability level.....	127
3.19: Partial structure of the complex C4 that emphasises the displacement of the central oxygen atom O7 by 0.335(5) Å and the coordination by the pyridines (Ry = the rest of the ligand that connects to the second triangular unit, Fe-cyan, N-blue,	

O-red, C-brown, all the H are omitted for clarity); ORTEP view at 25% probability level.....	129
3.20: Selected H-bond contacts within the complex C4 drawn in brown dotted lines, Fe-cyan, N-blue, O-red, C-brown, all the H atoms except the ones bound to tertiary nitrogen atoms and the ones involved in forming H bonds and the axial pyridine molecules are omitted for clarity]; ORTEP view at 10% probability level.....	130
3.21: Plot of $\chi_M T$ product vs T for the complex C4	131
3.22: M vs. H/T plot for C4	132
3.23: The metallic core of the complex C6 (Fe-cyan, N-blue, O-red); ORTEP view at 10% probability level.....	134
3.24: Plot of $\chi_M T$ product vs T for the complex C6 ·7BF ₄ ⁻ ·6H ₂ O	137
3.25: M vs. H/T plot for C6 ·7BF ₄ ⁻ ·6H ₂ O	137
3.26: Selected H-bond contacts within the complex, C9 drawn in brown dotted lines, Fe-cyan, N-blue, O-red, C-brown. H atoms except the ones involve in forming H-bonds are omitted for clarity; ORTEP view at 50% probability level.....	141
3.27: Plot of $\chi_M T$ product vs T for the complex C9 ·3BF ₄ ⁻ ·2PF ₆ ⁻ ·3H ₂ O.....	142
3.28: M vs. H/T plot for C9 ·3BF ₄ ⁻ ·2PF ₆ ⁻ ·3H ₂ O.....	143
3.29: ⁵⁷ Fe Mössbauer spectra of the complex C8 (raw data with error bar lines – spikey lines, simulated – continuous lines) at high and low temperature.....	149
3.30: ⁵⁷ Fe Mössbauer spectra of the complex C10 (raw data with error bar lines – spikey lines, simulated – continuous lines) at high and low temperature	149
3.31: ⁵⁷ Fe Mössbauer spectra of the complex C4 [raw data with error bar lines – spikey lines, simulated – continuous lines (red and blue lines - different species, black line – the overall fit] at high and low temperature.....	151
3.32: ⁵⁷ Fe Mössbauer spectra of the complex C9 [raw data with error bar lines – spikey lines, simulated – continuous lines (red and blue lines - different species, black line – the overall fit]	

at high and low temperature.....	151
3.33: ^{57}Fe Mössbauer spectra of the complex C6 [raw data with error bar lines – spikey lines, simulated – continuous lines (red and blue lines – different species, black line – the overall fit] at high and low temperature.....	152
4.1: Structural representation of the dimetallic core of the complex C1 ; ORTEP view at 50% probability level.....	157
4.2: Metallic core of the structure C10 ; ORTEP view at 50% probability level.....	157
4.3: Metallic core, $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L5-2H})_3]^{3+}$ of the complex, C8 emphasising the hydrogen bond contact (dark green dotted line) between the central oxygen atoms (O10 and O11) of the lower and upper triangles and the internal hexagon (O15 through O20, shown in dotted light green line) (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level.....	159
4.4: The metallic cores of the two crystallographic independent molecules of $[\text{Fe}_6\text{O}(\text{OH})_7(\text{L1-H})_5(\text{L1-2H})]^{2+}$ C2 (Fe-cyan, N-blue, O-red); ORTEP view at 50% probability level.....	160
4.5: Metallic core, $[\text{Fe}_7\text{O}_2(\text{OH})_6(\text{L5-2H})_3]^{5+}$ of the complex, C4 emphasising anti-prismatic arrangement of the N-O bridging oximic bonds (Fe-cyan, N-blue, O-red); ORTEP view at 30% probability level.....	161
4.6: A representative simple salicylaldoxime where X is a more bulky group...	164

LIST OF TABLES

1.1: Derivatized salicylaldehydes utilized in the project.....	32
2.1: Derivatized ‘single-headed’ salicylaldehydes utilized in the project.....	58
2.2: Metal salts utilized in the project.....	59
2.3: H-bond lengths for L2	61
2.4: Selected bond lengths of the complex C1 ·4MeOH.....	64
2.5: Distorted tetrahedral angles of a boron atom and Fe(III) atom of the complex C1 ·4MeOH	65
2.6: Selected H-bond lengths of the complex C1 ·4MeOH	67
2.7: Charge balance analysis of the complex C1	68
2.8: Bond lengths around the Fe(III) atoms of the complex C2	72
2.9: Bond angles around Fe(III) atoms of the complex C2	73
2.10: Selected H-bond distances of the asymmetric unit of the complex C2	74
2.11: Torsion angles around Fe(III) atoms of the complex C2	77
2.12: Charge balance analysis of the complex C2	78
2.13: Fe/R-sao ²⁻ complexes with the [Fe ₃ (μ ₃ -O)] ⁷⁺ core.....	78
2.14: Distorted octahedral bond lengths around the Fe ₂ (III) atom.....	79
2.15: Distorted octahedral angles of Fe ₂ (III) atoms on the plane For complex C3	79
2.16: Selected H-bond lengths of the complex C3	82
2.17: Charge balance analysis of the complex C3	82
2.18: Crystallographic details of the complexes, C1-C3 and L2	85
2.19: Fitting parameters of ⁵⁷ Fe on C1-C3 at low temperature and higher temperature (δ = isomer shift, ΔE _Q = electric quadrupole splitting, Γ _L = line width of the left peak, Γ _R = line width of the right peak, I = intensity).....	93
3.1: Selected bond distances for complex C5 ·3H ₂ O·3MeOH.....	106
3.2: Selected bond angles for complex C5 ·3H ₂ O·3MeOH.....	106
3.3: Selected H-bond distances for complex C5 ·3H ₂ O·3MeOH.....	106
3.4: Charge balance analysis of the complex C5	107
3.5: Selected bond lengths around Cu ions of complex C7 ·MeOH·Py.....	110
3.6: Selected bond angles around the Cu(II) ions of complex C7 ·MeOH·Py.....	110

3.7: Selected H-bond distances for C7 ·MeOH·Py.....	110
3.8: Charge balance analysis of the complex C7	111
3.9: Crystallographic details of the complexes C5 and C7	111
3.10: Selected bond lengths around the metal ions for the complex C10 ·2H ₂ O·MeOH·Py.....	114
3.11: Selected bond angles for the complex C10 ·2H ₂ O·MeOH·Py	114
3.12: Selected H-bonds for the complex C10 ·2H ₂ O·MeOH·Py	116
3.13: Charge balance analysis of the complex C10	116
3.14: Selected bond lengths around metal ions of the complex C8 ·7H ₂ O·Py.....	122
3.15: Selected bond angles around the metal centres of the complex, C8 ·7H ₂ O·Py.....	122
3.16: Selected H-bond lengths of the complex C8 ·7H ₂ O·Py.....	122
3.17: Charge balance analysis of the complex C8	123
3.18: Selected bond lengths around the metal centres of the complex C4 ·7H ₂ O·3Py.....	128
3.19: Selected bond angles around the metal centres of the complex C4 ·7H ₂ O·3Py.....	128
3.20: Important H-bond distances and angles within the complex C4 ·7H ₂ O·3Py.....	130
3.21: Charge balance analysis of the complex C4	131
3.22: Selected bond lengths around the metal centres of the complex C6 ·5PF ₆ ⁻ ·2H ₂ O	134
3.23: Selected bond angles around the metal centres of the complex C6 ·5PF ₆ ⁻ ·2H ₂ O.....	135
3.24: Selected torsion angles of the complex C6 ·5PF ₆ ⁻ ·2H ₂ O.....	135
3.25: CHN results for the complex C6 ·5PF ₆ ⁻	136
3.26: Charge balance analysis of the complex C6 ·5PF ₆ ⁻	136
3.27: Selected bond lengths around the metal centres of the complex C9 ·3BF ₄ ·3H ₂ O·2Py.....	139
3.28: Selected bond angles around the metal centres of the complex C9 ·3BF ₄ ·3H ₂ O·2Py.....	139
3.29: Important H-bond distances and angles within the complex C9 ·3BF ₄ ·3H ₂ O·2Py.....	140

3.30: Charge balance analysis of the complex C9 ·7BF ₄	140
3.31: CHN results for the complex C9 ·3BF ₄ ⁻ ·2PF ₆ ⁻ ·3H ₂ O	141
3.32: Iron clusters of double-headed salicylaldoxime derivatives.....	145
3.33: Crystallographic details of the complexes, C10 , C8 , C4 , C6 and C9	146
3.34: Fitting parameters of ⁵⁷ Fe on C8 , C4 , C9 , C10 and C6 at low temperature and higher temperature (δ = isomer shift, ΔE_Q = electric quadrupole splitting, Γ_L = line width of the left peak, Γ_R = line width of the right peak, I = intensity).....	148
4.1: Crystallographical formulae of the complexes.....	155
4.2: Complexes with low nuclearity.....	156
4.3: Complexes with high nuclearity.....	158
4.4: Comparison of IR data, Fe ^{III} μ -oxo/hydroxo bond lengths and displacements of the central oxygen atoms from the metal planes with each other and literature.....	162

ABBREVIATIONS

AF	Antiferromagnetic exchange
SMMs	Single molecule magnets
SCMs	Single chain magnets
ZFS	Zero field splitting parameter (<i>D</i>)
M	Magnetisation
H	External magnetic field
χ	Magnetic susceptibility
T _c	Curie temperature
T _N	Néel temperature
VT	Variable temperature
QTM	Quantum tunnelling of magnetisation
QPI	Quantum phase interference
MeOH	Methanol
EtOH	Ethanol
MeCN	Acetonitrile
EtOAc	Ethyl acetate
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
Et ₂ O	Diethylether
Et ₃ N	Triethylamine
Py	Pyridine
CDCl ₃	Deuterated chloroform
T	Temperature
RT	Room temperature
MP	Melting point
dc	Direct current
br	Broad
m	Medium
s	Strong
saoH ₂	Salicylaldoxime
Me-saoH ₂	Methyl salicylaldoxime
Et-saoH ₂	Ethyl salicylaldoxime

Ph-saoH ₂	Phenyl salicylaldoxime
MRI	Magnetic resonance imaging
XRD	X-ray diffraction
SQUID	Superconducting quantum interference device
TLC	Thin layer chromatography
NMR	Nuclear magnetic resonance
ESI-MS	Electrospray ionisation mass spectrometry
IR	Infra-red
UV-Vis	Ultraviolet-visible
TMS	Trimethylsilane