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The Synthesis and Magnetic Properties of Fe-based Homo- and Heterometallic Clusters.

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A Thesis Submitted for the Degree of Doctor of Philosophy



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Abstract

Historically, polynuclear Fe^{III}-O clusters have been at the heart of the study of molecular magnetism. From the study of [Fe^{III}₂-(μ-O)] dimers detailed magneto structural correlations were developed that can be applied to larger clusters.¹ Larger antiferromagnetic wheels revealed interesting magnetic properties manifesting in stepped magnetisation.² The second known single molecule magnet (SMM) was the [Fe₈] cluster synthesised by the hydrolysis of the FeCl₃(tacn) (tacn = triazacyclononane) monomer.

One particularly interesting aspect of Fe^{III} clusters is their potential to grant access to large ground state spins. Molecules with such properties include the [Fe_{17/19}] twin clusters³ and the [Fe₁₇] “molecular mineral” species’ which show a huge ground state spin of 35/2.⁴

The discovery of such clusters using relatively simple organic ligands has prompted us to speculate that new Fe^{III}-O clusters may be synthesised that can display larger spin ground states and that new geometries may provide a pathway to interesting magnetic frustration effects. This thesis reports the synthesis and magnetic properties of new homo- and heterometallic Fe^{III} based clusters each chapter aims to form these clusters using different methodologies and ligands.

Chapter 2 discusses work which expands the “molecular mineral” family of clusters reporting 3 new clusters [Fe₃₄], [Fe₃₀] and [Fe₈] prepared from reactions involving monodentate pyridine-type ligands. The synthesis of these clusters is described alongside their magnetic properties, all 3 compounds exhibit antiferromagnetic interactions leading to non-zero ground state spins.

Chapter 3 reports new structures built using Fe^{III} ions and the alkoxide ligand triethanolamine. Both homo and heterometallic species are reported. The homometallic [Fe₁₅] describes a centred tetrakis-hexahedron a topology previously unseen in Fe^{III} cluster chemistry. The heterometallic ring compounds [Fe₁₁Zn₄] and [Fe₁₂Zn₄] represent some of the largest Fe^{III} ring-type compounds to date with [Fe₁₁Zn₄] being the only odd numbered Fe^{III} ring type cluster reported. The magnetic data of all three clusters is reported all show strong antiferromagnetic interactions, with the [Fe₁₅] and [Fe₁₁Zn₄] clusters also exhibiting frustration effects at low temperature.

Chapter 4 reports a series of heterometallic Anderson-type wheel clusters built with Fe^{III}, another transition metal (Ni^{II}, Co^{II} and Zn^{II}) and the 2-pyridinemethanol ligand. Characterisation of their structures shows that the metal ions are disordered over multiple sites. Magnetic measurements elucidate competing interactions between with the Fe^{III} ions showing antiferromagnetic behaviour.

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Lay Summary

The work described in this thesis aims to prepare molecular iron cluster compounds containing a high amount of metal ions and study their physical properties with a focus on their magnetic behaviour. The first chapter sets out a brief outline of the field to date focusing on iron clusters with interesting magnetic behaviours. Chapter 2 details new compounds prepared through a relatively simple methodology. Chapter 3 and 4 discusses compounds which have been prepared using organic “bridging ligands” which connect the iron atoms together to form the molecule. Magnetic measurements of these compounds have been carried out and studied furthering our understanding of the magnetic behaviour of these relatively large molecules.

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Secondly, I want to thank the other members of the Brechin group which has only grown in number since I first joined. In particular Marco and Alvaro, who have been around from the very start it's been a privilege to work alongside you every day and to have shared some brilliant times both here in Edinburgh and across the world. My fellow Brechin group members, Lucy, Emily, Mukesh, Eri and Angelos, it has been inspiring to have you as colleagues and friends, I look forward with excitement to seeing what you all do in the future.

This work would not have been possible without the expertise of external collaborators. I wish to extend my gratitude to our collaborators, Prof Jürgen Schnack, Dr Marco Evangelisti and Prof Hiroyuki Nojiri. A special mention is required for Prof Gopalan Rajaraman and the Rajaraman group who made my visit to Mumbai in 2019 an exciting and enriching time despite the complications that ensued.

Finally, I wish to thank my friends and family both those here in Edinburgh and further afield. No one expects to be doing their PhD studies during a global pandemic. Thank you for being there, whether for a well needed chat over a video call, or for a beer and lunch in person once we were allowed out again.

Declaration

I hereby declare that except where specific reference is made to other sources, the work contained in this thesis is the original work of the author. It has been composed by the candidate and has not been submitted, in whole or in part, for any other degree, diploma, or qualification.

Daniel Cutler

Format of Thesis

Each chapter of this thesis, with the exception of Chapter 1, is made up of contributions to peer-reviewed publications which have already been published, submitted for publication or in preparation for publication. To fulfill the requirements of The University of Edinburgh regarding the preparation and submission of a thesis for the degree of PhD, they have been reformatted accordingly.

Chapter 1: Introduction

An outline of the field to date giving examples of Fe-based cluster compounds interesting to the field of molecular magnetism.

Chapter 2: Fe^{III} Molecular Minerals

Investigations into the synthesis, structures and magnetic properties of three novel Fe^{III}-oxo clusters prepared with monodentate pyridine-type ligands.

Chapter 3: Triethanolamine based Fe^{III} Clusters

Investigations into the synthesis, structures and magnetic properties of three novel Fe^{III} clusters (one homometallic and two heterometallic) prepared using two metal salts and the flexible chelate triethanolamine.

Chapter 4: 2-Pyridinemethanol [Fe^{III}₂M^{II}₂] Wheels (M = Ni, Co, Zn)

Investigations into the synthesis, structure and magnetic properties of a family of heterometallic wheel clusters containing the Fe^{III} metal ion and prepared with the pyridyl alcohol chelate 2-pyridinemethanol.

External Contributions

Chapter 2:

Single Crystal X-ray Crystallography – Measurements and structure solution:

Dr Gary Nichol (The University of Edinburgh), Dr Lauren McCormick (University of Southampton)

Computational Calculations:

Sourav Dey and Prof Gopalan Rajaraman (IIT Bombay), Dr Mukesh Singh (The University of Edinburgh)

Magnetic data fitting:

Prof Jürgen Schnack (Bielefeld University)

Heat Capacity:

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Chapter 3:

Single Crystal X-ray Crystallography – Measurement:

Dr Gary Nichol (The University of Edinburgh)

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Chapter 4:

Single Crystal X-ray Crystallography – Measurement:

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Publications

In press

- “Solvent Dictated Odd and Even Numbered Ferric Wheels” **Angew. Chem. Int. Ed.**, 2022
Daniel J. Cutler, Angelos B. Canaj, Mukesh K. Singh, Marco Evangelisti, Leroy Cronin, Juergen Schnack, Stergios Piligkos and Euan K. Brechin.

- “An [Fe₈] molecular oxyhydroxide” **Angew. Chem. Int. Ed.**, 2022
Daniel J. Cutler,* Marco Coletta* Mukesh K. Singh, Angelos B. Canaj, Laura J. McCormick, Simon J. Coles, Leroy Cronin, Juergen Schnack, Stergios Piligkos and Euan K. Brechin.

2022

- “An [Fe^{III}₃₀] molecular metal oxide” **Chem. Commun.**, 2022,58, 52-55
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- “[Fe₁₅]: a frustrated, centred tetrakis hexahedron.” **Chem. Commun.**, 2021, 57, 8925 – 8928.
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D. Nirosha T. De Silva, Tyson N. Dais, Geoffrey B. Jameson, Daniel J. Cutler, Euan K. Brechin, Casey G. Davies, Guy N. L. Jameson, Paul G. Plieger.

2020

- “Magneto-structural studies of an unusual [Mn^{III}Mn^{II}Gd^{III}(OR)₄]⁴⁻ partial cubane from 2,2'-bis-p-^tBu-calix[4]arene” **Dalton Trans.**, 2020, 14790-14797.
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Thomais G.Tziotzi, Evangelos K. Andreou, Eirini Tzanetou, Dimitris A. Kalofolias, **Daniel J. Cutler**, Marek Weselski, Milosz Siczek, Tadeusz Lis, Euan K. Brechin, Constantinos J. Milios.

2019

- “An $[Fe^{III}_{34}]$ Molecular Metal Oxide” **Angew. Chem. Int. Ed.**, 2019, 17059-17062.
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- “New salicylaldoximato-borate ligands resulting from anion hydrolysis and their respective copper and iron complexes” **Dalton Trans.**, 2019, 11872-11881.
Sidney S. Woodhouse, D. Nirosha, T. De Silva, Geoffrey B. Jameson, **Daniel J. Cutler**, Sergio Sanz, Euan K. Brechin, Casey G. Davies, Guy N. L. Jameson and Paul G. Plieger.

Conferences Attended

2021

Virtual Poster Presentation, Joint Dalton Meeting (2021).

Virtual Poster Presentation, International Conference on Molecular Magnets (2021).

2020

Virtual Poster Presentation (Awarded CrysEngComm Poster Prize), Crystallography and Emerging Materials Workshop for Ontario and Quebec 6.5 (Virtual Conference, 2020)

2019

Invited Speaker, Symposium on Magnetism and Photo-magnetism (2019), IIT Bombay (Mumbai, India)

Poster Presentation, Modern Trends in Molecular Magnetism (2019), IISER Bhopal (Bhopal, India)

Poster Presentation, European Conference of Molecular Magnetism (2019), University of Florence (Florence, Italy)

Poster Presentation, Universities of Scotland Inorganic Conference (2019), University of Glasgow, (Scotland,UK)

Poster Presentation, New Horizons in Chemistry and Materials Science Workshop (2019), Nagoya University (Nagoya, Japan).

Chapter 1: Introduction

Chapter 1: Introduction

Iron is the most abundant metal in the Earth's crust, has been used by mankind for centuries and is found in materials worldwide. Iron is extracted in the form of various iron oxide minerals such as magnetite, hematite, ferritin and maghemite.¹ Due to their abundance, low toxicity and variety of electronic and magnetic properties iron oxides are being increasingly seen as an important route towards the preparation of functional materials for a variety of applications including biomedicine,² energy storage,³ catalysis⁴ and magnetism.

In the field of magnetism, iron oxides have been studied extensively. The mineral magnetite ($\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}_4$) is possibly the earliest known magnetic material. Iron oxides have become essential in the application of information storage for example in previously widely used video/audio cassettes and the increasingly important devices of payment swipe cards and computer hard disk drives.⁵

Miniaturisation and Single Molecule Magnets.

The term miniaturisation is widely used in the field of micro-electronics often referring to Moore's law which correctly predicted the doubling of the number of transistors on silicon base integrated circuits approximately every 12 months.⁶ Although a popular term in this field miniaturisation is a concept that has been applied to other materials including magnets which have a particular significance in a variety of industries and emerging technologies including information storage,⁷ medical imaging,⁸ quantum computing,⁹ spintronics¹⁰ and magnetic refrigeration.^{11,12} Traditional bulk magnets are made using paramagnetic alloys (e.g. SmCo_5 , $\text{Nd}_2\text{Fe}_{14}\text{B}$) or metal oxides such as magnetite (Fe_3O_4).¹³ Often made via expensive, energy intensive methods, the magnetic properties of these materials arises through long-range ferromagnetic interactions.

The process of making smaller magnetic particles of bulk magnets can be thought of as a "top-down" approach. This strategy has resulted in the magnetic materials seen today in the applications previously mentioned. This approach has the drawback that bulk magnetic materials rely upon the alignment of magnetic domains to produce their magnetic behaviour. However, as bulk materials are reduced in size these domains begin to break down at sizes lower than the nanoscale, removing the useful magnetic behaviour required in devices.

An alternative to the “top-down” strategy is a so-called “bottom-up” approach. This strategy takes paramagnetic centres, most often metal ions, and builds up structures to form larger structures of varying topologies including 0D discrete clusters, 1D chains, 2D sheets and 3D lattices or frameworks (Figure 1). Such molecule-based materials owe their magnetic properties to short range interactions between neighbouring paramagnetic centres. The synthesis of such compounds often uses the concept of molecular self-assembly. An important concept in supramolecular chemistry¹⁴ self-assembly has been a successful method in building inorganic molecular clusters.^{15,16} Unlike the self-assembly of supramolecular species, which can be somewhat controlled with an understanding of intermolecular interactions, the synthesis of molecular coordination species, such as polymetallic clusters, is less predictable. As such the synthesis of such compounds is often labelled serendipitous self-assembly. This approach has been successfully applied to a range of metallic elements producing clusters in a range of sizes for various applications including the synthesis of molecular magnets.^{17–20} When applied to iron ions and small iron clusters this methodology has led to the discovery of multiple polymetallic clusters with interesting magnetic behaviour.

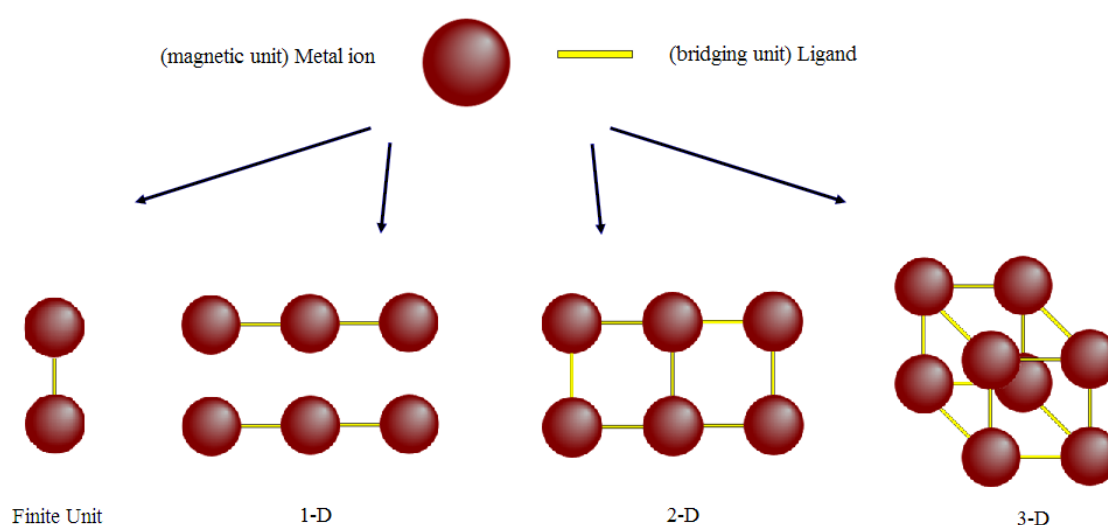


Figure 1: Illustration of the “bottom-up” approach towards building molecular magnets.

Iron in molecular magnetism

Iron ions present an opportunity to magnetochemists because they possess a high number of unpaired *d*-orbital electrons (5 and 4 for high spin, octahedral Fe^{III} and Fe^{II} respectively). Polymetallic clusters of Fe ions can therefore have large total spin values, a property which is sought after in magnetic materials for applications as molecular magnets²¹ and magnetic refrigerants.²² A further advantage of iron is its abundance and low cost. Widespread use and the relative lability of Fe^{II/III} lead to the characterisation of numerous coordination complexes, which allowed chemists to develop quantitative magneto-structural correlations, particularly for Fe-O-Fe moiety.

Magneto-structural correlations in Fe^{III}-O-Fe^{III} bridges.

Two neighbouring spins connected via an intervening bridge, X, can interact via a process called magnetic superexchange, described by the magnetic exchange parameter (*J*). Through magnetic exchange spins align either in parallel (a ferromagnetic interaction) or antiparallel (an antiferromagnetic interaction). The sign and magnitude of *J* signifies the strength and nature of this interaction (Figure 2).

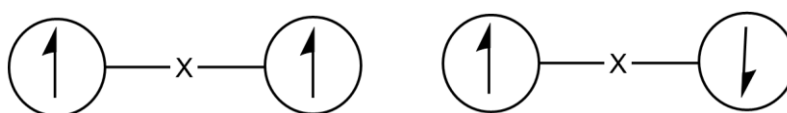


Figure 2: Magnetic exchange of two spins in a ferromagnetic interaction (left) and antiferromagnetic interaction (right).

Magneto-structural correlations seek to decipher the relationship between the magnetic exchange parameter *J* and structural characteristics such as the distance between the paramagnetic centres, the angle of the M-X-M bridge (where M = metal and X = bridging atom(s)) and the identity of the bridging and metal atoms. The latter is important as magneto-structural correlations are only applicable in molecules that have the same metal and bridging atoms as the dimers used to build the correlations.

Some of the first magneto-structural correlations developed were on oxygen-bridged Fe^{III} dimers. The first, reported in 1991, was designed using empirical methods. 36 Fe^{III} dimers containing one oxygen-type bridge (oxo, alkoxo or hydroxo) and one other bridge

(carboxylate, sulfate or phosphate) were studied experimentally to provide a single parameter equation (P) defined as half of the shortest superexchange pathway between the two metals. Equation 1 describes the relationship between J (cm^{-1}) and P ($\text{\AA}$).²³

$$J = 8.763 \times 10^{11} \exp(-12.663P) \quad \text{Equation 1}$$

This approach suggests a correlation between the magnetic exchange parameter and the average $\text{Fe}^{\text{III}}-(\mu\text{-O})$ distances only. The authors attempt to correlate J with other structural parameters (such as the Fe-O-Fe bond angle) were unsuccessful, therefore the correlation shows no angular dependence. A large disadvantage of this model is that, due to the reliance upon the average Fe-($\mu\text{-O}$) distance, it is not valid for singly bridged dinuclear species. Weihe and Güdel²⁴ proposed a semi-empirical model whereby 32 Fe^{III} dimers were studied using an angular overlap model. The resulting equation (Equation 2) accounts for dependence of J on both the Fe-O distance (r , $\text{\AA}$) and the Fe-O-Fe bond angle (φ , $^\circ$).

$$J = 1.337 \times 10^8 (3.536 + 2.488 \cos \varphi + \cos^2 \varphi) \times \exp(-7.909r) \quad \text{Equation 2}$$

In contrast to the previously described model, this semi-empirical model describes a dependence on both r and φ , although at larger values of r the angular dependence becomes less pronounced. These models present useful correlations for Fe-O-Fe dimers. However, they become less accurate upon application to larger polynuclear cluster compounds, which is the focus of this thesis. Mitchel *et al.*²⁵ found that developing a model for these larger compounds required an adjustment to Equation 2 to provide Equation 3. Despite the adjustment of constant values Equation 3 does not change the central concept of Equation 2, that the two most important structural parameters for magnetic exchange in a Fe-O-Fe bridge is the Fe-O-Fe bridging angle and the Fe-Fe distance.

$$J = 1.29 \times 10^9 (-0.12 + 1.57 \cos \varphi + \cos^2 \varphi) \times \exp(-8.99r) \quad \text{Equation 3}$$

As this thesis will describe the synthesis and characterisation of large Fe^{III} and $\text{Fe}^{\text{III}}/\text{M}$ clusters the following section provides a brief overview of such compounds that have been characterised up to this point.

Building Fe^{III} clusters

The first polynuclear iron cluster with interesting magnetic properties to be reported was the octametallic cluster $[\text{Fe}_8(\text{tacn})_6(\mu_3\text{-O})_2(\mu\text{-OH})_{12}]\text{Br}_7\cdot\text{H}_2\text{O}$ (tacn = 1,4,7-triazacyclononane, $[\text{Fe}_8(\text{tacn})]$). First synthesised in 1984 by the hydrolysis of the monomeric species $[(\text{tacn})\text{FeCl}_3]$ ²⁶ the magnetic properties of $[\text{Fe}_8(\text{tacn})]$ were not investigated until 1993 shortly after the discovery of a Mn_{12} acetate cluster as the first single molecule magnet (SMM).²⁷ SMMs are compounds with a unique magnetic property. When a paramagnetic material is subjected to an external magnetic field the unpaired spins in the paramagnet align with the magnetic field, the sample becomes magnetised. Upon the removal of the magnetic field a non-SMM paramagnet will return to its demagnetised state quickly (i.e. its T_1 relaxation process is short). On the other hand SMMs continue to retain their magnetisation so long as they are below their blocking temperature (i.e. an SMM's T_1 relaxation is much longer especially below their blocking temperature). This behaviour is attributed to zero field anisotropy within the spin states of the SMM. Mn_{12} was the first SMM to be characterised with the second, $[\text{Fe}_8(\text{tacn})]$, characterised shortly after.

Variable temperature magnetic susceptibility measurements of $[\text{Fe}_8(\text{tacn})]$ indicated that the compound has significant antiferromagnetic interactions. Despite this, $[\text{Fe}_8(\text{tacn})]$ displays a non-zero ground state which low-temperature/high field magnetisation measurements showed to be between $S = 9$ and $S = 10$. Originally this was attributed to magnetic frustration effects.²⁸ Further studies using High Frequency EPR^{29,30} and Inelastic Neutron Scattering³¹ (INS) have shown that this is indeed due to frustrated spin arrangement whereby the six outer Fe^{III} ions are spin up and the two central Fe^{III} ions are spin down, resulting in ground state spin of $S = 10$ (Figure 3). This large ground state spin is then coupled with a small but significant zero field splitting attributed to single ion anisotropy of the Fe^{III} ions, ($D_{\text{cluster}} = -0.522 \text{ cm}^{-1}$) affording $\text{Fe}_8(\text{tacn})$ its SMM properties.

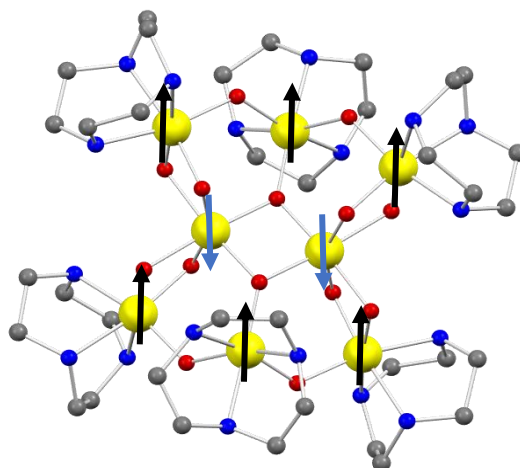


Figure 3: Structure of the cation of $[\text{Fe}_8(\text{tacn})_6(\mu_3\text{-O})_2(\mu\text{-OH})_{12}]\text{Br}_7\cdot\text{H}_2\text{O}$ alongside a pictorial representation of the exchanged coupled spins on each Fe^{III} ion. Colour code: Fe, Yellow ; O, Red; N, Blue; C, grey. Hydrogens, solvates and counterions omitted for clarity

After the discovery of $[\text{Fe}_8(\text{tacn})]$ research into large Fe^{III} -O clusters continued. In 1994 Taft *et al.* synthesised the decanuclear ferric wheel $[\text{Fe}(\mu\text{-OMe})_2(\text{O}_2\text{CCH}_2\text{Cl})]_{10}$ ($[\text{Fe}_{10}]$, Figure 4) consisting of 10 Fe^{III} ions linked by chloroacetate and methoxide bridges.³² Synthesised by the dissolution of the Fe^{III} -chloroacetate triangle $[\text{Fe}_3(\mu_3\text{-O})(\text{O}_2\text{CCH}_2\text{Cl})_6(\text{H}_2\text{O})_3]$ and $\text{Fe}(\text{NO}_3)_3$ in methanol this is a beautiful example of using smaller Fe^{III} -O clusters as building blocks to make larger clusters. Magnetic susceptibility measurements of Fe_{10} show behaviour typical of an antiferromagnetic wheel with a ground state spin of $S = 0$. Low temperature magnetisation data measured in fields up to 20 T showed that magnetisation (M) increased with applied field (H) in a stepped pattern. This was one of the first instances that the quantum nature of magnetic molecules was shown experimentally. Due to the proportional relationship of the Zeeman energy to the applied field a crossover of excited spin states with the ground state as the field increases is observed (Figure 5).

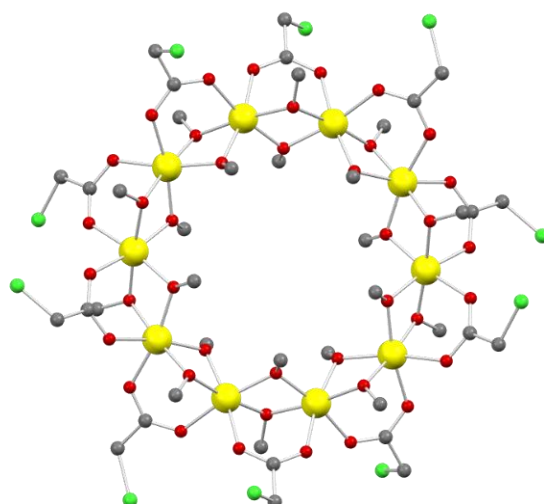


Figure 4: Structure of $[\text{Fe}(\mu\text{-OMe})_2(\text{O}_2\text{CCH}_2\text{Cl})]_{10}$. Colour code: Fe, Yellow ; O, Red; Cl, Green; C, grey. Hydrogens, solvates omitted for clarity.

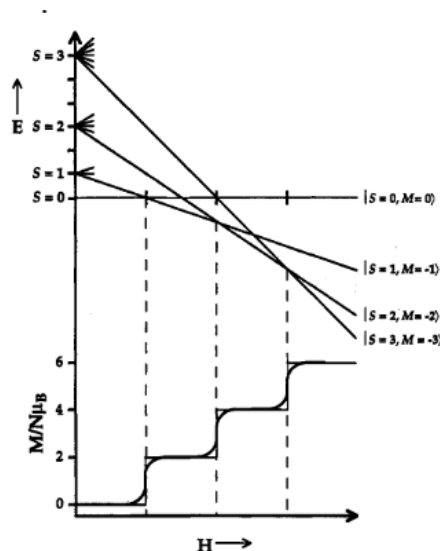


Figure 5: Illustration of the MvH plot and crossover of spin states with increasing applied field in Fe_{10} . Taken from reference 15.

Two of the largest known Fe^{III} -oxo clusters are found in the co-crystal $\text{Fe}_{17/19}$ which contains the two cluster units $[\text{Fe}_{19}(\mu_3\text{-O})_6(\mu_3\text{-OH})_6(\mu\text{-OH})_8(\text{heidi})_{10}(\text{H}_2\text{O})_2]^+$ and $[\text{Fe}_{17}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu\text{-OH})_{10}(\text{heidi})_8(\text{H}_2\text{O})_{12}]^{3+}$ (H_3heidi = N-(2-hydroxyethyl)iminodiacetic acid)). Referred to by the authors as “captured rust” $[\text{Fe}_{17}/\text{Fe}_{19}]$ (Figure 6) was synthesised in 1992³³ via the hydrolysis of an iron salt and the use of a capping ligand. In this case the ligand H_3heidi is added to an aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and treated with pyridine to afford crystals of $[\text{Fe}_{17}/\text{Fe}_{19}]$.

These “captured rust” clusters crystallise in the triclinic space group $P\bar{1}$ and the unit cell contains one each of the $[\text{Fe}_{17}]$ and $[\text{Fe}_{19}]$ and 4 charge balancing $[\text{NO}_3]^-$ counter ions. Variable temperature magnetic susceptibility measurements of $[\text{Fe}_{17}/\text{Fe}_{19}]$ elucidated ferrimagnetic behaviour indicative of a large spin ground state in one or both of the cluster cations. Magnetisation measurements at high fields and low temperatures provided a M_{sat} value of $65 \mu_B$, suggesting a ground state spin of no lower than $33/2$ and $27/2$ for $[\text{Fe}_{19}]$ and $[\text{Fe}_{17}]$, respectively.³⁴

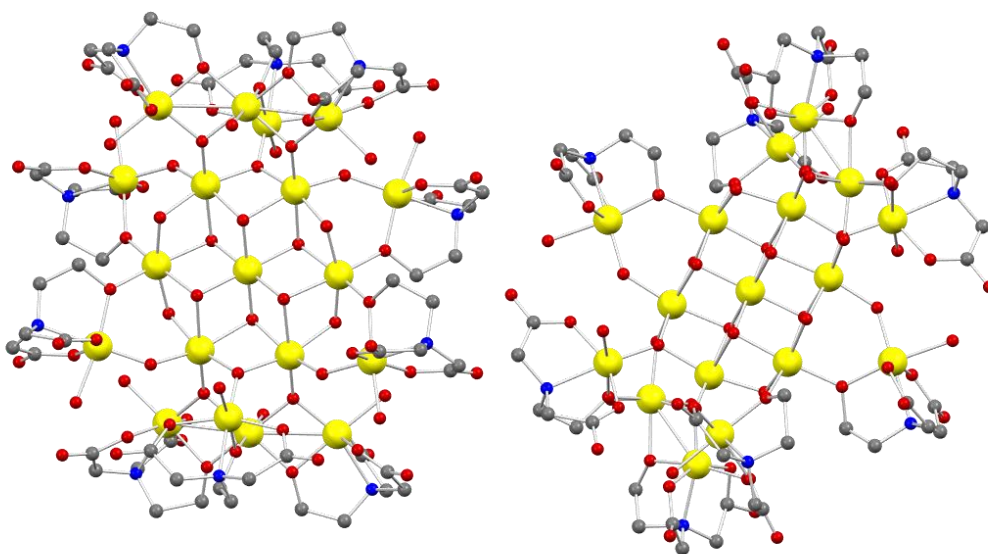


Figure 6: Crystal structure of the $[\text{Fe}_{17}/\text{Fe}_{19}]$ co-crystal. Colour code: Fe, yellow; O, red; N, blue; C, grey. Hydrogen atoms, solvates and counterions omitted for clarity.

In 1997 whilst attempting to prepare Fe^{III} coordination polymers from triethanolamine and dinitrile ligands, Saalfrank *et al.* synthesised a series of Fe^{III} coronate rings. Dissolution of FeCl_3 , triethanolamine, fumaric acid and an alkali metal hydride (Li/Na/Cs) affords rings with a formulae of $[\text{Fe}_6(\text{tea})_6\text{Na}]\text{Cl}$ and $[\text{Fe}_8(\text{tea})_8\text{Cs}]\text{Cl}$ (Figure 7) in which the alkali metal ion is encapsulated by the metallo-coronate ring, thus acting as a template for the different ring sizes.³⁵ As expected, these Fe^{III} rings showed antiferromagnetic nearest neighbour interactions resulting in a diamagnetic $S = 0$ ground state.³⁶ These templated rings proved to be of interest synthetically, as they provide a route to direct the self-assembly process. Further investigations have afforded a variety of structures with various substituted *N*-diethanolamines whereby changing alkyl side chains produces different crystal packing effects and the formation of interesting morphologies when adsorbed to a surface.^{37,38}

In 2002 an $[\text{Fe}_{13}]$ cluster was reported with a particularly interesting topology. First reported by Bino *et al.* $(\text{Hpy})_5[\text{Fe}_{13}\text{O}_4\text{F}_{24}(\text{OMe})_{12}]$, $[\text{Fe}_{13}]$, was synthesised by the reaction of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ with pyridine in hot methanol.³⁹ The structure of $[\text{Fe}_{13}]$ (Figure 8) represents first Fe^{III} Keggin ion and indeed the first open-shell Keggin ion of any transition metal. Seen predominately in the chemistry of polyoxometalates (POMs) the Keggin structure usually consists of a central tetrahedral heteroatom (e.g. P, S, Fe^{II}) bridged to high oxidation state octahedral metal ions (e.g., Mo, W) which are bonded to terminal oxygen ligands capping the cluster. In the case of $[\text{Fe}_{13}]$, Fe^{III} ions take up both the tetrahedral and octahedral sites.

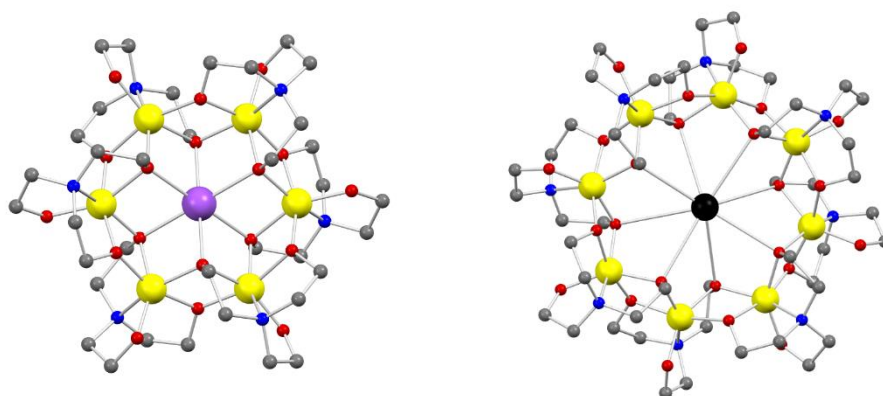


Figure 7: Alkali metal templated Fe^{III} rings. Left $[\text{NaFe}_6]$, right $[\text{CsFe}_8]$. Colour code: Fe, yellow; O, red; N, blue; C, grey; Na, pink; Cs, black. Hydrogen atoms, solvates and counterions omitted for clarity.

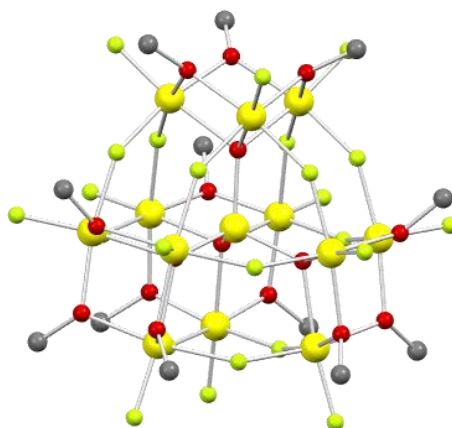


Figure 8: Structure of the anion of the Fe_{13} cluster, $[\text{Fe}_{13}\text{O}_4\text{F}_{24}(\text{OMe})_{12}]^{5-}$. Colour code: Fe, yellow; O, red; F, light green; C, grey. Hydrogen atoms, solvates and counterions omitted for clarity.

The tetradecanuclear Fe^{III} cluster $[\text{Fe}_{14}(\text{bta})_6\text{O}_6(\text{OMe})_{18}\text{Cl}_6]$ (where btaH = benzotriazole) ($[\text{Fe}_{14}]$, Figure 9) was reported in 2003. Unlike previously described clusters $[\text{Fe}_{14}]$ was prepared by solvothermal synthesis: Superheating the Fe carboxylate triangle $[\text{Fe}_3(\mu_3\text{-O})(\text{OAc})_6(\text{H}_2\text{O})_3]\text{Cl}$ in methanol with the btaH ligand and slow cooling produces crystals of $[\text{Fe}_{14}]$. The authors attribute the molecule's high symmetry to this high pressure method, with the metallic skeleton describing a hexacapped hexagonal prism. The first magnetic studies of $[\text{Fe}_{14}]$ elucidated antiferromagnetic exchange which results in a ground state spin value of $S = 25$.⁴⁰

Inspection of the Fe-O-Fe bond angles reveals they can be separated into two distinct categories. Those that connect apical Fe^{III} ions to the core hexagonal prism, with angles of $113^\circ - 125^\circ$, and those that connect all other Fe^{III} centres, with angles below 102° . Application of the magneto-structural correlations developed by Weihe and Güdel means that the larger bridging angles provide much stronger antiferromagnetic interactions dominating the magnetic exchange. This leads to the model seen in Figure 10 whereby 12 of the 14 Fe^{III} centres are spin up and 2 centres are spin down. DFT calculations corroborated the nature and magnitude of the magnetic exchange. 4 distinct J parameters were calculated (using a hamiltonian in the form of $\hat{H} = \sum_{i<j} -J_{ij}S_iS_j$), $J_1 = -22.0 \text{ cm}^{-1}$, $J_2 = -8.7 \text{ cm}^{-1}$, $J_3 = 29.7 \text{ cm}^{-1}$ and $J_4 = 3.7 \text{ cm}^{-1}$ where the more antiferromagnetic interactions (J_1 and J_3) are between the outer Fe^{III} ions and the apical Fe^{III} ions and the less antiferromagnetic interactions (J_2 and J_4) are between the outer Fe^{III} ions.⁴¹

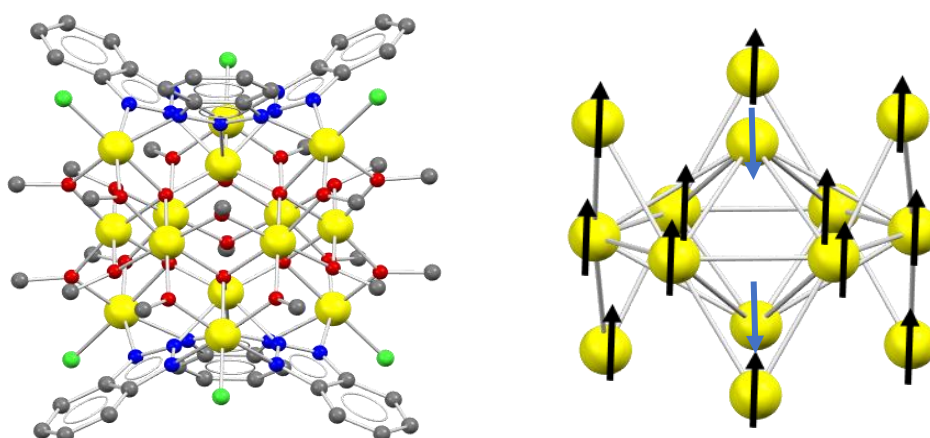


Figure 9: Crystal Structure of $[\text{Fe}_{14}(\text{bta})_6\text{O}_6(\text{OMe})_{18}\text{Cl}_6]$ (left) with the spin model of the metallic skeleton (right). Colour code: Fe, yellow; O, red; N, blue; Cl, green; C, grey. Hydrogen atoms omitted for clarity.

In 2004 Powell *et al.*⁴² extended the family of “POM-type” Fe-oxo molecules with the heptadecametallic cluster $(\text{pyH})[\text{Fe}_{17}(\mu_4\text{-O})(\mu_3\text{-O}_{15})(\mu\text{-OH})_{12}(\text{py})_{12}\text{Br}_4]\text{Br}_4$, $[\text{Fe}_{17}]$ (Figure 10). $[\text{Fe}_{17}]$ has an incredibly simple yet thought provoking preparation. Dissolution of an anhydrous iron(III) halide (Cl/Br) in pyridine, followed by filtration and slow evaporation of the solvent affords dark red crystals of $[\text{Fe}_{17}]$ in remarkably good yields. The authors postulate that as no water or other oxygen containing species are added to the reaction the oxide and hydroxide ions are supplied aerobically and from the water found in the “wet” pyridine solvent. In 2007 Gass *et al.* reported that this behaviour was seen across multiple pyridine-type ligands, reporting isostructural $[\text{Fe}_{17}]$ clusters with β -picoline, 3,5-lutidine and isoquinoline.⁴³ The magnetic properties of all reported $[\text{Fe}_{17}]$ clusters are the same. Variable temperature magnetic susceptibility and magnetisation measurements indicate ferrimagnetic behaviour and spin state of $S = 35/2$. This was later confirmed with very low temperature magnetisation data, heat capacity and neutron diffraction.⁴⁴ As in $[\text{Fe}_{14}]$ the ferrimagnetic behaviour of $[\text{Fe}_{17}]$ is explained well by the magento-structural correlations discussed above. The large Fe-O-Fe bond angles between tetrahedral Fe^{III} ions and octahedral Fe^{III} afford strong antiferromagnetic interactions whereas the smaller Fe-O-Fe angles found between octahedral Fe^{III} ions afford much weaker antiferromagnetic interactions resulting in all the tetrahedral Fe^{III} ions “spin down” and the octahedral “spin up” (Figure 10).

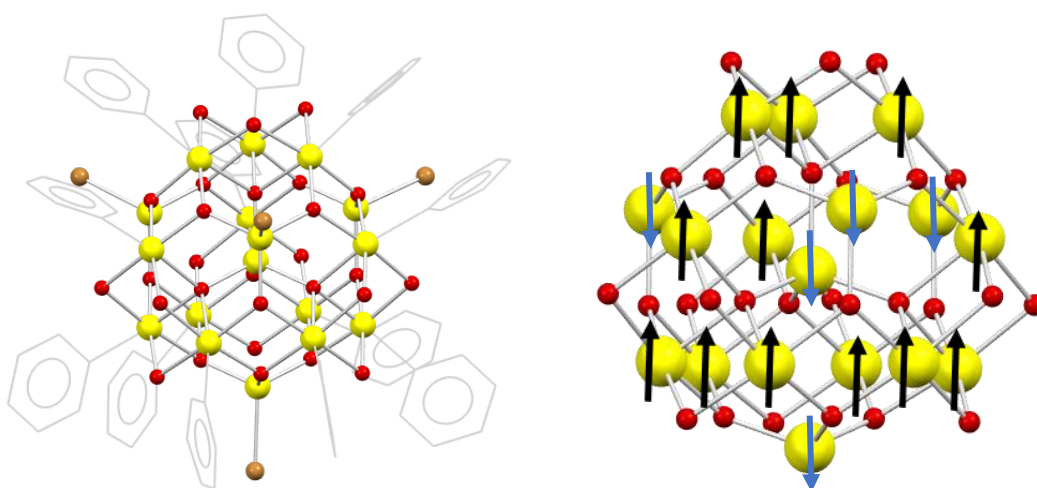


Figure 10: Structure of the heptadecametallic cluster Fe_{17} (left) alongside a spin model over the Fe-oxo core of the cluster (right). Colour code: Fe, yellow; O, red; Br, brown; C and N, grey wireframe. Hydrogen atoms, solvates and counterions omitted and pyridine ligands in wireframe format for clarity.

A particularly interesting aspect to the Fe-oxo cores of $[\text{Fe}_{17}]$ (and to lesser extent Fe_{13}) is the resemblance to the lattice structure of molecular minerals magnetite (Fe_3O_4) and maghemite (Fe_2O_3) made up of alternating shells of tetrahedral and octahedral Fe^{III} ions (Figure 11). It is this resemblance to bulk minerals that the authors refer to when naming these compounds “molecular minerals”. The synthesis of $[\text{Fe}_{13}]$ and $[\text{Fe}_{17}]$ suggest that it is possible for Fe^{III} to form large cluster compounds which take on topologies seen in POM chemistry. Following this theory it would be possible to synthesise giant Fe^{III} -O clusters en route to the 3D mineral phases, with nuclearities of >100 metal ions such as is seen in POMs; the largest POM having a nuclearity of 368.⁴⁵

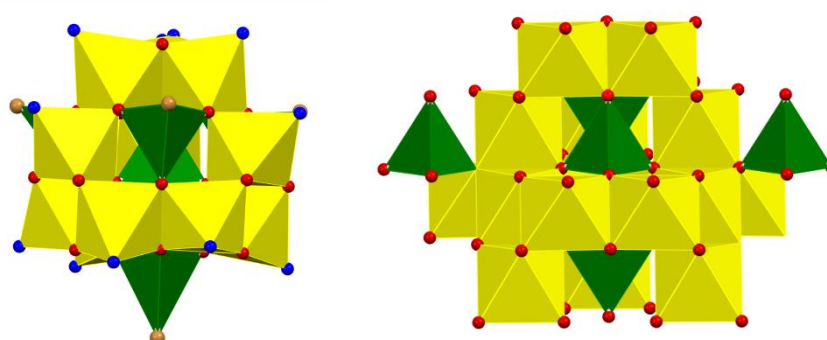


Figure 11: Polyhedral representations comparing Fe_{17} (left) to a piece of the magnetite lattice (right). Colour code: Fe(octahedral), yellow; Fe(tetrahedral), green; O, red; Br, brown; N, blue.

The Fe^{III} -oxo compounds described above present a brief introduction to the role of iron oxide compounds in the field of molecular magnetism. However there are other iron based clusters which present larger nuclearities and larger spin ground states than those mentioned above. The $\{[\text{Fe}_8(\text{tea})(\text{teaH})_3(\text{HCOO})_{12}]_8(\text{HCOO})_{12}\}(\text{ClO}_4)_{12}$ cluster, (teaH_3 = triethanolamine) $[\text{Fe}_{64}]$, is the largest Fe^{III} cluster built using a self-assembly approach in which 8 $\{\text{Fe}_8\}$ building blocks are coupled together.⁴⁶ The second largest Fe^{III} cluster, $\{[\text{Fe}_6\text{O}(\text{thme})_4\text{Cl}_3]_4[\text{Fe}_4(\text{thme})_2(\text{MeOH})_2(\text{H}_2\text{O})_4]_6[\text{Fe}(\text{Tp})(\text{CN})_3]_{12}\}\text{Cl}_5$, (thmeH_3 = 1,4,7-trimethyl-1,4,7-triazacyclononane, Tp = tris(pyrazoyl)borate) $[\text{Fe}_{60}]$, takes a similar approach linking three separate building blocks into one tetrahedral cage.⁴⁷ Due to the presence of antiferromagnetic interactions $[\text{Fe}_{64}]$ has an $S = 0$ ground state spin, and no ground state value could be assigned to $[\text{Fe}_{60}]$. Reported in 2015 $\text{Li}\{[\text{Fe}(\text{Tp})(\text{CN})_3]_{24}[\text{Fe}(\text{H}_2\text{O})_2]_6[\text{Fe}(\text{dpp})(\text{H}_2\text{O})]_{12}(\text{CF}_3\text{SO}_3)_6\}$, (dpp = 1,3-di(4-pyridyl)propane) $[\text{Fe}_{42}]$, currently has the largest ground state spin of any Fe^{III} polymetallic cluster⁴⁸ in which

cyanide bridging groups facilitate ferromagnetic exchange between $S = 5/2$ centres leading to a ground state spin of $S = 45$.

Iron based heterometallic polynuclear clusters.

Heterometallic $\text{Fe}^{\text{III}}\text{-O-M}$ compounds also have a range of applications in multiple fields including catalysis,⁴⁹ coordination polymers,⁵⁰ bioinorganic chemistry⁵¹ and molecular magnetism. Despite the plethora of homometallic $\text{Fe}^{\text{III}}\text{-O}$ complexes reported there has been much less work on large heterometallic $\text{Fe}^{\text{III}}\text{-O-M}$ clusters. This becomes clear when searching the Cambridge Structural Database (CSD). A search of compounds with an Fe-O-M moiety (where $M = 3d$ and $4f$ metal ions excluding Fe) and with a number of iron ions larger than 1 gives less than 500 hits. Of these just under half (222 compounds) are $\text{Fe}/4f$ complexes, with the remaining half (225 compounds) being $\text{Fe}/3d$ complexes. There are only a few $\text{Fe}^{\text{III}}\text{-M}$ clusters that are of interest to a magnetochemist. Such examples include variations of Mn_{12} which incorporate Fe^{III} ions.⁵²

More recent examples of Fe/M clusters are based upon $[\text{Fe}_4]$ star-shaped clusters. Synthesised by reaction of FeCl_2 , Hdpm (dipivoly methane) and either LiOMe or NaOMe $[\text{Fe}_4(\mu\text{-OMe})_6(\text{dpm})_6]$ ($[\text{Fe}_4]$, Figure 12) displays antiferromagnetic behaviour with the outer Fe^{III} ions “spin up” and the central Fe^{III} ion “spin down” leading to a ground state spin of $S = 5$.⁵³ These $[\text{Fe}_4]$ stars behave as SMMs, and work on their surface deposition have shown them to maintain their magnetic behaviour on a variety of substrates.^{54,55} This prompted further investigation into the preparation of analogous heterometallic stars $[\text{Fe}_3\text{Cr}^{\text{III}}(\mu\text{-OMe})_6(\text{dpm})_6]$, $[\text{Fe}_3\text{Cr}]$,⁵⁶ and $[\text{Fe}_3\text{V}^{\text{III}}(\text{L}^{\text{Et}})_2(\text{dpm})_6]$, ($\text{H}_3\text{L}^{\text{Et}} = 2\text{-ethyl-2-(hydroxymethyl)propane-1,3-diol}$) $[\text{Fe}_3\text{V}]$,⁵⁷ (Figure 13) thus increasing the spin ground state to $S = 6$ and $S = 13/2$, respectively.

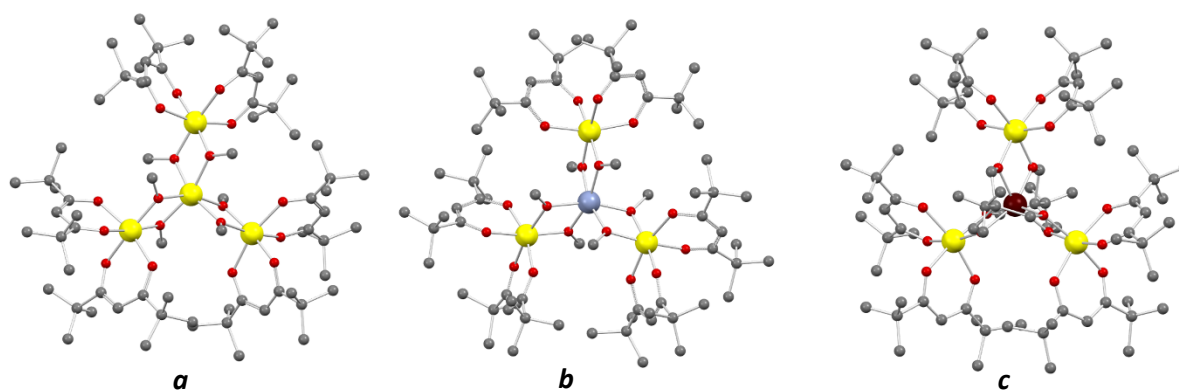


Figure 12: Structures of the “star” clusters $[Fe_4]$ (a), $[Fe_3Cr]$ (b) and $[Fe_3V]$ (c). Colour code: Fe, yellow; Cr, light blue; V, brown; O, red; C, grey. Hydrogen atoms, solvates and counterions omitted for clarity.

Other heterometallic Fe/M clusters have been investigated in an effort to utilise the enormous size of POMs to build high spin compounds by combining paramagnetic Fe^{III} ions with classical POM metals such as Mo. The icosidodecahedron capsule compound $[H_4Mo^{VI}_{72}Fe^{III}_{30}(OAc)_{15}O_{254}(H_2O)_{98}]$ ($[Mo_{72}Fe_{30}]$, Figure 13) was first synthesised by the degradation of a larger $[Mo_{132}]$ POM in the presence of $FeCl_3$.⁵⁸ The capsule is made up of 12 $\{(Mo)Mo_5\}$ pentagons which are bridged together by Fe^{III} octahedra leading to approximate icosahedral symmetry when considering the centres of the $\{(Mo)Mo_5\}$ pentagons. The 30 Fe^{III} ions present describe the vertices of an icosidodecahedron, an Archimedean solid. Magnetic measurements reveal highly frustrated behaviour resulting from the triangular and pentagonal arrangements of the Fe^{III} ions. Indeed, $[Mo_{72}Fe_{30}]$ is a molecular analogue of the 2D kagome lattice and as such has been the subject of many experimental and theoretical studies. In fact, to date, more than 100 papers on $[Mo_{72}Fe_{30}]$ have been published.^{59–62} $[Mo_{72}Fe_{30}]$ has also proven to have interesting host-guest chemistry in which a Keggin ion $[H_xPMo_{12}O_{40}]^{3-}$ ($x = 1, 2$) templates the formation of the capsules, leading to both discrete host-guest complexes⁶³ and 2D layer compounds of Keggin encapsulating $[Mo_{72}Fe_{30}]$ units bridged through Fe^{III} -O- Fe^{III} bonds.⁶⁴

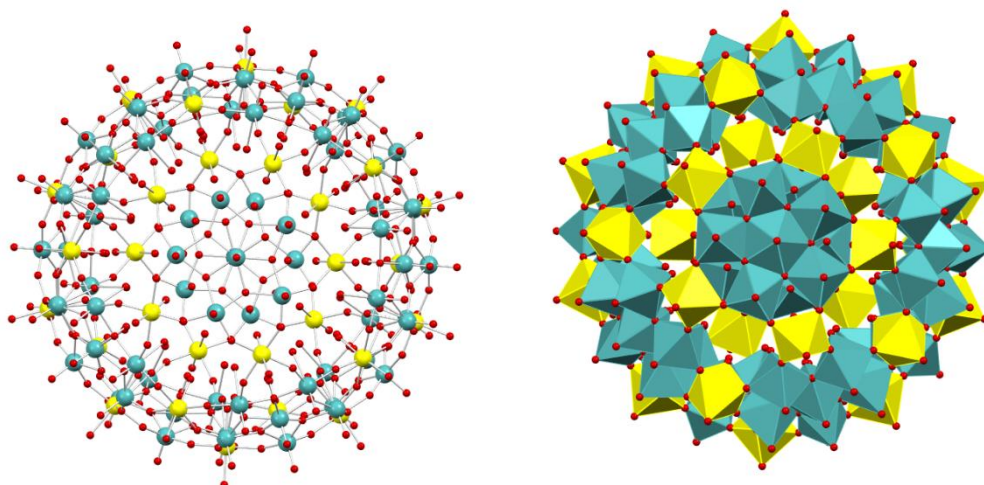


Figure 13: Structure of the $[H_4Mo^{VI}_{72}Fe^{III}_{30}(OAc)_{15}O_{254}(H_2O)_{98}]$ icosidodecahedron in ball and stick (left) and polyhedral representation (right). Colour code; Fe, yellow, Mo, light blue; O, red. Hydrogen and carbon atoms omitted for clarity.

The heterometallic species $Bi_6[Fe_{13}O_{16}(OH)_{12}(O_2CCCl_3)_{12}](O_2CCCl_3) \cdot 14H_2O$ ($[Bi_6\{Fe_{13}\}]$, Figure 14) contains an $[Fe_{13}]$ Keggin in its core, with the peripheral Bi ions providing structural and solution stability. Interestingly, it is prepared from aqueous solution from the reaction of $Bi(NO_3)_3$ with $Fe(NO_3)_3$, trichloroacetic acid and sodium bicarbonate, and recrystallised from THF. The core-shell nature of this cluster suggests that iron based minerals may be constructed from polymetallic building blocks rather atom by atom, and it also hints that core-shell species in which an outer, stabilising shell, which may be inorganic or organic, may be an interesting route to multifunctional molecule iron oxides. ^{65 66}

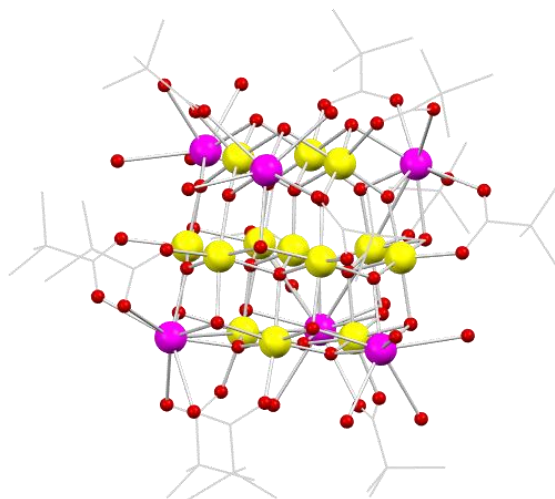


Figure 14: Crystal Structure of the water soluble Fe^{III} Keggin complex $\text{Bi}_6[\text{Fe}_{13}\text{O}_{16}(\text{OH})_{12}(\text{O}_2\text{CCCl}_3)_{12}](\text{O}_2\text{CCCl}_3)_{12} \cdot 14(\text{H}_2\text{O})$. Colour code: Fe, yellow; Bi, pink; O, red; C and Cl, grey wireframe. Solvates, counterions omitted and trichloroacetate ligands in wireframe for clarity.

Heterometallic species containing iron and lanthanide ions are plentiful.^{67–69} Often, such species lead to high nuclearity clusters with aesthetically pleasing structures and large spin ground states. A prominent example are the high-spin wheels of formula $[\text{Fe}_{10}\text{Ln}_{10}(\text{Me-tea})_{10}(\text{Me-teaH})_{10}(\text{NO}_3)_{10}] \cdot 20\text{MeCN}$ (Me-tea = *N,N*-bis-(2-hydroxyethyl)amino-2-propanol, Ln = Gd, Dy, Tb, Ho, Er, Tm, Yb, Lu, Y) ($[\text{Fe}_{10}\text{Ln}_{10}]$). Synthesised by heating an acetonitrile/methanol solution of $\text{Fe}(\text{NO}_3)_3$, $\text{Ln}(\text{NO}_3)_3$, NEt_3 and the Me-teaH₃ ligand these clusters are made up of alternating $\text{Ln}^{\text{III}}/\text{Fe}^{\text{III}}$ ions bridged by alkoxo ligands. In the $[\text{Fe}_{10}\text{Gd}_{10}]$ (Figure 15) this alternating pattern of *3d/4f* metal ions results in ferromagnetic exchange between adjacent Fe^{III} and Gd^{III} ions, leading to a ground state spin of $S = 60$, currently the largest ground state spin reported for a molecular species.

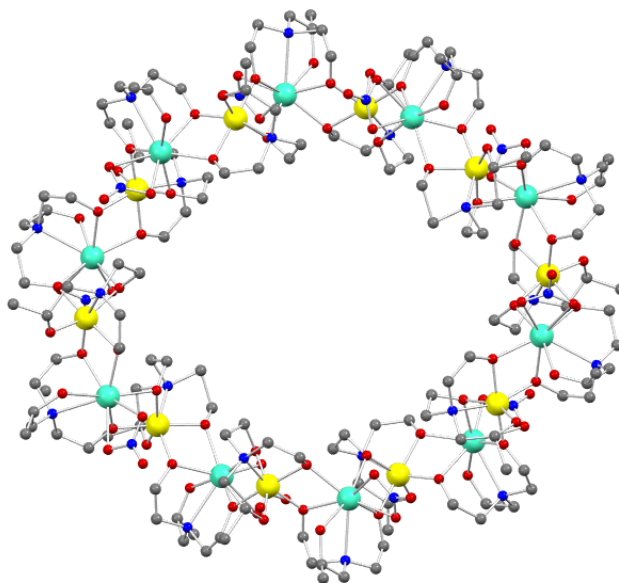


Figure 15: Crystal structure of $[Fe_{10}Gd_{10}(Me-tea)_{10}(Me-teaH)_{10}(NO_3)_{10}] \cdot 20MeCN$. Colour code; Fe, yellow, Gd, cyan; O, red; N, dark blue; C, grey. Solvates and hydrogen atoms omitted for clarity.

This introduction has given a brief summary of some important Fe-based clusters in the history of molecular magnetism, particularly those based on Fe oxyhydroxides and alkoxides. Chapter 2 aims to extend the family of Fe^{III} molecular minerals building upon the syntheses of clusters such as Fe_{17} and Fe_{13} to make new high nuclearity Fe^{III} – oxo clusters. Chapter 3 reports chemistry of iron salts with the triethanolamine ligand and other transition metal salts to form magnetically frustrated compounds. Finally, chapter 4 reports the synthesis and characterisation of a family of heterometallic $[Fe^{III}/M^{II}]_7$ Anderson wheels using the ligand 2-pyridinemethanol.

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Chapter 2: Fe^{III} Molecular Minerals

Chapter 2: Fe^{III} molecular minerals

As discussed in chapter 1 it is interesting to note the enormous size difference between the largest polyoxometalates (POMs), most commonly constructed from high oxidation state, diamagnetic metal ions,^{1–3} and molecules built from the high spin (d⁵), paramagnetic Fe^{III} ion,^{4–6} despite both often containing similar metal oxide cores.^{7,8} The most pertinent examples of Fe^{III} clusters conforming to POM-like architectures are [Fe₁₃]^{9–14} and [Fe₁₇];^{15,16} both are structurally related with alternating layers/shells of tetrahedral and octahedral metal ions—the former has the a-Keggin structure,⁹ and the latter the e-Keggin structure with four additional capping metal ions.¹⁷ In addition, the much studied [Mo₇₂Fe^{III}₃₀] icosidodecahedron,¹⁸ demonstrates that very large (heterometallic) molecular metal oxides containing paramagnetic metal ions can (a) be synthesized, (b) retain POM-like architectures, and (c) possess fascinating physical properties—the high symmetry icosidodecahedron possessing geometric spin frustration.^{19,20} This has prompted us to speculate that large and very large Fe^{III} molecular metal oxides, approaching the size and structural diversity of POMs, can be constructed, but with the terminal oxides replaced by simple monodentate ligands. There appears to be no chemical reason why such species cannot form, and their synthesis would help bridge the “gap” between the fields of molecular magnetism (where the vast majority of molecules have nuclearities less than twenty) and POM chemistry (where complexes can be an order of magnitude larger), producing species with a myriad of potentially interesting physical properties, with applications in chemistry, physics, materials science, biology and medicine.^{21–24} The [Fe₁₇] complex in particular hints at a potentially successful route to the synthesis of such species. It is made very simply by dissolving anhydrous FeX₃ (X=Cl, Br) in wet pyridine (or any analogous liquid base such as b-picoline, isoquinoline, ethyl-pyridine, lutidine, etc).²⁵ The wet pyridine appears to fulfil at least five simultaneous roles: it is the solvent, the base, the source of water (hence oxide), monodentate ligand (with the halide ions) that encases the metal oxide core, and source of the charge balancing pyridinium cations. Interestingly, in POM chemistry the addition of (bulky) organic amine cations is thought to aid the self-assembly of large nuclearity species by isolating the smaller building blocks, preventing rapid aggregation into complexes with (smaller) stable spherical topologies.²⁶ Herein we discuss the synthesis, structure and magnetic behaviour of 3 novel metal oxide clusters of with nuclearities ranging from 8 to 34

which expand the family of Fe^{III} based “molecular minerals” currently composed of [Fe₁₃] and the various analogues of [Fe₁₇].

Results and Discussion

The largest of these clusters is the [Fe^{III}₃₄(μ₄-O)₄(μ₃-O)₃₄(μ-OH)₁₂Br₁₂(py)₁₈]Br₂ (**1**) (Figure 16) which is made via a strategy based upon the synthesis of [Fe₁₇]. Dissolution of anhydrous FeBr₃ and an organic base (hexamethyltetramine, (hmta) /morpholine/N-methyl morpholine) into a mixture of acetonitrile and pyridine followed by crystallisation via an acetone vapour diffusion affords crystals of compound **1**. The synthesis bears similarities with the preparation of [Fe₁₇] with key differences. As discussed above pyridine has multiple roles in the synthesis of [Fe₁₇], the synthesis of compound **1** reduces the amount of pyridine in the overall reaction and adds other reagents to the reaction to fulfil some of these roles; acetonitrile as the solvent and an organic amine (hmta/morpholine/N-methyl morpholine) as a base. The result of these changes is a cluster twice the size of the original [Fe₁₇] cluster.

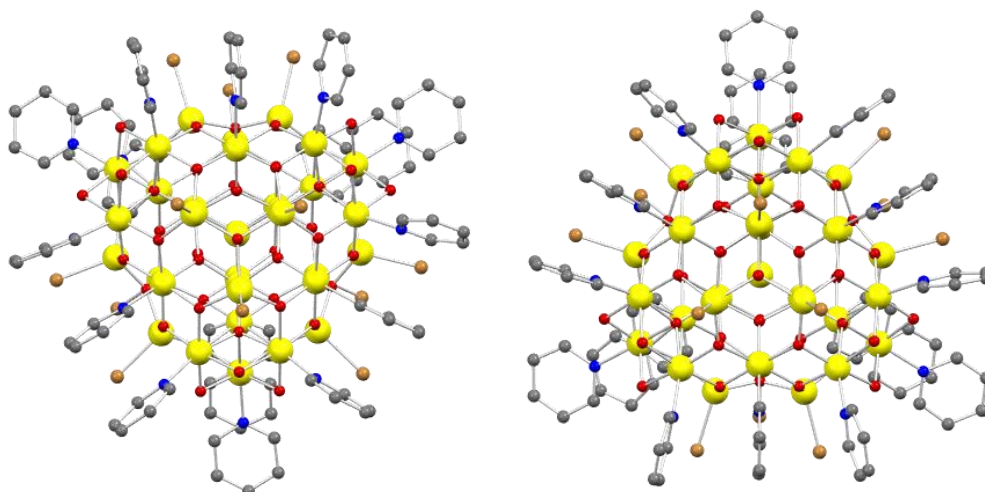


Figure 16: Orthogonal views of the [Fe^{III}₃₄(μ₄-O)₄(μ₃-O)₃₄(μ-OH)₁₂Br₁₂(py)₁₈]²⁺ cluster. Colour Code: Fe^{III}, yellow; O, red; Br, brown; N, blue; C, grey. Cations, solvates and hydrogen atoms omitted for clarity.

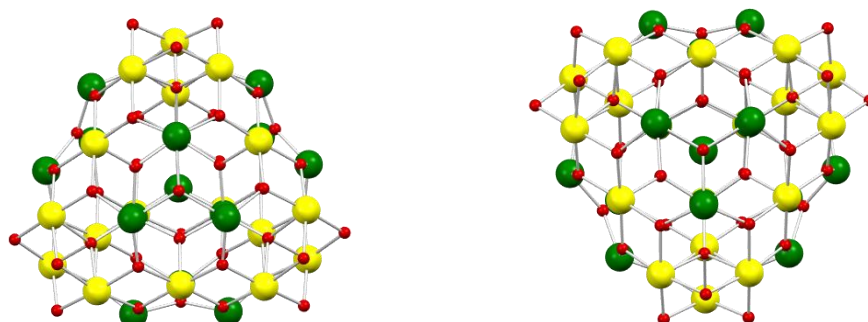


Figure 17: Orthogonal views of the metal-oxygen core of compound **1**. Colour Code: $\text{Fe}^{\text{III}}_{\text{octahedral}}$, yellow; $\text{Fe}^{\text{III}}_{\text{tetrahedral}}$, green; O, red.

Compound **1** crystallises in the monoclinic space group $P2_1/n$ with the full complex in the asymmetric unit. The metallic skeleton (Figure 17) describes a $[\text{Fe}^{\text{III}}_4]$ tetrahedron encapsulated within a $[\text{Fe}^{\text{III}}_{18}]$ truncated tetrahedron, whose large faces are capped by $[\text{Fe}^{\text{III}}_3]$ triangles. The (sixteen) metal ions in the inner tetrahedron and the outer triangles are all tetrahedral and the (eighteen) Fe ions in the truncated tetrahedron are all octahedral. The presence of tetrahedral-octahedral-tetrahedral “shells” of metal ions is as found in the $[\text{Fe}_{13}]$ and $[\text{Fe}_{17}]$ complexes (Figure 18) and Fe containing minerals, such as magnetite and maghemite.

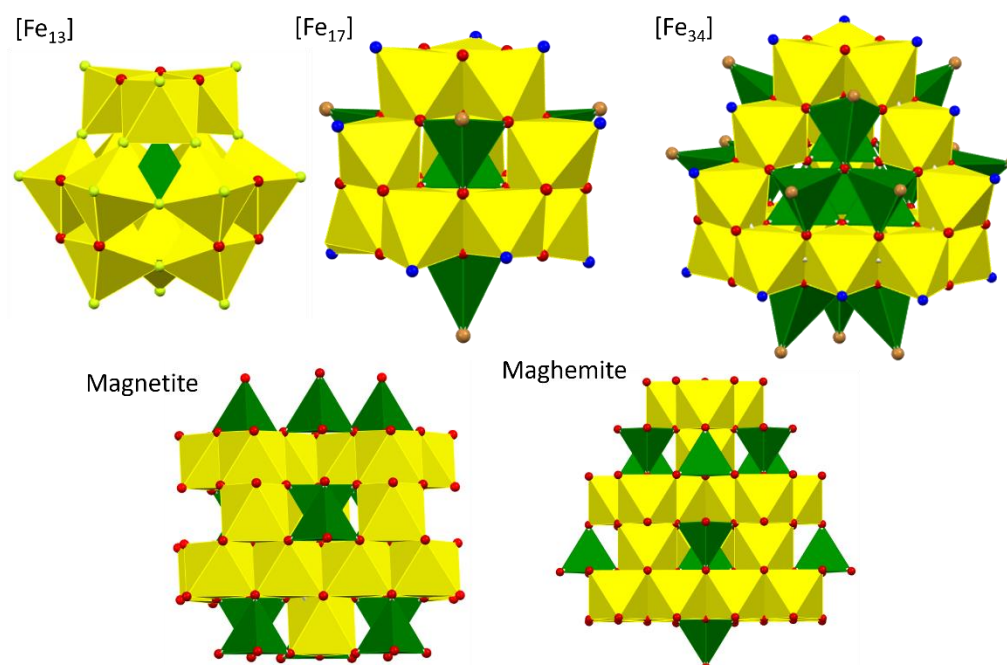


Figure 18: Polyhedral diagrams of the cores of $[\text{Fe}_{13}]$, $[\text{Fe}_{17}]$, compound **1** ($[\text{Fe}_{34}]$) and the minerals magnetite and maghemite. Colour Code: $\text{Fe}^{\text{III}}_{\text{octahedral}}$, yellow; $\text{Fe}^{\text{III}}_{\text{tetrahedral}}$, green; O, red; N, blue.

The inner tetrahedron is connected to the $[\text{Fe}^{\text{III}}_{18}]$ truncated tetrahedron via ten ($4 \mu_4$; $6 \mu_3$) O^{2-} ions. Each face-capping, oxo-centred $[\text{Fe}^{\text{III}}_3]$ triangle is connected to the $[\text{Fe}^{\text{III}}_{18}]$ truncated tetrahedron via six $\mu_3\text{-O}^{2-}$ ions. The remaining twelve $\mu_2\text{-OH}^-$ ions link the metal ions situated on the triangular faces on the truncated tetrahedron. Each of the octahedral metal ions in the $[\text{Fe}_{18}]$ truncated tetrahedron and tetrahedral metal ions in the face capping $[\text{Fe}_3]$ triangles have their coordination geometries completed through the presence of a pyridine (py) molecule and a bromide, respectively. The Br^- counter anions are associated with the triangular faces of the truncated tetrahedron with $\text{Br}\cdots(\mu_2\text{-})\text{O}$ distances in the range 3.21–3.48 Å, and the py C-atoms on a neighbouring molecule ($\text{Br}\cdots\text{C}$, 3.46 Å). The other prevalent intermolecular interactions occur between adjacent Br^- ions and py molecules ($\text{Br}\cdots\text{C}$, 3.50 Å). Magnetic measurements of **1** strongly hint at rather large, competing, antiferromagnetic exchange interactions between the Fe centres. The susceptibility data ($T=350\text{--}2\text{ K}$, $B=0.1\text{ T}$; Figure 19a) shows that the χT value at $T = 350\text{ K}$ ($\approx 60\text{ K cm}^3\text{ mol}^{-1}$) is well below the Curie constant expected for thirty four uncoupled Fe^{III} ions ($150\text{ K cm}^3\text{ mol}^{-1}$). As temperature is decreased the value of χT first increases to a broad maximum of $\approx 75\text{ K cm}^3\text{ mol}^{-1}$ centred around $T = 150\text{ K}$, before dropping slowly to a value of $\approx 70\text{ K cm}^3\text{ mol}^{-1}$ at $T = 50\text{ K}$. Below this temperature the value drops significantly and is strongly field dependent. Magnetisation (M) data (Figure 19b) show an initial, fairly rapid, increase to a value of $\approx 12\ \mu_{\text{B}}$ (for $T=2\text{ K}$, $B < 2\text{ T}$) before first plateauing and then increasing in a more linear fashion to $B = 7\text{ T}$ where $M \approx 15\ \mu_{\text{B}}$. This linear like increase is continued in the $B = 7\text{--}35\text{ T}$ field range (Figure 19b inset), where M reaches a maximum value of $\approx 30\ \mu_{\text{B}}$. The low temperature susceptibility and magnetisation data suggest a relatively small magnetic moment, in agreement with heat capacity measurements where the zero-field magnetic entropy content reaches just $S = 1.6R$ at $T = 2\text{ K}$ (Figure 20). A explanation of the temperature and field dependence of the magnetic data is not straightforward.

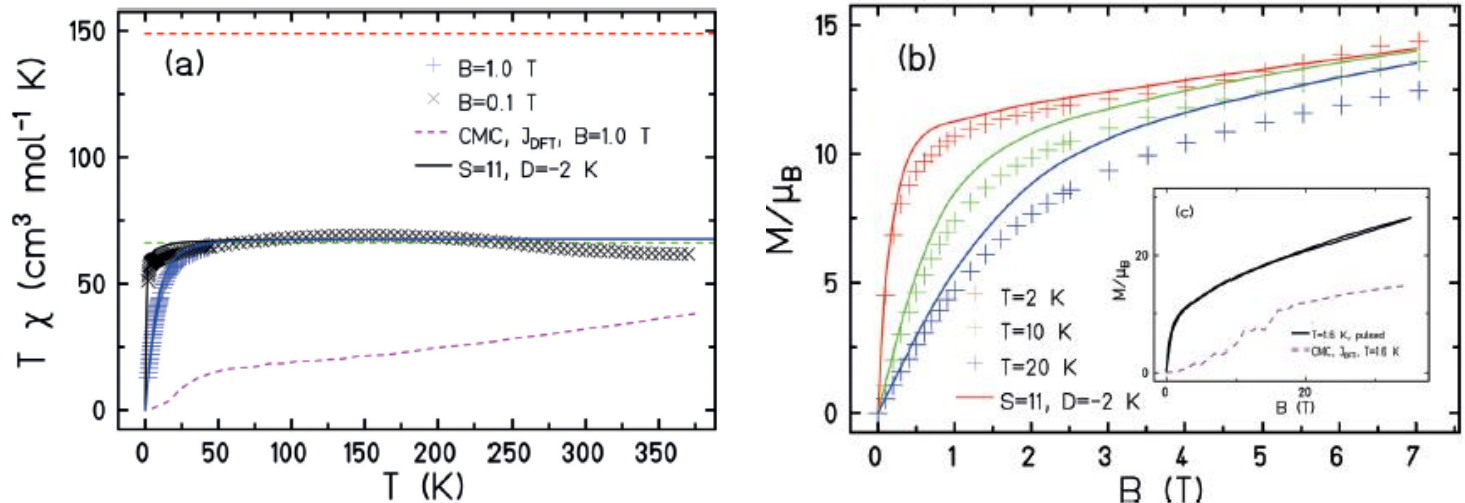


Figure 19: a) Magnetic susceptibility: symbols denote measurements, the red dashed line marks the paramagnetic limit for thirty four $S=5/2$ ions, the green dashed line the respective value for $S=11$. The solid curves belong to single-spin calculations, the dashed magenta curve to CMC simulations based of J_{DFT} values. b) Low-field magnetisation: the solid curves depict the single-spin magnetisation. c) Pulsed-field magnetisation, $T=1.6$ K and $B=0-34$ T (solid black curve) compared to (b) and CMC simulations based on J_{DFT} values (dashed magenta curve).

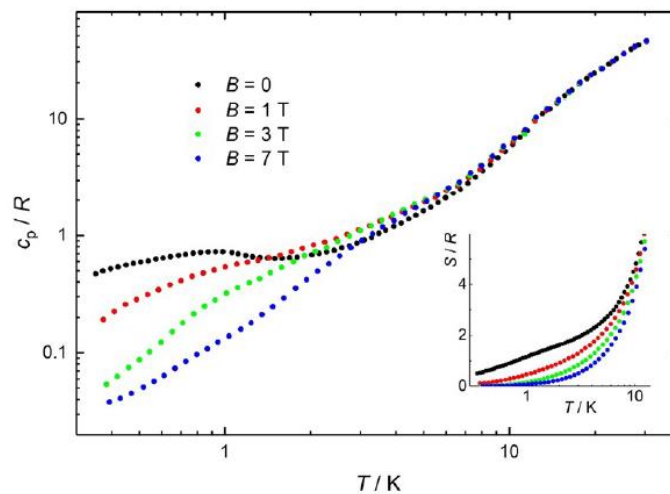


Figure 20: Temperature dependence of the low-temperature experimental heat capacity, c_p/R , and entropy, $S/R = \int c_p/RdT$ (inset), normalised to the gas constant, R , for selected values of the applied magnetic field, B , as labelled. In agreement with the susceptibility data, both sets of data become field-dependent on lowering the temperature below ~ 10 K, weakly at first and then stronger for $T < 2$ K. In further agreement with the magnetic data, the heat capacity and entropy are very small at the lowest temperatures. For instance, the zero-field magnetic entropy content reaches ca. $S = 1.6 R$ at $T = 2$ K, which is significantly smaller than that expected for 34 uncoupled Fe^{III} spins, i.e., $S = 34 \times \ln(6) = 60.9 R$.

Since the cluster is much too large for a quantum calculation in a spin model such as the Heisenberg model, we resort to two approximations. Classical Monte Carlo calculations (CMC) of a classical Heisenberg model, that often deliver accurate results in the temperature and field regions where quantum effects are of minor importance, that is, at elevated temperatures compared to the exchange couplings,¹⁹ suggest an even smaller susceptibility and magnetisation compared to the experiment, when using the exchange parameters provided by DFT (Table 1). In view of the relatively strong exchange, we surmise that we are always in the quantum regime, where the classical calculations point us in the right direction but are poor approximations otherwise. Guided by the nearly flat high temperature χT data, we investigated a quantum model where we assume a low-lying level structure similar to a zero-field split total spin $S = 11$ with g fixed at $g = 2.04$, as obtained from High Field Electron Paramagnetic Resonance (HFEPR) measurements (Figure 21). This effective model fits both χT vs. T and M vs. B (Figures 4a and b) astonishingly well, and it also explains why specific heat measurements detect very few low-lying levels (compared to a total of 2.8×10^{26} levels). While the absolute numbers in this effective model should be taken with a pinch of salt, they do hint at the presence of non-negligible anisotropy. We also expect that the true low-energy spectrum contains numerous additional (small) spin states, and in the absence of any out-of-phase χ'' signals in the ac susceptibility, that may not be of perfect easy axis character.

In order to estimate the magnitude of the magnetic exchange interactions in **1** we have employed a DFT methodology (B3LYP/TZVP) known to yield excellent numerical estimates of J values.^{27–29} Calculations were performed upon model structures derived from **1** (Appendix 1) using a Hamiltonian with the form $\hat{H} = \sum_{i<j} -J_{ij} S_i S_j$. In order to reduce the complexity of the calculations the number of unique exchange interactions in **1** was reduced to five (J_{1-5}) based upon Fe-O-Fe angle and Fe-Fe distance. Calculation of these interactions suggests all interactions are antiferromagnetic in nature and strongly correlated to the Fe-O distances and Fe-O-Fe angles, with larger angles and shorter bonds enhancing the antiferromagnetic part of the exchange, in agreement with the magneto-structural correlation developed by Weihe and Güdel.³⁰

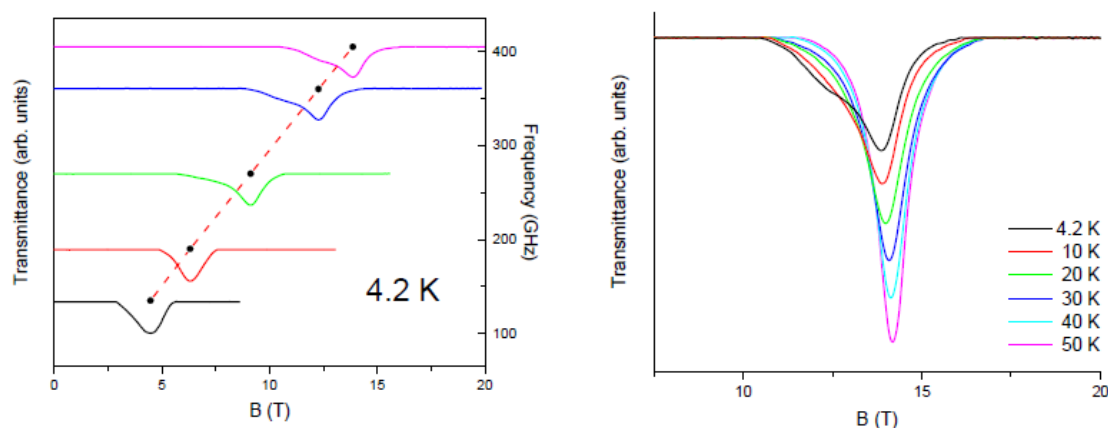


Figure 21: (left) HFEPR spectra of a polycrystalline sample of **1** recorded at 4.2 K and frequencies between 135-405 GHz. A linear fit of field-frequency plot affords a g -value of 2.04 ± 0.01 , and extrapolation of the field-frequency plot gives a zero field resonance frequency of 8.10 GHz (0.26 cm^{-1}). (right) HFEPR spectra at 405 GHz and temperatures between 4.2 - 50 K, revealing a narrowing and shift of the resonance field position to higher field with increasing temperature. The asymmetry / line broadening observed is likely due to one of, or a combination of (a) multiple transitions within multiple S states, (b) anisotropy, and (c) correlation effects. [4b] The Fe_{34} cluster demonstrates very strong exchange coupling between the Fe centres, and given the relative symmetry, one would expect the local anisotropies of different Fe sites to cancel out and the effective local anisotropy of the whole cluster to be small.

To further investigate the nature of these interactions the overlap integrals for the singly occupied molecular orbitals (SOMOs) of the Fe^{III} ions in the model complexes were calculated (Appendix 1). These show a direct correlation between the number of orbital interactions and the magnitude of the antiferromagnetic exchange. For example, for J_3 only two dominant overlaps ($d_{xy}||d_{xy}$ and $d_{x^2-y^2}||d_{xy}$) are detected leading to the smallest calculated J value (-15.7 cm^{-1}), whereas there are seven different, large interactions for J_5 , resulting in the largest J value (-68.2 cm^{-1}). Note that in the latter, the d_{xz} orbital of the tetrahedral Fe^{III} ion is found to overlap significantly with all the d-orbitals of the octahedral Fe^{III} ion, with the exception of the d_{xy} orbital.

Table 1: Calculated J_{DFT} values for the five unique exchange interactions in **1**, alongside the average Fe-O-Fe angles and Fe-O, Fe...Fe distances per interaction. For visualisations of the model complexes used for calculations see Appendix 1.

	Fe-O-Fe (°)	Fe-O (Å)	Fe – Fe (Å)	J_{DFT} (cm ⁻¹)
J_1	118	1.86	3.19	-24.2
J_2	121	1.95	3.39	-38.4
J_3	95.5	1.97	2.92	-15.7
J_4	119	1.92	3.32	-47.3
J_5	129	1.92	3.47	-68.2

In the preparation of [Fe₁₇] the pyridine ligand can be replaced by other “pyridine type” ligands. These include 4-ethylpyridine, β-picoline, 3,5-lutidine and isoquinoline.³¹ It stands to reason that this same principle would apply to the synthesis of compound **1**, however, this is not the case. In a similar reaction to the synthesis of compound **1** the dissolution of anhydrous FeBr₃ to a mixture of acetonitrile and 3,4-lutidine (lut) in the presence of hmta followed by vapour diffusion with isopropyl alcohol affords crystals of (lutH)[Fe^{III}₃₀(μ₄-O)₆(μ₃-O)₂₆(μ-OH)₁₅Br₉(lut)₁₅]Br₃ (**2**). The use of a 4-ethylpyridine (Et-py) in place of 3,4-lutidine and diethyl ether in place of isopropyl alcohol affords the analogous compound (Et-PyH)[Fe^{III}₃₀(μ₄-O)₆(μ₃-O)₂₆(μ-OH)₁₅Br₉(Et-py)₁₅]Br₃·Et-py (**2a**). Due to the analogous nature of these two compounds only compound **2** is discussed further.

Compound **2** crystallises in the monoclinic space group *Pn* with two [Fe₃₀] complexes in the asymmetric unit (Figure 22). The metallic skeleton of the [Fe₃₀] cage (Figure 23) is constructed from alternate layers of tetrahedral and octahedral Fe^{III} ions. In the centre of the cage is a [Fe^{III}₃] triangle of tetrahedral Fe ions. This is surrounded by a partial [Fe^{III}₁₈] supertetrahedron of octahedral Fe ions in which three of the corners are truncated into three-membered rings, and one corner is truncated into a six membered ring. The [Fe^{III}₁₈] cage is surrounded by a partial [Fe^{III}₉] cuboctahedron of tetrahedral Fe ions. Thus, in total, there are twelve tetrahedral Fe^{III} sites and eighteen octahedral Fe^{III} sites. The Fe ions in the inner [Fe^{III}₃O₉]⁹⁻ triangle are linked to each other and to the metal ions in the [Fe^{III}₁₈] unit through six μ₄- and three μ₃-O²⁻ ions. Twenty two μ₃-O²⁻ ions then link the octahedral Fe ions in the [Fe^{III}₁₈O₂₂]¹⁰⁺ unit to each

other and to the tetrahedral Fe ions in the outer $[\text{Fe}^{\text{III}}_9]$ partial cuboctahedron. The remaining $\mu_3\text{-O}^{2-}$ ions link three tetrahedral Fe ions in the $[\text{Fe}^{\text{III}}_9]$ partial cuboctahedron. The fifteen hydroxide ions are all located in the $[\text{Fe}^{\text{III}}_{18}]$ cage and are of two types: six are μ -bridging between Fe ions in the $[\text{Fe}_6]$ ring and the remaining nine are μ -bridging between Fe ions in the $[\text{Fe}_3]$ rings. The monodentate 3,4-lutidine ligands are all bonded to octahedral Fe ions in the $[\text{Fe}^{\text{III}}_{18}]$ moiety, while the nine tetrahedral iron ions in the outer partial $[\text{Fe}^{\text{III}}_9]$ cuboctahedron are each capped by a terminal Br ion. The Fe-O-Fe angles fall into two distinct categories: those connecting the tetrahedral metal ions to tetrahedral/octahedral metal ions are much larger ($115.5(7)^\circ$ – $134.9(6)1^\circ$) than those connecting octahedral metal ions to other octahedral metal ions ($90.1(5)^\circ$ – $104.9(6)1^\circ$). The $[\text{Fe}_{30}]$ cage has an overall charge of 2+, balanced by the presence of three Br^- counter anions (H-bonded to the m-OH ions associated with the truncated $[\text{Fe}_3]$ rings (Appendix 2) $\text{OH}\cdots\text{Br}$, ≈ 3.3 Å), and one lutH cation. The closest inter-cluster interactions occur between neighbouring Me (lut) groups ($\text{C}\cdots\text{C}$, ≈ 3.2 – 3.6 Å) and between the terminal Br ions and Me(lut) groups ($\text{Br}\cdots\text{C}$, ≈ 3.2 – 3.6 Å).

A structural comparison to the previously described molecular Fe oxides $[\text{Fe}_{17}]$ and $[\text{Fe}_{34}]$ (**1**) (Figure 24) and to the $[\text{Fe}_{13}]$ Keggin ion, shows some striking similarities. In each case the cluster is built up from alternate layers of tetrahedral and octahedral Fe ions. In $[\text{Fe}_{13}]$ and $[\text{Fe}_{17}]$ there is a single tetrahedral Fe ion in the centre, surrounded by a truncated tetrahedron of octahedral metal ions. $[\text{Fe}_{17}]$ has an additional outer shell of four tetrahedral metal ions arranged in a tetrahedron. $[\text{Fe}_{34}]$ contains a central tetrahedron of tetrahedral metal ions, surrounded by a truncated tetrahedron of octahedral metals ions, surrounded by a truncated tetrahedron of tetrahedral metal ions. $[\text{Fe}_{30}]$ has a central triangle of tetrahedral metal ions, rather than a tetrahedron, which clearly modifies the subsequent self-assembly process. The resultant changes in structure and symmetry have significant consequences for the magnetic behaviour (vide infra). The structural similarities across the $[\text{Fe}_{13}]$, $[\text{Fe}_{17}]$, $[\text{Fe}_{30}]$ and $[\text{Fe}_{34}]$ series do therefore hint that the growth of these complexes occurs layer by layer through addition of polynuclear building blocks.

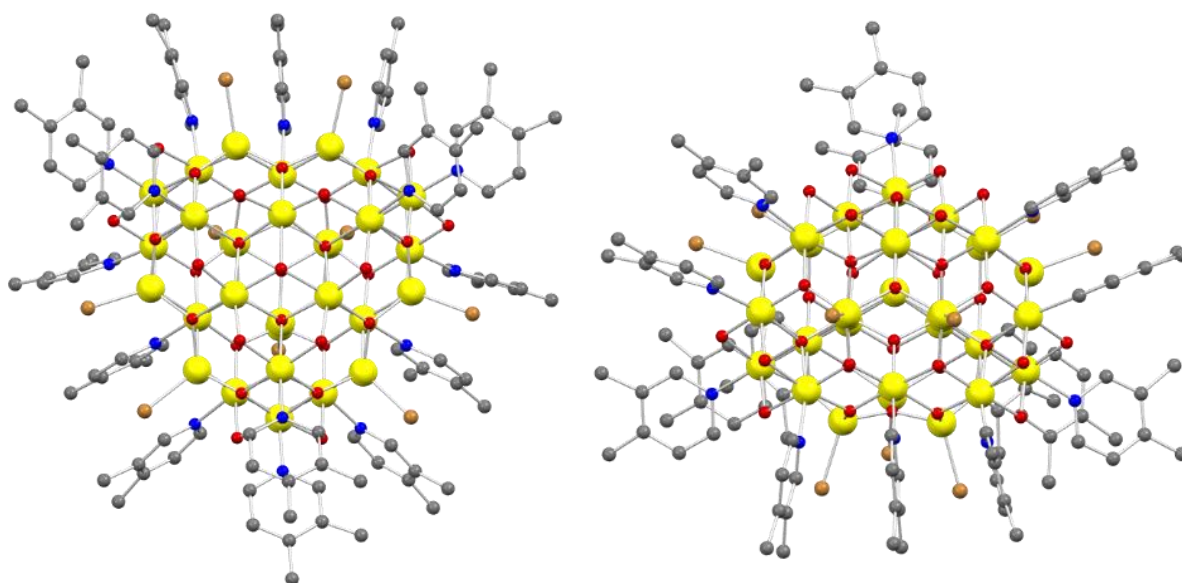


Figure 22: Orthogonal views of the molecular structure of the cluster cation of compound **2**. Colour Code: Fe^{III} , yellow; O, red; Br, brown; N, blue; C, grey. Cations, solvates and hydrogen atoms omitted for clarity.

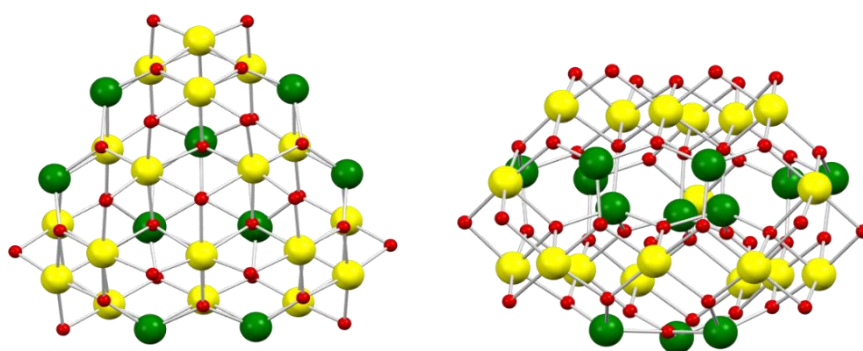


Figure 23: Orthogonal views of the metal-oxygen core of compound **2**. Colour Code: Fe^{III} octahedral, yellow; Fe^{III} tetrahedral, green; O, red.

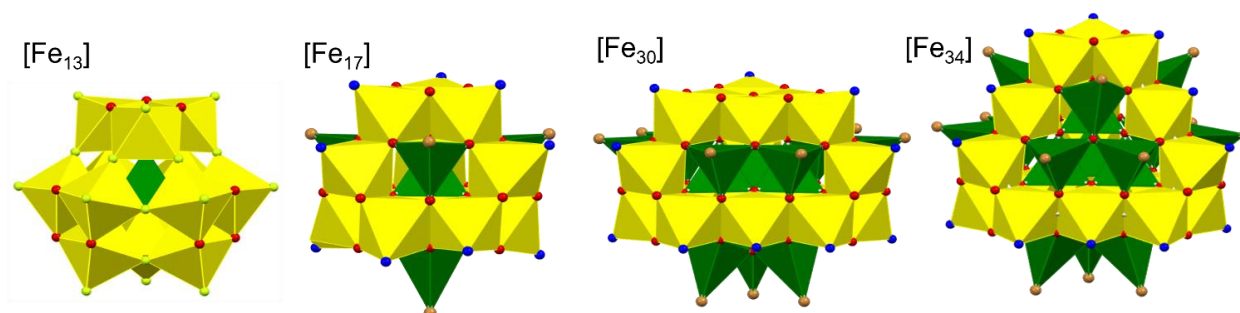


Figure 24: Polyhedral representations of the metal-oxygen cores of $[\text{Fe}_{13}]$, $[\text{Fe}_{17}]$, $[\text{Fe}_{30}]$ (**2**) and $[\text{Fe}_{34}]$ (**1**). Colour Code: Fe^{III} octahedral, yellow; Fe^{III} tetrahedral, green; O, red; N, blue.

Mass spectrometry (see the Experimental for full details) of the initial reaction solution indicates that the $[\text{Fe}_{30}]$ species is formed quickly with the $t = 0$ spectrum showing peaks corresponding to the $[[\text{Fe}_{30}]-2(\text{lut}) + 2(\text{MeCN})]^{2+}$ and $[[\text{Fe}_{30}]-3(\text{lut}) + 2(\text{MeCN})]^{2+}$ fragments. The cluster continues to be present throughout the reaction time with measurements at $t = 2$ hours and $t = 4$ hours also showing these peaks (Figures 25 and 26, Appendix 2). Mass spectrometry of crystalline **2** redissolved in a 20/80 mix of lut/MeCN shows the $[\text{Fe}_{30}]$ cage is present with one, two and three ligands removed, with measurements repeated over a period of 24 hours showing that the molecule is present in solution for at least 1 day.

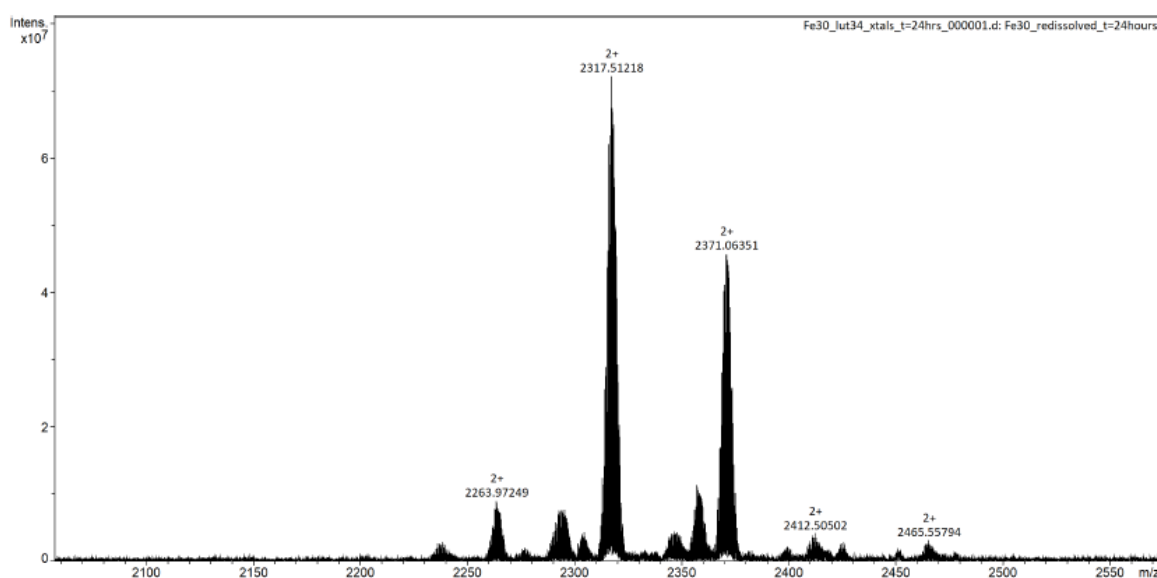


Figure 25: Mass spectrum of crystals of **2** re-dissolved in a 20/80 mix of lut/MeCN. The most intense peaks correspond to $[[\text{Fe}_{30}]-2(\text{lut})+2(\text{MeCN})]^{2+}$ and $[[\text{Fe}_{30}]-3(\text{lut})+2(\text{MeCN})]^{2+}$ (2371 and 2317 m/z respectively). Less intense peaks correspond to fragments and adducts of $[\text{Fe}_{30}]$ and common MS impurities, including $[[\text{Fe}_{30}]-4(\text{lut})+2(\text{MeCN})]^{2+}$ (m/z = 2263), $[[\text{Fe}_{30}]-2(\text{lut})+2(\text{H}_2\text{O})]^{2+}$ (m/z = 2295) and $[[\text{Fe}_{30}]+(\text{CH}_3\text{COCH}_3)]^{2+}$ (m/z = 2412).

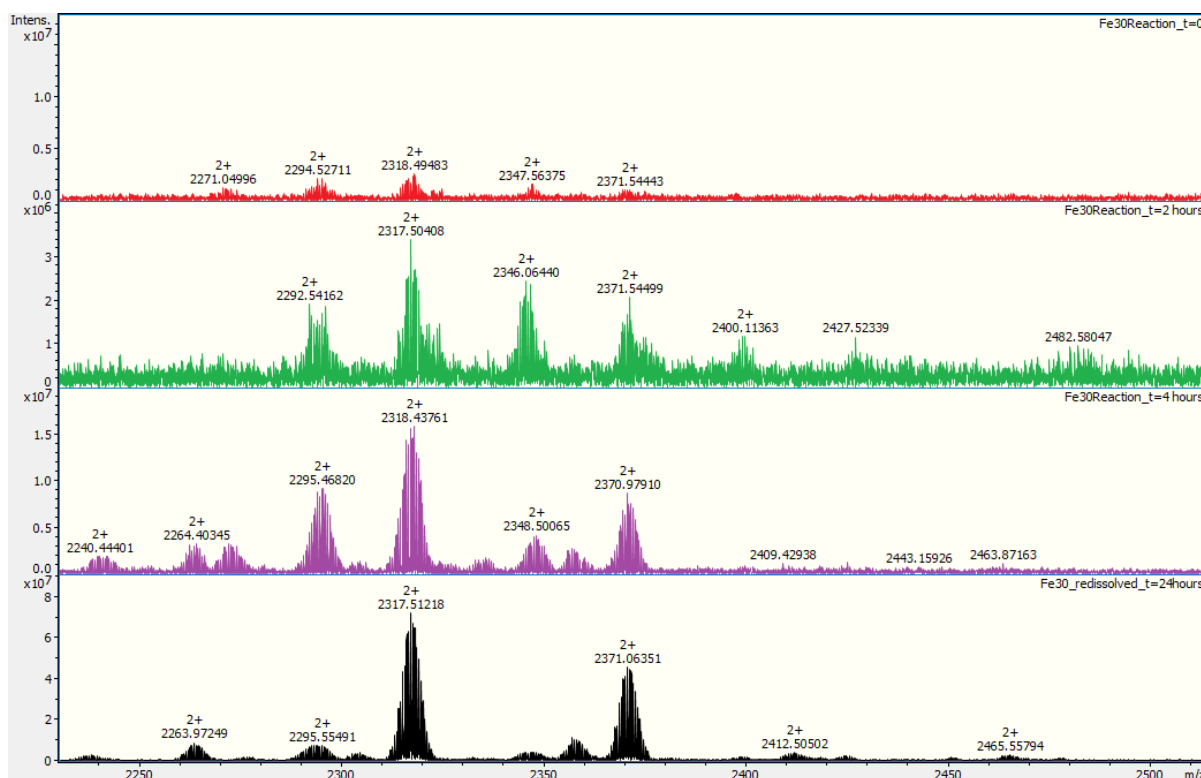


Figure 26: Time resolved mass spectra of the initial reaction mixture used to make compound **2** showing the characteristic peaks for $[\text{Fe}_{30}]$ at 2317 and 2371 m/z at $t = 0$ (red); $t = 2$ hours (green); $t = 4$ hours (purple). The mass spectrum of crystalline **2** re-dissolved in a 20/80 mix of lut/MeCN (black) is shown for comparison.

Magnetic measurements of **2** reveal relatively strong antiferromagnetic interactions between the Fe centres. The experimental dc susceptibility data ($T = 2\text{--}400\text{ K}$, $B = 0.1\text{ T}$) for **2** is plotted in Figure 27 as the χT product versus T , where χ is the molar magnetic susceptibility, T is the temperature, and B the applied magnetic field. The value of χT at $T = 300\text{ K}$ is $\approx 45\text{ K cm}^3\text{ mol}^{-1}$, significantly lower than that expected for the sum of the Curie constants for thirty Fe^{III} ($S = 5/2$) ions with $g_{\text{Fe}} = 2.00$ ($131.25\text{ K cm}^3\text{ mol}^{-1}$). As the temperature decreases, the magnitude of χT decreases rapidly, reaching a value of $\approx 3.5\text{ K cm}^3\text{ mol}^{-1}$ at $T = 2\text{ K}$, suggestive of a small/diamagnetic spin ground state. At $T \geq 300\text{ K}$, the χT value increases slowly, with no sign of an inflection or jump in value. Magnetisation data ($T = 2\text{--}7\text{ K}$, $B = 0.5\text{--}7\text{ T}$) appear somewhat S-shaped, with the low field data appearing to saturate at $\approx 2\text{ T}$ before increasing rapidly up to $\approx 5\text{ T}$, and then increasing more gradually up to 7 T . This is indicative of the presence of multiple low lying spin states, stabilised through increasing field strength. Similar to the behaviour shown by the $[\text{Fe}_{10}]$ ring described in chapter 1.³²

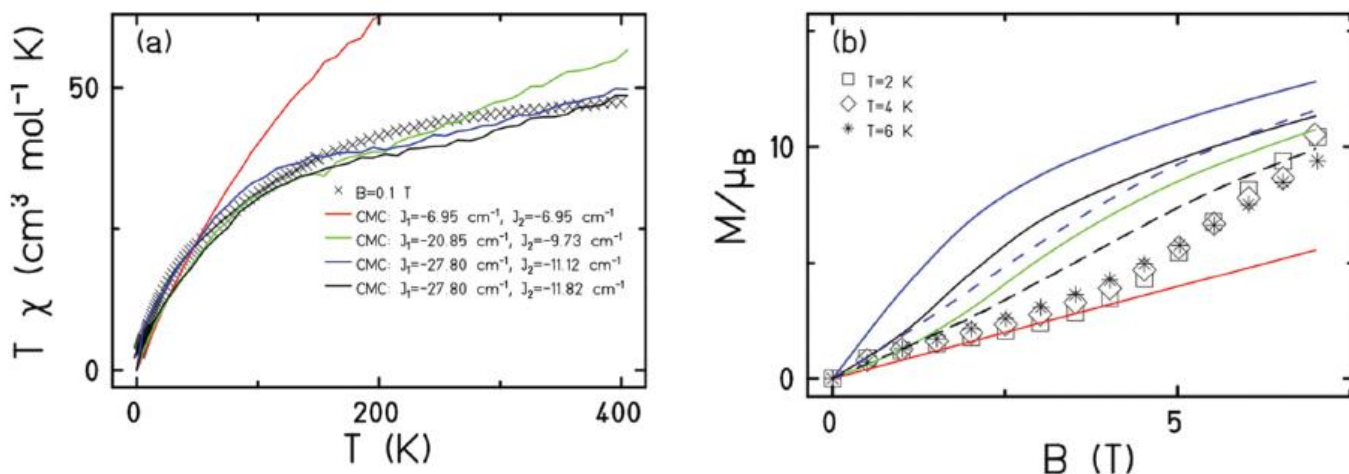


Figure 27: (a) Plot of the χT product versus T in the 400–2 K temperature range in an applied field, $B = 0.1 \text{ T}$. (b) Plot of M versus B in the 2–6 K range for 0.5 - B - 7T. In the latter the solid curves are for $T = 2 \text{ K}$, dashed curves for $T = 6 \text{ K}$. The colour coded CMC simulation values in (b) are the same as those provided in (a).

As with compound **1** it is computationally impossible to quantitatively analyse the magnetic data of a molecule containing thirty $S = 5/2$ spins via conventional matrix diagonalisation techniques. Even the finite-temperature Lanczos method^{33,34} which can approximately solve problems in Hilbert spaces with dimensions up to 10^{11} cannot be applied here. Therefore a classical spin model and classical Monte Carlo (CMC) has been used.³⁵ This allows approximations of the magnetisation and the magnitude of the exchange interactions to be obtained. Note however that classical spin models constitute a high-temperature approximation and thus can be inaccurate at (low) temperatures smaller than the typical interaction strength. Although there are nine different exchange interactions present in **2**, DFT calculations (vide infra, Table 2) suggest they can be grouped into two categories: strongly antiferromagnetic and weakly ferro- or antiferromagnetic based on the larger Fe(tet)-O-Fe(tet/oct) angles and the smaller Fe(oct)-O-Fe(oct) angles, respectively. Therefore, the numerical simulations were simplified by employing a model with just two different J values representing these two different Fe-O-Fe exchange pathways. Simulations with one strong AF coupling of $-20.85 \leq J_s \leq -27.80 \text{ cm}^{-1}$ and one weak AF coupling of $-6.95 \leq J_w \leq -11.82 \text{ cm}^{-1}$ ($\hat{H} = \sum_{i<j} -J_{ij}S_iS_j$) come closest to replicating the magnetic

observables (Figure 27), being superior to a model containing just one exchange interaction, $J = -6.95 \text{ cm}^{-1}$.

To further support the relative sign and magnitude of the coupling constants obtained above, DFT calculations have been performed (see the Experimental for computational details) on model complexes derived from complex **2** (Appendix 3). These suggest that the nine independent exchange interactions are in the range $|J| = 6\text{--}71 \text{ cm}^{-1}$ (Table 2). All the computed exchange interactions are antiferromagnetic, with the exception of J_5 where a relatively weak ferromagnetic exchange of $+14.3 \text{ cm}^{-1}$ has been estimated. The large antiferromagnetic interactions originate from multiple strong overlap integrals between the SOMOs of the Fe^{III} centres bridged by $\mu_3/\mu_4\text{-O}^{2-}$ ions in the model complexes (Appendix 2). The overlap integrals are smaller for the J_5 exchange pathway resulting in a small contribution to the antiferromagnetic part of the interaction affording the small ferromagnetic interaction calculated. These results are in agreement with previous magneto-structural correlations developed for oxo-bridged Fe^{III} complexes in which the magnitude of J is dictated by the Fe-O-Fe angle and Fe-O-Fe distances, and with the results observed for $[\text{Fe}_{17}]$ and **1** in which $J_{(\text{tet-oct})} \gg J_{(\text{oct-oct})}$.^{9,14,15,30}

Table 2: The nine DFT computed magnetic exchange interactions with average Fe-O-Fe angles and average Fe-O and Fe – Fe distances for each interaction.

	Fe-O-Fe (°)	Fe-O (Å)	Fe – Fe (Å)	$J_{\text{DFT}} (\text{cm}^{-1})$
J_1	117.5	1.88	3.17	-30.6
J_2	121.2	1.93	3.36	-6.3
J_3	122.7	1.96	3.45	-19.2
J_4	94.9	1.97	2.92	-7.3
J_5	94.9	2.12	3.29	+14.3
J_6	99.6	2.00	3.05	-14.0
J_7	118.8	1.91	3.28	-60.0
J_8	130.3	1.89	3.44	-70.9
J_9	119.1	1.97	3.40	-24.9

The change in structure between compounds **1** and **2** upon adjustment of peripheral positions on the pyridine-type ligand and the previous work with $[\text{Fe}_{17}]$ and various pyridine derivatives discussed in chapter 1 (*vide supra*)²⁵ prompted the re-examination of the original methodology using pyridine ligands with various functional groups. A result of this study is the synthesis of the smallest member of the “molecular mineral” family.

Dissolution of FeBr_3 in 4-methoxypyridine (MeO-py) with stirring for 3 hours, followed by filtration and vapour diffusion with acetone results in the formation of orange plate-like crystals in 1 week. Crystals of $[\text{Fe}^{\text{III}}_8(\mu_3\text{-O}_6)(\mu\text{-OH})_6(\text{MeO-py})_{12}\text{Br}_2]\text{Br}_4\cdot 3\text{H}_2\text{O}\cdot 2\text{MeO-py}$ (**3**· $3\text{H}_2\text{O}\cdot 2\text{MeO-py}$; Figure 28) are in a monoclinic crystal system and structure solution was performed in the space group $C2/c$ (Appendix 3). The asymmetric unit contains half the formula. The metallic skeleton of **3** (Figure 29) describes a hexagonal bipyramid, in which a ring of six octahedral Fe^{III} ions (Fe1-3 and symmetry equivalent, s.e.) is capped top and bottom by a tetrahedral Fe^{III} ion (Fe4 and s.e.).

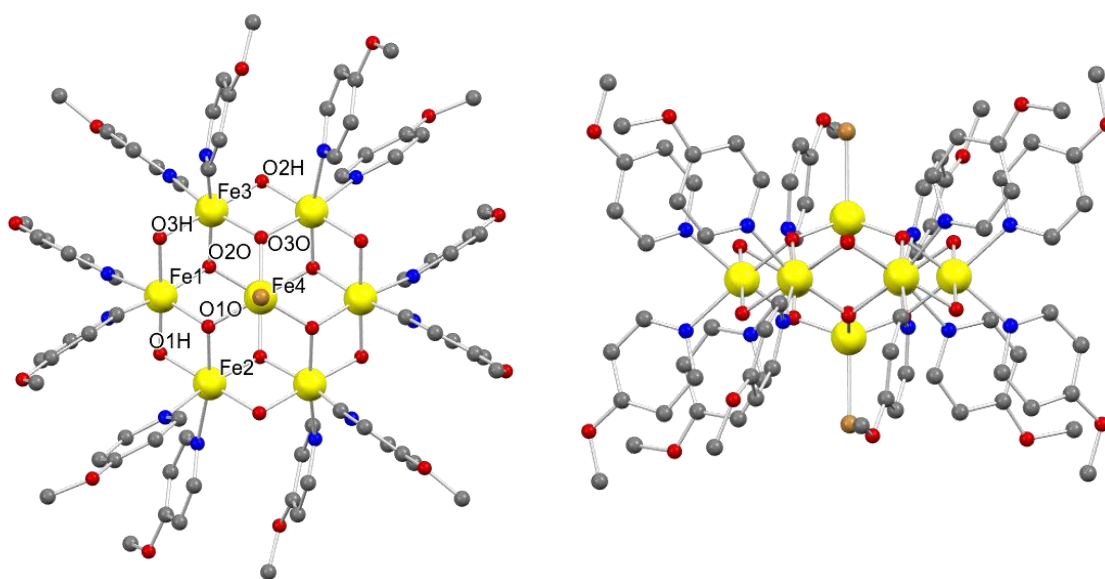


Figure 28: Orthogonal views of the molecular structure of the cation of **3**. Colour code: Fe = yellow, O = red, N = blue, Br = brown, C = black. H atoms, counter anions and solvates omitted for clarity.

The tetrahedral Fe^{III} ions are linked to the $[\text{Fe}_6]$ ring through three $\mu_3\text{-O}^{2-}$ ions (O10, O20, O30 and s.e.), which further bridge two octahedral Fe ions around the inner rim of the wheel. The outer rim is bridged by six $\mu\text{-OH}^-$ ions (O1H, O2H, O3H and s.e.). The coordination sphere of the tetrahedral Fe ion is completed by the presence of a terminal Br^- ion (Br3 and s.e.), and those of the octahedral Fe ions by two MeO-py molecules. Fe-O-Fe bond angles fall in the

ranges Fe(tet)-O-Fe(oct), 122.62-123.42°, and Fe(oct)-O-Fe(oct), 95.25-98.38°; note that the former are very much bigger than the latter. The Br⁻ counter anions (Br1, Br2 and s.e.) are H-bonded to the μ -OH ions (Br...O, 3.199-3.227 Å), as are the two MeO-py and three H₂O molecules of crystallisation (Br...O, 3.365-3.674 Å; N...O, 2.847 Å; Appendix 3). The closest inter-cluster interactions are between neighbouring MeO-py molecules with C/O...C/O distances ≥ 3.45 Å (Appendix 3). The structural similarity between **3** and [Fe₁₇] is remarkable with the [Fe₈] cation able to be directly mapped onto half of the [Fe₁₇] framework (Figure 30).

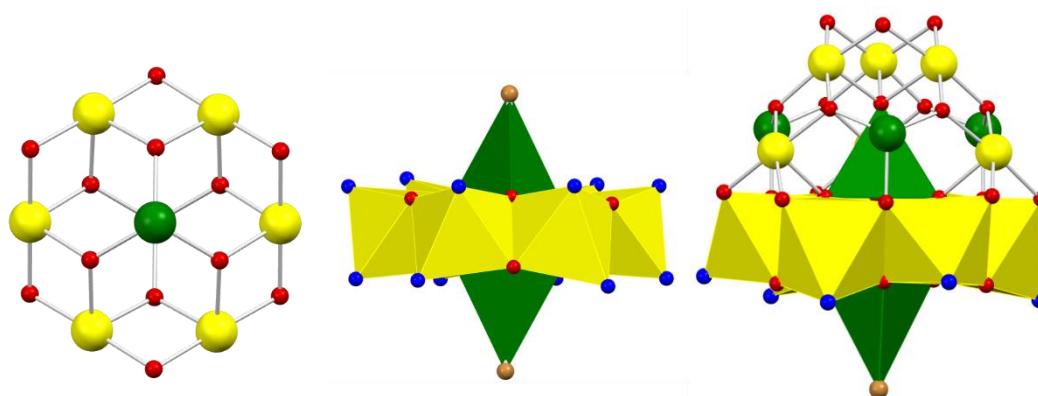


Figure 29: The metal-oxo core of compound **3** in ball and stick format (left), polyhedral format (centre) and mapped onto half of the [Fe₁₇] cluster represented (right). Colour Code: Fe^{III}_{octahedral}, yellow; Fe^{III}_{tetrahedral}, green; O, red; N, blue.

The hexagonal bipyramidal core of **3** is unique amongst the [Fe₈] clusters reported in the Cambridge Structural Database, but the same unit exists in two [Fe₁₄] clusters, the [Fe₁₄(bta)₆O₆(OMe)₁₈Cl₆]⁷ cluster discussed in chapter 1 (*vide supra*) and [Gd₁₂Fe₁₄O₁₂(OH)₁₈(tea)₆(CH₃COO)₁₆(H₂O)₈]₃₆ whose Fe metallic skeletons both describe hexacapped hexagonal bipyramids albeit with Fe ions being all octahedral.

Magnetic measurements of **3** reveal strong antiferromagnetic interactions between the Fe^{III} ions. The experimental dc susceptibility data ($T = 2$ -300 K, $B = 0.1$ T, Figure 30) for **3** are plotted as the χT product versus T , where χ is the molar magnetic susceptibility, T is the temperature, and B the field. The value of χT at $T = 300$ K is ~ 38 K cm³ mol⁻¹, larger than that expected for the sum of the Curie constants for eight Fe^{III} ($S = 5/2$) ions with $g_{\text{Fe}} = 2.00$ (35 K cm³ mol⁻¹). As the temperature decreases, the magnitude of χT increases rapidly, reaching a maximum value of ~ 57 K cm³ mol⁻¹ at $T = 16$ K, where it then plateaus before decreasing slightly to a value of ~ 55 K cm³ mol⁻¹ at $T = 2$ K. The data are clearly indicative of a ferrimagnetic system, with the maximum in χT suggesting a ground state spin value of $S = 10$. This is corroborated by

magnetisation data ($T = 2-7$ K, $B = 0.5 - 7$ T; Figure 30) which rise rapidly with increasing field strength and saturate just below $M = 20 \mu_B$. Given the large discrepancy in the Fe(tet)-O-Fe(oct) and Fe(oct)-O-Fe(oct) bond angles, the data suggest a strong antiferromagnetic interaction between the tetrahedral and octahedral Fe ions, entirely analogous to that seen for $[\text{Fe}_{17}]$,^{15,25,31} and consistent with published magneto-structural studies of O-bridged Fe^{III} compounds.³⁰ The magnetic data can be simulated using exact diagonalization^{37,38} and an isotropic spin-Hamiltonian ($\hat{H} = \sum_{i<j} J_{ij} S_i S_j$) with a coupling scheme that assumes just two independent exchange interactions, J_{ring} and J_{cap} (Figure 31), describing the interaction between the octahedral ions in the $[\text{Fe}_6]$ wheel and between the tetrahedral and octahedral Fe ions, respectively. This affords $J_{\text{ring}} = +5$ K ($+3 \text{ cm}^{-1}$) and $J_{\text{cap}} = -25$ K (-17 cm^{-1}) resulting in a spin ground state, $S = 10$.

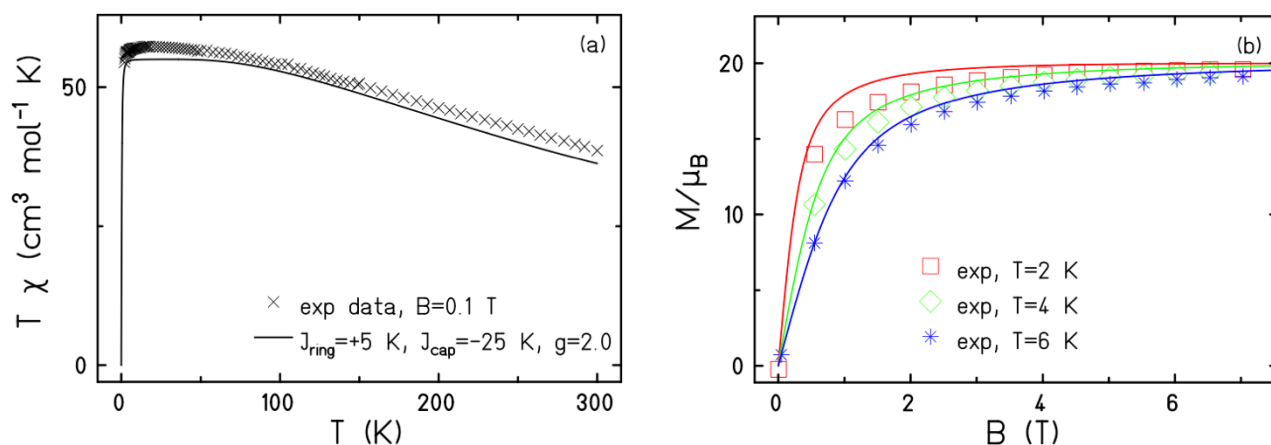


Figure 30: (a) Plot of the χT product versus T in the 300-2 K temperature range in an applied field, $B = 0.1$ T. (b) Plot of M versus B in the 2-7 K range for $0.5 \leq B \leq 7$ T.

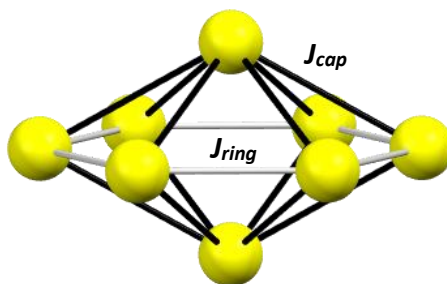


Figure 31: The magnetic skeleton of **1** highlighting the two magnetic exchange interactions, J_{cap} (black) and J_{ring} (white).

To further support the relative sign and magnitude of the coupling constants obtained, we have performed DFT calculations on two diamagnetic substituted set of models derived from **3** (Appendix 3) using a methodology similar to that used for compound **1** and **2** (see Experimental for full computational details). The J_{ring} exchange interaction between $\text{Fe}_{\text{Oct}}\text{-Fe}_{\text{Oct}}$ with bridging groups of types $\mu_2\text{-OH}^-$ and $\mu_3\text{-O}^{2-}$, average $\text{Fe-(}\mu_{2/3}\text{-O)-Fe}$ angle 97.2° and average $\text{Fe-(}\mu_{2/3}\text{-O)}$ distance $1.975 \text{ \AA}$, is calculated to be weakly ferromagnetic ($+2.1 \text{ cm}^{-1} \leq J_{\text{ring}} \leq +4.1 \text{ cm}^{-1}$). Whereas, the J_{cap} exchange interaction between $\text{Fe}_{\text{Oct}}\text{-Fe}_{\text{Tetr}}$ with $\mu_3\text{-O}^{2-}$ bridging groups, average $\text{Fe-}\mu_3\text{O-Fe}$ angle 123.1° and average $\text{Fe-(}\mu_3\text{-O)}$ distance $1.927 \text{ \AA}$, is calculated to be relatively strongly antiferromagnetic ($-30.4 \text{ cm}^{-1} \leq J_{\text{cap}} \leq -30.4 \text{ cm}^{-1}$). These calculated values fit well with the magneto-structural correlations previously developed³⁰ while also showing good agreement to the fit of the experimental data. As with compounds **1** and **2** orbital overlap calculations were performed for the SOMOs of the Fe^{III} ions of the model complexes, this suggests moderate overlap of three magnetic orbitals for the J_{ring} , resulting in small ferromagnetic interactions (Appendix 3). Whereas for J_{cap} magnetic exchange interaction, one large and ten moderate overlaps result in strong anti-ferromagnetic interaction (Appendix 3).

Summary and Conclusions

In conclusion the family of “molecular minerals”, previously made up of only $[\text{Fe}_{13}]$ and $[\text{Fe}_{17}]$ derivatives, has been expanded to include 3 new Fe^{III} clusters. Compounds **1**, **2** and **3** are synthesised by adjusting the simple methodology used to prepare $[\text{Fe}_{17}]$ affording clusters with nuclearities of 34, 30 and 8 Fe^{III} ions respectively. This therefore provides an attractive methodology for building large molecular metal oxides. Magnetic measurements of **1** indicate antiferromagnetic behaviour leading to a non-zero ground state spin of approximately $S = 11$, magnetisation data at high field and low temperature does not show a saturation of magnetisation up at $B = 34 \text{ T}$, $T = 2 \text{ K}$. Further studies including heat capacity and HFEPR measurements provide further evidence of a cluster exhibiting strong antiferromagnetic interactions leading to a non-zero ground state with non-negligible anisotropy. DFT calculations on model complexes of **1** back this up further with all calculated exchange parameters being antiferromagnetic ($-15 \text{ cm}^{-1} \leq J_{1-5} \leq -68 \text{ cm}^{-1}$). Magnetic studies of **2** present a similar challenge as compound **1**, using a classical spin approach the high temperature data can be modelled with a $2J$ model where J_s is strongly antiferromagnetic and J_w weakly

antiferromagnetic. DFT calculations of **2** agree with this model with calculated J values being dominated by antiferromagnetic interactions. Mass spectrometry studies on **2** indicate that the compound is solution stable when crystals are redissolved in mixture of lutidine and acetonitrile. Furthermore, mass spectrometry of the reaction solution of **2** indicates that the cluster is formed rapidly once the reaction is started. Finally, magnetic susceptibility and magnetisation data of compound **3** can be fit using a simple $2J$ model where J_{ring} is strongly antiferromagnetic ($J_{ring} = -3.4 \text{ cm}^{-1}$) and J_{cap} is weakly ferromagnetic ($J_{cap} = -17.375 \text{ cm}^{-1}$) leading to an $S = 10$ ground state spin, displaying ferrimagnetic behaviour reminiscent of $[\text{Fe}_{17}]$. DFT calculations on **3** support this model with calculated exchange parameter values closely matching the values found in fitting the experimental data ($J_{ring} \approx 30 \text{ cm}^{-1}$ and $J_{cap} \approx 3 \text{ cm}^{-1}$).

Experimental

Materials and physical measurements

All starting materials were procured from commercial suppliers and used as received. Elemental analysis C H and N of all compounds were performed by the service at the School of Geoscience, The University of Edinburgh.

Synthesis of $[\text{Fe}^{\text{III}}_{34}(\mu_4\text{-O})_4(\mu_3\text{-O})_{34}(\mu\text{-OH})_{12}\text{Br}_{12}(\text{py})_{18}]\text{Br}_2$ (**1**)

FeBr_3 (0.591 g, 2 mmol), hexamethylenetetramine (HMTA; 0.476 g, 3.4 mmol) and pyridine (1 mL, 12.3 mmol) were dissolved in MeCN (25 mL). The reaction was left for 2h 45mins with continuous stirring at room temperature. The resulting solution was filtered and left to stand overnight, during which time a small amount of precipitate formed. The precipitate was filtered off and the supernatant layered with acetone. After two weeks, this yielded dark brown, rod-shaped crystals suitable for X-ray diffraction. Elemental Analysis (% C H N) calculated (found), for $\text{C}_{90}\text{H}_{102}\text{Br}_{14}\text{Fe}_{34}\text{N}_{18}\text{O}_{50}$: C 20.58 (19.98), H 1.96 (2.01), N 4.80 (4.52). Yield: 15% based on Fe.

Compound **1** can also be prepared by replacing the HMTA in the above reaction with morpholine (4 mmol) or N-methylmorpholine (4 mmol).

Synthesis of $(\text{lutH})[\text{Fe}^{\text{III}}_{30}(\mu_4\text{-O})_6(\mu_3\text{-O})_{26}(\mu\text{-OH})_{15}\text{Br}_9(\text{lut})_{15}]\text{Br}_3$ (**2**)

FeBr_3 (0.591 g, 2 mmol) was dissolved with hexamethylenetetramine (0.476 g, 3.4 mmol) MeCN (25ml) and 3,4-lutidine (0.35 ml, 3.1 mmol) was added. The reaction was stirred for four hours and then filtered and allowed to stand undisturbed overnight. Diffusion of iPrOH into this solution afforded dark brown plate-shaped crystals suitable for X-ray diffraction after 3 weeks. Elemental analysis (% C H N) calculated (found) for $\text{Br}_{12}\text{C}_{112}\text{Fe}_{30}\text{H}_{159}\text{N}_{16}\text{O}_{47}$: C 26.30 (25.81), N 4.38 (3.62) H 3.13 (2.84). Yield $\leq$ 10% based on Fe.

Synthesis of $(\text{Et-PyH})[\text{Fe}^{\text{III}}_{30}(\mu_4\text{-O})_6(\mu_3\text{-O})_{26}(\mu\text{-OH})_{15}\text{Br}_9(\text{Et-py})_{15}]\text{Br}_3\cdot\text{Et-py}$ (**2a**)

Synthesis as for compound **1**, replacing 3,4-lutidine (0.35 ml) with 4-ethylpyridine (1 ml, 8.8 mmol) and iPrOH with diethylether. Elemental analysis (% C H N) calculated (found) for $\text{Br}_{12}\text{C}_{119}\text{Fe}_{30}\text{H}_{169}\text{N}_{17}\text{O}_{47}$: C 27.36 (26.72), N 4.56 (4.03) H 3.26 (2.95). Yield $\leq$ 10% based on Fe.

Synthesis of $[\text{Fe}^{\text{III}}_8(\mu_3\text{-O})_6(\mu\text{-OH})_6(4\text{-MeOpy})_{12}\text{Br}_2]\text{Br}_4\cdot(4\text{-MeOpy})$ (**3**)

FeBr_3 (2 mmol, 0.591 g) was dissolved in 4-methoxypyridine (4-MeOpy, 200 mmol, 20 ml). The resulting dark orange solution was stirred at room temperature for 2.5 hours. The solution was filtered under gravity. Vapour diffusion of acetone into the filtrate resulted in plate-shaped orange crystals suitable for Single Crystal X-ray diffraction. Elemental analysis: C, 36.84 (36.65); H, 3.84 (4.15); N, 7.16 (7.17). Yield: $\leq 10\%$.

Single Crystal X-ray Crystallography.

Diffraction data for compounds **1** and **2a** were collected on a Rigaku Oxford Diffraction Supernova diffractometer. The crystals were kept at a steady temperature of $T = 120.0$ K throughout data collection using an Oxford Cryosystems Cryostream. The structures were solved using ShelXT and refined with ShelXL interfaced through Olex2.^{39,40}

Diffraction data for compound **2** was collected on a Diamond Light Source I-19 EH1 diffractometer. The crystal was kept at a steady temperature of $T = 100.0$ K throughout data collection. The structure was solved using the Superflip solution program and refined using ShelXL interfaced through Olex2.^{39,40}

Diffraction data for compound **3** was collected on a Rigaku FRE+ diffractometer. The crystal was kept at a steady temperature of $T = 100$ K throughout data collection. The structure was solved using ShelXT and refined using ShelXL interfaced through Olex2.^{39,40}

Powder X-ray diffraction

Diffraction data of compounds **1**, **2** and **3** were collected on polycrystalline powders using a Bruker D2 PHASER with nickel filtered Cu radiation at power 30 kW and current 10mA. Diffraction measured from $2\theta = 5^\circ - 40^\circ$; step size, 0.0101° .

Magnetic Measurements (≤ 7 T)

Magnetic measurements of compounds **1**, **2** and **3** were performed on microcrystalline samples placed in a gelatine capsule and immobilised using eicosane. DC susceptibility and magnetisation data within the temperature and field ranges of $T = 2\text{-}300$ K and $B = 0\text{-}7$ T were performed on a Quantum Design MPMS XL SQUID magnetometer equipped with a 7 T DC magnet. Diamagnetic corrections were applied to the data using Pascal's constants.

High field Pulsed Magnetisation (>7 T)

Low-temperature magnetisation data of compound **1** was measured by use of a conventional inductive probe in pulsed magnetic fields, where the temperature reached as low as 1.6 K. The maximum field reached was 35 T. Polycrystalline samples with a typical mass of 15 mg were mounted in a capillary tube made of polyimide. The sample, which was not fixed within the sample tube, was aligned along the magnetic field direction. Magnetisation curves were found to be identical after application of the magnetic field several times due to the saturation of the orientation effect.

Heat Capacity

Heat capacity data of compound **1** was collected in the temperature range 0.3–20 K using a Quantum Design PPMS equipped with a ^3He cryostat. The powdered, polycrystalline sample of **1** was pressed into a thin pellet with mass of about 0.5 mg. Apiezon-N grease was used to facilitate the sample thermalization at low temperatures, and its contribution to the heat capacity was subtracted using a phenomenological expression.

High Field, High Frequency Electron Paramagnetic Resonance (HFEPR)

HFEPR spectra for polycrystalline samples of compound **1** were obtained on the Terahertz ESR Apparatus (TESRA-IMR) installed in the magnetism division of Institute of Material Research, Tohoku University. A case made of polyethylene was used for packing the sample. The radiation was produced by Gunn oscillators and backward traveling wave oscillators (BWO).

Mass Spectrometry

Mass spectrometry of compound **2** was performed on a 7 T Solarixr FT-ICR MS (Bruker Daltonics, Bremen, Germany) with an ESI source. The spectrum was acquired in positive ion mode (ESI+). The broadband spectrum was acquired with 16 summed scans between 101 - 6000 m/z . Samples were solubilized in a 20:80 3,4-lutidine/acetonitrile mix at 230 μM and sprayed by direct infusion into the ESI source. Data were analysed using Bruker Compass DataAnalysis software. Time resolved mass spectrometry was performed on the preparatory mixture used to synthesised **2**, under the same conditions as the re-dissolved crystalline sample. Aliquots of the reaction were taken at $t = 0$, $t = 2$ hours and $t = 4$ hours. The latter spectrum was measured after filtering the solution to remove precipitated material. Aliquots

were diluted to 230 μM (*wrt* initial concentration of FeBr_3) with a 20/80 mix of 3,4-lutidine and acetonitrile

Computational Methods

The diamagnetic substitution method was used to calculate the exchange coupling constants in **1** employing the Gaussian 09 suite.⁴¹ Since the calculation on the full structure of **1** is prohibitively expensive and time-consuming, the $[\text{Fe}_{34}]$ cluster was divided into five model complexes in order to calculate the five exchange coupling constants (J_1 – J_5), see Appendix 1. In these models, the surrounding Fe^{III} ions not involved in the pairwise exchange interaction under investigation were substituted by diamagnetic Ga^{III} ions in order to maintain the same coordination environment. The exchange coupling constants were estimated using the broken symmetry approach developed by Noodleman.⁴² Ahlrichs' triple- ξ plus polarisation basis set was used for the Fe, O, Br and N atoms, while the split valence plus polarisation basis set was used for Ga, C, and H atoms.⁴³ All theoretical calculations have been performed using the B3LYP functional since it has been proven to produce excellent estimates of J values.^{44,45} Exchange coupling constants have been derived from the difference between the broken symmetry (BS) and high spin (HS) state, and the quadratic conversion method.

A similar method to that used for **1** was used to calculate the exchange coupling constants for compounds **2** with nine model complexes used derived from the structure of **2**. Calculations of compound **3** used a similar method with 3 model complexes two of which are "dimer" models and 1 "trimer". The basis sets used in the calculations for **2** were the same as those used for **1**. For **3** the following were used: TZV for Fe atoms; SVP for Ga, O and N atoms; SV for C and H atoms; SDD for Br atoms.

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Chapter 3: Triethanolamine based Fe^{III} Clusters

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The preceding chapter discusses clusters formed using pyridine-type monodentate ligands whereby the core of the compound is formed of Fe^{III} ions bridged by oxide and hydroxide ions. While this strategy has been successful there are other methods available for the synthesis of polymetallic clusters. One such strategy is the use of small chelating/bridging organic ligands. This strategy has afforded a variety of systems with interesting magnetic behaviour such as those discussed in Chapter 1 ([Fe_{17/19}], [Fe₁₄], [Fe₈(tacn)]).^{1–3}

One subset of such ligands are N-O alkoxides. Such ligands include the pyridyl alcohols 2-pyridinemethanol and 2,6-pyridinedimethanol, the former of which is further discussed in Chapter 4. Some of the most basic forms of N-O chelating/bridging ligands, the aminoalcohols, are shown in Figure 32 and include ethanolamine, diethanolamine and triethanolamine. These three ligands have a proven track record in the synthesis of polymetallic compounds of both transition metals and lanthanides, with the ethanolamine ligand seen predominantly as a co-ligand in multiple reported structures (CCDC search = 49 structures)^{4–6}. On the other hand diethanolamine – and N-substituted derivatives – is found in a larger number of clusters (CCDC search [excluding triethanolamine] = 219 structures) as both a co-ligand^{7,8} and in homoleptic clusters.^{9,10} The coordination chemistry of triethanolamine is extensive (CCDC search = 128 structures), with a plethora of polymetallic cluster compounds known, including the [Ln₁₀Fe₁₀] clusters discussed in Chapter 1.¹¹ Despite this there are surprisingly few homometallic Fe^{III} clusters reported with triethanolamine. These are limited to [Fe₅],¹² [Fe₆] wheels (both unsupported¹² and supported¹³), [Fe₇],¹⁴ [Fe₈]^{15–19} (including an [Fe₈] cluster self-assembled into a [Fe₆₄] cage²⁰), and [Fe₁₀].²¹ Heterometallic Fe-Ln species are far more prevalent.^{22,23}

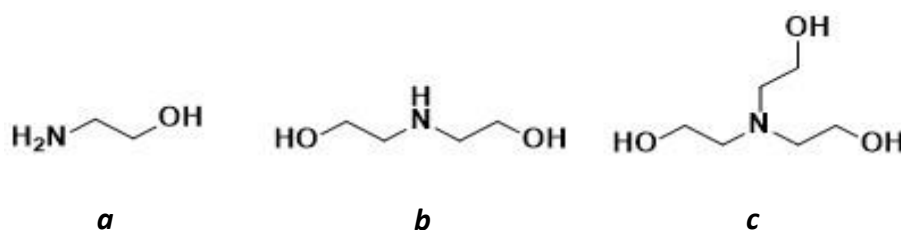


Figure 32: Aminoalcohol type ligands a) ethanolamine (eaH) b) diethanolamine (R-deaH₂) c) triethanolamine (teaH₃).

In this chapter an [Fe₁₅] cluster with a topology not previously reported for Fe^{III} clusters and two Fe^{III}/Zn^{II} heterometallic wheels, including the first odd numbered ferric wheel, are reported.

Results and Discussion

Among the structural properties sought after in polymetallic clusters high symmetry is of particular interest to the molecular magnetism community as such clusters may possess geometric spin frustration.^{24–29} Frustration can lead to some unusual and potentially useful low-temperature magnetic behaviour, an example being the [Mo₇₂Fe₃₀] icosidodecahedron which shows anomalous magnetisation in an applied magnetic field.³⁰

One synthetic methodology proven to enable the construction of high symmetry species is hydro/solvothermal synthesis, which typically exploits superheating reaction solutions under autogenous pressure. In the chemistry of polynuclear cluster compounds of paramagnetic transition metal ions, the temperature regimes employed (which are typically below 250 °C) can lead to enhanced solubility, reduced solvent viscosity and increased reagent diffusion. The result is often the synthesis of metastable kinetic products of high symmetry, with slow cooling enabling pristine crystal growth directly from the reaction mixture.³¹

The solvothermal reaction of FeCl₃, Fe(ClO₄)₃·6H₂O and teaH₃ in a MeOH solution in the presence of NEt₃ results in the formation of red/brown crystals upon cooling (see the experimental section for full details). Crystals of [Fe^{III}₁₅O₆(tea)₈Cl₆](ClO₄)₂(OH) (**4**, Figure 33, Appendix 4) were found to be in a trigonal crystal system, and structure solution was performed in the *R*-3 space group (see Experimental and Appendix 4 for full details). The metallic skeleton of **4** describes a centred tetrakis hexahedron (Figure 34), a Catalan solid which is the dual of the truncated octahedron, an Archimedean solid. The central Fe ion (Fe4) is octahedral, being bonded to six oxide ions ([FeO₆]; O5 and s.e ; Fe-O5 = 1.999 Å). O5 bridges to two further Fe ions in the peripheral shell (O5-Fe1 = 1.925 Å; O5-Fe2 = 2.025 Å) and is thus three coordinate and trigonal planar. There is a fourth, longer contact to Fe3 (O5-Fe3 = 2.492 Å), so O5 may be considered pseudo-tetrahedral if one considers this interaction significant (Figure 34 and 35). The outer shell is decorated with a combination of halide and tea³⁻ ions. The former are monodentate, coordinated to Fe2 (Fe2-Cl, 2.315 Å). The latter are tetradentate, chelating either Fe1 or Fe3 with each O-atom μ -bridging to a second Fe ion (Fe2). Thus Fe1 is five-coordinate ([FeO₄N])

and trigonal pyramidal, Fe2 is six-coordinate ($[\text{FeO}_5\text{Cl}]$) and octahedral, and Fe3 is four coordinate ($[\text{FeO}_3\text{N}]$) and trigonal prismatic, or seven coordinate ($[\text{FeO}_6\text{N}]$) and a capped octahedron if the Fe-O5 bonds are included (Figure 35). A review of the Cambridge Structural Database (CSD) for Fe-O bond lengths in any Fe-O-Fe moiety produces 3378 different compounds and 12361 bond lengths ranging from a minimum value of 1.651 Å to a maximum value of 2.629 Å, as depicted in the histogram in Appendix 4.

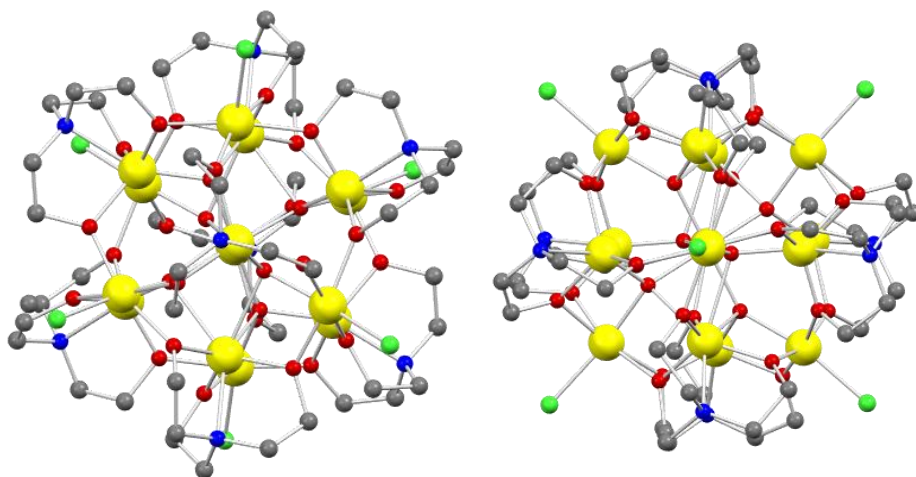


Figure 33: Orthogonal views of the $[\text{Fe}_{15}]$ cluster of compound **4**: Colour Code: Fe, yellow; O, red; Cl, green; N, blue; C, grey. Counter-ions and hydrogen atoms omitted for clarity.

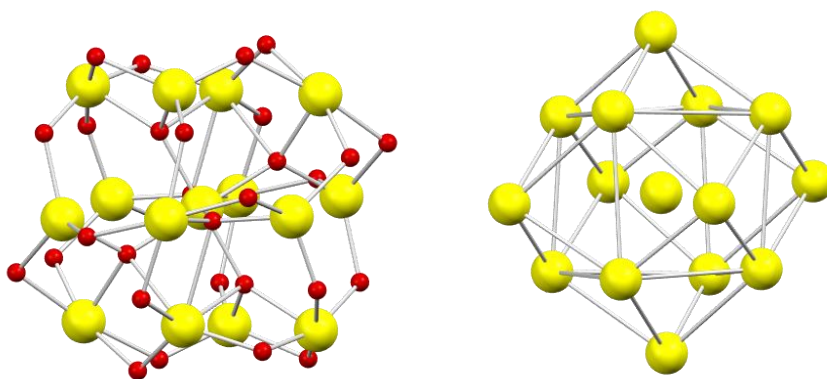


Figure 34: Metal-oxygen core of **4** (left) alongside the metal skeleton of **4** (right) to show the centred tetrahexahedron topology of the cluster. Colour Code Fe, yellow; O, red.

The $[\text{Fe}_{15}\text{O}_{30}]$ core displays a breadth of different Fe-O-Fe angles, ranging from a minimum of 86.67° (Fe4-O5-Fe3) to a maximum of 140.82° (Fe4-O5-Fe2). Angles from the central Fe4 ion to the peripheral Fe1 and Fe2 ions via the O5 oxide are 140.82° and 117.41° , while those connecting the outer Fe1, Fe2 and Fe3 ions together via the oxides and alkoxides range

between 86.7-129.39° (Table 3). The closest intermolecular interactions are between the monodentate Cl ions on Fe2 and the C-atoms of the tea³⁻ ligands on neighbouring molecules (Cl1...C7, ~3.43 Å), and between the perchlorate O-atoms and the C-atoms of the tea³⁻ ligands (O6...C4, ~3.43 Å; Fig. S6-7). This results in an aesthetically pleasing honeycomb-like network when viewed down the *c*-axis of the cell (Appendix 4). A search of the CSD reveals that just three [Fe₁₅] clusters have been reported previously,^{32–34} with **4** being the first example of a centred tetrakis hexahedron.

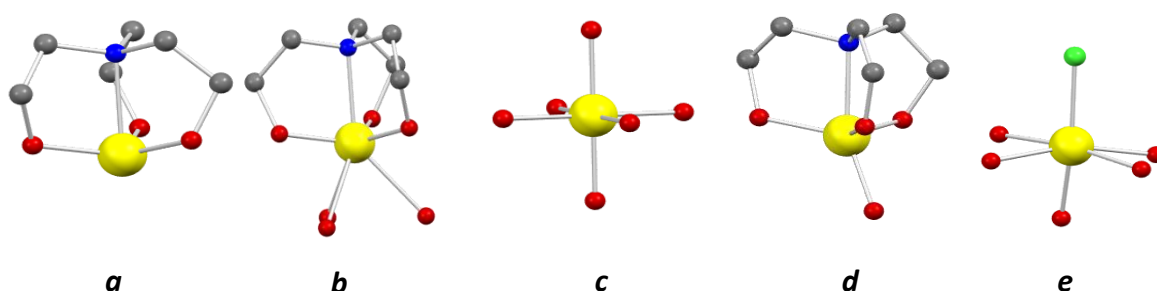


Figure 35: Coordination environments of the Fe^{III} ions present in **4**. a) Fe3 four coordinate, b) Fe3 seven coordinate, c) Fe4 six coordinate octahedral, d) Fe1 five coordinate, e) Fe2 six coordinate. Colour Code: Fe, yellow; O, red; Cl, green; N, blue; C, grey.

The direct-current (dc) molar magnetic susceptibility, χ , of a polycrystalline sample of **4** was measured in an applied magnetic field, B , of 0.1 T, over the 2–300 K temperature, T , range. The results are plotted in Figure 36 in the form of χT product, where $\chi = M / B$ with M the magnetisation. At room temperature, the χT product is 28.67 emu K mol⁻¹, much lower than the Curie constant expected for fifteen uncorrelated $S = 5/2$ centres (65.625 emu K mol⁻¹) with $g = 2$. On lowering the temperature, the χT product decreases rapidly, reaching a value of 11.05 emu K mol⁻¹ at $T = 10$ K, before decreasing even more abruptly to a value of 7.74 emu K mol⁻¹ at $T = 2$ K. The data is therefore indicative of competing antiferromagnetic exchange interactions, and a ground state spin of $S \approx 9/2$ (Figure 36). Variable-temperature-variable-field (VTVB) dc magnetisation measurements in the temperature range 2–6 K and in applied magnetic fields up to 7 T reach a maximum value of just $M = 8.35 \mu_B$ (Figure 36), well below the upper limit expected for a ferromagnetically coupled system ($M = 75 \mu_B$ for $g = 2$). This behaviour is clearly indicative of relatively strong antiferromagnetic interactions between the Fe^{III} ions, consistent with the Fe-O distances and Fe-O-Fe angles present.³⁵

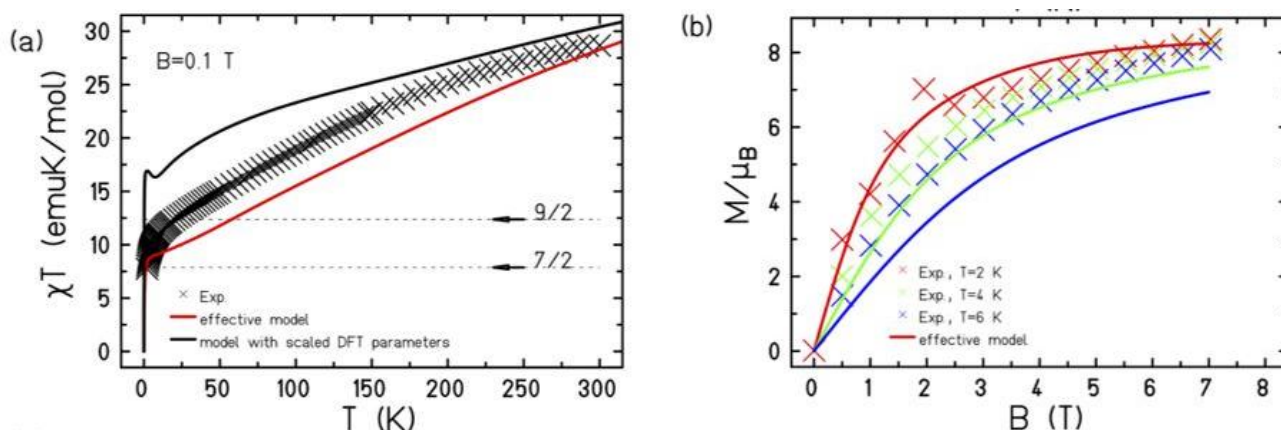


Figure 36: (a) Magnetic susceptibility (χT) versus temperature (T) data for **4** measured in an applied field, $B = 0.1$ T in the $T = 300$ – 1.80 K temperature range. (b) Magnetisation (M) versus field (B) data in the 2 – 6 K temperature and 0 – 7 T field ranges. The solid lines are a simulation of the experimental data (x) using the finite-temperature Lanczos method. The effective model denotes a Heisenberg model with high symmetry, as described in the main text. The black line in (a) denoted the model employing DFT parameters given in Table 3 in a Heisenberg model scaled by $25/9$ taking into account the use of spins, $S = 3/2$.

It is computationally impossible to quantitatively analyse the magnetic data of a molecule containing $15 \times S = 5/2$ spins via conventional matrix diagonalisation techniques since the dimension of the Hilbert space is 470,184,984,576, and thus as in Chapter 2 with compounds **1** and **2** we turn to the finite-temperature Lanczos method.^{36,37} Even here, several assumptions must be made. (A) Despite the presence of eight independent exchange interactions, we reduce this to four based on similar Fe–O bond lengths and Fe–O–Fe angles (Figure 37). These are: J_{cube} along edges of the cube; J_{pyramid} along the four edges from the top of each pyramid to the respective base square of cube; $J_{\text{c,cube}}$ from central Fe inside the cube to vertices of the cube; and $J_{\text{c,pyramid}}$ from central Fe ion to the tops of pyramids. (B) We simulate the data using isotropic $S = 3/2$ spins rather than isotropic $S = 5/2$ spins and scale the resulting data accordingly. The corresponding isotropic spin-Hamiltonian is: $\hat{H} = -2 \sum_{i < j} J_{ij} \hat{s}_i \cdot \hat{s}_j$, where J_{ij} denotes the four employed exchange constants, respectively. A rather good theoretical representation of the data (Figure 36) was obtained with $J_{\text{cube}} = -17.4$ cm⁻¹, $J_{\text{pyramid}} = -17.4$ cm⁻¹, $J_{\text{c,cube}} = -17.4$ cm⁻¹ and $J_{\text{c,pyramid}} = -3.5$ cm⁻¹, scaled by $9/25$ to meet a Hamiltonian with spins $S = 5/2$. Such a scaling approach can only provide “an order of magnitude” estimate of the exchange constants, rather than a precise derivation, albeit the

numbers are entirely consistent with experimentally and computationally derived magneto-structural correlations for previously reported O-bridged Fe^{III} clusters.^{38,39} The exchange constants are indicative of a highly frustrated system, as one might expect from the structural symmetry.

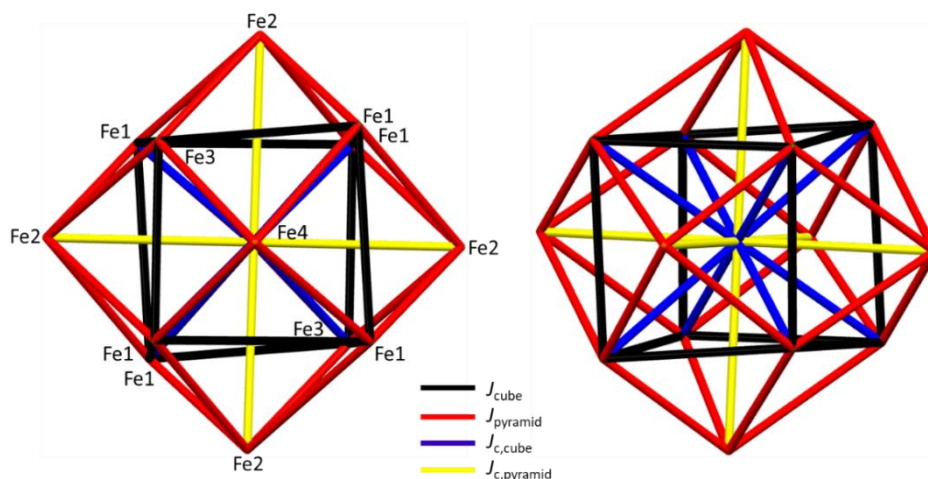


Figure 37: Exchange interaction scheme employed to simulate the magnetic susceptibility and magnetisation data of **4** using four J values (legend) and the finite temperature Lanczos method. The two figures show different orientations of the same scheme for clarity.

Heat capacity, C , measurements were collected between ~ 0.3 K and 30 K, for $B = 0, 3$ and 7 T (Figure 38). Below ~ 3 K, the heat capacity depends significantly on B , the zero-field C showing essentially flat behaviour and reaching values close to $\sim 0.5R$, where R is the gas constant. This behaviour is similar to that reported for an $[\text{Fe}^{\text{III}}_{10}\text{Gd}^{\text{III}}_{10}]$ wheel¹¹ and consistent with the presence of a large density of low-lying states, likely resulting from competing antiferromagnetic interactions.

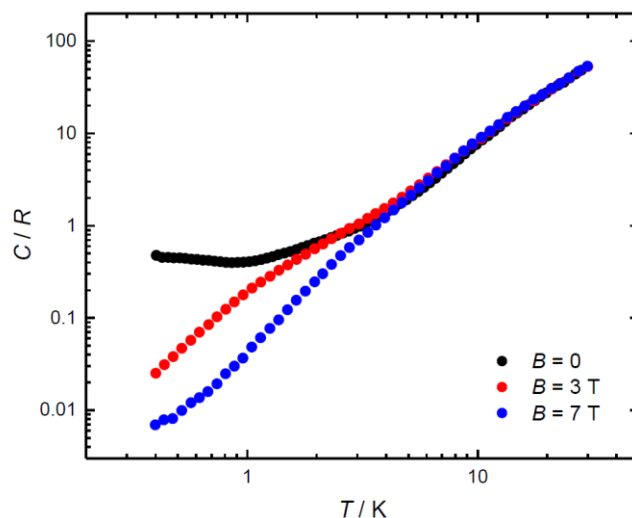


Figure 38: Heat capacity data for **4** in the indicated temperature and field ranges.

To further support the relative sign and magnitude of the coupling constants obtained, DFT calculations were performed (see Experimental for the computational details) on a model complex, **4A**, derived from complex **4** (Figure 39, Appendix 4). These suggest that the eight independent exchange interactions are in the range $|J| = 4.6\text{--}16.4\text{ cm}^{-1}$ (Table 3), in good agreement with the experimental simulations. All are antiferromagnetic in nature, with the exception of the $\text{Fe4-(}\mu_4\text{-O}^{2-}\text{)}_3\text{-Fe3}$ interaction, which affords a weakly ferromagnetic exchange parameter of $J = +4.6\text{ cm}^{-1}$, on account of the large Fe-O bond lengths and small Fe-O-Fe bond angles present, which lead to orbital orthogonality. Overlap integral calculations²³ using metal-based singly occupied molecular orbitals (SOMOs) reveal that the strongest antiferromagnetic interactions occur where there are a higher number of strong or moderate overlap integrals and vice versa (Appendix 4). For the $\text{Fe4-(}\mu_4\text{-O}^{2-}\text{)}_3\text{-Fe3}$ interaction (J_1 in Table 3), there is only one strong interaction ($d_z^2 || d_{xz}$) with the remaining 24 interactions being weak. The overall result is a weak/moderate ferromagnetic interaction.

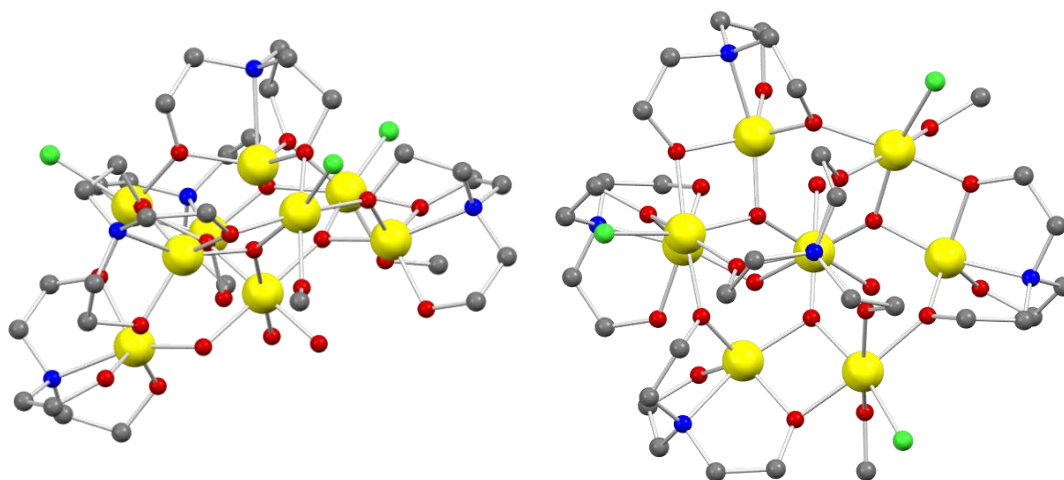


Figure 39: Orthogonal views of the model complex, derived from **4**, used in DFT calculations.

It is somewhat unusual to synthesise homometallic transition metal clusters by employing two different metal salts. Often the metal salts are viewed purely as a source of metal ions and the counterions are considered solely as charge balancing moieties. The synthesis of compound **4** shows how these counterions can play separate roles in cluster formation with **4** comprising terminal chloride ligands and charge balancing perchlorate anions, this realisation prompted further work with this strategy in mind.

Table 3: DFT computed magnetic exchange interactions calculated for model complex 1A, together with pertinent structural parameters for 1. N = total number of individual interactions present. $\sum |S_{AB}|$ represents the total overlap integrals.

J_{DFT}	Bridging group(s)	J / cm^{-1}	Avg. Fe-O distance (Å)	Avg. Fe-O-Fe angle (°)	Fe-Fe distance (Å)	$\sum S_{AB}$
J_1	3 $\mu_4\text{-O}^{2-}$	+4.6	2.245	86.7	3.102	0.433
J_2	$\mu_2\text{-O-CH}_2\text{-CH}_2\text{-N(R)}$,	-1.8	2.103	102.1	3.246	0.570
J_3	$\mu_2\text{-O-CH}_2\text{-CH}_2\text{-N(R)}$,	-6.8	1.985	99.1	3.022	0.761
J_4	$\mu_4\text{-O}^{2-}$	-9.8	2.208	111.1	3.657	0.800
J_5	$\mu_2\text{-O-CH}_2\text{-CH}_2\text{-N(R)}$	-9.5	1.991	116.7	3.390	0.799
J_6	$\mu_2\text{-O-CH}_2\text{-CH}_2\text{-N(R)}$	-14.7	1.935	129.4	3.500	1.054
J_7	$\mu_4\text{-O}^{2-}$	-16.4	1.963	117.4	3.354	1.221
J_8	$\mu_4\text{-O}^{2-}$	-14.7	2.012	140.8	3.791	1.063

Compound **4** exhibits magnetic frustration due to competing antiferromagnetic interactions. This is one form of magnetic frustration which results in low lying excited ground spin states. Odd numbered wheels present another more classical form of frustration. Even numbered homometallic wheels are well known, including Fe^{III} wheels, and in the main display antiferromagnetic nearest-neighbour exchange leading to a diamagnetic ground state spin.^{40–}

⁴² Studies of these species have revealed interesting quantum phenomena, including tunnelling of the Néel vector,⁴³ spin-multiplet mixing effects⁴⁴ and magnetic level repulsions.⁴⁵

Finite-size effects dictate that even-numbered wheels possess a discrete (and relatively simple) energy spectrum, with the lowest-lying excited states approximated by the Landé interval rule.⁴⁵ Frustration in odd-numbered AF wheels dramatically changes this picture and can lead to the emergence of a magnetic Möbius strip in the ground state, and the breakdown of the rotational band structure observed for bipartite systems.⁴⁶ Odd numbered transition metal wheels with $N > 3$ (where N is the number of metal ions) are remarkably rare with a CCDC search revealing only six molecules. These are $[\text{Cu}^{\text{II}}_5]$,⁴⁷ $[\text{V}^{\text{IV}}_7]$,⁴⁸ $[\text{Ti}^{\text{IV}}_9]$ and $[\text{Ti}_8\text{M}^{\text{III}}]$,⁴⁹ $[\text{Cr}^{\text{III}}_8\text{M}^{\text{II}}]$ ^{50–52} and $[\text{Cr}^{\text{III}}_9]$.⁵³ The remainder of this chapter reports the synthesis of the first Fe^{III}

odd-membered ring $[\text{Fe}^{\text{III}}_{11}\text{Zn}^{\text{II}}_4(\text{tea})_{10}(\text{teaH})_1(\text{OMe})\text{Cl}_8]$ (**5**) and its even-numbered analogue $[\text{Fe}^{\text{III}}_{12}\text{Zn}^{\text{II}}_4(\text{tea})_{12}\text{Cl}_8]$ (**6**).

Reaction of FeCl_3 and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with H_3tea in a basic MeOH/MeCN solution (see the Experimental for full details) leads to the formation of **5** after 2 days following diffusion of IPA into the mother liquor (Figure 40). **5** crystallises in the monoclinic space group $P2_1/n$ (Appendix 5), with the asymmetric unit comprising the whole cluster. The metallic $[\text{Fe}^{\text{III}}_{11}]$ skeleton is somewhat S-shaped rather than planar (Figure 41), with all neighbouring Fe ions bridged by two O-atoms from two tea^{3-} ligands, $[\text{Fe}-(\mu\text{-O}_{\text{tea}})_2\text{-Fe}]$. The only exception to this is between Fe6 and Fe8 where one of the triethanolamine arms is protonated/non-bonded and replaced in the bridging unit by the sole $\mu\text{-OMe}$ ligand in the cluster, $[\text{Fe}-(\mu\text{-O}_{\text{tea}})(\mu\text{-OMe})\text{-Fe}]$. This moiety is therefore responsible for the asymmetry of the wheel, with the magnetic core of the molecule being $[\text{Fe}_{11}(\mu\text{-O}_{\text{tea}})_{21}(\mu\text{-OMe})_1]$. The triethanolamine ligands are of three types. Seven are μ_4 -bridging ($[\text{Fe}_3\text{Zn}]$) with two O-atoms bridging two Fe ions, and one O-atom bridging between Fe-Zn. Three are μ_3 -bridging ($[\text{Fe}_3]$) with two O-atoms bridging two Fe ions, and one O-atom being terminally bonded. The remaining ligand is μ_3 -bridging ($[\text{Fe}_3\text{Zn}]$) with one O-atom bridging two Fe ions, one bridging between Fe and Zn, and the third being non-bonded.

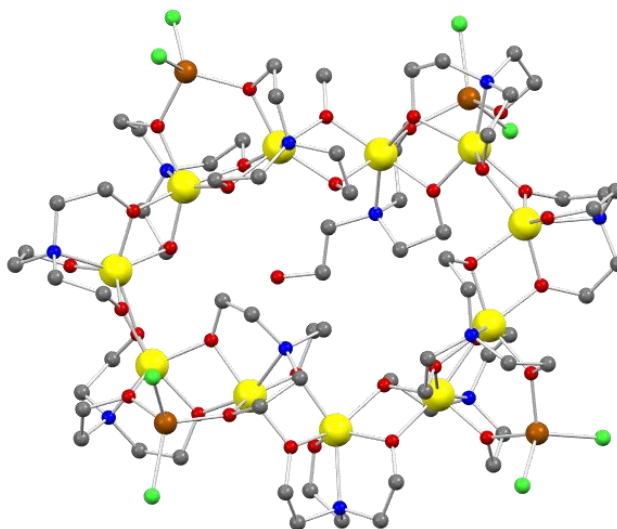


Figure 40: Structure of the neutral cluster of compound **5**. Solvates and hydrogen atoms omitted for clarity. Colour code: Fe, yellow; Zinc, brown; O, red; Cl, green; N, blue; C, grey.

The Fe-O-Fe angles fall within the range 101.61° - 107.66° . The Fe ions are all six coordinate and in distorted octahedral geometries, while the Zn ions are four coordinate and tetrahedral

- the remaining two coordination sites on each Zn ion being occupied by Cl ions. The non-bonded HO-arm of the Htea ligand is H-bonded to a CH₂(tea) moiety on a neighbouring cluster (O(H)⋯(H)C, 3.126 Å), as are the Cl ions (Cl⋯(H)C, 3.420 Å). The result is a rather complicated network of H-bonded clusters in the extended structure (Appendix 5).

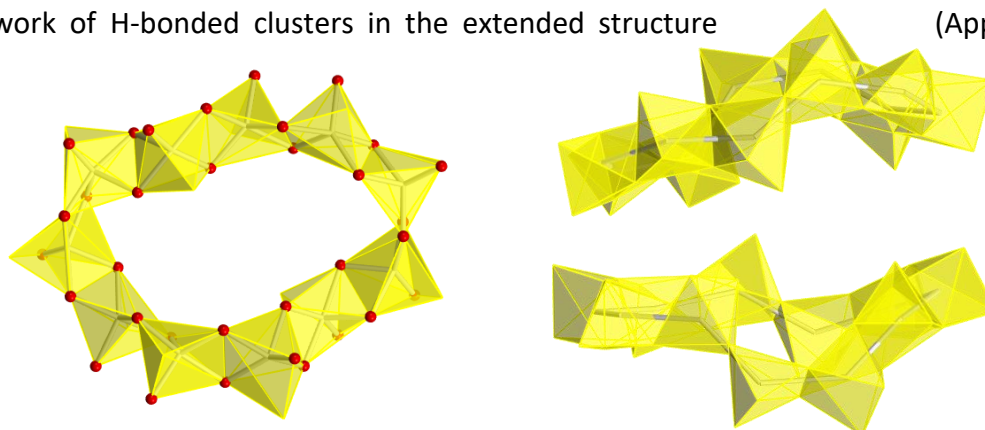
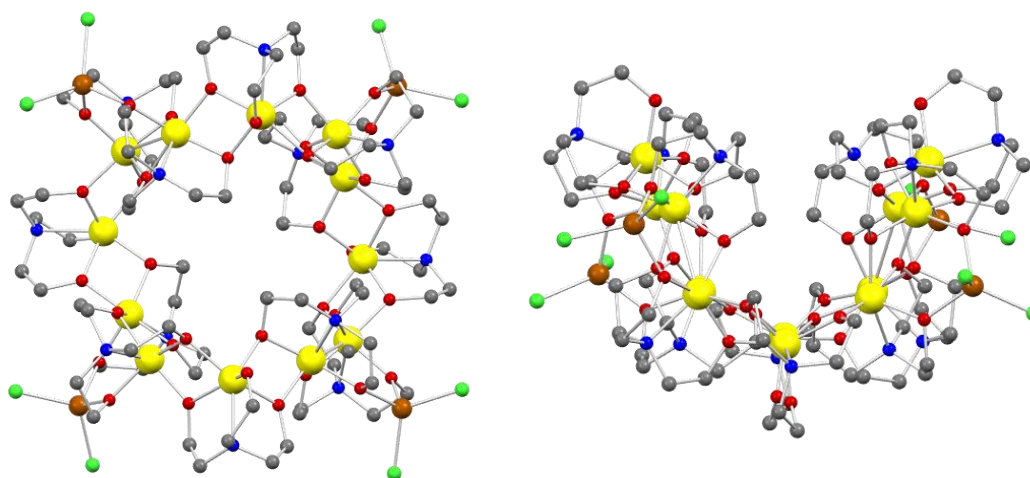


Figure 41: A view of the Fe^{III} oxygen core of **5** (left) alongside orthogonal views of the metal skeleton of **5** displaying the slightly S-shaped topology (right). Colour code: Fe, yellow polyhedral; O, red spheres.

Repetition of the synthetic procedure that produces **5**, but in a mixture of ethyl acetate/acetonitrile and diffused with hexane, affords **6** after 4 days (Figure 42). **6** crystallises in two separate forms **6a**, [Fe^{III}₁₂Zn^{II}₄(tea)₁₂Cl₈]·2(MeCN)(AcOEt), and **6b**, [Fe^{III}₁₂Zn^{II}₄(tea)₁₂Cl₈]·4(MeCN)(H₂O). **6a** crystallises in the monoclinic space group C2/c with half the cluster in the asymmetric unit, while **6b** crystallises in the tetragonal space group I4₁/a, with the asymmetric unit being composed of one quarter of the molecule (Appendix 6). While **6a** and **6b** have different unit cells and crystal symmetry this does not appear to be due to a fundamental change in the structure of the [Fe₁₂Zn₄] cluster; the main contributing factor being the solvates present in the extended structure. **6a** contains one ethyl acetate solvate molecule in the asymmetric unit along with 2 acetonitrile solvates, on the other hand while **6b** also contains two acetonitrile solvates a water molecule is present in the ASU rather than ethyl acetate. It should be mentioned that the differences in the solvate make up of these two structures may extend further as the discussion above is limited only to well defined solvates as a solvent mask was used in the solution of both **6a** and **6b**. Structural similarity between **6a** and **6b** is reflected in the the Fe-O-Fe bond angles and average Fe-O distances (Appendix 6); **6a** = 101.53° - 106.45°, **6b** = 101.61° - 106.21°, **6a** = 1.991 Å, **6b** = 1.987 Å. In essence,

compound **6** is the symmetric analogue of **5**, with the twelve tea ligands now of just two types: one μ_3 -bridging ligand ($[\text{Fe}_3]$) followed by two μ_4 -bridging ligands ($[\text{Fe}_3\text{Zn}]$) as the wheel is circumnavigated. The result is that the metallic skeleton becomes bowl- or U-shaped rather than S-shaped, with the magnetic core of the molecule being $[\text{Fe}_{12}(\mu\text{-O}_{\text{tea}})_{22}]$ (Figure 43). There are no significant intermolecular interactions seen in the extended structure of **6** in either crystal system, with closest contacts between two clusters coming between the Cl ions bonded to the Zn ions and the C atoms of the tea ligands of neighbouring wheels, $\text{Cl}\cdots\text{N}$, >3.5 Å in both **6a** and **6b**. The packing arrangement of **6** is also similar in both systems with the



wheels forming layers separated by solvate filled voids (Appendix 6).

Figure 42: Orthogonal views of the neutral cluster of compound **6**. Solvates and hydrogen atoms omitted for clarity. Colour code: Fe, yellow; Zinc, brown; O, red; Cl, green; N, blue; C, grey.

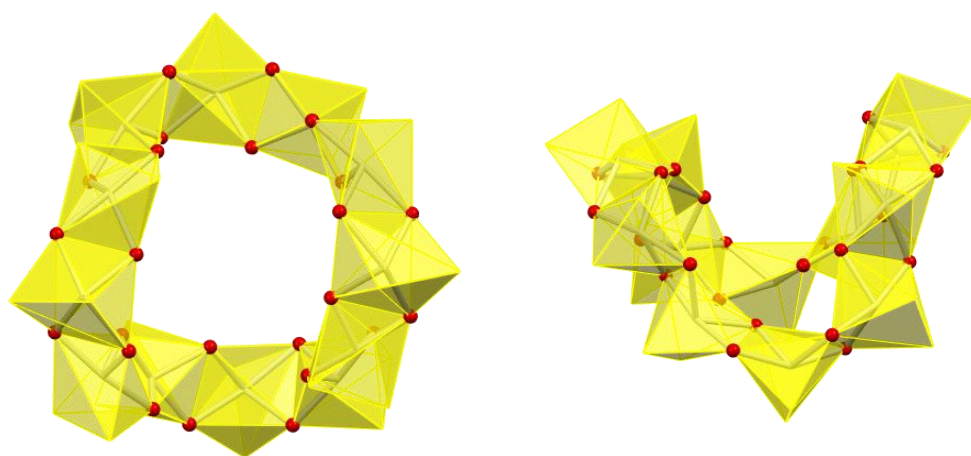


Figure 43: Orthogonal views of the Fe^{III} oxygen core of **6**. Colour code: Fe, yellow polyhedral; O, red spheres.

Variable temperature molar magnetic susceptibility measurements, χ , were performed on a polycrystalline sample of **5** with an applied magnetic field, B , of 0.1 T over a temperature range, T , of 2 – 270 K. The results are plotted as the χT product versus temperature (Figure 44). The high temperature value of χT of $16.95 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ is well below the value expected for eleven isolated Fe^{III} ions with $S = 5/2$ (expected: $48.125 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$). From 270 – 50 K χT steadily decreases to a value of $3.25 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. Below 50 K the χT value continues to decrease but begins to plateau, eventually reaching a value of $0.43 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at $T = 2 \text{ K}$. This is indicative of a system with strongly antiferromagnetic exchange interactions but with a non-zero ground state spin. The variable field variable temperature magnetisation data, taken over the field range $B = 0 - 5 \text{ T}$ and a temperature range $T = 2-5 \text{ K}$, support this hypothesis with the magnetisation, M , reaching a value of $\sim 0.8 \mu_{\text{B}}$ at $T = 2 \text{ K}$ and $B = 5 \text{ T}$. The susceptibility and magnetisation data are suggestive of an $S = \frac{1}{2}$ ground state. A fit of the data is currently in progress, as is EPR spectroscopy.

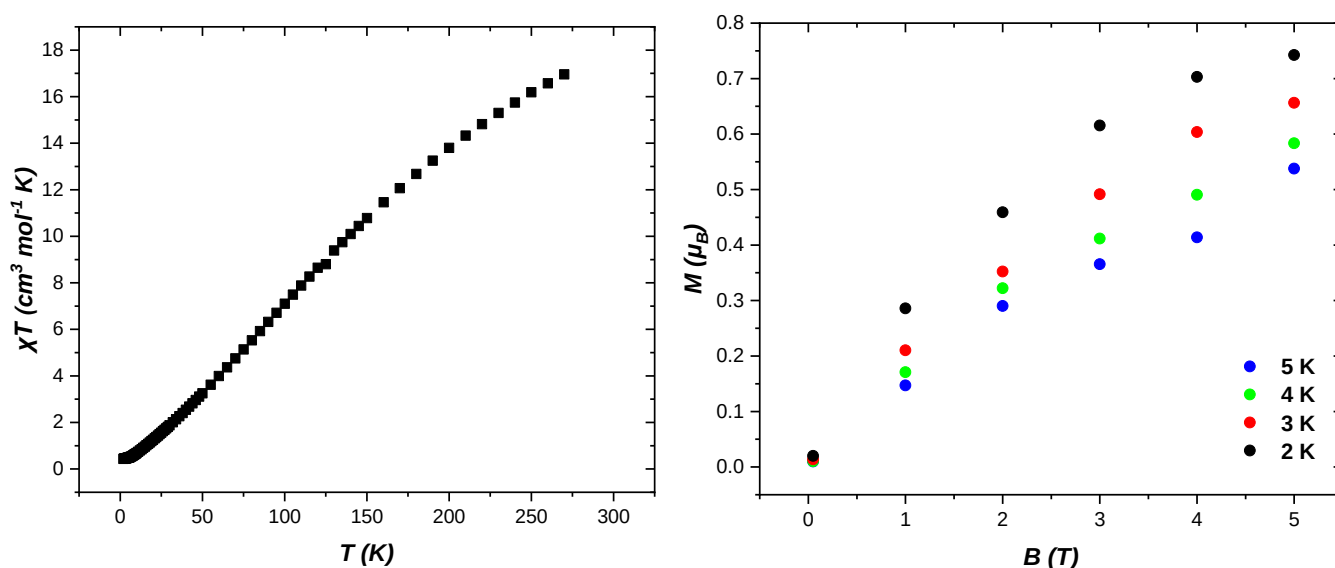


Figure 44: Magnetic susceptibility measurements (χT) of **5** (left). Magnetisation measurements (right) in the ranges $B = 0-5 \text{ T}$, $T = 2-5 \text{ K}$.

The magnetic behaviour of **6** is expected to show strong antiferromagnetic behaviour leading to a diamagnetic ground state, as seen for all other even-membered Fe^{III} wheels. These magnetic measurements are in progress.

To gain further understanding of the magnetic exchange present in compounds **5** and **6** DFT calculations were performed using model complexes derived from their crystal structures. For **6** the full structure of **6a** was used (Appendix 6). In both complexes all exchange parameters are calculated to be antiferromagnetic ($-3.5 \text{ cm}^{-1} \leq J \leq -12.9 \text{ cm}^{-1}$), in line with both magneto-structural correlations previously reported³⁵ and, in the case of **5**, the observed magnetic susceptibility behaviour.

Summary, Conclusions and Future work

It is somewhat unusual for the synthesis of polymetallic clusters to invoke the use of two different metal salts. The use of one salt is often viewed as being sufficient, particularly if the anion employed aids crystallisation. Here it is shown that the use of multiple anions of the same metal ion may be a useful/alternative route to obtaining novel structure types. This chapter reports three new Fe^{III} based clusters prepared with the flexible ligand triethanolamine. All of which demonstrate new and interesting topologies.

Compound **4** is just the fourth $[\text{Fe}_{15}]$ cluster reported and the only homometallic Fe cluster whose metallic skeleton conforms to a centred tetrakis hexahedron. Synthesised via solvothermal methods **4** continues to prove this technique useful for making high symmetric compounds. The magnetic data of **4** shows the compound has competing antiferromagnetic interactions leading to a non-zero ground state spin.

Compound **5** is the first reported odd numbered ferric wheel - a heterometallic $[\text{Fe}^{\text{III}}_{11}\text{M}^{\text{II}}_4]$ cluster where the M positions are occupied by diamagnetic Zn^{II} ions. Magnetic measurements of **5** indicate strong antiferromagnetic interactions leading to a non-zero (expected: $S = \frac{1}{2}$) ground state. Further work with this compound is in progress to fit the magnetic data and perform lower temperature and higher field magnetic measurements to probe the magnetic characteristics of this frustrated species. The identity of M will also be modified to include paramagnetic centres including, Co^{II} , Ni^{II} , Mn^{II} , Cu^{II} , Fe^{II} .

Compound **6** can be seen as the even numbered analogue of **5** - a heterometallic $[\text{Fe}^{\text{III}}_{12}\text{M}^{\text{II}}_4]$ cluster with diamagnetic Zn^{II} in the M positions. Compound **6** crystallises in two separate forms **6a** and **6b** differing only in the nature of crystallised solvate molecules. Further work on **6** is in progress including measurements to probe the magnetic behaviour which is expected

to show antiferromagnetic interactions leading to a diamagnetic ground state, as predicted by computational methods and seen in previous even numbered Fe^{III} wheels.

Experimental

Materials and physical measurements

All starting materials were procured from commercial suppliers and used as received. Elemental analysis C H and N of all compounds were performed by the service at the School of Geoscience, The University of Edinburgh. Metal analysis (Fe Zn) was performed by the Service at the School of Chemistry, The University of Edinburgh.

Synthesis of [Fe₁₅O₆(tea)₈Cl₆](ClO₄)₂(OH) (4)

FeCl₃ (0.162 g, 1 mmol) and Fe(ClO₄)₂·6H₂O (0.254 g, 1 mmol) were dissolved in methanol (25 cm³). Triethanolamine (0.198 cm³, 1.5 mmol) was added dropwise to the orange solution. Triethylamine (0.418 cm³, 3 mmol) was added dropwise and the darkened solution was stirred at room temperature overnight. The dark orange solution was then filtered under gravity and 12.5 cm³ samples of the filtrate were transferred to Teflon-lined autoclaves and heated to 100°C for 24 hrs. The reaction vessels were left to cool and stand for 48 hrs yielding dark red rod-shaped crystals suitable for X-ray diffraction. Yield = 0.096 g [0.041 mmol] (31.5% by Fe). Elemental analysis (% C H N) calculated (found) for C₄₈H₉₆Cl₈Fe₁₅N₈O₃₈: C 24.9 (24.35), H 4.18 (4.28), N 4.84 (4.40).

Synthesis of [Fe^{III}₁₁Zn^{II}₄(tea)₁₀(teaH)(OMe)Cl₈] (5)

FeCl₃ (1 mmol, 0.162 g) and Zn(ClO₄)₂·6H₂O were dissolved in a 50:50 mixture of acetonitrile and methanol (25 ml). Triethanolamine (teaH₃, 1.5 mmol, 0.198 ml) and triethylamine (3 mmol, 0.418 ml) were added dropwise. The cloudy yellow solution was stirred at room temperature overnight and filtered by gravity. Vapour diffusion of isopropanol into the filtrate produced pale yellow rod shaped crystals suitable for X-ray diffraction after 48 hours. Crystals were washed with a 10:1 methanol:water solution to remove any [teaH₄]Cl salt impurity. Yield = 0.008 g [0.0028 mmol] (3.03% by Fe). Elemental analysis (% C H N) calculated (found) for

$C_{67}H_{148}Cl_8Fe_{11}N_{11}O_{40}Zn_4$: C 27.68 (27.43), H 5.13 (4.91), N 5.30 (5.17). Metal analysis by ICP-MS (%wt Fe Zn) calculated (found): Fe 21.94 (21.52) Zn 9.34 (9.35).

Synthesis of $[Fe_{12}Zn_4(tea)_{12}Cl_8]$ (**6**)

$FeCl_3$ (1 mmol, 0.162 g) and $Zn(ClO_4)_2 \cdot 6H_2O$ were dissolved in a 50:50 mixture of acetonitrile and ethyl acetate (25 ml). Triethanolamine ($teaH_3$, 1.5 mmol, 0.198 ml) and triethylamine (3 mmol, 0.418 ml) were added dropwise. The cloudy orange solution was stirred at room temperature overnight and filtered by gravity. Vapour diffusion of hexane into the filtrate produced pale yellow rod shaped crystals suitable for X-ray diffraction after 24 hours. Crystals were washed with a 10:1 acetonitrile:water solution to remove any $[teaH_4]Cl$ salt impurity. Yield = 0.006 g [0.0018 mmol] (2.18 % by Fe). Elemental analysis (% C H N) calculated (found) for $C_{72}H_{140}Cl_8Fe_{12}N_{16}O_{36}Zn_4$: C 31.93 (32.48), H 5.24 (5.53), N 6.77 (7.08). Metal analysis by ICP-MS (%wt Fe Zn) calculated (found): Fe 20.25 (19.88) Zn 7.90 (7.53)

Single Crystal X-ray diffraction

Diffraction data for compounds **4** and **6 (6b)** were collected on a Rigaku Oxford Diffraction Xcalibur diffractometer. The crystals were kept at a steady temperature of $T = 120.0$ K throughout data collection using an Oxford Cryosystems Cryostream. The structure was solved using ShelXT and refined with ShelXL interfaced through Olex2.^{54,55}

Diffraction data for compound **5** was collected on a Bruker APEX-II CCD diffractometer. The crystals were kept at a steady temperature of $T = 100.4$ K throughout data collection using an Oxford Cryosystems Cryostream. The dataset was truncated at $1 \text{ \AA}$ due to rapidly rising values of R_{int} at higher resolution. The structure was solved using ShelXT and refined with ShelXL interfaced through Olex2.^{54,55}

Diffraction data for compound **6 (6a)** was collected on a Rigaku Oxford Diffraction Supernova diffractometer. The crystals were kept at a steady temperature of $T = 120.0$ K throughout data collection using an Oxford Cryosystems Cryostream. The structure was solved using ShelXT and refined with ShelXL interfaced through Olex2.^{54,55}

Powder X-ray diffraction

Diffraction data of compound **4** was collected on polycrystalline powders using a Bruker D2 PHASER with nickel filtered Cu radiation at power 30 kW and current 10mA. Diffraction measured from $2\theta = 5^\circ - 40^\circ$; step size, 0.0101°

Diffraction data of compounds **5** and **6** was collected on polycrystalline powders using a Bruker D8 ADVANCE with copper radiation at 40 kV, 40 mA and a Johansson monochromator, 2 mm divergence slit and 2.5 degree Soller slits on the incident beam side. LynxEye detector and Bruker DIFFRAC software. Diffraction measured from $2\theta = 5^\circ - 40^\circ$; step size, 0.0101°

Magnetic Measurements (≤ 7 T)

Magnetic measurements of compounds **4**, and **5** were performed on microcrystalline samples placed in a gelatine capsule and immobilised using eicosane. DC susceptibility and magnetisation data within the temperature and field ranges of $T = 2-300$ K ($2 - 270$ K for **5**) and $B = 0-7$ T ($0-5$ T for **5**) were performed on a Quantum Design MPMS XL SQUID magnetometer equipped with a 7 T DC magnet. Diamagnetic corrections were applied to the data using Pascal's constants.

Heat Capacity

Heat capacity data of compound **4** was collected in the temperature range 0.3–30 K using a Quantum Design PPMS equipped with a ^3He cryostat. The powdered, polycrystalline samples were pressed into a thin pellet with mass of about 0.5 mg. Apiezon-N grease was used to facilitate the sample thermalization at low temperatures, and its contribution to the heat capacity was subtracted using a phenomenological expression.

Computational Details

The diamagnetic substitution method was used to calculate the exchange coupling constants in **4** employing the Gaussian 16 suite.⁵⁶ Based on symmetry there are 8 there are a total of eight unique magnetic exchange interactions (J_1-J_8) present in **4**. These interactions are calculated using a model complex (Appendix 4). For each calculation Fe^{III} ions not involved in the pairwise exchange interaction under investigation were substituted by diamagnetic Ga^{III} ions in order to maintain the same coordination environment. The exchange coupling constants were estimated using the broken symmetry approach developed by Noodleman.⁵⁷

Ahlrichs' TZV polarisation basis set was used for the Fe and Ga ions, while a 6-31G* basis set was used for O, N, C, and H atoms.

A similar method to that used for compound **4** was employed to calculate the exchange parameters of compounds **5** and **6** with some differences. Due to the asymmetry of **5** five model complexes were derived and the J values were calculated for each Fe-O₂-Fe unit, a total of 11 parameters (Appendix 5). For **6** 4 models were derived and 6 individual parameters calculated (Appendix 6). The basis sets used for compounds **5** and **6** were also adjusted with the TZV basis set being used for Fe ions, SVP for Ga, Zn, O, and N atoms and SV for Cl, C and H atoms.

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Chapter 4: 2-Pyridinemethanol [$\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}_5$] Wheels (M = Ni, Co, Zn)

Chapter 4: 2-Pyridinemethanol [$\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}_5$] Wheels ($\text{M} = \text{Ni}, \text{Co}, \text{Zn}$)

A particularly prominent class of flexible chelates used for the synthesis of polymetallic clusters are the pyridyl alcohols. These compounds can be seen as an alternative to the aminoalcohols discussed in Chapter 3 with the N atom of the ligand now part of a pyridine ring. Two well studied pyridyl alcohols are 2-pyridinemethanol (or 2-hydroxymethylpyridine, hmpH) and 2,6-pyridinedimethanol (pdmH₂). The coordination chemistry of these two ligands (Figure 47) has afforded a library of polynuclear transition metal clusters with various topologies. Indeed, a search of the CCDC database for hmpH-based clusters with three or more transition metal atoms gives 223 structures while the same search for pdmH₂ affords a further 64 structures.

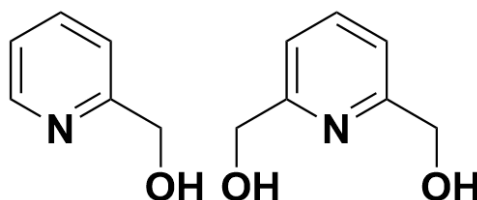


Figure 45: Structures of the pyridyl alcohol ligands hmpH (left) and pdmH₂ (right).

One of the more interesting cluster topologies hmpH can form is the planar seven-membered Anderson-type wheel that describes a centred hexagon. A well-known topology in polymetallic cluster chemistry this structural motif is present in number of homometallic complexes both as $[\text{M}_7]^{1-5}$ wheels and larger clusters exhibiting interesting physical properties such as $[\text{Ni}_{10}]^6$ a high nuclearity SMM, $[\text{Co}_{13/14}]$ a mixed valence compound showing ferromagnetic exchange,⁷ and a $[\text{Mn}_{19}]$ cluster displaying ferrimagnetic exchange.⁸ Heterometallic Anderson-type clusters are rarer but with a growing library containing complexes where the metal sites are both ordered and disordered, some of which are prepared with the hmpH ligand.⁹⁻¹²

When looking exclusively at wheels comprised of Fe-O units there are several $[\text{Fe}_7]$ Anderson-type clusters,^{4,13-15} while larger Fe^{III} clusters containing the wheel motif include the $[\text{Fe}_{17/19}]$ planar “captured rust” clusters discussed in Chapter 1.¹⁶ Heterometallic Fe-O based Anderson wheels are limited to just two examples; an hmpH-based $[\text{Cr}^{\text{III}}_2\text{Fe}^{\text{II}}_5]$ molecule as part of a large family of $[\text{Cr}^{\text{III}}_2\text{M}^{\text{II}}_5]$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Ni}, \text{Co}, \text{Cu}$ and Zn) complexes¹⁷ synthesised under solvothermal conditions, and an $[\text{Fe}^{\text{III}}_3\text{Mn}^{\text{II}}_4]$ wheel synthesised using a phenyl substituted diethanolamine ligand.¹⁸

Due this gap in the literature, the interesting magnetic features of previously reported Anderson-type clusters and previous success within the group in synthesising such compounds with hmpH it seemed reasonable to attempt the preparation of Fe^{III}-based mixed metal wheels. This chapter reports the successful synthesis of three such clusters of general formula [Fe^{III}₂M^{II}₅(hmp)₁₂](ClO₄)₄ (M = Ni (**7**), Co (**8**), Zn (**9**)) and the initial solid state studies of these complexes, including their magnetic properties.

Results and Discussion

The syntheses of **7**, **8** and **9** follow the same general procedure (see the Experimental section for full details). Metal salts were dissolved in MeOH, hmpH and NEt₃ were added, and the solutions stirred overnight at room temperature. After filtration the solutions were transferred to Teflon lined autoclaves and heated to 100°C for 24 hrs (**7** and **8**) or 12 hrs (**9**). After cooling the autoclaves were left to stand for 48 hrs affording crystals suitable for X-ray crystallography.

All three wheel clusters are isostructural, crystallising in the trigonal *R*-3 space group with the asymmetric unit containing just the central metal ion, one outer metal ion, two hmp⁻ ligands and two halves of two separate perchlorate counterions. The structure describes a seven membered wheel, or centred hexagon, with the central metal ion bridged to the six outer metal ions via six O_{hmp}⁻ atoms and the outer metal ions bridged to nearest neighbours around the wheel by a further six O_{hmp}⁻ atoms (Figure 48). Bond valence sum (BVS) calculations (Appendix 7) indicate that the central metal ion is always a M^{II} ion in octahedral geometry. The six outer metal ions are crystallographically equivalent and bond valence sum calculations do not provide a definitive identity of these ions, indicating the remaining two Fe^{III} ions and four M^{II} ions are disordered over the six sites with each site containing 1/3 Fe^{III} and 2/3 M^{II}. This has been modelled crystallographically by separating the unique site into two parts with identical constrained co-ordinates and anisotropic displacement parameters (see crystal structure files for more information). This disorder over the outer metal sites indicates the existence of 3 isomers of the cluster present within the crystal, where the Fe^{III} ions occupy the 1,2 1,3 and 1,4 positions in the outer ring (Figure 49). As well as bridging them to the central M^{II} ion the μ_3 -O bridges, along with a further six μ_2 -O units, bridge the outer metal ions around the ring. The result is that each outer metal ion is bonded to two μ_3 -O_{hmp}⁻ units and two μ_2 -O_{hmp}⁻ units, the pseudo-octahedral geometry being completed by two terminally bonded N_{hmp}⁻

atoms from the same ligands as the bridging O atoms. The twelve hmp⁻ ligands sit alternately above and below the metal plane of the molecule (Figure 50). Charge balance is maintained with the presence of four ClO₄⁻ counterions per formula unit. The wheels pack together in layers visible along the *a* and *b* axes with the perchlorates situated between the layers. Any voids in the crystal packing are likely filled with disordered methanol solvents masked out during structure refinement (see crystal structure files for more information).

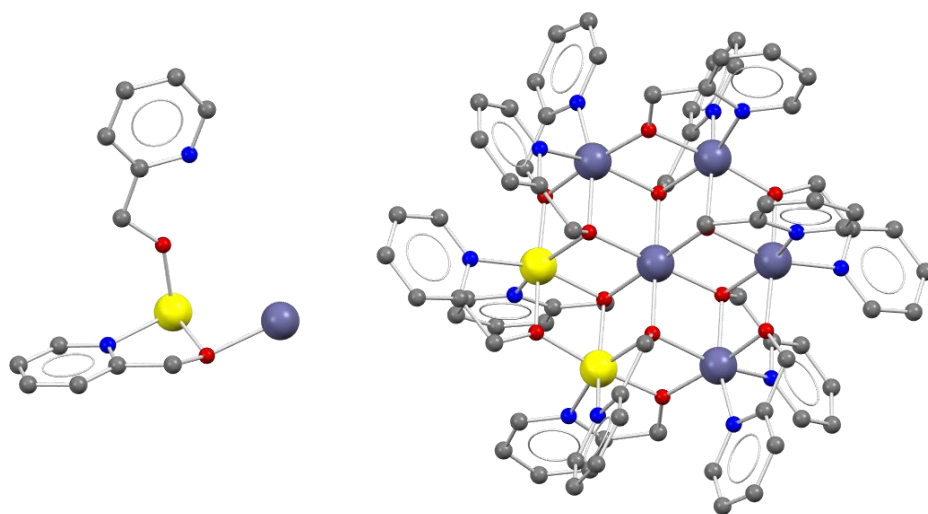


Figure 46: Asymmetric unit of the Anderson-type clusters of **7**, **8** and **9** (left) alongside the full molecular unit (right). Colour Code: Fe^{III}, yellow; M^{II}, dark blue/grey; O, red; N, blue; C, grey. Hydrogens and counterions removed for clarity

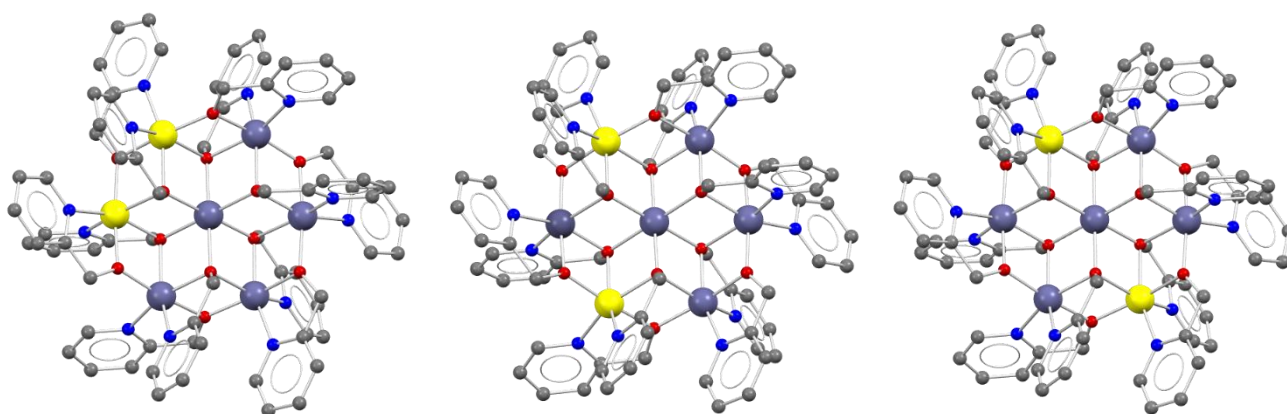


Figure 47: Visualisation of the three different isomers present in the cations of **7**, **8**, and **9**. Colour Code: Fe^{III}, yellow; M^{II}, dark blue/grey; O, red; N, blue; C, grey.

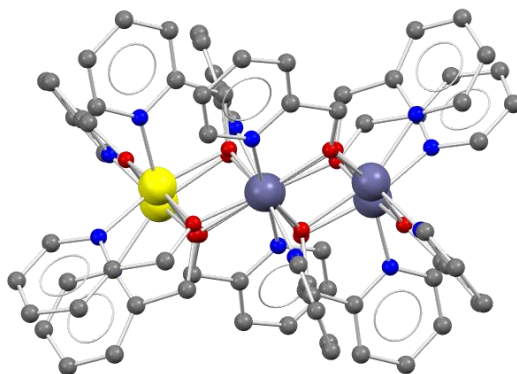


Figure 48: Side on view of the cationic cluster of **7**, **8** and **9** showing the ligands bonding from above and below the $[M_7]$ plane of the cluster. Colour Code: Fe^{III} , yellow; M^{II} , dark blue/grey; O, red; N, blue; C, grey. Hydrogens and counterions removed for clarity

Variable temperature direct current molar magnetic susceptibility, χ , measurements were performed on polycrystalline powders of **7-9** under an applied magnetic field, B , of 0.1 T over the temperature, T , range 2 – 300 K. The results of these measurements are presented in a plot of the χT product versus T (Figure 51). For each of the wheel complexes the experimentally obtained value for χT is close to the expected value for two Fe^{III} and five M^{II} non-interacting metal ions, 14.83 K cm³ mol⁻¹ for **7** (expected: 14.8 K cm³ mol⁻¹ $g_{Fe} = 2.0$); 19.80 K cm³ mol⁻¹ for **8** (expected: 18.1 K cm³ mol⁻¹ $g_{Fe} = 2.0$, $g_{Ni} = 2.2$) and 8.43 K cm³ mol⁻¹ for **9** (expected: 8.75 K cm³ mol⁻¹ $g_{Fe} = g_{Co} = 2.0$). As temperature decreases from 300 – 100 K the χT product for all three complexes steadily decreases at similar rates. From 100 – 25 K the behaviour of **7** and **8** diverges from **9** with a sharp decrease in χT . Below 25 K the χT product for all three complexes sharply decreases reaching 4.73 K cm³ mol⁻¹ (**7**), 8.17 K cm³ mol⁻¹ (**8**) and 5.5 K cm³ mol⁻¹ (**9**), respectively. The behaviour seen in **7** and **8** is indicative of weakly/competing antiferromagnetic interactions similar to those seen in the analogous $[Cr^{III}_2M^{II}_5(hmp)_{12}]^{4-}$ wheels.^{10,17} In the $[Cr^{III}_2M^{II}_5]$ analogues the Cr-Cr interaction is weakly antiferromagnetic ($J_{Cr-Cr} = -1.0$ cm⁻¹). An examination of the M-($\mu_{2/3}$ -O)-M bridges in **7**, **8** and **9** shows the bond angles between two outer metal ions to be 97° and 104° (Appendix 7). Considering the magneto-structural correlations previously reported for Fe-O-Fe bridges,¹⁹ an antiferromagnetic interaction of similar magnitude would therefore be expected. This hypothesis is supported by the data for **9** which originates from the exchange between just two Fe^{III} ions, albeit a mixture of three isomers. Variable field magnetisation data collected at $T = 2 - 7$ K in applied fields of $B = 0 - 7$ T supports the presence of weak/competing exchange

interactions, with M rising slowly with increasing B for each compound without reaching saturation (Figure 52). Fitting of this data with a similar model to that used for the $[\text{Cr}^{\text{III}}_2\text{Ni}^{\text{II}}_5]$ analogue in which approximate J values could be estimated using three model complexes weighted to 1/3 each, is in progress.¹⁰

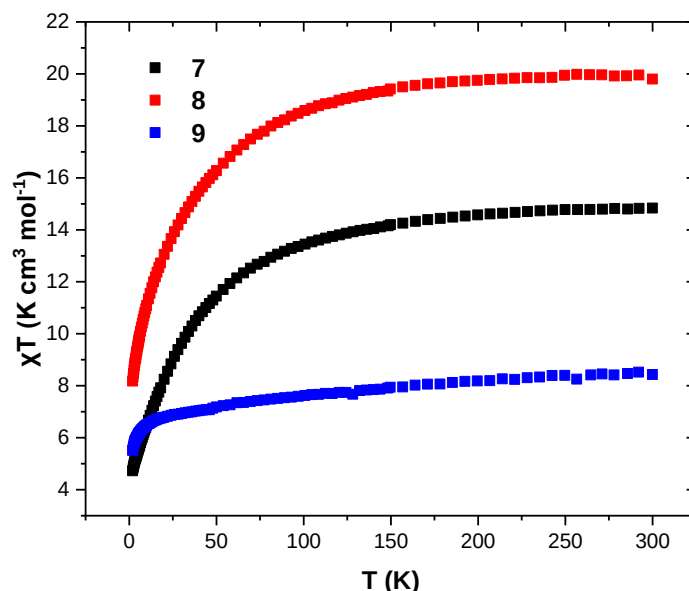


Figure 49: Magnetic susceptibility data as χT versus T for **7** (black), **8** (red) and **9** measured with an applied field of 0.1 T over a temperature range of 300 – 2 K.

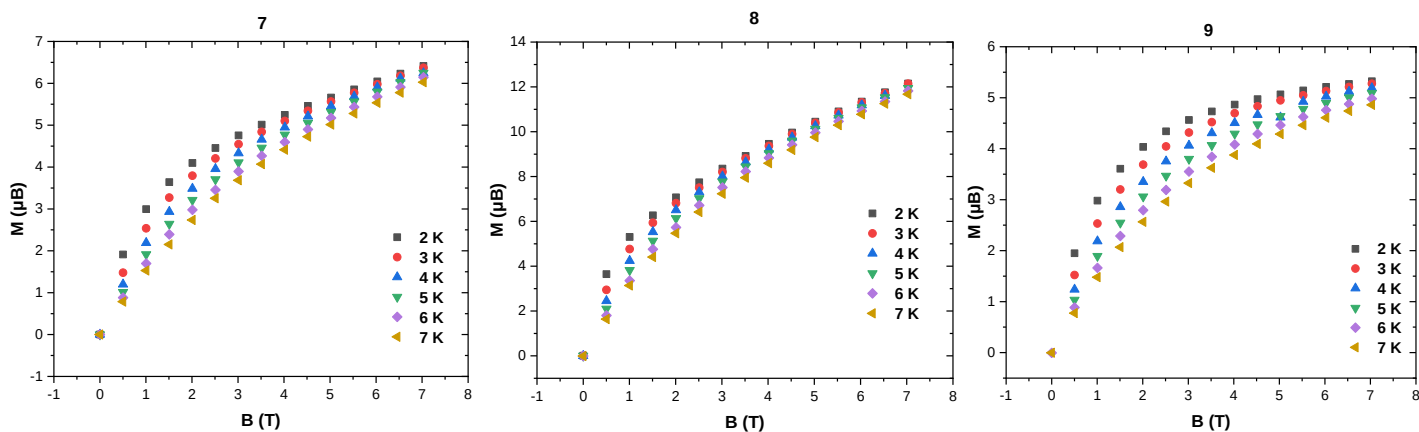


Figure 50: Variable field magnetisation data for **7**, **8** and **9** measured over an applied field range of $B = 0 - 7$ T and temperatures $T = 2 - 7$ K.

Summary, Conclusions and Future Work

In summary three novel heterometallic Anderson wheels with the general formula $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}_5(\text{hmp})_{12}](\text{ClO}_4)_4$ have been synthesised using solvothermal methods. The pseudo-hexagonal symmetry of the molecule and bond valence sum considerations indicate that the central metal ion is always a M^{II} ion while the two Fe^{III} ions and remaining four M^{II} ions are disordered over the six outer metal sites. Magnetic susceptibility and magnetisation measurements indicate weak/competing antiferromagnetic exchange between the constituent metal ions, in line with similar compounds previously reported, and as expected from the topology of the triangular subunits. The disorder of metal ions over multiple sites makes it difficult to quantitatively analyse the magnetic data by conventional methods. A methodology similar to the one used in the previously reported in analogous $[\text{Cr}^{\text{III}}_2\text{M}^{\text{II}}_5]$ wheels is currently being examined and may prove useful in obtaining a semi-quantitative/qualitative analysis of the data.

Future work will include the targeted synthesis of further $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}_5]$ structures including $\text{M} = \text{Mn}^{\text{II}}$ and $\text{M} = \text{Cu}^{\text{II}}$.

Experimental

Materials and physical measurements

All starting materials were procured from commercial suppliers and used as received. Elemental analysis C H and N of all compounds were performed by the service at the School of Geoscience, The University of Edinburgh. Electron Dispersive Spectroscopy was performed for metal analysis (Fe Ni Co) was performed by the electron microscope service at the School of Geoscience, The University of Edinburgh.

Synthesis of $[\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}_5(\text{hmp})_{12}](\text{ClO}_4)_4$ (7)

FeCl_3 (81 mg, 0.5 mmol) and $\text{Ni}(\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$ (365 mg, 1 mmol) were dissolved in methanol (25 ml). HmpH (0.298 ml, 3 mmol) and NEt_3 (0.418 ml, 3 mmol) were added and the brown/green solution stirred overnight at room temperature. The resulting cloudy green solution was filtered by gravity and the filtrate transferred to Teflon lined autoclaves which were sealed and heated to 100°C for 24 hrs. After cooling, the autoclaves were left to stand for 48 hrs. Single crystals suitable for X-ray crystallography were collected and washed with diethyl ether. Yield: 0.120 g (22.9% by Fe). Elemental analysis % CHN calculated (found): C 40.75 (41.17) H 3.46 (3.45) N 8 (7.82). Metal analysis %wt calculated (found): Fe 5.32 (5.20) Ni 14.97 (15.36).

Synthesis of $[\text{Fe}^{\text{III}}_2\text{Co}^{\text{II}}_5(\text{hmp})_{12}](\text{ClO}_4)_4$ (8)

FeCl_3 (81 mg, 0.5 mmol) and $\text{Co}(\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$ (365 mg, 1 mmol) were dissolved in methanol (25 ml). hmpH (0.298 ml, 3 mmol) and NEt_3 (0.418 ml, 3 mmol) were added and the orange-brown solution stirred overnight at room temperature. The resulting cloudy orange-brown solution was filtered by gravity and the filtrate transferred to Teflon lined autoclaves which were sealed and heated to 100°C for 24 hrs. After cooling the autoclaves were left to stand for 48 hrs. Single crystals suitable for X-ray crystallography were collected and washed with diethyl ether. Yield: 0.135 g (25.7 % by Fe). Elemental analysis % CHN calculated (found): C 40.58 (41.15) H 3.45 (3.38) N 8 (7.78). Metal analysis %wt: Fe 5.31 (5.22) Co 14.02 (14.41)

Synthesis of $[\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}_5(\text{hmp})_{12}](\text{ClO}_4)_4$ (9)

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (202 mg, 0.5 mmol) and $\text{Zn}(\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$ (372 mg, 1 mmol) were dissolved in methanol (25 ml). hmpH (0.298 ml, 3 mmol) and NEt_3 (0.418 ml, 3 mmol) were added, and

the orange solution stirred overnight at room temperature. The resulting cloudy green solution was filtered by gravity and the filtrate transferred to Teflon line autoclaves which were sealed and heated to 100°C for 12 hrs. After cooling the autoclaves were left to stand for 48 hrs. Single crystals suitable for X-ray crystallography were collected and washed with diethyl ether. Yield: 0.129 g (24.2 % by Fe). Elemental analysis % CHN calculated (found): C 39.75 (40.53) H 3.40 (3.37) N 6.65 (6.01).

Single Crystal X-ray Diffraction

Diffraction data for compound **7** were collected on a Rigaku Oxford Diffraction Xcalibur diffractometer. The crystals were kept at a steady temperature of $T = 120.0$ K throughout data collection using an Oxford Cryosystems Cryostream. The structure was solved using ShelXT and refined with ShelXL interfaced through Olex2.^{20,21}

Diffraction data for compounds **8** and **9** were collected on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystals were kept at a steady temperature of $T = 120.0$ K throughout data collection using an Oxford Cryosystems Cryostream. The structure was solved using ShelXT and refined with ShelXL interfaced through Olex2.^{20,21}

Powder X-ray Diffraction

Diffraction data for compounds **7**, **8** and **9** were collected on polycrystalline powders using a Bruker D2 PHASER with nickel filtered Cu radiation at power 30 kW and current 10mA. Diffraction measured from $2\theta = 5^\circ - 40^\circ$; step size, 0.0101°

Magnetic Measurements (≤ 7 T)

Magnetic measurements of compounds **7**, **8** and **9** were performed on microcrystalline samples placed in a gelatine capsule and immobilised using eicosane. DC susceptibility and magnetisation data within the temperature and field ranges of $T = 2-300$ K and $B = 0-7$ T were performed on a Quantum Design MPMS XL SQUID magnetometer equipped with a 7 T DC magnet. Diamagnetic corrections were applied to the data using Pascal's constants.

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Chapter 5: Conclusions and Future Outlook

Chapter 5: Conclusions and Future Outlook.

The aim of this thesis was to synthesise novel Fe-based polymetallic clusters which could have interesting magnetic properties. This aim was approached from different angles.

Chapter 2 discussed three novel Fe^{III} – oxo clusters prepared using monodentate pyridine-type ligands. By adjusting the [Fe₁₇] synthetic procedure the [Fe₃₄] cluster **1** was prepared. Further investigation of the synthesis of **1** led to the preparation of the related [Fe₃₀] cluster **2**. Approximations made using classical spin models indicate that **1** has a non-zero ground state of at least $S = 11$ with multiple low lying excited states. This hypothesis is supported by HFEPR, high field ($B = 34\text{T}$) magnetisation, and heat capacity measurements. The magnetic susceptibility of **2** indicates antiferromagnetic interactions with the data modelled with two J values - one strongly antiferromagnetic and one weakly antiferromagnetic. Mass spectrometry performed on the reaction mixture of **2** shows that the cluster is formed rapidly in solution. Chapter 1 concludes by reporting the [Fe₈] cluster **3**. Prepared from 4-methoxypyridine and anhydrous FeBr₃, magnetic measurements of **3** reveal ferrimagnetic behaviour leading to a ground state spin of $S = 10$. Experimental data fitting combined with computational calculations help explain this behaviour with the exchange interaction between the central Fe^{III} ions and the Fe^{III} ions in the outer ring being strongly antiferromagnetic, and the interactions between outer ring Fe^{III} ions weakly ferromagnetic. Future work will include investigation of POM/Fe^{III}-oxo compounds to create core-shell species with enhanced functionality.

Chapter 3 reported three novel triethanolamine Fe^{III} clusters displaying unique topologies. Compound **4** is just the fourth [Fe₁₅] cluster reported. The metallic skeleton conforms to a centred tetrakis hexahedron, a unique geometry in homometallic Fe^{III} cluster chemistry. Magnetic measurements of **4** reveal competing antiferromagnetic interactions resulting a non-zero ground state. DFT calculations corroborate this, with calculated J values predicting dominant antiferromagnetic interactions. The heterometallic (Fe/Zn) ring clusters **5** and **6** represent the first odd numbered Fe^{III} ring and its even numbered analogue. Magnetic measurements of **5** reveal frustrated behaviour with an $S = \frac{1}{2}$ ground state. EPR, heat capacity and high field, low temperature magnetisation measurements are in progress. Future work will target the synthesis of derivatives of **5** and **6** where the M^{II} position is occupied by paramagnetic metal ions ($M = \text{Mn, Fe, Co, Ni, Cu}$).

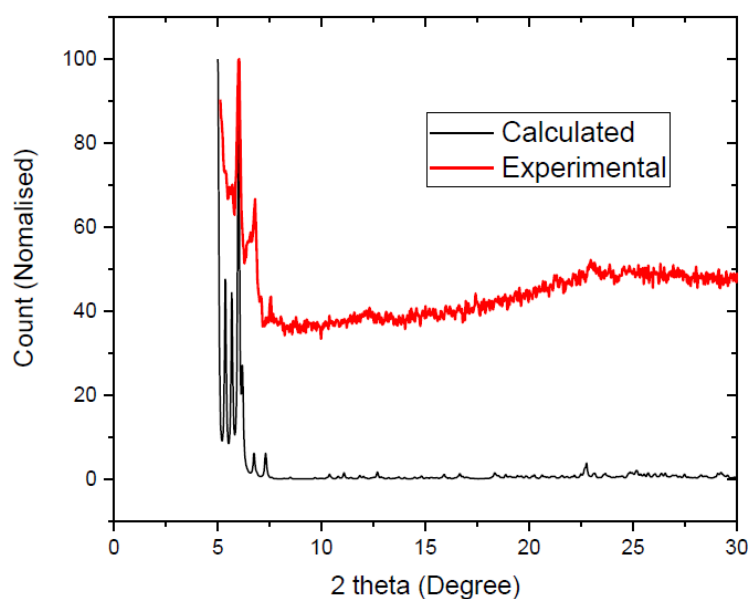
Chapter 4 reported a family of heterometallic Fe^{III} containing Anderson wheels with the general formula [Fe^{III}₂M^{II}₅(hmp)₁₂](ClO₄)₄. **7**, **8** and **9** are isostructural with the metallic skeleton conforming to a centred hexagon. Crystallographic analysis and BVS calculations indicate that two Fe^{III} ions and four M^{II} ions are disordered over the outer six metal sites due to isomerisation of the structure. Magnetic measurements indicate competing interactions in **7** and **8**. Fitting of the magnetic data, using a model that takes into account the isomerisation present is ongoing. Further work will include expanding the family of [Fe^{III}₂M^{II}₅] wheels with M = Mn and Cu, and trimetallic species with other transition / lanthanide metal ions.

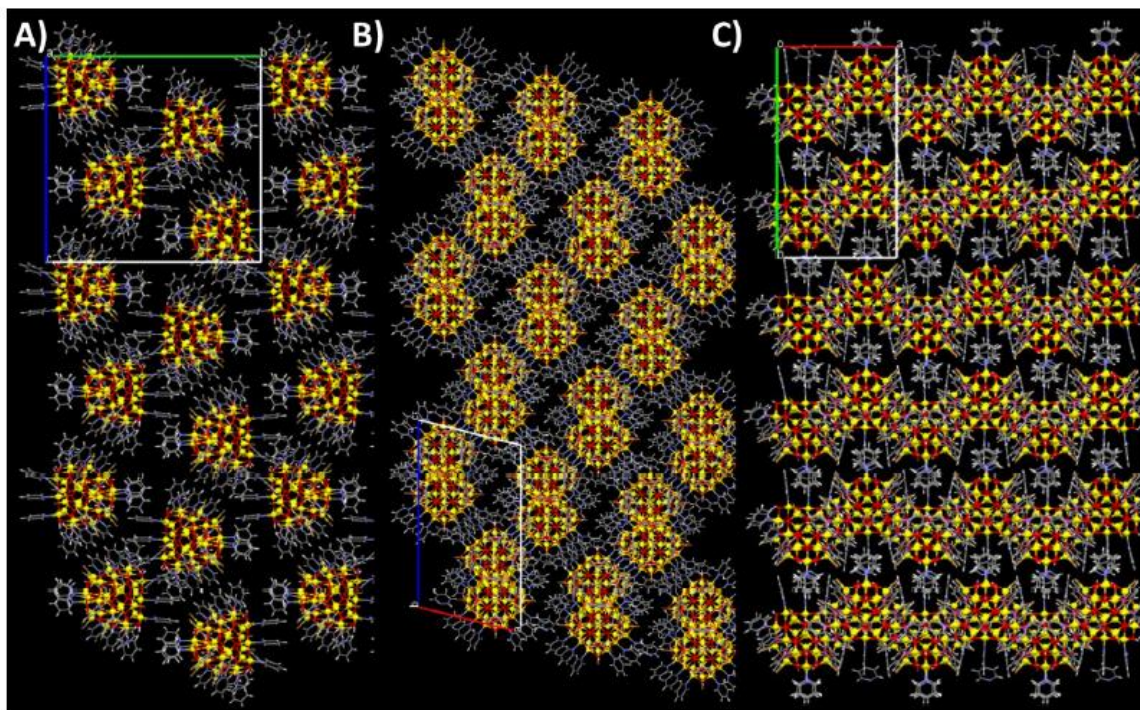
The synthesis of homo- and heterometallic Fe^{III} cluster compounds provides a route towards molecules unique structures with interesting magnetic behaviour. The preparation of large molecular metal oxides in particular suggests the possibility of bridging the gap between giant diamagnetic POMs and smaller paramagnetic clusters. Such species can potentially find application in diverse fields, ranging from catalysis and medicine to cryogenic refrigerations

Appendix

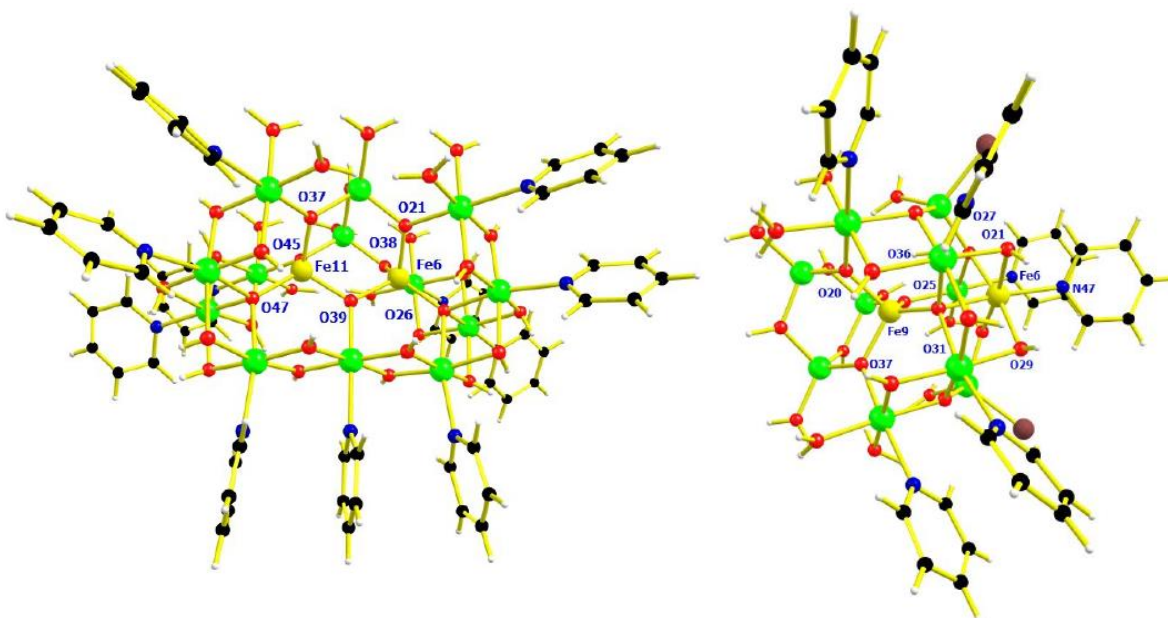
Appendix 1**Appendix 1.1: Crystallographic details for compound 1**

Formula	C ₉₅ H ₁₀₇ Br ₁₄ Fe ₃₄ N ₁₉ O ₅₀	Z'	1
D_{calc}/g cm⁻³	1.777	Wavelength/Å	1.54184
μ/mm⁻¹	22.968	Radiation type	CuK _α
Formula Weight	5332.63	Θ_{min}/°	3.378
Colour	Dark red	Θ_{max}/°	68.251
Shape	Block	Measured Refl.	297235
Size/mm × mm × mm	0.45 × 0.21 × 0.17	Independent Refl.	36505
T/ K	120.0	Reflections Used	23404
Crystal System	Monoclinic	R_{int}	0.2035
Space Group	<i>P</i> 2 ₁ / <i>n</i>	Parameters	1897
a/ Å	18.4222(5)	Restraints	120
b/ Å	32.8959(10)	Largest Peak	2.270
c/ Å	33.9586(9)	Deepest Hole	-1.311
α/°	90	GooF	0.995
β/°	104.44(3)	wR₂ (all data)	0.2880
γ/°	90	wR₂	0.2598
V/Å³	19928.9(10)	R₁ (all data)	0.1309
Z	4	R₁	0.1044

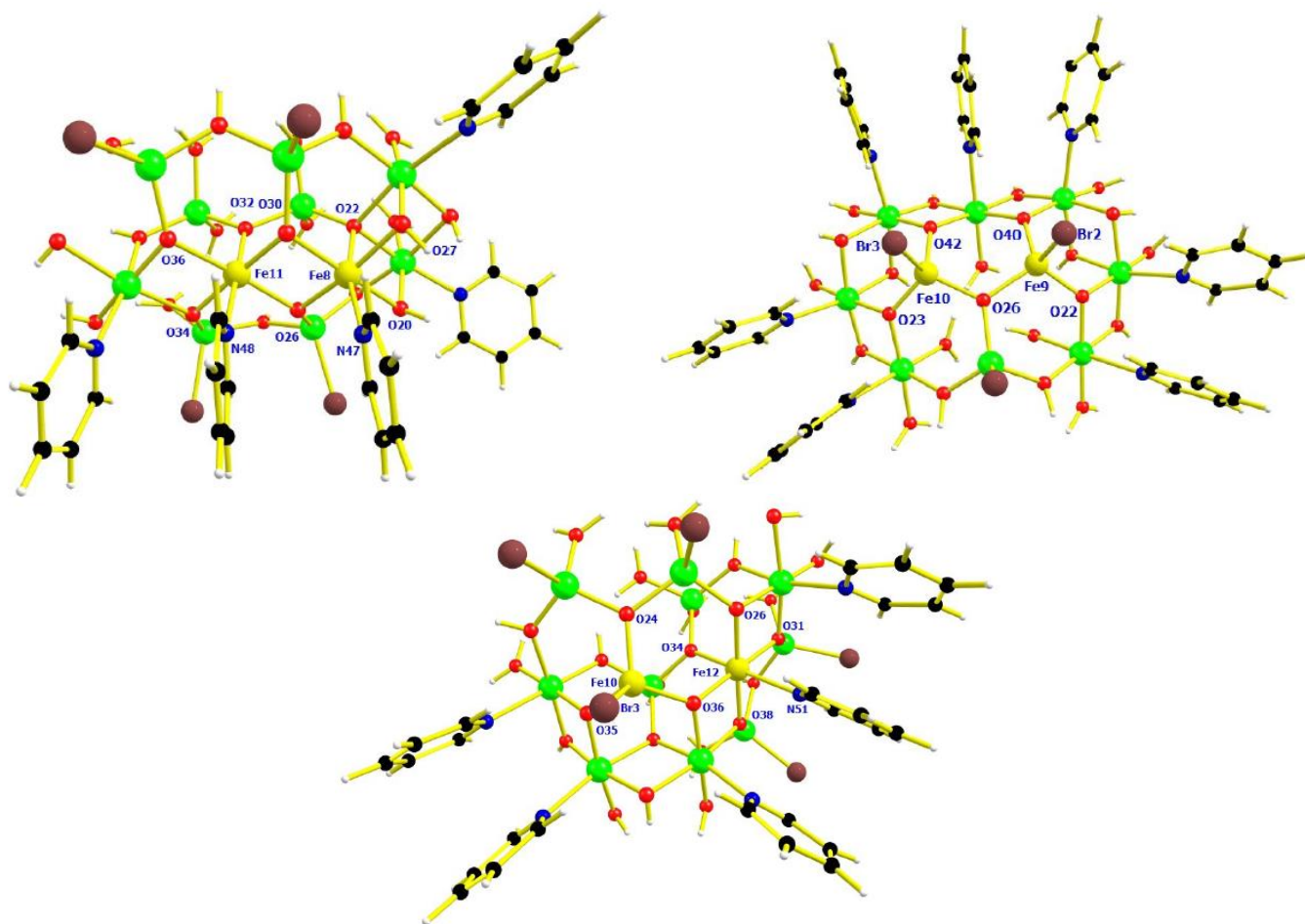
**Appendix 1.2: Powder X-ray diffraction pattern of compound 1.**



Appendix 1.3: Crystal packing diagram showing the extended structure in **1** in ball and stick representation viewed down the *a*-, *b*- and *c*- axes of the unit cell (left-right respectively). Br counter anions omitted.



Appendix 1.2: Model complexes used to computationally calculate the J_1 (left) and J_2 (right) exchange parameters in compound **1**. Models derived from **1**. Colour code: Fe^{III}, yellow; Ga^{III}, green; O, red; N, blue; Br, purple; C, black; H, white.



Appendix 1.3: Model complexes used to computationally calculate the J_3 (upper left), J_4 (upper right) and J_5 (lower centre) exchange parameters in compound **1**. Models derived from **1**. Colour code: Fe^{III}, yellow; Ga^{III}, green; O, red; N, blue; C, black; H, white.

Appendix 1.4: Overlap integral between the 3d orbitals of the Fe^{III} ions in the J_{1-5} exchange pathways. The most significant are highlighted in yellow.

J_1

Beta→ Alpha	d_{z^2}	d_{xy}	d_{xz}	$d_{x^2-y^2}$	d_{yz}
d_{yz}	0.175	-0.027	0.175	-0.000	-0.234
d_{xy}	0.021	0.041	0.076	0.041	-0.082
d_{z^2}	-0.073	0.013	-0.144	-0.093	-0.216
$d_{x^2-y^2}$	-0.066	0.063	-0.024	-0.331	0.058
d_{xz}	-0.262	0.003	-0.143	0.153	-0.058

J_2

Beta→ Alpha	d_{yz}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{z^2}
$d_{x^2-y^2}$	0.141	-0.007	0.184	-0.236	-0.098
d_{yz}	-0.033	0.319	0.081	-0.202	-0.151
d_{xz}	0.123	0.196	0.062	0.036	-0.270
d_{xy}	0.117	-0.089	-0.103	0.243	0.282
d_{z^2}	-0.013	0.071	0.035	-0.113	0.099

J_3

Beta→ Alpha↓	d_{xz}	d_{xy}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}
d_{xz}	0.021	0.011	-0.003	0.014	-0.044
d_{xy}	-0.041	0.197	-0.047	-0.036	-0.121
d_{yz}	-0.110	-0.002	-0.158	0.045	-0.178
$d_{x^2-y^2}$	-0.027	-0.317	-0.081	-0.171	-0.068
d_{z^2}	-0.106	0.047	0.031	-0.012	-0.017

 J_4

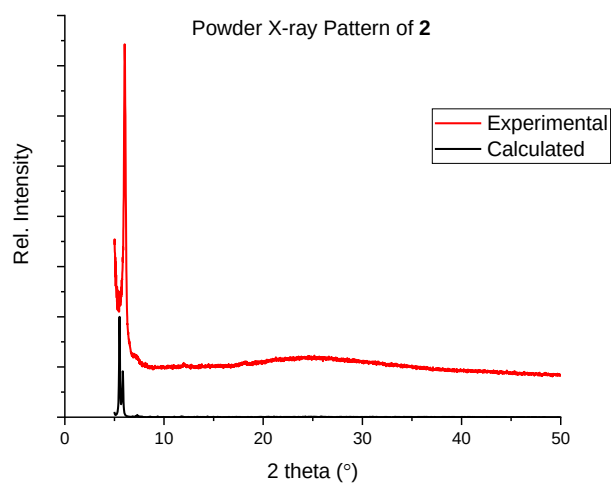
Beta→ Alpha	d_{z^2}	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$
d_{z^2}	0.264	0.266	-0.037	0.032	0.103
d_{xy}	0.077	0.053	0.024	0.018	-0.008
d_{xz}	-0.068	0.119	0.119	-0.285	-0.177
$d_{x^2-y^2}$	0.014	0.000	0.364	-0.113	0.001
d_{yz}	-0.012	-0.038	-0.087	0.019	-0.213

 J_5

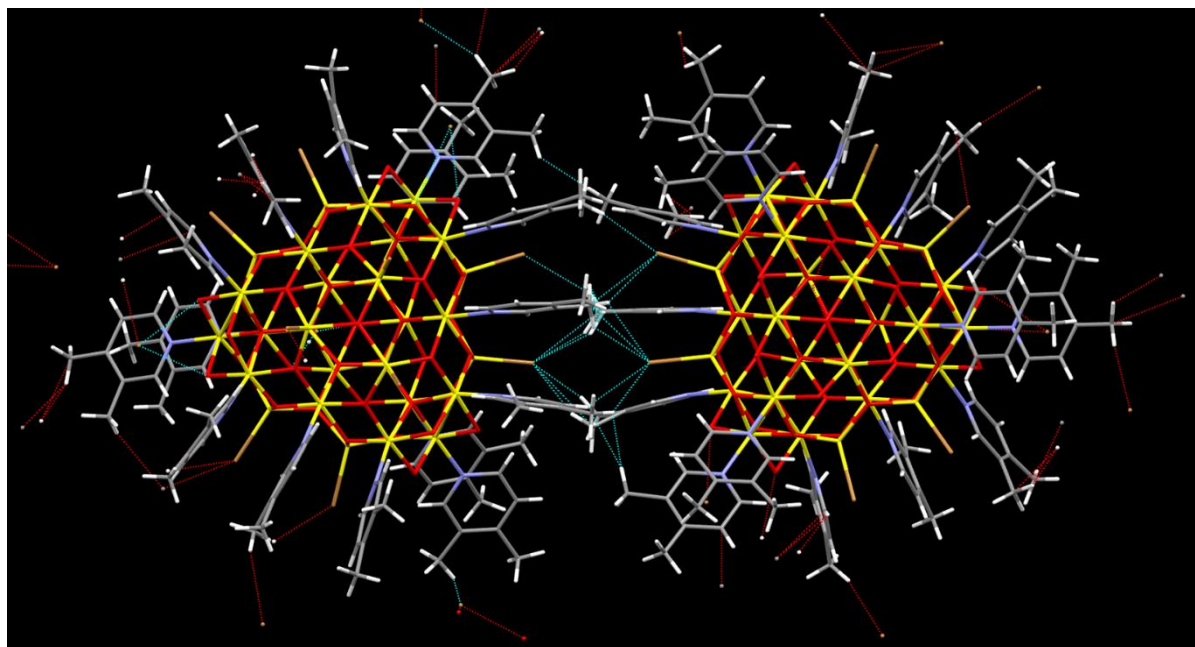
Beta→ Alpha↓	$d_{x^2-y^2}$	d_{yz}	d_{xz}	d_{xy}	d_{z^2}
d_{z^2}	0.106	0.220	0.262	0.025	-0.011
d_{xy}	0.071	-0.007	-0.011	-0.148	-0.005
$d_{x^2-y^2}$	-0.136	0.223	0.238	0.013	-0.002
d_{yz}	-0.002	0.054	0.212	-0.073	0.027
d_{xz}	-0.005	0.117	0.278	-0.055	-0.264

Appendix 2**Appendix 2.1: Crystallographic details for compound 2 and 2a.**

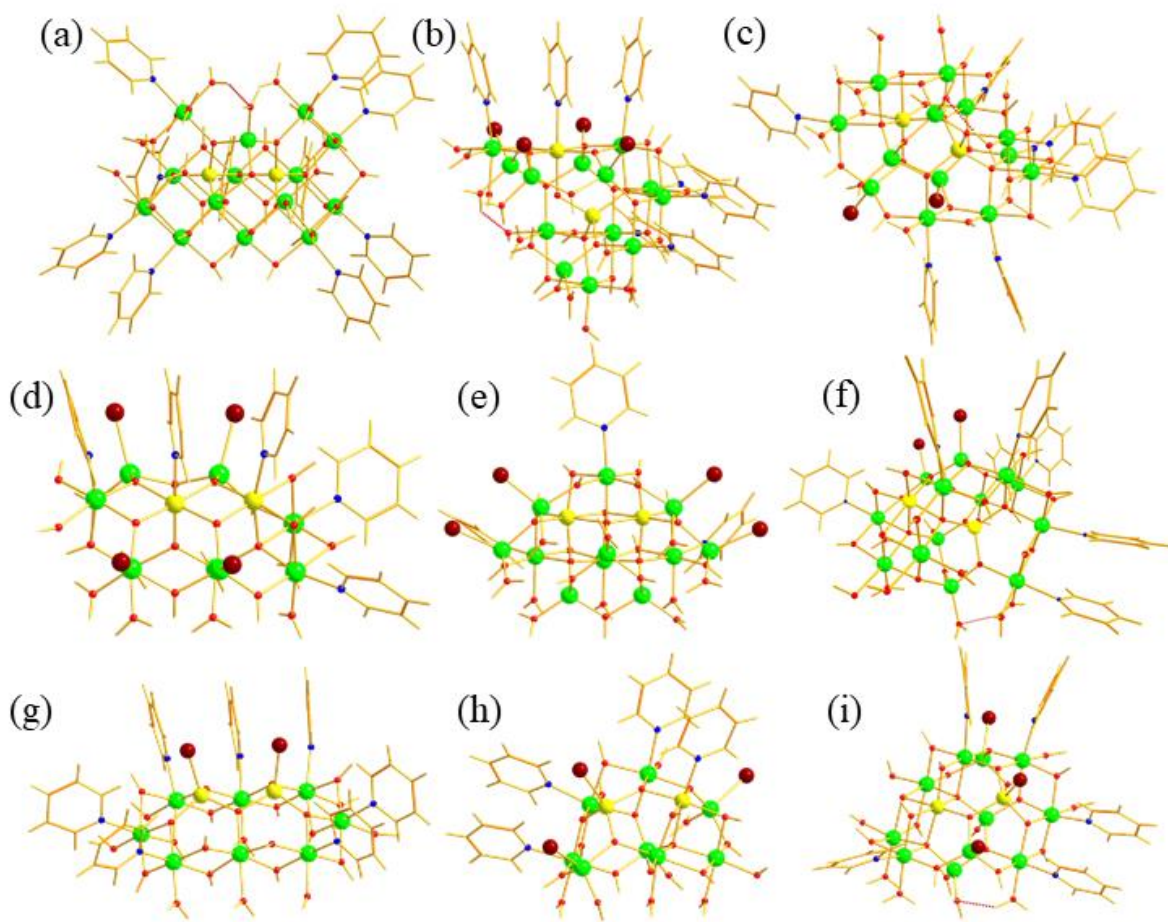
Compound	2	2a
Formula	C ₁₁₂ H ₁₅₉ Br ₁₂ Fe ₃₀ N ₁₆ O ₄₇	C ₁₁₉ H ₁₆₉ Br ₁₂ Fe ₃₀ N ₁₇ O ₄₇
$D_{calc.}/\text{g cm}^{-3}$	1.575	1.643
μ/mm^{-1}	3.885	19.117
Formula Weight	5115.96	5224.12
Colour	brown	dark brown
Shape	plate	block
Size/mm ³	0.15×0.12×0.04	0.17×0.09×0.06
T/K	100.0	120.0
Crystal System	monoclinic	triclinic
Space Group	Pn	$P-1$
Flack Parameter	0.159(10)	-
Hooft parameter	0.192(4)	-
$a/\text{\AA}$	30.929(3)	20.7362(5)
$b/\text{\AA}$	21.777(2)	22.7181(4)
$c/\text{\AA}$	32.273(4)	25.0130(4)
$\alpha/^\circ$	90	95.425(2)
$\beta/^\circ$	96.882(2)	97.928(2)
$\gamma/^\circ$	90	113.427(2)
$V/\text{\AA}^3$	21580(4)	10563.0(4)
Z	4	2
Z'	2	1
Wavelength/ $\text{\AA}$	0.6889	1.54178
Radiation type	Synchrotron	CuK α
$\theta_{\min}/^\circ$	0.835	3.617
$\theta_{\max}/^\circ$	20.136	76.143
Measured Refl.	168652	174652
Independent Refl.	44728	43629
Reflections with $I > 2(I)$	32432	29952
R_{int}	0.0752	0.0982
Parameters	3442	2012
Restraints	9631	950
Largest Peak	0.614	1.506
Deepest Hole	-0.468	-1.245
GooF	1.038	0.984
wR_2 (all data)	0.1530	0.1791
wR_2	0.1405	0.1618
R_1 (all data)	0.0794	0.0890
R_1	0.0549	0.0633
CCDC	2105690	2105691



Appendix 2.2: Powder x-ray diffraction pattern of compound **2**.



Appendix 2.3: Closest intermolecular interactions in **1** between the lutidine molecules and Br^- ions, highlighted by the dashed blue lines at $\text{C}\cdots\text{C}/\text{Br}$ distances of $\geq 3.2 \text{ \AA}$.



Appendix 2.4: The nine models employed to estimate the magnetic exchange interactions in the (a) J_1 (b) J_2 (c) J_3 (d) J_4 (e) J_5 (f) J_6 (g) J_7 (h) J_8 (i) J_9 exchange pathways. Colour Code: Fe, Yellow; Ga, Green; Br, Brown; O, Red; N, Blue; C, Black; H, white.

Appendix 2.5: Overlap integral between the 3d orbitals of the Fe^{III} ions in the J_{1-9} exchange pathways. The most significant are highlighted in yellow.

J_1

Beta→ Alpha↓	d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}
d_{xz}	-0.122	0.132	-0.216	-0.223	0.095
d_{yz}	0.030	0.057	0.040	0.108	-0.071
$d_{x^2-y^2}$	-0.048	0.013	-0.012	0.236	-0.028
d_{xy}	0.026	-0.081	0.018	0.042	-0.029
d_{z^2}	-0.007	0.121	0.046	0.017	-0.038

J_2

Beta→ Alpha↓	d_{z^2}	d_{yz}	d_{xz}	$d_{x^2-y^2}$	d_{xy}
d_{z^2}	-0.010	-0.179	-0.019	-0.018	-0.029
d_{yz}	-0.018	-0.069	0.114	0.176	0.080

d_{xz}	-0.001	0.058	-0.012	-0.002	-0.062
d_{x2-y2}	0.030	0.268	-0.036	0.162	-0.025
d_{xy}	0.050	-0.017	-0.051	-0.019	0.232

 J_3

Beta→ Alpha↓	d_{z2}	d_{yz}	d_{xz}	d_{x2-y2}	d_{xy}
d_{z2}	-0.059	0.111	-0.090	0.037	-0.022
d_{yz}	-0.137	-0.091	-0.192	0.068	0.028
d_{xz}	0.120	0.044	-0.002	0.022	-0.018
d_{x2-y2}	0.098	0.062	-0.041	-0.026	-0.019
d_{xy}	-0.227	-0.168	0.002	0.130	-0.060

 J_4

Beta→ Alpha↓	d_{xy}	d_{x2-y2}	d_{xz}	d_{z2}	d_{yz}
d_{z2}	-0.138	0.259	0.144	-0.080	0.046
d_{yz}	0.104	-0.216	0.138	0.014	-0.045
d_{xz}	0.241	0.091	-0.104	0.055	0.057
d_{x2-y2}	0.198	0.187	-0.149	0.122	-0.025
d_{xy}	0.012	0.140	-0.110	-0.078	-0.081

 J_5

Beta→ Alpha↓	d_{yz}	d_{x2-y2}	d_{xz}	d_{xy}	d_{z2}
d_{yz}	-0.006	-0.049	0.069	-0.017	-0.065
d_{xz}	0.107	0.086	-0.056	0.028	-0.159
d_{x2-y2}	0.040	0.049	-0.101	-0.192	-0.040
d_{xy}	-0.152	-0.077	-0.113	0.185	-0.048
d_{z2}	-0.128	-0.041	-0.123	0.058	-0.261

 J_6

Beta→ Alpha↓	d_{z2}	d_{yz}	d_{xz}	d_{x2-y2}	d_{xy}
d_{z2}	0.326	0.013	-0.091	0.033	0.079
d_{yz}	0.211	0.001	-0.161	0.090	0.040
d_{xz}	0.074	-0.006	-0.098	-0.297	-0.003
d_{x2-y2}	-0.037	-0.071	0.139	0.057	-0.125
d_{xy}	-0.095	-0.000	-0.016	-0.140	0.009

 J_7

Beta→ Alpha↓	d_{xy}	d_{x2-y2}	d_{xz}	d_{yz}	d_{z2}
d_{xy}	0.189	0.204	-0.084	0.045	-0.053
d_{x2-y2}	-0.140	-0.050	-0.036	0.099	0.024

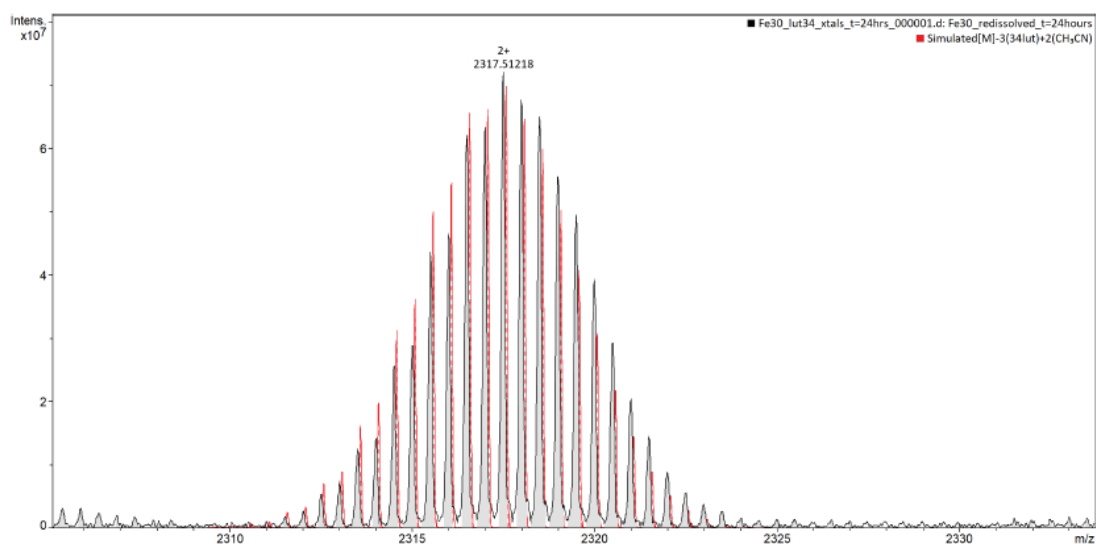
d_{xz}	0.365	0.038	0.022	0.068	0.081
d_{z2}	0.027	0.163	0.014	0.053	-0.075
d_{yz}	0.217	0.039	-0.236	0.003	0.099

J₈

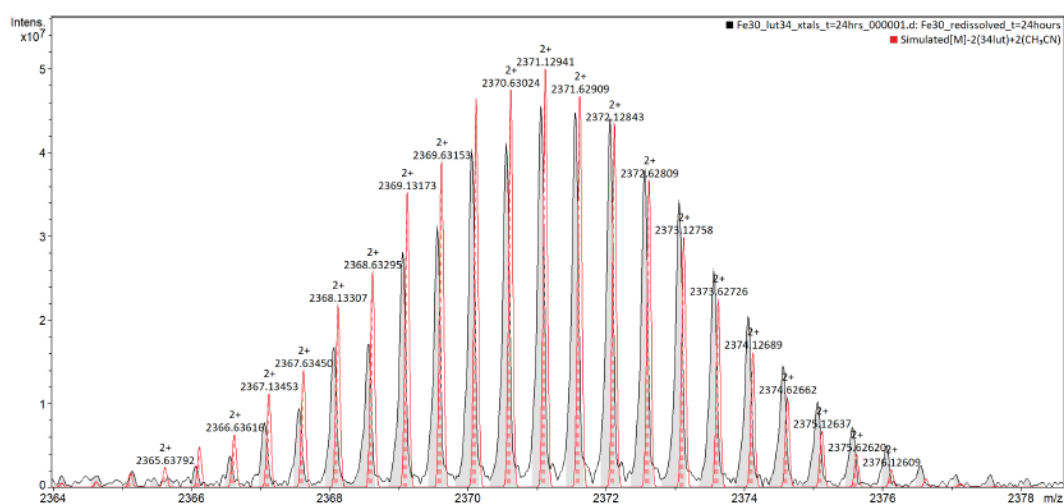
Beta→ Alpha↓	d_{x2-y2}	d_{xy}	d_{z2}	d_{xz}	d_{yz}
d_{xy}	-0.037	0.285	0.014	0.001	-0.066
d_{yz}	0.116	-0.043	-0.107	-0.099	-0.162
d_{x2-y2}	0.071	-0.180	0.103	-0.051	-0.102
d_{xz}	-0.221	-0.188	-0.099	-0.236	0.043
d_{z2}	0.174	0.148	0.014	-0.132	-0.126

J₉

Beta→ Alpha↓	d_{z2}	d_{yz}	d_{xz}	d_{xy}	d_{x2-y2}
d_{z2}	-0.096	0.046	0.109	0.010	0.010
d_{yz}	0.070	0.044	-0.002	-0.018	0.022
d_{xz}	0.145	0.091	-0.192	0.028	0.068
d_{xy}	-0.087	-0.168	0.002	-0.060	0.130
d_{x2-y2}	0.203	0.062	-0.041	-0.019	-0.026



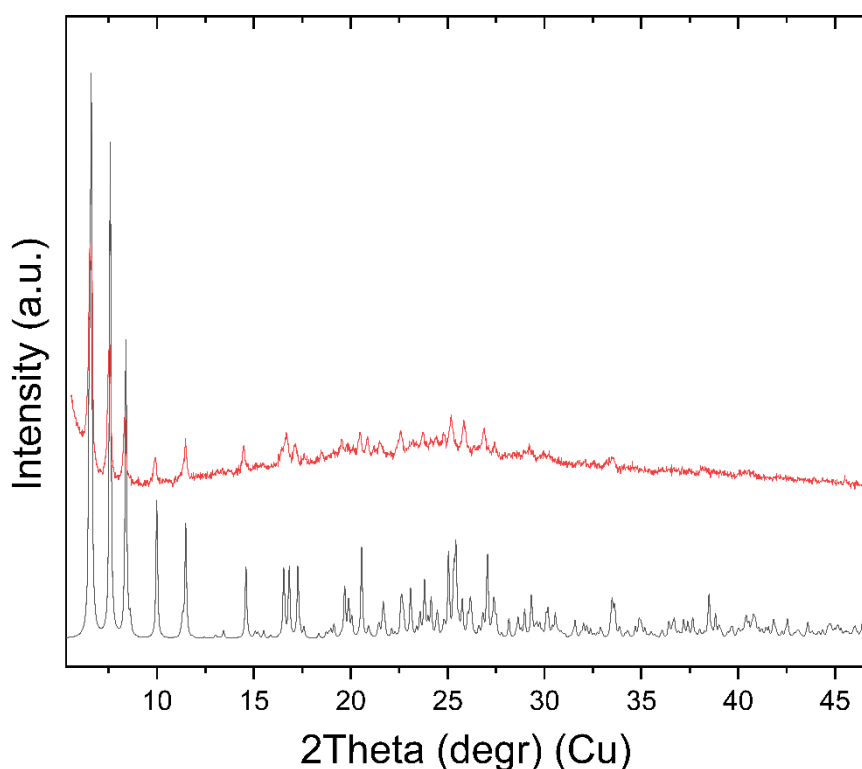
Appendix 2.6: Mass spectrum highlighting the $[[Fe_{30}]-2(lut)+2(MeCN)]^{2+}$ ion at $m/z = 2317$. The experimental data is in grey and the simulation in red.



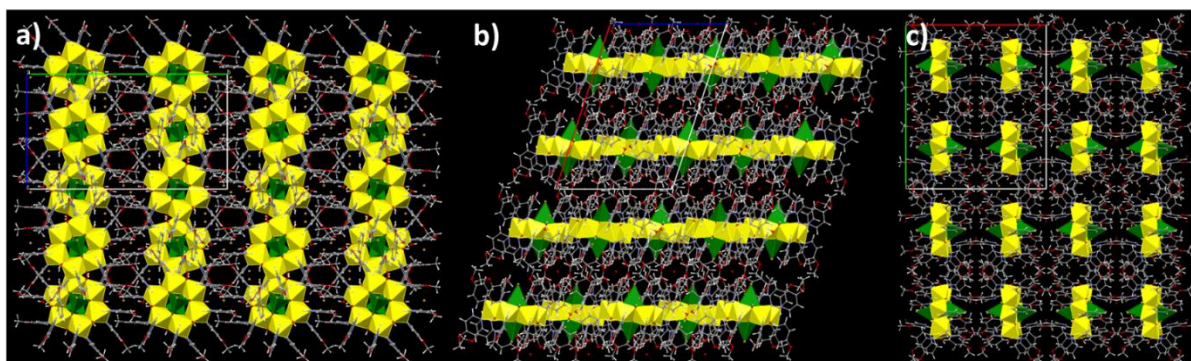
Appendix 2.7: Mass spectrum highlighting the $[[Fe_{30}]-3(lut)+2(MeCN)]^{2+}$ ion at $m/z = 2317$. The experimental data is in grey and the simulation in red.

Appendix 3**Appendix 3.1: Crystallographic details for compound 3.**

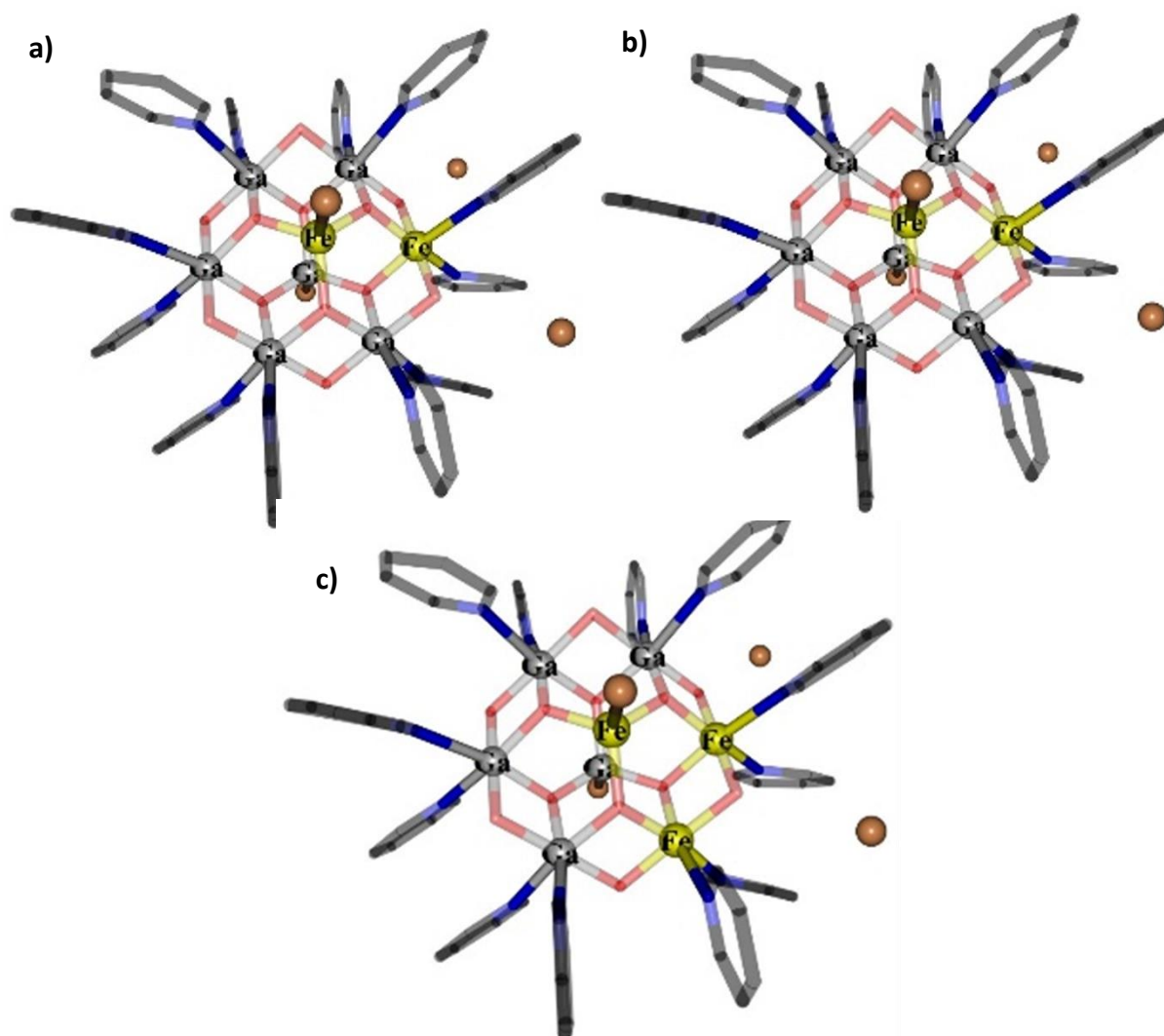
Formula	C ₈₄ H ₁₀₉ Br ₆ Fe ₈ N ₁₄ O _{28.5}	Z'	0.5
<i>D</i>_{calc.}/ g cm⁻³	1.717	Wavelength/Å	0.71073
μ/mm⁻¹	3.457	Radiation type	Mo Kα
Formula Weight	2697.11	θ_{min}/°	1.496
Colour	orange	θ_{max}/°	27.101
Shape	plate-shaped	Measured Refl's.	80637
Size/mm³	0.12×0.06×0.02	Indep't Refl's	11498
T/K	100(2)	Refl's I≥2 (I)	8514
Crystal System	monoclinic	R_{int}	0.1172
Space Group	C2/c	Parameters	736
<i>a</i>/Å	24.5496(9)	Restraints	26
<i>b</i>/Å	27.2170(10)	Largest Peak	1.057
<i>c</i>/Å	16.4374(7)	Deepest Hole	-0.692
α/°	90	GooF	1.018
β/°	108.242(4)	wR₂ (all data)	0.1148
γ/°	90	wR₂	0.1044
<i>V</i>/Å³	10430.9(7)	R₁ (all data)	0.0732
Z	4	R₁	0.0456



Appendix 3.2: Powder X-Ray diffraction pattern of compound 3. Colour code: calculated, black; experimental, red.



Appendix 3.3: Packing diagram of **3** viewed down the three unit cell axes, highlighting the layered packing of the cluster cations in the extended structure. The Fe ions are shown in polyhedral format with octahedral ions in yellow and tetrahedral ions in green.



Appendix 3.4: Dimetallic (a-b) **1A** and **1B**; and (c) trimetallic **1C** iron model complexes for estimating J_{ring} ($\text{Fe}_{\text{Oct}}\text{-Fe}_{\text{Oct}}$) and J_{cap} ($\text{Fe}_{\text{Oct}}\text{-Fe}_{\text{Tetr}}$) magnetic exchange interactions.

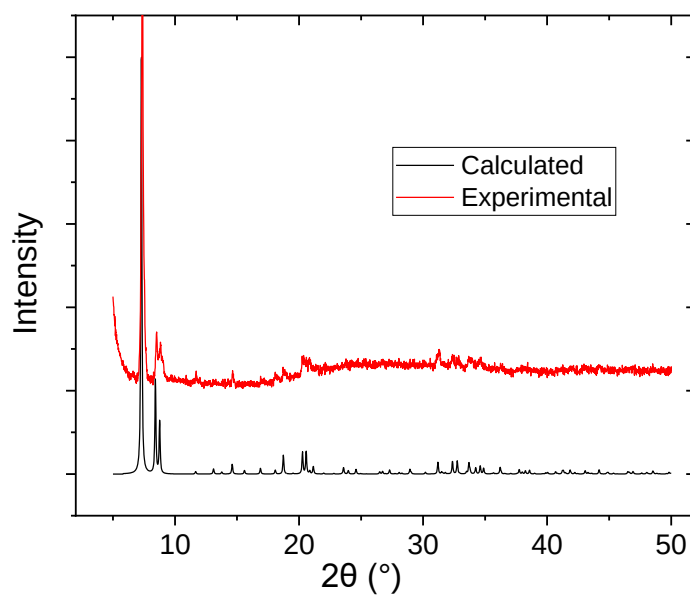
Appendix 3.5: Overlap integral between the 3d orbitals of the Fe^{III} ions in the J_{ring} and J_{cap} exchange pathways. The most significant are highlighted in yellow.

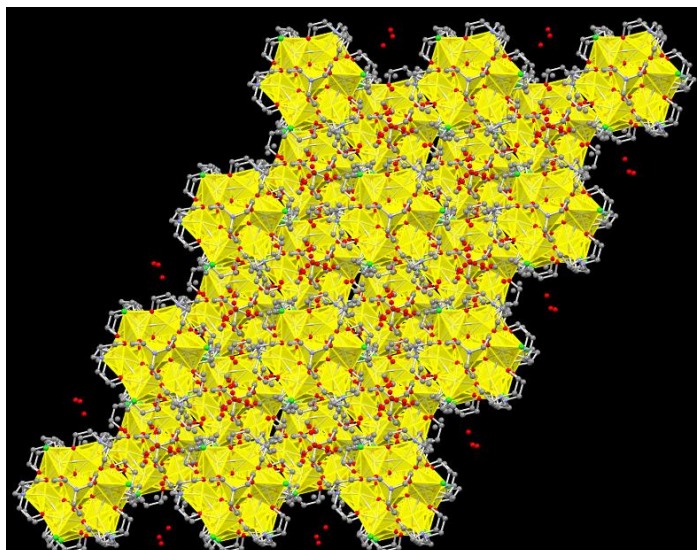
J_{ring}	$\text{Fe}_{\text{Oct}}(\alpha)$	d_{yz}	d_{xy}	d_{xz}	$d_{x^2-y^2}$	d_z^2
$\text{Fe}_{\text{Oct}}(\beta)$	d_{yz}	0.055	0.017	0.011	0.070	0.008
	d_{xy}	0.028	0.021	0.030	0.040	0.041
	d_{xz}	0.028	0.036	0.040	0.056	0.030
	$d_{x^2-y^2}$	0.007	0.035	0.047	0.014	0.015
	d_z^2	0.008	0.001	0.013	0.015	0.001

J_{cap}	$\text{Fe}_{\text{Tetr}}(\alpha)$	d_{yz}	d_{xz}	d_z^2	d_{xy}	$d_{x^2-y^2}$
$\text{Fe}_{\text{Oct}}(\beta)$	d_{yz}	0.079	0.064	0.054	0.023	0.034
	d_{xy}	0.048	0.087	0.000	0.093	0.070
	d_{xz}	0.056	0.006	0.047	0.010	0.006
	$d_{x^2-y^2}$	0.045	0.001	0.066	0.056	0.099
	d_z^2	0.004	0.013	0.023	0.042	0.050

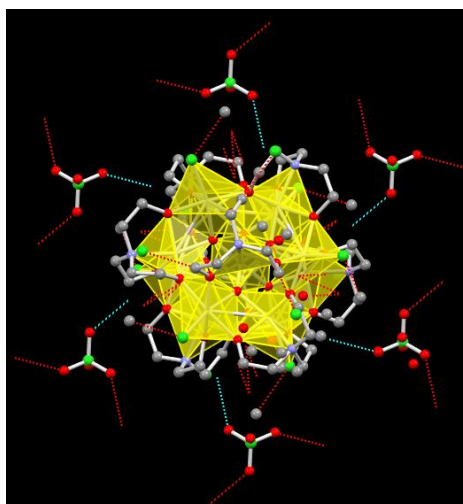
Appendix 4**Appendix 4.1: Crystallographic details of compound 4.**

Formula	C ₄₈ H ₉₇ Cl ₈ Fe ₁₅ N ₈ O ₃₉	Z'	0.166667
<i>D</i>_{calc.}/ g cm⁻³	2.014	Wavelength/Å	0.71073
<i>μ</i>/mm⁻¹	2.865	Radiation type	Mo K _α
Formula Weight	2531.68	θ_{min}/°	3.363
Colour	dark red	θ_{max}/°	29.352
Shape	block-shaped	Measured Refl's.	15300
Size/mm³	0.80×0.50×0.30	Indep't Refl's	3385
<i>T</i>/K	120.0(2)	Refl's I≥2 (I)	2914
Crystal System	trigonal	<i>R</i>_{int}	0.0219
Space Group	<i>R</i> -3	Parameters	304
<i>a</i>/Å	15.1578(5)	Restraints	276
<i>b</i>/Å	15.1578(5)	Largest Peak	1.682
<i>c</i>/Å	31.4738(12)	Deepest Hole	-1.384
α/°	90	GooF	1.134
β/°	90	<i>wR</i>₂ (all data)	0.1400
γ/°	120	<i>wR</i>₂	0.1348
<i>V</i>/Å³	6262.6(5)	<i>R</i>₁ (all data)	0.0756
<i>Z</i>	3	<i>R</i>₁	0.0646

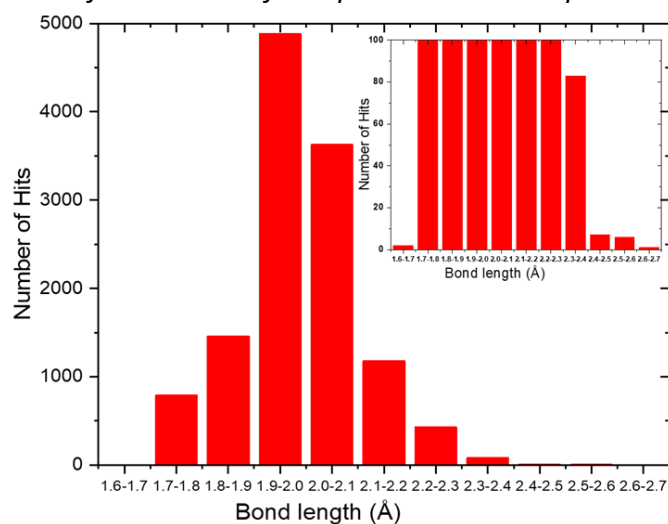
**Appendix 4.1: Powder diffraction pattern of compound 4**



Appendix 4.3: Packing of **4** viewed down the *c* axis



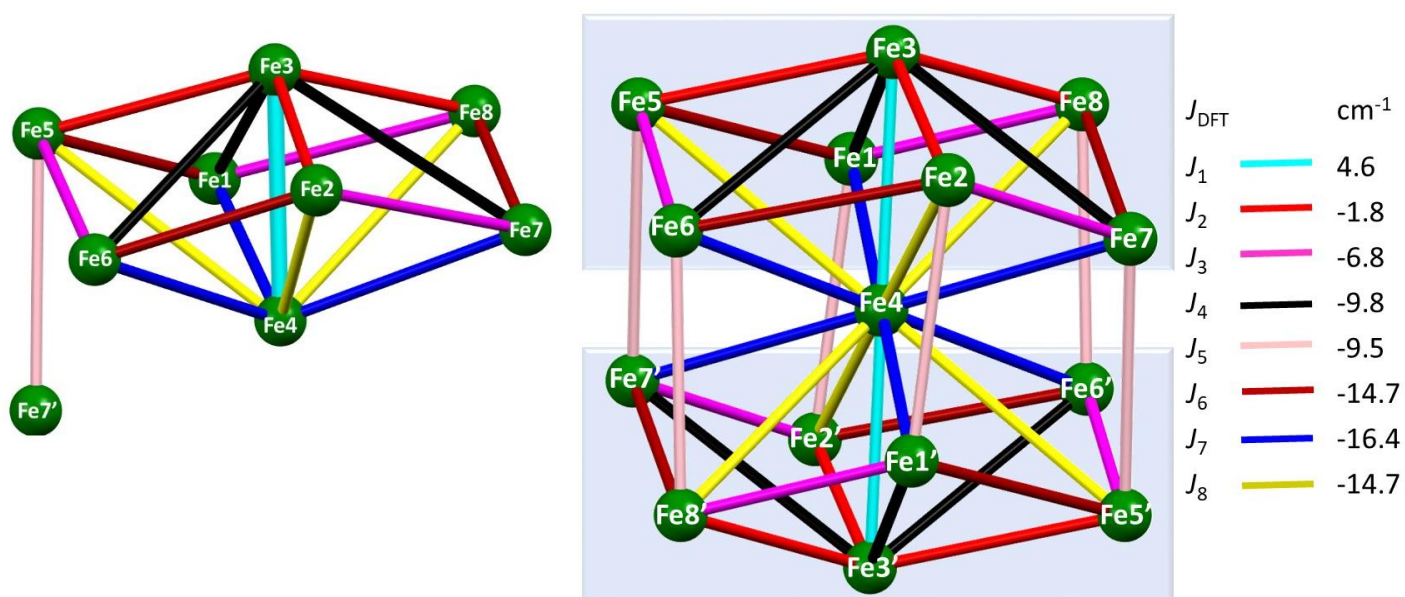
Appendix 4.4: Contacts of the cluster of compound **4** with the perchlorate counterions.



Appendix 4.5: Histogram showing the hits resulting from a bond length search of the Cambridge Structural Database for compounds containing the Fe-O-Fe moiety, with no other restrictions. There are a total of 3378 compounds and 12361 Fe-O bonds. The shortest bond length is 1.651 Å and the longest bond length is 2.629 Å.

Appendix 4.6: Pertinent bond distances and angles of **4**.

Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/ °
Fe1	O1	1.824(8)	Fe1	O1	Fe2	129.4(4)
Fe1	O2	1.986(10)	Fe1	O2	Fe2	116.7(4)
Fe1	O3	1.976(9)	Fe1	O3	Fe2	98.4(3)
Fe1	O5	1.925(4)	Fe1	O5	Fe2	99.8(18)
Fe1	N1	2.226(5)	Fe1	O5	Fe4	117.4(19)
Fe2	Cl1	2.315(15)	Fe3	O4	Fe2	112.9(3)
Fe2	O1	2.047(8)	Fe3	O5	Fe4	86.7(4)
Fe2	O2	1.996(9)	Fe4	O5	Fe2	140.8(2)
Fe2	O3	2.015(8)				
Fe2	O4	1.978(7)				
Fe2	O5	2.025(4)				
Fe3	O4	1.917(7)				
Fe3	O5	2.492(9)				
Fe3	N2	2.336(8)				
Fe4	O5	1.999(4)				



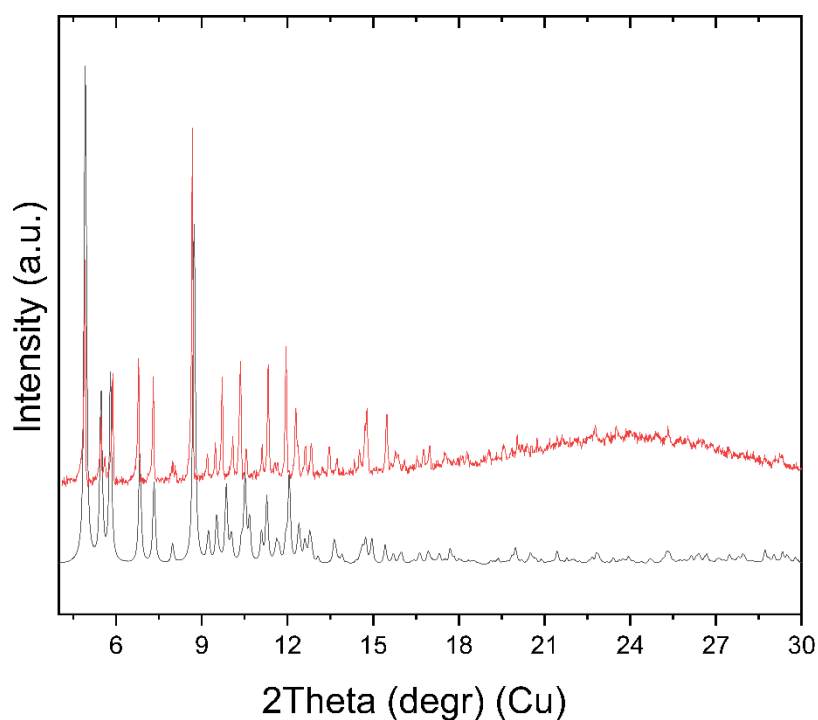
Appendix 4.7: Orbital overlap integrals for compound **4**. $\sum |S_{AB}|$ represents the total OIs between Fe^{III} - Fe^{III} SOMOs. Significant values are highlighted in yellow.

$J_1 = 4.6 \text{ cm}^{-1} (\alpha/\theta)$	$3d_{yz}$	$3d_{xz}$	$3d_z^2$	$3d_{xy}$	$3d_{x^2-y^2}$	$\sum S_{AB} $
$3d_{yz}$	0.028	0.013	0.033	0.013	0.017	0.433
$3d_{xy}$	0.043	0.005	0.035	0.041	0.019	
$3d_{xz}$	0.000	0.001	0.104	0.012	0.004	
$3d_z^2$	0.004	0.012	0.001	0.002	0.008	
$3d_{x^2-y^2}$	0.011	0.006	0.006	0.004	0.011	
$J_2 = -1.8 \text{ cm}^{-1} (\alpha/\theta)$	$3d_{yz}$	$3d_{xz}$	$3d_z^2$	$3d_{xy}$	$3d_{x^2-y^2}$	$\sum S_{AB} $
$3d_{yz}$	0.054	0.007	0.010	0.054	0.004	0.570
$3d_{xy}$	0.003	0.003	0.025	0.017	0.020	
$3d_{xz}$	0.068	0.005	0.009	0.009	0.009	
$3d_{x^2-y^2}$	0.005	0.001	0.006	0.029	0.010	
$3d_z^2$	0.046	0.039	0.018	0.060	0.059	
$J_3 = -6.8 \text{ cm}^{-1} (\alpha/\theta)$	$3d_{yz}$	$3d_{xy}$	$3d_{xz}$	$3d_{x^2-y^2}$	$3d_z^2$	$\sum S_{AB} $
$3d_{yz}$	0.071	0.006	0.037	0.002	0.033	0.761
$3d_{xy}$	0.000	0.004	0.004	0.023	0.095	
$3d_z^2$	0.019	0.032	0.050	0.011	0.022	
$3d_{xz}$	0.029	0.003	0.044	0.162	0.014	
$3d_{x^2-y^2}$	0.012	0.041	0.005	0.024	0.018	
$J_4 = -9.8 \text{ cm}^{-1} (\alpha/\theta)$	$3d_{yz}$	$3d_{xz}$	$3d_z^2$	$3d_{xy}$	$3d_{x^2-y^2}$	$\sum S_{AB} $
$3d_{yz}$	0.040	0.004	0.074	0.011	0.016	0.800
$3d_{xy}$	0.104	0.043	0.026	0.020	0.005	
$3d_{xz}$	0.091	0.029	0.033	0.003	0.005	
$3d_z^2$	0.092	0.041	0.027	0.024	0.012	
$3d_{x^2-y^2}$	0.018	0.003	0.016	0.027	0.036	

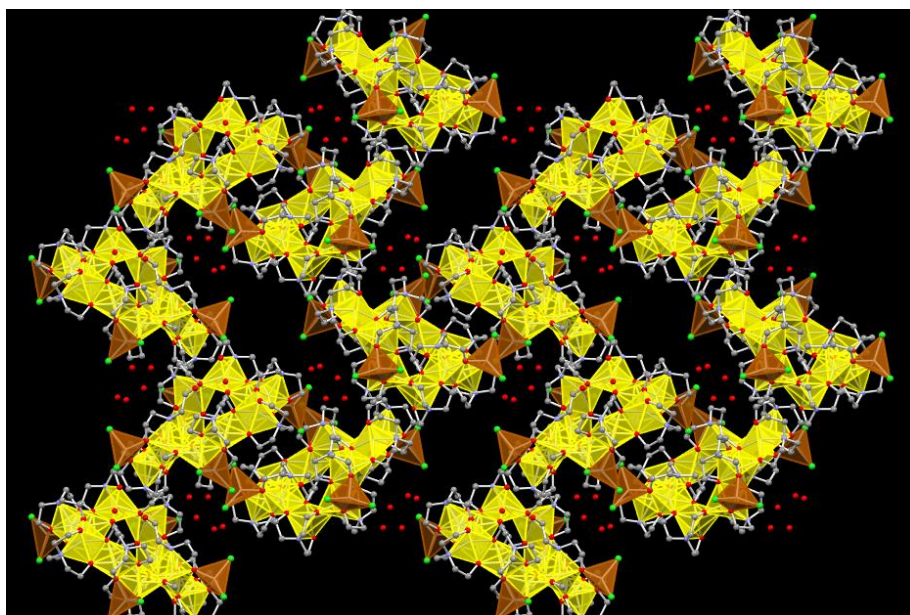
$J_5 = -9.5 \text{ cm}^{-1} (\alpha/8)$	$3d_{yz}$	$3d_{xy}$	$3d_{xz}$	$3d_{x^2-y^2}$	$3d_z^2$	$\Sigma S_{AB} $
$3d_{yz}$	0.033	0.006	0.027	0.004	0.078	0.799
$3d_{xy}$	0.010	0.010	0.014	0.027	0.020	
$3d_{xz}$	0.020	0.026	0.015	0.015	0.054	
$3d_z^2$	0.045	0.010	0.028	0.097	0.040	
$3d_{x^2-y^2}$	0.012	0.062	0.004	0.117	0.025	
$J_6 = -14.7 \text{ cm}^{-1} (\alpha/8)$	$3d_{yz}$	$3d_{xy}$	$3d_{xz}$	$3d_{x^2-y^2}$	$3d_z^2$	$\Sigma S_{AB} $
$3d_{yz}$	0.050	0.088	0.073	0.011	0.014	1.054
$3d_{xy}$	0.013	0.013	0.029	0.088	0.084	
$3d_{xz}$	0.001	0.034	0.009	0.000	0.041	
$3d_z^2$	0.010	0.012	0.006	0.109	0.007	
$3d_{x^2-y^2}$	0.011	0.047	0.002	0.226	0.076	
$J_7 = -16.4 \text{ cm}^{-1} (\alpha/8)$	$3d_{xy}$	$3d_{yz}$	$3d_{xz}$	$3d_z^2$	$3d_{x^2-y^2}$	$\Sigma S_{AB} $
$3d_{yz}$	0.029	0.105	0.047	0.009	0.103	1.221
$3d_{xy}$	0.02	0.068	0.012	0.072	0.066	
$3d_{xz}$	0.006	0.009	0.018	0.025	0.005	
$3d_z^2$	0.005	0.038	0.037	0.129	0.092	
$3d_{x^2-y^2}$	0.095	0.052	0.025	0.139	0.015	
$J_8 = -14.7 \text{ cm}^{-1} (\alpha/8)$	$3d_{yz}$	$3d_{xy}$	$3d_{xz}$	$3d_z^2$	$3d_{x^2-y^2}$	$\Sigma S_{AB} $
$3d_{yz}$	0.007	0.011	0.013	0.006	0.001	1.063
$3d_{xy}$	0.010	0.204	0.166	0.097	0.020	
$3d_{xz}$	0.026	0.002	0.006	0.037	0.019	
$3d_{x^2-y^2}$	0.008	0.044	0.049	0.091	0.066	
$3d_z^2$	0.027	0.038	0.007	0.055	0.053	

Appendix 5**Appendix 5.1: Crystallographic details for 5.**

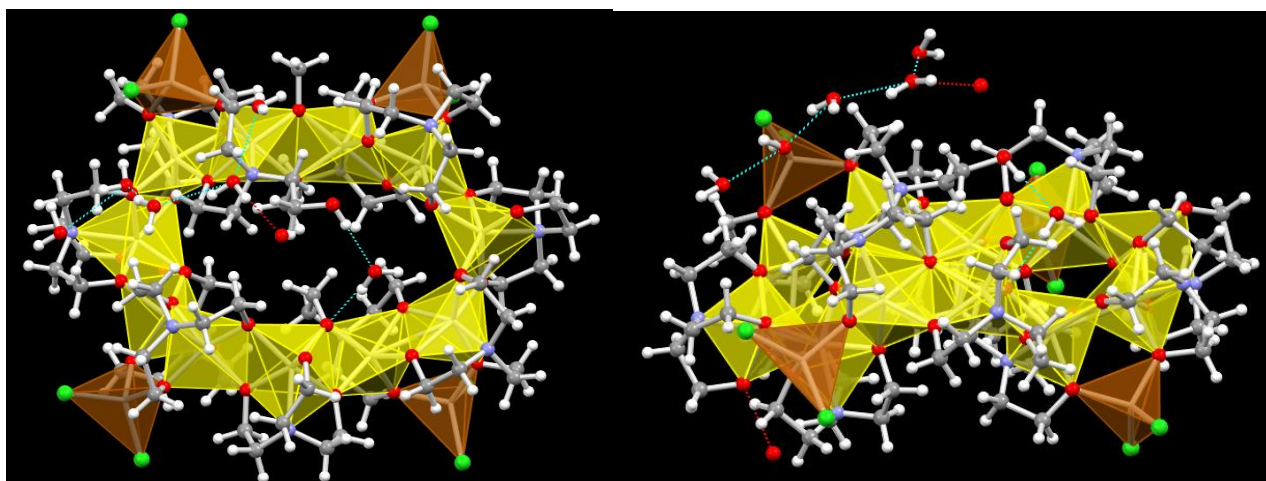
Formula	C ₆₇ H ₁₄₈ Cl ₈ Fe ₁₁ N ₁₁ O ₄₀ Zn ₄	Z'	1
<i>D</i>_{calc.}/ g cm⁻³	1.494	Wavelength/Å	0.71073
<i>μ</i>/mm⁻¹	2.155	Radiation type	MoK _α
Formula Weight	2907.39	θ_{min}/°	2.116
Colour	yellow	θ_{max}/°	20.831
Shape	rod-shaped	Measured Refl's.	303804
Size/mm³	0.18×0.06×0.04	Indep't Refl's	13524
<i>T</i>/K	100.4	Refl's I≥2 (I)	11513
Crystal System	monoclinic	<i>R</i>_{int}	0.0896
Space Group	<i>P</i> 2 ₁ / <i>n</i>	Parameters	1272
<i>a</i>/Å	18.5721(9)	Restraints	19
<i>b</i>/Å	32.2714(16)	Largest Peak	0.777
<i>c</i>/Å	21.8429(11)	Deepest Hole	-0.569
α/°	90	GooF	1.019
β/°	99.171(2)	<i>wR</i>₂ (all data)	0.0707
γ/°	90	<i>wR</i>₂	0.0670
<i>V</i>/Å³	12924.1(11)	<i>R</i>₁ (all data)	0.0396
<i>Z</i>	4	<i>R</i>₁	0.0307



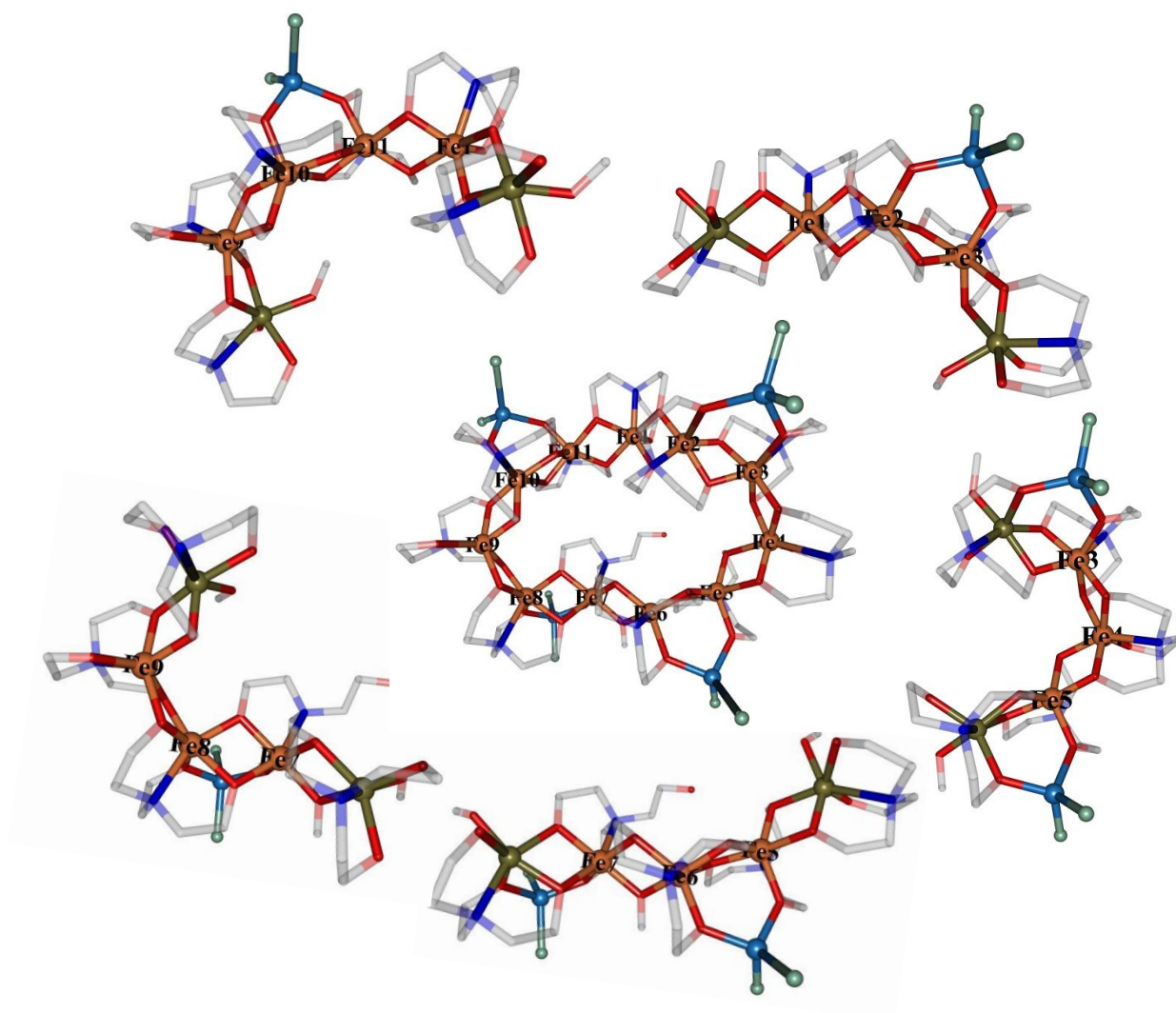
Appendix 5.2: Powder diffraction pattern of compound 5. Colour code: Black, predicted pattern; Red, experimentally determined pattern.



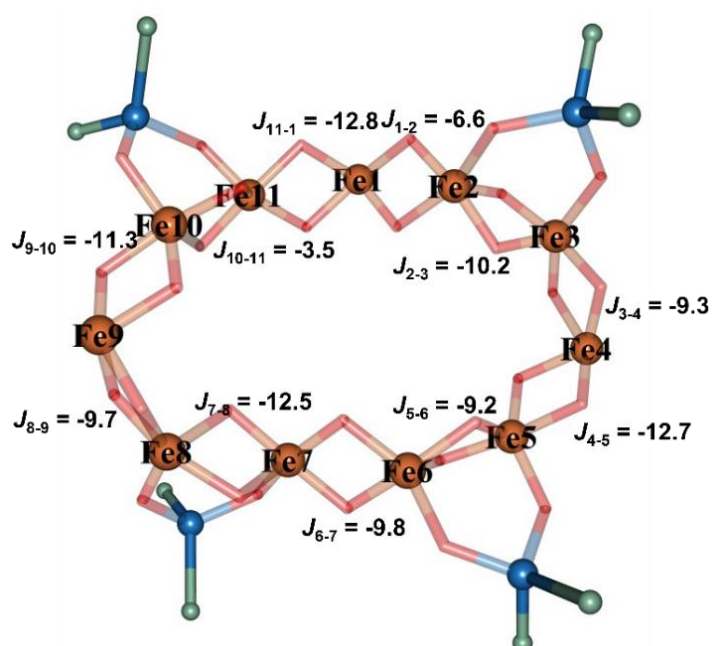
Appendix 5.3: Packing of **5** viewed down the *a* axis.



Appendix 5.4: Orthogonal views of **5** showing the network of H-bonded water solvates present between clusters.



Appendix 5.5. The model complexes used for the DFT calculations of **5** (outer circle) in a visualisation of their derivation from the cluster of **5** (centre). Colour Code: Fe, orange; Zn, cyan; Ga, brown; Cl, green; N, dark blue; O, red; C, grey. Hydrogens omitted for clarity.



Appendix 5.6: Metal-oxo core of **5** with the calculated J_{DFT} values for each bridge labelled. (Units of $J_{\text{DFT}} = \text{cm}^{-1}$). Colour Code: Fe, orange; Zn, cyan; Cl, green; O, red; Hydrogens omitted for clarity

Appendix 5.7: Results of bond valence sum calculations of **5**

Atom	FeIII	ZnII
Zn01	2.454	2.04
Zn02	2.43	2.02
Zn03	2.4	2
Zn04	2.35	1.96
Fe01	2.91	2.52
Fe02	3.223	2.786
Fe03	3.05	2.64
Fe04	2.9	2.5
Fe05	2.95	2.55
Fe06	2.89	2.5
Fe07	3.01	2.6
Fe08	3.02	2.61
Fe09	2.95	2.55
Fe10	2.93	2.54
Fe11	2.98	2.57

Appendix 6**Appendix 6.1: Crystallographic details for compound 6 in both crystal systems 6a and 6b.**

Compound	6a	6b
Formula	C ₉₅ Cl ₈ Fe ₁₂ H _{178.5} N _{19.5} O ₄₀ Zn ₄	C ₉₆ Cl ₈ Fe ₁₂ H ₁₇₈ N ₂₄ O ₃₇ Zn ₄
$D_{calc.}/\text{g cm}^{-3}$	1.589	1.545
m/mm^{-1}	12.553	1.972
Formula Weight	3309.69	3475.89
Colour	yellow	light yellow
Shape	rod-shaped	rod-shaped
Size/mm ³	0.37×0.08×0.06	0.34×0.11×0.10
T/K	120.00(10)	120.00(10)
Crystal System	monoclinic	tetragonal
Space Group	$C2/c$	$I4_1/a$
$a/\text{\AA}$	35.0610(3)	35.7793(4)
$b/\text{\AA}$	11.66710(10)	35.7793(4)
$c/\text{\AA}$	33.8615(2)	11.6698(3)
$\alpha/^\circ$	90	90
$\beta/^\circ$	93.1460(10)	90
$\gamma/^\circ$	90	90
$V/\text{\AA}^3$	13830.52(19)	14939.2(5)
Z	4	4
Z'	0.5	0.25
Wavelength/ $\text{\AA}$	1.54184	0.71073
Radiation type	Cu K_α	Mo K_α
$Q_{min}/^\circ$	3.534	3.340
$Q_{max}/^\circ$	75.899	25.671
Measured Refl's.	74972	74482
Indep't Refl's	14317	7077
Refl's $I \geq 2\sigma(I)$	12850	6165
R_{int}	0.0712	0.0573
Parameters	765	396
Restraints	49	0
Largest Peak	0.906	1.170
Deepest Hole	-0.874	-1.112
GooF	1.030	1.127
wR_2 (all data)	0.1591	0.1496
wR_2	0.1532	0.1451
R_1 (all data)	0.0615	0.0789
R_1	0.0568	0.0693

Appendix 6.2 Selected bond distances of compound **6** in crystal systems **6a** and **6b**.

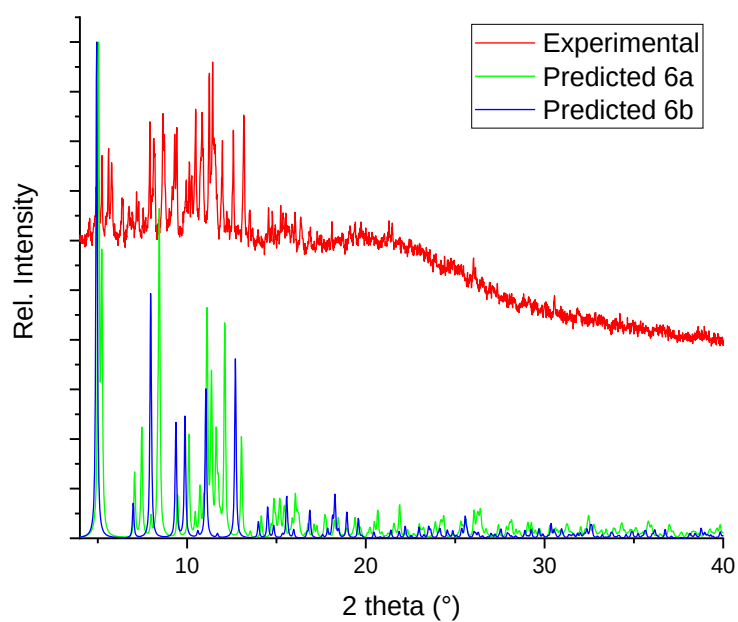
6a	C2/c		6b	I41/a	
Atom	Atom	Distance (Å)	Atom	Atom	Distance(Å)
Fe1	O1	1.976	Fe1	O9 ¹	1.99
Fe1	O2	2.031	Fe1	O3	1.982
Fe1	O5	1.961	Fe1	O2	2.029
Fe1	O3	1.965	Fe1	O4	1.954
Fe4	O12	2.021	Fe1	O1	1.978
Fe4	O10	1.983	Fe3	O9	1.971
Fe4	O11	1.960	Fe3	O3 ²	2.086
Fe4	O13	1.973	Fe3	O6	2.017
Fe4	O9	1.998	Fe3	O8	1.872
Fe6	O18	1.969	Fe3	O7	2.014
Fe6	O11	2.117	Fe2	O5	1.954
Fe6	O16	2.031	Fe2	O2	1.979
Fe6	O15	2.026	Fe2	O6	1.981
Fe6	O17	1.871	Fe2	O4	2.028
Fe3	O10	2.096	Fe2	O7	1.976
Fe3	O6	2.033			
Fe3	O9	1.973			
Fe3	O7	2.011			
Fe3	O8	1.868			
Fe2	O2	1.970			
Fe2	O6	1.979			
Fe2	O5	2.015			
Fe2	O7	1.985			
Fe2	O4	1.977			

Appendix 6.3: Selected bond angles of compound **6** in crystal systems **6a** and **6b**.

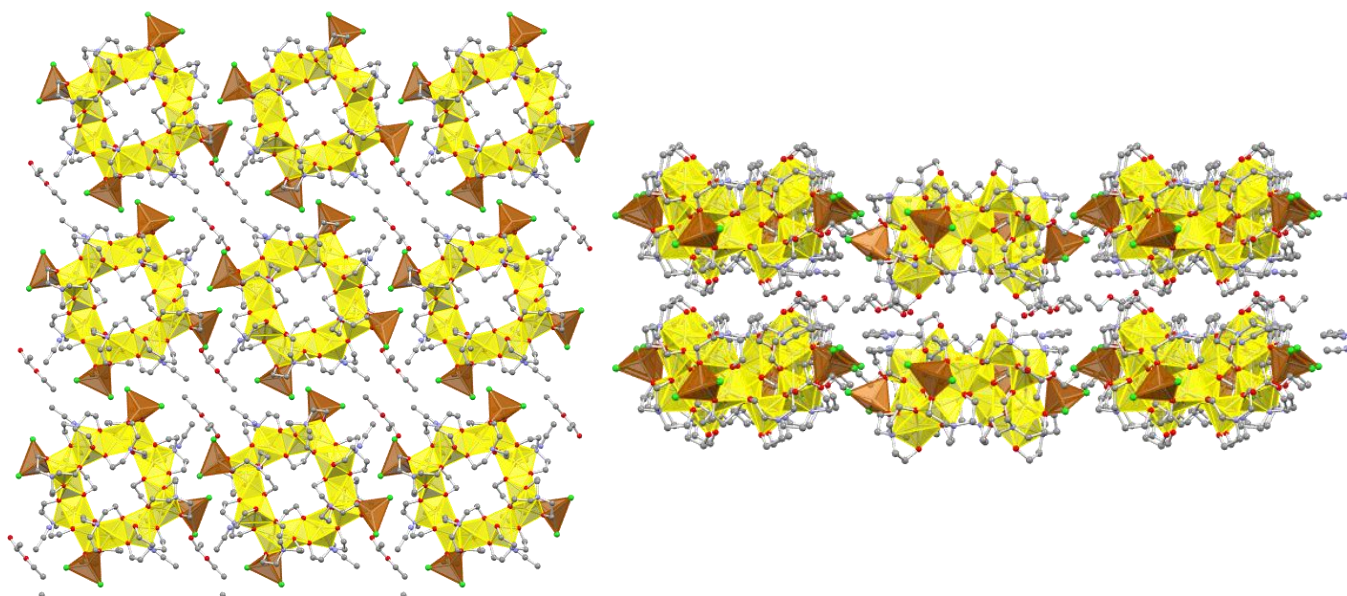
6a				6b			
C2/c				I41/a			
Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
Fe5	O12	Fe4	103.04	Fe3	O9	Fe1 ²	105.55
Fe6	O18	Fe1 ¹	106.1	Fe1	O3	Fe3 ²	101.61
Fe4	O10	Fe3	101.53	Fe2	O2	Fe1	102.21
Fe1	O1	Fe6 ¹	101.7	Fe2	O6	Fe3	105.91
Fe2	O2	Fe1	102.36	Fe1	O4	Fe2	103.17
Fe4	O11	Fe5	103.61	Fe2	O7	Fe3	106.21
Fe2	O6	Fe3	105.73				
Fe5	O16	Fe6	106.31				
Fe1	O5	Fe2	103.24				
Fe3	O9	Fe4	105.45				
Fe5	O15	Fe6	106.45				
Fe2	O7	Fe3	106.35				

Appendix 6.4: Results of Bond valence sum calculations for **6** (taken from **6a**).

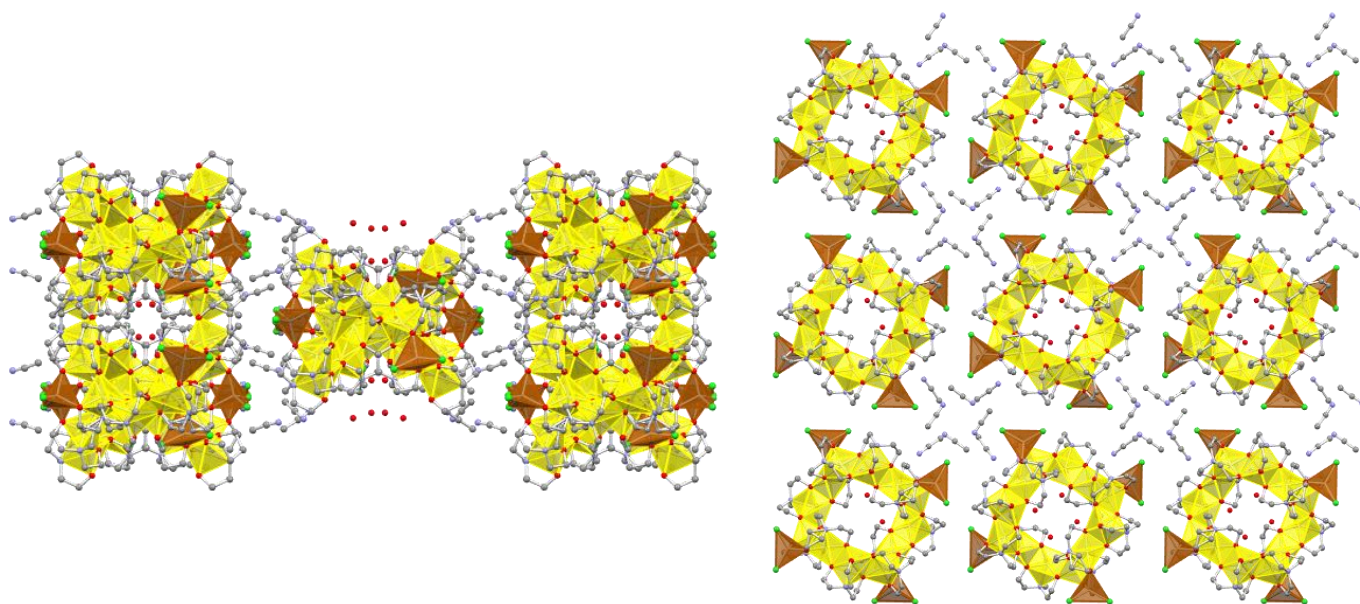
Atom	Fe ^{III}	Zn ^{II}
Zn1	2.36	2.04
Zn2	2.39	1.98
Fe1	3.01	2.69
Fe2	3.02	2.61
Fe3	2.95	2.55
Fe4	3.02	2.62
Fe5	2.95	2.55
Fe6	2.93	2.53



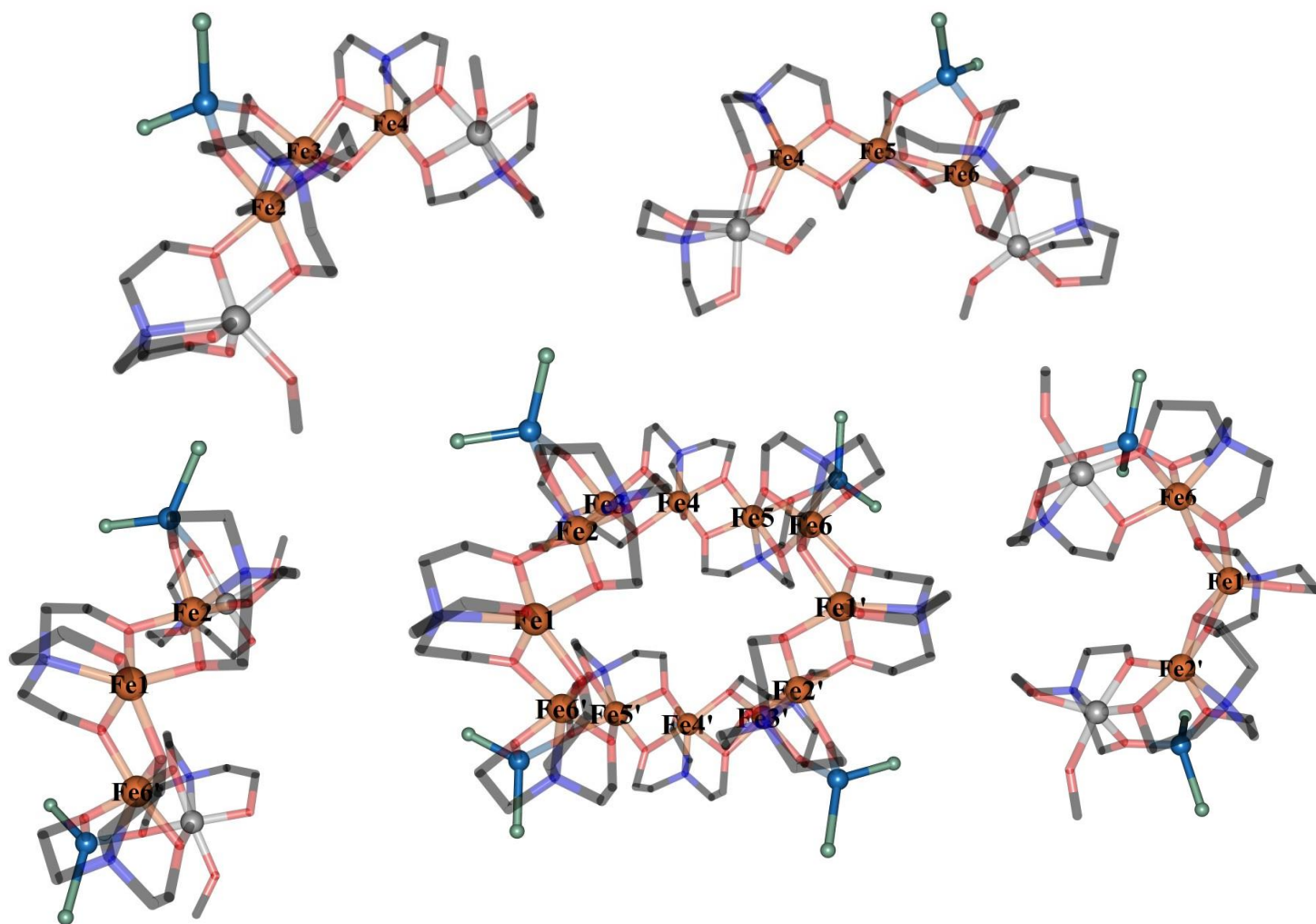
Appendix 6.5: Powder diffraction pattern of **6**. The experimental pattern contains the peaks expected for both **6a** and **6b** indicating that both systems are present in the powder.



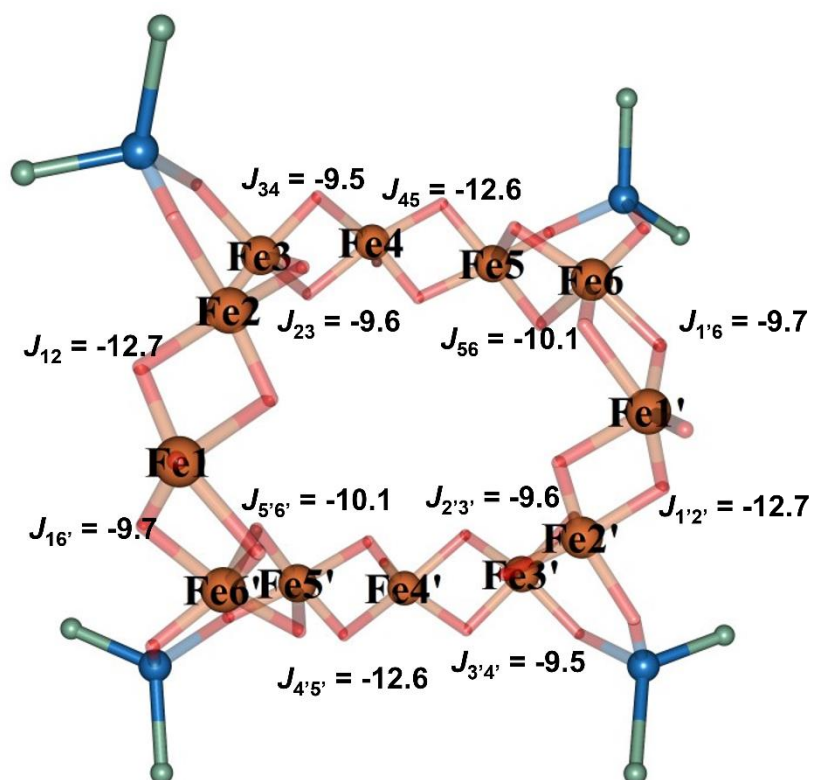
Appendix 6.6: Packing of **6** in crystal system **6a** viewed down the *a* (left) and *c* (right) axes.



Appendix 6.7: Packing of **6** in crystal system **6b** viewed along the *a* (left) and *c* (right) axes.



Appendix 6.8: The model complexes used for the DFT calculations of **6** (outer circle) in a visualisation of their derivation from the cluster of **6** (centre). Colour Code: Fe, orange; Zn, cyan; Ga, light grey; Cl, green; N, dark blue; O, red; C, dark grey. Hydrogens omitted for clarity



Appendix 6.9: Metal-oxo core of **6** with the calculated J_{DFT} values for each bridge labelled. (Units: $J_{\text{DFT}} = \text{cm}^{-1}$). Colour Code: Fe, orange; Zn, cyan; Cl, green; O, red; Hydrogens omitted for clarity

Appendix 7**Appendix 7.1: Crystallographic details for compounds 7, 8 and 9.**

Compound	7	8	9
Formula	C ₇₂ H ₇₂ Cl ₄ Fe ₂ N ₁₂ Ni ₅ O ₂₈	C ₇₂ H ₇₂ Cl ₄ Co ₅ Fe ₂ N ₁₂ O ₂₈	C ₇₂ H ₇₂ Cl ₄ Fe ₂ N ₁₂ O ₂₈ Zn ₅
$D_{calc.}/g\text{ cm}^{-3}$	1.478	1.484	1.478
m/mm^{-1}	1.465	10.847	5.404
Formula Weight	2100.46	2101.56	2133.76
Colour	dark green	black	brownish red
Shape	irregular-shaped	block-shaped	irregular-shaped
Size/mm ³	0.79×0.54×0.23	0.21×0.09×0.06	0.15×0.11×0.08
T/K	120.02(18)	120.00(10)	120.01(10)
Crystal System	trigonal	trigonal	trigonal
Space Group	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$
$a/\text{\AA}$	14.6722(5)	14.6653(4)	14.6917(2)
$b/\text{\AA}$	14.6722(5)	14.6653(4)	14.6917(2)
$c/\text{\AA}$	37.9658(11)	37.8761(10)	38.4674(7)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	90	90	90
$\gamma/^\circ$	120	120	120
$V/\text{\AA}^3$	7078.0(5)	7054.7(4)	7190.6(2)
Z	3	3	3
Z'	0.166667	0.166667	0.166667
Wavelength/ $\text{\AA}$	0.71073	1.54184	1.54184
Radiation type	Mo K_α	Cu K_α	Cu K_α
$Q_{min}/^\circ$	3.381	3.671	4.166
$Q_{max}/^\circ$	29.379	75.774	75.861
Measured Refl's.	27277	25228	16239
Indep't Refl's	3904	3261	3292
Refl's $I \geq 2\sigma(I)$	3317	2641	2951
R_{int}	0.0301	0.0788	0.0466
Parameters	177	186	177
Restraints	0	0	0
Largest Peak	1.220	0.985	1.677
Deepest Hole	-2.123	-1.363	-1.043
GooF	1.044	1.052	1.057
wR_2 (all data)	0.1847	0.1836	0.1915
wR_2	0.1741	0.1726	0.1858
R_1 (all data)	0.0650	0.0737	0.0642
R_1	0.0569	0.0627	0.0598

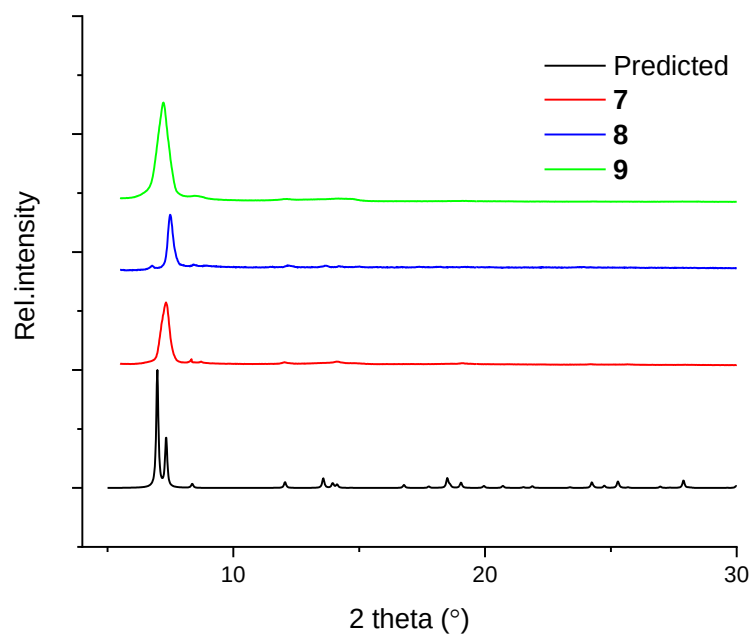
Appendix 7.2: Results of bond valence sum calculations for metal sites of **7**, **8** and **9**.

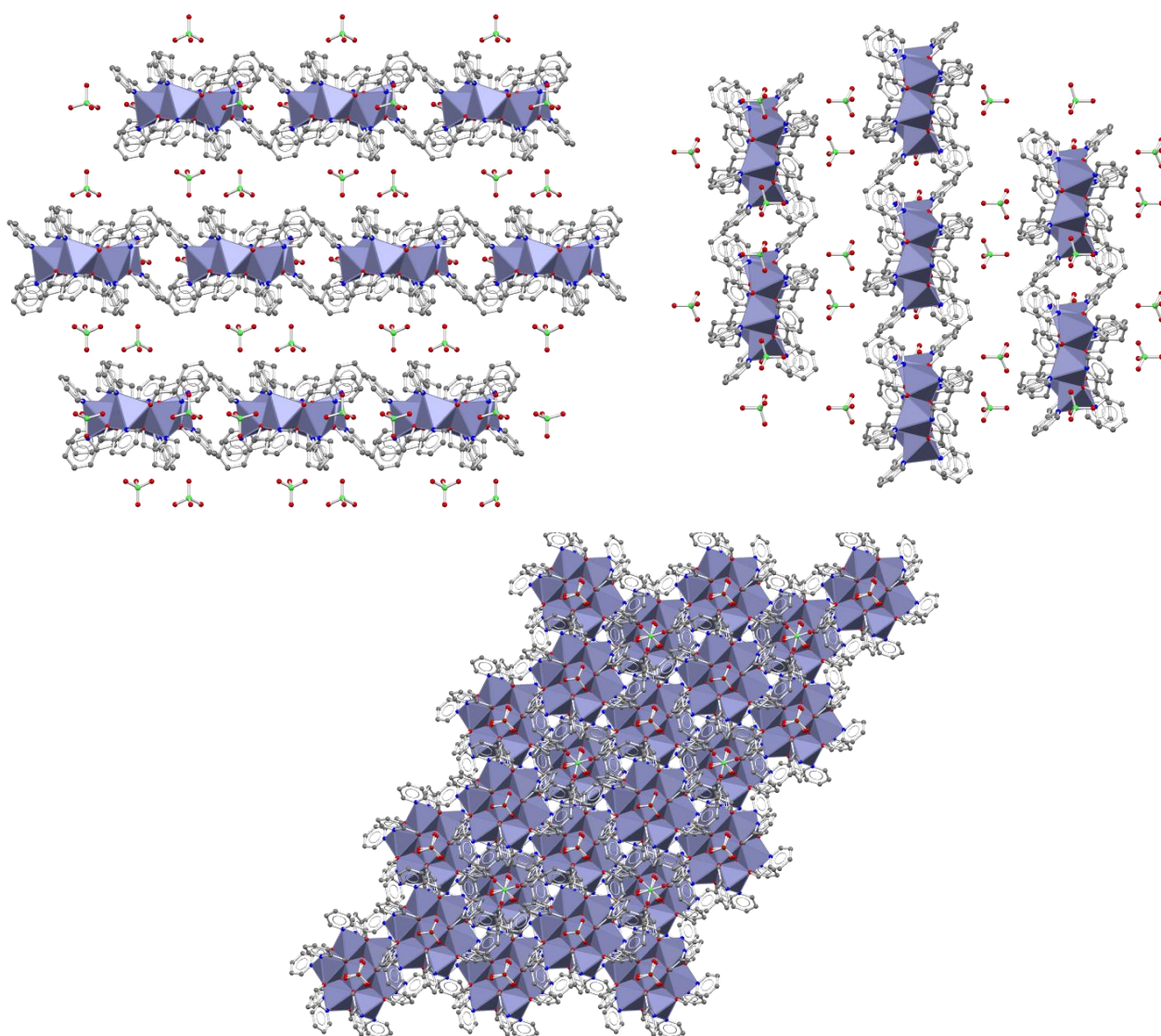
7	Fe	M	8			9		
Ni1	2.61	2.01	Co1	2.32	1.91	Zn1	2.35	2.02
M2	2.87	2.21	M2	2.75	2.21	M2	2.59	2.25

Appendix 7.3: Selected bond angles for **7**, **8** and **9**.

7				8			
Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
Ni01	O1	M02 ²	96.16(9)	Co1	O1	M2 ²	95.69(10)
M02	O1	M02 ²	96.85(9)	M2	O1	M2 ²	97.40(10)
M02	O1	Ni01	98.73(9)	M2	O1	Co1	98.81(11)
M02	O2	Ni02 ²	103.69(10)	M2	O2	M2 ²	104.98(12)

9			
Atom	Atom	Atom	Angle (°)
Zn01	O1	M02 ²	96.84(10)
M02	O1	M02 ²	97.41(10)
M02	O1	Zn01	99.77(10)
M02	O2	M02 ²	105.22(11)

**Figure 7.3:** Powder diffraction patterns of **7**, **8** and **9**.



Appendix 7.4: Crystal packing of **7**, **8** and **9** along the *a* axis (above left), *b* axis (above right) and *c* axis (below center).