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Exploring synthetic strategies towards novel magnetic materials – A structural, magnetic and spectroscopic study

By

Edel-Lisa Houton

Presented for the degree of Ph.D. at the

School of Chemistry

National University of Ireland, Galway

April 2015

Supervisor: Dr. Leigh F. Jones

Head of School: Dr. Andrea Erxleben
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Declaration

I hereby declare that the work carried out in this thesis is my own. No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification, at this, or any other university or institute of higher learning.

Signature

____________________
Edel-Lisa Houton
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And not to forget Holly – my four legged partner in crime!
Abstract

This thesis reports the exploration of various synthetic strategies towards the synthesis of novel magnetic materials, which were studied both structurally and spectroscopically. An outline of results chapters is given below.

Chapter Two reports the synthesis, structural and magnetic characterization of a pair of model Mn dimers with formulas: \([\text{Mn}^{\text{III}}_2\text{Zn}^{\text{II}}_2\text{(Ph-sao)}_2\text{(Ph-saoH)}_4\text{(hmp)}_2]\) (2.1) (where Ph-saoH_2 = (2-hydroxyphenyl)(phenyl)methanone oxime and hmp = 2-hydroxymethylpyridine) and \([\text{Mn}^{\text{III}}_2\text{(Naphth-sao)}_2\text{(Naphth-saoH)}_2\text{(MeOH)}_2]\cdot4\text{MeOH} \) (2.2) (where Naphth-saoH_2 = 2-hydroxy-1-naphthaldehyde oxime) constructed via oxime ligands. These dimers were used as model complexes with which to examine the magneto-structural relationship in oxime-bridged Mn^{III} complexes.

In an attempt to examine the effect of sterically demanding oximes and carboxylate co-ligands towards Fe-oxime cage formation, Chapter Three presents the synthesis and magnetic behavior of the hexametallic siblings \([\text{Fe}^{\text{III}}_6\text{O}_2\text{(Naphth-sao)}_2\text{(O}_2\text{C-C}_{10}\text{H}_{8})_{10}\text{(H}_2\text{O})_2]\cdot8\text{MeCN} \) (3.1) (where \text{O}_2\text{C-C}_{10}\text{H}_{8} = 1-naphthoate and Naphth-saoH_2 = 2-hydroxy-1-naphthaldehyde oxime) and \([\text{Fe}^{\text{III}}_6\text{O}_2\text{(Naphth-sao)}_2\text{(O}_2\text{C-C}_{14}\text{H}_{10})_{10}\text{(H}_2\text{O})_2]\cdot8\text{MeCN} \) (3.2) (where \text{O}_2\text{C-C}_{14}\text{H}_{10} = 9-anthracenecarboxylate and Naphth-saoH_2 = 2-hydroxy-1-naphthaldehyde oxime), along with the tetrannuclear cube-like cage \([\text{Fe}^{\text{III}}_4\text{(tert-butyl-sao)}_4\text{(MeOH)}_4\text{Cl}_4]\) (3.3), constructed using the 3,5-di-tert-butyl salicylaldoxime (tert-butyl-saoH_2) ligand.

In a similar vein to the work described in Chapter Three, we report in Chapter Four the solvothermal synthesis and structural and magnetic characterisation of a family of discrete Cr^{III} cages (4.1-4.3) and extended network materials (4.4 and 4.5), each comprising trimetallic oxo-centred \(\{\text{Cr}^{\text{III}}_2\text{O}(\text{O}_2\text{C}_{\text{R}})_3\text{(R}_2\text{-sao)}_3\}\cdot2\) (R_1 = H, CH_3, C(CH_3)_3, C_{14}H_{9}, R_2 = Me, \text{'Bu, Naphth, Ph}) units linked via connector Na^+ cations. The structural characterisation of a \([\text{Cr}_4]\) complex (4.6) is also discussed here.

The final research chapter (Five) reports on the facile synthesis and D tensor elucidation of a family of Mn(III) monomers using an efficient (5 minute duration) synthetic route. These complexes are: \([\text{Mn}^{\text{III}}_3\text{F}_3\text{(H}_2\text{O})(\text{L}_1)]\) (5.1), \([\text{Mn}^{\text{III}}_3\text{F}_3\text{(H}_2\text{O})(\text{L}_2)]\)
Abstract

(5.2), \([\text{Mn}^{III}F_3(H_2O)(L_3)]\) (5.3), \([\text{Mn}^{III}F_3(H_2O)(L_4)]\) (5.4), \([\text{Mn}^{III}F_3(H_2O)(L_5)]\) (5.5) and \([\text{Mn}^{III}F_3(H_2O)(L_6)]\) (5.6), where \(L_1 = 2,2'\text{-bipyridine}, L_2 = 1,10\text{-phenanthroline}, L_3 = 6\text{-methyl-2,2'-dipyridyl}, L_4 = 4,4'\text{-dimethyl-2,2'-dipyridyl}, L_5 = 5,5'\text{-dimethyl-2,2'-dipyridyl}\) and \(L_6 = 5\text{-chloro-1,10-phenanthroline}\).
List of Publications

1. Accidentally on purpose: construction of a ferromagnetic, oxime-based [Mn$^{III}$]$_2$ dimer

2. Ferromagnetic exchange in a twisted, oxime-bridged [Mn$^{III}$]$_2$ dimer


4. Solvothermal-Assisted Synthesis of Discrete Cages and Extended Networks Comprising \{(Cr$_3$O(O$_2$CR)$_3$(oxime)$_3$)$_2$\} (R = H, CH$_3$, C(CH$_3$)$_3$, C$_{14}$H$_9$) Building Blocks

5. A Facile Synthetic Route to a Family of Mn(III) Monomers and their Structural, Magnetic and Spectroscopic Studies
Conference Proceedings, Modules and Awards

Conference Proceedings
- RSC Young Researchers Symposium. University of Warwick, September ‘11.
- 64th Irish Universities Chemistry Research Colloquium. University of Limerick, June ‘12.
- ECMM (European Conference on Molecular Magnetism), October ‘13, Germany.

Modules
- Core Skills for Chemistry Research.
- Teaching and Learning.
- Graduate Information Skills.
- ICGEE (International Centre for Graduate Education in Micro and Nano-Engineering) course on semi-conductor LASER fabrication. Tyndall Institute, Cork.
- Three month internship. Seagate™ Technology, Derry (August-October ‘12).

Award
- BOC Postgraduate Award, April ’15.
Chapter One

Introduction
1.1 History and Background to Magnetism

Magnetism is a physical process which involves the motion of electric charge, leading to the attraction and repulsion between materials. It is an ancient phenomenon and there are a number of theories as to where the term ‘magnetism’ was derived. It has been proposed that magnetite (Fe₃O₄, an oxide of iron containing a mixture of Fe²⁺ and Fe³⁺ ions) and its fascinating properties were first explored by the Greeks. Large black rocks known as ‘lodestones’ meaning ‘leading stone’ or the more common term ‘compass’ were found to show affinities for metals. These lodestones may have earned their name from the region in which they were mined, ‘Magnesia’. On the same note, others give reference to the Shepard Magnes, ‘the nails of whose shoes and the tip of whose staff stuck fast in a magnetick field while he pastured his flocks’. In the 1500s, William Gilbert, an English man, became known as the ‘father of magnetism’. He wrote and published the book *De Magnete* in 1600 in which he was the first to suggest that the earth itself was a large magnet.

An apparent link between electricity and magnetism was not discovered until 1820 when Hans Christian Ørsted noticed, during a public demonstration, that a hanging compass needle was deflected once an electric current was turned on. This discovery prompted further investigations with André-Marie Ampère explaining the dynamics of magnetic forces between parallel current carrying wires (as the magnets travel in the same or opposite direction the wires were attracted to or repelled by each other respectively). Further to this, Michael Faraday formulated the theory of a magnetic field. Using an electromagnet he discovered electromagnetic induction (changing of the magnetic field to induce the flow of electricity), this then led to what is still commonly known as the ‘Faraday effect’, when the plane of polarized light is rotated by a magnetic field.

Nearing the latter years of the nineteenth century, a huge aid in the elementary understanding of magnetism was discovered, the electron. The Irish scientist George Johnstone Stoney described the concept of an electron in 1891.[1] J. J. Thompson later conducted experiments on cathode rays which led to the
determination of the mass to charge ratio of the electron. It was soon realised that these electrons, which are moving charged particles, played a vital role in the theory of magnetisation; they were what carried electric current and were the sole magnetic components of atoms and solids.

Some time later, quantum mechanics became a crucial part in the understanding of magnetic theory. Weiss, Bohr, Heisenberg, Pauli, Dirac, Landau and their ideas in physics all contributed to this step forward. It was hypothesized that each electron had an intrinsic angular momentum and magnetic moment (electron spin) and that a force, namely ‘exchange’, existed between pairs of these electrons.\[2\] \[3\] \[4\] \[5\] \[6\]

In more recent times magnets have become involved in competitive industries and are used all around us in the world today, for example, in electronic devices involving information storage or telecommunications. Magnets also have their use in medicine within techniques such as Magnetic Resonance Imaging (MRI), which contain huge super-conducting magnets used to apply the external magnetic field.

**Table 1.1.** The seven ages of magnetism adapted from J. M. D. Coey’s publication in the *Journal of Magnetism and Magnetic Materials.*\[2\]
Magnets are not only involved in the technological lifestyle in which we lead today, for instance, magnetite (Fe$_3$O$_4$) is a naturally occurring mineral and is found as intracellular microcrystals in the brains of birds and is used for navigation purposes.\cite{7} In fact, iron and its magnetic properties have a number of roles in nature, including its involvement with the enzyme Cytochrome C in the human body.\cite{8} Magnetism in the 21\textsuperscript{st} century calls for a search for a combination of or an individual raw material which can further develop the field of magnetism in terms of robustness and efficiency. A more detailed understanding of such materials is acquired through their study at the molecular level, an area known as molecular magnetism on which this thesis is heavily based.\cite{9}

### 1.2 Electrons and their Involvement in Magnetism

Magnetism is fundamentally reliant on the properties and actions of electrons. Electrons are charged particles with direction or spin and therefore produce a magnetic field or moment. Electrons could be described as minute magnets leading to the idea that all magnetic materials must possess unpaired electrons.

Unpaired electrons have the ability to move in two ways, spinning on their axis (spin angular momentum, quantum number S) and orbiting their nucleus (orbital angular momentum, quantum number L). Collectively these two sources of

<table>
<thead>
<tr>
<th>Age</th>
<th>Time</th>
<th>Key Names</th>
<th>Driver</th>
<th>Achievements</th>
<th>Materials</th>
<th>Applications/ Devices</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High Frequency</strong></td>
<td>1935-1960</td>
<td>Dirac</td>
<td>Bloch</td>
<td>Microwaves, EPR, NMR</td>
<td>Ferrites</td>
<td>Radar, Television, MRI</td>
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<td></td>
<td></td>
<td>Landau</td>
<td>Pound</td>
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<td></td>
<td>Purcell</td>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>Applications</strong></td>
<td>1960-1995</td>
<td>-</td>
<td>Industry</td>
<td>Miniaturisation of magnetic circuits</td>
<td>Nd-Fe-B, Sm-Co</td>
<td>Consumer electronics</td>
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<td></td>
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<td></td>
<td>(consumer)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>Spin Electronics</strong></td>
<td>1995-Present</td>
<td>-</td>
<td>Industry</td>
<td>Thin film devices</td>
<td>Multilayers</td>
<td>High Density, Magnetic Recording, MRAM etc.</td>
</tr>
<tr>
<td></td>
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<td>(consumers)</td>
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</tbody>
</table>
magnetic field are known as the total angular momentum (quantum number J) and therefore \( J = S + L \). Electrons have a magnetic moment and spin quantum number of \( S = +\frac{1}{2} \) or \(-\frac{1}{2}\) which are known as microstates \( (M_s) \) (Fig. 1.1).

**Figure 1.1.** This is a schematic representation of the two microstates \( (M_s) \) which can be generated when an electron either lines itself parallel or anti-parallel to an external magnetic field (Zeeman Effect).

### 1.3 Types of Magnetic Behaviour

**Figure 1.2.** Illustration representing the individual magnetic moments in A) paramagnetic, B) ferromagnetic, C) antiferromagnetic and D) ferrimagnetic systems respectively.
1.3.1 Diamagnetism

Diamagnetism is a property of all matter whereby both magnetisation (M) and susceptibility (χ) carry a negative value. The electron spins in diamagnetic materials are aligned anti-parallel to one another. Therefore, interaction of these electron pairs with the external field (H) generates a field opposing H, producing the negative value for M. Diamagnetic materials have a tendency to repel magnetic fields and accordingly repel magnetic lines of flux (Fig. 1.3) and are attracted to areas of minimal energy and lowest field strength. The diamagnetic contribution to the magnetic susceptibility can be calculated using a table of known susceptibilities for atoms and bonds known as Pascal’s constants, thus, the diamagnetic contribution is additive, although it is more favourable to be measured using direct methods.

![Diamagnetic Material and Paramagnetic Material](image)

Figure 1.3. Illustrations showing the effect that diamagnetic and paramagnetic material have on the magnetic lines of flux in an applied magnetic field.

1.3.2 Paramagnetism

Paramagnetism is prevalent in materials with unpaired electrons in the presence of a magnetic field; here magnetisation carries a positive value. In the presence of this magnetic field, electrons align in a uniform manner in the same direction as H, shown in Fig. 1.2, (A). If however, the direction of this field is reversed the electron spins will follow, as a result the substances do not show the indicative signs of hysteresis. In the absence of a magnetic field spins have a randomised orientation,
thus paramagnetism is independent of field strength with temperature being the deciding factor. Paramagnetic materials are attracted into a magnetic field and therefore their magnetic lines of flux are drawn into the material (Fig. 1.3). This form of material tends to be attracted to areas of high energy and maximum field strength. All paramagnetic materials have a diamagnetic component which must also be calculated due to paired electrons simultaneously present in the material, this can likewise be calculated using Pascal’s constants, mentioned in the previous section. This diamagnetic component must be accurately accounted for if the magnetic susceptibility of a material is to be calculated / measured precisely.

1.3.3 Ferromagnetism

Here, the spin moments line parallel with one another, all pointing in the same direction to produce a directional net magnetic moment (Fig 1.2, (B)). This only occurs once the material is below the Curie temperature \(T_c\) in the absence of a magnetic field (Fig 1.5). Above this temperature spins become randomised and permanent magnetic behaviour is lost in a scenario akin to paramagnetic behaviour.

![Figure 1.4. Bulk ferromagnetism; (top) net magnetic moment of magnetic domains are randomly aligned with respect to one another, (bottom) uniform alignment of spin throughout the material upon application of an external magnetic field (H).](image)

Bulk ferromagnets are composed of many atoms in 3D extended solids; subsequently magnetic domains assemble which are regions of uniform alignment
and intense magnetisation. In the absence of a magnetic field, the net magnetic moment within each of these domains are aligned randomly with regards to one another (Fig. 1.4, top). Once the external magnetic field is applied, the direction of spins between domains synchronises and the sample becomes magnetised leading to a net magnetic moment along the direction of H (Fig. 1.4, bottom). A distinct property of ferromagnetic materials is that they may remain magnetised once the external magnetic field has been removed, forming a permanent magnet and therefore display magnetic hysteresis.

1.3.4 Antiferromagnetism

Antiferromagnetism leans towards being the most common form of magnetic behaviour where electron spins align anti-parallel to one another (Fig. 1.2, (C)). Individual spin moments are equal in magnitude and effectively cancel each other out leading to a net magnetic moment of zero. Antiferromagnetic behaviour occurs below the Néel temperature (TN) (Fig. 1.5).

1.3.5 Ferrimagnetism

The individual spins or magnetic moments in a ferromagnetic material align in an antiparallel arrangement as illustrated in Fig. 1.2, (D)). However, the magnitude of every other spin is unequal and results in an overall net magnetic moment in the direction of the spin with the greater magnitude. A prominent example of a ferrimagnet is the naturally occurring iron ore ‘magnetite’ ([Fe$^{III}_2$Fe$^{II}$O$_4$]), as it contains a mixture of Fe$^{II}$ and Fe$^{III}$ ions with spins of differing magnitude. This behaviour is observed below the materials Curie temperature (T$c$) (Fig. 1.5).
1.3.6 Metamagnetism

Metamagnetism is prevalent in materials that possess traits of both ferromagnetic and antiferromagnetic behaviour within the crystal lattice that undergo a phase transition, upon application of an external magnetic field. For example, within the lattice of FeCl₂, two forms of magnetic interactions are witnessed. The coupling within each layer of Fe²⁺ ions is ferromagnetic while concurrently there is a weak antiferromagnetic interaction between layers. Below ~24 K antiferromagnetic behaviour is dominant, in response to the application of an applied magnetic field, the Fe²⁺ dipoles align in the same direction overriding the antiferromagnetic component of the material leading to overall ferromagnetic behaviour.¹⁰

1.3.7 Superparamagnetism

Superparamagnetism is a phenomenon characteristic of ferromagnetic or ferrimagnetic nanoparticles that are single domain, typically with a particle size of ~10 nm and often referred to as ferrofluids. These materials reach a state of magnetic saturation quite easily under the influence of an applied magnetic field but have no remnant magnetisation (i.e. no magnetisation remains upon the removal of the magnetic field). When in their superparamagnetic state these
particles can flip the direction of their magnetic moments in response to
temperature, usually below the particles Curie temperature ($T_c$), while the time
between flips is known as the Néel relaxation time. This behaviour is the reverse of
regular ferrimagnetic and ferromagnetic material behaviour. If the particle has a
preferred direction for its magnetic moment (i.e. it is anisotropic), two stable
configurations will dominate anti-parallel to one another; these stable orientations
define the nanoparticles ‘easy axis’. The blocking temperature ($T_B$) of a particle is
defined as the temperature limit at which its magnetisation will be retained in a
specific direction.\textsuperscript{[11]}

1.4 Curie and Curie-Weiss Laws

The Curie law explains the relationship between magnetisation and temperature in
a paramagnet. It states that magnetisation is inversely proportional to temperature;
hence, the thermal energy and therefore thermal agitation of a material at higher
temperatures outweighs its magnetic energy, described by the equation below:

$$\chi_m = \frac{C}{T}$$

where $C$ is the Curie constant and can be extracted from a plot of $1/\chi_m$ vs. $T$ which in
theory gives a straight line (Fig. 1.6) that passes through or within close proximity to
the origin. The slope is $C^{-1}$, $\chi_m$ is the magnetic molar susceptibility and $T$ is
temperature. Paramagnetic materials that obey Curie law are rare due to their
ability to partake in weak intermolecular interactions; therefore a Weiss constant ($\theta$)
must be applied to give the Curie-Weiss law described below:

$$\chi_m = \frac{C}{(T-\theta)}$$

In this case, a plot of $1/\chi_m$ vs. $T$ gives a straight line, with $\theta$ as its intercept. The sign
of this $\theta$ value supplies information on the type of magnetic behaviour in force and
is characteristic of an individual substance. A positive $\theta$ value at low temperatures is
indicative of dominant ferromagnetic behaviour while a negative $\theta$ value suggests the behaviour is antiferromagnetic in origin (Fig. 1.6).

![Curie-Weiss plot](image)

Figure 1.6. Curie-Weiss plot of $1/\chi$ vs. $T$ with the intercept equal to $\theta$.

A common plot used to confirm or determine the category of magnetic behaviour and to detect deviation from Curie law, is a graph of $\chi_mT$ vs. $T$ (Fig 1.7). This plot also gives information on the magnitude of the magnetic coupling present in a molecule. Figure 1.7 presents deviations from the Curie law for ferromagnetic, antiferromagnetic and ferrimagnetic materials. It can be noted that the $\chi_mT$ product deviates significantly form Curie law particularly at lower temperatures.

![χₘT vs. T graph](image)

Figure 1.7. $\chi_mT$ vs. $T$ curves indicative of various types of magnetic behaviour. Colour code: Red – Paramagnetic, Green – Ferromagnetic, Orange – Antiferromagnetic and Blue – Ferrimagnetic.
1.5 Magnetic Hysteresis

Magnetic hysteresis, also known as the memory effect, is the phenomenon of a sample retaining its magnetisation once the external magnetic field has been switched off (i.e. a sample remains magnetised upon removal of H). The concept of hysteresis leads to magnetic bi-stability in materials, whereby, in the dearth of a magnetic field the remnant magnetisation can either be ‘spin up’ or ‘spin down’. This topic will be covered in more detail in section 1.14 - 1.14.5 and can be represented by ‘b’ and ‘e’ in Figure 1.8.

![Figure 1.8](image-url)  
**Figure 1.8.** Schematic representation of a typical hysteresis loop. Index: \( a = \) magnetisation saturation, \( b = \) retentivity, \( c = \) coercivity, \( d = \) magnetisation saturation in opposing direction, \( e = \) retentivity and \( f = \) coercivity.

Figure 1.8, is representative of a typical hysteresis curve, the magnetisation (B) is being quantified while the field (H) is being altered. The dashed line represents a material which has never previously been magnetised, as the field is switched on and increased, it initiates magnetic ordering within the solid leading to point \( a \). At \( a \), the material is said to be saturated, this infers that a high number of magnetic domains have aligned in the one direction and an increase of field intensity will
have little to no effect; leading to ‘magnetic saturation’. As H is reduced to zero a follows the path to b known as retentivity. Here, some of the magnetisation still remains; as mentioned previously it is a material’s ability to retain magnetisation once a magnetic field has been removed following saturation. Some domains remain aligned while others return to their previous state, also known as remnant magnetisation. As the field is reversed, the loop moves to point c, the point of coercivity where the field is now zero. Reversal of the field has flipped enough domains that the net magnetisation is now zero. The force needed to return this net magnetisation to zero is known as coercivity. As the field is increased in the opposing direction, the material will once again become magnetically saturated (d) in this opposite direction. The value of residual magnetisation will be equal in both directions, positive and negative (i.e. b = e). Increasing the external magnetic field back to zero brings the loop to f, however it has not returned to its original position (0,0) as a certain amount of force is required to remove all residual magnetisation from a material.

![Hysteresis Loops](image)

**Figure 1.9.** Hysteresis loops for a hard magnet and a soft magnet representing the difference in coercive field and retentivity for each class of compound while saturation remains uniform.

The nature of the hysteresis curve verifies if a magnet is hard or soft. A hard magnet will hold onto its magnetisation for a considerably longer period of time that a soft
magnet and following the same trend will also require a strong opposing magnetic field to return its magnetisation to zero. That is, the retentivity and coercivity of a hard magnet are much larger than those of a soft magnet. The area encased by a hysteresis curve is known as its coercive field, the larger this area the harder the magnet concerned (Fig. 1.9), with superparamagnets exhibiting hysteresis functions below their blocking temperatures ($T_B$).

### 1.6 Magnetic Susceptibility ($\chi$)

Magnetic susceptibility is a measure of the increase in magnetic moment upon application of a magnetic field. In the sections which follow, two methods used to measure magnetic susceptibility ($\chi$) will be discussed, namely, the Gouy Balance method and SQUID magnetometry.

#### 1.6.1 Gouy Balance Method

The Gouy balance (Fig. 1.10) uses force methods to quantify $\chi$. A powdered sample of the material is placed in a quartz tube and is suspended centrally between the opposing poles of a magnet, on a precise balance. The sample in the bottom of the quartz tube is hanging in a homogenous magnetic field, while the top of the tube is held in a zero or very weak magnetic field and thus a displacement force is exerted upon it. This results in a change in the materials weight with the difference being proportional to the molar magnetic susceptibility ($\chi_m$). A weight increase is indicative of a paramagnetic material and the contrary a diamagnetic material. The Gouy method is not as sensitive as SQUID Magnetometry (discussed in section 1.6.2, below), which is more commonly used today.
1.6.2 Superconducting Quantum Interference Device (SQUID) Magnetometry

SQUID magnetometry is a very sensitive technique used to measure the magnetisation of a sample and magnetic fields as small as $10^{-15}$ tesla (T) can be quantified. The resulting magnetisation obtained from a SQUID experiment is documented as a single figure, but is in fact the combination of all magnetic moments within a sample. A very small sample size is required (~20-40 mg) and is usually suspended in Eicosane, a low melting point wax which prevents torquing and solvent loss. The main measuring components of a SQUID are a superconducting magnet (which generates the field) and Josephson junctions which are small gaps between semiconductors (Fig. 1.11). Electrons pass through these junctions and demonstrate quantum interference. In other words, the sample is placed in the centre of a sensing coil which in turn is coupled to a second loop, as the sample (which at this point is magnetised) is passed though the coil, a current is induced in the circuit. These minute magnetic signals are converted into large...
electrical signals at output. Measurements are usually conducted at very low temperatures in the 3 – 400 K range and these temperatures are created via liquid helium, which also aids the electromagnet in maintaining its superconducting state. Therefore, the magnetic flux being measured is both temperature and field dependant.

Figure 1.11. Schematic representation of the main working component of a Superconducting Quantum Interference Device (SQUID).\textsuperscript{[12]}

1.7 Magnetic Anisotropy

Magnetic anisotropy can be described as the directional dependence of a material’s magnetic property (\textit{i.e.} a preferred direction of orientation). It is contradictory to that of an isotropic material, whose magnetic moment has no directional dependence, in an external magnetic field. The direction at which an anisotropic material aligns its magnetic moment is usually known as its ‘easy axis’ or $z$ axis. Magnetic anisotropy is a consequence of spin-orbit coupling and is responsible for zero-field splitting (these topics will be discussed in sections 1.9 and 1.10), and is important in the area of molecular magnetism for the retention of magnetisation upon removal of an external magnetic field. Magnetic hardness (mentioned in section 1.5) is also related to magneto-anisotropy (\textit{i.e.} the width of the hysteresis curve). The average susceptibility ($\bar{\chi}$) is described using the formula below:
If $\chi_x = \chi_y = \chi_z$ then the material is said to be isotropic whereas, if $\chi_x = \chi_y \neq \chi_z$ the magnetic susceptibility of the material is said to be axial. There are different forms of anisotropy which lead to a materials magnetic susceptibility differing from its model isotropic value. These include g-anisotropy and zero-field splitting which will be discussed as the chapter progresses.

### 1.8 g-Anisotropy

The g-value links a particle’s magnetic moment ($\mu$) with its orbital angular momentum to give a value of $\mu_B$ (in Bohr magnetons). Consequently the $\mu$ and therefore $\chi$ are highly influenced by spin-orbit coupling. The energy gap between microstates ($M_s$) and the applied field ($H$) are linked by the g-value presented in the equation below:

$$\Delta E(M_s) = g \beta M_s H_0$$

The g-value of a free electron is ~ 2.0023 ($g_e$). When the g-value is quoted to be ~ 2, particles are considered to be isotropic. When spin-orbit coupling begins to dominate results tend to differ with the value of $g$ diverging from 2, indicating an anisotropic arrangement. The deviation from a $g$ value of 2 is dependent on the energy gap between the excited state and the ground state, described in the equation below:

$$\Delta g_e = E_{es} - E_{gs}$$

When an unpaired electron pairs to an unoccupied orbital (e.g. $d^1$), $g < g_e$. However if the unpaired electron couples to an orbital which already contains electrons (e.g. $d^9$), $g > g_e$. In addition to this, the $g$-value is dependent on the orientation of the orbital containing the unpaired electron with respect to field direction ($H$); this governs which excited state may couple with the ground state.
Chapter One: Introduction

The magnitude of the spin-orbit coupling constant is also a contributing factor referred to as $\lambda$, in the equation below:

$$\Delta g = \frac{n\lambda}{E_{es} - E_{gs}}$$

‘g-values’ are best measured via electron paramagnetic resonance (EPR) spectroscopy, as outlined in section (1.13).

### 1.9 Zero-Field Splitting

Zero-field splitting (ZFS), also known as the D parameter or ‘single ion anisotropy’ occurs in the absence of an external magnetic field ($H$). Each microstate is degenerate with equal energy (i.e. $M_s = -\frac{1}{2} = +\frac{1}{2}$) due to spin-orbit coupling or the mixing of empty excited states into a ground state and is attributed to the lowering of symmetry around a metal’s centre.\(^{[13]}\) The number of $M_s$ states or spin multiplicity of a system can be calculated, based on the spin quantum number ‘$S$’ shown later in Figure 1.12, and described in the equation below:

$$M_s = 2S + 1$$

ZFS can only occur in atoms or complexes with a ground spin state of $S > \frac{1}{2}$. The energies of $M_s$ states in zero-field can be calculated using the equation below:

$$\Delta E = M_s^2 D$$

For an $S = 1$ system, the microstates split into $M_s = 0$ and $M_s = +/- 1$ in the absence of an applied magnetic field. The separation between these states is known as the zero-field splitting parameter and is quantified as $D$ (Fig. 1.12). The value of $D$ can take both positive and negative values. In the case of a negative value, the lowest energy level contains the larger $M_s$ number and vice versa for a positive $D$ value. In the case of an $S = 1$ system with a positive $D$ value the ground state is $M_s = 0$. If the value of $D$ is very large, at low temperatures (T), molecules occupy this $M_s = 0$ state.
Therefore, as T approaches zero, population of the $M_s = 0$ state increases to near 100% leading to negligible magnetic susceptibility ($\chi$) and $\mu_{\text{eff}}$ values.\textsuperscript{[14]}

\[ S = 1 \quad S = \frac{3}{2} \quad S = 2 \quad S = \frac{5}{2} \]

\[ M_s = 0 \quad M_s = \pm \frac{1}{2} \quad M_s = \pm 1 \quad M_s = \pm \frac{3}{2} \quad M_s = \pm 2 \quad M_s = \pm \frac{5}{2} \]

**Figure 1.12.** Schematic diagram representing the separation of $M_s$ in a variety of spin systems exhibiting zero-field splitting (given in units of $D$).

**1.10 Spin-Orbit Coupling**

Spin-orbit coupling (SOC) can be described as the spin angular momentum ($S$) and the orbital angular momentum ($L$) of a sample communicating in order to create a magnetic moment. The spin and angular magnetic momenta are no longer considered to be independent of each other and so the total angular momentum quantum number ‘$J$’ must be used and takes the absolute values $|L+S| \leftrightarrow |L-S|$. For spin-orbit coupling to occur two necessary principles must be fulfilled: (1) an empty or half-filled orbital must be present with comparable energy and symmetry to the orbital containing the unpaired electron; (2) this orbital must not contain an unpaired electron with an identical spin to the first (Hund’s Rule states that each orbital must first be singly occupied by electrons with identical spins and, Pauli Exclusion principle states two electrons with equal spin may not occupy the same orbital). These rules are fulfilled when one or two of the three $t_{2g}$ orbitals ($d_{xy}$, $d_{yz}$, $d_{xz}$) contain an odd number of electrons (e.g. Fig. 1.13). Correspondingly, deviations from spin-only values tend to be significant for 3d$^5$ (low-spin Fe$^{III}$),\textsuperscript{[15]} 3d$^6$ (high-spin Fe$^{II}$)\textsuperscript{[16]} and 3d$^7$ (Co$^{II}$)\textsuperscript{[17]} complexes.
Figure 1.13. Crystal field diagram of a high-spin 3d⁶ complex, the distance between t₂g and e₈ orbitals increases for high-spin complexes.

Orbital angular momentum (µₗ) is generated when such electrons move or jump between orbitals. Degenerate orbitals containing the spinning electron rotate on their axis to find an orbital vacancy. There are five different d orbitals (Fig. 1.14) and as a result this leads to an availability of possible transformations.

For example, a dₓᵧ orbital via rotation about the easy z-axis can be transformed to the dₓ²−ᵧ² orbital (Fig. 1.15). However, an electron in a dₑ² orbital cannot communicate with a degenerate dₓᵧ orbital, as such orbitals are non-exchangeable via rotation about the z-axis. Therefore, these orbital transformations cause deviation from the spin-only value due to the orbital momentum (µₗ) combining with the spin magnetic moment (µₗₒ). This moving electron and therefore moving
charged particle rotating around the atom creates a magnetic dipole moment perpendicular to the plane of motion, electronic spins can couple with this dipole, which leads to the concept of spin-orbit coupling.

![orbital transformation diagram]

*Figure 1.15. An example of an orbital transformation from a $d_{xy}$ orbital to a $d_{x^2-y^2}$ orbital through the medium of spin-orbit coupling, the electron moves from the $xy$ to the $x^2-y^2$ orbital via a 45° rotation.*[^18]

If there is a large energy cost associated with a transition such as the one depicted above, the orbital angular momentum ($\mu_L$) is said to be quenched and therefore will not contribute to the overall magnetic moment ($\mu_{\text{eff}}$). Energy costs include large ligand field splitting or electron-electron repulsion. For instance, bound ligands remove the five-fold d-orbital degeneracy *via* crystal field splitting and significantly quench the orbital contributions (Fig. 1.16).
If we take a $3d^3$ Cr$^{III}$ free ion as an example, $S = 3/2$ and $L = 3$, the $J$ energies will be $9/2, 7/2, 5/2$ and $3/2$. For a shell which is less than half full ($d^1$-$d^4$), the minimum $J$ value is the ground state (in this example $J$ would be equal to $3/2$), and for systems with shells greater than half full ($d^6$-$d^9$) the maximum $J$ value will be the ground state (in this case $J = 9/2$). For half-filled shells, such as that of a high-spin $d^5$ complex the angular momentum quantum number ($L$) will be zero and therefore there will be only one value as $J$ will be equal to $S$.

### 1.11 Exchange Interactions

Magnetic exchange occurs in polynuclear complexes when neighbouring paramagnetic metal ions in a system interact and magnetically couple with one another. It can take place via two methods: direct exchange or superexchange, details of which follow in the coming sections. But before we go into detail, we will take time to consider the parameter used to measure the strength and nature of a magnetic exchange interaction; the isotropic exchange parameter known as the 'J value', not to be mistaken for the $J$ parameter relating to spin-orbit coupling.

If we consider a dimeric Cu$^{II}$ complex in which each Cu$^{II}$ ion has a $d^9$ configuration, the spins on the unpaired electron from each of the Cu centres can interact in one of two ways; align anti-parallel creating an antiferromagnetic interaction ($S = 0$) or
align in a parallel manner creating a ferromagnetic interaction ($S = 1$). It is only possible for one of these scenarios to dominate at any one time.

![Diagram representing the interaction between two unpaired electrons on two transition metal (TM) ion centres (1 and 2) connected by two bridging ligands (L). The $J$ value provides information on the size and magnitude of exchange between two metal centres.](image)

**Figure 1.17.** Diagram representing the interaction between two unpaired electrons on two transition metal (TM) ion centres (1 and 2) connected by two bridging ligands (L). The $J$ value provides information on the size and magnitude of exchange between two metal centres.

If the $J$ value is large and negative the interaction is antiferromagnetic. Conversely, if the $J$ value is large and positive the exchange interaction is said to be ferromagnetic in origin. This net interaction can be viewed in Figure 1.17 and described by the isotropic exchange Hamiltonian below, where $\hat{S}_1$ and $\hat{S}_2$ are the local spins on metal centres 1 and 2 respectively:

$$\hat{H} = -2J \hat{S}_1 \cdot \hat{S}_2$$

**1.11.1 Direct Exchange**

Direct exchange occurs when there is a head-on overlap of the magnetic orbitals (orbitals containing the unpaired electrons). This direct overlap of two atomic orbitals in turn gives rise to a bonding ($\sigma$) and an anti-bonding ($\sigma^*$) molecular orbital (MO), (Fig. 1.18 (A)). Direct exchange usually results in antiferromagnetic exchange between metal centres. This is due to that fact that the anti-bonding state is usually too high in energy and is therefore thermally inaccessible at room temperature. If however, overlap is weak and the energy gap ($\Delta E$) is small enough, the excited state can be thermally populated, for instance overlap of orbitals with $\delta$ symmetry. The
weak side-on overlap of the aforementioned orbitals leads to a small energy gap ($\Delta E$) and accordingly a thermally populated excited state ($\delta^*$), (Fig. 1.18 (B)).

![Diagram](image)

**Figure 1.18.** A) Two possible energy states from the direct overlap of atomic orbitals. B) Overlap of orbitals with $\delta$ symmetry.\[18\]

### 1.11.2 Superexchange

Superexchange arises in inorganic complexes with two or more paramagnetic centres, separated by ligand atoms (*i.e.* an inorganic core encased with an organic exterior). Direct exchange does not tend to occur in these types of complexes as the metal centres are too far apart to communicate, this is when superexchange comes into play and the metal-metal interaction occurs *via* an intermediate diamagnetic ligand. The magnitude and nature (antiferromagnetic or ferromagnetic) of magnetic exchange interactions between two metal ions are now reasonably well understood in terms of the energetics and the overlap of magnetic orbitals.\[19\] The connection between such magnetic behaviour and the structure of a compound has been a strong interest for chemists for decades. Libraries of molecules have been synthesised and their magnetic properties measured in order to establish and develop a theory in this structure-property relationship. Distortion of bond angles (M-L-M), torsion angles (M-L-L-M), the distance between metal centres (M–M) and steric factors all contribute to this effect. Such a study was carried out by Hatfield et al. on a planar hydroxide bridged dinuclear CuII complex in 1976. They explored the magneto-structural correlation between the Cu-O-Cu angle and the sign and magnitude of the $J$ value.\[20\] It was found that the $J$ value depended on this dihedral angle (Cu-O(H)-Cu), with the oxygen atom being supplied by the diamagnetic hydroxide bridging ligand. It was also found that if the angle was greater than 97.5°
the interaction was antiferromagnetic \((J < 0)\) while ferromagnetic exchange \((J > 0)\) was observed when the Cu-O(H)-Cu angle was less than 97.5°.

With respect to the copper complex illustrated in Fig. 1.19, if the Cu-O-Cu dihedral angle \((\theta)\) is -90° then the oxygen atom from the diamagnetic ligand will bond with one Cu\(^{II}\) centre \textit{via} its \(P_x\) orbital and the other Cu\(^{II}\) ion \textit{via} its \(P_y\) orbital (Fig. 1.20, A). A single unpaired electron from each Cu centre will lie in their respective \(dx^2-y^2\) orbitals. This gives a total of six electrons with involvement in the magnetic exchange (Fig. 1.20, B), giving rise to an \(S = 1\) ground state and consequently ferromagnetic exchange.

![Figure 1.19. Structure of the \([\text{Cu}^{II}_2(OH)_2(L)_4]\) complex illustrating the dihedral/torsion angle \((\theta)\), where \(L\) = organic ligand.](image)

![Figure 1.20. A) Schematic of the hydroxide bridged orbital overlap in the \([\text{Cu}^{II}_2(OH)_2(L)_4]\) complex where Cu-O-Cu angle ~90° and \(L\) = ligand. B) Molecular orbital diagram depicting ferromagnetic exchange, \(S = 1\).](image)

If however, the Cu-O-Cu torsion angle is ~180°, four electrons are involved in the exchange; two single electrons from each Cu\(^{II}\) ion in the \(dx^2-y^2\) orbitals and two electrons form the oxygen orbital, in this case the \(P_y\) orbital (Fig. 1.21, B). The
oxygen atom only uses one orbital to bridge the two copper centres leading to antiferromagnetic exchange and a resultant $S = 0$ ground spin state (Fig. 1.21, A).

It is important to note that if the unpaired electrons are in orthogonal orbitals (right angles to one another), no overlap will occur and the exchange will be ferromagnetic, this is known as the orthogonality principle. It appears that the more obtuse an angle the stronger the antiferromagnetic exchange and therefore the larger and more negative the $J$ value.

### 1.11.3 Magneto-Structural Correlation

Magneto-structural correlation studies have extensively been carried out by Brechin et al. in Edinburgh, on Mn$^{III}$ complexes built using salicylaldoxime ligands (discussed later in section 1.16). Firstly, a large family of sixty [Mn$_6$] and thirty [Mn$_3$] clusters$^{[21]}$ were synthesised and studied,$^{[22]}$ resulting in the conclusion that the dominant structural factor dictating the pairwise magnetic exchange within the {Mn$_3$O} triangular units was the twisting of the Mn–O–N–Mn torsion angle. Steric factors and bulkiness of the salicylaldoxime ligands controlled the degree of twisting within these triangular moieties. Following this study, a simple model complex was desired, a complex with only one exchange pathway, to prove this linear relationship between the Mn-O-N-Mn torsion angle and the magnitude of $J$ (Fig. 1.22, B).
The Mn dimers in the study by Brechin et al.\textsuperscript{[23]} differ from the examples in this thesis (Chapter 2) as they are bridged by one $\mu$-O\textsuperscript{2-} ion and the -N-O- moiety of the phenolic oxime and not solely by oxime -N-O- moieties. It was concluded from this dimeric magneto-structural study, that the greater the torsion angle (Mn-N-O-Mn) the greater the magnitude of the ferromagnetic interaction present (Fig. 1.22, A).

In larger clusters containing more paramagnetic metal centres the number of exchange pathways also increases.\textsuperscript{[22]} This type of polynuclear complex has been explored in this thesis (Chapter 2, 3 and 4).

1.12 Methods Used to Study Superexchange - DFT

Density functional theory (DFT) is used to probe the electronic structure of complexes. Superexchange leads to spin / electron densities on ligand atoms, giving a function of speed and time; from this the energy in the system can be calculated and likewise the ground state energy.\textsuperscript{[24]} Thus, detailed analysis of magnetic exchange within such complexes can be elucidated. Indeed, DFT was used in Chapter 2 of this thesis to access the spin density of model [Mn\textsuperscript{III}]\textsubscript{2} oxime dimers.
**1.13 Electron Paramagnetic Resonance (EPR) Spectroscopy**

EPR spectroscopy supplies electronic information on paramagnetic materials by probing the Zeeman splitting of unpaired electrons and is utilised in this work. EPR spectra supply information on compounds through a series of lines, which vary depending on the interaction of the unpaired electrons with their surrounding environment and framework. The peak intensities, widths and the sheer amount of lines present all supply details on the complex in question, supplying the parameters \( g \), \( S \) and \( D \) directly. The measurement is conducted by increasing the external magnetic field and concurrently probing the resonance using microwave energy (Fig. 1.23).

![Figure 1.23. Illustrative diagram displaying the Zeeman splitting of the \( M_s \) states associated with a single electron. The energy difference (\( \Delta E \)) increases with increasing magnetic field and is probed using microwave frequency radiation in EPR.](image)

As mentioned in Section 1.2, an unpaired electron has a spin quantum number of \( S = \frac{1}{2} \). For a system with two unpaired electrons, \( S = 1 \). Using the formula \( (2S + 1) \) the spin multiplicity can be calculated and in this instance is \( 2 \times \frac{1}{2} + 1 = 3 \). Therefore there are three possible spin states for this complex \( M_s = +1 \), \( M_s = 0 \) and \( M_s = -1 \), the positive of these corresponds to the parallel alignment of the electrons magnetic moment with the field (H) and the negative represents an antiparallel configuration (Fig. 1.24).

![Figure 1.24.](image)
In advance of a magnetic field being turned on all states are said to be degenerate, the application of the magnetic field leads to splitting of the energy levels known as Zeeman splitting. The energy separation between $M_s$ states is calculated using the formula below:

$$\Delta E = g_e \mu_B H$$

Where $g$ is the electron g-factor (dimensionless), $\mu_B$ is the Bohr magneton and $H$ is the applied magnetic field. This energy difference can be directly probed in EPR through the absorption of a photon of energy (typically microwave frequency), which initiates a transition between microstates. As $\Delta E$ is proportional to the magnetic field ($H$), by altering photon frequency or $H$ while simultaneously keeping the other constant, $\Delta E$ can be distinguished.\cite{25}
Figure 1.25. Example of an EPR signal. **A)** Original output through absorption of a photon of microwave frequency. **B)** First derivative of this resonance response given as an EPR spectrum. The red circle is indicative of the g-value and is usually ~ 2.

EPR spectra are recorded in the first derivative of its absorption peaks (Fig. 1.25) and can be measured for samples in solution, frozen and powdered samples and single crystals. A value for $g_x$, $g_y$ and $g_z$ can be obtained from an EPR spectrum by means of measurement along different directions and from this, information relating to the molecular symmetry of a complex can be obtained. A complex with axial molecular symmetry (i.e. $D_{4h}$) will deliver two peaks in an EPR spectrum, one for $g_z$ and one for $g_x$ and $g_y$ combined (i.e. $g_z \neq g_x = g_y$). Whereas a species with symmetry lower than axial (i.e. rhombic, $C_{2h}$) will present three separate peaks (i.e. $g_z \neq g_x \neq g_y$). It is important to establish efficient band splitting, to ensure all complexes are not deemed to be axial, this can be satisfied through the amplitude of H or microwave frequency used.

### 1.14 Single-Molecule Magnets

Single-Molecule Magnets (SMMs) have attracted a wealth of interest over the past decades due to their unique magnetic properties. SMMs are a class of compounds best described as discrete polymetallic complexes comprising paramagnetic centres linked with bridging organic ligands. These superparamagnetic entities can retain their magnetisation when cooled at or below a certain blocking temperature ($T_B$), in the absence of a magnetic field (Fig. 1.26).
This magnetization occurs because there is a large energy barrier between the ‘spin-up’ and the ‘spin-down’ states. Single-Molecule Magnets display magnetic bi-stability due to the presence of a large spin ground state ($S$) and a large negative anisotropy ($D$) as a result of zero-field splitting within the ground state. They also display magnetic hysteresis of molecular origin,[26] due to a barrier to the reversal of magnetization ($U_{eff}$), where:

$$\Delta E = S^2 D$$

As a result of their bi-stability SMMs have potential for information storage at the molecular level. In theory, maximising $S$ and $D$ simultaneously should lead to a huge improvement in SMM behaviour.

The first complex to display SMM behaviour was a dodecanuclear manganese cluster of formula $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ (often written as $[\text{Mn}_{12}\text{OAc}]$) (Fig. 1.27) and is now known to be the prototypical SMM.[27] [28] [26] $[\text{Mn}_{12}\text{OAc}]$ has eight outer $S = 2 \text{ Mn}^{III}$ ions, which are antiferromagnetically coupled to the four inner $S = 3/2 \text{ Mn}(IV)$ ions giving an overall net spin ($S$) of $(8 \times 2) – (4 \times 3/2) = 10.$

Figure 1.26. Illustration representing the ‘memory effect’, an established trait of Single-Molecule Magnets.[18]
Figure 1.27. The prototype [Mn$_{12}$] acetate with a ground state of $S = 10$. Colour code: Purple – Mn$^{IV}$, Green – Mn$^{III}$, Red and Grey – Oxygen, Black – Carbon.

This molecule was first synthesised in the 1980s by Lis et al.\(^{(29)}\) but it was not until 1991 that its magnetic properties were perceived and [Mn$_{12}$OAc] was seen to display slow magnetic relaxation below 10 K.\(^{(30)}\) On the basis that [Mn$_{12}$OAc] displayed slow magnetisation reversal and therefore hysteresis of molecular origin, this lead to the emergence of the concept of ‘Single-Molecule Magnetism’ and the conceptualisation that these singular units may behave as tiny magnets.\(^{(31)}\)

[Mn$_{12}$OAc] has a blocking temperature ($T_B$) of $\sim 4$ K and was the lowest recorded blocking temperature for over 15 years until 2007 when Brechin et al. broke the record by reporting a [Mn$_6$] cluster in possession of a blocking temperature of -4.5 K and a reversal of magnetisation barrier of 60 cm$^{-1}$.\(^{(32)}\) In 2011, a blocking temperature of 8.3 K at a sweep rate of 0.08 T s$^{-1}$ was recorded for a N$_2$ bridged [Dy$^{III}_{12}$] complex further increasing the record. The crystal structure and hysteresis curve for the dysprosium complex can be seen in Figure 1.28.\(^{(33)}\) In the same year Rinehart et al., broke their own record in the synthesis of a [Tb$^{III}_{12}$] analogue of the aforementioned [Dy$^{III}_{12}$] complex. Currently this remains the record holder with a $T_B$ of 13.9 K and a $U_{eff}$ of 326.62 K.\(^{(34)}\)
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1.14.1 Applications of Single-Molecular Magnets

Each of these molecular nanomagnets which are no more than a few nm$^3$ in size have a huge and varied range of potential applications including: information storage, quantum computing, molecular spintronics and molecular coolants which are outlined in more detail in the sections which follow.\[35\] All of the functionalities mentioned fundamentally depend on a detailed knowledge and understanding of the bi-stability and the structure-property relationship in SMMs which is somewhat explained in Section 1.14.

1.14.2 Information Storage and Quantum Tunnelling of Magnetisation

Data storage is one of the most conventional uses of magnets; thus by decreasing particle size and working at lower temperatures so as to retain information over a long period of time, nanomagnets could be proposed as possible candidates for the construction of quantum computers.\[13a\] These single molecules have the capability of acting as binary units, with a spin-up and a spin-down value which can be related to a qubit or ‘quantum bit’ and the binary system used in digital electronics. With reference to qubits, they can hold position at 0, 1 or a super-position of both states. A super-position arises from their ability to tunnel through their magnetisation reversal barrier and is known as quantum tunnelling of magnetisation (QTM), which
is illustrated via the red arrows in Figure 1.29. Here the positive and negative microstates come into resonance, thus permitting their electrons to tunnel through the energy barrier, $S^2D$. To date, such miniaturized systems are not applicable to everyday life due to the extremely low temperatures at which they are functional.\cite{36}

![Figure 1.29. Schematic diagram depicting the process of quantum tunnelling through the energy barrier $S^2D$ (red arrows).](image)

1.14.3 Molecular Spintronics

Molecular spintronics (aka. spin transport electronics) takes advantage of the dual functionality of an electron, its ability to carry an electric charge along with its intrinsic magnetic moment or spin. In electronic devices spins are randomly aligned, the contrary is observed in spintronic models where the spins are polarized or ‘pinned’ in a desired direction. Accordingly, information can be processed by both the charge and spin direction of the electron in question.\cite{37} Giant magneto-resistance (GMR) was discovered in the 1980s during the hunt for smaller nanoelectronic devices, for example; molecular transistors and semi-conductors. Their minute size and perfect homogeneity make them ideal candidates for the miniaturisation of such electronic circuit components. The GMR in hard drives is considered an archetype of spin transport electronics. These class of materials are
considered to be thin films composed of alternating layers of ferromagnetic (F) and non-magnetic (NM) materials (Fig. 1.30).

The ferromagnetic layer (top layer; commonly synthesised using an alloy of iron and nickel) is considered to be the ‘free layer’ whereby its magnetic field is switchable. The non-magnetic layer (frequently copper based), functions as a spacer to buffer the two magnetic layers. The bottom or ‘pinned’ layer (often comprising cobalt), is permanently ferromagnetic in a specified direction. As the read head hovers over the hard drive, moving from side to side while passing over a specific ‘bit’ the free (top) layer re-orientates its magnetic moment to replicate that of the bit. Resistance can be controlled through the manipulation of the direction of magnetisation of the top layer (Fig. 1.31). The two magnetic layers can have spins aligned parallel or anti-parallel to one another, manipulated through the use of the external magnetic field (H). These spin combinations and variability of exchange result in either high (AF exchange) or low (F exchange) current resistances which can be represented as 0s and 1s respectively and therefore comfortably interpreted by a computer.\cite{38}

Figure 1.30. Layers of a Giant magneto-resistance read head.

Figure 1.31. Diagram showing the effect of an external magnetic field on the current/resistance of a GMR (Giant magneto-resistance).
1.14.4 Molecular Coolants

Molecular coolants, more commonly referred to as molecular refrigerants, are an application of the magneto-calorific effect (MCE). The magneto calorific effect is based on the change of magnetic entropy ($\Delta S_m$) in relation to the application of an externally applied magnetic field ($H$). In advance of a magnetic field being applied, the spin magnetic moments are randomly aligned, once applied the spins become ordered and align in the direction of $H$. This initiates a reduction in the materials magnetic entropy and heat capacity as a result of less disorder in the system. These materials are in an adiabatic environment meaning that they are insulated from their surroundings and transfer of energy in the form of heat does not occur. Such an environment rules that the change in entropy must be counter-balanced by an equal but opposite change in entropy of the lattice, resulting in the temperature of the material being raised.\[39\] As the magnetic field is gradually removed, disorder returns to the material via absorption of heat by magnetic moments, entropy and heat capacity increase in a process known as adiabatic demagnetisation.\[40\] This phenomenon allows for cooling at the molecular level and could lead to a more economical method towards refrigeration. However, in order for a material to be a magnetic coolant it must possess a large value of $\Delta S_m$. In order for this pre-requisite to be satisfied, the system must have a large spin ground state ($S$), a negligible anisotropy ($D$) and negligible interactions between its magnetic ions or centres (\textit{i.e.} $J$ and $D \sim 0$).\[41\] In more recent times polynuclear Ln$^{III}$ complexes have become popular for their MCE properties, for example a \{Zn$^{II}_2$Dy$^{III}_2$\} complex synthesised by Ruiz \textit{et al.} in 2014 exhibited a large magneto-calorific effect (Fig. 1.32).\[42\]
1.14.5 Spin-Crossover Complexes

The occurrence of Spin-crossover (SCO) behaviour of a material was first discovered by Cambi and Szego in 1931. It is a characteristic displayed by certain complexes whereby they can flip between magnetic spin states (Fig. 1.33) upon a perturbation of an external stimulus such as heat (T), light (hv), and pressure (p). Considering the spin state of metals involved in a complex is important when it comes to SMM behaviour. This flip in magnetic spin state often brings with it a colour change in the material (i.e. a change in both electronic and physical properties).\cite{43}

Figure 1.32. (left) Crystal structure of the [Zn$^{II}_2$Dy$^{III}_2$] complex synthesised by Ruiz et al. (top right) Magnetic entropy change of [Zn$^{II}_2$Dy$^{III}_2$] and (bottom right) adiabatic temperature change for magnetic field changes.

Figure 1.33. Schematic example of spin-crossover in a 3d$^6$ Fe$^{II}$ complex, in some cases a ligands ability to absorb light masks a SCO colour change.
Magnetic susceptibility curves for spin-crossover complexes have a distinct shape or curvature as shown in Figure 1.34, more specifically, a rapid transition from low spin (LS) to high spin (HS) can be observed at the transition temperature ($T_c$) with a dramatic drop in magnetic moment, $\chi$.

![Figure 1.34. Typical $\chi_mT$ curve observed for a spin-crossover complex displaying the rapid transition from low-spin to high-spin.](image)

### 1.15 Ligand Choice

Choosing a ligand for the rational design of polymetallic clusters and coordination polymers is a crucial factor. Ligands are molecules which bind to a central metal ion to form a cluster; they can be neutral molecules, anions or cations. They usually include at least one donor atom (for example N or O), with a non-bonding electron pair used in the formation of covalent bonds. They can act as terminal units creating complexes of known nuclearity or as connecting blocks forming infinite arrays.

### 1.16 An Introduction to Salicylaldoximes

Salicylaldoximes are a class of compounds with the generic formula 2-OH-Ph-HC=NOH. Phenolic oximes with the generic structure as shown in Figure 1.35, have had many uses in industry including metal extraction$^{[44]}$ and as anti-corrosives in protective coatings.$^{[45]}$ Oximes are versatile ligands with a variety of favourable
characteristics including, multiple coordination modes (e.g. μ_1-, μ_2- and μ_3-) which lead to the formation of poly-nuclear complexes and mixed metal chemistry with interesting magnetic properties.

**Figure 1.35.** Generic phenolic oxime structure referred to throughout this thesis as R-saoH_2.

When these phenolic oximes are involved in the formation of metal complexes, the phenolic proton is exchanged; this is also possible for the less acidic proton on the oximic oxygen atom.[46] Some R-saoH_2 (sao = salicylaldoxime) ligands adopt the more common η^1:η^1:η^1: μ_2- coordination mode (Fig. 1.36, A), while others can adopt the rarer η^1:η^2:η^1: μ_3- mode (Fig. 1.36, B) among others.[47] [48]

**Figure 1.36.** Examples of coordination modes for phenolic oximes, using the ligand 2-hydroxy benzaldehyde oxime, η^1:η^1:η^1: μ_2- for A and η^1:η^1:η^2: μ_3- for B.

Complexes built using these ligands have been reported with 1st, 2nd and 3rd row transition metals. However, the formation of polynuclear metal complexes is the most established with the early first row transition elements, especially those in medium or high oxidation states. The synthesis of such clusters is assisted by
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bridging which involves the oximato or phenolato oxygen atoms in the doubly deprotonated ligands.\[49\] These phenolic oximes are easily synthesised through the addition of hydroxylamine to an aldehyde or a ketone leading to a condensation reaction.\[48\] The phenolic oximes ligands synthesised and subsequently utilised are shown below (Fig. 1.37).

![Figure 1.37. Structures of the salicylaldoxime ligands used throughout this thesis.](image)

1.17 Co-Ligands

Bulky aromatic carboxylic acid co-ligands, with their $\eta^1:\eta^1: \mu_2$-coordination mode, were employed as bridging ligands to work in combination with the salicylaldoximes (Section 1.16), in chapters three and four. They act as chelating agents and aid in the completion of coordination spheres around metal ions. Their bulky aromatic nature, lead to the formation of attractive forces such as $\pi - \pi$ stacking which lead
to improved chances of product crystallisation. These carboxylic acids (Fig 1.38) were purchased commercially and converted into their sodium salts, using standard methods for easier manipulation and greater affinity for the metal centre.

![9-Anthracenecarboxylic Acid](image1) ![1-Naphthalenecarboxylic Acid](image2)

**Figure 1.38.** Bulky carboxylate ligands used throughout this work.

### 1.18 Synthetic Methodologies - Solvothermal Oven Synthesis

Before use in the area of inorganic cluster chemistry, solvo / hydrothermal techniques were widely used in the synthesis of zeolites.[50] Solvothermal synthesis involves the heating of a reaction mixture in a sealed stainless steel vessel or autoclave; to a temperature higher than that of the boiling point of the solvent in use. The typical temperatures employed are in the range of 100-250 °C. High pressures inside these vessels are autogenous and hence are not externally applied. These high temperature and high pressure conditions mentioned lead to maximum coordination of bridging ligands and high nuclearity compounds.[51] Slow cooling times (i.e. Fig. 1.39) offered by this technique have proved successful in the crystallisation of inorganic clusters.[52] Solvents heated to above their boiling temperature in sealed vessels exhibit very different properties to those at room temperature and pressure in that solubility tends to increase and the solution becomes more viscous. Indeed, this is witnessed in the work described in Chapter 4, where ambient CrIII reactions gave no crystalline output.[53] Moreover, in some cases, different products were obtained from solvothermal reaction conditions than those of ambient conditions (for example a study by Eslava et al. generating two different titanium oxide clusters).[54]
1.19 Project Aims

This thesis describes the synthesis of numerous 1st row transition metal complexes built through a combination of salicylaldoxime and carboxylate ligands and their full structural and magnetic properties probed using a myriad of techniques. A brief description of each chapter is given below:

- **Chapter Two:** A rare Mn-oxime complex was constructed. Its rarity is derived from the fact that it does not contain the ubiquitous [Mn$^{III}$O(R-sao)$_3$]$^{1+}$ triangle. We have used this complex as a simple model to test an assumption previously employed in the magneto-structural correlation study of [Mn$_3$] and [Mn$_6$] SMMs.$^{[22]}$

- **Chapter Three:** Examines the role of sterically demanding oximes and carboxylate co-ligands towards the formation of Fe-oxime cages.

- **Chapter Four:** Use of solvothermal synthesis to synthesise Cr$^{III}$ cages comprising various salicylaldoxime ligands towards magneto-structural correlations akin to those observed by the [Mn$_3$] and [Mn$_6$] SMM family.$^{[21a]}$

- **Chapter Five:** MnF$_3$ has been utilised as a precursor towards new Mn$^{III}$ magnetic complexes and their magnetic properties elucidated.
1.20 References


Chapter Two

Ferromagnetic exchange in twisted, oxime-bridged $[\text{Mn}^{\text{III}}_2]$ and $[\text{Mn}^{\text{III}}_2\text{Zn}^{\text{II}}_2]$ dimers
Chapter 2: Ferromagnetic exchange in twisted, oxime-bridged \([\text{Mn}^{\text{III}}]^2\) and \([\text{Mn}^{\text{III}}]^2\text{Zn}^{\text{II}}]^2\) dimers

2.1 Introduction

The relationship between the structure of a molecule and its magnetic properties has fascinated chemists for decades. For example, in complexes containing the \([\text{Cr}^{\text{III}}(\text{OH})]^2\) core the dominant structural factor was the variation of the angle between the \(\text{O}–\text{H}\) vector and the \(\text{Cr}_2\text{O}_2\) plane.\(^{[1]}\) Another example would be the families of \(\text{Cu}^\text{II}\) dimers which have been extensively studied for magneto-structural correlations in the past decades, where coordination geometry and the nature of the bridge between \(\text{Cu}\) atoms play a major role in this relationship.\(^{[2]}\) While more recent papers in molecular magnetism have concentrated on sub-topics such as (amongst others) single-molecule magnetism,\(^{[3]}\) quantum information processing\(^{[4]}\) and magnetic cooling,\(^{[5]}\) they still all fundamentally rely on a detailed understanding and exploitation of the structure property relationship. However, the structural complexity of large polynuclear cluster compounds and the presence of multiple exchange pathways make a detailed, quantitative analysis of the magneto-structural relationship extremely problematic.\(^{[6]}\)

Indeed studies of di-, tri- and tetra-metallic compounds have shown that the type and magnitude of magnetic exchange interaction can depend on many factors including the bridge identity, metal–metal separation, bond angles subtended at the bridging atoms, dihedral angles between coordination planes containing the metal ions, metal–ligand bond lengths and/or the metal ion stereochemistry.\(^{[7]}\)

However, given that many large clusters contain the same, well-known building blocks (\(e.g.\) \([\text{M}_3]\) triangles or \([\text{M}_4]\) butterflies),\(^{[8]}\) a possible solution to the problem lies firstly in making and understanding, both experimentally and theoretically, the chemistry and physics of these small molecular sub-units and then secondly, exploiting their coordination chemistry to construct larger molecular arrays in which the magnetic properties can be, at least to some extent, tailored.
Chapter 2: Ferromagnetic exchange in twisted, oxime-bridged [Mn$^{III}$]$^n$ and [Mn$^{III}$]$^2$Zn$^{II}$] dimers

![Chemical structures](image)

**Figure 2.1.** Structures of the derivatised salicylaldoximes, R-saoH$_2$. R = H, saoH$_2$; R = Me, Me-saoH$_2$; R = Et, Et-saoH$_2$, R = Ph, Ph-saoH$_2$.

One class of molecule in which this kind of exploitation is possible is the [Mn$^{III}$]$_n$ (n = 3, 6) family of clusters constructed with derivatised salicylaldoxime ligands (R-saoH$_2$; Fig. 2.1).[9] By building a family of over fifty [Mn$^{III}$]$_6$ and thirty [Mn$^{III}$]$_3$ complexes, a semi-quantitative magneto-structural correlation could be established and indicated that the **dominant** structural factor dictating the pairwise magnetic exchange within the triangular unit was the twisting of the Mn–O–N–Mn moiety (Fig. 2.2).[10] If the Mn–O–N–Mn torsion angle was greater than ~31° the pairwise exchange was ferromagnetic and if the torsion angle was less than ~31° the pairwise exchange was antiferromagnetic.
Chapter 2: Ferromagnetic exchange in twisted, oxime-bridged [Mn$^{III}$]$^{2}_{2}$ and [Mn$^{III}$]$^{2}$Zn$^{II}$]$^{2}$ dimers

Figure 2.2. (a) Generic structure of the phenolic oxime, R-saoH$_{2}$. (b) Structure of the Naphth-saoH$_{2}$ ligand. Magnetic cores present in the complexes (c) [Mn$^{III}$]$_{6}$ and (d) [Mn$^{III}$]$_{3}$, whose magnetic exchange can be controlled by the structural distortion of the Mn-O-N-Mn moiety. Colour code: Mn = purple, O = red, N = blue, C = grey.

Controlling the degree of twisting is relatively trivial, requiring the simple substitution of the H-atom on the oximic C-atom with more sterically demanding R-groups (Me, Et, Ph, Naphth etc.). Despite the relative structural simplicity of these molecules, extracting a simple quantitative magneto-structural correlation is not trivial.

The "ideal" model molecule to make and study would be a simple dinuclear complex consisting of two Mn$^{III}$ ions linked to each other through only one –N–O– bridge, with different analogues differing only in their Mn–N–O–Mn torsion angle. However specifically building such molecules is a difficult task because, when given the freedom to react “how it pleases” with Mn$^{III}$ (in alcohol), the R-sao$^{2-}$ ligand will inevitably try to form structures based on the oxocentred [Mn$^{III}$]$_{3}$O(R-sao)$_{3}$]$_{1+}$ triangle. This has both advantages and disadvantages. While the rational construction of molecules and molecule-based materials based on this moiety is
made much easier,\cite{11} allowing vast room for exploitation in disparate directions, it somewhat restricts serendipity and therefore restricts the variety of products one might expect to be associated with the use of such flexible bridging ligands. Many would perhaps perceive this solely as an enormous advantage, but it also potentially masks the discovery of unknown complexes that may possess fascinating structural / magnetic properties.

We therefore began a program of research designed simply to try to make polymeric cluster compounds using R-saoH₂ ligands whose building blocks were not [Mn₃O(R-sao)₃]^{1+} triangles. There has been some success in this field with the synthesis of a [Mn₃] double-decker wheel,\cite{12} a chiral [Mn₅] partial super-tetrahedron,\cite{13} and [Mn₃Ln₂] hexagonal prisms.\cite{14} One simple approach is to employ co-ligands that are able to compete with the oximes for the metal coordination sites and / or to make heterometallic clusters in which the second (dia- or para-magnetic) metal ion would not favour the formation of the oxocentred triangle.

This chapter focuses on the synthesis, structural and magnetic characterization of a pair of Mn dimers which were the initial model complexes for a further Mn dimer study which has more recently been put to publication by Brechin and co-workers.\cite{15} To this end we present the siblings [Mn₃₂Zn₂(Ph-sao)₂(Ph-saoH)₄(hmp)₂] (2.1) (where Ph-saoH₂ = (2-hydroxyphenyl)(phenyl)methanone oxime and hmp = 2-hydroxymethylpyridine) and [Mn₃₂(Naphth-sao)₂(Naphth-saoH)₂(MeOH)₂]·4MeOH (2.2) (where Naphth-saoH₂ = 2-hydroxy-1-naphthaldehyde oxime) constructed via oxime ligands.

**2.2 Results and Discussion**

2.2.1 Structural Descriptions

[Mn₃₂Zn₂(Ph-sao)₂(Ph-saoH)₄(hmp)₂] (2.1) crystallises in the triclinic P-1 space group and lies about an inversion centre. The structure contains a planar-diamond or butterfly-like core of four metal ions with the Mn₃⁺ ions (Mn1 and symmetry
equivalent, s.e.) at the central or body positions and the Zn\textsuperscript{II} ions (Zn1 and s.e.) at the peripheral or wing-tip positions (Fig. 2.3). The oxime ligands are of two types: Ph-sao\textsuperscript{2-} and PhsaoH\textsuperscript{-} (Fig. 2.4). The former are $\mu_3$-bridging linking the two central Mn\textsuperscript{III} ions together and further bridging to one of the peripheral Zn\textsuperscript{II} ions; the latter are simply chelating - one on each of the four metal centres, with their protonated oximic O-arm H-bonded to a neighbouring terminally bonded phenolate O-atom (O29(H29O)…O43 = 1.827 Å; O48(H48O)…O15 = 1.760 Å). The two hmp\textsuperscript{-} (2-hydroxymethylpyridine) ions are $\mu$-bridging and link Zn1 to Mn1 (and s.e.). The Mn\textsuperscript{III} ions are six-coordinate in Jahn-Teller (JT) distorted octahedral geometries with [O\textsubscript{4}N\textsubscript{2}] coordination spheres. The JT axes are defined by the O4-Mn1-N28 (and s.e.) vector (Mn1…O4 = 2.184 Å; Mn1…N28 = 2.238 Å). The Zn\textsuperscript{II} ions are 5-coordinate and square-pyramidal in geometry in [O\textsubscript{3}N\textsubscript{2}] coordination spheres, with a sixth longer (axial) contact to the phenolic O-atom of the Ph-sao\textsuperscript{2-} ligand (Zn1…O15 = 2.654 Å). The two Mn ions are connected to each other by only two –N–O– bridges from the two $\mu_3$-bridging Ph-sao\textsuperscript{2-} ligands and thus the magnetic core of the complex is the very simple [Mn\textsuperscript{III}(NO)]\textsubscript{2} moiety. In the crystal the molecules form super-imposable columns in all three directions in the cell, as expected with a P-1 space group. Despite the large number of phenyl groups around the [Mn\textsubscript{2}Zn\textsubscript{2}] molecules, there are only four C–H⋯π interactions [one unique: C27–H271⋯π(C21, C22, C32, C33, C34, C35), H⋯centroid 2.82 Å, C⋯centroid 3.63 Å, C–H⋯centroid 144°] that hold the molecules together forming a chain running along the $\alpha$-axis (Fig. 2.5). The closest inter-molecular contacts are between C-atoms on the phenyl rings of neighbouring Ph-sao\textsuperscript{2-} ligands (C⋯C, 3.294 Å).
Chapter 2: Ferromagnetic exchange in twisted, oxime-bridged $[\text{Mn}^\text{III}_2]$ and $[\text{Mn}^\text{III}_2\text{Zn}^\text{II}_2]$ dimers

**Figure 2.3.** a) The molecular structure of complex 2.1. Colour code: Mn = purple, Zn = green, O = red, N = blue, C = black. b) The $[\text{Mn}^\text{III}(\text{NO})]_2$ magnetic core present in 2.1. H-atoms have been omitted for clarity.

**Figure 2.4.** Bonding modes of Naphth-sao in 2.1, the bonding mode on the right can involve a Zn$^{II}$ or Mn$^{III}$ ion, in this instance Mn is illustrated. Colour code: Mn = purple, Zn = green, O = red, N = blue, C = grey. H-atoms have been omitted for clarity.
Chapter 2: Ferromagnetic exchange in twisted, oxime-bridged $[\text{Mn}^{	ext{III}}_{2}]$ and $[\text{Mn}^{	ext{III}}_{2}\text{Zn}^{	ext{II}}_{2}]$ dimers

Figure 2.5. A view of the $[\text{Mn}_2\text{Zn}_2]$ chains running along the $a$-axis in 2.1 emphasising the inter-molecular C-H···π interactions (blue dashed lines) and the intra-molecular O-H···O hydrogen bonds (red dashed lines).

$[\text{Mn}^{	ext{III}}_{2}(\text{Naphth-sao})_{2}(\text{Naphth-saoH})_{2}(\text{MeOH})_{2}]\cdot4\text{MeOH}$ (2.2) crystallises in the orthorhombic Pbca space group. The molecule describes a dimer of symmetry equivalent $\text{Mn}^{	ext{III}}$ ions which are six-coordinate and in Jahn–Teller (JT) distorted octahedral geometries with $[\text{O}_4\text{N}_2]$ coordination spheres. The JT axes are defined by the $\text{O}_2$-(oximic O)–$\text{Mn}_1$–$\text{O}_5$(MeOH) (and s.e.) vector ($\text{Mn}_1$⋯$\text{O}_5 = 2.333 \, \text{Å}$; $\text{Mn}_1$⋯$\text{O}_2 = 2.197 \, \text{Å}$). The oxime ligands are of two types: Naphth-sao$^2$ and Naphth-saoH$^-$ (Fig 2.7). The former are μ-bridging linking the two $\text{Mn}^{	ext{III}}$ ions together via the (very twisted) –O–N– oxime linkage ($\text{Mn}$–O–N–$\text{Mn}$, 80.28°); the latter are simply chelating - one on each of the two $\text{Mn}^{	ext{III}}$ ions, with their protonated oximic O-arm (O4) H-bonded to a bridging oximic O-atom (O4⋯O2 = 2.573 Å) and with a further longer contact to the terminally bonded phenolate O-atom (O4⋯O1 = 3.404 Å). The sixth coordination site on the two $\text{Mn}^{	ext{III}}$ ions is completed by the presence of a terminally bonded MeOH molecule. It is these and the terminally bonded phenolate O-atoms that propagate the extensive inter-molecular H-bonded interactions via the interstitial MeOH solvate molecules (Fig. 2.6). The terminally bonded MeOH molecule (O5) is H-bonded to one MeOH of crystallisation (O5⋯O7 = 2.654 Å), which in turn is H-bonded to a second MeOH molecule of crystallisation (O7⋯O6 = 2.672 Å), which in turn is H-bonded to the two terminally bonded phenolate O-
atoms on the neighbouring cluster molecule (O6⋯O1 = 2.936 Å; O6⋯O3 = 2.956 Å).
The result is the formation of a H-bonded 2D sheet in the ac plane, with the inter-
plane interactions occurring via the C–H⋯π interactions of the ‘interdigitated’
naphthalene moieties, with typical C⋯centroid distances of 3.560 Å. Complex 2.2 is
only the second example of an oxime-bridged MnIII dimer and indeed is a very rare
example of an oxime bridged Mn dimer at any oxidation level. Its closest analogue
was the heterometallic complex 2.1, which also displays the very simple [MnIII(NO)]2
magnetic core. More recently a new family of Mn-oxime dimers have appeared in
the literature as mentioned in Section 1.11.3, Chapter one.\textsuperscript{15}
Figure 2.6. (a) and (b) Orthogonal views of the molecular structure of $[\text{Mn}^{III}_2(\text{Naphth-sao})_2(\text{Naphth-saoH})_2(\text{MeOH})_2] \cdot 4\text{MeOH}$ 2.2. (c) Space-fill representation of 2.2. (d) Packing of molecules of 2.2 in the crystal viewed down the $b$ axis. Colour code: Mn = purple, O = red, N = blue, C = grey. H-atoms and solvent molecules of crystallisation have been omitted for clarity.
2.2.2 SQUID Magnetometry

$Dc$ magnetic susceptibility measurements were performed on powdered microcrystalline samples of complexes 2.1 and 2.2 in an applied magnetic field of 0.1 T and in the temperature range 300 to 5 K for complex 2.1 and 275 to 5 K for complex 2.2. The results for 2.1 are plotted as the $\chi_M T$ product vs. $T$ in Fig. 2.8. The $\chi_M T$ value of $\sim 6.2$ cm$^3$ K mol$^{-1}$ at 300 K is close to the spin-only value of 6 cm$^3$ K mol$^{-1}$ expected for two non-interacting high-spin Mn$^{III}$ (3d$^4$) ions, assuming $g = 2$. This value increases constantly as the temperature is decreased, reaching a maximum of $\sim 9.2$ cm$^3$ K mol$^{-1}$ at 11 K before decreasing to a value of $\sim 8.7$ cm$^3$ K mol$^{-1}$ at 5 K. The results for 2.2 are plotted as the $\chi_M T$ product vs. $T$ in Fig 2.10. The high temperature $\chi_M T$ value of 5.92 cm$^3$ K mol$^{-1}$ is again very close to that expected from the spin-only value (6.00 cm$^3$ K mol$^{-1}$) for two non-interacting high-spin Mn$^{III}$ (3d$^4$) ions, assuming $g = 2$. This value increases constantly as the temperature is decreased, reaching a maximum of $\sim 9.66$ cm$^3$ K mol$^{-1}$ at 6 K before decreasing slightly to a value of $\sim 9.60$ cm$^3$ K mol$^{-1}$ at 5 K. This behaviour is indicative of the presence of an intramolecular ferromagnetic exchange interaction between the two Mn$^{III}$ ions in both complexes 2.1 and 2.2. The small drop in the $\chi_M T$ product below 11 K (2.1) and 6 K (2.2) is ascribed to inter-molecular interactions and/or zero-field splitting of their ground spin-state. As different Hamiltonians were used in the fitting of [Mn$^{III}_2$Zn$^{II}_2$(Ph-
sao)₂(Ph-saoH)₄(hmp)₂ 2.1 and [MnIII₂(Naphth-sao)₂(Naphth-saoH)₂(MeOH)₂]·4MeOH 2.2, the interpretation of each of their magnetic properties will be described separately (below).

Magnetic Characterisation of Complex 2.1

For the interpretation of the magnetic properties of 2.1 we employed the spin-Hamiltonian as shown below in Equation 2.1:

\[
\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 + \mu_B g \sum_{1,2} B \cdot \hat{S}_i + D \sum_{1,2} \hat{S}^2_{i,z} - S(S + 1)/3
\]

Equation 2.1.

where \( J \) is the isotropic exchange interaction parameter, \( \hat{S} \) is a spin-operator, \( i \) runs from 1 to 2, \( \mu_B \) is the Bohr magneton, \( B \) is the applied magnetic field, \( g = 2 \) is the \( g \)-factor of the Mn III ions, \( D \) is the uniaxial anisotropy parameter of Mn III and \( S = 2 \) is the electronic spin of Mn III. Inter-molecular interactions were taken into account in the frame of mean-field theory, by use of the Curie-Weiss temperature, \( \theta \).

The \( \chi_M T \) product of 2.1 was numerically fitted to the spin-Hamiltonian (Equation 2.1) by use of a simplex algorithm,\(^{[16]}\) and the best-fit parameters obtained following various fit strategies are shown in Table 2.1. If the drop at low temperatures in the \( \chi_M T \) product of 2.1 is assumed to be solely due to inter-molecular interactions (completely neglecting single-ion anisotropy), then the determined best-fit \( J \) parameter is \( J = +2.24 \) cm\(^{-1}\) and the Curie-Weiss temperature is \( \theta = -0.88 \) K. This exchange is of the same order of magnitude as that seen previously in the related [MnIII₆] and [MnIII₃] complexes.\(^{[17]}\) If the drop in the \( \chi_M T \) product of 2.1 at low temperatures is assumed to be solely due to the single-ion anisotropy of the Mn III centres, then the obtained best-fit values for the \( J \) and \( D \) parameters vary depending on the sign of the initial guess value of the Mn III single-ion anisotropy, \( D \) (Table 2.1). Using an initial guess value \( D = -3.00 \) cm\(^{-1}\), a typical value for Mn III, one obtains \( J = +1.89 \) cm\(^{-1}\) and \( D = -9.00 \) cm\(^{-1}\). While the determined \( J \) value is perfectly sensible, the value of \( D \) appears rather unrealistic. If one inverses
the sign of the initial guess value of the \( \text{Mn}^{\text{III}} \) single-ion anisotropy (i.e. \( D = +3.00 \text{ cm}^{-1} \)), a similar situation arises (Table 2.1). On this occasion both the sign and magnitude of \( D \) are not what would be expected for \( \text{Mn}^{\text{III}} \). Thus, in order to successfully account for the \( \chi_M T \) product of 2.1 over the whole temperature range (and in a 0.1 T applied magnetic field) it appears that both contributions should be taken into account. Thus, we finally fit the experimental \( \chi_M T \) product of 2.1 employing both single-ion anisotropy and inter-molecular interaction terms. The obtained best-fit parameters are given in Table 2.1, where it can be seen that, irrespective of the sign of the initial guess-value of \( D \), \( J \) is determined to be of the order of \( +2.2 \text{ cm}^{-1} \) and \( \theta \) of the order of \( -0.8 \text{ K} \).

**Table 2.1.** Best-fit parameters obtained by numerically fitting the \( \chi_M T \) product of 2.1 to spin-Hamiltonian (Equation 2.1), as described in the text.

<table>
<thead>
<tr>
<th>( D_{\text{guess}} / \text{cm}^{-1} )</th>
<th>( J / \text{cm}^{-1} )</th>
<th>( D / \text{cm}^{-1} )</th>
<th>( \theta / \text{K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0°</td>
<td>2.24</td>
<td>0.00°</td>
<td>-0.88</td>
</tr>
<tr>
<td>-3.0</td>
<td>1.89</td>
<td>-9.00</td>
<td>0.00°</td>
</tr>
<tr>
<td>3.0</td>
<td>1.93</td>
<td>6.61</td>
<td>0.00°</td>
</tr>
<tr>
<td>-3.0</td>
<td>2.24</td>
<td>-0.97</td>
<td>-0.81</td>
</tr>
<tr>
<td>3.0</td>
<td>2.22</td>
<td>1.55</td>
<td>-0.75</td>
</tr>
</tbody>
</table>

\( ^a \) The value of this parameter was kept fixed to the reported value.
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Figure 2.8. Plot of the \(\chi M T\) product of 2.1 vs. \(T\) in the 300–5K temperature range in an applied field of 0.1 T. The solid red line is the best-fit of the data to Hamiltonian (Equation 2.1) with \(J = +2.24\;\text{cm}^{-1}\), \(D = -0.97\;\text{cm}^{-1}\) and \(\theta = -0.81\;\text{K}\).

Figure 2.9. Plot of reduced magnetisation \((M/N\mu_B)\) of 2.1 vs. \(\mu_B B/kT\) in the 2–7 K temperature range and at the indicated field strengths. The solid red lines are the best-fit of the data to spin-Hamiltonian (Equation 2.1) with \(J = 2.24\;\text{cm}^{-1}\), \(D(\text{Mn}^{\text{III}}) = -3.23\;\text{cm}^{-1}\) and \(\theta = 0.03\;\text{K}\).
Under these conditions these two parameters are relatively well defined. However, even if the magnitude of the obtained best-fit $D$ values are now closer to what would be expected for Mn$^{III}$, albeit tending to the small side, their sign is still dependent on the sign of the initial guess-value of $D$. This is a clear indication that the $\chi_M T$ product of 2.1 cannot be used to determine $D$. This is of course to be expected since anisotropy effects are of importance at low temperatures. Thus, in order to determine the sign and magnitude of $D$, we have numerically fitted\cite{16} the magnetisation data collected on 2.1 to the spin-Hamiltonian given in Equation 2.1, at temperatures between 2 and 7 K in magnetic fields ranging from 1 to 7 T, keeping $J$ constant to $J = +2.24$ cm$^{-1}$ as determined by fitting the $\chi_M T$ product. The obtained best-fit parameters are given in Table 2.2. When $J$ is fixed the sign of the obtained best-fit $D$ parameter still depends on the initial guess of sign of this parameter. However, the quality of fit, measured by $\chi^2$, is better by an order of magnitude when associated to the negative sign solution. In none of the previously discussed cases did the order of magnitude of $\chi^2$ depend on the initial guess-value of the $D$ parameter. Thus, the retained best-fit value for the uniaxial anisotropy of Mn$^{III}$ in 2.1 is $D = -3.23$ cm$^{-1}$. This value is in good agreement in both magnitude and sign with previous studies of related [Mn$^{III}_6$] and [Mn$^{III}_3$] complexes, and with that expected for a Jahn-Teller distorted Mn$^{III}$ ion.

Table 2.2. Best-fit parameters obtained by numerically fitting the low-temperature field-dependent magnetisation data of 2.1 to spin-Hamiltonian (Equation 2.1), as described in the text.

<table>
<thead>
<tr>
<th>$D_{\text{guess}}$ / cm$^{-1}$</th>
<th>$J$ fixed / cm$^{-1}$</th>
<th>$D_{\text{best-fit}}$ / cm$^{-1}$</th>
<th>$\theta$ / K</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.0</td>
<td>2.24$^a$</td>
<td>-3.23</td>
<td>0.03</td>
<td>0.0399</td>
</tr>
<tr>
<td>3.0</td>
<td>2.24$^a$</td>
<td>3.62</td>
<td>-0.11</td>
<td>0.5512</td>
</tr>
<tr>
<td>-3.0</td>
<td>199.97</td>
<td>-3.18</td>
<td>0.03</td>
<td>0.0366</td>
</tr>
<tr>
<td>3.0</td>
<td>119.38</td>
<td>4.31</td>
<td>-0.09</td>
<td>0.5078</td>
</tr>
</tbody>
</table>

$^a$ The value of this parameter was kept fixed to the reported value.
Interestingly, the fit of the low-temperature field-dependent magnetisation data leads to negligible values of inter-molecular exchange, as evidenced by the small values of θ (Table 2.2). This is likely due to the fact that in fields of 1 T (corresponding to approximately 1.5 K) or higher, the effect of the small inter-molecular interactions operating for 2.1 in the solid state (of the order of 1.0 K as determined by fitting the $\chi_M T$ product) is quenched by the magnetic field. Furthermore, if the $J$ parameter is included in the fit as a free fit parameter, $\chi^2$ decreases with increasing magnitude of ferromagnetic interactions (albeit, very slowly). This indicates a very flat error surface with respect to this parameter. This is shown in Table 2.2 where a very slight improvement in the $\chi^2$ is observed when $J$ is left free to vary in, for example, the interval -200 to 200 cm$^{-1}$. For both signs of the initial guess-value of the $D$ parameter, the quality of fit increases only slightly for a large variation of $J$. This behaviour confirms that low temperature field dependent magnetisation data are, in general, not a sensitive probe for the determination of the isotropic exchange parameter.

**Magnetic Characterisation of Complex 2.2**

For the interpretation of the magnetic properties of 2.2 the isotropic spin-Hamiltonian shown in Equation 2.2 (below) was employed:

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 + \sum_{i=1,2} \{\mu_B \vec{B} \cdot \hat{S}_i\}$$

*Equation 2.2.*

where $J$ is the isotropic exchange interaction parameter, $\hat{S}$ is a spin-operator, $i = 1, 2$, $\mu_B$ is the Bohr magneton, $\vec{B}$ is the applied magnetic field vector, and $g = 2.00$ is the $g$-factor of the Mn$^{III}$ ions. The $\chi_M T$ product of 2.2 was numerically fitted, by use of the simplex algorithm,$^{[16]}$ to this spin-Hamiltonian by numerical diagonalisation of the full spin-Hamiltonian matrix. The best-fit parameter was $J = +1.24$ cm$^{-1}$, affording an $S = 4$ ground state, with the first excited state ($S = 3$) approximately 10 cm$^{-1}$ higher in energy. In addition, inter-molecular interactions were taken into account in the frame of mean-field theory, by use of the Curie–Weiss temperature.
A Curie-Weiss constant of \( \theta = -0.54 \) K, was necessary to reproduce the small drop of the \( \chi_M T \) product below 6 K. Inclusion of axial anisotropy to the above isotropic spin-Hamiltonian did not increase the quality of fit in a significant way (f-test of 0.97), leaving the \( J \) and \( \theta \) parameters essentially unaltered, and resulted in a relatively low best-fit single-ion axial anisotropy (-0.55 cm\(^{-1}\)) for the Mn\( ^{\text{III}} \) centres. This is not surprising since anisotropy effects are predominant at very low temperatures and thus, do not weight significantly in the fitting of the \( \chi_M T \) product of 2.2.

Figure 2.10. Plot of the \( \chi_M T \) product of 2.2 vs. \( T \) in the 275–5 K temperature range in an applied field of 0.1 T. The solid red line is the best-fit of the data with \( J = +1.24 \) cm\(^{-1}\) and \( g = 2.0 \).[18]
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Figure 2.11. Plot of reduced magnetisation in the 2.0 to 7.0 K temperature range and at the indicated field strengths for 2.2. The solid red lines are the best fit of the data with \(J = +1.24\) cm\(^{-1}\), \(g = 2.0\) and \(D = -3.64\) cm\(^{-1}\).

The ferromagnetic nature of the exchange between the two metals in 2.2, mediated via the oximate -N-O- bridges, was expected on the basis of previous magneto-structural correlations in phenolic oxime based \([\text{Mn}^{\text{III}}_3]\) and \([\text{Mn}^{\text{III}}_6]\) clusters that have suggested that Mn-N-O-Mn torsion angles above approximately 31° are likely to result in ferromagnetic pairwise exchange.\(^{[17]}\) The magnitude of the exchange is also similar to that seen in the complex \([\text{Mn}^{\text{III}}_2\text{Zn}^{\text{II}}_2(\text{Ph-sao})_2(\text{Ph-saoH})_4(\text{hmp})_2]\) (2.1).\(^{[19]}\)

In order to determine the single-ion axial anisotropy parameter for the Mn\(^{\text{III}}\) centres in 2.2, variable-temperature-variable-field dc magnetisation experiments were performed in the 2.0–7.0 K and 0.5–5.0 T temperature and magnetic field ranges, respectively. These experimental data are presented as reduced magnetisation \((M/N\mu_B vs. \mu_B/kT)\), with \(N\) being Avogadro’s number and \(k\) the Boltzmann constant) in Fig. 2.11. They were numerically fitted, by use of the simplex algorithm,\(^{[16]}\) to the axially anisotropic spin-Hamiltonian (Equation 2.3), by numerical diagonalisation of the full spin-Hamiltonian matrix.
\[
\hat{H} = -2J \hat{S}_1 \cdot \hat{S}_2 + \sum_{i=1,2} \left\{ \mu_B \vec{B} \hat{g} \hat{S}_i + D \hat{S}_{z,i}^2 - S_i (S_i + 1) / 3 \right\}
\]

Equation 2.3.

Here $D$ is the uniaxial anisotropy, and $S = 2$ the total spin of the Mn$^{III}$ ions. The best fit $D$ parameter, keeping $J$ fixed to +1.24 cm$^{-1}$ (as determined by fitting the $\chi_M T$ product of 2.2), was $D = -3.64$ cm$^{-1}$.

### 2.2.3 Ac Magnetic Susceptibility Studies

Ac magnetic susceptibility measurements were performed on a polycrystalline sample of [Mn$^{III}$$_2$Zn$^{II}_2$(Ph-sao)$_2$(Ph-saoH)$_4$(hmp)$_2$] 2.1 in the 1.8 – 10 K range in zero applied dc field and a 3.5 G ac field oscillating in the 50 – 1000 Hz frequency range (Fig. 2.12). 2.1 does display frequency-dependent out-of-phase, $\chi_M''$, signals but no peaks are observed down to 2 K. Ac measurements were not performed on complex 2.2 as whole ac peaks were not expected.

![Figure 2.12](image-url)  
**Figure 2.12.** Out-of-phase ($\chi_M''$) ac susceptibility versus temperature in the indicated frequency and temperature ranges for [Mn$^{III}_2$Zn$^{II}_2$(Ph-sao)$_2$(Ph-saoH)$_4$(hmp)$_2$] 2.1.
2.2.4 High Field Electron Paramagnetic Resonance (HFEPR) Spectroscopy

Single-crystal High-Frequency EPR (HFEPR) measurements were performed on complexes 2.1 and 2.2 by Professor Stephen Hill and his associates at the National high Magnetic Field Laboratory, Florida State University. These studies were performed in order to directly extract D parameters associated with the aforementioned Mn dimers, 2.1 and 2.2.

2.2.4.1 HFEPR measurements of [MnIII2ZnII2(Ph-sao)2(Ph-saoH)4(hmp)2]·3.6 MeCN (2.1)

HFEPR measurements were performed on 2.1 primarily with a view to determining the magnetic anisotropy associated with its ground state. However, as shall be seen, it is also possible to estimate the exchange coupling strength within the molecule from such measurements. Experiments were conducted in a spectrometer that enabled in-situ rotation of the sample about a fixed axis[20],[21] Variable frequency (60 - 410 GHz) and variable temperature measurements were thus performed with the field aligned both in the hard-plane and at an orientation close to the easy axis of the molecules under scrutiny.

Fig. 2.13 shows representative spectra obtained at 171 GHz with the external field applied in the hard plane. The sharp transition seen at ~6 T at all temperatures is due to a paramagnetic impurity (with $g = 2.00$) in the sample and is ignored in the ensuing data analysis. A cluster of transitions seen in the 12-13 T range increases in intensity with decreasing temperature, indicating that it involves excitations from the ground state. Likewise, a broad, featureless dip centered at ~7.5 T is also seen to strengthen with decreasing temperature. The observation of multiple excitations from the ground state can be attributed to weak disorder in the sample. Indeed, essentially identical behavior is seen in the hard-plane spectra of the [Mn12-acetate][22] and [Ni4][23] SMMs. The cluster of fine structure peaks at the highest fields is likely caused by a discrete disorder associated with either the ligand
or solvent molecules that gives rise to distinct species with slightly different transverse anisotropy parameters, hence the observation of several resolved peaks in the hard plane spectra (as denoted by the vertical arrows in Fig. 2.13).\cite{22b,c} The broad feature can be attributed to a very slight tilting of the zero-field-splitting (zfs) tensors associated with the different species such that the field is not perfectly aligned in the hard plane for all of the molecules.\cite{22b} The easy axis spectra (not shown) also reveal clear evidence for this same disorder, with the effect most pronounced for the ground state transition, as expected on the basis of D-strain.\cite{24}

**Figure 2.13.** Hard plane HFEPR spectra of complex 2.1 obtained at 171 GHz as a function of temperature from 20 K (top) to 2.5 K (bottom).

Fig. 2.14 shows the frequency dependence of EPR peak positions observed with the field applied (a) close to the molecular easy axis and (b) exactly in the hard plane; we include only peaks that can clearly be identified and assigned to known transitions. As can clearly be seen in (a), four branches of resonances are observed which are labeled $A_1$, $A_2$, $A_3$ and $A_4$, where $A_i$ denotes the transition from $m_s = -i$ to $-(i-1)$ ($i$=integer). $m_s$ is the spin projection onto the easy-axis ($A_4'$ is the $m_s = +4$ to $+3$ transition and $B_4$ is a shoulder on $A_4$ attributed to disorder). The resonances in Fig. 2.14(b) have been labeled according to the same scheme except that $m_s$ now corresponds to the spin projection onto the high-field quantisation axis, which necessarily corresponds to the applied field direction. The observation of four
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resonance branches with positive zero-field intercepts in Fig. 2.14(a) confirms the $S = 4$ ground state spin value, while the fact that the $A_4$ transition persists to the lowest temperatures suggests easy-axis anisotropy. We note that the diminished sensitivity of the spectrometer at higher frequencies required data above 360 GHz to be recorded at 2 K, where only the $A_4$ transition is observed. It is noticeable in Fig. 2.14(a) that the spacing between the four main branches is non-uniform. It is well documented that this is indicative of weak coupling, i.e., $J \sim |D|^{[25]}$. In the strong coupling limit ($J \gg |D|$), only 2nd order zfs ($D\hat{S}_z^2$) is expected within the $S = 4$ ground state, which would result in equal spacing between the easy-axis peaks. Thus, the uneven spacing provides an additional handle on the exchange coupling parameter $J$.

Figure 2.14. Frequency dependence of EPR peak positions observed for 2.1 with the field applied (top) close to the molecular easy axis and (bottom) exactly in the hard plane. The data were mainly collected at 15 K; however, data above 360 GHz were collected at 2 K. The solid lines are the simulations of the peak positions employing the Hamiltonian and parameters provided in the main text.
The solid lines in Fig. 2.14 represent the best simulations of the peak positions using Equation 2.1 with the following parameters: \( D(\text{Mn}^{III}) = -3.83 \text{ cm}^{-1} \), \( J = +2.33 \text{ cm}^{-1} \) and \( g = 2.00 \). Fig. 2.14(a) required an 18° field misalignment due to the fact that one cannot guarantee exact coincidence with the easy axis when rotating about a single-axis. Furthermore, in order to obtain a good simulation for the hard plane data in Fig. 2.14(b), a rhombic zfs term was included for each Mn^{III} ion with \( E = 0.18 \text{ cm}^{-1} \); the data points represent the strongest central resonance within each cluster of peaks, with the error bars spanning the adjacent peaks/shoulders (see vertical arrows in Fig. 2.13). It should be noted that the obtained \( E \) value represents a lower bound because the precise field orientation within the hard plane was not known. As can be seen, the simulations provide good overall agreement for all plotted EPR transitions observed in both orientations. The easy axis data are relatively insensitive to \( E \) and, thus, provide the main constraints on \( D \) and \( J \). We note the excellent agreement between these parameters and those obtained via the preceding analysis of magnetic data, thereby providing further confidence in the overall conclusions of this work.

### 2.2.4.2 HFEPR measurements of [Mn^{III}]_{2}(Naphth-sao)_{2}(Naphth-saoH)_{2}(MeOH)_{2}\cdot4\text{MeOH} (2.2)

HFEPR measurements were also performed on a powdered crystalline sample of 2.2. Fig. 2.15 separately displays the temperature dependence of parallel (\( B//z \)) and perpendicular (\( B\perp z \)) components of representative powder spectra obtained for complex 2.2. Due to the significant zero-field splitting experienced by 2.2, these two measurements were performed at quite different frequencies (406.4 (a) and 165.6 GHz (b) for \( z \) and \( xy \), respectively) in order to match the most prominent features to the available field window. For an easy-axis (\( D < 0 \)) system at low temperatures, one expects the strongest parallel components to occur on the low-field side of the \( g = 2.00 \) position (indicated in both panels of Fig. 2.15), while the stronger perpendicular components should occur on the high-field side, as is clearly the case in Fig. 2.15.
Figure 2.15. Temperature dependent powder HFEPR spectra recorded in field derivative mode in the temperature range from 2.5 to 30 K: the measurements in (a) were recorded at 406.4 GHz, emphasizing the parallel (B||z) components of the spectrum; those in (b) were recorded at 165.6 GHz, emphasizing the perpendicular (B⊥z) components. The main resonance features are labeled according to the scheme described in the main text. The inset (top) depicts a typical T = 0 derivative mode powder spectrum for a biaxial system, illustrating the line shapes expected for the x, y and z components of the spectrum.

The spectra were recorded in field-derivative mode (dI/dB, where I denotes the absorption intensity), making it relatively straightforward to determine which peaks correspond to which components of the spectrum. The inset to Fig. 2.15(a) displays a trivial example of a T = 0 derivative mode powder spectrum for a biaxial system for which three features are observed: the z-component corresponds to the onset of absorption and appears as a peak in the derivative; the x component corresponds to the cessation of absorption and thus appears as a dip in the derivative; meanwhile, the y component occurs at the maximum in absorption and therefore looks like the derivative of the z-component. Examination of the first few resonances in Fig. 2.15(a) indicates that they are indeed peaks, confirming their
assignment to the parallel part of the spectrum. However, the resonances change to more of a derivative shape as the center \((g = 2)\) position of the spectrum is approached.

Based on simulations (vide infra), the peaks in Fig. 2.15(a) have been labeled according to the notation \(z_{S,ms}\), where \(S\) denotes the spin multiplet state associated with the excitation, and \(m_s\) denotes the magnitude of the spin projection associated with the state from which the transition was excited. Accordingly, the strongest low-temperature peak is \(z_{4,4}\) corresponding to the lowest-lying \(m_s = -4\) to \(-3\) excitation associated with the \(S = 4\) ground state multiplet. We note that, as the temperature is increased, many more features emerge in the spectrum, especially as one approaches the isotropic \(g = 2.00\) position. It is possible to assign many of these features to transitions within excited spin multiplet states (vide infra), e.g., \(z_{3,3}\). Finally, we note that the strongest peak in Fig. 2.15(a) displays fine structures that are most likely attributable to multiple molecular microenvironments with slightly different \(zfs\) parameters.\(^{22a}\) Such strains are very common in molecular clusters and we shall see similar evidence for such behavior in the perpendicular spectra.\(^{10a, 22a, b, 23a}\)
Figure 2.16. Frequency dependence of the main HFEPR peak positions (see main text for explanation of labeling) determined from parallel spectra such as those in Fig. 2.15(a). The solid curves represent the best simulation of the data according to the Hamiltonian of Equation 2.4. The lower right inset depicts the perpendicular Zeeman diagram, illustrating the origin of the $\alpha$ and $\beta$ resonances seen in Fig. 2.15(b) and Fig. 2.17 (see main text for further explanation).

Fig. 2.15(b) clearly contains two distinct types of excitation: those observed as double dips, which we assign to the $x$ components, and those that appear as derivatives, which we assign to the $y$ components. The two dips in the $x$-component spectrum again suggest multiple microenvironments. The resonances in Fig. 2.15(b) have been labeled according to a scheme developed previously for the [Mn$_{12}$] SMM.$^{[22b]}$ At the lowest frequencies, the excitations may be further grouped into two types, $\alpha$ and $\beta$, depending on whether they occur between pairs of levels that are nearly degenerate ($\alpha$), or separated by a gap ($\beta$) in zero field. This is illustrated in the inset to Fig. 2.16, which shows the perpendicular ($B//xy$) Zeeman diagram associated with the low-energy portion of the $S = 4$ ground state, and where the $\alpha$ and $\beta$ transitions are indicated with black and blue arrows, respectively. This distinction will become important below when we attempt to simulate the powder spectra. The resonances in Fig 2.15(b) are thus labeled either $\alpha$ or $\beta$, with subscripts that denote (i) the approximate $m_S$ value (even for $\alpha$ and odd for $\beta$) associated with the state from which the transition was excited, and (ii) whether the excitation
belongs to the $x$ or $y$ part of the spectrum. The $m_s$ values are only exact in the very high-field/frequency limit in which the quantisation axis is determined by the applied magnetic field vector.

Fig. 2.15 plots the positions of main peaks observed in the parallel spectra determined from measurements spanning a wide range of high-frequencies, while Fig. 2.16 displays similar plots corresponding to the perpendicular spectra. Included in the Figures are the best simulations (solid curves) of the combined data sets employing the anisotropic spin-Hamiltonian as shown in Equation 2.4:

$$
\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 + \sum_{i=1,2} \{\mu_B g \hat{B} \cdot \hat{S}_i + D[\hat{S}_{z,i}^2 - S_i (S_i + 1)/3] + E(\hat{S}_{x,i}^2 - \hat{S}_{y,i}^2)\}
$$

Equation 2.4.

where $E$ is the rhombic anisotropy parameter associated with the Mn$^{III}$ ions. One of the major advantages of performing multi-frequency measurements is that different features in the combined data sets separately constrain each of the free parameters in the above Hamiltonian.$^{[23b]}$ To start with, we have previously argued$^{[25a]}$ that, for a ferromagnetic molecule with parallel $D$ tensors, the zero-field intercept ($zfs$) associated with the parallel ground state transition ($z_{4,4}$ in Fig. 2.16) depends only on $D$, i.e., it is completely insensitive to any of the other parameters in the above Hamiltonian. Given that this is the most prominent feature in the entire study, we use it to fix $D$. The locations of the 2$^{nd}$ and 3$^{rd}$ ground state parallel resonances ($z_{4,3}$ and $z_{4,2}$ in Fig. 2.16) then constrain $J$, while the slopes of the lines in Fig. 2.16 constrain the $z$-component of the $g$ tensor. The effect of $J$ is to introduce higher (> 2$^{nd}$) order interactions into the effective description of the $S = 4$ ground state (not considered here) that result in uneven field spacing of the corresponding resonance branches. This is clearly the case in Fig. 2.16, and it is this uneven spacing (i.e. the locations of $z_{4,3}$ and $z_{4,2}$ relative to $z_{4,4}$) that constrains $J$.

We next turn to the perpendicular spectra in Fig. 2.17. Introduction of a rhombic $E$ term together with a tuning of the $x$ and $y$ components of the Landé $g$-tensor
produces near perfect agreement in terms of the \( \alpha \) resonances (thick black curves). The rhombic interaction effectively splits the \( x \) and \( y \) components, shifting the former (latter) to higher (lower) fields, while the \( g \) values again determine the slopes. The only remaining issue concerns the low-frequency behavior of the \( \beta \) resonances (blue data points), which deviate dramatically from \( x \) and \( y \) component expectations (thick blue curves).

The low-frequency behavior of the \( \beta \) resonances is not new, having been documented previously by other authors\(^{[26]}\) as well as by some of the authors collaborating on this work (while they looked at the [Mn\textsubscript{12}] SMM).\(^{[22b]}\) The simple 2\textsuperscript{nd} order Hamiltonian above possesses \( D_{2h} \) symmetry. In the strict high field limit (\( B \gg DS/g\mu_B \)), it gives rise to resonant (EPR) excitations that have turning points when the field is applied along each of the three principal Cartesian axes \( x \), \( y \) and \( z \), i.e., when rotating in one of the three Cartesian planes (\( xy \), \( yz \) or \( zx \)), the field location of each resonance will oscillate from a minimum to a maximum, with the extrema (turning points) located exactly along the Cartesian axes. It is these turning points that dominate the powder derivative spectrum. However, if the high field criterion is not met, these turning points need not necessarily lie along the Cartesian axes. This can give rise to what are termed ‘off-axis resonances’ in powder measurements at low frequencies.\(^{[22b, 26]}\) This is precisely the explanation for the low frequency behavior of the \( \beta \) resonances, and very similar effects have been observed in [Mn\textsubscript{12}].\(^{[22b, 27]}\)
Figure 2.17. Frequency dependence of the main HFEPR peak positions (see main text for explanation of labeling) determined from $x$ (a) and $y$ (b) components of spectra such as those displayed in Fig. 2.15(b). The thick solid curves represent the best simulation of the $\alpha$ (black) and $\beta$ (blue) resonances according to the spin-Hamiltonian of Equation 2.4. The thin blue curves correspond to simulations with the field applied away from the $xy$-plane (in $2^\circ$ increments); these curves account for the low-frequency off-axis $\beta$ resonances (see main text for further explanation).

To demonstrate the above assertion, we include additional simulations in Fig. 2.17, corresponding to field orientations away from the $xy$ plane in $2^\circ$ increments (thin blue curves). At the highest frequencies, the off-axis curves all occur to the low-field side of the $B//xy$ curve (thick blue line), i.e., the turning points lie exactly along $x$ and $y$. However, at the lowest frequencies, the simulations move initially to higher fields, but then retreat again to lower fields (i.e. as expected the turning points lie out of the $xy$ plane). The field orientations corresponding to the turning points (maximum field) are frequency dependent. Nevertheless, by plotting a series of such curves, one indeed finds that they tend to the locations of the observed low-frequency $\beta$ resonances. In other words, a single parameterisation accounts perfectly for all aspects of the powder measurements. The optimum simulation
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parameters are: $D = -3.49\text{ cm}^{-1}$, $|E| = 0.16\text{ cm}^{-1}$, $J = +1.17\text{ cm}^{-1}$ (ferromagnetic) and $g = 2.00$.

Finally, we comment on the obtained parameters. There is excellent agreement between the single-ion uniaxial anisotropy and isotropic exchange parameters obtained from the HFEPR measurements and the fitting of the susceptibility and reduced magnetisation data ($D = -3.64\text{ cm}^{-1}$, $J = +1.24\text{ cm}^{-1}$). EPR studies are normally insensitive to exchange. However, as we have recently shown, one can indirectly determine $J$ rather precisely in the case of simple clusters for which the exchange is comparable to, or weaker than the anisotropy associated with the constituent ions.$^{[23b]}$ This condition is present in the current example, again illustrating the utility of HFEPR for such studies. We note that the obtained value for $D$ is exactly in the same range of -3.4 to -3.6 cm$^{-1}$ as found for many related Mn$^{III}$ complexes.$^{[10a, 10d, e, 19, 25a, 28]}

2.2.5 DFT Analysis

2.2.5.1 DFT Analysis of [Mn$^{III}_2$Zn$^{II}$$^2_2$(Ph-sao)$^2_2$(Ph-saoH)$^4$hmp$^2_2$]$\cdot$3.6 MeCN (2.1)

For complex 2.1, calculations (carried out by Dr. Gopalan Rajaraman and co-workers; University of Mumbai) were performed with the Gaussian09 package using the B3LYP functional and the quadratic convergence approach.$^{[29]}$ Triple-$\xi$ and double-$\xi$ all electron basis sets, as proposed by Ahlrichs et al., were used for the metal ions, and the rest of atoms, respectively.$^{[30]}$ The broken symmetry approach was employed to describe the unrestricted solutions of the antiferromagnetic spin states,$^{[31]}$ which were obtained from the guess functions generated with the fragment tool implemented in the Gaussian code. The full geometry was used for 2.1. We also used a polarisable continuum model with the parameters corresponding to the acetonitrile solvent but similar results for the magnetic coupling constant, $J$, were found and preserved. Therefore, they have not been included in the discussion.$^{[32]}$ The broken-symmetry methodology allows for the determination of all the exchange coupling constants present in a polynuclear
transition metal complex.\textsuperscript{[31]} Since our system contains only two Mn\textsuperscript{III} (\(S = 2\)) paramagnetic centres, the magnetic coupling constant in 2.1 can be inferred from the energies of a nonet and a singlet spin function, displaying a parallel and antiparallel alignment of the local spin moments.

\textit{DF} calculations on the experimental geometry of complex 2.1 were performed in order to estimate the magnetic coupling constant between the two Mn\textsuperscript{III} centres. The obtained \(J\) value, +1.5 cm\(^{-1}\), is in excellent agreement with that found experimentally. In an attempt to understand the factors responsible for the ferromagnetic nature of the coupling, \textit{DF} calculations were performed on the dinuclear model complex shown in Fig. 2.18, in which there is only one bridging oximato (-N-O-) group between the metal centres, the Ph-sao\textsuperscript{2-} ligand has been simplified (to H\textsubscript{2}CNO) and the peripheral ligands replaced with F\textsuperscript{-} atoms. The distances from the Mn atoms to the peripheral ligands were optimised in order to tune the strength of the ligand field, but the direction of the Jahn-Teller axis was preserved and all other distances and angles retained.

In our model complex, one of the Mn\textsuperscript{III} ions has been placed in the same plane formed by the C-, N- and O-atoms of the oxime ligand, with the Mn-O vector of the other metal quasi-perpendicular to the oxime plane. For the latter Mn\textsuperscript{III} ion, the experimentally observed Mn-O-N angle is 119.3° and the Mn-O-N-C dihedral angle (\(\theta\)) is 96.1°. A constant \(J\) dependence on the \(\theta\) angle was calculated to examine the effect of the Mn-O-N-C dihedral angle on the nature of the magnetic coupling. The results are displayed in Fig. 2.19. For \(\theta = 90^\circ\) [close to that observed in the crystal structure], a \(J\) value of +1.0 cm\(^{-1}\) is found. Despite the simplifications employed in building our model, this is remarkably close to the experimentally determined value of +2.2 cm\(^{-1}\). An analysis of the contributions to the magnetic coupling is shown in Fig. 2.20 and in Table 2.3. For a Jahn-Teller distorted Mn\textsuperscript{III} ion in octahedral geometry the \(d_x^2-y^2\) orbital is non-magnetic, and contributions from the \(d_{xy}\) magnetic orbitals were ignored because this orbital is unable to delocalise its electronic density onto the oxime ligand.
Figure 2.18. The dinuclear model complex employed to investigate the magnetic coupling present in 2.1. Color code, Mn = dark pink, O = red, N = blue, C = grey, H = light pink, F = green.

Fig. 2.20 shows that the ferromagnetic nature of some contributions is due to an orthogonality between the magnetic orbitals. For example, this is the case for the $z^2$-$z^2$ magnetic contribution when $\theta = 90^\circ$, where the spin density is delocalised through the $\pi$ pathway of the oxime ligand for one metal, but the $\sigma$ pathway for the second. For $\theta = 90^\circ$ there are clearly more ferromagnetic contributions to the exchange than antiferromagnetic contributions and the net result is ferromagnetic coupling, as experimentally observed. When the $\theta$ angle decreases, the ferromagnetic contributions become weaker because the orthogonality is lost. However, when $\theta$ is close to $0^\circ$, some of the antiferromagnetic contributions become ferromagnetic and the total number of ferromagnetic contributions present is large. The result is the observation of a minimum in the plot of $J$ versus $\theta$, and net ferromagnetic coupling when $\theta = 0^\circ$. However we stress that this observation is qualitative. Since many contributions are present, subtle changes can result in a modification of the observed results.
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Figure 2.19. Dependence of the magnetic coupling constant $J$ (cm\textsuperscript{-1}) with the dihedral angle $\theta$ (°). The grey horizontal hairline shows the separation between ferromagnetic and antiferromagnetic regions.

Figure 2.20. Schematic view of the magnetic orbitals and their delocalization onto the bridging ligand for each metal center for $\theta = 0^\circ$ and $90^\circ$. 
Table 2.3. Nature of each contribution to the magnetic coupling for θ = 0° and 90°. F = ferromagnetic, AF = antiferromagnetic.

<table>
<thead>
<tr>
<th>Contribution</th>
<th>θ = 90°</th>
<th>θ = 0°</th>
</tr>
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<tbody>
<tr>
<td>$z^2-z^2$</td>
<td>F</td>
<td>AF</td>
</tr>
<tr>
<td>$z^2-xz$</td>
<td>AF</td>
<td>F</td>
</tr>
<tr>
<td>$z^2-yz$</td>
<td>F</td>
<td>F</td>
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<tr>
<td>$xz-z^2$</td>
<td>AF</td>
<td>F</td>
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<tr>
<td>$xz-xz$</td>
<td>F</td>
<td>F</td>
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<tr>
<td>$xz-yz$</td>
<td>F</td>
<td>AF</td>
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<tr>
<td>$yz-z^2$</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>$yz-xz$</td>
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<td>AF</td>
</tr>
<tr>
<td>$yz-yz$</td>
<td>AF</td>
<td>F</td>
</tr>
</tbody>
</table>

Since there have been no previous reports of solely oxime-bridged MnIII dimers it is impossible to discuss our results in the context of literature precedents, but it is possible to extract some useful information from other complexes in the Cambridge Structural Database that, while differing in nuclearity and / or oxidation levels, have some structural similarities. The cube-like complex [MnIII₄(Me-sao)₄(Me-saoH)₄], which contains dinuclear moieties and arrangements of MnIII ions relative to the ONC (oxime) plane similar to those present in 2.1,[33] displays global ferromagnetic coupling. The majority of the magnetic contributions present in the complexes, [LMnIII(dfmp)₃MnII₂]MnIII[L](ClO₄) and [LMnIV{(dfmp)₃MnII₂}MnIVL](ClO₄)₃ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane; H₃dfmp = 2,6-diformyl-4-methylphenol oxime) are also present in 2.1.[34] Ferromagnetic exchange is observed for the MnIII-MnII and MnIV-MnII pairs when the manganese ions are placed in the ONC plane and the results obtained are in agreement with the sum of contributions given in Table 2.1.
and the calculated $J$ values in Fig. 2.19. In the trinuclear complex $[\text{Mn}^{IV}_3(dpo)_6]$, the magnetic exchange is mediated by three -N-O- bridges with only one manganese ion out of the ONC plane.\cite{35} This case can therefore be used to visualize the net $t_{2g}-t_{2g}$ magnetic contribution in 2.1, which was observed to be ferromagnetic. In agreement with these observations, three important ferromagnetic contributions and one antiferromagnetic contribution co-exist in $[\text{Mn}^{IV}_3(dpo)_6]$ and a global ferromagnetic coupling could be expected. With more recent literature in sight, a family of Mn dimers has emerged in which two Mn\textsuperscript{III} ions are bridged by one $\mu$-O\textsuperscript{2-} ion and an –N-O- moiety of an oxime, with the dominant structural factor being as the Mn-O-N-Mn torsion angle increases antiferromagnetic exchange decreases. As a result of mixed bridging this family cannot be directly compared to 2.2 with solely oxime bridged exchange.

2.2.5.2 DFT Analysis of $[\text{Mn}^{III}_2(\text{Naphth-sao})_2(\text{Naphth-saoH})_2(\text{MeOH})_2]\cdot 4\text{MeOH}$ (2.2)

All calculations (carried out by Prof. Joan Cano and co-workers; University of Valencia) were performed with version 2.8 of the program ORCA,\cite{36} with the TZVP basis set proposed by Ahlrichs used in all cases.\cite{30a, 30b} For density functional theory (DFT) calculations, \textit{resolution of the identity (RI)} approximation with the auxiliary TZV/J Coulomb fitting basis sets were employed.\cite{37} For \textit{Complete Active Space (CAS)} calculations, these were replaced by TZV/C.\cite{38} In certain cases, the electronic effects of the acetonitrile solvent were introduced \textit{via the conductor-like screening model (COSMO)}.\cite{39} DFT calculations on the zero-field splitting (zfs) were carried out using the coupled perturbed and Pederson-Khanna methods, as well as quasi-restricted theory.\cite{7d, 40} The spin-orbit and spin-spin coupling operators employed are based in the \textit{SOMF} scheme.\cite{7d}

Models A and B (Fig. 2.21) were built from the experimental molecular geometry of the dinuclear complex (Fig. 2.21). In Model A one Mn\textsuperscript{III} ion has been replaced by a diamagnetic Zn\textsuperscript{II} ion, and in Model B the molecule has been cleaved in half to produce a mononuclear Mn\textsuperscript{III} complex. Contributions to the axial ($D$) and rhombic
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$(E)$ magnetic anisotropy from second-order spin-orbit and spin-spin coupling were calculated from methods based on density-functional theory (DFT) and post-Hartree-Fock methods based on the CAS treatment,$^{[7d]}$ and used as implemented in ORCA. Those based on DFT calculations were incorporated by means of mean-field approximations. The choice of conditions for the calculations were made using a combination of literature precedents and tests performed by G. Rajaraman et al. using different functionals (including hybrid functionals) and different methods to calculate the spin-orbit coupling (coupled perturbed, quasi-restricted (QRO) and Pederson-Khanna techniques) in the complex $[\text{Mn}^{\text{III}}(\text{bpea})\text{F}_3]$ (bpea = N,N-bis(2-pyridylmethyl)-ethylamine).$^{[7d, 40-41]}$ Results with the BLYP functional and QRO technique provide $D$ values closest to experiment and therefore they will be the only ones presented in this work. The chosen active space in CAS was composed of the five manganese $d$ orbitals occupied by four electrons, with the diagonalised SOC matrix derived from the 5 lowest quintet and 35 lowest triplet states.

Figure. 2.21. Model A (top) and model B (bottom) constructed from the crystal structure of 2.2. Colour code, Mn = pink; Zn = brown; N = blue; O = red; C = grey; H = white.

High-spin Mn$^{\text{III}}$ ions possess a $d^5$ electronic configuration with a quintuplet ground state. The Jahn-Teller effect results in one of the $e_g$ orbitals being unoccupied and non-magnetic. In axially-elongated complexes this is the $x^2-y^2$ orbital, and in axially
compressed complexes this is the $z^2$ orbital. This is normally reflected in negative and positive values of the axial magnetic anisotropy ($D$) parameter, respectively. However in some cases distributions in the metal-ligand bond lengths, which is particularly relevant when a variety of donor atoms are present in the coordination sphere, do not permit such a simple analysis (see section 2.2.1). Complex 2.2 is indeed such a case. In these situations, calculations of the electronic structure provide invaluable support. In the present work both DFT and CAS methods have been employed in order to evaluate the contributions to the axial ($D$) and rhombic ($E$) magnetic anisotropy, originating from the spin-orbit and spin-spin coupling. The results from calculations performed on Models A and B are summarised in Table 2.4.

As has been observed in previous studies, better agreement with experiment was found from CASSCF calculations; albeit with a slight overestimation of the $D$ parameter in some cases. Results based on DFT and CAS calculations provide negative values for the $D$ parameter that correspond to an axially elongated molecular geometry. In model B, DFT calculations provide a positive value of $D$. However, inclusion of the electronic effects from neighbouring molecules propagated via the acetonitrile results in an inversion of sign (see values in parentheses in Table 2.4). These new values are close to that found in Model A, in the presence or absence of solvent. Since DFT calculations tend to overestimate electron delocalisation, molecules in which (highly) negatively charged ligands are coordinated to the (positively charged) metal ions can be somewhat unstable, causing partial charge transfers or the inversion of the $e_g$ magnetic orbital. This can be avoided through the inclusion of an adaptable cavity with a dielectric constant that allows for simulation of intermolecular electronic interactions, stabilising the surplus electronic density on the ligands. Even if the spin-orbit contribution is predominant, the spin-spin contribution is non-negligible and must be considered in the quantitative evaluation of the $D$ parameter.
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**Table 2.4.** Calculated values of $D$ (cm$^{-1}$), its components (spin-spin, $D_{ss}$; spin-orbit, $D_{so}$), and $E/D$ ratio for Models A and B using DF (BLYP functional and QRO method) and CAS techniques. The values in parentheses are those found when solvent effects are included through the COSMO approach.

<table>
<thead>
<tr>
<th></th>
<th>Model A</th>
<th>Model B</th>
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<tr>
<td></td>
<td>BLYP</td>
<td>CAS</td>
</tr>
<tr>
<td>$D_{so}$</td>
<td>-2.25</td>
<td>-3.56</td>
</tr>
<tr>
<td>$D_{ss}$</td>
<td>-0.38</td>
<td>-0.50</td>
</tr>
<tr>
<td>$D$</td>
<td>-2.63</td>
<td>-4.04</td>
</tr>
<tr>
<td>$E/D$</td>
<td>0.129</td>
<td>0.071</td>
</tr>
</tbody>
</table>

**Figure 2.22.** Schematic view of the orthogonality between the magnetic orbitals, which are displayed in different colours (blue and red) for each metal centre. The electronic densities delocalised for each Mn$^{III}$ ion meet at the nitrogen atoms in an orthogonal fashion.
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The nature and magnitude of the magnetic coupling were also examined using DFT calculations on the nonet and broken-symmetry singlet spin states of 2.2, resulting in a weak ferromagnetic coupling constant ($J = +0.5 \text{ cm}^{-1}$) between the two paramagnetic quintet Mn$^{\text{III}}$ ions, in excellent agreement with the experimental data. As suggested in previous work by G. Rajaraman et al., the nature of pairwise magnetic coupling can be explained by an accidental orthogonality between the Mn-N-O plane of the first Mn$^{\text{III}}$ ion and the Jahn-Teller axis of the second Mn$^{\text{III}}$ ion (Fig. 2.22). The result is no overlap between $z^2$ orbitals on adjacent metal ions, which are only able to delocalise electron density through the $\sigma$-pathway.

2.2.6 FT-IR and RAMAN Spectroscopy

2.2.6.1 FT-IR and Raman Measurements on $[\text{Mn}^{\text{II}}_2(\text{Naphth-sao})_2(\text{MeOH})_2].4\text{MeOH}$ (2.2)

Raman spectra were obtained from a polycrystalline sample of Naphth-saoH$_2$ and a 1.5% in KBr solid matrix of complex 2.2, while FT-IR spectra were obtained from polycrystalline samples of 2.2 and Naphth-soaH$_2$. The Raman spectra provide information in the 250 to 700 cm$^{-1}$ spectral region that is not accessible by our FT-IR measurements. For Naphth-saoH$_2$, the Raman spectrum shows two peaks at 425 and 530 cm$^{-1}$ with smaller associated bands at 448 and 518 cm$^{-1}$ respectively. These we tentatively ascribe to out-of-plane ring deformation vibrations. In the complex, only a single band at 507 cm$^{-1}$ is observed, and this may arise because of the increased rigidity of the complex (Fig. 2.23).

The intense IR peaks observed at 743 cm$^{-1}$ (Naphth-saoH$_2$) and 753 cm$^{-1}$ (2.2) respectively are attributed to aromatic $\nu$(C-H) out-of-plane deformation vibrations, readily observed for 1, 2-disubstituted naphthalene moieties. The equivalent Raman bands are known to be weak in nature and this is confirmed in our Raman measurement where we do not observe any significant bands here (Fig. 2.26). Likewise the IR (weak) and Raman (strong and sharp) bands in the 1587-1614 cm$^{-1}$ and 1368-1379 cm$^{-1}$ regions respectively (Fig. 2.27 and 2.28) are due to multiple aromatic $\nu$(C=C) stretching vibrations. The bands centred at 1633 cm$^{-1}$ may be
tentatively attributed to the $\nu$(C=N) oxime stretching mode, as observed elsewhere.$^{[44]}$ Attempts at assigning the $\nu$(N-O) stretching modes in Naphth-saoH$_2$ and 2.2 are severely hampered by the significant spectral overlap in the 900-1150 cm$^{-1}$ region of both the IR and Raman spectra (Fig. 2.23 and 2.24). Previous reports on ligating aromatic oximes have documented $\nu$(N-O) stretching IR bands in the ~1050-1250 cm$^{-1}$ spectral range and so should be considered here.$^{[45]}$ However, we cannot rule out the presence of multiple C-H out-of-plane deformation vibrational bands.$^{[43]}$ This uncertainty is further compounded by the multiple N-O bonding environments observed in 2.2.

Figure 2.23. Overlay of Raman spectra obtained from Naphth-saoH$_2$ (LH$_2$ - black line) and 2.2 (red).
Chapter 2: Ferromagnetic exchange in twisted, oxime-bridged $[\text{Mn}^{III}_2]$ and $[\text{Mn}^{III}_2\text{Zn}^{II}_2]$ dimers

Figure 2.24. Overlay of FT-IR and Raman spectra obtained from Naphth-saoH$_2$ (LH$_2$ - black and grey lines respectively) and 2.2 (red and blue lines respectively).

Figure 2.25. Raman spectra (black and red lines) in the 250-600 cm$^{-1}$ region obtained from crystalline sample of Naphth-saoH$_2$ (LH$_2$) and 2.2. All data were normalised and baseline corrected using standard methods.
Figure 2.26. Infra-Red (black and red lines) and Raman spectra (green and blue lines) obtained from crystalline sample of Naphth-saoH$_2$ (LH$_2$) and 2.2 in the 1300-1400 cm$^{-1}$ region highlighting the v(C-H) out-of-plane deformed vibrations. Data were normalised and baseline corrected using standard methods.

Figure 2.27. Infra-Red (black and red lines) and Raman spectra (green and blue lines) obtained from crystalline sample of Naphth-saoH$_2$ (LH$_2$) and 2.2 as viewed in the 1300-1420 cm$^{-1}$ spectral range.
2.3 Concluding Remarks

This chapter has described the serendipitous self-assembly of two model Mn dimer complexes. Firstly, a tetranuclear [Mn$^{III}_2$Zn$^{II}_2$] complex which has provided a model complex with which to examine the magneto-structural relationship in oxime-bridged Mn$^{III}$ complexes. SQUID magnetometry revealed ferromagnetic exchange ($J = +2.24$ cm$^{-1}$) through the highly twisted Mn-N-O-Mn unit, stabilising an $S = 4$ ground state. Magnetisation measurements confirmed the presence of significant anisotropy originating from the high spin d$^4$ Mn$^{III}$ ions. ac susceptibility confirmed slow relaxation of the magnetisation and SMM behaviour. HF EPR spectroscopy confirmed the magnetic analysis, affording the spin Hamiltonian parameters $D$(Mn$^{III}$) = -3.83 cm$^{-1}$ and $J = +2.33$ cm$^{-1}$. DFT calculations on a simplified model complex of 2.1 revealed a pronounced dependence of the exchange coupling on the relative twisting of the oxime moiety with respect to the metal ion positions, as suggested previously in more complicated [Mn$^{III}_3$] and [Mn$^{III}_6$] clusters.
Complex **2.2** is a symmetric dimer with a very simple [Mn-O-N-Mn]$_2$ magnetic core, allowing it to be an excellent and even more simple model complex with which to examine the magneto-structural relationship. SQUID magnetometry revealed weak ferromagnetic exchange ($J = +1.24$ cm$^{-1}$) mediated through the heavily twisted Mn-O-N-Mn moiety, with high field, high frequency EPR data determining a single ion anisotropic value ($D$(Mn$^{III}$) of -3.94 cm$^{-1}$. Theoretical studies afford calculated values of the exchange coupling and the anisotropy that are in excellent agreement with both SQUID and EPR experiments, and suggest that the weak ferromagnetism results from an accidental orthogonality between the Mn-N-O plane of one Mn$^{III}$ ion and the Jahn-Teller axis of the other.
2.4 Experimental

2.4.1 Instrumentation

2.4.1.1 Carbon, Hydrogen and Nitrogen Micro-analysis

C, H and N elemental analysis were performed using a Perkin Elmer Series II CHNS / O Analyser (2400 Series).

2.4.1.2 Infrared Spectroscopy

Infra-red spectra were recorded on a Perkin Elmer FT-IR Spectrum One spectrometer equipped with a Universal ATR Sampling accessory (ZnSe diamond).

2.4.1.3 $^1$H NMR Spectroscopy

Nuclear Magnetic resonance (NMR) Spectroscopic analysis was performed using a JEOL ECX-400 $^1$H NMR Spectrometer. NMR spectra were recorded at room temperature in CDCl$_3$. Chemical shifts ($\delta$) are indicated in ppm.

2.4.1.4 Raman Spectroscopy

Raman spectra were obtained in conjunction with Dr Alan G. Ryder, Director at the Nanoscale Biophotonics Laboratory situated within the School of Chemistry, NUI Galway. Raman measurements were recorded at room temperature using a Kaiser Optical Systems Raman spectrometer (RamanRxn2$^{TM}$ 1000 Analyzer) equipped with a 993 nm laser diode excitation source and an InGaAs array detector. A laser power of ~200 mW (at the sample) with an exposure time of 10 x 8 seconds was used and spectra were collected from 250 to 4000 cm$^{-1}$ (at a resolution of 5 cm$^{-1}$). Raman spectra of the coloured complex 2.2 were collected from a solid dispersion (approximately 1.5% by weight of complex) in dry KBr which was pressed into a disk using a hydraulic press and a 13 mm die set. This was done to minimise sample burning due to excessive absorption of excitation light. All data were normalised to the peak of maximum intensity and baseline corrected using standard methods.
2.4.1.5 Magnetic Susceptibility Measurements

Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 1.8 K and alternating current (ac) magnetic susceptibility data were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal’s constants. Each sample was set in an eicosane wax to avoid torqueing of the crystalline material. Magnetic measurements were performed by the Brechin group at the University of Edinburgh, Scotland, UK.

2.4.1.6 Single-Crystal X-ray diffraction

Diffraction data for 2.1 were collected at 100 K on an Oxford Diffraction SuperNova Dual diffractometer equipped with an Oxford Cryosystems LT device using Cu radiation (by Dr. A. Prescimone at the University of Edinburgh). The structure was solved by direct methods and refined by full-matrix least squares techniques on $F^2$ using all the reflections in the program CRYSTALS. The MeCN solvents of crystallisation in 2.1 were modelled as disordered and refined isotropically. DFIX and DANG restraints were also used.

X-ray diffraction studies on 2.2 were performed using an Oxford Xcalibur S Kappa CCD system using an enhanced Mo source (School of Chemistry, NUI Galway). Each data collection / reduction was carried out on the CrysAlisPro software package. The structures were solved by direct methods (SHELXS-97) and refined by full matrix least squares using SHELXL-97. SHELX operations were automated using the XSEED and OSCAIL software packages. All hydrogen atoms were modelled isotropically and assigned to idealised positions. All MeOH solvents of crystallisation were also modelled isotropically.

2.4.1.7 Electron Paramagnetic Resonance (EPR) Spectroscopy

High-frequency Electron Paramagnetic Resonance (HFPR) data were collected for complexes 2.1 and 2.2 on finely ground powder samples pressed into a KBr pellet (102 mg) in order to avoid field-alignment of the micro-crystallites within the
Chapter 2: Ferromagnetic exchange in twisted, oxime-bridged $[\text{Mn}^{III}_2]$ and $[\text{Mn}^{III}_2\text{Zn}^{II}_2]$ dimers

Measurements were performed in the temperature range 2.5 to 30 K and at high-frequencies between 100 and 430 GHz. The HF-EPR spectra were obtained using a broadband transmission-type probe that employs cylindrical light-pipes. Microwaves were generated using a phase-locked Virginia Diodes solid-state source operating at $13\pm1$ GHz, followed by a chain of multipliers. High magnetic fields were provided by an Oxford Instruments superconducting magnet.
2.4.2 Crystal structure information

Table 2.5. Crystallographic data for complexes 2.1 – 2.2.

<table>
<thead>
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<th>Complex</th>
<th>2.1.3.6MeCN</th>
<th>2.2.4MeOH</th>
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</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{97.2}H_{80.8}Mn_{2}N_{11.6}O_{14}Zn_{2}</td>
<td>C_{50}H_{54}N_{4}O_{14}Mn_{2}</td>
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<tr>
<td>( M_r (g \text{ mol}^{-1}) )</td>
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<td>1044.85</td>
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</tr>
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<td>( \beta/^\circ )</td>
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<td>90</td>
</tr>
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<td>( \gamma/^\circ )</td>
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<td>4735.0(2)</td>
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<td>4</td>
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<td>( T/K )</td>
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<td>14243 / 4330 (0.0264)</td>
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<td>( R^1 \text{ (ref)} )</td>
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</table>
Chapter 2: Ferromagnetic exchange in twisted, oxime-bridged [Mn$^{III}$]$_2$ and [Mn$^{III}$Zn$^{II}$]$_2$ dimers

<table>
<thead>
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<th>Complex</th>
<th>2.1.3.6MeCN</th>
<th>2.2.4MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goodness of fit on $F^2$</td>
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<td>1.133</td>
</tr>
</tbody>
</table>

$^a$ Includes guest molecules. $^b$ Mo-κ radiation, graphite monochromator. $^c$ $wR^2 = [\sum w(I_F - I_c)^2 / \sum wI_F^2]^{1/2}$. $^d$ For observed data. $^e$ $R1 = \sum \|I_F\| - \|I_c\| / \sum \|I_F\|$. 

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Chapter 2: Ferromagnetic exchange in twisted, oxime-bridged \([\text{Mn}^\text{III}_2]\) and \([\text{Mn}^\text{III}_2\text{Zn}^\text{II}_2]\) dimers

2.4.3 Synthetic Procedures

All manipulations were carried out under aerobic conditions using materials as received (reagent grade). Caution! Although we encountered no problems, care should be taken when using the potentially explosive perchlorate ion. Ph-saoH\textsubscript{2} and Naphth-saoH\textsubscript{2} were synthesised by the reaction of the precursor ketone / aldehyde with hydroxylamine and sodium acetate in EtOH as described in the text below.

2.4.3.1 Synthesis of (2-Hydroxyphenyl)(Phenyl)Methanone Oxime (Ph-SaoH\textsubscript{2})

![Chemical structure of Ph-SaoH\textsubscript{2}]

2-hydroxybenzophenone (25 g, 126.1 mmol, 1 eq.) and hydroxylamine hydrochloride (8.8 g, 126.1 mmol, 1 eq.) were dissolved in ethanol (200 cm\textsuperscript{3}) before adding sodium acetate (10.4 g, 126.1 mmol, 1 eq.) and, with constant stirring, heated under reflux for 4 hours at 100 °C. The precipitated salt was removed via filtration and the desired product obtained after solvent removal (under reduced pressure) and subsequent drying on a vacuum line in approximately 89% yield.

C, H, N Elemental Analysis

Calculated for: C\textsubscript{14}H\textsubscript{14}O\textsubscript{2.5}N\textsubscript{1} (Ph-saoH\textsubscript{2} 0.5H\textsubscript{2}O)

Theory (%): C 71.19, H 5.93; N 5.93.

Found (%): C 71.37, H 6.06; N 6.20.

Infrared Spectroscopy (cm\textsuperscript{-1}):

3354(b), 3052(w), 1626(m), 1606(m), 1494(w), 1444(s), 1415(m), 1375(m), 1326(m), 1291(m), 1241(s), 1220(s), 1155(m), 1074(w), 1102(m), 1033(m), 1016(m), 1000(s), 943(s), 932(s), 915(m), 827(m), 756(vs), 725(s), 697(vs), 687(vs).
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$^1H$ NMR (400 MHz, $\text{CDCl}_3$)

$\delta$ 6.73-7.61 (m, 9H, Ar-H), 12.06 (s, 1H, O-H).

2.4.3.2 Synthesis of 2-Hydroxy-1-Naphthaldehyde Oxime (Naphth-SaoH$_2$)

2-hydroxy-1-napthaldehyde (28.7 g, 166.9 mmol, 1.0 eq.) and hydroxylamine hydrochloride (11.6 g, 166.9 mmol, 1.0 eq.) were dissolved in ethanol (200 cm$^3$) before adding sodium acetate (13.7 g, 166.9 mmol, 1.0 eq.) and, with constant stirring, heated under reflux for 4 hours at 100 °C. The precipitated salt was removed via filtration and the desired product obtained after solvent removal (under reduced pressure) and subsequent drying on a vacuum line in approximately 92% yield.

C, H, N Elemental Analysis

Calculated for: C$_{11}$H$_9$O$_2$N$_1$

Theory (%): C 70.58, H 4.85; N 7.48.

Found (%): C 69.23, H 4.59; N 7.18.

Infrared Spectroscopy (cm$^{-1}$):

3309(b), 3012(w), 1632(m), 1590(m), 1525(w), 1481(m), 1464(m), 1413(m), 1368(w), 1345(w), 1268(s), 1239(s), 1182(s), 1161(m), 1143(m), 1079(m), 1033(m), 1012(s), 956(w), 934(s), 879(s), 853(s), 814(vs), 781(s), 772(vs), 742(vs), 717(vs), 678(s).

$^1H$ NMR (400 MHz, $\text{CDCl}_3$)

$\delta$ 7.19-7.98 (m, 6H, Ar-H), 9.14 (s, 1H, N=C-H), 10.89 (s, 1H, O-H).
2.4.3.3 Synthesis of $[\text{Mn}^{III}_2\text{Zn}^{II}_2\text{(Ph-sao)}_2\text{(Ph-saoH)}_4\text{(hmp)}_2] (2.1)$

$\text{Mn(ClO}_4)_2.6\text{H}_2\text{O} (0.36 \text{ g}, 1.0 \text{ mmol}, 1 \text{ eq.}), \text{Zn(NO}_3)_2.6\text{H}_2\text{O} (0.297 \text{ g}, 1.0 \text{ mmol}, 1 \text{ eq.}), \text{Ph-saoH}_2 (0.213 \text{ g}, 1 \text{ mmol}, 1 \text{ eq.}), \text{Hhmp} (0.22 \text{ g}, 2.0 \text{ mmol}, 2 \text{ eq.) and NEt}_3 (0.101 \text{ g}, 1.0 \text{ mmol}, 1 \text{ eq.) were stirred in MeCN (20 cm}^3) \text{ for 2 hours, filtered and allowed to stand. Black diamond shaped crystals formed upon slow evaporation of the mother liquor in approximately 40% yield over a period of 5 days. The crystals were removed from the liquor and dried \textit{in vacuo}.}$

$C, H, N \text{ Elemental Analysis}$

Calculated for: C$_{98}$H$_{81}$Mn$_2$N$_{12}$O$_{14}$Zn$_2$

Theory (%): C 61.99, H 4.34; N 8.94.

Found (%); C 61.83, H 4.72; N 8.77.

2.4.3.4 Synthesis of $[\text{Mn}^{III}_2\text{(Naphth-sao)}_2\text{(Naphth-saoH)}_2\text{(MeOH)}_2].4\text{MeOH} (2.2)$

$\text{MnCl}_2.4\text{H}_2\text{O} (0.25 \text{ g}, 1.3 \text{ mmol}, 1 \text{ eq.}), \text{Naphth-saoH}_2 (0.236 \text{ g}, 1.3 \text{ mmol}, 1 \text{ eq.}), \text{sodium 1-naphthoate} (0.25 \text{ g}, 1.3 \text{ mmol}, 1 \text{ eq.) and NaOMe (0.068 \text{ g}, 1.3 \text{ mmol}, 1 \text{ eq.) were stirred in MeOH (30 cm}^3) \text{ for 2 hours, filtered and allowed to stand. Black diamond shaped crystals were formed upon slow evaporation of the mother liquor in approximately 15% yield over a period of 7 days. The crystals were removed from the liquor and dried \textit{in vacuo}.}$

$C, H, N \text{ Elemental Analysis}$

Calculated for: C$_{50}$H$_{54}$N$_4$O$_{14}$Mn$_2$.3H$_2$O

Theory (%): C 54.64, H 4.49; N 5.09.

Found (%); C 54.73, H 4.36; N 5.44.

$\text{Infrared Spectroscopy (cm}^{-1})$

3383(vb), 1679(w), 1614 (s), 1592(s), 1570(m), 1555(m), 1533(s), 1504(m), 1453(s), 1427(s), 1388(s), 1324(s), 1300(m), 1282(s), 1247(s), 1192(s), 1163(m), 1146(m),
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1092(m), 1050(vs), 1029(m), 1014(w), 950(s), 926(w), 883(w), 865(m), 826(s), 776(s), 753(vs), 679(w).

*Raman Spectroscopy (993 nm excitation) (cm$^{-1}$):*

236(w), 241(w), 335(w), 354(w), 369(w), 428(w), 467(w), 505(m), 530(w), 556(w), 635(w), 650(s), 682(m), 761(m), 774(w), 879(w), 925(w), 957(w), 1028(m), 1049(w), 1091(w), 1142(w), 1194(m), 1215(w), 1247(w), 1377(s), 1427(w), 1427(s), 1454(m), 1528(m), 1564(w), 1591(w), 1614(w).
2.5 References


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Chapter Three

Bulking Up: Hexanuclear Oximato Fe$^{III}$ Complexes Surrounded by Sterically Demanding Co-Ligands
3.1 Introduction

Functionalised phenolic oximes have extensive application as ligands in the solvent extraction of copper, accounting for roughly 25% of worldwide production.\[1\] Complex stability upon binding is (at least in part) due to the formation of pseudo macrocyclic $[\text{Cu}(\text{L})_2]$ (where $\text{L}$ = phenolic oxime) moieties. Recent studies by Forgan et al have shown that extractant strength may be tuned by controlling the extent of outer sphere H-bonding interactions.\[2\] Although exhibiting a great affinity towards copper, oximes have also formed many interesting (often polymetallic) coordination complexes with other f row transition metals.\[3\] A good example is the use of derivatised salicylaldoximes (R-saoH$_2$; R = H, Me, Et, Ph, 'Bu etc.) in the formation of a large family of $[\text{Mn}_3]$ and $[\text{Mn}_6]$ Single-Molecule Magnets (SMMs).\[4\] Moreover it was shown inextricably that the ground spin states of these magnetic cages could be tuned and controlled by modification of the bridging salicylaldoxime ligands at their R positions.\[5\] Although $[\text{Mn}_3]$ and $[\text{Mn}_6]$ cage formation was found to be predictable and under near complete synthetic control, investigations into the coordination chemistry of the same salicylaldoximes with iron has proven to be far more difficult and less predictable, giving rise to ferric cages of numerous sizes (ranging from $\{\text{Fe}_2\}$\[6\] to $\{\text{Fe}_{12}\}$\[7\]) and topologies, depending on specific synthetic factors, such as the type of oxime,\[8\] the nature of the co-ligand (e.g. carboxylate), solvent identity and temperature/pressure.\[9\]

With these thoughts in mind we decided to examine the role of sterically demanding oximes and carboxylate co-ligands towards Fe-oxime cage formation\[10\] and quickly settled on investigating combinations of 2-hydroxy-1-naphthaldehyde oxime (Naphth-sao, C$_{11}$H$_9$N$_1$O$_2$; Scheme 3.1) and the carboxylate anions 1-naphthoate ($\text{O}_2\text{C-C}_9\text{H}_8$) and 9-anthracenecarboxylate ($\text{O}_2\text{C-C}_{14}\text{H}_{10}$) (Scheme 3.1). To this end we present the hexametallic siblings $[\text{Fe}^{\text{III}}_6\text{O}_2(\text{Naphth-sao})_2(\text{O}_2\text{C-C}_{10}\text{H}_8)_{10}(\text{H}_2\text{O})_2]\cdot8\text{MeCN \hspace{1cm} (3.1)}$ and $[\text{Fe}^{\text{III}}_6\text{O}_2(\text{Naphth-sao})_2(\text{O}_2\text{C-C}_{14}\text{H}_{10})_{10}(\text{H}_2\text{O})_2]\cdot8\text{MeCN \hspace{1cm} (3.2)}$, and the tetranuclear cube-like cage $[\text{Fe}^{\text{III}}_4(\text{tert-butyl-sao})_4(\text{MeOH})_4(\text{Cl})_4] \hspace{1cm} (3.3)$ constructed using 3,5-di-tert-butyl salicylaldoxime (Scheme 3.1).\[11\]
3.2 Results and Discussion

The reaction of FeCl₂·4H₂O, Naphth-saoH₂, sodium 1-naphthoate and NaOMe in MeOH resulted in the formation of a black solid after evaporation of the mother liquor. Subsequent dissolution of this solid in a 50:50 MeCN:CH₂Cl₂ solvent mixture, followed by filtration and slow evaporation of the mother liquor afforded dark red crystals of [Fe₆O₂(Naphth-sao)₂(O₂C-C₁₀H₈)₁₀(H₂O)₂]·8MeCN (3.1) in 20% yield. As anticipated, employing Sodium 9-Anthracenecarboxylate gave rise to the analogous hexanuclear complex [Fe₆O₂(Naphth-sao)₂(O₂C-C₁₄H₁₀)₁₀(H₂O)₂]·8MeCN (3.2) in 15% yield. Complexes 3.1 and 3.2 both crystallise in the triclinic P-1 space group. Their inorganic cores consist of two fused [Fe₃(µ₃-O)(O₂-CR)₅] triangular units (where R = C₁₀H₈ in 3.1; R = C₁₄H₁₀ in 3.2), lying off-set to one another (Fig. 3.1 and 3.2). Complexes 3.1 and 3.2 join a small group of previously reported oxime-based hexametallic cages which include [Fe₆O₂(O₂CPh)₁₀(salox)₂] (salox = salicylaldoxime)⁹ and [Fe₆O₂(O₂CPh)₁₀(R-sao)₂] (R-saoH₂ = 3-^Bu-5-NO₂-
salicyaldoxime and 3-tBu-salicyaldoxime).\[9b\] They also have structural similarity to another family of hexanuclear cages of general formula \([\text{Fe}_6\text{O}_2\text{(OH)}_2\{(\text{O}_2\text{C-}R)_{10}\text{(L)}_2\}] (\text{R} = \text{tBu}, \text{L} = 2-(2-hydroxyethyl)-pyridine[12]; and \text{R} = \text{tBu} \text{ or Me}, \text{L} = 2-(2-hydroxyethyl)-pyridine or 6-methyl-2-(hydroxymethyl)pyridine),[13] whose inorganic cores differ only in the presence of two \(\mu_2\)-bridging \text{OH}^- anions.[14]

Each Fe\text{III} centre exhibits a distorted octahedral geometry. The triangular units in 3.1 and 3.2 closely resemble the classic, ubiquitous oxo-bridged trimeric species of general formula \([\text{M}_3(\mu_3-\text{O})\{(\text{O}_2\text{-CR})_6\text{(L)}_3\}]^{n+} (n = 0, 1),[15]\ differing only in the replacement of one carboxylate bridging ligand with one Naphth-sao\(^2^-\) ligand per \{Fe\text{III}_3(\mu_3-\text{O})\{(\text{O}_2\text{-CR})_5\}^2\) unit. Indeed these \(\eta^1:\eta^1:\eta^2: \mu_3\)-bridging oxime ligands are responsible for joining the trimeric units together via their oximic O atoms (O2 in 3.1 and O3 in 3.2) with angles of \(\text{Fe3-O2-Fe3} = 104.48\)° and \(\text{Fe3-O3-Fe3} = 106.49\)°, respectively. Moreover, each of these doubly deprotonated oxime ligands (Naphth-sao\(^2^-\) or \text{t}er-t-butyl-sao\(^2-\)) are able to bridge one Fe\text{III} edge of each \{Fe\text{III}_3(\mu_3-\text{O})\} unit (Fe1…Fe3 in 3.1 and Fe2…Fe3 in 3.2) to form Fe-N-O-Fe pathways (Fig. 3.1). The coordination spheres at Fe2 in 3.1 and Fe1 in 3.2 (and symmetry equivalents) are completed by terminal \text{H}_2\text{O} ligands (Fe2-O14 = 2.118 Å, Fe1-O14 = 2.103 Å). Eight MeCN solvents of crystallisation per [Fe\text{III}_6] cage are also present in both crystal structures, H-bonding \text{via} their N atoms to nearby carboxylate and \text{H}_2\text{O} ligands (e.g. C43(H43)…N5 = 2.690 Å and O14…N2 = 2.812 Å in 3.1; C50(H50)…N2 = 2.671 Å and O14…N2 = 2.834 Å in 3.2). Both complexes 3.1 and 3.2 exhibit intra-molecular \(\pi-\pi\) interactions \text{via} their naphthoate and anthracenolate rings, in the form of \(\pi-\pi\) contacts (e.g. [C\text{46}-C\text{55},\text{centroid}]^-[C\text{35}-C\text{40},\text{centroid}] = 4.042 Å (3.1) and [C\text{13}-C\text{26}]^-[C\text{58}-C\text{71}] = 3.988 Å (3.2)) (Fig. 3.3).

The individual \{Fe\text{III}_6\} units in 3.1 arrange in superimposable 1-D rows along the \text{b} cell direction (Fig. 3.2). These rows stack on top and by the side of one another (along the \text{ac} plane) in an interdigitated fashion, propagated through C-H-\(\pi\) interactions between \{Fe\text{III}_6\} moieties (e.g. C9(H9)…[C\text{14}-C\text{19}] = 2.934 Å) (Fig. 3.3). The MeCN molecules of crystallisation lie in between the cages in 3.1, stabilising this packing arrangement through the aforementioned inter-molecular interactions.
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The individual {Fe$_6$} units in 3.2 arrange themselves into superimposable rows along the $c$ cell direction and are linked via symmetry related inter-molecular $\pi-\pi$ interactions ([C$_{29}$-C$_{34}$]$_{\text{centroid}}$–[C$_{29'}$–C$_{34'}$]$_{\text{centroid}} = 3.842$ Å) (Fig. 3.2). These rows then stack in off-set parallel rows in both the $a$ and $b$ cell directions. MeCN molecules of crystallisation lie in between the 1-D rows and are held by hydrogen bonding, as observed previously in 3.1.

![Diagram of crystal structure and bonding modes](image)

**Figure 3.1.** (left) Crystal structure of 3.1 as viewed perpendicular to the {Fe$_6$} plane. (right) The $\eta^1:\eta^1:\eta^2$: $\mu_3$-bonding mode demonstrated by the oxime ligands in 3.1 and 3.2. Colour code: Orange (Fe), Red (O), Blue (N), Grey (C). Hydrogen atoms omitted for clarity.
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Figure 3.2. Crystal structure of 3.2 as viewed perpendicular (top) and parallel (bottom) to the [7] plane. Colour code as used previously. Hydrogen atoms omitted for clarity.

Figure 3.3. Space-fill representations of 3.2 as viewed parallel (top) and perpendicular (bottom) to the $\{\text{Fe}_2\text{O}\}$ planes within the $\{\text{Fe}_6\}$ core.
Figure 3.4. Polyhedral representation of the packing observed in the crystal structures of 3.1 (left) and 3.2 (right) as viewed along the b and c axes of their unit cells, respectively. Hydrogen atoms and MeCN molecules of crystallisation have been omitted for clarity in both cases.

Figure 3.5. 1-D row of \{Fe₆\} units in 3.2 propagated by inter-molecular π-π interactions along the c cell direction. Hydrogen atoms have been omitted for clarity. See main text for details.

Reactions of the rarely employed 3,5-di-tert-butyl-salicylaldoxime (tert-butyl-saoH₂; Scheme 3.1) in combination with bulky carboxylates proved fruitless, but omission of the co-ligand resulted in formation of \([\text{Fe}^{III}_4(\text{Tert-butyl-sao})_4(\text{MeOH})_4(\text{Cl})_4]\) (3.3) via the simple reaction of FeCl₃·₄H₂O and tert-butyl-saoH₂ in a basic methanolic solution (Fig. 3.6). Dark red crystals of 3.3 were obtained in 45% yield and crystallised in the monoclinic C2/c space group (Z = 4). The inorganic core in 3.3 comprises four Fe³⁺ ions (Fe1, Fe2 and symmetry equivalents) linked into a distorted tetrahedral arrangement via four doubly deprotonated Tert-butyl-sao²⁻ ligands,
each employing an $\eta^1:\eta^1:\eta^2: \mu_3$-bonding motif (Fig. 3.6). The result is the formation of a severely distorted \( \{\text{Fe}^{III}_4(\text{NO})_4\}^{4+} \) cube, a topology observed only once previously in Fe-oxime chemistry.\(^6\) Each Fe\(^{III} \) ion exhibits a distorted octahedral geometry, with their coordination spheres completed by one Cl\(^- \) ion (Fe1-Cl2 = 2.313 Å; Fe2-Cl1 = 2.301 Å) and one terminal MeOH ligand (Fe1-O5A = 2.097 Å; Fe2-O6A = 2.093 Å). The intra-molecular Fe1=Fe1', Fe1=Fe2 and Fe2=Fe2' distances are (Å): 4.043, 3.581 and 4.152. Interestingly, and despite huge efforts, no other ferric cages were obtained with or without the inclusion of co-ligands during our synthetic investigations with 3,5-di-\text{tert}-butyl-salicylaldoxime. This may tentatively be attributed to the steric nature of the 3,5-di-\text{tert}-butyl-salicylaldoxime ligand.

Figure 3.6. (left) Crystal structure of 3.3. (right) The $\eta^1:\eta^1:\eta^2: \mu_3$-bonding mode demonstrated by the 3,5-di-\text{tert}-butyl salicylaldoxime (\text{tert}-butyl-sao\(^- \)) ligands in 3.3. Colour code as used previously in the text (yellow = Cl). Hydrogen atoms have been omitted for clarity.

Intra-molecular interactions are observed in 3.3 in the form of rather long $\pi-\pi$ interactions ($[\text{C}_2-\text{C}_7]_{\text{centroid}} - [\text{C}_2-\text{C}_7]_{\text{centroid}} = 4.587 $ Å) and hydrogen bonding between the terminal Cl\(^- \) ligands (Cl1) and juxtaposed terminal MeOH ligands (Cl1=H5A(O5A) = 2.266 Å). The \{Fe\(_4\)\} units in 3.3 pack in a brickwork motif along the \textit{ab} cell plane.
These 2D sheets then stack in an off-set parallel arrangement along the $c$ direction of the unit cell (Fig. 3.7). The individual $\{\text{Fe}_4\}$ moieties are connected through a combination of inter-molecular C-H-$\pi$ exchanges (i.e. $C31(H31B)^{-}\text{[C17-C22]}_{\text{centroid}} = 2.888 \text{ Å}$ and $C32(H32B)^{-}\text{[C2-C7]}_{\text{centroid}} = 3.174 \text{ Å}$) and H-bonding interactions between the terminal Cl$^-$ ions (Cl1) and methyl protons belonging to $^{t}$Bu groups of adjacent tert-butyl-sao$^2$ ligands (Cl1–H29(C29) = 2.911 Å).

Figure 3.7. Packing observed in the crystal structure of 3.3 as viewed along the $c$ (left) and $b$ (right) axes of the unit cell. Hydrogen atoms have been omitted for clarity. Colour code as used previously in the text.

Infra-red spectroscopic studies were carried out on air dried crystalline samples of 3.1-3.3. Weak IR bands were observed in the 1555-1597 cm$^{-1}$ region of the spectra and are attributed to multiple aromatic $\nu$(C=C) stretching vibrations.$^{[16]}$ The multiple bands centred on the 1578-1616 cm$^{-1}$ region of the spectra comprise indistinguishable $\nu$(CO) carboxylate and $\nu$(C=N) oxime stretching modes, as observed elsewhere.$^{[17]}$ Attempts at assigning the $\nu$(N-O) oxime stretching modes in 3.1-3.3 were severely hampered by the significant spectral overlap in the 900-1150 cm$^{-1}$ region of the IR spectra. Previous reports on ligating aromatic oximes have documented $\nu$(N-O) stretching IR bands in the ~1050-1250 cm$^{-1}$ spectral range and so should be considered here.$^{[18]}$ Quenching due to Fe$^{III}$ ligation in complexes 3.1 and 3.2 rendered all solid state fluorescence studies fruitless.
3.2.1 Magnetic Susceptibility Studies

Magnetic susceptibility ($\chi_M$) measurements were carried out on powdered polycrystalline samples of 3.1 and 3.3 in the 300-5 K temperature range, in an applied dc field of 0.1 T (Fig. 3.9). The room temperature $\chi_M T$ values of 6.38 (3.1) and 9.54 (3.3) cm$^3$ mol$^{-1}$ K are significantly lower than expected for six and four non-interacting Fe$^{III}$ ions (26.25 (3.1) and 17.5 (3.3) cm$^3$ mol$^{-1}$ K, assuming $g = 2.0$), respectively. Such observations are indicative of dominant antiferromagnetic interactions between the Fe$^{III}$ ions in both complexes. For 3.1 the $\chi_M T$ product decreases gradually with decreasing temperature, before a steeper decline is witnessed below approximately 50 K, reaching a minimum value of 1.46 cm$^3$ mol$^{-1}$ K at 5 K. Fitting of the experimental data for (3.1) required use of the 3-J model ($J_1$ mediated by carboxylate and oxide; $J_2$ by carboxylate, oxide and oxime; and $J_3$ by alkoxide) described in Fig. 3.8 and equation 3.1, affording the best-fit parameters $J_1 = -69.35$ cm$^{-1}$, $J_2 = -41.66$ cm$^{-1}$ and $J_3 = -0.32$ cm$^{-1}$, with $g$ fixed to $g = 2.00$, resulting in a $S = 0$ ground state. Such values are consistent with those obtained from previously reported analogues.$^{[9a]}

$$
\hat{H} = -2J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_1' \cdot \hat{S}_2' + \hat{S}_2' \cdot \hat{S}_3') - 2J_2(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_1' \cdot \hat{S}_3') - 2J_3(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_1' \cdot \hat{S}_3')$

Equation 3.1.

$$
\hat{H} = -2J_1(\hat{S}_1 \cdot \hat{S}_1' + \hat{S}_2 \cdot \hat{S}_2') - 2J_2(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1' \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1' \cdot \hat{S}_2')$

Equation 3.2.
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**Figure 3.8.** Schematic of the models used to fit the magnetic susceptibility data of complex 3.1 (left) and complex 3.3 (right). Note: for clarity not all magnetic exchange pathways have been labelled. See main text for details.

The $\chi_{M\text{T}}$ vs. T plot for complex 3.3 is also indicative of dominant antiferromagnetic exchange and a diamagnetic ground state (Fig. 3.9). Fitting of the magnetic susceptibility data employed the 2-J model of Equation 3.2, illustrated in Fig. 3.8, in which $J_1$ represents the Fe$1\ldots$Fe$1'$ and Fe$2\ldots$Fe$2'$ vectors comprising $2 \times$ Fe-N-O-Fe oxime bridging pathways, and $J_2$ represents the Fe$1\ldots$Fe$2$, Fe$1'+\ldots$Fe$2'$, Fe$1\ldots$Fe$2'$ and Fe$1'+\ldots$Fe$2$ vectors comprising $1 \times$ Fe-N-O-Fe and $1 \times$ Fe-O-Fe magnetic exchange pathway (Fig. 3.8). The best fit afforded $J_1 = -16.0$ cm\textsuperscript{-1} and $J_2 = -2.0$ cm\textsuperscript{-1}, with $g$ fixed to $g = 2.00$, which are comparable to the parameters fitted from the structurally similar [Fe$4$(Me-sao)$4$(Me-saoH)$_4$] (where Me-saoH$_2$ = 2'-hydroxyacetophenone oxime) (Table 3.1.).\textsuperscript{[6]}

**Table 3.1.** Equivalent Spin Hamiltonian parameters obtained from 3.3 and its previously reported analogue.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$J_1$ (cm\textsuperscript{-1})</th>
<th>$J_2$ (cm\textsuperscript{-1})</th>
<th>$g$</th>
<th>Ground Spin State (S)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>-16.0</td>
<td>-2.0</td>
<td>2.00</td>
<td>0</td>
<td>This work</td>
</tr>
<tr>
<td>[Fe$4$(Me-sao)$_4$(Me-saoH)$_4$]\textsuperscript{*}</td>
<td>-12.4</td>
<td>-5.5</td>
<td>2.01</td>
<td>0</td>
<td>[6]</td>
</tr>
</tbody>
</table>

(* Me-saoH$_2$ = 2’-hydroxyacetophenone oxime)
3.3 Concluding Remarks

We have described the synthesis of two hexanuclear ferric cages \([\text{Fe}^{III}_6\text{O}_2\text{Naphth-sao}_2\text{O}_2\text{C-C}_{10}\text{H}_{8}\text{H}_2\text{O}]\cdot8\text{MeCN}\) (3.1) and \([\text{Fe}^{III}_6\text{O}_2\text{Naphth-sao}_2\text{O}_2\text{C-C}_{14}\text{H}_{10}\text{H}_2\text{O}]\cdot8\text{MeCN}\) (3.2). The core topologies in 3.1 and 3.2 are derived from the fusion of two \(\{\text{Fe}^{III}_3\text{O}[\text{O}_2\text{CR}]_5\}^{2+}\) triangular units \((R = \text{C}_{10}\text{H}_{8}; \text{C}_{14}\text{H}_{10})\) and are encased by an organic sheath provided by the combination of extremely bulky polyphenolic oxime and carboxylate ligands. The bulky 3,5-di-tert-Butyl-salicylaldoxime (tert-butyl-saoH) ligand led to the formation of the distorted cubane complex \([\text{Fe}^{III}_4(\text{tert-butyl-sao})_4\text{MeOH}_4\text{Cl}]_4\) (3.3). Magnetic susceptibility data obtained for 3.1 and 3.3 revealed relatively strong antiferromagnetic exchange between nearest neighbours in both cases, leading to diamagnetic ground states. Best-fit spin Hamiltonian parameters were \(J_1 = -69.35 \text{ cm}^{-1}, J_2 = -41.66 \text{ cm}^{-1}, J_3 = -0.23 \text{ cm}^{-1}\) (3.1) and \(J_1 = -16.0 \text{ cm}^{-1}, J_2 = -2.0 \text{ cm}^{-1}\) (3.3).
3.4 Experimental

3.4.1 Instrumentation

3.4.1.1 Carbon, Hydrogen and Nitrogen Micro-analysis
C, H and N elemental analysis were performed using a Perkin Elmer Series II CHNS / O Analyser (2400 Series).

3.4.1.2 Infrared Spectroscopy
Infra-red spectra were recorded on a Perkin Elmer FT-IR Spectrum One spectrometer equipped with a Universal ATR Sampling accessory (ZnSe diamond).

3.4.1.3 $^1$H NMR Spectroscopy
Nuclear Magnetic resonance (NMR) Spectroscopic analysis was performed using a JEOL ECX-400 $^1$H NMR Spectrometer. NMR spectra were recorded at room temperature in CDCl$_3$. Chemical shifts (δ) are indicated in ppm.

3.4.1.4 Magnetic Susceptibility Measurements
Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 1.8 K and alternating current (ac) magnetic susceptibility data were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal’s constants. Each sample was set in an eicosane wax to avoid torqueing of the crystalline material. Magnetic measurements were performed by the Brechin group at the University of Edinburgh, Scotland, UK.

3.4.1.5 Single-Crystal X-ray diffraction
Complexes 3.1-3.3 were collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source. Each data reduction was carried out on the CRYSALISPRO software package. The structures were solved by direct methods (SHELXS-97)$^{[19]}$ and refined by full matrix least squares using SHELXL-97.$^{[20]}$ SHELX operations were automated using the OSCAIL software package.$^{[21]}$ All
hydrogen atoms in 3.1-3.3 were assigned to calculated positions. All non-hydrogen atoms were refined as anisotropic. A DFIX restraint was placed on a single MeCN solvent of crystallisation in 3.2 (labelled C93-C94-N5). Crystal data and refinement parameters are tabulated in Table 3.2. Single crystals of complex 3.2 were found to be weakly diffracting at higher angles and therefore several collections were attempted. Our best data set has been supplied in this work (R1 = 0.1285).
### 3.4.2 Crystal structure information

Table 3.2. Single crystal X-ray diffraction data collected on complexes 3.1-3.3

<table>
<thead>
<tr>
<th></th>
<th>3.1</th>
<th>3.2</th>
<th>3.3</th>
</tr>
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<td><strong>Formula</strong>&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>C&lt;sub&gt;64&lt;/sub&gt;H&lt;sub&gt;100&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;Cl&lt;sub&gt;4&lt;/sub&gt;Fe&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>monoclinic</td>
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<td>P-1</td>
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<td>16.5927(17)</td>
<td>25.946(3)</td>
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<td>17.0191(15)</td>
<td>18.4694(9)</td>
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<tr>
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<td>17.936(2)</td>
<td>20.669(2)</td>
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<td><strong>β (°)</strong></td>
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<tr>
<td><strong>γ (°)</strong></td>
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<td><strong>Meas./indep.(R&lt;sub&gt;int&lt;/sub&gt;) refl.</strong></td>
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<td>14712/3444 (0.203)</td>
<td>6792/4247 (0.070)</td>
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<td>0.944</td>
<td>1.036</td>
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</table>

<sup>a</sup> Includes guest molecules.  
<sup>b</sup> Mo-Kα radiation, graphite monochromator.  
<sup>c</sup> wR<sub>2</sub> = [Σw(F<sub{o}</sub>-F<sub>c</sub>)<sup>2</sup>]/ [Σw(F<sub{o}</sub>)<sup>2</sup>]<sup>1/2</sup>.  
<sup>d</sup> For observed data.  
<sup>e</sup> R<sub>1</sub> = Σ||F<sub{o}</sub>||-|F<sub>c</sub>||/ Σ||F<sub{o}</sub>||.
3.4.3 Synthetic Procedures

All reactions were performed under aerobic conditions and all reagents and solvents were used as purchased. Ligands Naphth-saoH₂ and Tert-butyl-saoH₂ were synthesised using literature methods.[22] Carboxylic acids used (1-Naphthoic acid and 9-Anthracene carboxylic acid) were converted to their sodium salts via a two hour reaction with NaOMe in MeOH. Solvent was removed via rotary evaporation.

3.4.3.1 Synthesis of 2-Hydroxy-1-Naphthaldehyde Oxime (Naphth-SaoH₂)

2-hydroxy-1-napthaldehyde (28.74 g, 166.9 mmol, 1.0 eq.) and hydroxylamine hydrochloride (11.6 g, 166.9 mmol, 1.0 eq.) were dissolved in ethanol (200 cm³) before adding sodium acetate (13.7 g, 166.9 mmol, 1.0 eq.) and, with constant stirring, heated under reflux for 4 hours at 100 °C. The precipitated salt was filtered off and the solvent was removed on a rotary evaporator until an oily substance appeared then dried using vacuum pump in approximately 92% yield.

C, H, N Elemental Analysis

Calculated for: C₁₁H₉O₂N₁

Theory (%): C 70.58, H 4.85; N 7.48.

Found (%): C 69.23, H 4.59; N 7.18.

Infrared Spectroscopy (cm⁻¹):

3309(b), 3012(w), 1632(m), 1590(m), 1525(w), 1481(m), 1464(m), 1413(m), 1368(w), 1345(w), 1308(m), 1268(s), 1239(s), 1182(s), 1161(m), 1143(m), 1079(m), 1033(m), 1012(s), 956(w), 934(s), 879(s), 853(s), 814(vs), 781(s), 772(vs), 742(vs), 717(vs), 678(s).
Chapter Three: Hexanuclear Oximato Fe\textsuperscript{III} Complexes Surrounded by Sterically Demanding Co-Ligands

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})

\[ \delta 7.19-7.98 \text{ (m, 6H, Ar-H), 9.14 (s, 1H, N=C-H), 10.89 (m, 2H, O-H).} \]

3.4.3.2 Synthesis of 3,5-di-tert-butyl-salicyladoxime (Tert-butyl-SaoH\textsubscript{2})

3,5-Di-tert-butyl-2-hydroxybenzaldehyde (5.00 g, 21.34 mmol, 1.0 eq.) and hydroxylamine hydrochloride (1.50 g, 45.45 mmol, 2.13 eq.) were dissolved in ethanol (100 cm\textsuperscript{3}) before adding sodium acetate (1.75 g, 21.34 mmol, 1.0 eq.) and, with constant stirring, heated under reflux for 4 hours at 100 °C. The precipitated salt was filtered off and the solvent was removed on a rotary evaporator until an oily substance appeared then dried using vacuum pump in approximately 95% yield.

\textit{C, H, N Elemental Analysis}

Calculated for: C\textsubscript{15}H\textsubscript{23}N\textsubscript{1}O\textsubscript{2}

Theory (%): C 72.23, H 9.30; N 5.62.

Found (%): C 72.07, H 9.28; N 5.51.

\textit{Infrared Spectroscopy (cm\textsuperscript{-1})}:

3433(m), 2954(m), 2871(w), 1635(w), 1607(w), 1483(w), 1462(m), 1437(s), 1391(m), 1361(m), 1312(m), 1289(m), 1264(w), 1241(s), 1173(m), 1132(w), 1025(w), 1005(s), 977(w), 957(m), 927(w), 902(w), 883(m), 827(m), 800(m), 749(s), 728(s), 707(s).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})

\[ \delta 1.27 \text{ (s, 9H, C(CH}_3)_3), 1.42 \text{ (s, 9H, C(CH}_3)_3), 7.00-7.35 \text{ (m, 2H, Ar-H), 8.23 (s, 1H, N=C-H), 10.02 (s, 2H, O-H).} \]
3.4.3.3 Synthesis of $[\text{Fe}^{III}_6\text{O}_2(\text{Naphth-sao})_2(\text{O}_2\text{C-C}_{10}\text{H}_8)_{10}(\text{H}_2\text{O})_2]\cdot8\text{MeCN}$ (3.1)

$\text{FeCl}_2\cdot4\text{H}_2\text{O}$ (0.25 g, 1.26 mmol), $\text{Naphth-saoH}_2$ (0.235 g, 1.26 mmol), Sodium 1-Naphthoate (0.242 g, 1.25 mmol) and NaOMe (0.068 g, 1.26 mmol) were stirred in $\text{MeOH}$ (30 cm$^3$) for 2 h, filtered and allowed to evaporate to dryness. The resultant solid was dissolved in a 1:1 MeCN:$\text{CH}_2\text{Cl}_2$ solvent mixture, filtered and left to stand. Dark red crystals of 3.1 were formed upon slow evaporation in 20% yield over a period of 5 days.

$C, H, N$ Elemental Analysis

Calculated for: C$_{148}$H$_{112}$N$_{10}$O$_{28}$Fe$_6$

Theory (%): C 63.18, H 4.01; N 4.98.

Found (%): C 63.37, H 3.84; N 4.55.

Infrared Spectroscopy (cm$^{-1}$):

3051(w), 1617(w), 1597(w), 1578(w), 1541(m), 1525(m), 1509 (m), 1459(w), 1408(s), 1375(s), 1343(vs), 1257(m), 1209 (w), 1184(w), 1157(w), 1139(w), 1077(w), 1037(w), 1010(w), 998(w), 941(m), 870(vw), 826(w), 782(vs), 757(m), 750(m), 672(w).

3.4.3.4 Synthesis of $[\text{Fe}^{III}_6\text{O}_2(\text{Naphth-sao})_2(\text{O}_2\text{C-C}_{14}\text{H}_{10})_{10}(\text{H}_2\text{O})_2]\cdot8\text{MeCN}$ (3.2)

$\text{FeCl}_2\cdot4\text{H}_2\text{O}$ (0.25 g, 1.26 mmol), $\text{Naphth-saoH}_2$ (0.235 g, 1.26 mmol), Sodium 9-Anthracene carboxylate (0.307 g, 1.26 mmol) and NaOH (0.05 g, 1.25 mmol) were stirred in $\text{EtOH}$ (30 cm$^3$) for 2 h, filtered and allowed to evaporate to dryness. The resultant solid was then dissolved in a 1:1 MeCN:$\text{CH}_2\text{Cl}_2$ solvent mixture, filtered and left to stand. Dark red crystals of 3.2 were formed upon slow evaporation in 15% yield after 5 days.

$C, H, N$ Elemental Analysis

Calculated for C$_{188}$H$_{132}$N$_{10}$O$_{28}$Fe$_6$:

Theory (%): C 68.13, H 4.01; N 4.23.

Found (%): C 68.37, H 3.84; N 4.11.
Infrared Spectroscopy (cm$^{-1}$):

2982(vb), 1616(w), 1555(s), 1529(m), 1487 (w), 1425(s), 1391(s), 1317(s), 1279(m), 1248(w), 1187(w), 1143(w), 1092(w), 1034(w), 1014(m), 954(m), 884(w), 866.2(w), 846(w), 825(w), 782(w), 729(s), 679(m), 662(m).

3.4.3.5 Synthesis of $[\text{Fe}^{\text{III}}]_{4}\text{(Tert-butyl-sao)}_{4}\text{(MeOH)}_{4}\text{(Cl)}_{4}$ (3.3).

FeCl$_2$·4H$_2$O (0.25 g, 1.26 mmol) in MeOH (25 cm$^3$), 3,5-di-tert-butyl-salicylaldoxime (0.313 g, 1.26 mmol) and NaOH (0.05 g, 1.26 mmol) were stirred in EtOH (30 cm$^3$) for 2 h after which it was filtered to afford a purple-black mother liquor. Slow evaporation of the solvent afforded X-ray quality crystals of 3.3 in 45% yield.

C, H, N Elemental Analysis

Calculated for C$_{64}$H$_{100}$N$_4$Cl$_4$Fe$_4$O$_{12}$:

Theory (%): C 51.87, H 6.80; N 3.78.

Found (%): C 51.42, H 6.54; N 3.30.

Infrared Spectroscopy (cm$^{-1}$):

3243(w), 2956(m), 2905(w), 2869(w), 1602(w), 1586(m), 1548(w), 1534(w), 1478(w), 1460(w), 1423(m), 1387(w), 1363(m), 1296(m), 1273(m), 1253(s), 1232(w), 1201(m), 1174(m), 1136(w), 1118(w), 1005(m), 973(s), 954(s), 930(w), 902(w), 874(w), 842(s), 817(w), 775(m), 749(m), 711(s).
3.5 References


Chapter Four

Solvothermal-Assisted Synthesis of Discrete Cages and Extended Networks

Comprising

\[ \{\text{Cr}_3\text{O(O}_2\text{CR})_3(\text{oxime})_3\}\text{}^{2-} \quad (R = \text{H, CH}_3, \text{C(CH}_3)_3, \text{C}_{14}\text{H}_9) \]

Building Blocks
4.1 Introduction

Hydro / solvo-thermal synthesis comprises the oven heating of reaction mixtures within Teflon receptacles encased inside the confines of a spring loaded stainless steel reaction vessel. The high temperatures and hydrostatic pressures achieved can often lead to products previously unattainable under ambient conditions,\(^\text{[1]}\) while crystallisation is greatly influenced by employing slow (and controllable) cooling rates.\(^\text{[2]}\) Moreover the hydrostatic pressure within the reaction vessels has regularly shown to promote the synthesis and crystallisation of highly symmetrical polynuclear complexes,\(^\text{[1, 3]}\) which often result in non-zero ground spin states and thus interesting magnetic behaviour such as the magneto-caloric effect (MCE).\(^\text{[1]}\)

Building upon our previous work concerning the magnetic tuning of salicylaldoxime bridged [Mn\(_3\)] and [Mn\(_6\)] Single-Molecule Magnets,\(^\text{[4]}\) we have employed in this chapter solvothermal synthesis in order to encourage Cr\(^{\text{III}}\)-oxime coordination, while probing this technologies influence on resultant cage topologies. A complication lies in the inert nature of the aqueous Cr\(^{\text{III}}\) ion whose polynuclear cage formation requires extreme reaction conditions such as reflux, solid state or hydro / solvo-thermal heating. Although there are other examples in the literature,\(^\text{[1-2, 5]}\) this area has been significantly enhanced by the extensive work of Winpenny, Timco, McInnes and co-workers, having developed high yielding synthetic routes to numerous Cr\(^{\text{III}}\) complexes which include the elegant extended families of homometallic (i.e. [Cr\(_8\)],\(^\text{[6]}\) [Cr\(_9\)]\(^\text{[7]}\) and [Cr\(_{10}\)]\(^\text{[8]}\)) and heterometallic (i.e. [Cr\(_7\)M\(_1\)]; M = Ni\(^{\text{II}}\), Co\(^{\text{II}}\), Fe\(^{\text{II}}\), Mn\(^{\text{II}}\), Cd\(^{\text{II}}\)\(^\text{[9]}\)) ring structures as well as their deliberately distorted horseshoe siblings.\(^\text{[10]}\) These versatile ring architectures have also proven to be excellent models for molecular qubits with respect to quantum information processing,\(^\text{[11]}\) while other developments have focused on their use as the macrocyclic element of a rotaxane based molecular shuttle\(^\text{[12]}\) and more recently as building blocks in the self-assembly of larger premeditated multi-component architectures.\(^\text{[13]}\)

With these thoughts in mind we report here the solvothermal synthesis and structural and magnetic characterisation of a family of discrete cages (4.1-4.3) and
extended network materials (4.4 and 4.5), each comprising trimetallic oxo-centred 
\( \{\text{Cr}^{III}_3\text{O(O}_2\text{C}_1\text{R}_1\text{)}_3(R\text{2-sao})_3\}^{2-} \) \( (R_1 = \text{H, CH}_3, \text{C(CH}_3)_3, \text{C}_1\text{4H}_9; R_2 = \text{Me, } ^{t}\text{Bu, Naphth, Ph}) \) units linked via connector \( \text{Na}^+ \) cations. Interestingly the formation of 4.1-4.5 are in total contrast to Choudhuri’s previously reported family of \( \text{Cr}^{III}\)-oxime complexes: 
\[ \{\text{Cr}^{III}_6\text{O}_2\text{O}_2\text{C}_1\text{R}_1\text{)}_2\text{salox}_6\text{H}_2\text{O}_2\text{R}_2\text{CN}_2\} \] \( (R_1 = \text{CH}_3, \text{C(CH}_3)_3, \text{C}_6\text{H}_5; R_2 = \text{CH}_3, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9; \text{salox} = \text{salicylaldoxime}) \), whose structures are analogues to our previously described \([\text{Mn}_6]\) SMMs, although Choudhuri employed reflux reaction conditions.\[14\]
An alternative synthetic route and the structural characterisation of a \( \text{Cr}_4 \) complex (4.6) will also be discussed later in this chapter.

4.2 Results and Discussion

The aerobic stirring in acetonitrile of \( \text{CrCl}_3.6\text{H}_2\text{O} \) along with equimolar amounts of the ligands Naphth-saoH\text{2} and sodium-9-anthracene carboxylate and a suitable base (\( \text{NEt}_4\text{(OH)} \)) gives a green slurry which does not produce any discernible products upon manipulation. However, when this slurry solution is placed in a spring loaded stainless steel digestion vessel and lodged in a solvothermal oven for a period of 24 hours (\( T = 100 ^\circ\text{C} \)), crystals of the heptanuclear complex 
\[ (\text{H}_3\text{O})(\text{NEt}_4)\text{2}[\text{Na}_1\text{Cr}^{III}_6\text{O}_2\text{O}_2\text{C}_1\text{4H}_9\text{)}_6\text{Naphth-sao}_6\].26\text{H}_2\text{O}.2\text{MeCN} \] (4.1) are obtained after a slow cool down period (24 hours). Longer and shorter cool down periods have no effect on yield and crystal quality. Complex 4.1 crystallises in the triclinic P-1 space group and two half \([\text{Na}_3\text{Cr}^{III}_6]\)^3- units lie within the asymmetric unit and therefore we will describe just one complete \([\text{Na}_3\text{Cr}_6]\) cage here. For all pertinent crystal data on 4.1 (and 4.2-4.5) please refer to Tables 4.1 – 4.2. All \( \text{Cr}^{III} \) and \( \mu_3-\text{O}^– \) oxidation states in 4.1 (and subsequently 4.2-4.5) were confirmed using bond valence sum (BVS) calculations and bond length and charge balancing considerations.

The core in 4.1 has a sandwich-like shape whereby a central \( \text{Na}^+ \) ion (Na1) lies at the midpoint of two \( \{\text{Cr}^{III}_3\text{O(O}_2\text{C-C}_1\text{4H}_9\text{)}_3\text{Naphth-sao}_3\}^{2-} \) triangular units which are related by an inversion centre lying at the \( \text{Na}^+ \) position (Fig. 4.1). The carboxylate / oxime ligand distribution observed in these \( \{\text{Cr}^{III}_3\text{O(O}_2\text{C-C}_1\text{4H}_9\text{)}_3\text{Naphth-sao}_3\}^{2-} \) moieties in 4.1 (and subsequently 4.2-4.5) have been previously observed only in \( \text{Mn}^{III} \) coordination chemistry\[15\] and are adaptations on the classic and ubiquitous
trinuclear $[\text{Cr}_3\text{O}(\text{O}_2\text{C})_6(\text{L})_3]^{10+/}$ species ($\text{L} = \text{H}_2\text{O}$, pyridine etc.),\textsuperscript{16} whereby the \{Cr\textsuperscript{III}O\textsuperscript{7+}\} core is maintained while substituting half the carboxylates for three Naphth-sao\textsuperscript{2-} ligands to give the structure in 4.1 (Fig. 4.1). Each edge of these trinuclear fragments are bridged by one $\mu$-O$_2$C-anthracenoate (O$_2$C-C$_{14}$H$_9$) and one $\eta^1:\eta^1:\eta^2$, $\mu_3$-Naphth-sao\textsuperscript{2-} ligand which occupy opposite sides of the \{Cr\textsuperscript{III}O\textsuperscript{7+}\} planes (Fig. 4.1). The O donor atoms of the carboxylates exclusively bridge the Cr\textsuperscript{III} centres within the triangular units. The Naphth-sao\textsuperscript{2-} ligands also achieve this, while also connecting the \{Cr\textsuperscript{III}O\textsuperscript{7+}\} units to the central Na\textsuperscript{+} ion via six oximic O atoms (O5, O11, O13 and s.e.) with distances lying in the 2.374-2.419 Å range (Fig. 4.2). The resultant $[\text{NaCr}_{6}\text{O}(\text{O}_2\text{C-C}_{14}\text{H}_9)_6\text{(Naphth-sao)}_6]^{3-}$ anionic clusters are charge balanced by two (NEt$_4$)$^+$ counter ions and an oxonium species.

**Figure 4.1.** Crystal structure of 4.1 as viewed perpendicular (left) and parallel (right) to the \{Cr\textsuperscript{III}O\textsuperscript{7+}\} planes. Colour code (used throughout the chapter): Cr (green), O (red), N (blue), Na (yellow), C (grey). All hydrogen atoms have been omitted for clarity.
Figure 4.2. (Top left) Core in 4.1 highlighting the major connection pathways between the two \(\{\text{Cr}^\text{III}_3\text{O}\}^{7+}\) triangular units and the central Na\(^+\) ion. (Bottom left) Core in 4.1 illustrating the oximic (Cr-N-O-Cr) and carboxylate (Cr-O-C-O-Cr) bridges within the \([\text{Cr}_3]\) triangular units. (Right) Bonding mode exhibited by the Naphth-sao\(^2\) ligands in 4.1.

The \((\text{NEt}_4)^+\) counter anions in 4.1 each sit within pockets formed by two neighbouring \(\{\text{NaCr}_6\}\) units and are held in position by numerous C-H–\(\pi\) interactions between their ethyl protons and the surrounding aromatic rings of the Naphth-sao\(^2\) and \(\text{O}_2\text{C}-\text{C}_{14}\text{H}_9\) ligands (\(i.e.\ C93(\text{H}121)\cdots[C_{149}-C_{154}] = 2.620\ \text{Å}\) and \(\text{C91(\text{H}12B)}\cdots[C_{97}-\text{C}_{102}] = 2.887\ \text{Å}\)). MeCN solvents of crystallisation also lie in the solvent accessible voids in 4.1 at distances commensurate with H-bonding interactions with nearby aromatic protons (\(i.e.\ C101(\text{H}101)\cdots\text{N}10 = 2.819\ \text{Å}\)). The \(\{\text{Na}_3\text{Cr}_6\}\) units arrange into 2D brickwork sheets (\(bc\) plane) which are stacked in superimposable and parallel rows along the \(a\) unit cell axis.
Figure 4.3. Two adjacent \( \text{NaCr}_6\text{O}_2\left(\text{O}_2\text{C-C}_{14}\text{H}_{9}\right)_6(\text{Naphth-sao})_6 \) cages in 4.1 forming a hydrophobic pocket accommodating a space-fill represented \((\text{NEt}_4)^+\) counter anion.
Despite the steric bulk of both the Naphth-sao$^{2-}$ and anthracene-9-carboxylate bridging ligands utilised in 4.1, the oxo-centred trinuclear $\{\text{Cr}^{III}_{3} \text{O}\}^{7+}$ arrangement so prominent in 1$^{\text{st}}$ row transition metal chemistry was once again observed here. We therefore elected to investigate the employment of less bulky ligands (with respect to both oxime and carboxylate ligands) in a systematic fashion in order to assess their influence on the connectivity’s and topologies of our resultant materials.
We began our study by selecting the least bulky carboxylate in the form of the formate anion and although no other products were obtained when employing the oxime Naphth-saoH₂ co-ligand in this work, the solvothermal (in MeCN) heating of chromic chloride, Ph-saoH₂ and sodium formate in the presence of a suitable base (NEt₄(OH)) gave rise to the complex \([\text{Na}_2\text{Cr}^{II}_{6}(\text{O})_{2}({\text{O}_2\text{CH}})_{6}(\text{Ph-sao})_{6}(\text{MeCN})_{2}({\text{H}_2\text{O}})_{2}]\cdot 2\text{H}_2\text{O}.4\text{MeCN}\) (4.2) (Fig. 4.5b). Complex 4.2 crystallised in the monoclinic P2_1/n space group in 10% yield. Interestingly the core in 4.2 comprises two triangular \([\text{Cr}^{III}_{3}O({\text{O}_2\text{CH}})_{3}(\text{Ph-sao})_{3}]^{2-}\) units that unlike in 4.1, are linked via two distorted octahedral Na⁺ ions (Na1 and s.e.), whose role apart from achieving electroneutrality are to fuse the two trimetallic units along a common edge and form the near planar \{Na₂Cr₆\} core in 4.2 (Fig. 4.5b). The coordination spheres at the two central Na⁺ centres are each completed by a terminal H₂O and MeCN ligand (Na1-N4 = 2.442 Å, Na1-O14 = 2.330 Å), while an inversion centre lies at the midway point between the two alkali metal centres.

**Figure 4.5.** (a) The asymmetric unit in 4.2 highlighting the \([\text{Cr}^{III}_{3}O({\text{O}_2\text{CH}})_{3}(\text{Ph-sao})_{3}]^{2-}\) triangular unit and one of the connector Na⁺ ions. (b) Crystal structure of 4.2 minus all hydrogen atoms and solvents of crystallisation (H₂O and MeCN). (c) Bonding modes exhibited by the formate (top) and Ph-sao²⁻ (middle and bottom) ligands in 4.2.
The role of the bridging Ph-sao\(^{2-}\) and \(^{-}\)O\(_2\)CH ligands differ slightly to those observed in 4.1. More specifically two of the six carboxylate anions in 4.2 bridge the Cr\(^{-}\)Cr edges exclusively (\(\mu\)-bridging mode), while the remaining four use their \(\eta^1:\eta^2\), \(\mu_3\)-bonding motifs to fuse the central Na\(^+\) ions to the \{Cr\(_{3}\)O\}\(^{7+}\) units, while also linking Cr\(^{\text{III}}\) centres within the triangular moieties (Fig. 4.5c). A similar pattern of coordination behaviour is observed by the six Ph-sao\(^{2-}\) ligands in 4.2 using both the \(\eta^1:\eta^1:\mu_2\)- and \(\eta^3:\eta^1:\mu_4\)-bonding modes as shown in Fig. 4.5c. Water and acetonitrile solvents of crystallisation occupy the lattice voids in 4.2 and in doing so forge H-bonds with each other (N5\(\cdots\)O15 = 3.077 Å and N6\(\cdots\)O15 = 2.938 Å) and with juxtaposed [Na\(_2\)Cr\(_6\)] cages (i.e. O15\(\cdots\)O11 = 2.919 Å). The individual [Na\(_2\)Cr\(_6\)] units in 4.2 arrange in the space efficient brickwork motif along the bc plane of the cell and these 2D sheets align in parallel off-set rows along the a cell direction (Fig. 4.4b).

![Figure 4.6. Bonding mode exhibited by the 3,5-di-tert-Bu-sao\(^{2-}\) ligands in 4.3.](image)

Employment of the ligand 3,5-di-tert-butyl salicylaldoxime and pivalate co-ligands in the synthon used to create 4.1 and 4.2 gives rise to the complex [Na\(_4\)Cr\(_{3}\)\(_{3}\)(O\(_2\)CC(CH\(_3\))\(_3\))\(_6\)(3,5-di-\text{Bu-sao})\(_6\)(MeCN)\(_6\)].1.5MeCN (4.3). Complex 4.3 crystallises in the trigonal R-3c space group and shares a similar core to that in 4.1 by exhibiting a sandwich type arrangement (Fig. 4.7c vs. Fig. 4.1). However in this particular case the two \{Cr\(_{3}\)O(O\(_2\)CC(CH\(_3\))\(_3\))\(_3\)(3,5-di-\text{Bu-sao})\(_3\)\}\(^{2-}\) moieties are connected through a belt of four Na\(^+\) ions (Na1-2 and s.e.) as opposed to the single
Na$^+$ centre employed in 4.1 (Fig. 4.7c). Na2 (as in 4.1) is bound by oximic O atoms (O2, O6 and s.e.) and lies at the centre of the cage and equidistant between the two central O$^2-$ ions (O5 and O7) located at the centre of each \{Cr$^{III}$O\}_7$^+$ unit. The three symmetry related sodium centres (Na1 and s.e.) are situated in the same plane as the central Na2 and together form a star shaped arrangement (Fig. 4.7a). The coordination spheres at Na1 (and s.e.) are completed by two terminal MeCN ligands (Na1-N2 = 2.490 Å, Na1-N3 = 2.449 Å) (Fig. 4.7b and 4.7d). As observed in 4.1, the carboxylates in 4.3 bridge only the Cr$^{III}$ ions within each trinuclear unit using the common µ-bridging mode. As a result the tBu-sao$^{2-}$ ligands must assume the role of connecting the \{Cr$^{III}$O\}_7$^+$ units to the central belt of Na$^+$ linkers and this is achieved using a η$^2$::η$^1$::η$^3$, μ$^5$-bonding motif (Fig. 4.6). As we move from complex 4.1 to 4.3, it becomes apparent that the number of Na$^+$ linker ions increases from one (in 4.1) to four (in 4.3) and may be attributed to the decreasing steric nature of the oxime and carboxylate ligands employed as we move along the series. In the crystal of 4.3 the [Na$_4$Cr$_6$] moieties stack on top of one another resulting in a unit cell possessing pseudo-superimposable 1D columns with each unit linked by a 120 ° rotation (Fig. 4.8).
A combination of the Me-saoH₂ ligand and acetate co-ligand in conjunction with previous synthons (producing 4.1-4.3) lead to the production of 
\[ [\text{Na}_4\text{Cr}^{III}_6(O)_2(O_2CCH_3)_6(\text{Me-sao})_6(\text{MeCN})]_n \] (4.4). Complex 4.4 crystallises in the
monoclinic I2/a space group and is the first example of an extended network in this work, comprising \(\text{Cr}^{III}_3\text{(O)(O}_2\text{CCH}_3)_3\text{(Me-sao)}_3\)\(^{2-}\) nodes linked into a 3D diamondoid topology via charge balancing Na\(^+\) connector ligands. The connectivity within each \(\text{Cr}^{III}_3\text{O}\)\(^{7+}\) node is as follows. Two of the three Me-sao\(^2-\) ligands located within each \([\text{Cr}_3]\) moiety exhibit \(\eta^2:\eta^1\):\(\eta^2\), \(\mu_4\)-bonding modes while the third oxime bridges in the \(\eta^2:\eta^1\):\(\eta^1\), \(\mu_3\)-fashion (Fig. 4.9-right). As a result each ligand spans an edge of a trinuclear unit while also providing a connection to a Na\(^+\) connector node (Fig. 4.9-left). An identical role is adopted by the three acetate ligands within each \(\text{Cr}^{III}_3\text{O}\)\(^{7+}\) unit in 4.4, using a combination of \(\eta^1:\eta^2\), \(\mu_3\)- and \(\eta^2:\eta^2\), \(\mu_4\)-bonding motifs in the process (Fig. 4.9-right). As a result the central \(\text{Cr}^{III}_3\text{O}\)\(^{7+}\) nodes lie in a distorted tetrahedral hole with respect to the four surrounding Na\(^+\) ions that lie at the vertices, as shown in Fig. 4.10 (middle). Moreover each of these alkali metal centres link to another \([\text{Cr}_3]\) unit to form the diamondoid topology in 4.4 (Fig. 4.10-bottom). Centres Na1 and Na3 exhibit distorted octahedral geometries while Na2 possesses a distorted square based pyramidal configuration (\(\tau = 0.10\)).\(^{17}\) A single acetonitrile ligand completes the coordination requirements at Na1 (Na1-N4 = 2.445 Å). No accessible voids and therefore lattice solvent are observed in the crystal structure of 4.4. The extended connectivity in 4.4 is enhanced by numerous C-H\(^{−}\)π interactions between aromatic oxime and juxtaposed aliphatic acetate protons (i.e. C24(H24B)\(^−\)[C9-C14]\(_{\text{centroid}}\) = 3.381 Å and C20(H20)\(^−\)[C1-C6]\(_{\text{centroid}}\) = 2.796 Å).
Figure 4.9. Crystal structure of 4.4 as viewed perpendicular (top left) and parallel (bottom left) to the \([\text{Cr}^{III}O(O_2CCH_3)_3(\text{Me-sao})_3]^{2-}\) triangles that make up the \([\text{Na}_1\text{Cr}_6]\) sandwich node. The remaining three bridging Na\(^+\) ions (Na2-4), MeCN solvent of crystallisation and all H atoms have been omitted for clarity. (Right) The two distinct bridging arrangements exhibited by the Me-sao\(^2-\) and acetate anions in the 3D network in 4.4.
Figure 4.10. A single \(\{\text{Cr}^{III}O(\text{O}_2\text{CCH}_3)_3(\text{Me-sao})_3\}^{2-}\) node surrounded by four connecting \(\text{Na}^+\) ions to form a tetrahedral array as viewed perpendicular (a) and parallel (b) to the \(\{\text{Cr}^{III}O\}^{7+}\) plane in 4.4. The majority of the acetate carbon atoms and all hydrogen atoms have been omitted for clarity. (c) A fragment of the 3-D diamondoid network in 4.4. The red vertices represent the O atom at the centre of the \([\text{Cr}_3]\) triangular nodes and the yellow vertices represent the bridging \(\text{Na}^+\) ions in 4.4.

Figure 4.11. The bridging arrangements exhibited by the Me-sao\(^{2-}\) and acetate anions in the 2D network in 4.5.
It was decided to attempt to duplicate the synthon in 4.4 under ambient conditions in order to probe directly the influence solvothermal heating (and associated hydrostatic pressure) has on our CrIII cage formation and resultant topology. To this end the ambient reaction of chromium acetate, Me-saoH2 and NaOH in MeOH gave rise to a green slurry from which no discernible product was obtained. However, by evaporating down this methanolic solution under reduced pressure, X-ray quality crystals of [Na2CrIII3O(O2CCH3)3(Me-sao)3(H2O)6]n·3MeCN (4.5) were obtained via re-crystallisation from acetonitrile. Although complex 4.4 and 4.5 have comparable chemical formulae their structural connectivity’s and topologies differ considerably. Complex 4.5 crystallises in the trigonal R-3 space group (cf. monoclinic I2/a space group of 4.4) and is best described as a 2D [3,6] extended network comprising \{CrIII3O(O2CCH3)3(Me-sao)3(H2O)6\}2- nodes linked by Na+ connector ions (Na1 and s.e.) into a hexagonal honeycomb array (Fig. 4.12 and 4.13).\cite{18} To create this 2D topology the Me-sao2- and ¯O2CCH3 ligands each bridge four metal centres (2 × CrIII and 2 × Na+) by adopting η3:η1:η1,µ4 and η2:η2,µ4 bonding modes respectively (Fig. 4.11). Two terminal H2O ligands (O6 and O7) bind to each sodium linker ion (Na1-O6 = 2.372 Å, Na1-O7 = 2.371 Å) and in doing so lie within the hexagonal cavity while effectively completing their distorted octahedral geometries. The individual 2D sheets in 4.5 pack in a parallel fashion along the c direction of the unit cell as illustrated in Fig. 4.14 (inter-sheet distance: Na1−Na1′ = 12.271 Å). Moreover these individual sheets arrange in a staggered parallel arrangement in relation to one another and therefore no significant pores or channels are observed in 4.5. However, MeCN solvents of crystallisation occupy the spaces in-between each of the 2D sheets in 4.5 and do so by arranging themselves into symmetry related triads around the three fold axis of the cell (down c).(Fig. 4.13 and 4.14).
Figure 4.12. A single $\{\text{Cr}^{\text{III}}_3\text{O}\}^{2+}$ unit along with the linker Na$^+$ ions (yellow spheres) as viewed perpendicular (a) and parallel (b) to the triangular plane in 4.5. (c) An array of six $\{\text{Cr}_3\text{O(O}_2\text{CCH}_3\text{j}_3\text{(Me-sao)}_3\}^{2-}$ units linked by Na$^+$ ions to form the hexagonal honeycomb topology in 4.5.
Figure 4.13. (top) The [3,6] 2D extended network in 4.5 as viewed along the c axis of the unit cell. Solvent molecules of crystallisation (MeCN) have been omitted for clarity. (bottom) Three symmetry equivalent MeCN solvents of crystallisation lying perpendicular to the three fold axis along c and reside in-between the individual 2D sheets in 4.5.

Figure 4.14. Space-fill representation of the parallel stacking of the individual (colour coded) 2D [6,3] nets in 4.5, highlighting their staggered arrangements with respect to one another. All MeCN solvent molecules and H atoms have been omitted for clarity.
Siblings 4.1-4.5 emphasise the stability of the \([\text{Cr}^{\text{III}}_3\text{O}]^{2+}\) building block observed in many \(\text{Cr}^{\text{III}}\) (and other transition metal) polymetallic cages. Despite numerous attempts, no sodium free cages were produced in this work, thus highlighting the important charge balancing and \(\{\text{Cr}^{\text{III}}_3\text{O(O}_2\text{CR})_3(\text{R-sao})_3\}_^{2-}\) unit-linking role undertaken by these ions.

We also report here the synthesis and structural characterisation of the \(\text{Cr}^{\text{III}}\) complex \((\text{NEt}_4)[\text{Cr}^{\text{III}}_4(\text{OH})(\text{Naphth-saoH})_2(\text{Naphth-sao})_5(\text{H}_2\text{O})].3\text{MeCN.H}_2\text{O } (4.6)\), which is structurally different to the aforementioned family of discrete molecules and extended complexes 4.1-4.5. Indeed this was the only complex from a myriad of reactions to portray major structural differences in this family of chromium species. Interestingly, despite many attempts, the synthesis of 4.6 represents the only example in this work of a sodium and carboxylate free structure.

Akin the synthons in 4.1-4.5, the aerobic stirring of \(\text{CrCl}_3.6\text{H}_2\text{O}, \text{Naphth-saoH}_2\) and the base tetraethylammonium hydroxide (\(\text{NEt}_4(\text{OH})\)) in acetonitrile afforded a dark green slurry. This slurry was then transferred to a spring loaded stainless steel digestion vessel and placed in a solvothermal oven at 100 °C for a period of 24 hours to produce crystals of the tetranuclear complex \((\text{NEt}_4)[\text{Cr}^{\text{III}}_4(\text{OH})(\text{Naphth-saoH})_2(\text{Naphth-sao})_5(\text{H}_2\text{O})].3\text{MeCN.H}_2\text{O } (4.6)\). Complex 4.6 crystallises in the monoclinic C2/c space group. This \([\text{Cr}_4]\) complex has a butterfly-like core comprising of four distorted octahedral \(\text{Cr}^{\text{III}}\) centres bridged by a combination of five doubly deprotonated Naphth-sao\(^2-\) ligands (bonding mode: \(\eta^1:\eta^1:\eta^1\mu^-\)) and two singly protonated Naphth-saoH\(^+\) moieties (chelating \(\eta^1:\eta^1\) bonding mode)(Fig. 4.15, 4.16 and 4.17). A bridging OH\(^-\) anion (O13(H13)) also aids the construction of the tetranuclear core in 4.6 by linking the Cr1 and Cr3 centres. A terminal H\(_2\)O completes the co-ordination sphere at Cr1 (Cr1-O16 = 2.041 Å) while three MeCN and one H\(_2\)O (O8) solvent molecules of crystallisation are located at the periphery of the structure in 4.6, both of which are partaking in intermolecular H-bonding (\(i.e. \ \text{N9}^-\text{H5(C5)} = 2.583 \text{ Å and O8}^-\text{O16} = 2.577 \text{ Å). A single charge balancing [NEt}_4]^+ counter ion resides a short distance from the core in 4.6 and partakes in hydrogen bonding interactions with juxtaposed Naphth-saoH- ligand (\(i.e. \ \text{O5}^-\text{H84A(C84)} = 2.488 \text{ Å and O7}^-\text{H83B(C83)} = 2.679 \text{ Å).} \)
Intermolecular H-bonding connections \( (i.e. \text{O15(H15)-O15(H15)} = 2.967 \text{ Å}) \) add to the extended connectivity along with C-H-π short contact interactions which occur between the aromatic Naphth-saoH and the oximatic proton \( (i.e. \text{C14(H14)-[C69-C74] centroid} = 2.510 \text{ Å}) \). Such interactions connect individual molecules together leading to layered columns within the unit cell.

**Figure 4.15.** The \([\text{Cr}_4]\) core in 4.6. Colour code: Cr (green), O (red), N (blue), C (grey). Hydrogen atoms have been omitted for clarity.

**Figure 4.16.** The Crystal structure of 4.6 illustrating its butterfly-like core. Colour code: Cr (green), O (red), N (blue), C (grey). All hydrogen atoms have been omitted for clarity.
4.2.1 TGA Measurements

The TG trace of \([\text{Na}_4\text{Cr}^{III}_6(\text{O})_2(\text{O}_2\text{CC(CH}_3)_3)_6(3,5-\text{di-}^{1}\text{Bu-sao})_6(\text{MeCN})_6].1.5\text{MeCN}\) \(4.3\) shows two distinct weight loss regions, with the initial weight loss of 10.4 % corresponding to the loss of all (7.5 per cage) MeCN solvents of crystallisation (calculated as 11.1 %). The second (and much steeper) weight drop occurs at \(~420 ~{^\circ}\text{C}\) and is attributed to the initiation of the decomposition of \(4.3\). The corresponding trace of \([\text{Na}_2\text{Cr}^{III}_3\text{O}(\text{O}_2\text{CCH}_3)_3(\text{Me-sao})_3(\text{H}_2\text{O})_6]_n.3\text{MeCN}\) \(4.5\) exhibits three weight loss regions. The initial loss (in the 50-100 \({^\circ}\text{C}\) range) of 18.1 % is attributed to the removal of interstitial MeCN solvent molecules and terminal H\(_2\)O solvent ligands (calculated at 21.3 %). The closely related second and third weight loss steps between 300 \({^\circ}\text{C}\) and 475 \({^\circ}\text{C}\) represent an 18 % material loss and is tentatively attributed to acetate ligand loss (calculated as 16.3 %), which is rapidly followed by further ligand loss (Me-sao\(^{2-}\)) and eventual decomposition of \(4.5\) (Fig. 4.18).
Figure 4.18. TGA trace obtained on crystalline samples of and 4.3 (top) and 4.5 (bottom) analysed in the 25-600 °C temperature range in an N₂ atmosphere.

4.2.2 Magnetic Susceptibility Studies

Magnetic susceptibility (\(\chi_{M}\)) measurements were carried out on powdered polycrystalline samples of \([\text{Na}_2\text{Cr}^{III}_6\text{(O)}_2\text{(O}_2\text{CH)}_6\text{(Ph-sao)}_6\text{(MeCN)}_2\text{(H}_2\text{O)}_2\].2\text{H}_2\text{O}.4\text{MeCN} \ (4.2)\) and \([\text{Na}_4\text{Cr}^{III}_6\text{(O)}_2\text{(O}_2\text{CCH}_3)_6\text{(Mes-sao)}_6\text{(MeCN)}]_n \ (4.4)\) in the 300-5.5 K temperature range, in an applied dc field of 0.1
The \(\{\text{Cr}^{III}_3\text{O}((\text{O}_2\text{CR})_3}\text{(R}_2\text{-sao)}_3\}\text{)}^{2-}\) building blocks in 4.2 and 4.4 are magnetically well separated and therefore their magnetic data was treated as such. The room temperature \(\chi_M T\) (per \([\text{Cr}_3]\) unit) values of 5.59 (4.2) and 4.56 (4.4) cm\(^3\) mol\(^{-1}\) K are lower than expected for three non-interacting Cr\(^{III}\) ions (5.63 cm\(^3\) mol\(^{-1}\) K, assuming \(g = 2.0\)), respectively. Such observations are indicative of dominant antiferromagnetic interactions between the Cr\(^{III}\) ions in both the complex in 4.2 and extended network in 4.4. The \(\chi_M T\) products for 4.2 and 4.4 both decrease with lowering temperature (although 4.2 is more gradual than 4.4), before a steeper decline is witnessed below approximately 100 K in both cases. The resting values of 1.78 (4.2) and 1.48 (4.4) cm\(^3\) mol\(^{-1}\) K (obtained at 5.5 K) are commensurate with \(S = 3/2\) ground spin states and is indicative of spin frustration within the \([\text{Cr}_3]\) triangles that compose the cores in 4.2 and 4.4. In order to further determine the ground state of complexes 4.2 and 4.4 further, variable temperature and variable field dc magnetisation data were collected in the ranges 2–7 K and 0.5–7 T and these are plotted as reduced magnetisation \((M/N\beta)\) vs. \(H/T\) in Figure 4.20. Magnetisation saturation is observed at 7 T with \(M/N\beta\) values of 3.33 (4.2) and 2.69 (4.4) confirming \(S = 3/2\) ground spin states in both cases.

![Figure 4.19. \(\chi_M T\) (per \([\text{Cr}_3]\) unit) vs. T plots obtained from polycrystalline samples of 4.2 (□) and 4.4 (Δ) within the 300-5.5 K temperature range and a 0.1 T external magnetic field.](image-url)
Figure 4.20. Reduced magnetisation (M / Nβ) vs. field (H / T) plots obtained from 4.2 (top) and 4.4 (bottom) in the 0.5 – 7 T and 2- 7 K magnetic and temperature field ranges respectively. The solid lines are guides for the eye only.
4.3 Concluding Remarks

The solvothermal heating of Cr$^{III}$ salts in the presence of bulky R-saoH$_2$ oxime ligands (*i.e.* Naphth-saoH$_2$ and Ph-saoH$_2$) alongside $^\ddag$O$_2$C-R co-ligands of varying sizes (R = H, CH$_3$, C(CH$_3$)$_3$, C$_{14}$H$_9$) produce a series of structurally related discrete cages each comprising Na$^+$ linked {Cr$_{3}^{III}$O(O$_2$CR)$_3$(R-sao)$_3$}$^{2-}$ units. However the combinatory reaction of less bulky oxime and carboxylate ligands in the form of ligands Me-saoH$_2$ and $^\ddag$O$_2$CCH$_3$ leads to the formation of either 2D or 3D extended networks containing {Cr$_{3}^{III}$O(O$_2$CCH$_3$)$_3$(Me-sao)$_3$}$^{2-}$ nodes and Na$^+$ secondary building units, depending on whether ambient or solvothermal heating synthetic methods are employed. Lacking one or more of these contributory factors, be it a Na$^+$ anion or a carboxylate ligand, a structurally altered molecule is synthesised in the form of a [Cr$_4$] species (4.6). Magnetic susceptibility and magnetisation vs. field data obtained for 4.2 and 4.4 revealed significant antiferromagnetic exchange between the Cr$^{III}$ ions in both cases, leading to spin frustration within their triangular cores and resultant S = 3/2 ground spin states in both cases.
4.4 Experimental

4.4.1 Instrumentation

4.4.1.1 Carbon, Hydrogen and Nitrogen Micro-analysis

C, H and N elemental analysis were performed using a Perkin Elmer Series II CHNS/O Analyser (2400 Series).

4.4.1.2 Infrared Spectroscopy

Infra-red spectra were recorded on a Perkin Elmer FT-IR *Spectrum One* spectrometer equipped with a Universal ATR Sampling accessory (ZnSe diamond).

4.4.1.3 $^1$H NMR Spectroscopy

Nuclear Magnetic resonance (NMR) Spectroscopic analysis was performed using a JEOL ECX-400 $^1$H NMR Spectrometer. NMR spectra were recorded at room temperature in CDCl$_3$. Chemical shifts ($\delta$) are indicated in ppm.

4.4.1.4 Magnetic Susceptibility Measurements

Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 5.5 K and alternating current (ac) magnetic susceptibility data were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal’s constants. Each sample was set in an eicosane wax to avoid torqueing of the crystalline material. Magnetic measurements were performed by the Brechin group at the University of Edinburgh, Scotland, UK.

4.4.1.5 Thermogravimetric Analysis

TGA measurements were carried out using a Rheometric Scientific STA 625 by Dermot McGrath (NUI Galway).
4.4.1.6 Single-Crystal X-ray diffraction

The structures of 4.1-4.6 were collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source. Each data reduction was carried out on the CrysAlisPro software package. The structures were solved by direct methods (SHELXS-97)[19] and refined by full matrix least squares using SHELXL-97.[20] SHELX operations were automated using the OSCAIL software package.[21] All hydrogen atoms were placed in calculated positions. All non-hydrogen atoms were refined as anisotropic. Despite numerous attempts each single crystal data set obtained from 4.1-4.3 were found to consistently diffract poorly at higher angles. Our best data sets have been supplied in this work. Residual electron densities in solvent accessible voids and channels were observed in 4.1, 4.3 and 4.5 and so were modelled using the SQUEEZE program.[22] The two large channels (volumes ~970 Å³) in 4.1 contained extremely diffuse electron density and were assumed to contain numerous waters of crystallisation along with the required oxonium charge balancing cation. CHN analysis on 4.1 supported these observations.
### 4.4.2 Crystal structure information

#### Table 4.1 Crystal data obtained from complexes 4.1-4.6.

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<th>4.3 ( 1.5\text{MeCN} )</th>
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\(^a\) Includes guest molecules apart from the guest H\(_2\)O in 1 and MeCN solvents in 3, these were calculated using the SQUEEZE program. \(^b\) Mo-Kα radiation, graphite monochromator.  
\(^c\) \(wR2= [\Sigma w(\mid F_o^2\mid - \mid F_c^2\mid)^2/ \Sigma w\mid F_o^2\mid]^{1/2} \). For observed data.  
\(^d\) \(R1= \Sigma \mid F_o\mid - \mid F_c\mid / \Sigma \mid F_o\mid \).
### Table 4.2 Crystal data obtained from complexes 4.4-4.6.

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<sup>a</sup> Includes guest molecules.  
<sup>b</sup> Mo-Kα radiation, graphite monochromator.  
<sup>c</sup> wR² = [Σw(|F_o|²-|F_c|²)²] / ΣwF_o²]² / 2.  
<sup>d</sup> For observed data.  
<sup>e</sup> R₁ = Σ||F_o|-|F_c|| / Σ|F_o|.  

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4.4.3 Synthetic Procedures

All solvothermal reactions were carried out in a Heraeus (UT6420-Thermo Scientific) oven using spring loaded stainless steel digestion vessels (23 cm$^3$ capacity) produced by the Parr Instrument Company. All reagents and solvents were used as purchased. The salicylaldoxime ligands were synthesised by the reaction of the precursor ketone with hydroxylamine and sodium acetate in ethanol, as described in the literature.[23] The synthesis of chromium pivalate was adapted from established methods[24] while chromium acetate was purchased from Sigma Aldrich and used without purification. Complex 4.5 was carried out on the bench top under ambient conditions using solvents that were used as purchased without further purification.

4.4.3.1 Synthesis of (2-Hydroxyphenyl)(Phenyl)Methanone Oxime (Ph-SaoH$_2$)

2-hydroxybenzophenone (25 g, 126.1 mmol, 1 eq.) and hydroxylamine hydrochloride (8.8 g, 126.1 mmol, 1 eq.) were dissolved in ethanol (200 cm$^3$) before adding sodium acetate (10.4 g, 126.1 mmol, 1 eq.) and, with constant stirring, heated under reflux for 4 hours at 100 °C. The precipitated salt was filtered off and the solvent was removed on a rotary evaporator until an oily substance appeared then dried using vacuum pump in approximately 89% yield.

C, H, N Elemental Analysis

Calculated for: C$_{14}$H$_{14}$O$_{2.5}$N$_1$ (Ph-saoH$_2$.0.5H$_2$O)

Theory (%): C 71.19, H 5.93; N 5.93.

Found (%); C 71.37, H 6.06; N 6.20.
Infrared Spectroscopy (cm\(^{-1}\)):

3354(b), 3052(w), 1626(m), 1606(m), 1494(w), 1444(s), 1415(m), 1375(m), 1326(m),
1291(m), 1241(s), 1220(s), 1155(m), 1074(w), 1102(m), 1033(m), 1016(m), 1000(s),
943(s), 932(s), 915(m), 827(m), 756(vs), 725(s), 697(vs), 687(vs).

\(^1\)H NMR (400 MHz, CDCl\(_3\))

\(\delta\) 6.73-7.61 (m, 9H, Ar-H), 12.06 (s, 1H, O-H).

4.4.3.2 Synthesis of 2-Hydroxy-1-Naphthaldehyde Oxime (Naphth-SaoH\(_2\))

![Chemical structure]

2-hydroxy-1-napthaldehyde (28.7 g, 166.9 mmol, 1 eq.) and hydroxylamine hydrochloride (11.6 g, 166.9 mmol, 1 eq.) were dissolved in ethanol (200 cm\(^3\))
before adding sodium acetate (13.7 g, 166.9 mmol, 1 eq.) and, with constant stirring, heated under reflux for 4 hours at 100 °C. The precipitated salt was filtered off and the solvent was removed on a rotary evaporator until an oily substance appeared then dried using vacuum pump in approximately 92% yield.

C, H, N Elemental Analysis

Calculated for: C\(_{11}\)H\(_9\)O\(_2\)N\(_1\)

Theory (%): C 70.58, H 4.85; N 7.48.

Found (%): C 69.23, H 4.59; N 7.18.

Infrared Spectroscopy (cm\(^{-1}\)):

3309(b), 3012(w), 1632(m), 1590(m), 1525(w), 1481(m), 1464(m), 1413(m),
1368(w), 1345(w), 1308(m), 1268(s), 1239(s), 1182(s), 1161(m), 1143(m), 1079(m),
1033(m), 1012(s), 956(w), 934(s), 879(s), 853(s), 814(vs), 781(s), 772(vs), 742(vs),
717(vs), 678(s).
Chapter 4: Solvothermal-Assisted Synthesis of Discrete Chromium Cages and Extended Networks

$^{1}H$ NMR (400 MHz, CDCl$_3$)

$\delta$ 7.19-7.98 (m, 6H, Ar-H), 9.14 (s, 1H, N=C-H), 10.89 (s, 1H, O-H).

4.4.3.3 Synthesis of 2-Hydroxyacetophenone oxime (Me-SaoH$_2$)

\[
\begin{array}{c}
\text{C}_{8}\text{H}_{9}\text{O}_{2}\text{N} \\
\text{Calculated for: C 63.56, H 6.00; N 9.27.} \\
\text{Found (%): C 62.48, H 5.78; N 8.07.} \\
\text{Infrared Spectroscopy (cm}^{-1}: \text{)} \\
3328(w), 2542(w), 1633(m), 1614(m), 1589(m), 1497(m), 1469(w), 1408(m), 1369(m), 1314(w), 1287(s), 1251(s), 1159(m), 1126(w), 1073(w), 1046(m), 1015(s), 943(m), 849(m), 834(m), 780(m), 746(s). \\
\end{array}
\]

$^{1}H$ NMR (400 MHz, CDCl$_3$)

$\delta$ 2.37 (s, 3H, CH$_3$), 6.91-7.44 (m, 4H, Ar-H), 12.27 (s, 1H, O-H).
4.4.3.4 Synthesis of 3,5-di-tert-butyl-salicyladoxime (tert-butyl-SaoH₂)

3,5-Di-tert-butyl-2-hydroxybenzaldehyde (5.0 g, 21.3 mmol, 1 eq.) and hydroxylamine hydrochloride (1.5 g, 45.5 mmol, 2 eq.) were dissolved in ethanol (100 cm³) before adding sodium acetate (1.8 g, 21.34 mmol, 1 eq.) and, with constant stirring, heated under reflux for 4 hours at 100 °C. The precipitated salt was filtered off and the solvent was removed on a rotary evaporator until an oily substance appeared then dried using vacuum pump in approximately 95% yield.

C, H, N Elemental Analysis

Calculated for: C₁₅H₂₃N₁O₂

Theory (%): C 72.23, H 9.30; N 5.62.

Found (%): C 71.07, H 9.28; N 5.51.

Infrared Spectroscopy (cm⁻¹):

3433(m), 2954(m), 2871(w), 1635(w), 1483(w), 1462(m), 1437(s), 1391(m), 1361(m), 1312(m), 1289(m), 1264(w), 1241(s), 1173(m), 1132(w), 1025(w), 1005(s), 977(w), 957(m), 927(w), 883(m), 827(m), 800(m), 749(s), 728(s), 707(s).

¹H NMR (400 MHz, CDCl₃)

δ 1.27 (s, 9H, C(CH₃)₃), 1.42 (s, 9H, C(CH₃)₃), 7.00-7.35 (m, 2H, Ar- H), 8.23 (s, 1H, N=C-H), 10.02 (s, 1H, O-H).

4.4.3.5 (H₂O)[(NEt₄)₂[NaCrIII₆(O)₂(O₂C-C₁₄H₉)₆(Naphth-sao)₆].26H₂O.2MeCN (4.1)

CrCl₃.6H₂O (0.1 g, 0.4 mmol, 1 eq.), Naphth-saoH₂ (0.07 g, 0.04 mmol, 1 eq.), sodium-9-anthracene carboxylate (0.09 g, 0.04 mmol, 1 eq.) and
tetraethylammonium hydroxide (0.2 cm$^3$, 0.15 mmol, 1 eq.) were stirred in MeCN (10 cm$^3$) for 6 hours. This slurry solution was then transferred to a 23 cm$^3$ capacity Teflon vial which was then placed in a spring loaded stainless steel digestion vessel in a solvothermal oven. The oven temperature was then raised to 100 °C over a period of 5 minutes and held at this temperature for 24 hours. The temperature was then lowered gradually down to room temperature over a period of 24 hours. Dark green rhombic shaped crystals of 4.1 were collected and air dried to give a yield of 11%.

$C, H, N$ Elemental Analysis

Calculated for: $C_{176}H_{196}N_{10}O_{53}NaCr_6$

Theory (%): C 58.16, H 5.44; N 3.85.

Found (%): C 58.14, H 4.93; N 3.68.

Infrared Spectroscopy (cm$^{-1}$):

3046(w), 1613(m), 1596(m), 1559(s), 1503(m), 1487(w), 1457(m), 1427(s), 1383(s), 1322(s), 1276(m), 1249(m), 1181(m), 1141(w), 1087(w), 1041(m), 1025(m), 951(s), 885(w), 864(w), 822(m), 785(m), 750(m), 735(s), 678(s).

Figure 4.21. Crystal of 4.1 mounted on glass fibre for diffraction.
4.4.3.6 *Synthesis of* \[\text{[Na}_2\text{Cr}^{III}_6(\text{O})_2(\text{O}_2\text{CH})_6(\text{Ph-sao})_6(\text{MeCN})_2(\text{H}_2\text{O})_2].2\text{H}_2\text{O}.4\text{MeCN} (4.2)\]

CrCl$_3$.6H$_2$O (0.1 g, 0.4 mmol, 1 eq.), Ph-saoH$_2$ (0.08 g, 0.4 mmol, 1 eq.), Na-formate (0.05 g, 0.7 mmol, 1 eq.) and tetraethylammonium hydroxide (0.2 cm$^3$, 0.15 mmol, 1 eq.) were stirred in MeCN (10 cm$^3$) for 2 hours. This slurry solution was then transferred to a 23 cm$^3$ capacity Teflon vial which was then placed in a spring loaded stainless steel digestion vessel in a solvothermal oven. The oven temperature was then raised to 100 °C over a period of 5 minutes and held at this temperature for 24 hours. The temperature was then lowered gradually down to room temperature over a period of 24 hours. Dark green rhombic shaped crystals of 4.2 were collected and air dried to give a yield of 10%.

*C, H, N Elemental Analysis*

Calculated for: C$_{96}$H$_{98}$N$_{12}$O$_{30}$Na$_2$Cr$_6$

Theory (%): C 51.07, H 4.38; N 7.44.

Found (%): C 51.01, H 4.65; N 7.76.

*Infrared Spectroscopy (cm$^{-1}$):*

3368(b), 1576(s), 1490(w), 1470(w), 1435(m), 1393(w), 1358(m), 1310(s), 1250(w), 1155(w), 1044(m), 1026(m), 956(s), 846(w), 759(s), 672(s).

*Figure 4.22.* Rhombic shaped crystal of 4.2 mounted on glass fibre for diffraction.
4.4.3.7 Synthesis of $[\text{Na}_4\text{Cr}^{III}_6\text{O}_2\text{O}_2\text{CC(CH}_3)_3\text{3}(\text{3,5-di-tBu-sao})_6(\text{MeCN})_6].1.5\text{MeCN}$ (4.3)

Chromium pivalate (0.1 g, 0.2 mmol, 1 eq.), 3,5-di-tert-butyl-saoH$_2$ (0.15 g, 0.6 mmol, 3 eq.) and NaOH (0.03 g, 0.8 mmol, 4 eq.) were stirred in MeCN (10 cm$^3$) for 2 hours. This slurry solution was then transferred to a 23 cm$^3$ capacity Teflon vial which was then placed in a spring loaded stainless steel digestion vessel in a solvothermal oven. The oven temperature was then raised to 100 °C over a period of 5 minutes and held at this temperature for 24 hours. The temperature was then lowered gradually down to room temperature over a period of 24 hours. Dark green rhombic shaped crystals of 4.3 were collected and air dried to give a yield of 12%.

$C, H, N$ Elemental Analysis

Calculated for: C$_{132}$H$_{198}$N$_{12}$O$_{26}$Na$_4$Cr$_6$

Theory (%): C 57.17, H 7.20; N 6.06.

Found (%): C 57.01, H 7.45; N 6.26.

$\text{Infrared Spectroscopy (cm}^{-1})$:

3405(vb), 2956(w), 1588(w), 1548(s), 1483(m), 1459(w), 1419(s), 1377(m), 1360(m), 1295(w), 1276(w), 1255(m), 1229(m), 1201(m), 1169(m), 1020(m), 986.60(w), 955.95(w), 897(w), 872(w), 835(m), 811(w), 788(m), 746(w), 714(s), 694(m).

Figure 4.23. Rhombic shaped crystal of 4.3 mounted on glass fibre for diffraction.
4.4.3.8 Synthesis of \([\text{Na}_4\text{Cr}^{III}_6\text{O}_2\text{O}_2\text{CCH}_3]_6\text{Me-sao}_6\text{Me-CN}]_n\) \(4.4\)

Chromium acetate (0.1 g, 0.17 mmol, 1 eq.), Me-saoH₂ (0.08 g, 0.53 mmol, 3 eq.) and NaOH (0.03 g, 0.75 mmol, 4 eq.) were stirred in MeCN (10 cm³) for 1.5 hours. This slurry solution was then transferred to a 23 cm³ capacity Teflon vial which was then placed in a spring loaded stainless steel digestion vessel and then placed inside a solvothermal oven. The oven temperature was then raised to 100 °C over a period of 5 minutes and held at this temperature for 24 hours. The temperature was then lowered gradually down to room temperature over a period of 24 hours. Dark green rhombic shaped crystals of \(4.4\) were collected and air dried to give a yield of 15%.

\(C, H, N\) Elemental Analysis

Calculated for: \(C_{62}H_{69}O_{29}N_{7}Na_{4}Cr_{6}\text{ (}4.4\text{.3H}_{2}O)\):

Theory (%): C 41.83, H 3.91; N 5.50.

Found (%): C 41.58, H 4.43; N 5.75.

Infrared Spectroscopy (cm\(^{-1}\)):

3360(w), 2988(w), 2215(w), 1614(w), 1594(m), 1536(m), 1506(m), 1454(m), 1427(s), 1379(s), 1329(s), 1292(s), 1247(m), 1184(s), 1143(m), 1090(w), 1044(s), 952(s), 881(w), 858(w), 823(s), 786(s), 776(s), 742(s).

\textbf{Figure 4.24.} Rhombic shaped crystal of \(4.4\) mounted on glass fibre for diffraction.
4.4.3.9 Synthesis of $[\text{Na}_2\text{Cr}^{III}_3\text{O}(\text{O}_2\text{CCH}_3)_3\text{(Me-sao)}_3(\text{H}_2\text{O})_6]_{\text{n}}.3\text{MeCN}.\text{H}_2\text{O}$ (4.5)

Chromium acetate (0.25 g, 0.4 mmol, 1 eq.), Me-saoH$_2$ (0.19 g, 1.3 mmol, 3 eq.) and NaOH (0.07 g, 1.65 mmol, 4 eq.) were dissolved in MeOH (30 cm$^3$) and stirred for 2 hours. The solvent was then removed under reduced pressure and the green solid redissolved in MeCN and the resultant solution filtered. X-ray quality crystals of 4.5 were obtained upon slow evaporation of the mother liquor in 10% yield after 6 days.

$C, H, N$ Elemental Analysis

Calculated for: C$_{30}$H$_{54}$O$_{25}$N$_3$Na$_2$Cr$_3$ (4.5.6H$_2$O):

Theory (%): C 34.03, H 5.14; N 3.96.

Found (%): C 33.85, H 4.64; N 3.79.

Infrared Spectroscopy (cm$^{-1}$):

3357(b), 2167(vw), 1581(m), 1550(vs), 1481(w), 1430(vs), 1301(vs), 1244(s), 1164(w), 1138(w), 1080(w), 1054(m), 1020(s), 971(s), 860(s), 754(s), 706(s), 649(vs).

Figure 4.25. Crystal of 4.5 mounted on glass fibre for diffraction.

4.4.3.10 Synthesis of (NEt$_4$)[Cr$^{III}_4$(OH)(Naphth-saoH)$_2$(Naphth-sao)$_3$(H$_2$O)].3MeCN.H$_2$O (4.6)

CrCl$_3$.6H$_2$O (0.1 g, 0.4 mmol, 1 eq.), Naphth-saoH$_2$ (0.07 g, 0.04 mmol, 1 eq.), and tetraethylammonium hydroxide (0.2 cm$^3$, 0.15 mmol, 1 eq.) were stirred in MeCN (10 cm$^3$) for 2 hours. This solution was then transferred to a 23 cm$^3$ capacity Teflon
vial which was then placed in a spring loaded stainless steel digestion vessel and
placed in a solvothermal oven. The oven temperature was then raised to 100 °C
over a period of 5 minutes and held at this temperature for 24 hours. The
temperature was then lowered slowly down to room temperature over a period of
24 hours. Upon cooling the mother liquor was filtered and allowed to stand. Dark
brown plate-like crystals of 4.6 were obtained upon slow evaporation of the mother
liquor in 10% yield after 6 days.

_C, H, N Elemental Analysis_

Calculated for: C_{91}H_{81}O_{17}N_{11}Cr_{4}

Theory (%): C 58.45, H 4.91; N 6.42. (4.6·3H_{2}O)

Found (%): C 58.59, H 4.65; N 6.76.

_Infrared Spectroscopy (cm⁻¹):_

3050(w), 1615(m), 1595(m), 1535(w), 1506(m), 1455(m), 1427(m), 1383(m),
1329(m), 1293(m), 1248(m), 1185(m), 1143(w), 1091(w), 1043(m), 1024(m), 949(s),
882(w), 859(w), 822(s), 786(m), 777(m), 741(s).

*Figure 4.26.* Crystal of 4.6 mounted on glass fibre for diffraction.
4.5 References


Chapter Five

A Facile Synthetic Route to a Family of Mn$^{III}$ Monomers and their Structural, Magnetic and Spectroscopic Studies
5.1 Introduction

Commercially available and synthetically viable sources of the Mn$^{III}$ ion are scarce and this has connotations for synthetic chemists working in many facets of research. An example of a commercially available Mn salt would be Mn(acac)$_3$ (where acac = acetylacetonate). For instance, Mn$^{III}$ species are common catalytic reagents$^{[1]}$ in various organic transformations such as alkane oxidations$^{[2]}$ and oxidative radical cyclizations,$^{[3]}$ while manganese complexes have been extensively studied as model compounds towards elucidating the function of specific metalloenzymes.$^{[4]}$ In the field of molecular magnetism, the Mn$^{III}$ ion is an excellent source of single-ion anisotropy and when aggregated into polymetallic topologies can often effect global anisotropy and magnetic bistability upon their resultant architectures.$^{[5]}$ Synthetic chemists in this field predominantly rely on the redox manipulation of Mn$^{II}$, Mn$^{IV}$ and Mn$^{VII}$ precursors to produce Mn$^{III}$ rich polymetallic cages.$^{[6]}$

An alternative strategy is to synthesise new simple Mn$^{III}$ complexes as preludes towards larger architectures. With these thoughts in mind, two such examples in the literature caught our eye in the form of the monometallic complexes $[\text{Mn}^{III} \text{F}_3(\text{H}_2\text{O})(\text{L})) \cdot x\text{H}_2\text{O} \ (L_1 = 2,2\text{-bipyridine}, \ x = 0 \ (5.1')) \text{ or } L_2 = 1,10\text{-phenanthroline, } x = 1 \ (5.2'))$. These siblings were first synthesised as powders by Chaudhuri et al. $^{[7]}$ and subsequently characterised crystallographically by the Núñez $^{[8]}$ (5.1’) and Rajasekharan $^{[9]}$ (5.2’) groups respectively. Synthesis of these complexes involved the careful manipulation of hot toxic 48% HF solutions requiring manipulation in well ventilated areas. Drawing on our previous experience using anhydrous MnF$_3$ as a precursor to larger polymetallic architectures,$^{[10]}$ we herein report its utilisation in the synthesis of $5.1' \cdot 2\text{H}_2\text{O}$ (the hydrated analogue to $5.1'$) and $5.2$ (the dehydrated analogue to $5.2'$), using a facile reaction route which may be performed in just 5 minutes (Fig. 5.1). We also demonstrate the robust nature of this synthetic route by describing the formation of their siblings: $[\text{Mn}^{III} \text{F}_3(\text{H}_2\text{O})(\text{L}_3)] \ (5.3)$, $[\text{Mn}^{III} \text{F}_3(\text{H}_2\text{O})(\text{L}_4)] \ (5.4)$, $[\text{Mn}^{III} \text{F}_3(\text{H}_2\text{O})(\text{L}_5)] \ (5.5)$ and $[\text{Mn}^{III} \text{F}_3(\text{H}_2\text{O})(\text{L}_6)] \ (5.6)$ ($L_3 = 6\text{-methyl-2,2'}\text{-dipyridyl, } L_4 = 4,4\text{-dimethyl-2,2'}\text{-dipyridyl, } L_5 = 5,5\text{-dimethyl-2,2'}\text{-dipyridyl and } L_6 = 5\text{-chloro-1,10-phenanthroline}$) (Fig. 5.2).
Figure 5.1. Crystal structures of [Mn(F)₃(H₂O)(L₁)].2H₂O (5.1) (top) and [Mn(F)₃(H₂O)(L₂)] (5.2) (bottom). Colour code: Purple (Mn), Red (O), Blue (N), Grey (C), Yellow (F) and Black (H). Aromatic protons have been omitted for clarity. Selected H-bond distances given as dashed red lines: F₂⁻H¹₂'(O₂') = 1.923 Å, F₃⁻H¹₃'(O₃') = 1.989 Å; F₁⁻H¹B'(O¹') = 1.884 Å.

Figure 5.2. Ligands used in the synthesis of 5.1-5.6.
5.2 Results and Discussion

Each of the monometallic complexes shown in Figures 5.1 and 5.3 are synthesised by heating (in a fumehood) a methanolic solution of anhydrous Mn\textsuperscript{III}F\textsubscript{3} and your 1,2-diimine ligand (L\textsubscript{x}) of choice at 50 °C until a dark red / orange colour has formed. Such heating is required to break down and dissolve the extended network structure of MnF\textsubscript{3}. Red / orange crystalline solids of \textbf{5.1-5.6} subsequently precipitate slowly in substantial yields. Slow Et\textsubscript{2}O diffusion may also be employed to facilitate X-ray quality crystal growth of all members. The structures of \textbf{5.1-5.6} each comprise of a single Jahn-Teller elongated distorted octahedral Mn\textsuperscript{III} centre, chelated by a single heterocyclic 1,2-diimine ligand ‘L\textsubscript{x}’, while three terminal F\textsuperscript{-} ions and a H\textsubscript{2}O ligand complete their coordination geometries. The axial distortions in these systems are consistently observed in the form of elongated Mn1-N1 and Mn1-O1 bonds with distances ranging between 2.146 and 2.309 Å, while the shorter terminal Mn-F bonds range from 1.805 to 1.884 Å (Table 5.1). Full crystallographic data on all siblings can be found in Tables 5.11 and 5.12.

\textbf{Figure 5.3.} Crystal structures of complexes \textbf{5.3-5.6}. Colour code: Purple (Mn), Red (O), Blue (N), Grey (C), Yellow (F) and Black (H). Aromatic protons omitted for clarity. H-bond distance in \textbf{5.3} given as dashed red line (C11(H11C)\textsuperscript{-}F2 = 2.232 Å).
### Table 5.1. Angles and distances concerning the J-T elongation axes in complexes 5.1-5.6.

<table>
<thead>
<tr>
<th>Complex</th>
<th>J-T elongation distances (Å) (Mn-N and Mn-OH₂)</th>
<th>J-T elongation angle (°) (O-Mn-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MnF₃(H₂O)(L₁)].2H₂O (5.1)</td>
<td>2.220; 2.176</td>
<td>168.95</td>
</tr>
<tr>
<td>[MnF₃(H₂O)(L₂)] (5.2)</td>
<td>2.260; 2.166</td>
<td>166.98</td>
</tr>
<tr>
<td>[MnF₃(H₂O)(L₃)] (5.3)</td>
<td>2.309; 2.193</td>
<td>164.91</td>
</tr>
<tr>
<td>[MnF₃(H₂O)(L₄)].2H₂O (5.4)</td>
<td>2.261, 2.146</td>
<td>166.67</td>
</tr>
<tr>
<td>[MnF₃(H₂O)(L₅)].0.5MeOH (5.5)</td>
<td>2.246; 2.170</td>
<td>168.60</td>
</tr>
<tr>
<td>[MnF₃(H₂O)(L₆)] (5.6)</td>
<td>2.261; 2.153</td>
<td>167.28</td>
</tr>
</tbody>
</table>

The discrete moieties in 5.1-5.3 each pack within their unit cells in a similar manner (Fig. 5.4). The [Mn⁺⁺⁺F₃(H₂O)(Lₙ)] units in each case arrange in superimposable stacks along the b direction of their cells to give intermolecular Mn1⁻⁻⁻Mn1’ distances of (Å): 7.404 (5.1), 7.294 (5.2) and 7.500 (5.3) respectively. These individual columns of monomeric units arrange along their ac planes in an interdigitated fashion with respect to their adjacent rows, forming close contacts primarily in the form of strong H-bonding interactions between the terminal F⁻ ligands and protons of juxtaposed terminal H₂O ligands (i.e. F⁻⁻⁻H16’(O1’) = 1.832 Å in 5.1; F⁻⁻⁻H1B’(O1’) = 1.884 Å in 5.2, F⁻⁻⁻H1H’(O1’) = 1.879 Å in 5.3), as well as via waters of crystallisation in the case of 5.1 (F3⁻⁻⁻H13’(O3’) = 1.989 Å). Secondary interactions are also observed in the form of off-set πcentroid…πcentroid stacking interactions (i.e. [C1⁻⁻⁻N5]⁻⁻⁻[C1’⁻⁻⁻N5’] = 3.843 Å in 5.1; [C1⁻⁻⁻N1]⁻⁻⁻[C4-C12] = 3.784 Å in 5.2 and [C6⁻⁻⁻N2]⁻⁻⁻[C6’⁻⁻⁻N2’] = 3.901 Å in 5.3). For a list of all intermolecular interactions in 5.1-5.6 and their corresponding distances see Table 5.2.
Figure 5.4. Packing arrays observed in 5.1 (a), 5.2 (b) and 5.3 (c) as viewed along the $a$ direction of their unit cells. All hydrogen atoms and solvents of crystallisation (in 5.1) have been omitted for clarity. Colour code: Purple (Mn), Red (O), Blue (N), Grey (C) and Yellow (F).

The {Mn} moieties in 5.4 are linked via multiple hydrogen bonding interactions concerning metal bound $F^-$ ligands with nearby $H_2O$ solvents of crystallisation (as in 5.1) and not with ligated $H_2O$ moieties as observed in 5.2 and 5.3 (see Table 5.2 for details). Off-set $\pi_{\text{centroid}}$/ $\pi_{\text{centroid}}$ arrangements are also forged along the $a$ direction of the unit cell in 5.4 and are separated at a distance of 3.678 Å ([C1-N1]…[C7′-N2′])(Fig. 5.5).
Figure 5.5. Crystal packing arrangement in 5.4 as viewed along the b unit cell direction. All hydrogen atoms and solvents of crystallisation have been omitted for clarity. Purple (Mn), Red (O), Blue (N), Grey (C) and Yellow (F).

Table 5.2. List of all intermolecular interactions observed in 5.1-5.6.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Atom Labelling F-H</th>
<th>(Intermolecular Distance, Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>F1...H16'(O1')</td>
<td>1.832</td>
</tr>
<tr>
<td></td>
<td>F1...H3'(C3')</td>
<td>2.584</td>
</tr>
<tr>
<td></td>
<td>F1...H8'(C8')</td>
<td>2.624</td>
</tr>
<tr>
<td></td>
<td>F1...H9'(C9')</td>
<td>2.635</td>
</tr>
<tr>
<td></td>
<td>F2...H12'(O2')</td>
<td>1.923</td>
</tr>
<tr>
<td></td>
<td>F2...H8'(C8')</td>
<td>2.601</td>
</tr>
<tr>
<td></td>
<td>F3...H13'(O3')</td>
<td>1.989</td>
</tr>
<tr>
<td></td>
<td>F3...H15'(O1')</td>
<td>1.827</td>
</tr>
<tr>
<td>5.2</td>
<td>F1...H1B'(O1')</td>
<td>1.884</td>
</tr>
<tr>
<td></td>
<td>F1...H8'(C8')</td>
<td>2.326</td>
</tr>
<tr>
<td></td>
<td>F2...H2'(C2')</td>
<td>2.485</td>
</tr>
<tr>
<td>Complex</td>
<td>Atom Labelling F-H</td>
<td>(Intermolecular Distance, Å)</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td></td>
<td>F2...H10'(C10')</td>
<td>2.540</td>
</tr>
<tr>
<td></td>
<td>F3...H1A'(O1')</td>
<td>1.874</td>
</tr>
<tr>
<td></td>
<td>F3...H3'(C3')</td>
<td>2.391</td>
</tr>
<tr>
<td><strong>5.3</strong></td>
<td>F1...H1H'(O1')</td>
<td>1.879</td>
</tr>
<tr>
<td></td>
<td>F1...H3'(C3')</td>
<td>2.332</td>
</tr>
<tr>
<td></td>
<td>F1...H11A'(C11')</td>
<td>2.456</td>
</tr>
<tr>
<td></td>
<td>F2...H1'(C1')</td>
<td>2.413</td>
</tr>
<tr>
<td></td>
<td>F2...H4'(C4')</td>
<td>2.665</td>
</tr>
<tr>
<td></td>
<td>F3...H2H'(O2')</td>
<td>1.951</td>
</tr>
<tr>
<td></td>
<td>F3...(H8'(C8'))</td>
<td>2.357</td>
</tr>
<tr>
<td><strong>5.4</strong></td>
<td>F1...O3'</td>
<td>2.779</td>
</tr>
<tr>
<td></td>
<td>F2...O2'</td>
<td>2.865</td>
</tr>
<tr>
<td></td>
<td>F2...O3'</td>
<td>2.689</td>
</tr>
<tr>
<td></td>
<td>F3...O2'</td>
<td>2.775</td>
</tr>
<tr>
<td></td>
<td>F3...H8'(C8')</td>
<td>2.561</td>
</tr>
<tr>
<td><strong>5.5</strong></td>
<td>F1...H1B'(O1')</td>
<td>1.751</td>
</tr>
<tr>
<td></td>
<td>F2...H1A'(O1')</td>
<td>1.896</td>
</tr>
<tr>
<td></td>
<td>F2...H3A'(C3')</td>
<td>2.481</td>
</tr>
<tr>
<td></td>
<td>F2...H11A'(C11')</td>
<td>2.388</td>
</tr>
</tbody>
</table>
Chapter 5: A Facile Synthetic Route to a Family of Mn\textsuperscript{III} Monomers

<table>
<thead>
<tr>
<th>Complex</th>
<th>Atom Labelling F-H</th>
<th>(Intermolecular Distance, Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F3…O2′</td>
<td>2.640</td>
</tr>
<tr>
<td>5.6</td>
<td>F1…H1A′(O1′)</td>
<td>1.797</td>
</tr>
<tr>
<td></td>
<td>F2…H1B′(O1′)</td>
<td>1.848</td>
</tr>
<tr>
<td></td>
<td>F2…H8′(C8′)</td>
<td>2.508</td>
</tr>
<tr>
<td></td>
<td>F3…H10′(C10′)</td>
<td>2.616</td>
</tr>
<tr>
<td></td>
<td>F3…Cl1′</td>
<td>2.873</td>
</tr>
</tbody>
</table>

The packing arrangements in 5.5 and 5.6 share similarities in that they both comprise superimposable columns of \{Mn\} units along the $b$ and $a$ cell directions respectively to give Mn1−Mn1′ internodal distances of 7.624 Å (5.5) and 7.315 Å (5.6). More specifically these monomers arrange in brickwork sheets (propagating along the $ab$ planes in 5.5 and $ac$ plane in 5.6) which are held in place by interdigitated off-set $\pi_{\text{centroid}}$...$\pi_{\text{centroid}}$ close contacts at distances of 3.886 Å in 5.5 ([C7-N2]...[C7′-N2′]) and 3.681 Å in 5.6 ([C1-N1]...[C1′-N1′]). These 2D sheets align in parallel motifs across the $ac$ plane in 5.5 and along the $bc$ plane in 5.6 and are held in position via numerous H-bonding interactions between terminal F\textsuperscript{−} ions and ligated water protons of juxtaposed monomers (i.e. F1−H1B′(O1′) = 1.751 Å in 5.5 and F1−H1A′(O1′) = 1.797 Å in 5.6). Moreover, Cl−F dipole-dipole interactions also influence the overall packing in 5.6 (F3−Cl1′ = 2.873 Å) and leads to the slight packing differences observed between the two complexes (Fig. 5.6).
Figure 5.6. Crystal packing in 5.5 (top) and 5.6 (bottom) as viewed along the c direction of their unit cells. All hydrogen atoms and solvents of crystallisation have been omitted for clarity. Purple (Mn), Red (O), Blue (N), Grey (C) and Yellow (F).

An extensive study was carried out in the literature to account for the number of Mn monomers with reported anisotropic ‘D values’. Approximately six hundred Mn$^{III}$ monomers were found but only a small percentage (~5%) with reported D values. This highlights how such materials have not been extensively considered as good sources of Mn$^{III}$ starting materials in the field of molecular magnetism. These monomeric complexes with reported D values are in the scientific papers referenced [13-34], in section 5.5.\[^8, 11\] Details of Mn$^{III}$ monomers with reported D values are reported in Table 5.3, below.\[^12\]

Table 5.3. Mn monomers in the literature with reported D values from magnetism or EPR studies.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Jahn-Teller Elongation /Compression Distances (Å)</th>
<th>Spin Hamiltonian Parameters (from $\chi_M T$ data unless stated otherwise)</th>
<th>Spin Hamiltonian Parameters (from EPR)</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| 1.      | [Mn$^{III}$(sal)(bpy)(MeOH)Cl].MeOH | Mn-Cl 2.495(2)  
Mn-O(2) 2.315(4) | D = -3.46 cm$^{-1}$  
g = 2.00 | Not Available | \[^13\] |
<table>
<thead>
<tr>
<th>Complex</th>
<th>Jahn-Teller Elongation / Compression Distances (Å)</th>
<th>Spin Hamiltonian Parameters (from $\chi_T$ data unless stated otherwise)</th>
<th>Spin Hamiltonian Parameters (from EPR)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>[Mn$^{III}$]<a href="O$_2$CMe">H$_2$O</a>(3-OEtalen).CH$_3$CN</td>
<td>Mn-O(28) 2.347(2)  Mn-O(29) 2.125(2) D = -1.76 cm$^{-1}$ *Fitted as an intermolecular H-bonded dimer</td>
<td>Not Available</td>
<td>[14]</td>
</tr>
<tr>
<td>3.</td>
<td>[Mn$^{III}$(tolylerpy)$_2$][PF$_6$]$_2$.2CH$_3$CN</td>
<td>Mn-N(2) 1.9749(12) J-T compressed Mn$^{III}$ centre</td>
<td>M vs. H data fitted equally well with the following two sets of parameters: D = -3.89 cm$^{-1}$, E/D = 0.09, $g_{x,y} = 2.09$, $g_z = 1.95$. D = +4.82 cm$^{-1}$, E/D = 0.27; $g_x = 2.09$, $g_y = 2.11$, $g_z = 1.95$.</td>
<td>No HF-EPR transition observed in any spectra at temperatures between 5 and 30 K. Frequency-domain magnetic resonance spectroscopy (FDMRS) also showed no signal. May be attributed to large D strain or fast spin-lattice relaxation.</td>
</tr>
<tr>
<td>5.</td>
<td><a href="PF$_6$">Mn$^{III}$L</a></td>
<td>Mn-N(2) 2.162(3) Mn-N(3) 2.106(3)</td>
<td></td>
<td>$</td>
</tr>
<tr>
<td>6.</td>
<td>[Mn$^{III}$($L^{SO}$)$_2$(L$^{N\pi}$)] $L^{AP}$ = aminophenolate(-)-form of 2-anilino-4,6-di-tert-butylphenol $L^{ISO} = \pi$ radical form of o-iminobenzosemiquinonate. $L^{ISO}$ = the monoanionic $\pi$ radical form o-iminobenzosemiquinonate(-)</td>
<td>Mn-N(1) 2.345(3) Mn-N(2) 2.082(3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$D = -1.76$ cm$^{-1}$

$|D| = 4.53$ cm$^{-1}$ (from ESI of ref 4)

$|D| = 4.15$ cm$^{-1}$

$|D| = 4.15$ cm$^{-1}$

$g = 2.00$

$|E| = 0.75$ cm$^{-1}$

$|D_{ox} - | = 3.4$ cm$^{-1}$

$J = -300$ cm$^{-1}$

*g = 2.00 (fixed)

* Strong AF exchange observed between the Mn$^{III}$
### Chapter 5: A Facile Synthetic Route to a Family of Mn\textsuperscript{III} Monomers

<table>
<thead>
<tr>
<th>Complex</th>
<th>Jahn-Teller Elongation /Compression Distances (Å)</th>
<th>Spin Hamiltonian Parameters (from $\chi_{MT}$ data unless stated otherwise)</th>
<th>Spin Hamiltonian Parameters (from EPR)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[L\textsuperscript{6}Mn\textsuperscript{III}(CH\textsubscript{3}OH)\textsubscript{2}]</td>
<td></td>
<td></td>
<td></td>
<td>[18]</td>
</tr>
<tr>
<td>(L^6 = 2)-hydroxy-N-(2-{(1E)-(2-hydroxyphenyl)methylene]amino]propyl) benzamide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn1-O3 = 2.264(2) Mn1-O4 = 2.290(1)</td>
<td>The best fit yields the parameters: (J = -0.2\ \text{cm}^{-1}), (g = 2.03) and (D = -0.01\ \text{cm}^{-1}). However, almost equally good fits may be obtained for (D) values ranging from 3 to (-3\ \text{cm}^{-1}). This indetermination of the axial single-ion ZFS of Mn\textsuperscript{III} was confirmed by an error-surface plot which showed that while the value of (J) was well determined by the fitting procedure, the value of (D) was not.</td>
<td></td>
<td>Not Available</td>
<td></td>
</tr>
<tr>
<td>[Mn\textsuperscript{III}(HphpzH)\textsubscript{2}Cl]</td>
<td></td>
<td></td>
<td></td>
<td>[19]</td>
</tr>
<tr>
<td>(HphpzH = 3(5)-(2\text{-hydroxyphenyl})pyrazole)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Not available</td>
<td>Fitted as intermolecular H-bonded AF 1D* ladder-like structure to give: (</td>
<td>J</td>
<td>/kB = 1.1\ \text{K}) (from $\chi_{MT}$ and specific heat measurements) and 1.2 K (from M vs. H)</td>
<td></td>
</tr>
</tbody>
</table>
### Table

<table>
<thead>
<tr>
<th>Complex</th>
<th>Jahn-Teller Elongation /Compression Distances (Å)</th>
<th>Spin Hamiltonian Parameters (from $\chi_mT$ data unless stated otherwise)</th>
<th>Spin Hamiltonian Parameters (from EPR)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn$^{III}$(HphpzH)$_2$Br]</td>
<td>Mn-Br(1) 2.6025(6) * 5 coordinate Mn$^{III}$ centre</td>
<td>Fitted as intermolecular H-bonded AF 1D* ladder-like structure to give: $</td>
<td>J</td>
<td>/K_B = 0.7$ K (from $\chi_mT$ and specific heat measurements) and 0.9 K (from $M$ vs. $H$) * 3D ordering below 1.5 K</td>
</tr>
<tr>
<td>[Mn$^{III}$(HphpzPh)$_2$Cl]</td>
<td>Two ASU in cell, both comprise 5 coordinate Mn$^{III}$ centres Mn(1)-Cl(1) 2.3889(13) Mn(2)OCl(2)</td>
<td>Intermolecular H-bonded AF 2D structure. No spin Hamiltonian parameters elucidated.</td>
<td>Not Available</td>
<td></td>
</tr>
</tbody>
</table>
### Chapter 5: A Facile Synthetic Route to a Family of MnIII Monomers

<table>
<thead>
<tr>
<th>Complex</th>
<th>Jahn-Teller Elongation /Compression Distances (Å)</th>
<th>Spin Hamiltonian Parameters (from $\chi_M$T data unless stated otherwise)</th>
<th>Spin Hamiltonian Parameters (from EPR)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>13. $[\text{Mn}^\text{III}(\text{HphpzPh})_2\text{Br}]$</td>
<td>Two ASU in cell, both comprise 5 coordinate MnIII centres</td>
<td>Intermolecular H-bonded AF 2D structure. No spin Hamiltonian parameters elucidated.</td>
<td></td>
<td>[20]</td>
</tr>
<tr>
<td>HphpzPh = 3(S)-(2-hydroxyphenyl)-5(3)-phenylpyrazole</td>
<td>Mn(1)-Br(1) 2.5441(12) Mn(2)-OBr(2) 2.5447(11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14. ${[\text{HimH}][\text{Mn}^\text{III}(\text{sal})_2(\text{py})\text{H}_2\text{O}]}_2^*$</td>
<td>Mn(1)-N(11) 2.368(8) Mn(1)-Ow(1) 2.213(7) Mn(2)-N(31) 2.369(7) Mn(2)-Ow(2) 2.225(7)</td>
<td></td>
<td>Not Available</td>
<td>[21]</td>
</tr>
<tr>
<td>sal = salicylate, py = pyridine, [HimH]$^+$ = imidazole cation, * H-bonded intermolecular dimer.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15. $[\text{Mn}^\text{III}(\text{dbm})_3]$</td>
<td>Not Available</td>
<td>Not available</td>
<td></td>
<td>[22]</td>
</tr>
<tr>
<td>Hdbm = 1,3-diphenyl-1,3-propanedione</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bpaeOH = $N,N'$-bis(2-pyridylmethyl)-2-aminoethanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17. ${[\text{py}_2(\text{NMe})_2]\text{Mn}^\text{III}\text{J}_3}_2^+$</td>
<td>Mn-N(2) 2.274(2) Mn-N(2') 2.278(2)</td>
<td></td>
<td></td>
<td>[24]</td>
</tr>
<tr>
<td>py$_2$(NMe)$_2$ = $N,N'$-dimethyl-2,11 diaza<a href="2,6">3,3</a>pyridinophane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18. $\text{(Me}_4\text{N})[\text{Mn}^\text{III}(\text{opba})\text{H}_2\text{O}]_2$</td>
<td>Not Available in paper</td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>obpa = o-phenylenebis(oxamate)</td>
<td>D = -7.4 cm$^{-1}$ g = 2.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19. $\text{(Ph}_3\text{P})[\text{Mn}^\text{III}(\text{opba})\text{py}]_2\text{H}_2\text{O}$</td>
<td>Not Available in paper</td>
<td></td>
<td></td>
<td>[26]</td>
</tr>
<tr>
<td>obpa = o-phenylenebis(oxamate)</td>
<td>D = -5.8 cm$^{-1}$ g = 2.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20. $\text{(NEt}_4)[(\text{Tp}^\ast)\text{Mn}^\text{III}(\text{CN})_3]$</td>
<td>No JT distortion</td>
<td></td>
<td></td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>D/kB = +9.4(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Complex</th>
<th>Jahn-Teller /Compression Distances (Å)</th>
<th>Spin Hamiltonian Parameters (from χ$_MT$ data unless stated otherwise)</th>
<th>Spin Hamiltonian Parameters (from EPR)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tp* = Tris[3,5-dimethylpyrazolyl]borate</td>
<td>observed</td>
<td>g = 2.09(2)</td>
<td>Not Available</td>
<td>[26]</td>
</tr>
</tbody>
</table>

21. | | | | |
| [Mn$^{III}$ (N$_3$)(DH$_3$)] | Mn–O(2) | D = -3.25 cm$^{-1}$ (from M vs. H data) | Not Available | [26] |
| L = 2,2-bis(hydroxymethyl)-2,2',2''-nitrilotriethanol | Mn–O(4) | | | |
| | 2.208(1) | | | |
| | 2.235(2) | | | |
| | | | | |

22. | | | | |
| [Mn$^{III}$ (valen)-(H$_2$O)(NCS)] .2CH$_3$CN | Mn–O(1) | D = -3.1 cm$^{-1}$ | Not Available | [27] |
| H$_2$valen = a bicompartimental Schiff base proligand, resulting from the 2:1 condensation of 3-methoxysalicylaldehyde with ethylenediamine | Mn–N(3) | g = 2.14 | | |
| | 2.263(2) | | | |
| | 2.214(2) | | | |
| | | | | |

23. | | | | |
| [Mn$^{III}$ (dbm)$_2$(py)$_2$](ClO$_4$) | Mn–N(1) | | Not Available | [28] |
| dbm = anion of 1,3-diphenyl-1,3 propanedione (dibenzoylmethane) | Mn–N(2) | | | |
| | 2.291(1) | | | |
| py = pyridine | 2.273(1) | | | |
| | | | | |

24. | | | | |
| (NH$_4$)$_5$[Mn$^{III}$ (C$_6$H$_4$O$_7$)$_2$].2H$_2$O | Mn–O(1) | D = 0.29 cm$^{-1}$ (from χ$_MT$) | EPR carried out but no D value elucidated | [29] |
| C$_6$H$_4$O$_7$ = citrate | Mn–O(1) | g = 1.95 | | |
| | 2.2244(14) | | | |
| | 2.2244(14) | | | |
| | | | | |

25. | | | | |
| [Mn$^{III}$ (cyclam)(NCH$_3$)$_2$][CF$_3$SO$_3$] | Mn–N1 | D = -4.65 cm$^{-1}$ | Not Available | [30] |
| cyclam = 1,4,8,11-tetraazacyclotetradecane | Mn–N2 | | | |
| | 2.209 | | | |
| | 2.215 | | | |
| | | | | |

26. | | | | |
| cyclam = 1,4,8,11-tetraazacyclotetradecane | | | | |
| | | | | |

27. | | | | |
| [Mn$^{III}$ (cyclam)(NCSe)$_2$][CF$_3$SO$_3$].H$_2$O | | | Not Available | [30] |
| cyclam = 1,4,8,11-tetraazacyclotetradecane | | | | |
| | | | | |

28. | | | | |
| [Mn$^{III}$ (terpy)(Cl)$_3$] | Mn–Cl(2) | | Not Available | [31] |
| terpy=2,2':6,2''-terpyridine | Mn–Cl(3) | | | |
| | 2.2933(6) | | | |

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<table>
<thead>
<tr>
<th>Complex</th>
<th>Jahn-Teller Elongation /Compression Distances (Å)</th>
<th>Spin Hamiltonian Parameters (from $\chi^*_T$ data unless stated otherwise)</th>
<th>Spin Hamiltonian Parameters (from EPR)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>29. $[{\text{Mn}^{III}(\text{Phterpy})(\text{Cl})<em>3}]</em>{\text{}}$ Phterpy=4'-phenyl-2,2':6',2''-terpyridine</td>
<td>Mn-Cl(2) 2.2719(6)</td>
<td>$g_y = g_z = 2.00(1)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30. $[{\text{(terpy)}\text{Mn}^{III}(\text{N}_3)<em>3}]</em>{\text{}}$ terpy = 2,2':6',2''-terpyridine</td>
<td>Mn-N(1) 2.293(2)</td>
<td>Not Available</td>
<td>$D = -3.53(3)$ cm$^{-1}$ $E = 0.30(2)$ cm$^{-1}$ $g_x = g_y = 1.98(1)$ $g_z = 1.95(1)$</td>
<td></td>
</tr>
<tr>
<td>31. $[{\text{Mn}^{III}(\text{bpea})(\text{F})<em>3}]</em>{\text{}}$ bpea = N,N-bis(2-pyridylmethyl)-ethylamine</td>
<td>Mn-N(2) 2.2673(18)</td>
<td>Not Available</td>
<td>$D = -3.29$ cm$^{-1}$ $E = 0.48$ cm$^{-1}$ $g_x = 2.00$ $g_y = 1.98$ $g_z = 2.01$</td>
<td></td>
</tr>
<tr>
<td>32. $[{\text{Mn}^{III}(\text{bpea})(\text{N}_3)<em>3}]</em>{\text{}}$ bpea = N,N-bis(2-pyridylmethyl)-ethylamine</td>
<td>Mn-N(5) 1.9695(15)</td>
<td>Not Available</td>
<td>$D = +3.50(1)$ cm$^{-1}$ $E = 0.82(1)$ cm$^{-1}$ $g_x = 2.02(1)$ $g_y = 1.98(1)$ $g_z = 1.95(1)$</td>
<td></td>
</tr>
<tr>
<td>33. $[{\text{Mn}^{III}(\text{terpy})(\text{F})<em>3}]</em>{\text{}}$ terpy = 2,2':6',2''-terpyridine</td>
<td>Mn-N(2) 2.2561(9)</td>
<td>Not Available</td>
<td>$D = -3.82(2)$ cm$^{-1}$ $E = 0.75$ cm$^{-1}$ $g_x = 1.97(2)$ $g_y = 2.04(1)$ $g_z = 1.96(1)$</td>
<td></td>
</tr>
<tr>
<td>34. $[{\text{Mn}^{III}(\text{vanoph})(\text{DMF})(\text{H}_2\text{O})}]\text{ClO}_4$ H$_2$vanoph = N,N'-((1,2-phenylene)-bis(3-</td>
<td>Mn(1)-O(5) 2.287(2)</td>
<td>Fitting as monomer unsuccessful.</td>
<td>Not Available</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 5: A Facile Synthetic Route to a Family of Mn$^{III}$ Monomers

### Table 5.4. Mn-F Raman peaks for MnF$_3$ (literature and used in this work) and complex 5.1.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(cm$^{-1}$)</th>
<th>(cm$^{-1}$)</th>
<th>(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnF$_3$ (literature)$^{[35]}$</td>
<td>184, 283, 311</td>
<td>513</td>
<td>651</td>
</tr>
<tr>
<td>MnF$_3$ (this work)</td>
<td>262*</td>
<td>491</td>
<td>574</td>
</tr>
<tr>
<td>5.1 (this work)</td>
<td>244*</td>
<td>481</td>
<td>582</td>
</tr>
</tbody>
</table>

*very broad peak

5.2.1 FT-IR and Raman Spectroscopy

Solid state Raman spectra were obtained from 1.5% in KBr solid matrixes of complex 5.1 and of the 2,2-bipyridine ligand and MnF$_3$ as purchased, while a FT-IR spectrum was obtained from a polycrystalline sample of 5.1 (Fig. 5.6 and 5.10). All data in this section were normalised and baseline corrected using standard methods unless otherwise stated. Raman spectra provide information in the 150 to 700 cm$^{-1}$ spectral region that is not accessible by our FT-IR measurements.

The experimental Raman spectrum of MnF$_3$ exhibits peaks at 262, 491 and 574 cm$^{-1}$. The literature reports peaks at 184, 283, 311, 513 and 651 cm$^{-1}$ referring to in complete literature data in their text.$^{[35]}$ A theoretical study carried out by Nguyen...
and co-workers proposed that MnF₃ has a T-shaped confirmation, with two longer and a shorter Mn-F bond as its lowest energy isomer. Their predicted IR spectra (vibrational modes (A₁)) of MnF₃ gave peaks centred at 760 and 720 cm⁻¹, along with a lower intensity band at 180 cm⁻¹. Note that these calculations were all done in the gas phase. Therefore, we can tentatively assign the peaks mentioned in Table 5.4 in our experimental spectra in this work to two stretching (491, 481 and 574, 582 cm⁻¹) and one bending mode (262 and 244 cm⁻¹). Intensities of these Raman bands when compared with the Mn-F bond lengths in 5.1 conditionally confirm this. The two Mn-F bonds with lengths of 1.835 and 1.833 Å compare to the peak of greater intensity at 582 cm⁻¹ whereas the less intense Raman peak at 481 cm⁻¹ compares to the Mn-F bond with a length of 1.844 Å. Peak intensities are indicative of population. Bands are observed in the Raman spectrum of complex 5.1 at 244, 481 and 574 cm⁻¹ which tentatively confirm the presence of Mn-F bonds as expected for these molecules. (Fig. 5.7-5.9 and Table 5.4).³⁶³⁷

Table 5.5. Main Raman peaks for 2,2-bipyridine (literature and used in this work) and complex 5.1.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2-bipyridine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(literature)⁴⁰</td>
<td>616</td>
<td>763</td>
<td>995</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2,2-bipyridine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(literature)⁴⁰</td>
<td>614</td>
<td>765</td>
<td>996</td>
<td>1046</td>
<td>1236</td>
</tr>
<tr>
<td>2,2-bipyridine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(this work)</td>
<td>626</td>
<td>766</td>
<td>1014</td>
<td>1059</td>
<td>1261</td>
</tr>
<tr>
<td>5.1 (this work)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.6. Main Raman peaks for 2,2-bipyridine (literature and used in this work) and complex 5.1 -continued.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2-bipyridine (literature)</td>
<td>1314</td>
<td>1448</td>
<td>1484</td>
<td>1564</td>
<td>1615</td>
</tr>
<tr>
<td>2,2-bipyridine (literature)</td>
<td>1308</td>
<td>1444</td>
<td>1481</td>
<td>1569</td>
<td>1587</td>
</tr>
<tr>
<td>2,2-bipyridine (literature)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2-bipyridine (literature)</td>
<td>1301</td>
<td>1446</td>
<td>1482</td>
<td>1573</td>
<td>1590</td>
</tr>
<tr>
<td>5.1 (this work)</td>
<td>1311</td>
<td>-</td>
<td>1489</td>
<td>1566</td>
<td>1593</td>
</tr>
</tbody>
</table>

Similarities between the Raman spectra of 5.1 and 2,2-bipyridine can be seen in Figures 5.6, 5.9 and 5.10 and are also tabulated in Tables 5.5 and 5.6. Castellucci and co-workers made reliable assignments of the internal Raman modes of 2,2-bipyridine \(^{38-40}\) and designated peaks at 616, 1056 and 1308 cm\(^{-1}\) to an in-plane ring deformation, ring-ring stretching and a C-H deformation respectively. These figures compare well with our experimental figures of 614, 1046 and 1301 cm\(^{-1}\) for 2,2-bipyridine. Related peaks are present in the spectrum of complex 5.1 at 626, 1059 and 1311 cm\(^{-1}\).
Figure 5.6. Overlay of FT-IR and Raman spectra obtained from 2,2-bipyridine and 5.1.

Figure 5.7. Raman spectra in the 200-400 cm\(^{-1}\) region obtained from crystalline sample of 5.1 and MnF\(_3\).
Figure 5.8. Raman spectra in the 320-700 cm⁻¹ region obtained from crystalline sample of 5.1 and MnF₃.

Figure 5.9. Raman spectra in the 320-700 cm⁻¹ region obtained from crystalline sample of 2,2-bipyridine, 5.1 and MnF₃.
Figure 5.10. Raman spectra in the 700-1500 cm⁻¹ region obtained from crystalline sample of 2,2-bipyridine and 5.1.

Solid state Raman spectra were also obtained from complex 5.2 and the as purchased MnF₃ and 1,10-phenanthroline ligand, while a FT-IR spectrum was obtained from a polycrystalline sample of 5.2 (Figures 5.11 and 5.15).

Table 5.7. Mn-F Raman bands for MnF₃ (literature and used in this work) and complex 5.2.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnF₃ (literature)</td>
<td>184, 283, 311</td>
<td>513</td>
<td>651</td>
</tr>
<tr>
<td>MnF₃ (this work)</td>
<td>262*</td>
<td>491</td>
<td>574</td>
</tr>
<tr>
<td>5.2 (this work)</td>
<td>276*</td>
<td>482</td>
<td>574</td>
</tr>
</tbody>
</table>

*very broad peak

The experimental Raman spectrum of MnF₃ exhibits peaks at 262, 491 and 574 cm⁻¹. As mentioned earlier in this section the literature reports peaks at 184, 283, 311, 513 and 651 cm⁻¹ referring to in complete literature data in their text. Raman bands are found in the Raman spectrum of complex 5.2 at 276, 482 and 574 cm⁻¹ tentatively confirming the presence of Mn-F bonds in our complex, similar to 5.1 (Fig. 5.12-5.14 and Table 5.7). Intensities of these Raman bands when compared with the Mn-F bond lengths in 5.2 conditionally confirm this. The two Mn-F bonds with lengths of 1.838 and 1.847 Å in 5.2 compare to the peak of greater intensity at 574 cm⁻¹ whereas the less intense Raman peak at 482 cm⁻¹ compares to the Mn-F
bond with a length of 1.808 Å. As mentioned previously peak intensities are indicative of population.

**Table 5.8.** Main Raman peaks for 1,10-phenanthroline (literature and used in this work) and complex 5.2.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(cm(^{-1}))</th>
<th>(cm(^{-1}))</th>
<th>(cm(^{-1}))</th>
<th>(cm(^{-1}))</th>
<th>(cm(^{-1}))</th>
<th>(cm(^{-1}))</th>
<th>(cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,10-phenanthroline (literature)(^{[41]})</td>
<td>410</td>
<td>551</td>
<td>706</td>
<td>1035</td>
<td>1293</td>
<td>1401</td>
<td>1448</td>
</tr>
<tr>
<td>1,10-phenanthroline (literature)(^{[42]})</td>
<td>411</td>
<td>552</td>
<td>711</td>
<td>1036</td>
<td>1295</td>
<td>1405</td>
<td>1446</td>
</tr>
<tr>
<td>1,10-phenanthroline (this work)</td>
<td>410</td>
<td>551</td>
<td>710</td>
<td>1035</td>
<td>1295</td>
<td>1406</td>
<td>1445</td>
</tr>
<tr>
<td>5.2 (this work)</td>
<td>420</td>
<td>556</td>
<td>735</td>
<td>1054</td>
<td>1308</td>
<td>1426</td>
<td>1454</td>
</tr>
</tbody>
</table>

Similarities between the spectra of 5.2 and 1,10-phenanthroline can be seen in Figure 5.14 and 5.15 and are also tabulated in Table 5.8. Peaks at 410, 710, 1035, 1295, 1406 and 1445 cm\(^{-1}\) are the most intense peaks observed in the Raman spectrum of 1,10-phenanthroline, which correlate with literature values shown in Table 5.8. These bands are due to in-plane modes (A\(_1\)).\(^{[41-42]}\)

**Figure 5.11.** Overlay of FT-IR and Raman spectra obtained from 1,10-phenanthroline and 5.2.
Figure 5.12. Raman spectra in the 100-400 cm\(^{-1}\) region obtained from crystalline sample of 5.2 and MnF\(_3\).

Figure 5.13. Raman spectra in the 320-700 cm\(^{-1}\) region obtained from crystalline sample of 5.2 and MnF\(_3\).
Solid state Raman spectra were also obtained from complexes 5.3-5.6; their as purchased corresponding ligands along with the MnF₃ precursor, while FT-IR spectra were also obtained from polycrystalline samples of 5.3-5.6. Overlays of these plots can be seen in Figures 5.16-5.25, which represent similar trends to complexes 5.1 and 5.2. Literature values for the Raman bands of 6-methyl-2,2′-dipyridyl, 4,4′-dimethyl,2,2′-dipyridyl, 5,5-dimethyl-2,2′-dipyridyl and 5-chloro-1-10-phenanthroline were not found as these ligands are not as widely used. Although these ligands are derivatives of 2,2'-bipyridine and 1,10-phenanthroline and
therefore present similar peaks. Table 5.9 below shows Mn-F Raman bands for each of the complexes 5.1-5.6.

**Table 5.9.** Mn-F Raman bands for MnF₃ (literature and used in this work) and complexes 5.1-5.6.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
<th>(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnF₃ (literature)</td>
<td>184, 283, 311</td>
<td>513</td>
<td>651</td>
</tr>
<tr>
<td>MnF₃ (this work)</td>
<td>262*</td>
<td>491</td>
<td>574</td>
</tr>
<tr>
<td>5.1 (this work)</td>
<td>244*</td>
<td>481</td>
<td>582</td>
</tr>
<tr>
<td>5.2 (this work)</td>
<td>276*</td>
<td>482</td>
<td>574</td>
</tr>
<tr>
<td>5.3 (this work)</td>
<td>275*</td>
<td>484</td>
<td>573</td>
</tr>
<tr>
<td>5.4 (this work)</td>
<td>264*</td>
<td>481</td>
<td>589</td>
</tr>
<tr>
<td>5.5 (this work)</td>
<td>271*</td>
<td>488</td>
<td>564</td>
</tr>
<tr>
<td>5.6 (this work)</td>
<td>279*</td>
<td>501</td>
<td>586</td>
</tr>
</tbody>
</table>

*broad peak

**Figure 5.16.** Overlay of FT-IR and Raman spectra obtained from 5.3.
Figure 5.17. Raman spectra in the 320-700 cm\(^{-1}\) region obtained from crystalline sample of 5.3 and MnF\(_3\).

Figure 5.18. Overlay of FT-IR and Raman spectra obtained from 4,4'-dimethyl,2,2'-dipyridyl and 5.4.
Figure 5.19. Raman spectra in the 320-700 cm\(^{-1}\) region obtained from crystalline sample of 5.4 and MnF\(_3\).

![Raman spectra in the 320-700 cm\(^{-1}\) region obtained from crystalline sample of 5.4 and MnF\(_3\).](image)

Figure 5.20. Raman spectra in the 320-700 cm\(^{-1}\) region obtained from crystalline sample of 4,4'-dimethyl,2,2'-dipyridyl, 5.4 and MnF\(_3\).

![Raman spectra in the 320-700 cm\(^{-1}\) region obtained from crystalline sample of 4,4'-dimethyl,2,2'-dipyridyl, 5.4 and MnF\(_3\).](image)
Figure 5.21. Overlay of FT-IR and Raman spectra obtained from 5,5-dimethyl-2,2'-dipyridyl and 5.5.

Figure 5.22. Raman spectra in the 320-700 cm$^{-1}$ region obtained from crystalline sample of 5.5 and MnF$_3$. 
Chapter 5: A Facile Synthetic Route to a Family of Mn$^{III}$ Monomers

Figure 5.23. Raman spectra in the 320-700 cm$^{-1}$ region obtained from crystalline sample of 5,5-dimethyl-2,2’-dipyridyl, 5.5 and MnF$_3$.

Figure 5.24. Overlay of FT-IR and Raman spectra obtained from 5.6.
5.2.2 Magnetic Susceptibility Studies

Dc magnetic susceptibility measurements were performed on powdered microcrystalline samples of 5.1-5.6 in an applied magnetic field of 0.1 T and in the temperature range 300 to 5 K. The results are plotted as $\chi_M T$ product vs. T in Figures 5.26, 5.27 and 5.28. The high temperature $\chi_M T$ values obtained range from 2.84 (in 5.2) to 3.29 (in 5.3) cm$^3$ K mol$^{-1}$ and are very close to that expected (3.00 cm$^3$ K mol$^{-1}$) for single high-spin Mn$^{III}$ ions (where $g = 2$). There values decrease gradually with lowering temperature before reaching plateaus in the ~50-100 K region. These initial drops in $\chi_M T$ may be attributed to the extensive intermolecular interactions observed in the crystal structures 5.1-5.6. A second more abrupt drop in their susceptibilities are attributed to zero-field splitting effects, as expected for such anisotropic ions. The final resting $\chi_M T$ products at 5 K range from 1.94 (in 5.2) to 2.57 (in 5.5) cm$^3$ K mol$^{-1}$. In order to determine the single-ion axial anisotropy parameter for the Mn$^{III}$ centres in 5.1-5.6 variable-temperature-variable-field dc magnetisation experiments were performed in the 2.0-7.0 K and 0.5-7.0 T temperature and magnetic field ranges, respectively. These experimental data are presented as reduced magnetisation (M/NμB vs. H, with N being Avogadro’s number and k the Boltzmann constant) in the inset panels of Figures 5.26, 5.27 and
5.28. They were numerically fitted, by use of the simplex algorithm,\textsuperscript{[43]} to the axially anisotropic spin-Hamiltonian (Equation 5.1) below, by numerical diagonalisation of the full spin-Hamiltonian matrix.

\[
\hat{\mathcal{H}} = \sum_{i=1} \{ \mu_B \vec{B} g \hat{S}_i + D[\hat{S}_{z,i}^2 - \hat{S}_i (\hat{S}_i + 1)/3]\}
\]

\textbf{Equation 5.1.}

Here $D$ is the uniaxial anisotropy, and $S = 2$ the total spin of the Mn$^{\text{III}}$ ion. The best fit $D$ parameters were $D$ (cm$^{-1}$) = -3.974 (5.1), -3.012 (5.2), -3.098 (5.3), -3.898 (5.4), -4.018 (5.5) and -3.971 (5.6) (Table 5.10).
Figure 5.26. Plots of magnetic susceptibility ($\chi_M T$) vs. temperature (T) and reduced magnetisation ($M/N\mu_B$) vs. Field (H) (insets) obtained from polycrystalline samples of 5.1 (top) and 5.2 (bottom) respectively. See main text and Table 5.10 for details.
Figure 5.27. Plots of magnetic susceptibility ($\chi_M T$) vs. temperature (T) and reduced magnetisation ($M/N\mu_B$) vs. Field (H) (insets) obtained from polycrystalline samples of 5.3 (top) and 5.4 (bottom) respectively. See main text and Table 5.10 for details.
Figure 5.28. Plots of magnetic susceptibility ($\chi_mT$) vs. temperature (T) and reduced magnetisation ($M/N\mu_B$) vs. Field (H) (insets) obtained from polycrystalline samples of 5.5 (top) and 5.6 (bottom) respectively. See main text and Table 5.10 for details.
Table 5.10. Zero-field splitting parameters obtained from 5.1-5.6 using magnetic susceptibility measurements.

<table>
<thead>
<tr>
<th>Complex</th>
<th>g value</th>
<th>D (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>2</td>
<td>-3.974</td>
</tr>
<tr>
<td>5.2</td>
<td>2</td>
<td>-3.012</td>
</tr>
<tr>
<td>5.3</td>
<td>2</td>
<td>-3.098</td>
</tr>
<tr>
<td>5.4</td>
<td>2</td>
<td>-3.898</td>
</tr>
<tr>
<td>5.5</td>
<td>2</td>
<td>-4.018</td>
</tr>
<tr>
<td>5.6</td>
<td>2</td>
<td>-3.971</td>
</tr>
</tbody>
</table>
5.3 Concluding Remarks

We have demonstrated a new and facile synthetic route to a family of Mn$^{III}$ monomers with general formula \([\text{Mn}^{III}_3\text{F}_3(\text{H}_2\text{O})(\text{L}_x)]\). Magnetic susceptibility and magnetisation studies were successfully employed to elucidate their D-tensor parameters, which are in line with literature values. Raman Spectroscopy was also used to look at Mn-F stretches and subsequently compared to literature values. Work is currently underway on using 5.1-5.6 as presursors to discrete polymetallic cages and as building blocks to 1-3D extended architectures using self-assembly routes (Fig. 5.29).

![Figure 5.29. Structures of Mn monomers discussed throughout this chapter.](image)
Chapter 5: A Facile Synthetic Route to a Family of Mn\textsuperscript{III} Monomers

5.4 Experimental

5.4.1 Instrumentation

5.4.1.1 Carbon, Hydrogen and Nitrogen Micro-analysis

C, H and N elemental analysis were performed using a Perkin Elmer Series II CHNS / O Analyser (2400 Series).

5.4.1.2 Infrared Spectroscopy

Infra-red spectra were recorded on a Perkin Elmer FT-IR Spectrum One spectrometer equipped with a Universal ATR Sampling accessory (ZnSe diamond).

5.4.1.3 Magnetic Susceptibility Measurements

Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 1.8 K and alternating current (ac) magnetic susceptibility data were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal’s constants. Each sample was set in an eicosane wax to avoid torqueing of the crystalline material. Magnetic measurements were performed by the Brechin group at the University Of Edinburgh, Scotland, UK.

5.4.1.4 Single-Crystal X-ray diffraction

Complexes 5.1-5.6 were collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source. Each data reduction was carried out on the CRYSALISPRO software package. The structures were solved by direct methods (SHELXS-97\textsuperscript{[44]}) and refined by full matrix least squares using SHELXL-97\textsuperscript{[45]}. SHELX operations were automated using the OSCAIL software package.\textsuperscript{[46]} All hydrogen atoms in 5.1-5.6 were assigned to calculated positions. All non-hydrogen atoms were refined as anisotropic. Single crystals of complexes 5.4-5.6 were found to be weakly diffracting at higher angles and therefore several collections were attempted. Our best data sets have been supplied in this work. Crystal data and refinement parameters are tabulated in Tables 5.11 and 5.12.
5.4.1.5 RAMAN Spectroscopy

Raman spectra were obtained at the Nanoscale Biophotonics Laboratory at the School of Chemistry, NUI Galway. Raman measurements were recorded at room temperature using a Kaiser Optical Systems Raman spectrometer equipped with a 785 nm laser diode excitation source. A laser power of ~200 mW (at the sample) with an exposure time of 4 × 10 seconds was used with mapping of 2 x 2 spots and spectra were collected from 150 to 4000 cm\(^{-1}\) (at a resolution of 5 cm\(^{-1}\)). Raman spectra of the complex 5.1-5.6 were collected from a solid dispersion (approximately 1.5% by weight of complex) in dry KBr which was pressed into a disk using a hydraulic press and a 13 mm die set. This was done to minimise sample burning due to excessive absorption of excitation light. All data were normalised to the peak of maximum intensity and baseline corrected using standard methods.
### 5.4.2 Crystal structure information

**Table 5.11.** X-ray crystallographic data obtained from complexes 5.1-5.3

<table>
<thead>
<tr>
<th></th>
<th>5.1.2H2O</th>
<th>5.2</th>
<th>5.3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>{10}$H$</em>{14}$N$<em>{2}$O$</em>{3}$F$<em>{3}$Mn$</em>{1}$</td>
<td>C$<em>{12}$H$</em>{10}$N$<em>{2}$O$</em>{1}$F$<em>{3}$Mn$</em>{1}$</td>
<td>C$<em>{11}$H$</em>{12}$N$<em>{2}$O$</em>{1}$F$<em>{3}$Mn$</em>{1}$</td>
</tr>
<tr>
<td><strong>M$_{w}$</strong></td>
<td>322.17</td>
<td>310.16</td>
<td>300.17</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2$_1$/n</td>
<td>P2$_1$/c</td>
<td>P2$_1$/c</td>
</tr>
<tr>
<td><strong>a/Å</strong></td>
<td>9.0453(2)</td>
<td>8.3759(17)</td>
<td>8.3482(4)</td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
<td>7.4043(2)</td>
<td>7.2941(15)</td>
<td>7.4997(3)</td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
<td>19.4455(4)</td>
<td>19.268(4)</td>
<td>18.7579(10)</td>
</tr>
<tr>
<td><strong>α/°</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>β/°</strong></td>
<td>95.425(2)</td>
<td>101.83(3)</td>
<td>102.664(4)</td>
</tr>
<tr>
<td><strong>γ/°</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>V/Å$^3$</strong></td>
<td>1261.51(5)</td>
<td>1152.2(4)</td>
<td>1145.84(9)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
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<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>T/K</strong></td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td><strong>λ/Å</strong></td>
<td>0.7107</td>
<td>0.7107</td>
<td>0.7107</td>
</tr>
<tr>
<td><strong>D$_c$/g cm$^{-3}$</strong></td>
<td>1.651</td>
<td>1.788</td>
<td>1.740</td>
</tr>
<tr>
<td><strong>μ(Mo-Kα)/ mm$^{-1}$</strong></td>
<td>1.060</td>
<td>1.177</td>
<td>1.180</td>
</tr>
<tr>
<td><strong>Meas./indep.(R$_{int}$)</strong></td>
<td>3156/2390 (0.0633)</td>
<td>2105/1840 (0.0297)</td>
<td>2089/1933 (0.0205)</td>
</tr>
<tr>
<td><strong>Restraints, Parameters</strong></td>
<td>9, 196</td>
<td>0, 180</td>
<td>0, 172</td>
</tr>
<tr>
<td><strong>wR2 (all data)</strong></td>
<td>0.0879</td>
<td>0.0944</td>
<td>0.0610</td>
</tr>
<tr>
<td><strong>R1</strong>$^{de}$</td>
<td>0.0564</td>
<td>0.0361</td>
<td>0.0595</td>
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<tr>
<td><strong>Goodness of fit on F$^2$</strong></td>
<td>1.047</td>
<td>1.132</td>
<td>1.125</td>
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</table>

$^a$ Includes guest molecules. $^b$ Mo-Kα radiation, graphite monochromator. $^c$ wR2 = [$\Sigma$(IF$_o$ - IF$_c$)$^2$/ $\Sigma$(IF$_o$)$^2$]$^{1/2}$. $^d$For observed data. $^e$ R1 = $\Sigma$|IF$_o$-IF$_c$|/ $\Sigma$IF$_o$. 

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Table 5.12. X-ray crystallographic data obtained from complexes 5.4-5.6

<table>
<thead>
<tr>
<th></th>
<th>5.4.2H2O</th>
<th>5.5.0.5MeOH</th>
<th>5.6</th>
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</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C_{12}H_{14}N_{2}O_{3}F_{3}Mn_{1}</td>
<td>C_{12.5}H_{14}N_{2}O_{1.5}F_{3}Mn_{1}</td>
<td>C_{12}H_{9}N_{2}O_{1}Cl_{1}F_{3}Mn_{1}</td>
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<tr>
<td><strong>M_w</strong></td>
<td>346.19</td>
<td>328.20</td>
<td>344.60</td>
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<tr>
<td><strong>Crystal System</strong></td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-1</td>
<td>I2/a</td>
<td>Pbca</td>
</tr>
<tr>
<td><strong>a/Å</strong></td>
<td>6.8782(5)</td>
<td>16.4291(7)</td>
<td>7.3151(5)</td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
<td>10.3111(14)</td>
<td>7.6236(4)</td>
<td>16.5375(14)</td>
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<tr>
<td><strong>c/Å</strong></td>
<td>10.6165(19)</td>
<td>23.0374(14)</td>
<td>20.773(2)</td>
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<tr>
<td><strong>α/°</strong></td>
<td>73.723(15)</td>
<td>90</td>
<td>90</td>
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<td><strong>β/°</strong></td>
<td>86.860(12)</td>
<td>102.176(5)</td>
<td>90</td>
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<tr>
<td><strong>γ/°</strong></td>
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<td>90</td>
<td>90</td>
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<td><strong>V/Å³</strong></td>
<td>720.17(17)</td>
<td>2820.5(3)</td>
<td>2513.0(4)</td>
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<tr>
<td><strong>T/K</strong></td>
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<td>150(2)</td>
<td>150(2)</td>
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<tr>
<td><strong>λ Å</strong></td>
<td>0.7107</td>
<td>0.7107</td>
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<td><strong>D_g/g cm⁻³</strong></td>
<td>1.596</td>
<td>1.546</td>
<td>1.822</td>
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<td><strong>µ(Mo-Kα)/mm⁻¹</strong></td>
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<td>0.969</td>
<td>1.295</td>
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<tr>
<td><strong>Meas./indep.(R_{int}) refl.</strong></td>
<td>2649/2065(0.0534)</td>
<td>2573/2226(0.0348)</td>
<td>2297/1224(0.2124)</td>
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<td><strong>Restraints, Parameters</strong></td>
<td>0, 196</td>
<td>0, 189</td>
<td>0, 186</td>
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<tr>
<td><strong>wR2 (all data)²</strong></td>
<td>0.3463</td>
<td>0.1113</td>
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<tr>
<td><strong>R1⁵</strong></td>
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<tr>
<td><strong>Goodness of fit on F²</strong></td>
<td>1.116</td>
<td>1.243</td>
<td>1.052</td>
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</tbody>
</table>

* Includes guest molecules. ¹ Mo-Kα radiation, graphite monochromator. ² wR2 = [Σw(IFo^2 - IFc^2)^2 / ΣwIFo^2]^(1/2). ³ For observed data. ⁴ R1 = Σ||Fo|| - ||Fc|| / Σ||Fo||.
5.4.3 Synthetic Procedures

All reactions were performed under aerobic conditions and all reagents and solvents were used as purchased.

5.4.3.1 Synthesis of \([\text{Mn}^{III}\text{F}_3(\text{H}_2\text{O})(\text{L}_1)]\cdot2\text{H}_2\text{O} \ (5.1)\)

Anhydrous MnF$_3$ (0.5 g, 4.47 mmol, 1 eq.) and 2,2'-Bipyridine (L$_1$) (0.70 g, 4.48 mmol, 1 eq.) were dissolved in 50 cm$^3$ of methanol. The solution was heated with constant stirring at 50 °C for 3-5 minutes until it turned a black-red colour; it was then cooled and filtered. Slow evaporation of the solvent afforded X-ray quality crystals of 5.1 in 35 % yield.

C, H, N Elemental Analysis

Calculated for: C$_{10}$H$_{14}$N$_2$O$_3$F$_3$Mn$_1$

Theory (%): C 37.28, H 4.38; N 8.90.

Found (%): C 36.96, H 4.00; N 8.92.

Infrared Spectroscopy (cm$^{-1}$):

3531(m), 3440 (m), 3312 (m, b), 3115 (m), 3083 (m), 1667(m), 1598(s), 1575(m), 1563(m), 1493(m), 1472(s), 1441(vs), 1421(m), 1316(m), 1247(m), 1222(w), 1173(w), 1154(m), 1098(w), 1073(w), 1058(w), 1042(w), 1015(m), 1029(s), 810(m), 772(s), 731(vs), 658(s).

Raman (cm$^{-1}$):

244(w), 356(w), 416(w), 451(w), 481(w), 539(w), 582(w), 626(w), 646(w), 689(w), 766(m), 817(w), 996(w), 1014(s), 1059(m), 1115(w), 1151(w), 1261(w), 1284(w), 1311(s), 1364(w), 1406(w), 1454(w), 1489(m), 1566(m), 1593(s).

5.4.3.2 Synthesis of \([\text{Mn}^{III}\text{F}_3(\text{H}_2\text{O})(\text{L}_2)] \ (5.2)\)

Anhydrous MnF$_3$ (0.5 g, 4.47 mmol, 1 eq.) and 1,10 - Phenanthroline (L$_2$) (0.81 g, 4.47 mmol, 1 eq.) were dissolved in 50 cm$^3$ of methanol. The solution was heated
with constant stirring at 50 °C for 3-5 minutes until it turned a black-red colour; it was then cooled and filtered. Slow evaporation of the solvent afforded X-ray quality crystals of 5.2 in 32 % yield.

**C, H, N Elemental Analysis**

Calculated for: C_{12}H_{10}N_{2}O_{1}F_{3}Mn_{1}

Theory (%): C 46.47, H 3.25; N 9.03.

Found (%): C 46.88, H 3.01; N 9.33.

**Infrared Spectroscopy (cm\(^{-1}\)):**

3305(vb), 3225(vb), 3063(m), 1650(m), 1623(m), 1604(m), 1583(m), 1516(s), 1492(m), 1452(w), 1427(vs), 1345(m), 1308(w), 1259(w), 1223(w), 1196(w), 1151(m), 1143(m), 1104(m), 1034(w), 1004(w), 993(w), 975(w), 959(w), 908(w), 866(s), 849(vs), 780(m), 733(s), 722(vs).

**Raman (cm\(^{-1}\)):**

249(w), 276(w), 289(w), 420(m), 454(w), 482(w), 519(w), 556(w), 574(w), 726(w), 735(m), 851(w), 869(w), 1054(m), 1106(w), 1146(w), 1209(w), 1259(w), 1308(m), 1344(m), 1416(m), 1426(s), 1454(s), 1518(w), 1588(w), 1604 (w), 1624(w).

**5.4.3.3 Synthesis of [Mn\(^{III}\)F\(_3\)(H\(_2\)O)(L\(_3\))] (5.3)**

Anhydrous MnF\(_3\) (0.65 g, 5.81 mmol, 1 eq.) and 6-Methyl-2,2'-dipyridal (L\(_3\)) (0.99 g, 5.81 mmol, 1 eq.) were dissolved in 50 cm\(^3\) of methanol. The solution was heated with constant stirring at 50 °C for 3-5 minutes until it turned a black-red colour; it was then cooled and filtered. Slow evaporation of the solvent afforded X-ray quality crystals of 5.3 in 36 % yield.

**C, H, N Elemental Analysis**

Calculated for: C\(_{11}\)H\(_{12}\)N\(_2\)O\(_2\)F\(_3\)Mn\(_1\)

Theory (%): C 44.01, H 4.03; N 9.33.
Infrared Spectroscopy (cm\(^{-1}\)):

3339(vb), 3088(w), 1645(w), 1596(m), 1571(m), 1488(w), 1456(s), 1390(w), 1319(w),
1301(w), 1249(m), 1184(w), 1158(m), 1103(w), 1091(w), 1033(s), 1013(w), 900(vw),
814(w), 778(vs), 744(m), 723(m).

Raman (cm\(^{-1}\)):

256(w), 274(w), 336(w), 379(w), 463(w), 484(w), 561(w), 573(m), 654(w), 724(w),
815(w), 1014(s), 1032(s), 1060(w), 1106(w), 1161(w), 1241(w), 1269(w), 1303(m),
1322(s), 1391(w), 1450(w), 1491(m), 1569(m), 1594(w).

5.4.3.4 Synthesis of \([\text{Mn}^{III}\text{F}_3(\text{H}_2\text{O})(\text{L}_4)]\cdot2\text{H}_2\text{O}\) (5.4)

Anhydrous MnF\(_3\) (0.3 g, 2.68 mmol, 1 eq.) and 4,4’-Dimethyl-2,2’-dipyridine (L\(_4\))
(0.49 g, 2.68 mmol, 1 eq.) were dissolved in 50 cm\(^3\) of methanol. The solution was
heated with constant stirring at 50 °C for 3-5 minutes until it turned a black-red
colour; it was then cooled and filtered. Slow evaporation of the solvent afforded X-
ray quality crystals of 5.4 in 31 % yield.

C, H, N Elemental Analysis

Calculated for: C\(_{12}\)H\(_{14}\)N\(_2\)O\(_3\)F\(_3\)Mn\(_1\)

Theory (%): C 41.63, H 4.08; N 8.09.


Infrared Spectroscopy (cm\(^{-1}\)):

3488(b), 3122(b), 1613(s), 1560(m), 1490(m), 1417(m), 1381(m), 1307(w), 1251(m),
1028(m), 1017(m), 923(w), 901(w), 836(vs), 741(m), 672(m).
Raman (cm$^{-1}$):

251(w), 264(w), 331(w), 386(w), 459(w), 481(w), 519(w), 545(m), 589(w), 609(w), 641(w), 669(w), 691(w), 739(m), 836(w), 923(w), 1014(s), 1114(w), 1204(w), 1243(w), 13006(w), 1321(s), 1386(w), 1411(m), 1488(m), 1556(m), 1612(w).

5.4.3.5 Synthesis of [Mn$^{III}$F$_3$(H$_2$O)(L$_5$)].0.5MeOH (5.5)

Anhydrous MnF$_3$ (0.5 g, 4.47 mmol, 1 eq.) and 5,5'-Dimethyl-2,2'-dipyridine (L$_5$) (0.82 g, 4.47 mmol, 1 eq.) were dissolved in 50 cm$^3$ of methanol. The solution was heated with constant stirring at 50 °C for 3-5 minutes until it turned a black-red colour; it was then cooled and filtered. Slow evaporation of the solvent afforded X-ray quality crystals of 5.5 in 29 % yield.

C, H, N Elemental Analysis

Calculated for: C$_{12.5}$H$_{14}$N$_2$O$_{1.5}$F$_3$Mn$_1$

Theory (%): C 45.70, H 4.27; N 8.53.

Found (%): C 44.33, H 3.69; N 8.83.

Infrared Spectroscopy (cm$^{-1}$):

3287(b), 3052(w), 1598(w), 1573(w), 1501(w), 1476(s), 1389(m), 1316(w), 1249(m), 1233(s), 1162(m), 1066(w), 1052(m), 1040(m), 986(w), 839(vs), 817(m), 731(s), 692(vs).

Raman (cm$^{-1}$):

271(w), 304(w), 359(w), 488(w), 564(w), 648(w), 663(w), 694(w), 840(w), 851(m), 874(w), 1041(w), 1053(w), 1146(w), 1162(w), 1226(m), 1248(w), 1259(w), 1295(m), 1309(m), 1319(s), 1377(w), 1501(m), 1598(m), 1610(m).

5.4.3.6 Synthesis of [Mn$^{III}$F$_3$(H$_2$O)(L$_6$)] (5.6)

Anhydrous MnF$_3$ (0.25 g, 2.23 mmol, 1 eq.) and 5-Chloro-1,10-phenanthroline (L$_6$) (0.47 g, 2.23 mmol, 1 eq.) were dissolved in 50 cm$^3$ of methanol. The solution was heated with constant stirring at 50 °C for 3-5 minutes until it turned a black-red
colour; it was then cooled and filtered. Slow evaporation of the solvent afforded X-ray quality crystals of 5.6 in 35 % yield.

C, H, N Elemental Analysis

Calculated for: C_{12}H_9N_2Cl_F_3Mn_1

Theory (%): C 41.83, H 2.63; N 8.13.

Found (%): C 41.10, H 2.36; N 7.27.

Infrared Spectroscopy (cm$^{-1}$):

3235(vb), 3072(w), 1642(m), 1578(m), 1517(m), 1481(m), 1428(s), 1415(s), 1372(w), 1340(w), 1258(m), 1204(m), 1144(m), 1035(w), 926(s), 891(vs), 822(w), 809(vs), 782(m), 728(vs).

Raman (cm$^{-1}$):

221(w), 279(w), 309(w), 369(w), 426(w), 459(w), 501(m), 586(w), 649(w), 728(m), 783(w), 894(w), 1056(m), 1096(w), 1179(w), 1206(w), 1261(w), 1296(m), 1309(m), 1331(w), 1339(w), 1375(w), 1416(s), 1429(s), 1449(s), 1516(w), 1556(w), 1584(w), 1601(w).
5.5 References


Chapter 5: A Facile Synthetic Route to a Family of MnIII Monomers


Chapter Six: Concluding Remarks and Future Outlook

Chapter 6

Concluding Remarks and Future Outlook
6.1 Concluding Remarks

This thesis comprises a collection of novel molecular assemblies (both discrete cages and extended network materials), which have been fully probed in the magnetic and structural studies described in Chapters 2 - 5. A brief summary of the outcomes from each research chapter is given below.

In Chapter two we reported the serendipitous self-assembly of two model Mn dimer complexes. Firstly, a tetranuclear [MnIII2ZnII2] dimer which has provided a model complex with which to examine the magneto-structural relationship in oxime-bridged MnIII complexes. SQUID magnetometry revealed ferromagnetic exchange ($J = +2.24 \text{ cm}^{-1}$) through the highly twisted Mn-N-O-Mn unit, stabilising an $S = 4$ ground state. HF-EPR spectroscopy confirmed the magnetic analysis, affording the spin Hamiltonian parameters $D_{\text{(MnIII)}} = -3.83 \text{ cm}^{-1}$ and $J = +2.33 \text{ cm}^{-1}$. Secondly we reported complex 2.2, which is a symmetric dimer with a very simple [Mn-O-N-Mn] magnetic core, affording it to be an ideal candidate with which to confirm the type of exchange in these Mn oxime species. SQUID magnetometry revealed weak ferromagnetic exchange ($J = +1.24 \text{ cm}^{-1}$) mediated through the heavily twisted Mn-O-N-Mn moiety, with high field, high frequency EPR data determining a single ion anisotropic value ($D_{\text{(MnIII)}}$ of $-3.94 \text{ cm}^{-1}$). These model complexes conclusively confirm that ferromagnetic exchange is indeed observed between the {MnIII3O(oxime)3(carboxylate)} triangular moieties within the [Mn6] Single-Molecule Magnets of Brechin et al.;[1] until this work this was merely a long held assumption, albeit a sound one.

In Chapter three we reported the synthesis of two hexanuclear ferric cages [FeIII6O2(Naphth-sao)2(O2C-C10H8)10(H2O)2]·8MeCN (3.1) and [FeIII6O2(Naphth-sao)2(O2C-C14H10)10(H2O)2]·8MeCN (3.2). The core topologies in 3.1 and 3.2 are derived from the fusion of two {FeIII3O(O2CR)5}$^{2+}$ triangular units ($R = \text{C}_{10}\text{H}_8; \text{C}_{14}\text{H}_{10}$) and are encased by an organic sheath provided by the combination of extremely bulky polyphenolic oxime and carboxylate ligands. We also reported the formation of the distorted cubane complex [FeIII4(tert-butyl-sao)4(MeOH)4(Cl)4] (3.3) via the bulky 3,5-di-tert-butyl-salicylaldoxime (tert-butyl-saoH2) ligand. Magnetic susceptibility data obtained for 3.1 and 3.3 revealed relatively strong
antiferromagnetic exchange between nearest neighbours in both cases, leading to diamagnetic ground states.

In Chapter four we employed solvothermal heating of Cr$^{\text{III}}$ salts in the presence of bulky R-saoH$_2$ oxime ligands (i.e. Naphth-saoH$_2$ and Ph-saoH$_2$) alongside $\text{O}_2C\text{-R}$ co-ligands of varying sizes (R = H, CH$_3$, C(CH$_3$)$_3$, C$_{14}$H$_9$) to produce a series of structurally related discrete cages, each comprising Na$^+$ linked (Cr$^{\text{III}}$)$_3(O_2\text{CR})_3$(R-sao)$_3$$^{2-}$ units (4.1-4.3). Moreover, we found that the combinatory reaction of less bulky oxime and carboxylate ligands (namely Me-saoH$_2$ and $\text{O}_2C\text{CH}_3$) leads to the formation of either 2D and 3D extended networks containing (Cr$^{\text{III}}$)$_3(O_2\text{CCH}_3)_3$(Me-sao)$_3$$^{2-}$ nodes and Na$^+$ secondary building units, depending on whether ambient or solvothermal heating synthetic methods were employed (4.4 and 4.5). Magnetic susceptibility and magnetisation vs. field measurements on select members of this family are indicative of dominant antiferromagnetic exchange between the Cr$^{\text{III}}$ centres in all cases.

In Chapter five we demonstrated a new and facile synthetic route to a family of Mn$^{\text{III}}$ monomers (5.1'-5.6) with general formula [Mn$^{\text{IIIF}_3}(\text{H}_2\text{O})(L_x)]$, where $L_1$ = 2,2'-bipyridine, $L_2$ = 1,10-phenanthroline, $L_3$ = 6-methyl-2,2'-dipyridyl, $L_4$ = 4,4'-dimethyl-2,2'-dipyridyl, $L_5$ = 5,5'-dimethyl-2,2'-dipyridyl and $L_6$ = 5-chloro-1,10-phenanthroline. Magnetic susceptibility and magnetisation studies were successfully employed to elucidate their D-tensor parameters; the best fit parameters were $D$ (cm$^{-1}$) = -3.974 (5.1), -3.012 (5.2), -3.098 (5.3), -3.898 (5.4), -4.018 (5.5) and -3.971 (5.6). Raman Spectroscopic studies were employed to probe the Mn-F stretches observed within each of these siblings.
Chapter Six: Concluding Remarks and Future Outlook

6.2 Future Work

Future work may include further investigations into the synthesis of analogous [Cr_3] cages and extended networks (as described in Chapter three) towards producing a large magneto-structural correlation; akin to those on the large families of [Mn_3] and [Mn_6] oxime species previously carried out by Brechin et al. (as discussed in Chapter two).[1b]

In relation to the family of Mn^{III} monomers synthesised in Chapter five; we propose that HF-EPR studies should be carried out on these complexes towards their D-tensor elucidation. Direct comparisons between EPR and SQUID magnetometer derived D values can then be made along with comparisons with all other magnetically studied Jahn Teller elongated Mn^{III} monomers in the literature (as shown in Chapter five).[2] Due to their large D values (ranging from -3.012 to -4.018 cm^{-1}) these complexes are on the edge of measurable range using standard EPR methods. Therefore it is expected that limited information can be extracted using this method and HF-EPR should provide better resolution. We propose that these Mn^{III} starting products (5.1′-5.6) then be used as building blocks toward novel and more elaborate magnetic architectures, although their use as homogenous catalysts should not be overlooked.
6.3 References
