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<td>Author(s)</td>
<td>Meally, Seán Tomás</td>
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<tr>
<td>Publication Date</td>
<td>2012-11-02</td>
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<tr>
<td>Item record</td>
<td><a href="http://hdl.handle.net/10379/3398">http://hdl.handle.net/10379/3398</a></td>
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By

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Thesis submitted for the degree of Ph.D. of the National University of Ireland, Galway

School of Chemistry,
National University of Ireland, Galway

2012

Supervisor: Dr. Leigh F. Jones
Head of School: Prof. Paul V. Murphy
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Declaration

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

Signature

___________________________
Seán T. Meally
Abstract

National University of Ireland, Galway

ABSTRACT OF THESIS submitted by Seán Tomás Meally for the degree of Ph.D., entitled
Investigating the Structural and Magnetic Characteristics of Polynuclear Complexes
including the Solid-State Hosting Abilities of \([M_7] \{M = \text{Ni(II), Zn(II), Co(II/III)}\}\)

Month and Year of Submission: November 2012

We report the synthesis, structural and magnetic characterisation of a family of planar,
pseudo metallocalix[6]arene disc-like complexes (1-10 and 14-21) of general formula
\([M_7(OH)_6(L_x)_6](NO_3)_2 \{M = \text{Ni(II), Zn(II), Co(II/III)}\}\) and \(L_xH\) are Schiff base ligands: \(L_1H = 2\text{-iminomethyl-6-methoxyphenol}, L_2H = 4\text{-bromo-2-iminomethyl-6-methoxyphenol}, L_3H = 2\text{-iminophenyl-6-methoxyphenol}\). Each member exhibits a double-bowl pseudo metallocalix[6]arene topology of which the \([M(II)_7]\) units in complexes 1-8 stack on top of one another to generate molecular host cavities in the solid-state, capable of encapsulating a wide variety of guest molecules (MeCN, NO_2Me, MeOH). Encapsulation of the reactive aromatic species 2-Furaldehyde and 3-Furaldehyde was also achieved in the form of complexes 14-18; presence of guest furaldehyde species being detected via spectroscopic methods. Dc magnetic susceptibility measurements were performed on complexes 2, 4, 8 and 9 which revealed weak ferromagnetic intramolecular exchange between the Ni(II) ions in both complexes \([(\text{MeOH})_2\subset\text{Ni(II)}_7(\text{OH})_6(L_1)_6](\text{NO}_3)_2\) (2) and \([(\text{MeCN})_2\subset\text{Ni(II)}_7(\text{OH})_6(L_2)_6](\text{NO}_3)_2\) (4), while similar studies on complexes (8-9) revealed weak ferro- and ferrimagnetic behaviour respectively. The ‘⊂’ notation is used to indicate guest presence. Attempts at extending the molecular cavities present in these systems via functionalisation of the utilised Schiff base ligand, led to the isolation of the heptanuclear complexes (19-21) of general formula \([\text{M(II)}_7(\text{OMe})_4(\text{OEt})_2(L_4)_6](\text{NO}_3)_2\) (where \(M = \text{Ni(II), Zn(II), Co(II)}\) and \(L_4H = 4\text{-phenyl-2-iminomethyl-6-methoxyphenol}\)).

In efforts to expand our family of solid-state host-guest disc-like complexes the Schiff base ligand was further functionalised and other M(II) salt precursors were utilised. These
investigations instead afforded entirely different complex topologies including the heterometallic tetranuclear complexes of general formula \([\text{Na(I)}_2\text{M}_2(\text{X})_2(\text{L}_1)_4(\text{Y})_2]\) \{where \(\text{M} = \text{Fe(III)}, \text{X} = \text{MeO}^-, \text{Y} = \text{NO}_3^- \) \((24)\); \(\text{M} = \text{Ni(II)}, \text{X} = \text{N}_3^- \) and \(\text{Y} = \text{MeCN} \) \((25)\)\}, each comprising the molecular butterfly topology. Magnetic susceptibility measurements of these complexes highlight antiferromagnetic and ferromagnetic coupling in \((24)\) and \((25)\) respectively, with the inclusion of the azide bridging anion \((\text{N}_3^-)\) in the latter affording the observed ferromagnetic coupling between the Ni(II) ions. We also report the formation of the heterometallic molecular cage \([\text{Na(I)}_2\text{Ni(II)}_2(\text{L}_1)_6](\text{ClO}_4)\) \((28)\) which exhibits a rare trigonal bipyramidal core topology. In addition we report the isolation of the tetranuclear cubane clusters \([\text{Mn(III)}_3\text{Mn(IV)}_1(\text{O})_3(\text{OEt})(\text{OAc})(\text{L}_1)_3]\) \((30)\) and \([\text{Ni(II)}_4(\mu_3-\text{OMe})_4(\text{L}_5)_4(\text{MeOH})_4]\) \((32)\) \{where \(\text{L}_5\text{H} = 2\text{-imino-6-methoxyphenol}\)\}. Dc and ac magnetic susceptibility studies on complexes \((30)\) and \((32)\) reveal \(S = 9/2\) and \(S = 4\) spin ground states, as a result of ferri- and ferromagnetic exchange coupling in complexes \((30)\) and \((32)\) respectively.
Acknowledgements

I would like to thank my supervisor Dr. Leigh Fôn Jones for all his guidance and support in the completion of this work. A HUGE THANK YOU.

I would like to thank my fellow Jones-group members Nelly Berg, Cecelia McDonald and Edel Houton for their camaraderie and support over the last three years.

Of course, I cannot forget my brothers-in-arms in Inorganic Chemistry: Noel Byrne, Robert Whiriskey, Pól MacFhionnghaile, Fergal Coleman and Peter Dunne. ‘The ladies’: Máiréad Crushell, Marian Vignoles, Yun Hu, Nicole Walshe, Jolanta Karpinska, and ‘Frau’ Nóra (Crushell eile!).

Neither can I forget our resident Cork man, Mr. Jim Cotter for his assistance (“James can I get into the store please?”) and entertainment. When you would least expect it, one would be in their office and hear the sound of either a fiddle or a tin-whistle coming from around the corner. Of course, Jim-Sir would always oblige you with a tune accompanied by a hearty laugh.

I gratefully acknowledge the assistance and wise council of Prof. Patrick McArdle not only during my postgraduate but also throughout my undergraduate years. Your stories will be retold for many years to come. I will always remember one story in particular: crystal growing via bag-pipes.

I would also like to thank Dr. Andrea Erxleben and Dr. Tim Higgins for their assistance over the last three years (not least of which been the organization of undergraduate practicals).

And an honorary mention to our very own Prof. Mike Hynes whose stories will always be formidable opposition to Pat’s best!

I would like to thank the following people for measurements and council:

Prof. Euan K. Brechin and the entire Brechin Group at the University of Edinburgh for magnetic measurements. A BIG THANK YOU!!!

Dr. Giannis S. Papaefstathiou for 3-D connectivity work.

Dr. Stergios Piligkos (University of Copenhagen) for fitting of magnetic data.
Prof. David Collison and the crew from the University of Manchester for EPR work.

Dr. Nicholas P. Power (London West Bank University) for advice on ligand synthesis.

Dr. Alan G. Ryder and Ms. Edel Houton for fluorescence measurements.

Dr. Guan-Nan Wang and Mr. Mark Farrell for advice on sugar work.

A word of mention to the Italians (past and present): Diego Montagner, Danielle Lo Re and Carmela ‘Melania’ Napolitano

Over the last three years, the Jones Laboratory has been host to several undergraduate 4th year guest students, not least of which been our very own Cecelia ‘Purple Fury’ McDonald. And also:

Patrick Kiely                        Gráinne Henry
Paul Joyce                          Rebecca Pigot
Nicholas Dolan                      Louise Macken
Kieran Connele                      Teresa Whyte

‘Best of luck to them all in their future studies and careers’

And just a few things from over the years:

Cecelia: You will, regardless of your future hair colour, always be known as ‘Purple Fury’.

Christopher: Like I said Chris we were never lost, just “masters of our own destiny”.

Edel: “Aw, it’s so cute”.

Pól: Pól Macfhi…..a…..e?

Nóra: “Frau”. “put on your damn safety glasses Nóra”.

Fergal: Galahad anyone? “But Seán, did you never just want to get locked?”


Jolanta: “…so where did you steal the car from Seán?”

Jim: “Fear mór macânta”.

13
Máiréad: “I will kill you with a spoon”

Rob: Nana nana nana nana nana nana nana nana……BATMAN

Noel: “But you need soakage Seán”.

Pat McArdle: “A wall built at night never looks good in the morning”.

Leigh: “they’re not crystals……just smeg”. Grrrrrr!!

I would like to thank all the academic staff in the School of Chemistry, in particular Dr. Dónal Leech and Prof. Patrick McArdle who were the referees for my IRCSET Scholarship.

I would also like to thank all the technical and secretarial staff in the School of Chemistry for all their assistance over the last three years without which this work would never have been possible: Bernie (baking discussions!!), Marian (CHN analyses…and lots of them!! AND MS Analyses – especially towards the end of my write-up!), Judy, Karen, Gerry (stores and a veritable lake of liquid N\textsubscript{2}!!), Séamus (you can fix anything) agus Séamus eile (Mr. NMR), Dermot, Róisín (Ms. NMR), Ger and last but not least Jim.

To all postgraduates (past and present) in the School of Chemistry: Thank You

And finally, thank you Dad, Mam, Elizabeth, Maria and Ted.

For the last time then (hopefully!),

*Slán go fóill,*

Seán J.
Publications

1. **A F-bridged Mn(II) Molecular Square**
   Meally, S. T., Mason, K., McArdle, P., Brechin, E. K., Ryder, A. G., Jones, L. F.
   *Chem. Commun.*, **2009**, *7024*-7026

2. **Planar [Ni(II)] discs as double-bowl, pseudo metallocalix[6]arene host cavities**
   Meally, S. T., Karotsis, G., Brechin, E. K., Papaeftathiou, G. S., Dunne, P. W.,

   Meally, S. T., McDonald, C., Karotsis, G., Papaeftathiou, G. S., Brechin, E. K.,

   Meally, S. T., McDonald, C., Kiely, P., Taylor, S. M., Brechin, E. K., Jones, L. F.,

5. **Homo- and Heterometallic Planes, Chains and Cubanes (Manuscript in Preparation)**
   Meally, S. T., Taylor, S. M., Brechin, E. K., Piligkos, S., Jones, L. F., To be submitted
   to *Dalton Transactions*.

‘The Changing Face of Chemistry’

The dictionary tells us that Chemistry is the “science that deals with the characteristics of simple substances (elements), the changes that take place when they combine to form other substances and the laws of their behaviour under various conditions”.1 It is essentially the study of matter and the changes which it may undergo. The first chemical reaction which human beings would have witnessed would have been the creation of fire arising from natural phenomena such as lightning striking the earth or in regions of volcanic activity. From these humble beginnings would spark millennia of chemical advances; the majority of which have arisen over the past 400 years or so. From iron smelting, gunpowder invention and early alchemic endeavours, to the discovery of the electron, synthesis of sugars and the development of the Haber-Bosch process for the industrial production of ammonia; essential in the manufacture of artificial fertilizers used in the agri-industry.

Monumental though they may be, the advance of chemistry has not halted at these discoveries and has over the last 50 years made giant leaps, penetrating every facet of society. Be it medicines, synthetic clothes, plastics, detergents and increasingly bio-fuels, modern society simply could not function without the ubiquitous presence of chemistry in our daily lives.
‘Thoughts on a PhD’

The beginning of any work is always difficult. The task at hand can seem daunting, overwhelming, intimidating and at times demoralising and disheartening. These adjectives and others (albeit less colourful) are certainly applicable to a postgraduate student (including this one) making those first few hammer-blows across the keyboard of their computer upon embarking on the adventure of writing up their PhD thesis. Fortitude is required, so they say, and one must persevere through thick and thin, through the sunny days and the rainy days, through the straight-forward chapters as well as those which prove considerably more involved. Perseverance throughout is what is required to get through as well as the knowledge that the task will eventually be complete.
DEO FAVENTE

With the favour of God

[Original Crest and Motto of UCG / NUIG]
Chapter One

Supramolecular Chemistry: An Introduction
1.1 Introduction

1.1.1 Overview

The work undertaken in this doctoral thesis, does not seek to re-invent the wheel, neither does it endeavor to revolutionise the field of inorganic chemistry or that of chemistry as a whole. The purpose of this thesis is to expose the reader to novel coordination compounds which exhibit interesting structural and magnetic characteristics and which may ultimately lead to the generation of functional materials for useful applications. The work presented here will, as intimated above, involve a thorough analysis of the structural and magnetic properties of a wide variety of polynuclear, coordination complexes and a discussion of the potential applications of same. Additional techniques including EPR spectroscopy (Appendix: Section B) and SQUID magnetometry (Section 1.5.3.3.1) will also be detailed; thus a concise discussion of the use of these analytical techniques in the study of polynuclear complexes will be given. One of the major elements to the research undertaken here, however, is that of supramolecular ordering of polynuclear systems and the generation of molecular cavities and containers for the encapsulation of a variety of guest species; thus a detailed review of such supramolecular systems and their many applications will also be undertaken.

1.2 Supramolecular Chemistry: Early Beginnings

**Container:** an object for holding or transporting something. At least that is the definition of ‘container’ which is afforded to us by the Oxford English Dictionary. Certainly a lackluster, clinical description for a rapidly-developing branch of supramolecular chemistry which has over the last 20 years become an increasingly important focus for research groups worldwide.

Little did Alfred Werner realize, in 1893, when he proposed his theory of coordination chemistry and the existence of a secondary valence for transition metal ions,\(^1\text{-}^4\) that coordinate-bond based systems would conceive disparate research offshoots such as supramolecular chemistry and protein / enzyme mimetics. Supramolecular chemistry, however, has given birth to an additional research field which exploits our aforementioned ‘container’; that of molecular containment and host-guest architectures.
1.2.1 Supramolecular Host-Guest Chemistry: The Torch is Lit

Supramolecular chemistry has fascinated and thrilled inorganic chemists, of wide ranging disciplines, for many years owing to its great use in the synthesis of polymetallic complexes towards important applications such as gas storage,\(^5\) catalysis,\(^6,7\) medical imaging (MRI contrast agents)\(^8-11\) and drug discovery.\(^12\) Often described as chemistry beyond the molecule, supramolecular methods involve the synthesis of covalently-bonded building blocks (molecules / complexes) linked together by non-covalent forces such as hydrogen bonding (H-bonding), \(\pi\)-\(\pi\) stacking and electrostatic interactions. Since nearly all biological behaviour, as well as many newly emerging materials, involve and / or are based almost entirely on non-covalent interactions, it is imperative that a brief description of H-bonding, arguably the most important of such interactions, be first given prior to delving deeper into more involved aspects of supramolecular chemistry.

1.2.2 Hydrogen Bonding

H-bonding is evident in \(\beta\)-pleated sheets and \(\alpha\)-helices of peptide chains (proteins) as well as in base pairing in DNA and involves electrostatic interactions between a donor H atom (D) {attached to a highly electronegative atom such as oxygen} and other electronegative species {acceptors (A)} including, but not limited to, N, O, and F i.e. a D-H-⋯A interaction (Figure 1). Hydrogen bonding distances typically range from 2.50-2.80 Å with intermolecular interactions over 3.0 Å also often observed. An important subclass of hydrogen bonding are C-H-⋯O interactions which are commonly observed in supramolecular systems. C-H-⋯O interactions are considerably weaker in comparison to their more electronegative counterparts (e.g. N-H-⋯O), although the acidity of the C-H proton can be augmented by nearby electronegative atoms. The H atom therefore acts as a bridge between two electronegative elements and although the strength of H-bonds is only about 10 % that of covalent bonds, the importance of hydrogen bonds cannot be underestimated. In modern materials (e. g. fire-resistant Kevlar), long chains of molecules line up parallel to each other and are held together strongly by hydrogen bonding which affords the material great durability.
**Fig. 1(a)** H-bonding is observed in α-helices and β-pleated sheets of a protein (EBF1).\textsuperscript{13} Black arrows illustrate H-bonding interactions (not all shown). Coils represent α-helices while folds represent β-pleated sheets.

![Diagram](image)

**Fig. 1(b)** Base pairing in DNA is effected by hydrogen bonding between hydrogen bond donor (D) atoms on one residue and hydrogen bond acceptor (A) atoms on another residue.

A rapidly growing research field incorporating supramolecular methods, and the focus of our studies, is that of the development of host-guest systems via the targeted structural manipulation of polymetallic complexes and their associated molecular assemblies (Figure 2).
Supramolecular host-guest interactions have been observed for a multitude of different systems in recent years. Some notable examples include a family of zinc-dimERIC capsules based on C-propylpyrogallol[4]arene (PgC₃), which contained a 3-Methylpyridine (3-MePy) guest molecule and which also incorporated eight 3-MePy molecules ligated at the metal centres of the resulting capsule (Figure 3).¹⁴

Host-guest systems have also been observed for resorcinarene-based species involving Co(II) ions, from which molecular cages are formed which selectively encapsulate isomers of xylene (i.e. encapsulation of p-xylene is 20 x 10³ times more favourable than that of m-xylene).¹⁵ This in itself is a prime example of how guest structure / conformation has such a
dramatic effect on the ability to interact with the host framework. Other examples of such host-guest capsules include anion encapsulation of $\text{PF}_6^-$ and $\text{ClO}_4^-$ within bowl-like shaped capsules formed by tetracopper(II) oxamato species,\textsuperscript{16} inclusion of neutral $\text{NO}_2\text{Me}$ and $\text{Et}_2\text{O}$ species within the cavities of $\pi$-metalated cyclotrimeratrylenes\textsuperscript{17} as well as encapsulation of magnetic nanoparticles, organic dyes and luminescent quantum dots within spherical cavities formed by $\text{Zn(II)}$-bix species (bix = 1,4-bis(imidazol-1-ylmethyl)benzene), developed by Imaz et al.\textsuperscript{18}

Host-guest chemistry was initially applied to purely organic systems such as calixarenes (cyclic arrays of n-phenol moieties linked by methylene groups), carcerands and cyclodextrins and the docking of yet further organic molecules therein.\textsuperscript{19-22} A representative calixarene species is illustrated in Figure 4 below with functionalisation of such species also possible. For instance, calixarenes may be functionalised at their upper or lower rim to allow for encapsulation of a variety of different guest species towards a myriad of applications.

![Fig. 4](image)

**Fig. 4** Functionalisation of calixarenes may be effected at the upper or lower rim of the ring.
The diagram above illustrates $p$-tert-butyl-calix[4]arene whereby the upper-rim position has been functionalised with a tert-butyl (tBu) group.

It soon became apparent that by incorporation of metal centres into these organic entities and the subsequent construction of supramolecular frameworks, based on intermolecular non-covalent interactions, it was possible to furnish architectures of far greater structural and chemical complexity; and thus materials with enhanced applications. Such self-assembled systems are being increasingly used towards encapsulation of more chemically robust and useful guest species.
1.2.3 Exemplar Host-Guest Systems: The Foundations are Laid

Fujita and co-workers recently described a wide range of polymetallic-based supramolecular containers and the individual building blocks which assemble these complex architectures.\textsuperscript{19} A brief discussion of these systems is vital as they essentially lay the foundation for more complex and intricate host-guest vessels upon which many modern applications of supramolecular host-guest systems are based. Particular attention will be afforded to the use of such containers as functional host-guest materials.

The founding member of the Fujita group’s cage-like supramolecular architectures was an octahedral cage based on Pd(en) and Pt(en) building blocks (Capsule A) (en = ethylenediamine), which occupy each of an octahedral assembly’s six corners and incorporating the planar, tridentate ligand 1,3,5-tris(4-pyridyl)triazine as scaffolding for four of this octahedron’s eight faces (Figure 5).\textsuperscript{19,23}

![Octahedral Capsule A](image)

**Fig. 5** Octahedral Capsule A developed by the Fujita group. The M vertices comprise individual ‘en’ building blocks.\textsuperscript{19,23}
It is reported that a hydrophobic cavity is generated from this octahedral geometry; a factor which plays a pivotal role in host-guest systems in general. For example, in systems where there is a desire to isolate reactive intermediates or molecules which, in general, have a fleeting existence in aqueous environments, trapping of these species within such hydrophobic cavities provides the facility to study them before decay. In addition, it is likely that the pronounced stability of this relatively complex architecture, as well as its ability to encapsulate a broad range of organic species including alkanes and aromatics stems from the occupancy of alternating faces of the octahedron by the chelating ligand 1,3,5-tris(4-pyridyl)triazine. Hypothetically, if all faces were occupied by this ligand the system as a whole would be far more unstable due to steric interactions between face-occupying units; thus less efficient an enclosure for molecular guests. In addition, it is also reported that the Pt(II) analogue of this octahedral system has a far greater capacity to exist in strongly acidic/basic environments; which is advantageous when attempting encapsulation of species which can only exist in such stark environmental conditions. An extension of this octahedral environment are the bowl- and prism-shaped supramolecular entities [Capsules B (Figure 6) and C (Figure 7) respectively] also developed by Fujita and co-workers, which again incorporate six Pd(II) ions and the face-occupying tris(3-pyridyl)triazine ligand.\textsuperscript{19,24,25}

\textbf{Fig. 6} Bowl-like architecture (Capsule B) developed by Fujita et al. Each Pd(II) unit comprises an ‘en’ moiety.\textsuperscript{19,24,25}

The bowl structure differs from the octahedral species in two respects: 1) the tip of the square-pyramidal architecture is essentially capped by two Pd(II) ions and 2) every face of the pyramid is capped by one triazine ligand. In addition the prism may be differentiated from
the octahedral species by virtue of inclusion of an additional ligand molecule (tetra-methyl-4,4-bipyridine) in the host framework (Figure 7). Fujita and co-workers also reported that the cavity could be expanded by extending the length of the bipyridine edge or ‘pillar’ ligand, for encapsulation of multiple hydrophobic and organic guest species.

**Fig. 7** Prism-like system (Capsule C) developed by Fujita and co-workers, with potential container applications.\(^{19,24,25}\)

A variety of other model systems have been reported which exhibit molecular flask characteristics. These utilise an array of non-covalent interactions to selectively encapsulate small guest molecules. One such model compound / flask and a striking example of the use of H-bonding towards the self-assembly of covalently-bound units, are the H-bonded supramolecular capsules (Capsules D1 and D2) developed by Rebek et al (Figures 9 and 10).\(^{26,27}\)

**Fig. 8** Glycoluril building block utilised in the synthesis of supramolecular cage D1.
The core architecture of the first capsule is purely organic based on the glycoluril building block (Figure 8), whilst that of the second comprises an aromatic-panel-capped calix[4]resorcinarene (Figure 10). The glycoluril building block (as will be seen later) is utilised in the construction of cucurbit[n]uril species (CBₙ), where n is the number of glycoluril moieties.

![Glycoluril-based capsule](image)

**Fig. 9** Glycoluril-based capsule (Capsule D1) exhibits a dome-like architecture.²⁶,²⁷

The cylindrical nature of the resultant capsule (akin to a double-bowl structure where the open end of one bowl is placed on top of another) is essentially an elongation of the glycoluril species and forms as a direct consequence of the presence of hydrogen-bond donors and acceptors located at the interface of the individual, interlocking capsular units. This breed of supramolecular host presents itself as a beautiful example of how solvent molecules, docked within cavities formed by the capsule components through H-bonding, may be replaced by larger, more useful, molecular species as chosen by the researcher.
Fig. 10 Double-bowl-like cylindrical species comprising aromatic-panel-capped calix[4]resorcinarene species.\textsuperscript{26,27}

For instance, Rebek and co-workers found that several solvent molecules could be replaced by a single, larger molecule such as adamantane (analogues of which have been used to combat flu and parkinsons disease)\textsuperscript{28} or ferrocene carboxylic acid (analogues of which have been used as novel anticancer species).\textsuperscript{29-34} They postulated that such substitution-based encapsulation was based on entropy effects; one bound molecule as opposed to many.

An increasingly popular interest of research clusters involves the development of synthetic, self-assembled systems capable of mimicking biological processes such as photosynthesis and metal-ion transport.\textsuperscript{19,35} Porphyrin building blocks are often used for this purpose stemming from their well-defined and characterized redox activity (of relevance in cytochrome P450 chemistry). To this end Slone and Hupp have developed two such porphyrin-based species (Capsules E\textbf{1} and E\textbf{2}): the former a molecular-square assembly incorporating a Re(I) metal centre and bis(pyridyl)porphyrinatozinc ligands (Figure 11),\textsuperscript{36} while the latter exhibits a cage-like architecture and incorporates Zn(II) and Sn(II) nuclear centres (Figure 12).\textsuperscript{37}
Fig. 11 Molecular-square assembly comprising a Re(I) centre and Zn(II)-based panels.\textsuperscript{36}

It was postulated that by utilising more-labile Zn-py bonds that the initial molecular-square assembly could be extended to generate a larger cavity; and likely then encapsulation of an array of guest entities. Functionalisation of such coordinating axial ligands affords an additional pathway for selective guest encapsulation. For instance Slone and Hupp reported that by utilising different ligands, cavities could be generated which are either sterically bulky (using ligand A) or one which is chiral in nature (using ligand B) (Figure 13).\textsuperscript{19,37}

Fig. 12 Extension of the molecular square in Figure 11 via incorporation of Sn(II) panels.\textsuperscript{37}
Fig. 13 Sterically bulky carboxylate ligand (left) and chiral ligand (right) utilised by Slone and Hupp in capsule generation.

Additionally since the initial report of Capsules **E1** and **E2**, Hupp and co-workers have succeeded in generating Zn(II)-porphyrin-based molecular prisms and boxes, with the box-like systems showing particular promise in catalysing the methanolysis reaction of aromatic phosphate triesters shown in Figure 14.\(^{38,39}\)

![Zn(II)-porphyrin building block and resultant cage](image)

Fig. 14 Zn(II)-porphyrin building block (left) and resultant cage (right) used to catalyse methanolysis in aromatic phosphate triesters.\(^{38,39}\)

Aromatic phosphate triesters are quite useful in evaluating the catalytic characteristics of such porphyrin systems as a result of their efficient turnover (Section 1.2.4.2), which in turn stems from weak binding between the host porphyrin and ester species.

Finally, a more recent addition to the breadth of techniques utilised for the generation of self-assembled molecular cavities is that of the hydrophobic effect. The theory behind cavity
formation (via the hydrophobic effect) is essentially the desire of hydrophobic molecules to exist in an environment as free from water as possible (Figure 15).

**Fig. 15** Schematic representation of the hydrophobic effect. H₂O = blue, organic hydrophobic molecules = green.

In terms of self-assembly, templating hydrophobic molecules (the guests) provide a platform for the non-covalent association of covalently-bound units. A prime example of such a hydrophobically-driven self-association has been reported by two of the forerunners in this research field, Gibb and Gibb, who were successful in isolating a dimeric cavitand capsule (Capsule F) (Figure 16).⁴⁰

**Fig. 16** Hydrophobically-generated self-assembly Capsule F.⁴⁰
The self-assembly of this capsule was reported to be unfeasible in the absence of the templating, hydrophobic guest. In addition to allowing for the existence of the cavitand species, it is reported that its kinetic stability depends on the size, shape and water solubility of the guest. Such supramolecular assemblies have also been utilised by Giles and co-workers in the preparation of carboxylate- (RCOO\(^{-}\)) and hydroxide (OH\(^{-}\))-coated cavitand frameworks (Figure 17), assembled via the hydrophobic effect and capable of encapsulating a wide variety of guest species within molecular capsules formed therein.\(^{41}\)

![Fig. 17 Cavitand cage framework developed by Giles and co-workers.\(^{41}\)](image)

Cavitand assemblies are not the only macrocyclic species utilised in hydrophobic cavity generation, as evidenced by the isolation of cyclodextrin-\(^{42}\), cucurbit[8]uril\(^{43}\) and porphyrin-based\(^{44}\) species towards the development of supramolecular host-guest architectures. Examples of these macrocyclic cavity-precursor species are shown in Figure 18 below.
1.2.4 Exploitation of Molecular Flasks: Towards Synthesis and Catalysis

We have already encountered a small subset of the wide-ranging variety of supramolecular, host-guest self-assemblies; popularly referred to as molecular flasks. It has been shown how these self-assembled systems can encapsulate a wide variety of small guest molecules ranging from simple solvent molecules (i.e. H₂O) to more structurally complex guests such as alkanes and planar aromatic species. The question arises however: *When complementary guest molecules are held, simultaneously, in such tightly-bound cavities, is there potential to effect a reaction between such guest species or even catalyse the reaction between same?* This was one of the most thought-provoking questions presented to chemists in the infancy of supramolecular host-guest chemistry and is one of continuing intrigue to this day.
The answer is a resounding yes. Molecular flasks have indeed been shown to act as molecular media for the facilitation of reactions between guest species (Figure 19); with initial theories of host-guest complexes (towards enzyme mimetics) having been proposed as early as the 1970s. Basic kinetic theory describes how the rate of a reaction is directly proportional to the concentration of reagents present and when guest molecules are isolated within such tightly-bound cavities, their effective concentration increases; consequently resulting in a dramatically increased reaction rate. While the ultimate goal of supramolecular chemists is to isolate host-guest systems exhibiting the naturally-occurring lock-and-key characteristics of enzymes (enzyme mimics), such success has not yet been fully realised; although quite interesting findings have been garnered in such pursuits. Reaction between two molecular entities will often be hindered due to steric factors. However, containment of these same molecules within the aforementioned tightly-enclosed cavities causes the guests to adopt conformations such that reaction between the two becomes favourable. These modified conformations would be exceedingly disfavoured exterior to the molecular flask (host). Preorganisation of these conformers (and transition states) allows for accelerated or unusual reactivity. Such ‘social isomers’ arise from this preorganisation and are realised as a result of intermolecular interactions between guests and ultimately their orientation with respect to the host framework. Specifically two (usually) guests within a molecular capsule have limited mobility and intermolecular interactions between the two can only occur at specific sites, thus reorientation of one (or both) molecules affords a pathway which allows the two guest species to react (Figure 20). Such social isomers are being increasingly used in the determination of reaction outcomes within host-guest architectures.
It is evident that a vast array of supramolecular host capsules exists and that intermolecular interactions between molecular building blocks are paramount in the self-assembly process. They have been shown to be capable of accommodating a broad range of guest species with the nature of a proposed guest being directly dependent on the interior chemical environment of the host capsule. The questions now arise however: What specific types of guests take up residence within the host cavity and what applications may be derived from such host-guest associations? The next section will strive to address these questions and afford a deeper insight into the self-assembly process.

1.2.4.1 Supramolecular Host Capsules: Ideal Candidates as Chemical Reactors

As intimated previously, molecular capsules rely on both the increased concentration and increased effective molarity which exists within the flask to yield reaction species which are otherwise extremely difficult to isolate and inherently unfavoured in the ‘regular’ chemical environment. As an introduction to the breadth of host capsules (and reactions which occur therein) which exist, the discussion will initially involve an overview of a recent article by Fujita and co-workers. Discussions will also highlight a tremendous range of example reactions, where the molecular capsule / cavity and increased effective molarity have allowed for investigations and analyses of everyday organic reactions on a molecular scale and hence the isolation of normally unfavored species. From Diels-Alder\textsuperscript{57,58} and photochemical dimerisations\textsuperscript{59,60} to radical additions\textsuperscript{61} and photochemical oxidation reactions, the molecular

![Fig. 20 Social isomerisation within supramolecular capsules, realised here in the reorientation of the aromatic species.\textsuperscript{56}](image)
cavity approach has penetrated deep within the heart of synthetic (particularly organic) chemistry.

The reaction between a diene and a dienophile, commonly known as the Diels-Alder reaction, has been widely exploited in terms of supramolecular host-guest chemistry and the design of molecular cavities for useful applications. The Diels-Alder reaction itself is one of the most important reactions in organic chemistry, stemming from its use in the synthesis of morphine, cholesterol, the anti-inflammatory cortisone, vitamin B12, the anti-cancer agent Taxol along with many others (Figure 21). The Diels-Alder reaction, reported by Rebek and co-workers, between p-benzoquinone and cyclohexadiene was observed to exhibit a dramatically increased reaction rate upon encapsulation of the dienophile (benzoquinone), within the ball-shaped cavity of Capsule D1 (discussed previously) and subsequent gradual addition of the diene to the host framework.  

![Fig. 21 Cholesterol (left) and morphine (right) are synthesized via the Diels-Alder reaction.](image)

NMR titrations are invaluable in the investigation of such molecular-level organic reactions for two principal reasons: 1) NMR spectroscopy is an extremely sensitive analytical tool and 2) guest diene occupancy can be monitored in real time. NMR titrations essentially monitor the difference in chemical shift between free and bound guest species and this can be used to determine such parameters as binding constants and bound guest concentration.

**1.2.4.2 Catalysis: Host-Guest Chemistry Picks up the Pace**

An increasingly popular use of supramolecular host-guest systems, from both an academic and industrial application perspective is their existence as catalytic incubators; mediums for the acceleration (or deceleration as the case may be) of chemical reactions followed by subsequent egress of reaction products. The ‘golden chalice’ of such research is the design of supramolecular architectures akin to the characteristics of naturally-occurring enzymes.
While progress to this end has been admirable, further synthetic strides need to be made before complexes, capable of acting as mimics for the active sites of naturally occurring enzymes, can be utilised to this effect.

**Fig. 22** Prostate-specific antigen (PSA) enzyme is one of many naturally-occurring enzymes, which chemists strive to mimic synthetically.\(^{13}\)

One of the key parameters used as a benchmark of catalyst efficiency is the turnover number (TON). This is essentially the number of molecules of substrate converted to product per active site, per unit of time. Thus the higher the turnover number, the more efficient the catalyst. Product inhibition is the principal obstacle to be overcome when attempting to generate catalytic systems; essentially a scenario which arises when the product of a catalytic interaction within the cavity is more stable (or more strongly bound) than the reactants (Figure 23).\(^{19,64}\) For instance the host capsule, acting as a platform for catalysis with the ability to orientate the reactive species into favorable conformations for accelerated reactions, binds one of the reactants (Reactant 1) at the active site. Reactant 2 then orientates itself such that Reactant 1 / Reactant 2 react with one another.
Fig. 23 Schematic representation of catalysis within molecular capsules: (a) ideal situation where product readily exits cavity, (b) product inhibition observed when product strongly binds host species.

Ideally then the host should relinquish control over the newly-formed product thus freeing up the active site to allow for further reaction and hence the formation of new product (scenario (a) in Figure 23). If, however, the host-product interaction is stronger than that between host and reactants, the product species will not depart and will block the active site of the enzyme. Thus the formation of new product will be hindered / inhibited (scenario (b) in Figure 23). It has also been reported how the products generated during such catalytic interactions may be too large for egress of the cavity to occur. This again leads to product inhibition and the stifling of further host-substrate interactions. The principal method by which catalysts operate / bind is by ‘complementing the shapes and characteristics of transition states’. Thus, in terms of supramolecular encapsulation of reactive substrates, the greater the ability of the capsule to orient the substrate into a conformation that resembles the transition state, the better the catalyst and the greater the acceleration of a given chemical reaction. In addition to mimicking the transition state, it is desired for the products of catalytic interactions to readily exit the host cavity (i.e. to limit product inhibition discussed previously). Fujita has described
several systems which involve limiting product inhibition through intelligent choice of host and substrate species. As an illustration of host-guest catalysis, the Diels-Alder reaction system developed by Rebek et al involving catalysis of the reaction between 2,5-dimethylthiophene dioxide and p-benzoquinone within the previously discussed Capsule D1 (Figure 24), sought to reduce product inhibition by loss of SO₂. Loss of SO₂ would, in theory, have altered the conformation of the transition state such that eventual egress of catalytic products would be expeditious and facile. While SO₂ was not lost (the high final yield has been attributed to weak interaction between host and product), the system was relatively efficient in terms of catalytic activity (TON = 7) and was indeed the first self-assembled molecular flask to exhibit catalytic activity.⁶⁸

![Diels-Alder reaction](image)

**Fig. 24** Diels-Alder synthesis of p-benzoquinone and 2,5-dimethylthiophene catalysed by encapsulation of reactive guests within Capsule D1.

Another prime example of an attempt to limit product inhibition with consequent dramatic increase in catalytic efficiency is that of the host-guest architecture developed by Caulder et al. This particular system utilizes Ga(III) in an anionic coordination cage (Capsule G) along with enammonium cationic substituents [Figure 25 (a)].⁶⁹
Fig. 25 (a) (left) Capsule G utilised in the catalysis of 3-aza Cope rearrangements of enammonium cationic species (right) [M = Ga(III)].  

Caulder et al utilised this breed of supramolecular capsule in the catalysis of 3-aza Cope rearrangements of such enammonium cationic species. Capsule G is considerably more tightly enclosed than other capsules (described previously in Section 1.2.3) and as such the enammonium substrates, once encapsulated, have no option but to alter their conformation [Figure 25 (b)]. The chair-like conformation adopted by the enammonium substrate (alkyl-based here) closely resembles the transition state with an observed reaction rate increase of 850 fold observed. There is a low binding constant associated with the host-altered substrate interaction and thus exclusion of catalytic products is facile and expeditious (scenario (b) in Figure 23).

Fig. 25 (b) Schematic showing the catalysis of 3-aza Cope rearrangements within Capsule G.
1.2.5 Modern Applications of Host-Guest Systems

1.2.5.1 Chemical Sensors

Chemical sensors are often described as being comprised of a recognition element coupled to a transducer.\(^1\) A rather apt description for the breadth of sensing materials described below which not only function as novel systems for the detection of a broad range of analytes in various media but also serve as prime examples of the rapidly developing interest and application of supramolecular host-guest architectures. The underlying principle of the sensing technique is illustrated in Figure 26, which shows a host cavity in the absence of a guest to exist in a given state (State A). Upon guest inclusion (analyte) the host-guest complex shifts to a different state (State B), resulting in a response.

![Figure 26](image)

**Fig. 26** Schematic illustrating the basic principle of chemical sensing as it applies to supramolecular host-guest architectures.

The chemistry of the host-guest complex, upon encapsulation, may change in terms of chemical reactivity / intermolecular interactions. This response may take one or more forms: mass differential, fluorescence (or its quenching) or electrochemical (Figure 26). A brief discussion of some of the most widely-exploited sensor systems will be given in the sections that follow, including those based on redox-active and fluorescence-based materials.
1.2.5.1.1 Redox-active Sensors

One of the first examples of a redox-active sensor, developed in 1997 by D’Souza and co-workers, involved the grafting of a thin β-cyclodextrin-based polymer film (Figure 27) to a gold (Au) surface for the detection of dissolved oxygen (O₂). Such cyclodextrin species have been widely identified as leading candidates for acting as host species for the generation of supramolecular host-guest architectures.⁷²

![Figure 27: β-Cyclodextrin macrocyclic species utilised by D’Souza and co-workers in O₂ detection.⁷²](image)

The guest of choice in this instance was a cobalt(II)tetrakisporpyrinh complex since such metalloporphyrins possess a rich and well-defined redox behaviour and also act as redox catalysts, as observed by the work of Kadish and co-workers.⁷³ D’Souza et al highlighted numerous advantages in coating cyclodextrin species as a polymer mixture onto an electrode surface: 1) increased stability of the supramolecular assembly, 2) high resistance to extremes of pH and various solvents (pronounced insolubility in both aqueous and organic media), 3) selective permeability through relatively narrow channels present therein (smaller molecules allowed through while larger molecules are prohibited) and 4) long shelf life in environments of suitable humidity.
Fig. 28 Oxidation of Co(II)→Co(III) and reduction of O₂ to H₂O₂ within β-cyclodextrin thin films observed via cyclic voltammetry (CV).⁷²

Cyclic voltammetry (CV) experiments undertaken on the cyclodextrin-coated assemblies in the presence of dioxygen (O₂) involved allowing O₂ to pass through the above polymer channels which resulted in its catalytic reduction to H₂O₂, while the porphyrin species is itself oxidised (Co(II)→Co(III)). The CV technique allows for the detection of these redox changes (Figure 28).

1.2.5.1.2 Mass Sensors

A now well established class of sensor materials incorporating self-assembled architectures involves the measurement of a mass differential for the quantitative detection of various analytes.⁷¹⁷⁴ The method utilises a quartz-crystal-microbalance (QMB) and exploits the intermolecular interactions which occur between organic host entities (grafted onto a quartz surface) and guest analytes (Figure 29). Pinalli and Suman both utilised another widely popular host architecture for supramolecular self-assembly; that of a cavitand species. Cavitands are particularly ideal frameworks towards sensor materials, not only because they have enforced concave surfaces of molecular dimensions but since they have also been previously shown to form host-guest inclusion complexes with myriad aliphatic and aromatic guests in the solid state.⁷⁵ A schematic illustrating the basic concept of the QMB technique is shown in Figure 29.
**Fig. 29** Schematic illustrating the basic operating principle of the quartz-crystal microbalance (QMB).

The mass differential / increment which results from intermolecular interactions such as C-H···π and H-bonding interactions reduces the fundamental resonance frequency of the oscillating signal by an amount proportional to the concentration of analyte / guest present. More specifically the mass increments change the resonance frequency of the quartz disc which lies beneath the sample.\(^7\) The QMB technique has been used for the selective detection of a variety of alcohol and acetate-based species which form inclusion complexes with the above cavitand host framework; with selectivity dependent on the possession of acidic methyl groups by the guest. Such facile detection of alcohol and acetate species has garnered considerable interest among researchers stemming from the ubiquitous nature of these compounds in consumer goods: For instance, the aroma of white wines stems from the presence of acetates.\(^7\)

### 1.2.5.1.3 Fluorescence-based Sensors

In 2010, Baumes and co-workers reported the use of an organic-based cucurbituril capsule host species for the colourimetric detection of the date-rape drug \(\gamma\)-hydroxybutyric acid (GHB) in aqueous media (Figure 30).\(^7\) Cucurbituril macromolecules in general have been proposed as potential vesicles for drug delivery, gas storage media and as molecular switches.\(^7\)
Fig. 30 γ-Hydroxybutyric acid (left) and Methylene blue dye (right) utilised in the colourimetric detection of GHB.

Baumes et al utilised over-the-counter fluorescent cationic dyes (Figure 30) such as methylene blue and thionine, which became encapsulated within the cucurbituril host capsule (Figure 31). The dyes, in general, emit an intense fluorescence in the visible spectral region upon illumination with UV light. The chosen host frameworks in this instance were two cucurbituril species CB[7] and CB[8] since these macrocycles form strong host-guest inclusion complexes with basic tricyclic dyes such as thionine and methylene blue. As described previously, these macromolecules comprise ‘n’ glycoluril building blocks (here n = 7 / 8 for CB[7] and CB[8] respectively) arranged in a cyclic array. The sensor response itself is due to the formation of such inclusion complexes and is largely based on fluorescence spectra intensity and how the fluorescence intensity varies between free and bound guest species. The fluorescent dye is already present within the cavity when GHB guest enters the cavity. The sensor response then is due to quenching of the fluorescence of the dye by the GHB guest.

Fig. 31 Cucurbit[7]uril and cucurbit[8]uril species utilised by Baumes and co-workers.
The inclusion complex generated was proposed for the detection of GHB, however, the selectivity of the sensor towards this analyte (with respect to other similar compounds such as γ-butyro lactone (GBL)) was vital. Baumes and co-workers were successful in this respect since the sensor they developed was indeed able to discriminate between GHB and GBL; commensurate with this selectivity the sensor affords facile and reliable detection of analytes. This is in stark contrast to traditional analytical methods such as gas chromatography (GC) which encounters great difficulty in attempting to differentiate between GHB and GBL solutions, largely as a result of GHB→GBL conversion at injector temperatures (Figure 32).

**Fig. 32** High-temperature conversion of GHB→GBL makes GC qualitative assay of GHB difficult.

The development of such supramolecular sensors for the detection of harmful substances such as GHB presents numerous advantages: greater reliability and accuracy, increased sensitivity and they are less cumbersome relative to other commercial techniques currently been utilised. In addition the computer system adopted in the sensor array also allows for a quantitative assay of drug concentration.\(^76\)

### 1.2.5.1.4 Calixarene Surface-Adsorbed Sensors: The SPR Technique

A particular branch of supramolecular-based chemical sensors increasingly utilised for the detection of a wide range of analytes involves the self-assembly and adsorption of calixarene compounds in monolayers onto the surface of gold nanoparticles aptly referred to as gold self-assembled monolayers (SAMs).\(^86\) The surface of these SAMs may be functionalised in a myriad of ways for selective detection of specific analytes. For instance crown ether and thiol species may be incorporated at the upper / lower rim of the calix[n]arenes respectively for detection of cations (Figure 33(b)).\(^87\)
Fig. 33 Self-assembled monolayer (SAM) (top) and crown-ether-functionalised SAM (bottom) utilised in chemical sensing.

Such gold nanoparticle-based systems rely on a phenomenon known as surface plasmon resonance (SPR) in order to facilitate detection of analytes. This phenomenon has been widely reported in the literature for the detection of small molecules and ions as well as larger biologically relevant molecules and occurs when the oscillations of the conduction electrons of the analyte are brought into resonance with the incident electromagnetic radiation used to probe the material.\textsuperscript{87,88} The essentials of the technique are illustrated in Figure 34.
Fig. 34 Schematic illustrating the basic principles of the Surface Plasmon Resonance (SPR) technique utilised in the detection of various analytes adsorbed onto surfaces.

One of the key parameters in determining the colour of a gold-nanoparticle solution is the distance between gold atoms. When this distance exceeds that of the Au-atoms’ diameters the solution appears red as a consequence of the surface plasmon resonance centred at 520 nm, while as the distance between Au atoms is progressively reduced (below that of the Au atoms’ diameters), a shift in the surface plasmon radiation band is observed and the solution appears blue. SPR, in conjunction with functionalised self-assembled monolayers of gold nanoparticles (via the grafting of calixarene species to the surface) have been used for the detection of cations\textsuperscript{89,90}, anions\textsuperscript{91} and organic molecules\textsuperscript{92}.

From the SPR angle shifts (not dissimilar to the colour variations of Au nanoparticle solutions described above and stem from adsorption of molecules onto the SAM surface), Chen and co-workers found that calix[4]-crown-5 SAM, formed on a gold surface, allowed for the selective detection of K\textsuperscript{+} ions over other alkali and alkaline earth metal ions (Figure 33(b)).\textsuperscript{89} Similarly, other calix-crown species can be used for the detection of Cs(I) and Na(I).\textsuperscript{90,93} Additionally anion sensing is possible using such a SPR methodology and has been highlighted by the work of Zhang and co-workers in their use of calix[6]arene species for the selective detection of F\textsuperscript{-} anions over, for example, Cl\textsuperscript{-}, Br\textsuperscript{-} and AcO\textsuperscript{-} species.\textsuperscript{94} The SPR technique, in conjunction with supramolecular host-guest architectures, can be used not only for the detection of simple anions and cations, it can also be used for the selective detection
more complicated biomolecules such as dopamine, a vital neurotransmitter. It was again Zhang and co-workers who demonstrated that a calix[6]arene species (calix[6]-crown-4) exhibited improved dopamine recognition in contrast to other organic-based charged species such as alkylammonium cations.\textsuperscript{92} A wide variety of other supramolecular-sensor systems, based on the SPR phenomenon, have been recently reported. These include calix[6]arene SAMs for the colourimetric detection of diaminobenzene isomers\textsuperscript{95} and 1,3-dialkoxy calix[4]arenes\textsuperscript{96} for the detection of quaternary ammonium cations as well as calix[8]arene SAM systems for the selective detection of \(C_{60}\) and \(C_{70}\) (Figure 35); with the latter (fullerenes) having potential application in medicine for the targeting of cancer cells.\textsuperscript{97}

**Fig. 35** Fullerene (\(C_{60}\)) (left) and fullerene-based carbon nanotube (right) are readily detected using SPR.
1.3 Aims and Objectives

The principal aim of the research undertaken here is to generate species which exhibit significant supramolecular extended architectures exhibiting host-guest relationships; specifically involving magnetically interesting host species towards potential multifunctional materials. In addition while attempting to isolate supramolecular host-guest species, other polynuclear systems will also be investigated and characterised from both a structural and magnetic viewpoint in efforts to garner a deeper understanding of such polymetallic metal-ligand associations. In doing so it is hoped that novel pathways and synthetic routes will emerge towards functional supramolecular host-guest systems. The methodology employed involves the use of polydendate Schiff base ligands towards supramolecular host-guest complex formation.

More specifically this thesis describes the use of the Schiff base ligand 2-iminomethyl-6-methoxyphenol (L₁H) and its analogues, functionalised on both the aromatic ring and at the imino-nitrogen to generate supramolecular host-guest systems upon metal ligation as well as species possessing unique and interesting structural and magnetic characteristics. These analogues include the aromatic ring functionalised Schiff base ligand 4-bromo-2-iminomethyl-6-methoxyphenol (L₂H) as well as the imino-N functionalised species 2-iminophenyl-6-methoxyphenol (L₃H) (Figure 36).

![Figure 36](image)

**Fig. 36** (a) o-Vanillin precursor, (b) L₁H and (c) functionalised Schiff base analogues: R = Br, R’ = Me (L₂H); R = H, R’ = Ph (L₃H); R = Ph, R’ = Me (L₄H), R = H, R’ = H (L₅H).

1.3.1 Ligand Choice: Why L₁H and its Analogues?

Ligand choice in the synthesis of polymetallic complexes is paramount as the ligand influences factors such as the stability of metal-ligand assemblies as well as the strength and type of intermolecular interactions which the complexes undergo. L₁H ticks all the boxes as
an ideal ligand for coordination to transition metal ions. It allows not only for ligation between multiple metal sites (via its methoxide, phenolate and imino-N sites respectively), but also for intermolecular π-π stacking and H-bonding interactions between individual metallo-organic units. Additionally, following on from the work of Dalgarno, Brechin and co-workers, who used a whole calix[4]arene macrocycle towards complex formation with commensurate Single-Molecule Magnet (SMM) and magnetic coolant applications,\textsuperscript{98-99} we postulated the effect ligand types equivalent to ¼ of such a calix[4]arene species, specifically an oxacalix[4]arene species, would have on final complex topology in conjunction with the presence of paramagnetic metal centres (Figure 37).

![Fig. 37](image)

**Fig. 37** (left) Structure of the macrocyclic compound oxacalix[4]arene. (right) Structure of L\textsubscript{1}H (effectively ¼ of an oxacalix[4]arene molecule), used extensively in this work.

We were confident in pursuing this line of research, with a view towards isolating supramolecular host-guest species, following the success of our pilot investigations using this ligand. We initially found that L\textsubscript{1}H, on complexation with the paramagnetic Ni(II) ion, resulted in the formation of heptanuclear double-bowl pseudo metallocalix[6]arene discs of formula [Ni(II)\textsubscript{7}(OH)\textsubscript{6}(L\textsubscript{1})\textsubscript{6}(NO\textsubscript{3})\textsubscript{2} (where L\textsubscript{1} = deprotonated L\textsubscript{1}H Schiff base ligand) (Figure 38). These complexes packed in 3D to form molecular cavities of appreciable dimensions. Calixarene (stemming from the term ‘calix’ meaning vase) species in general comprise cyclic arrays of n-phenol moieties which are linked by methylene groups. It was thus postulated that our molecular cavities may afford the potential for encapsulation of a variety of guest molecules, via intermolecular host-guest interactions. Such molecular cavities have been reported previously involving purely organic calixarene species with encapsulated guests such as solvent molecules. However, no examples of host-guest pseudo metallocalix[6]arene species have been reported to date.
Fig. 38 Molecular cavities encapsulating guest species within [Ni(II)$_7$] double-bowl units.

1.4 Concluding Remarks

We have thus encountered a vast range of polynuclear systems exhibiting host-guest characteristics and how these systems may be used for a myriad of useful applications including catalysis, sensing and drug delivery among others. It has been shown how functionalisation of the core architectures of calix[n]arenes and cyclodextrin species (among others) may be used for the selective encapsulation of different guest molecules and indeed how environmental factors such as pH and temperature can affect the inclusion of guests within the host framework.

The allure of such systems for researchers is ever-increasing with host-guest materials set to play an increasingly vital role in the development of novel drug delivery systems, in sensing technologies and the detection of harmful environmental pollutants as well as affording a deeper understanding of the range of intermolecular interactions which participate in the self-assembly process. As the research detailed in this thesis lies at the interface of supramolecular host-guest chemistry and molecular magnetism, an overview of some of the principal aspects of molecular magnetism and its applications must first be given.
1.5 Molecular Magnetism

1.5.1 Introduction

Magnetism is the study of the properties and interactions exhibited by magnetic materials and is by no means a modern phenomenon. It dates back thousands of years to the discovery of large black stones which were observed to attract pieces of iron-metal particles towards them. During the middle ages, Europeans discovered that an oblong piece of this stone would point to the north and south if it were hung by a string. The stones thus came to be known as leading stones or lodestones. These loadstones were the first magnets and ultimately led to the invention of compasses, which are used to this day by sailors to navigate without the reliance on stars to guide their way.

The interest in and reliance on magnetic materials is far greater today than it was in the middle ages, though the focus has since shifted towards their use in telephones, televisions and radios, where they help change electrical impulses into sounds as well as their use for data storage in computer systems on which modern society has come to rely. Magnetism and magnetic materials equate to a multi-billion euro industry and have applications in electronics as well as in medicine, where Gd(III) and Mn(II) macrocyclic complexes are used as paramagnetic magnetic resonance imaging (MRI) contrast agents. In addition, MRI machines contain huge superconducting magnets which are used to apply the necessary external magnetic field. While many of the everyday forms of magnetic materials are iron-based (i.e. the common bar magnet used in compasses), many materials exhibit some form of magnetic behaviour. In the case of d-block first-row transition metals (the focus of this thesis) the arrangements of valence electrons in the d-orbitals of the metal lead to a number of unpaired electrons whose individual spins produce a magnetic moment. It must also be remembered that magnetism was fundamental to the development of the theory of molecular and solid-state chemistry and physics and continues to play a role in testing new theories. Magnetic materials also have exceedingly important biological significance, a prime example of which exists in the form of the iron storage protein ferritin which exhibits superparamagnetic characteristics. Magnetic behaviour may also be observed in the interactions between Cu(II) and Fe(III) in cytochrome-c oxidase, an enzyme if displaying mutations may result in severe metabolic disorders (heart, brain). Additionally, the study of magnetic materials affords much useful information such as the ability to distinguish between
high and low spin compounds such as Fe(III) \((S=5/2): \text{high spin, } S=1/2: \text{low spin}\) as well as differentiation between compounds exhibiting completely different topologies / symmetries. For example, in the study of the magnetic properties of Ni(II) species, magnetic measurements can answer the question: \textit{Is a given Ni(II) system square planar \((S = 0)\) or tetrahedral in geometry \((S = 1)\)?} One may readily and visibly observe the bulk magnetic properties of certain materials, however a greater and even more fundamental understanding of magnetism is gained from a study of the magnetic properties of materials at the molecular level. Specifically isolated molecules and molecular crystals in which the molecules interact only very weakly with one another. This field is called Molecular Magnetism.

\subsection*{1.5.2 Molecular Magnetism: A Closer Look}

Molecular magnetism is often described as the study of the magnetic properties of isolated molecules and assemblies of molecules.\(^{104}\) Such assemblies include discrete molecular crystals (described above) as well as systems in which very strong intermolecular interactions (in 1D, 2D or 3D) are observed, resulting in long-range magnetic ordering (as seen by bulk ferromagnets). Magnetic materials used in industry incorporating metals such as Co, Fe, and Cr are prepared by high temperature metallurgical processes. Molecular magnets however are easily prepared as high quality single crystals formed by numerous crystallization techniques or via hydrothermal / solvothermal techniques.\(^{108}\) Indeed, the inherent homogeneity of single crystals eradicates problems encountered in solid-state metallurgical processes such as poor grain size monodispersity. The magnetic properties of desired compounds may also be altered by simple chemical methodologies in addition to been able to combine such magnetic properties with other mechanical, electrical or optical properties. Arising from such simplicity of fabrication and the ability to alter a materials magnetic properties led to the 1998 report by Kahn and co-workers regarding the potential for Fe(II) spin-crossover compounds for use in display devices and sensors (see Section 1.2.5.1).\(^{109}\)

\subsection*{1.5.3 Molecule-Based Magnets: The Key is the Electron}

Before discussing molecular magnetism in more detail, it is imperative that a thorough background on the fundamental concepts encountered in this field of chemistry be first given. This discussion will range from the general types of magnetic behaviour which are encountered to magnetic measurement methods, as well as potential future applications of magnetic materials including single-molecule magnets (SMMs) and magnetic refrigerants.
All electrons have associated with them a total angular momentum [quantum number J], which in turn has an associated magnetic moment, a vector quantity made up of two components: one component is due to the electron spinning on its own axis [quantum number S] and the other as a result of the electron orbiting the nucleus [quantum number L]. These two components of electron angular momentum are known as spin and orbital angular momentum respectively. Essentially, the magnetic moment arises because an electron is a moving charged particle and therefore produces a magnetic field (magnetic moment). A free electron can only have spin-angular momentum, however contribution from the orbital component in a process known as spin-orbit coupling dictates the need to modify calculations of angular momentum (see Section 1.5.3.8). Indeed, it is often the case that contributions from the orbital component of angular momentum are observed.

Paramagnetic materials possess unpaired electrons and their magnetic moments align with one another in the presence of an external magnetic field and are therefore attracted to the applied field (Figure 39). Opposed to this are diamagnetic materials in which the spins on the electrons are anti-parallel or spin paired and the motions of which result in a body been repelled by an external magnetic field. There also exist several sub-classes of paramagnetic behaviour. Ferromagnetic and antiferromagnetic interactions occur when the spins of the electrons align parallel and anti-parallel to one another, respectively, in the presence of an applied magnetic field. Ferrimagnetism is a type of antiferromagnetic behaviour, however there is a net magnetic moment due to the unequal magnitude of adjacent magnetic moments. The various forms of magnetic interactions will be re-visited in the sections that follow, when discussing magnetic susceptibility and the energy changes which occur when a material is exposed to an externally-applied magnetic field.
Fig. 39 Different forms of magnetic behaviour. The arrows represent the directions of the spin magnetic moments.\textsuperscript{110}

At the heart of molecular magnetism, as intimated above, lie the magnetic moments of the unpaired electrons in a given material. The effective magnetic moment $\mu_{\text{eff}}$, comprising contributions from both the intrinsic spin of the electrons and their orbital motion about the nucleus, may be described by Equation 1.

$$\mu_{\text{eff}} = [L(L+1) + 4S(S+1)]^{1/2} \quad \text{Equation 1}$$

When only spin-angular momentum contributes to the magnetic moment, the relationship above reduces to Equation 2; the spin-only formula.

$$\mu_{s,o} = 2[S(S+1)]^{1/2} \quad \text{Equation 2}$$

Equation 2 may be further reduced to Equation 3 which directly relates the spin-magnetic moment to the number of unpaired electrons ($n$) in a given system.

$$\mu_{s,o} = [g^2 S(S+1)]^{1/2} \approx [n(n+2)]^{1/2} \quad \text{Equation 3}$$

The $g$ value in the above expression (Equation 3), as will be seen later when discussing magnetic anisotropy characterises a particle’s magnetic moment and gyromagnetic ratio (see Section 1.5.3.7.1).
1.5.3.1 Polynuclear Complexes and Molecular Magnetism

While paramagnetic mononuclear complexes exhibit magnetic behaviour, a more interesting class of magnetic material are those based on highly paramagnetic polynuclear (polymetallic) complexes, whose magnetic properties can again be altered by structural variation at the molecular level. These polymetallic complexes typically comprise first-row transition metals and/or lanthanoid ions linked into certain topologies through one or a combination of bridging ligands. The coordination spheres at each metal centre are usually completed by terminal halogens and/or solvent molecules. The structural topologies of these complexes depend greatly on the various ligands used in their formation. The relationships that may be derived between the magnetic properties and structures of d/f block transition metal complexes are known as magneto-structural correlations (see Section 1.5.3.9) and have been widely studied in the case of [Mn₆] clusters, [Fe₄] butterflies, Fe(III) dimers and Cu(II) dimers.¹¹¹-¹¹⁵ An example of a polynuclear transition metal cluster is shown in Figure 40.

![Fig. 40 ORTEP Plot of a Typical [Fe₆] Wheel transition metal cluster: [Fe₆(bic)₆]₂ (where bic = bicine = 2-(Bis(2-hydroxyethyl)amino)acetic acid).¹¹⁶](image)

1.5.3.2 The Study of Molecular Magnetism

While a complete discussion of all the features of molecular magnetism would be rather involved, the sections which follow detail some of the most important aspects of this field. In all magnetic studies of transition metal complexes, one is effectively investigating how a given species responds to an externally applied magnetic field. The ability of a molecule to be magnetised is as a result of the difference between the magnetic field which exists within the molecule (in presence of applied magnetic field) and that of the free-space value (FSV) in the
absence of an applied field. The energy of the molecule changes as a result of exposure to the applied magnetic field and the rate of change of energy (E) of a given molecule as a function of the applied field (H) is known as the Magnetisation (M): (Equation 4).

\[-\frac{\partial E}{\partial H} = M\]  
Units: cm$^3$.G.mol$^{-1}$ (where G=Gauss) (Equation 4)

In turn, the rate of change of (M) as a function of the applied field (H) is, for molar amounts of compounds, known as the molar magnetic susceptibility ‘χ’: (Equation 5).

\[\chi = \frac{\partial M}{\partial H}\]  
Units: cm$^3$ mol$^{-1}$ (Equation 5)

The larger the value of χ the more easily and more strongly a given species is magnetized.

The measured magnetic susceptibility (χ) is made up of two components: a paramagnetic parameter χ$^P$ and a diamagnetic parameter χ$^D$ as given by Equation 6 below.

\[\chi = \chi^D + \chi^P\]  
(Equation 6)

χ is positive for paramagnetic species (independent of applied field but dependent on temperature) and negative for diamagnetic species (independent of both applied field and temperature). χ is often found to be inversely proportional to temperature (see Section 1.5.3.5) and can be directly related to the spin-only formula ($\mu_{s.o}$) by Equation 7.

\[\mu_{s.o} = 2.828(\chi T)^{1/2}\]  
(Equation 7)

### 1.5.3.3 Measuring the Magnetic Susceptibility

There are essentially two methods by which the magnetic susceptibility parameter (χ) may be measured: Force Methods (using the Gouy Balance) and Induction Methods (now widely performed using a Superconducting Quantum Interference Device (SQUID) magnetometer). A schematic representation of a Gouy balance is shown in Figure 41 and essentially determines ‘χ’ by measuring the change in weight of a sample when placed in an inhomogeneous magnetic field. The theory behind the Gouy method is very straightforward. The top of the sample container is kept in zero field while the bottom of the container is kept in high field. The weight change between the two (when exposed to the applied field), is proportional to the molar magnetic susceptibility. In such systems, diamagnetic compounds
are repelled by the applied magnetic field and thus appear lighter in mass with respect to its free space value (FSV). In contrast, a paramagnetic material is attracted by an applied field and appears to weigh more with respect to its FSV. SQUID measurements (described below) offer much greater sensitivity and are thus used for most magnetic studies; however a major downside is the increased complexity and cost associated with the technique.

Fig. 41 Schematic illustrating the principal features of a Simple Gouy Balance.

1.5.3.3.1 SQUID Magnetometry

The most widely utilised method for determining magnetic susceptibility is SQUID magnetometry. SQUID techniques have been utilised since the early 1960s and are far superior to Gouy methods in terms of the breadth of information they yield. The approach also offers far greater sensitivity ($10^{-12}$ emu vs. $10^{-6}-10^{-8}$ emu for Gouy method), in addition to offering variable temperature control and the ability to analyse single-crystal samples, as well as the more common powders. SQUID magnetometry is based on induction methods. The sample (loaded along with eicosane to avoid torquing) is surrounded by a superconducting ($S_c$) sensing coil, thus negating the possibility for loss / damping of signal (Figure 42).
Fig. 42 Schematic showing the mode of operation of a typical SQUID.

The coil which surrounds the sample is coupled to a second superconducting (S\textsubscript{c}) loop inside the SQUID itself. The movement of the magnetic material through the S\textsubscript{c} coil generates an electric current which is subsequently induced in the second S\textsubscript{c} loop (without loss of signal). The magnitude of the induced signal / voltage is thus proportional to the magnetic susceptibility of the sample under investigation. A standard SQUID is equipped with a 7 T dc magnet and usually performs solid-state dc magnetic susceptibility data down to 1.8 K. The only disadvantage of the SQUID technique is the expense and complexity of the equipment used, for example a standard SQUID system can cost as much as €500,000 with recurring costs associated with maintenance and the requirement for liquid He to allow for superconductivity in sensing coils. Indeed, the enduring necessity for analyses with increasing sensitivity assures the consistently steep cost associated with magnetic susceptibility measurements.

1.5.3.4 Influencing the Magnetic Susceptibility $\chi$

The magnetic susceptibility $\chi$ described above is affected, both in size and magnitude, by the nature and strength of the magnetic material being analysed. These variations ultimately
dictate the potential applications which a material may have; paramagnetic materials (including its various sub-classes: ferro-, antiferro- and ferrimagnetism) ultimately dominating in this respect. Diamagnetic materials exhibit a negative $\chi$ whose magnitude is independent of both the applied field and temperature with values varying between $-10^{-6}$ to $-10^{-4}$ cm$^3$ mol$^{-1}$. The susceptibility values obtained for diamagnetic materials are said to be approximately additive which implies that if the susceptibility values of the ligands in a coordination complex are known their combined contribution to the observed $\chi$ may be determined.\textsuperscript{104-106} Paramagnetic materials, in direct contrast, exhibit positive $\chi$ susceptibility values and are independent of the applied field $H_o$ but dependent on temperature. $\chi$ values for paramagnetic species vary from $+10^4$ to $+10^1$ cm$^3$ mol$^{-1}$ with the temperature dependence of such materials affording important information regarding the electronic structure of the paramagnet.\textsuperscript{104-106}

Before delving deeper into the various forms of magnetic interactions, an initial description of the underlying law relating magnetic susceptibility ($\chi$) to temperature must be given.

\subsection{1.5.3.5 The Curie and Curie-Weiss Laws}

The Curie Law states that the magnetic susceptibility $\chi$ observed for a given material is inversely proportional to the temperature (Equation 8 below).

$$\chi = \frac{C}{T} \quad \text{Equation 8}$$

The constant of proportionality relating magnetic susceptibility to temperature is known as the Curie constant (with units of cm$^3$ K mol$^{-1}$) and is characteristic of a given system. Thus the Curie constant ($C$) may be ascertained by plotting $1/\chi$ vs. $T$ (Figure 43).
Fig. 43 Plot of $1/\chi$ vs. $T$ for a system obeying the Curie Law. The best fit line through a given data set will intersect the origin.

Indeed it is often found that certain characteristic features of a given system are shrouded or concealed on a particular graphical plot of $\chi$ and $T$. It is thus highly informative to construct several different plots (Figure 44) such as $\chi$ vs. $T$ or $\chi$ vs. $1/T$ or $\chi T$ vs. $T$ which, when combined, afford a much more detailed picture of the magnetic behaviour of a given material. For instance if ferromagnetic behaviour is intimated by a plot of $\chi$ vs. $T$, plotting $1/\chi$ vs. $T$ (Figure 43) and isolating a positive Weiss constant $\theta$ [intercept with abscissa] confirms such magnetic behaviour.

Fig. 44 One of several types of plots relating magnetic susceptibility to temperature change. Axes: ordinate = $\chi M T$ and abscissa = $T$.

It is often a reality, however, that a material’s observed magnetic susceptibility cannot be fitted to the Curie Law. This is often found to arise in systems that exhibit weak intermolecular interactions, specifically weak magnetic interactions between neighbouring
paramagnetic centres, and for systems exhibiting multiple low-lying excited states or zero-field splitting effects. The latter will be discussed in the sections that follow. In these instances the systems’ magnetic behaviour may be fitted to the Curie-Weiss law (Equation 9), which introduces an additional parameter $\theta$ known as the Weiss constant; the sign of which dictates whether a system is ferromagnetic or antiferromagnetic.

$$\chi = \frac{C}{T - \theta} \quad \text{(Equation 9)}$$

The Weiss constant, $\theta$, with units of K may be ascertained by plotting $1/\chi$ vs. $T$ (with $\theta =$ intercept with abscissa) (Figure 45).

![Plot of $1/\chi$ vs. $T$](image)

**Fig. 45** Intercept of plot of $1/\chi$ vs. $T$ for a system exhibiting Curie-Weiss behaviour gives the Weiss Constant $\theta$.

The sign of $\theta$ is a strong indication of the type of magnetic behaviour corresponding to a given system. A positive $\theta$ indicates ferromagnetic exchange while a negative $\theta$ indicates the dominance of antiferromagnetic exchange. There are, as mentioned previously, a number of sub-classes of paramagnetic materials; those exhibiting ferromagnetic, antiferromagnetic and ferrimagnetic characteristics; all of which will be observed to an appreciable extent in this thesis (Figures 46-49).
Fig. 46 Paramagnetic behaviour exhibited above Curie temperature \( (T_C) \) and Néel temperature \( (T_N) \) for ferromagnetic and antiferromagnetic materials respectively.

Ferromagnetic materials are a class of paramagnetic materials in which the susceptibility \( \chi \) increases with decreasing temperature (Figure 47). There exists a transition temperature known as the Curie Temperature \( (T_C) \) below which the unpaired electron spin moments align parallel; above this temperature however the thermal energy of the surroundings overrides the electron spins’ tendency to align parallel in the absence of an applied field. Thus above this critical temperature the material behaves as a paramagnet.

Fig. 47 (left) Schematic of typical ferromagnetic behaviour. (right) A literature example of ferromagnetic exchange in a \([\text{Ni(II)}_4]\) tetranuclear cubane.\(^{117}\) Both plots show an increase in \( \chi \) as the temperature is reduced below the Curie temperature. Above \( T_C \), the plot is the same as
that shown in Figure 46. Black squares represent experimental data while the solid line indicates the best fit to the experimental data.

Antiferromagnetic materials exhibit magnetic susceptibilities which decrease with decreasing temperature. The critical temperature in this instance is known as the Néel temperature ($T_N$) and marks the point above which the material under investigation exhibits paramagnetic characteristics (Figure 46).

![Graph showing magnetic susceptibility vs temperature for antiferromagnetic materials.]

**Fig. 48** (left) Schematic of a typical antiferromagnet. (right) A literature example of antiferromagnetic exchange in the tetranuclear complex $[\text{Mn(II)}_4\text{F}_4(\text{phen})_4](\text{NO}_3)_4.12\text{H}_2\text{O}$ (where phen = 1,10-phenanthroline).\(^{118}\) Both plots show a decrease in $\chi$ as the temperature is reduced. Above $T_N$, the plot is the same as that shown in Figure 46.

Ferrimagnetic materials exhibit behaviour which lies between that of a ferro- and antiferromagnet. For instance, magnetite is found in bird skulls and is known to be ferrimagnetic. They use this to navigate in conjunction with the earth’s magnetic poles. Figure 49 illustrates ferrimagnetic exchange in a $[\text{Mn(II)}_3\text{Mo(V)}_2]$ polymetallic complex reported by Withers and co-workers.\(^{119}\)
1.5.3.6 The Van Vleck Equation

It is the enduring desire of magneto-chemists to be able to calculate theoretical values of $\chi$ in situations which deviate from those dictated by the Curie / Curie-Weiss equations. The derivation of the Curie Law was based on a number of underlying assumptions, namely the absence of spin-orbit coupling, the mixing of ground states with excited states, or zero-field field splitting of excited states (the latter will be discussed later). Indeed, the results which form the basis of this thesis will highlight polynuclear complexes which exhibit such deviations from the Curie / Curie-Weiss Laws. In order to derive a relationship which affords such theoretical $\chi$ values, it is necessary to determine the new energy levels in the applied field ($H_o$) and the Boltzmann distribution among them. In formulating such a relationship, it is necessary to make a number of assumptions, namely that the system under investigation is magnetically dilute i.e. the spin moments of the electrons on one atom are independent of those on a neighbouring atom and that the susceptibility $\chi$ is independent of $H_o$. Additionally, the number of spin states / sub-levels in a system is given by the spin multiplicity ($M_s = 2S+1$); the quantised orientations of the spin moments with respect to the applied field (Figure 51). The latter assumption above (regarding the independence of $\chi$) indicates that the thermal energy of the surroundings far exceeds that of the energy gap between $M_s$ sub-levels and thus each $M_s$ level has approximately the same population governed by the Boltzmann distribution. An expression describing the macroscopic magnetisation can be derived by summing the magnetic moments (or microscopic
magnetisation) for each $M_s$ level and weighting the value for each level by the Boltzmann distribution between them.

Energy of level ‘$n$’ in zero ‘applied’ field = $E_n^{(0)}$

$1^{st}$ order Zeeman coefficient = $E_n^{(1)}$

$2^{nd}$ order Zeeman coefficient = $E_n^{(2)}$

Microscopic Magnetisation = $-\frac{\partial E_n}{\partial H}$

The expression which is obtained for the macroscopic magnetisation ‘$M$’, in an applied field $H_o$, is given by Equation 10 below:

$$M = \frac{N H_o \sum_n \left( \frac{E_n^{(1)^2}}{kT} - 2E_n^{(2)} \right) \cdot \exp \left( \frac{-E_n^{(0)}}{kT} \right)}{\sum_n \exp \left( -\frac{E_n^{(0)}}{kT} \right)}$$  \hspace{1cm} \text{(Equation 10)}$$

From the initial discussion of magnetic susceptibility ‘$\chi$’, it is known that:

$$\chi = \frac{\partial M}{\partial H}$$

Assuming then that $H$ is small so that $\partial H$ is negligible, the susceptibility is given by:

$$\chi = \frac{M}{H_o}$$

The magnetic susceptibility then is given by Equation 11:

$$M = \frac{N \sum_n \left( \frac{E_n^{(1)^2}}{kT} - 2E_n^{(2)} \right) \cdot \exp \left( \frac{-E_n^{(0)}}{kT} \right)}{\sum_n \exp \left( -\frac{E_n^{(0)}}{kT} \right)}$$  \hspace{1cm} \text{(Equation 11)}$$
This expression describes the relationship between the macroscopic magnetisation $M$ and the Boltzmann distribution of the population of the $M_s$ levels (Equation 11) and is known as the \textit{Van Vleck Equation} (after John Hasbrouck Van Vleck). This equation can be used to derive the Curie Law (when specific assumptions are made), as well as being able to account for the magnetic behaviour of systems which cannot be fitted to the Curie / Curie-Weiss laws.

\subsection*{1.5.3.7 Magnetic Anisotropy: Which direction?}

It has been assumed up to now that there is no directional dependence of the magnetic susceptibility ($\chi$) with respect to the applied field $H_o$; in other words $\chi$ is isotropic and independent of molecular orientation with respect to $H_o$. This is not usually true as molecules and assemblies of molecules are generally anisotropic with respect to the applied field. In such anisotropic systems the magnetic moment will preferentially align in a certain direction (along its easy axis: usually defined as the $z$ axis). Indeed isotropic behaviour is often only found for systems exhibiting purely $O_h$ or $T_d$ symmetry.\textsuperscript{104-106} The magnetic susceptibility, $\chi$, is a tensor quantity and can thus be described by a $3 \times 3$ matrix (Figure 50).

$$
\begin{pmatrix}
\chi_{xx} & \chi_{xy} & \chi_{xz} \\
\chi_{yx} & \chi_{yy} & \chi_{yz} \\
\chi_{zx} & \chi_{zy} & \chi_{zz}
\end{pmatrix}
$$

\textbf{Fig. 50} Tensor representation of the Magnetic Susceptibility $\chi$.

The average susceptibility, $\bar{\chi}$, may be described by Equation 12:

$$
\bar{\chi} = \frac{\chi_{xx} + \chi_{yy} + \chi_{zz}}{3} \quad \text{(Equation 12)}
$$

If $\chi_{xx} = \chi_{yy} = \chi_{zz}$ the material / system under investigation possesses a $\chi$ which is isotropic while if $\chi_{xx} = \chi_{yy} \neq \chi_{zz}$ the material’s magnetic susceptibility is said to be axial. There are various forms of magnetic anisotropy which cause a material’s magnetic susceptibility to deviate from that of its idealised isotropic value. These include $g$-anisotropy and, more importantly, zero-field splitting effects.
1.5.3.7.1 g-anisotropy

The energy of a state / level in a magnetic field depends on the g-value; a parameter which characterises a particle’s magnetic moment (μ) and gyromagnetic ratio. The g-value links a particle’s magnetic moment with its angular momentum quantum number to give a real value of μB (in Bohr magnetons) and hence χ. Indeed the energy gap between Ms states and the applied field H₀ are linked by the g-value as shown in Equation 13:

$$\Delta E(M_s) = g\beta M_s H_o \quad \text{(Equation 13)}$$

For isotropic systems, g is often approximated as being equal to 2 i.e. g~2, however it is often found that g deviates from this isotropic value, which is indicative of anisotropic behaviour and hence a preference by spin magnetic moments to align in a particular direction.

1.5.3.7.2 Zero-Field Splitting

A much more pertinent realisation of the directional dependence of a material’s magnetic moment for an applied field H₀ lies in the phenomenon of zero-field splitting (ZFS). ZFS arises from mixing of ground states with excited states, in a process known as spin-orbit coupling (SOC) (see Section 1.5.3.8), due to lowering of symmetry around the metal centre. For instance, lowering of symmetry can be brought about by the introduction of two trans-ligands at the axial positions of an octahedral complex. SOC effects (for S>1/2 systems) result in the partial removal of the degeneracy of the Ms states (Figure 51) even in the absence of the applied field H₀, hence the term zero-field splitting (symbol D). In magnetic studies this is often referred to as the single-ion anisotropy and is exceedingly important in the study of Single-Molecule Magnet materials (SMMs) (See Section 1.4.3.4). The energies of the now separated Ms states in zero field are given by Equation 14.

$$\Delta E = M_s^2 D \quad \text{(Equation 14)}$$
Fig. 51 Removal of the degeneracy of $M_S$ states in zero field due to anisotropy effects. The $m_s$ values also represent the allowed quantised orientations of the spin moments with respect to the applied field ($H_0$). Examples of $S = 1/2$, $1$ and $3/2$ are given here.

1.5.3.8 Spin-Orbit Coupling: A Closer Look

As mentioned previously, spin-orbit coupling arises from the mixing of the ground state with excited spin states due to lowering of symmetry around the metal centre. If spin-orbit coupling is to be observed for a given system (either mononuclear or polymetallic) there are a number of prerequisites which need to be fulfilled, namely that 1) a half-filled or empty orbital similar in energy and symmetry to that of the unpaired electron must be available nearby and 2) the nearby orbital must not contain an electron with the same spin as the first electron (to obey Hund’s rule and Pauli exclusion principle). The electron in this orbital can make use of the nearby orbital vacancy via transformation processes to circulate around the centre of the complex. These transformation processes generate orbital momentum (orbital magnetic moment $\mu_L$) which combines with the spin-magnetic moment, thus transformation effects a deviation from the spin-only value (Figure 52). These processes can include the transformation of the $d_{xy}$ orbital into $d_{x^2-y^2}$ or $d_{xy} \rightarrow d_{xz}$ transformations etc via rotation about the easy $z$-axis, all as a result of electrons moving from one to the other. For instance, free ions may undergo a multitude of transformations (similar to those above); an orbital motion often referred to as first-order orbital angular momentum ($\mu_L$). The aforementioned prerequisites regarding nearby-orbital spin and energy are fulfilled when one or two of the three $T_{2g}$ orbitals ($d_{xy}$, $d_{xz}$, $d_{yz}$) contain an odd number of electrons.
Fig. 52 Spin-orbit coupling visualised as orbital transformations which are equivalent to one electron moving from one orbital to the other resulting in additional momentum ($\mu_L$). Here a $d_{xy}$ orbital is being transformed into a $d_{x^2-y^2}$ orbital via rotation about the easy $z$-axis.

Some recent examples of systems where spin-orbit coupling effects are considerably pronounced are those of low-spin $3d^5$ and high-spin $3d^6$ (Fe(III) and Fe(II) respectively),\textsuperscript{120,121} as well as high spin $3d^7$ species (Co(II)); the latter being of particular relevance to this thesis.\textsuperscript{122}

1.5.3.9 Magnetic Exchange: Metal Centres ‘Talk’ to One Another

Thus far the discussion has focused on individual metal ions and mononuclear transition metal complexes, so-called magnetically dilute systems. In reality such magnetic dilution is relatively rare, with metal ions in real systems interacting with their neighbours via a number of different processes; interactions known as magnetic exchange. Magnetic exchange is largely effected via 1) Direct exchange and 2) Super-exchange.\textsuperscript{104-110,123}

Before considering these processes in more detail, it is necessary to mention the parameter which is used to quantify the strength and nature of a magnetic exchange interaction. This is known as the isotropic exchange parameter (given as the J value with units of cm$^{-1}$ or K) and describes a magnetic exchange interaction. Its origin stems from the fact that when two paramagnetic centres interact, their local spins $S_A$ and $S_B$ are not good quantum numbers for the system. A spin Hamiltonian may be derived for the system (Equation 15) in which $\hat{S}_A$ and $\hat{S}_B$ are the spin operators for $S_A$ and $S_B$.

$$\hat{H} = -2J \hat{S}_A \cdot \hat{S}_B \quad (\text{Equation 15})$$
Various evolutions of this spin Hamiltonian may be formulated depending on the system under investigation. A number of important points may be derived from a study of the J value, namely if J is negative and large then the coupling is termed strongly antiferromagnetic. A positive (and large) J value, however, indicates strong ferromagnetic exchange between the paramagnetic ions under investigation (Figure 53).

**Fig. 53:** Schematic Representation of a magnetically coupled dimer with corresponding coupling parameter (J).

A representative magnetically coupled dimer is shown in Figure 53 above in which the transition metal centres (A and B) are bridged by atoms (X) and each metal centre has coordinated organic ligands (Y). As mentioned previously, the two paramagnetic centres may interact with one another via either direct-exchange or via a super-exchange mechanism. Direct exchange involves direct overlap of the magnetic orbitals of the two metal centres and gives rise to bonding (symmetric) and anti-bonding (anti-symmetric) molecular orbitals (MOs), analogous to a weak metal-metal bond, and often results in antiferromagnetic exchange between the two nuclei as a result of unpaired electrons pairing in the ground state bonding MO.

The second principal pathway by which two magnetic species may interact with their neighbours is by super-exchange; the exploitation of an intervening diamagnetic ligand species (X in Figure 53) to effect orbital overlap. The type and magnitude of the exchange interaction observed between two metal centres depends on the extent of orbital overlap between each metal centre and the intervening diamagnetic ligand. For instance in a
[Cu(II)$_2$(H$_2$O)$_2$] species (Figure 53) such magnetic exchange would involve orbital overlap between the $d_{x^2-y^2}$ magnetic orbitals of each Cu(II) (A and B metal centres in Figure 53) and the electron pair of the O species in the $p_y$ orbital (X in Figure 53).$^{104}$ For systems in which there is good overlap of electron clouds, antiferromagnetic behaviour (spins aligned antiparallel) is often observed while poor overlap is normally indicative of a ferromagnetic coupling interaction (parallel orientation of spin moments). Indeed it is a general observation for [Cu(II)$_2$] dimers that the more obtuse the bond angle ($>90^\circ$) between metal centres, the more antiferromagnetic the exchange. In more complex systems containing say six or more paramagnetic metal centres (e.g. [Mn$_6$] (Figure 54)),$^{111}$ many pathways exist along which the spin moments on the metal centres may interact. In the case of a simple dimer, there are only two such coupling pathways.

![Fig. 54](image_url)

**Fig. 54** Ball and stick representation of a [Mn$_6$] Single-Molecule Magnet (SMM) exhibiting numerous magnetic exchange pathways. The complex comprises two {Mn(III)$_3$} trinuclear assemblies within which the Mn(III) centres can undergo exchange via the $\mu_3$-bridging O1 and O1’ species. Exchange can also be effected between each {Mn(III)$_3$} assembly via N22 and O12.$^{124}$

In principle, both ferromagnetic and antiferromagnetic exchange interactions are possible for a given complex, however, for systems with large numbers of unpaired electrons, antiferromagnetic exchange often predominates. Indeed, this was found to be the exchange interaction pertaining to planar hydroxyl-bridged [Cu(II)$_2$] species in which a magnetostructural correlation was derived relating the Cu-O-Cu angle ($\theta$) to the observed magnetic characteristics (Figure 55). Below a certain angle $\theta$ the exchange interaction was observed to alternate from antiferro- to ferromagnetic and back again as $\theta$ was once again increased.$^{104}$
Magneto-chemists are currently investigating and deducing such relationships between the structure and magnetic properties of a broad range of transition metal complexes in attempts to glean important information about such systems for potential applications. Magneto-structural correlations on dinuclear first-row transition metal complexes have been widely studied in order to ascertain exactly which structural parameters such as M-M distance, M-L-M angle and M-L-L-M torsion angle (where L = bridging ligand) have most or any influence on the observed magnetic properties. By knowing exactly how certain magnetic interactions are linked to a molecular structure, scientists will be able to deliberately tune a material’s magnetic properties, which would be a powerful and much sought after tool towards future applications of molecular nanomagnets.

1.5.3.10 Further Measurements probed using SQUID Techniques

1.5.3.10.1 AC Susceptibility / Dynamic Susceptibility

Pilot investigations utilising SQUID magnetometry involve probing the sample with a direct current (DC) field whereby the sample under investigation is exposed to a constant applied field while the magnetic moment of the sample is measured. One of the principal reasons for incorporating alternating current (AC) methods is the ability of an AC field, unlike DC measurements, to probe time-dependent magnetic processes (magnetisation dynamics) as a result of the induced sample moment being time-dependent. Indeed, one of the principal advantages of AC measurements, as opposed to DC investigations, is its ability to detect small changes in magnetisation. The ability of AC measurements to detect such small changes in magnetisation allows one to determine whether or not a material possesses
When systems are probed at higher frequencies than those normally considered in DC measurements, the magnetisation may lag behind the AC field utilised, resulting in a phase shift between the two signals. Therein lies the utility of the AC technique, the ability to measure $\chi$ and this lag or phase shift. Translation of this phase shift into magnetic susceptibility affords two pseudo-susceptibilities (components of $\chi$), the in phase (real) $\chi'$ and out-of-phase (imaginary) $\chi''$. It is the latter parameter ($\chi''$) that is found to afford information on SMM behaviour; essentially if a material exhibits an out-of-phase signal it is said to exhibit SMM characteristics (Figure 56).

**Fig. 56** AC susceptibility plots for a [Mn(III)$_6$] Single-Molecule Magnet (SMM). (top) Plot showing the in phase real component ($\chi'$) and (bottom) plot depicting the out-of-phase imaginary component ($\chi''$). The out-of-phase (SMM) component for such [Mn(III)$_6$] species is realised by the observance of signals below $\approx$4 K in Figure 56. AC measurements also allowed Canaj and co-workers to detect the SMM behaviour of a blue emitting octahedral [Dy(III)$_7$] complex with potential applications in chemical sensing.

Additionally, AC measurements are performed on materials proposed for use as superparamagnetic and Single-Molecule Magnet (SMM) characteristics (See Section 1.5.4.2).
superconductors. It is clear that AC magnetic susceptibility experiments are of vital importance in the continued characterisation of the magnetic properties of polymetallic complexes. Through a combination of DC and AC measurements, it will be possible to devise synthetic strategies to tune the magnetic properties of such polynuclear assemblies to afford materials with useful applications. Indeed, such a methodology combined with previous discussions on host-guest chemistry could allow for the generation of multifunctional species such as spin-crossover materials.

1.5.4 A Closer Look: Further Applications of Magnetic Materials

The sections that follow serve as a brief overview of current applications of magnetic materials. Magnetic materials, however, have been in widespread use for many years in the form of magnetic resonance imaging (MRI) contrast agents, utilised for enhanced selectivity and tissue specificity in the MRI technique for detection of cancerous tumors (see Appendix: Section A).

1.5.4.1 Magnetic Coolant Materials

One of the more novel applications of molecular magnetic materials which have garnered increasingly widespread appeal is that of magnetic coolants (a.k.a molecular refrigerants). This application of molecular nanomagnets is based on the magnetocalorific effect which essentially relates the change in magnetic entropy and adiabatic temperature to a change in the externally applied magnetic field. The phenomenon (illustrated in Figure 57) allows for cooling at the molecular level and is reported, in some instances, to be superior to that of solid-state refrigerant materials in terms of cooling ability. The overriding principle is that spin magnetic moments (dipoles) undergo entropy changes (ΔS) as a result of the application/removal of an applied magnetic field (H_{APP}).
Fig. 57 Schematic showing the fundamental steps to magnetic refrigeration.
There are a number of pre-requisites which need to be fulfilled if a system is to possess coolant characteristics. These include the necessity for 1) a large ground-spin state, 2) negligible magnetic exchange between magnetic centres and 3) negligible or zero magnetic anisotropy ‘D’ (i.e. J and D ≈ 0). Observance of coolant characteristics is also dependent on the number of metal ions in a given system (with more metal ions corresponding to an enhanced coolant effect). Thus polynuclear Ln(III) species are invariably used as candidates for this purpose.  

Magnetic coolant properties have recently been observed in calix[4]arene mixed metal (3d/4f) systems (Figure 58) and dinuclear [Gd(III)₂] species as well as in [Gd(III)ₓMn(II)ₘ] and [Gd(III)ₓNi(II)ₘ] systems developed by the groups of Brechin and Winpenny respectively.  

This breed of polynuclear complex, based on the MCE phenomenon, promises to afford great utility in the future study and fabrication of molecular nanomagnets for functional applications.

**Fig. 58** (left) Crystal structure of a [Mn(III)₄Gd(III)₄] molecular coolant. (right) The observed magnetic susceptibility and (inset) magnetisation vs. field (M vs. H) data for this complex.

### 1.5.4.2 Single Molecule Magnets

One very important and extremely interesting sub-group in the field of molecular magnetism are the paramagnetic species known as Single-Molecule Magnets (SMMs), often referred to as molecular nanomagnets. The first polynuclear complex to show SMM behaviour was the Mn-based dodecanuclear complex [Mn₁₂O₁₂(C₂H₆CCH₃)₁₆(H₂O)₄] ([Mn₁₂]), which was first discovered in 1993, although initially synthesised in 1980 by Lis et al. SMMs are a class of magnetic material which are able to display magnetic hysteresis of molecular origin due to slow magnetisation relaxation (Figure 59). The point of difference with SMMs is that these
properties are exhibited by discrete molecules, as opposed to bulk magnets, where hysteresis is as a result of interactions between paramagnetic metals existing in magnetic domains, as is the case with common bar magnets. Magnetic hysteresis is a property associated all magnetic materials and is effectively the ability of a species to remain magnetised, even in the absence of an externally applied magnetic field (Figure 60).

![Figure 59](image1.png)

**Fig. 59** Magnetic Hysteresis behaviour observed for [Mn$_{12}$O$_{12}$(O$_2$CCH$_3$)$_{16}$(H$_2$O)$_4$].

![Figure 60](image2.png)

**Fig. 60** Magnetic hysteresis observed for a polymetallic [Mn$_{30}$] transition metal cluster. This data was obtained from single crystal measurements.
It is instructive to utilise a ‘real-world’ example of hysteresis, as it applies to SMM systems, as opposed to the idealised, perfectly symmetric hysteresis loop often used to explain this phenomenon. The sample being measured here is a [Mn$_{30}$] SMM developed by Soler and co-workers and the hysteresis curve for this system is shown in Figure 60. The sample is initially at zero-field within the SQUID when the applied field, directed along the easy axis of the complex, is gradually increased. The magnetisation of the [Mn$_{30}$] complex subsequently increases, reaching a maximum at Point A. This maximum magnetisation is known as magnetisation saturation. The applied field is then switched off, however, the magnetisation of the sample does not return to zero (Point B). The magnetic field at which the magnetisation would return to zero is known as the coercive field while the residual magnetisation, in the absence of an applied field, is known as the remnant magnetisation. For an ideal ferromagnet, the remnant magnetisation would be equal to the saturation magnetisation value (Point C). The applied field is then swept, in this case, at rates of between 0.14 and 0.008 T/s in the opposite (negative) direction. The [Mn$_{30}$] species again achieves magnetisation saturation (Point D) with remnant magnetisation (Point E) similarly been observed once again, but in the opposite direction. At the points of magnetic saturation the spin moments of electrons may be up or down with respect to the applied field; important for bistability in SMMs for information storage applications. Application of the magnetic field in the original direction completes the experiment, affording a hysteresis loop characteristic of an SMM.

1.5.4.2.1 Current Work with Single Molecule Magnets

Despite 15 years of intense research, it was only recently that an N$_2^3$-bridged [Dy(III)$_2$] dinuclear complex has shown a larger barrier to magnetisation reversal and higher working temperature than the previous record holders of general formula [Mn(III)$_6$O$_2$(sao)$_6$(O$_2$CPh)$_2$(EtOH)$_4$] (saoH$_2$ = salicylaldoxime). The characteristic hysteresis curve observed for this dinuclear complex (of formula {[([Me$_3$Si]$_2$N]$_2$(THF)Dy]$_2$(μ-η$_2^3$:η$_2^3$-$N_2$)}) is shown in Figure 61 below.
Fig. 61 (left) Crystal structure of an N$_2^3$-bridged [Dy(III)$_2$] complex and corresponding hysteresis curve (right) exhibiting the highest known blocking temperature of 8.3 K for a SMM.\textsuperscript{139}

Corresponding to this barrier to magnetisation reversal is the record-breaking blocking temperature of 8.3 K, with remnant magnetisations observable on the minutes timescale.\textsuperscript{139} It is worth noting, however, that by targeting specific structural distortions within the family of [Mn(III)$_6$] complexes mentioned above, scientists were able to tune and improve their SMM behaviour to generate the former record-holding SMM [Mn(III)$_6$O$_2$(Et-sao)$_6$(O$_2$CPh)$_2$(EtOH)$_6$], possessing an upper effective barrier to magnetisation reversal of S$^2$D = 86K as opposed to [Mn$_{12}$] complexes with U$_{\text{eff}}$ values up to 74K.

The importance and potential applications of SMMs cannot be under-estimated. The prospects are many and varied and include: information storage, quantum computing and molecular spintronics. The potential applications of SMMs stem from the aforementioned magnetic hysteresis in these materials and an overview of just some of these applications is given in the sections that follow.

\textit{1.5.4.2.1.1 Information Storage Devices}

Single-Molecule Magnets display magnetic hysteresis of molecular origin and thus possess magnetic-bistability.\textsuperscript{135} This bistable behaviour essentially arises as a result of an energy barrier (hill) to magnetisation reversal, effectively allowing the molecule to exist in one of two magnetic states (spin-up, spin-down) [shown by yellow arrows in Figure 62] at any given time. Molecules can switch between the two spin states if they can surmount the energy maximum in Figure 62; the relationship between the energy maximum (U$_{\text{eff}}$) and the total
spin of the system (S) is given by $U_{\text{eff}} = S^2 D$. Molecules may also switch between the two spin states by tunnelling through this energy barrier in a process called quantum tunnelling, described in Section 1.5.4.2.1.3.

![Energy vs Quantum Number Diagram](Image)

**Fig. 62** Bistability of spins observed in SMMs due to existence of energy barrier to magnetisation reversal given by $U_{\text{eff}} = S^2 D$.\textsuperscript{140}

This dual nature is analogous to the binary system (0,1) utilised in digital electronics and modern information storage devices. Thus SMMs could potentially function as information storage devices.\textsuperscript{141} Effectively, one molecule would be equivalent to one ‘bit’ of memory. In terms of a home PC, this could increase the density of information stored by at least 10000 times relative to conventional storage devices. As yet, however, realising such an application of SMM systems has not been possible due to the very-low temperatures at which this SMM behaviour is observed. The working temperatures of such materials would need to witness a pronounced increase for such data storage to be feasible.

**1.5.4.2.1.2 Molecular Spintronics**

Society today is in constant search of ever-smaller electronic devices. The ability of SMMs to store information in their spins (bistability) and their nano- and sub-nano level dimensions makes them ideal candidates for molecular spintronic devices: using an electron’s dual function of spin and electronic charge to produce miniaturised electronic components (molecular transistors, switches etc) for nanodevices.\textsuperscript{142} The move towards nano-scale
devices and the miniaturisation of device components has gained considerable impetus in recent years as evidenced by the extensive literature on the topic. For instance, Prasad and co-workers recently described a [Fe(III)$_4$] system possessing an azobenzene functionality with the potential for use as devices possessing optical and magnetic bistability. The well-defined redox nature of porphyrin species (mentioned previously) has also been combined with the bistability characteristics of SMM materials in the dinuclear Tb(III) systems (Figure 63), developed by Sakaue et al. The breadth of additional SMM systems which exist with potential spintronics applications is staggering and serves to highlight the growing desire to isolate functional magnetic species of molecular origin.

**Fig. 63** Three views of the [Tb(III)$_2$] dinuclear complexes developed by Sakaue and co-workers (a) side, (b) top and (c) bottom.

### 1.5.4.2.1.3 Quantum Information Technologies

As mentioned previously, there exists a barrier to magnetisation reversal in SMM systems. In regular bistable materials, the only way for a system to switch from spin-up to spin-down (i.e. between $M_S$ states) is to overcome this energy barrier. However, transition between the two states (and hence magnetisation reversal) can also be effected via quantum tunnelling of the spin ground state (magnetisation) through this energy barrier, between any two $M_s$ states which are in resonance (see blue arrow in Figure 62). Such behaviour has the potential for applications in quantum information processing (QIP) (or quantum computing), where one molecule would be equivalent to ‘one qubit’ (quantum bit). One of the first SMM systems to exhibit relatively pronounced quantum-tunnelling behaviour was the previously described [Mn$_{30}$] system developed by Soler et al, while recently synthetic realisation of...
materials possessing quantum-tunnelling characteristics has been demonstrated by the work of Gómez-Coca and Affronte in the form of \([\text{Ni(II)}_3\text{Mn(III)}_2]\) and \([\text{Cr(III)}_7\text{Ni(II)}_1]\) polynuclear architectures respectively (Figures 64 and 65 respectively).\(^{150,151}\)

**Fig. 64** Crystal structure of a \([\text{Ni(II)}_3\text{Mn(III)}_2]\) SMM which exhibits quantum tunnelling of the magnetisation barrier separating spin states.\(^{150}\)

**Fig. 65** The cyclic topology of the mixed-metal species \([\text{Cr(III)}_7\text{Ni(II)}_1]\), developed by Affronte and co-workers and utilised in quantum tunnelling studies.\(^{151}\)
1.6 References


(13) [www.rcsb.org/pdb](http://www.rcsb.org/pdb) *Protein Data Bank* Brookhaven, USA, 2012.


Chapter Two

Investigating the Solid-State Host-Guest Properties of Heptanuclear $[M_7]$ ($M = \text{Ni(II), Co(II/III), Zn(II)}$) Discs
2.1 Introduction

Supramolecular chemistry has rapidly become a vast and multidisciplinary field with applications including catalysis,\textsuperscript{1} anion sensing recognition,\textsuperscript{2-4} gas sequestration / storage\textsuperscript{5} and species transportation towards drug delivery,\textsuperscript{6-8} and consequently is of interest to scientists of wide ranging disciplines. One particularly interesting facet of supramolecular chemistry concerns the expression of high degrees of local and extended topological control onto a molecule (e.g. a host unit) in terms of its partaking in intermolecular interactions with other species (e.g. a guest molecule). This is achieved via careful structural manipulation of these molecules (and molecular assemblies) giving rise to complex molecular architectures possessing targeted synergic chemical and physical properties. Although supramolecular host-guest chemistry has been readily exhibited and widely reported with a vast array of organic receptor moieties,\textsuperscript{9-11} the engagement of magnetically interesting inorganic host units is still relatively rare.\textsuperscript{12-17} The complementarity which has long existed between the fields of supramolecular chemistry and molecular magnetism has fascinated scientists for many years.\textsuperscript{18} This was once again highlighted quite recently in the production of a tetranuclear [Mn\textsubscript{4}] Single-Molecule magnet\textsuperscript{19} and a [Mn\textsubscript{4}Gd\textsubscript{4}] magnetic cooler,\textsuperscript{20} each built entirely using bowl-like Calix[4]arene ligands - a cyclophane synonymous with host-guest supramolecular chemistry.\textsuperscript{21} By employing this particular ligand, the authors have purposefully exercised site specific cluster growth (i.e. the {Mn\textsubscript{4}} and {Mn\textsubscript{4}Gd\textsubscript{4}} motifs can only be formed at the lower rim of the Calix[4]arene ligands) and spatial separation of the individual [Mn\textsubscript{4}] units to promote magnetic dilution.

This chapter focuses on the synthesis, structural and magnetic characterization of a large family of heptanuclear, 1\textsuperscript{st} row transition metal complexes incorporating the Schiff base ligand 2-iminomethyl-6-methoxyphenol (L\textsubscript{1}H) or one of its analogues (L\textsubscript{1-4}H) (Figure 66).\textsuperscript{22,23} As mentioned previously the choice of ligand in the synthesis of polynuclear complexes exhibiting interesting structural / magnetic characteristics is of the utmost importance; especially from the point of view of their ability to influence complex stability, topology and the intermolecular interactions that occur therein. To this end employment of a Schiff base ligand such as 2-iminomethyl-6-methoxyphenol (L\textsubscript{1}H), or one of its analogues, was an obvious choice stemming from the reported utility of such species in isolating
coordination compounds possessing novel structural topologies. For instance compounds comprising Schiff base ligands, analogous to L₁H and synthesized from an o-vanillin precursor, have recently been reported in the generation of mixed-metal 3d/4f complexes.²⁴,²⁵

![Fig. 66](image)

Fig. 66 (a) o-Vanillin precursor, (b) the Schiff base ligand L₁H and (c) its functionalised Schiff base analogues; where R = Br, R’ = Me (L₂H); R = H, R’ = Ph (L₃H) and R = Ph, R’ = Me (L₄H).

Indeed L₁H and its analogues, which may be described as ¼ of a calix[4]arene unit fulfill all the requirements for generating large metal-ligand assemblies. Their structures allow not only for ligation between multiple metal sites (via their methoxide, phenolate and imino sites) but also afford the potential for intermolecular π-π stacking and H-bonding interactions. The complexes described herein not only exhibit quite interesting magnetic properties but they also possess another interesting property, that of solid-state host-guest characteristics.

### 2.2 Isolating the Founder Members of the [M(II)₇] Family

The first complex to be obtained using the Schiff base ligand 2-iminomethyl-6-methoxyphenol (L₁H) was the heptanuclear Ni(II) species [Ni(II)₇(OH)₆(L₁)₆(NO₃)₂] (I). The founder member of a family of heptanuclear pseudo metallocalix[6]arene discs, this complex was isolated following the reaction of Ni(NO₃)₂·6H₂O with L₁H and NaOH in ethanol. Filtration and subsequent slow evaporation of the mother liquor afforded 1 as green crystalline hexagons in 30 % yield (Figure 67). Complex 1 crystallises in the trigonal space group P-3c1 with corresponding unit cell parameters: a = 13.806(2) Å, b = 13.806(2) Å, c = 23.270(5) Å, α = 90°, β = 90°, γ = 120°. Complete X-ray structural details for 1 are given in Table 6 (Section 2.5).

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2.2.1 Topological Features of the [Ni(II)$_7$] System

The core in 1 comprises a body-centred hexagon whereby a central Ni(II) ion is surrounded by six peripheral Ni(II) ions to form a planar disc. Although topologically analogous [Mn$_7$]$_{26-30}$ [Fe$_7$]$^{31}$ and [Co$_7$]$^{32}$ complexes are known, the synthesis of 1 represents the first example for the paramagnetic Ni(II) ion (Figure 68).$^{22,23}$

**Fig. 67** (left) Crystal of 1 used in X-ray diffraction data collection. (right) The sample of 1 used for magnetic measurements, highlighting the hexagonal topology observed in the structure.

**Fig. 68** Heptanuclear disc-like topology exhibited by the inorganic core in 1 as viewed perpendicular to the [Ni(II)$_7$] plane. Colour code: Ni = green, O = red, N = blue, C = grey. Hydrogen atoms have been omitted for clarity.
All seven Ni(II) centres exhibit distorted octahedral geometries. The six $\mu_3$-bridging OH$^-$ ions (O1 and symmetry equivalent (s. e.)) link the central nickel (Ni1) to the six peripheral nickel ions (Ni2 and s. e.). The central Ni(II) ion is located at a site with imposed 3-bar symmetry with the NO$_3^-$ nitrogen atom (N2) sitting on a threefold axis. The remainder of the asymmetric unit consists of a second Ni(II) centre (Ni2) along with one L$_1^-$ unit (deprotonated L$_1$H) and one hydroxy group (O1-H1) occupying general positions. Each of the six trigonal pyramidal OH$^-$ ions is situated alternately above and below the [Ni(II)$_7$] plane. The six L$_1^-$ ligands are deprotonated at the phenolate site only and bridge the peripheral Ni(II) centres via an $\eta^1$:$\eta^2$:$\eta^1$-$\mu$ coordination motif (Figure 69).

Fig. 69 Schematic showing the coordination motif of L$_1$H with respect to the octahedral Ni(II) metal centres in 1.

The L$_1^-$ ligands are situated alternately above and below the [Ni(II)$_7$] plane resulting in a double-bowl conformation in which the [Ni(II)$_7$] core represents the basal plane, analogous to a metallocalix[6]arene concave unit. Further investigation of the double-bowl framework identifies approximate bowl dimensions of (Å) 6.20 x 4.21 x 11.70 (base (b) x depth (d) x rim diameter (r)) (Figure 70).
Fig. 70 (left) Double-bowl topology exhibited by 1. Hydrogen atoms have been omitted for clarity. (right) Schematic depicting the double-bowl unit in 1 and its dimensions (in Å) 6.20 x 4.21 x 11.70 (base (b) x depth (d) x rim (r)).

The [Ni(II)] units in 1 stack one on top of the other resulting in the formation of pseudo-superimposable 1D columns whereby each unit is spaced at a [Ni(II)] plane−[Ni(II)] plane distance of 11.64 Å.22-23 In the crystals of 1 the [Ni(II)] units stack on top of one another resulting in a unit cell possessing four pseudo-superimposable 1D columns of [Ni(II)] units with each unit linked by a 120° rotation (Figure 71).

Fig. 71 (left) Crystal packing observed in 1 as viewed down the c-axis of the unit cell. (right) View along a-axis of the cell in 1. Large spheres represent NO$_3^-$ counter anions. Colour code: Ni = green, O = red, N = blue, C = grey. Hydrogen atoms have been omitted for clarity.

The [Ni(II)] moieties are connected into 1D columnar arrays via zig-zag shaped belts of NO$_3^-$ anions (each comprising six NO$_3^-$ ions), located above and below the individual [Ni(II)] units with dipolar C-H···O bonding interactions between the NO$_3^-$ oxygen atoms (one unique O4) and protons (H1A and H5) of the L$_1^-$ ligands (H1A···O4 = 2.59Å and H5···O4 = 2.44Å). The NO$_3^-$ belts act as molecular zips by pairing up individual [Ni(II)] units to form molecular cavities each of approximate volume ~265.9 Å$^3$,33 formed by two juxtaposed pseudo metallocalix[6]arene [Ni(II)] bowl units (Figure 72).
2.2.2 Investigating the Hosting Potential of this [Ni(II)$_7$] Array

Although no guest species took up residence within the aforementioned molecular cavities in 1, the fascinating double-bowl metallocalix[6]arene cavities observed led to their investigation as potential paramagnetic host architectures. Initial work involved the replacement of EtOH (used as the reaction medium) with a MeOH solvent in order to ascertain whether this smaller solvent molecule (MeOH) might take up residence within the host cavity. This proved successful with the isolation of the solid-state host-guest complex [(MeOH)$_2$Ni(II)$_7$(OH)$_6$(L$_1$)$_6$(NO$_3$)$_2$]$_2$ (2), which crystallises as hexagonal blocks in the same trigonal P-3c1 space group as 1 in 40 % yield. The ‘⊂’ notation is used here to indicate guest inclusion of MeOH species within the host cavity. Complete X-ray structural details for 2 are given in Table 6 (Section 2.5). The improved yield of 2, when compared to the synthesis of 1, is likely due to the increased solubility of NaOH in MeOH. Complex 2 also exhibits a central Ni(II) (Ni1) of imposed 3-bar symmetry and a N atom (N2) of the NO$_3^-$ counter anion (N2) located on a three-fold axis. The molecular cavities in 2 are similar to those in 1 (6.20 x 4.16 x 11.81 Å (base x depth x rim diameter)), while the [Ni(II)$_7$]$_{plane}•••[Ni(II)$_7$]$_{plane}$ distance of 11.57 Å is also comparable to that of 1 (see Section 2.5: Table 4). The former differs with respect to its sibling only in that the H-bonded cavities in 2 (of calculated volume of
~293.7Å³) are of the required dimensions to accommodate two disordered guest MeOH molecules (Figure 73).

Fig. 73 (left) Intermolecular interactions (facilitated by NO₃⁻ counter anions) bind MeOH guests within molecular cavities generated in 2 as viewed parallel to the [Ni(II)₇] cores. (right) Space-filling representation of 2 showing hexagonal core and templating NO₃⁻ counter anions. Colour code: Ni = green, O = red, N = blue, C = grey, H = light blue.

When small molecules are located within such highly symmetrical molecular cavities, it is common to observe crystallographic disorder and the MeOH guest molecules in 2 are no exception. The first disordered MeOH guest (atoms C20-O10) has only 1/6th occupancy and occupies positions in between the NO₃⁻ counter anions. These NO₃⁻ anions form a zig-zag shaped belt as seen in 1 and lie in between the double-bowl units. This MeOH guest is H-bonded via the interaction between the oxygen atoms of the MeOH molecule and the bridging µ₃-OH⁻ (hydroxide) groups which line the basal plane of the heptanuclear core (O4(H4)···O10 = 2.86 Å). The second disordered MeOH guest (C21-O9) lies within the molecular cavity in 2 at the midpoint between the two [Ni(II)₇] planes (possessing a two-fold axis along the C-O vertex of the MeOH unit) and is disordered over three sites with respect to the three fold rotation axis inherent to the cell (Figure 74). The latter central MeOH guest shows no significant signs of supramolecular interactions within or outside its host cavity. This is not particularly surprising as the central MeOH guest moiety lies over 4 Å away from the nearest µ₃-OH⁻ proton (O1(H1)···O9 = 4.10 Å).
Fig. 74 Crystal packing observed in 2 with disordered MeOH guests depicted as space-filled spheres. Dashed lines represent H-bonding interactions in between the individual [Ni(II)] units in 2 (via the NO₃\(^-\) anions). Colour code: Ni = green, N = blue, O = red, C = grey.

It was decided to attempt the encapsulation of a larger guest molecule which would invoke H-bonding interactions within the molecular cavity and promote affinity towards its solid-state host receptor. It was decided to utilise the NO₂Me unit as a potential guest on the assumption that its O-atoms would interact with the hydrogen atoms of the µ₃-OH\(^-\) bridges within the [Ni(II)] host cavity units. Indeed, the symmetry inherent to the nitromethane molecule makes it an ideal candidate towards guest residency within the double-bowl cavity previously observed in 1 and 2. This was achieved with the isolation of the solid-state host-guest complex [(NO₂Me)₃−Ni(II)₇(OH)₆(L₁₆)₆(NO₃)₂] (3), formed by dissolution and recrystallization of 1 from NO₂Me in 15 % yield. Complete X-ray structural details for 3 are given in Table 6 (Section 2.5). The host cavity observed in 3 has a calculated volume of 283.8 Å\(^3\) and is occupied by three disordered NO₂Me guests which are related crystallographically via a three-fold rotation (Figure 75).
The trigonal planar NO$_2$Me guests in 3 are disordered as evidenced by the carbon atoms [C10 and symmetry equivalent (s.e.)] of the Me-groups in NO$_2$Me lying on a two-fold axis. These orientations are most likely to exist in the up-down-up anti-parallel configuration with respect to the three fold rotation symmetry they share, as any other spatial arrangement would result in significant steric effects (Figure 75). As predicted the three interact within the cavity via hydrogen bonding interactions between their O-atoms (O5 and O6) and the nearby µ$_3$-OH$^-$ protons of the two [Ni(II)$_7$] units which line the cavity floors (O1···O5 = 3.08 Å; O1···O6 = 3.25 Å).

### 2.2.3 Widening the Gap: Towards Selective Guest Encapsulation

In order to alter the interior size and shape of the molecular cavities highlighted in 1-3 towards subsequent modification and / or control of guest preference, it was decided to attempt to increase the bowl depth (in relation to complexes 1-3) by utilising the Br-analogue of the ligand L$_1$H, namely 4-bromo-2-iminomethyl-6-methoxy-phenol (L$_2$H) (Figure 66). Complexation using the functionalised Schiff base ligand L$_2$H was realised with the isolation
of the heptanuclear species \( [(\text{MeCN})_2\text{Ni(II)}_7(\text{OH})_6(\text{L}_2)_8](\text{NO}_3)_2 \) (4) upon reaction of an ethanolic solution of \( \text{Ni(NO}_3)_2\cdot6\text{H}_2\text{O} \) with \( \text{L}_2\text{H} \) and \( \text{NaOH} \). The mother liquor was then left to evaporate slowly, however no crystalline product was obtained. The subsequent green powder produced was redissolved in numerous potential guest solvents (MeOH, \( \text{NO}_2\text{Me} \), MeCN). Interestingly only the MeCN guest species was successfully incorporated in the form of complex 4 which was formed in 23 % yield (based on Ni used in original reaction). In contrast to the trigonal P-3c1 settings in 1-3, complex 4 crystallises in the monoclinic C2/c space group. Complete X-ray structural details for 4 are given in Table 6 (Section 2.5). The two MeCN guests within the cavity of 4, exhibit a head-to-tail conformation (Figure 76). Analogous to our previous discs (1-3) H-bonding is the dominant intermolecular interaction in the encapsulation of the MeCN guests within the host cavity. In this instance, H-bonding takes place between the N-atoms of the MeCN guests (N5) and the protons of the \( \mu_3-\text{OH}^- \) groups (H3A) of neighbouring \([\text{Ni}_7(\text{OH})_6]\) units (N5···H3A(O3) = 2.36 Å) (Figure 76).

**Fig. 76** (left) Interlocked [Ni(II)7] double-bowl units in 4 afford a tightly-enclosed cavity for encapsulation of two MeCN guests. (right) H-bonding interaction between a guest MeCN molecule (one shown) and the protons of a \( \mu_3-\text{OH}^- \) group. Colour code: Ni = green, Br = yellow, O = red, N = blue, C = grey, H = light blue.

The central Ni(II) ion located at the centre of 4 lies on an inversion centre with the remaining three metal centres (Ni1-Ni3) and all other atoms in the asymmetric unit occupying general
positions. It was proposed that by functionalising the original Schiff base ligand, the resultant molecular cavity may be modified towards encapsulation of a variety of different guest species. Employment of L2H in the synthesis of 4 results in a significantly altered cavity size and shape evidenced from the crystal structure of the 4, which shows the formation of a deeper bowl of dimensions of (Å) 6.22 x 6.18 x 11.90 (base x depth x rim diameter). As observed in 1-3, the individual [Ni(II)7] units in 4 stack into super-imposable 1D columns, which propagate along the $b$-direction of the unit cell (Figure 77).

![Crystal packing observed in 4](image)

**Fig. 77** Crystal packing observed in 4 (NO$_3^-$ anions omitted for clarity). Colour code: Ni = dark green, C = grey, N = blue, Br = yellow, O = red. Hydrogen atoms have been omitted for clarity.

The stacking of the [Ni(II)$_7$] units along the $b$-axis is bolstered by two complementary O-H···Br interactions which involve one $\mu_3$-OH$^-$ of a [Ni(II)$_7$] unit and the bromine atom of a neighbouring [Ni(II)$_7$] moiety (O(H)···Br = 2.82 Å). These hydrogen bonding interactions direct the formation of molecular cavities, which differ from those in 1-3 as they are tilted with respect to the [Ni(II)$_7$] planes and are interlocked in a staggered arrangement (Figure 78). The [Ni(II)$_7$]$_{\text{plane}}$-[Ni(II)$_7$]$_{\text{plane}}$ distance inside the cavity is 11.14 Å and represents a cavity-height reduction of $\sim$ 0.4 Å relative to that seen in 1-3.
**Fig. 78** Space-fill representations of 4 highlighting the interlocking, staggered arrangement of molecular cavities therein. The view on the right clearly shows the tilting of the cavities with respect to the [Ni(II)] planes. Colour code: C = grey, O = red, N = blue, Br = yellow. Hydrogen atoms have been omitted for clarity.

It is believed that reduction in cavity height is attributed to the significant H-bonding affinity of the pendant Br-atoms in 4, which generates a more tightly embraced cavity of approximate volume 155.9 Å³, which is significantly smaller than those of 1 (265.9 Å³), 2 (293.7 Å³) and 3 (283.8 Å³). Further details of cavity dimensions pertaining to complexes 1-4 are described in Table 4 (Section 2.5).

Investigations into whether or not selective guest encapsulation of MeCN and NO₂Me were possible within cavities formed in 2 and 4 respectively were unsuccessful. These investigations were two-fold. Firstly attempts were made at recrystallising 2 from a mixture of MeCN and NO₂Me. However, upon crystallisation, only NO₂Me was encapsulated within the double-bowl molecular cavity. Secondly, attempts at recrystallisation of 4 from a mixture of MeCN and NO₂Me afforded only the MeCN-encapsulated system with no NO₂Me guest. It was concluded that only those guest molecules which can orientate themselves into certain topologies comprising symmetry elements compatible with their host lattices can dock within the double-bowl molecular cavities. For instance the three-fold symmetry present in the cavity of 2 cannot accommodate the MeCN guest which possesses two-fold symmetry. This hypothesis is supported by the formation of complex 3, which crystallises in the trigonal P-3c1 space group, in which three NO₂Me guests linked via a three-fold rotation axis are accommodated inside the trigonal P-3c1 cell, whereas attempts at producing a MeOH guest analogue to 4 (in a monoclinic C2/c cell) remain fruitless. It must be noted that the size and
shape of the molecular cavities in such complexes will also reflect their resultant guests and must also be considered here.

### 2.2.4 3D Connectivity of (1-4)

Complexes 1-3 crystallize in the trigonal P-3c1 space group and only differ in terms of their guest occupancy and therefore are analogous in terms of their 3D connectivity. The [Ni(II)$_7$] columns in each of their unit cells are connected via H-bonds to adjacent 1D [Ni(II)$_7$] columns. These connections are manifested by a myriad of H-bonding interactions between the NO$_3^-$ counter anions and the individual [Ni(II)$_7$] moieties. More specifically each [Ni(II)$_7$] is H-bonded to twelve NO$_3^-$ counter anions, which in turn connect to six other [Ni(II)$_7$] units, thus creating a (6,12)-connected net with a $(4^{15})_2(4^{48}.6^{18})$-alb topology (Figure 79).$^{34,35}$

![Fig. 79 (6,12)-connected net with a $(4^{15})_2(4^{48}.6^{18})$-alb topology exhibited by 1-3 (blue spheres represent the 12-connected [Ni(II)$_7$] units while red spheres are representative of 6-connected NO$_3^-$ species).](image)

As mentioned previously, complex 4 crystallises in the monoclinic C2/c space group and as such possesses a 3D connectivity, which differs to that of 1-3. The 1D columnar stacks of [Ni(II)$_7$] units in 4 are linked by C-H···Br interactions through the Br-atoms (Br2 and Br3) of the bridging L$_2^-$ ligands and the –Me protons (H18B and H27B) of adjacent [Ni(II)$_7$] moieties (H18B···Br3 = 2.93 Å, H27B···Br2 = 2.70 Å and s.e.). The result is a 3D connectivity comprising a 10-connected net with a $(3^{12}.4^{28}.5^5)$-bct topology (Figure 80).$^{34,35}$
2.2.5 IR Evidence for Guest Encapsulation

IR spectroscopic studies on the host complexes 2-4 were performed to ascertain whether their guest molecules remained within their respective H-bonded cavities on drying. Elemental analyses on samples of 2-4 were consistent with retained guest. The IR spectrum of [(MeOH)$_2$Ni(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (2) showed broad OH stretching bands (centred at 3416 cm$^{-1}$) attributable to both the µ$_3$-OH bridges and MeOH guest solvent molecules. However, there was also a possibility that such bands were due to adsorbed MeOH solvent molecules and therefore the same sample was subsequently dried at room temperature under high-vacuum for 2 hours prior to re-analysis of its IR spectrum. It was found that the initial broad OH stretching band had lost intensity on drying and was now centred at 3406 cm$^{-1}$ (Section 2.5.3.3: Figure 113). Subsequent elemental analysis on this same sample analysed as guest-free [Ni(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (i.e. identical to that of complex 1). Similarly, the IR spectrum of 3 (NO$_2$Me species) gave peaks at 1337 and 1555 cm$^{-1}$, which are characteristic for the asymmetric and symmetric NO stretching of the guest NO$_2$Me molecules, respectively. Subsequent vacuum drying of a sample of 3, resulted in the loss of these vibrational bands indicating that the NO$_2$Me guests were weakly bound within the double-bowl cavity and had exited the molecular housing under high-vacuum conditions. This spectroscopic observation was reinforced by CHN elemental analysis of a sample of 3 which again analysed as [Ni(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (identical to complex 1).

The facile removal of the MeOH and NO$_2$Me guests in 2 and 3 respectively is consistent with their crystal structures and more specifically in the way that guests ‘dock’ within the host.
cavity i.e. via weak H-bonding interactions. Thus the molecular cavities formed in the crystalline architectures of these complexes are by no means tightly bound enclosures. The IR spectrum of \([(\text{MeCN})_2\subset\text{Ni(II)}(\text{OH})_6(\text{L}_2)_6](\text{NO}_3)_2\) (4) exhibits a weak resonance at 2256 cm\(^{-1}\) corresponding to a C≡N stretch, indicative of the enclosed MeCN guest molecules. This complex is unique (relative to complexes 1-3) in that the peak at 2256 cm\(^{-1}\) is not lost upon exposure to the same high-vacuum conditions as complexes 2-3 (Section 2.5.3.5: Figure 114). Commensurate with this spectroscopic observation, elemental analysis of a sample of 4, remained unchanged. These observations would indicate that the guest MeCN molecules in 4, are far more strongly encapsulated within their host cavity. This observation is likely as a result of the more tightly bound cavities generated in the crystal structure of 4, whereby adjacent [Ni(II)]-Br double-bowl units essentially interlock with one another (Figures 77 and 78).

2.2.6 NMR Titrations and the Isolation of Diamagnetic [Zn(II)]\(_7\) Systems

NMR titration studies were seen as a viable method to probe further the guests’ interactions within our host lattices (see Section 1.2.4.1 for further details). However, Ni(II) species are paramagnetic and thus cannot be readily analysed via NMR techniques. Thus, the [Zn(II)]\(_7\) analogues to our [Ni(II)]\(_7\) systems were isolated. The diamagnetic analogues to complexes 2-3 in the form of \([(\text{MeOH})_2(\text{H}_2\text{O})\subset\text{Zn(II)}(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2\) (5) and \([(\text{NO}_2\text{Me})_3\subset\text{Zn(II)}(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2\) (6) were successfully synthesized, with both analogues crystallising in the trigonal P-3c1 space group. Complete X-ray structural details for 5 and 6 are given in Table 6 (Section 2.5). Similarly, the core structure of the diamagnetic species 6 is analogous to that of its paramagnetic Ni(II) sibling 3 with a slightly larger cavity volume of 295.4 Å\(^3\). The connectivity in 5, however, differs to that of its paramagnetic sister complex 2. The [Zn(II)]\(_7\) units in 5 are held in 2D layers running parallel to the \(ab\)-plane via the NO\(_3\)- ions, which sit above and below the individual heptanuclear complexes with C-H⋯O bonding interactions exhibited between the NO\(_3\)- oxygen atoms (one unique, O4) and protons (one unique, H5) of the L\(_1\)- ligands (H5⋯O4 = 2.46 Å). In this arrangement, each [Zn(II)]\(_7\) is H-bonded to six NO\(_3\)- anions with the latter being connected to three [Zn(II)]\(_7\) units thus creating a (3,6) layer. Although the NO\(_3\)- ions do not hold the [Zn(II)]\(_7\) moieties of neighbouring layers, the (3,6) layers stack as [Zn(II)]\(_7\)-forming columnar arrays like those
found in complexes 1-3 giving rise to molecular cavities (each of approximate volume \( \approx 280.4 \, \text{Å}^3 \) with a \([\text{Zn(II)}_7]_{\text{plane}}-[\text{Zn(II)}_7]_{\text{plane}}\) distance of 11.68 Å), formed by two juxtaposed pseudo metallocalix[6]arene \([\text{Zn(II)}_7]\) bowl units. Such 1D columnar arrays are also observed for 6 with encapsulated \( \text{NO}_2\text{Me} \) guests (Figure 81).

![Crystal structure of 6](image)

**Fig. 81** (left) Crystal structure of 6 as viewed along a 1D column of \([\text{Zn(II)}_7]\) units and (right) as viewed parallel to the planar \{\text{Zn(II)}_7\} core highlighting the guest disordered \( \text{NO}_2\text{Me} \) molecules. Colour code: Zn = light blue, O = red, N = dark blue, C = grey. Hydrogen atoms have been omitted for clarity.

The cavities in 5 are of the required size and shape to accommodate two guest MeOH molecules and are related crystallographically via a three-fold rotation. The molecular cavity volumes of the various double-bowl heptanuclear disc species: 1 (265.9 Å\(^3\)), 2 (293.7 Å\(^3\)), 3 (283.8 Å\(^3\)), 5 (280.4 Å\(^3\)) and 6 (295.4 Å\(^3\)) indicates that the cavities in question are of comparable volume (Section 2.5: Table 4). The slight differences that do exist are due to the slightly different orientations of the [M(II)]\(_7\) units in their respective lattices. This intimates that the guests and / or H-bonding interactions between the [M(II)]\(_7\) units and the \( \text{NO}_3^- \) counter anions do not play an important role in the resultant cavity size. It was hoped that NMR host-guest titration studies of 5-6 would allow for further characterisation of guest interactions within the host cavity, however such analyses were not possible due to the extremely poor solubility of 5-6 in readily available NMR solvents (CDCl\(_3\), MeOH, Me\(_2\)SO (d\(_6\)), MeCN, D\(_2\)O) at concentrations sufficient for NMR studies.
2.2.7 UV-vis Solution Studies

Despite the rather poor solubility of this class of compound, UV-vis studies of [(MeOH)$_2$Ni(II)$_7$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (2) and [(MeOH)$_2$(H$_2$O)Zn(II)$_7$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (5) were successfully performed in both MeOH and MeCN. The UV-vis spectrum of 2 in MeOH showed absorptions centred at approximately 230, 270 and 356 nm. A fourth sharp transition in the methanolic solution of 2 is also observed at 205 nm, which has been cut off in the analogous MeCN solution spectrum (Figure 82).

![UV spectrum of 2 in MeOH](image)

**Fig. 82** UV spectrum of [(MeOH)$_2$Ni(II)$_7$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (2) in MeOH.

The transitions at ~ 205, 230 and 270 nm are as a result of π→π* excitations (ε values ranging from 42.8–110.2 x 10$^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$), while the absorption at 356 nm correspond to the n→π* excitations occurring in both solutions of 2. As expected, no absorptions indicative of d-d transitions are observed and if present are presumably masked by the presence of the deprotonated L$_1^-$ ligand species in 2. This assumption is supported by the UV-vis spectra of MeOH and MeCN solutions of the [Zn(II)$_7$] sibling 5 whose absorptions are analogous to those observed in 2, with only L$_1^-$ absorptions allowed and no possibility of any significant d-d transitions (Figure 83). Such d-d transitions would (if present) occur in the region dominated by the L$_1^-$ absorptions above (200-400 nm, visible region). Furthermore, the UV-vis spectra obtained from MeOH and MeCN solutions of L$_1$H and L$_2$H showed similar absorptions to those of 2 and 5 (see Section 2.5.3.1 for further details), although on comparison appearing less defined, presumably due to their more symmetric nature when incorporated into the [M(II)$_7$] complex.
Fig. 83 UV spectra of [(MeOH)$_2$(H$_2$O)$_2$Zn(II)$_7$(OH)$_6$(L$_1$)$_6$(NO$_3$)$_2$ (5) in MeOH (top) and MeCN (bottom).

### 2.2.8 Magnetic Susceptibility Studies of [Ni(II)$_7$] Species

Magnetic susceptibility measurements were performed on crystalline samples of [Ni(II)$_7$(OH)$_6$(L$_1$)$_6$(NO$_3$)$_2$ (1) and [(MeCN)$_2$Zn(II)$_7$(OH)$_6$(L$_2$)$_6$(NO$_3$)$_2$ (4) in the 300 to 5 K temperature range. The room temperature $\chi_M T$ values of 7.76 and 7.90 cm$^3$ K mol$^{-1}$, respectively obtained from these studies are slightly larger than expected for seven non-interacting Ni(II) ions (~ 7.7 cm$^3$ K mol$^{-1}$ assuming $g \approx 2.1$). As the temperature is lowered further, there is a gradual increase in the magnetic susceptibility reaching maxima of ~8.5 cm$^3$ K mol$^{-1}$ at 40 K for 1 and ~10 cm$^3$ K mol$^{-1}$ at a temperature of 25 K for 4 (Figure 84). The $\chi_M T$ values then decrease rapidly as the temperature is lowered once again, reaching minima of ~5.5 cm$^3$ K mol$^{-1}$ and ~7.9 cm$^3$ K mol$^{-1}$ at 5 K for 1 and 4 respectively. This behaviour is suggestive of very weak ferromagnetic intramolecular exchange between the
Ni(II) ions in both complexes, with their low temperature (T < 40 K) decreases in $\chi_m T$ ascribed to relatively strong intermolecular antiferromagnetic exchange, consistent with the extensive H-bonding observed in the crystals of 1 and 4. The maxima in $\chi_m T$ for 1 and 4 are well below that expected for an isolated $S = 7$ spin ground state which would give a $\chi_m T$ value of approximately 31 cm$^3$ K mol$^{-1}$ (assuming $g = 2.1$). Fitting of the $1/\chi_m$ versus $T$ data to the Curie-Weiss law using only the 300-50 K data affords Weiss constants ($\Theta$) of +18.7 K (1) and +29.0 K (4), suggestive of weak ferromagnetic exchange in both cases (Figure 85).

![Plot of $\chi_m T$ vs. $T$ for complexes 1(Δ) and 4 (o) in the 300-5 K temperature range (measured in an applied field of 0.1 T). (inset) Schematic representing the 1-J model employed to fit the magnetic data in 1 and 4. For specific spin Hamiltonian parameters see main text.](image)

**Fig. 84** Plot of $\chi_m T$ vs. $T$ for complexes 1(Δ) and 4 (o) in the 300-5 K temperature range (measured in an applied field of 0.1 T). (inset) Schematic representing the 1-J model employed to fit the magnetic data in 1 and 4. For specific spin Hamiltonian parameters see main text.
Fig. 85 (top) Plot of $1/\chi_M$ vs. $T$ for complex 1 and (bottom) plot of $1/\chi_M$ vs. $T$ for complex 4 giving Curie-Weiss constants ($\theta$) of +18.7 and +29.0 K respectively.

There are a variety of factors which preclude the simulation (fitting) of magnetic susceptibility data, such as the numerous exchange pathways present in both complexes 1 and 4. Specifically, there are $\mu$-bridging $O^{2-}$ ions between every pair of Ni(II) ions as well as $\mu_3$-bridging OH$^-$ groups, which each bridge three Ni(II) ions. There is relatively strong intermolecular antiferromagnetic exchange exhibited between neighbouring [Ni(II)$_7$] units, which makes fitting problematic. In addition, since the intramolecular ferromagnetic exchange in each [Ni(II)$_7$] unit is quite weak, there is a high probability that $J$ will be comparable to the single ion zero-field splitting parameter D (known as the weak exchange limit). Commensurate with this then is the possibility of the presence of multiple low-lying states which cannot be properly described as total $S$ states. This scenario is supported by the
magnetization versus field (M vs. H) data performed on 1 and 4 in the 2-7 K temperature and 0.5-7.0 T magnetic field ranges (Figure 86).

![Graph of M (Nµβ) vs. H (G)](image)

**Fig. 86** Plot of M (Nµβ) vs. H (G) carried out on complex 1 in the 2-7 K temperature range and 0.5 – 7 T magnetic field range.

For an isolated spin ground state, one would expect a rapid initial increase in M, with saturation of the magnetisation achieved for relatively low fields. In complexes 1 and 4, however, the magnetization increases only slowly with H, indicative of the population of low-lying levels with smaller magnetic moment, which only become depopulated when significantly larger magnetic fields are applied.

### 2.3 Coupling with Co(II): Expanding the [M(II)$_7$] Family

Stemming from our synthetic success in isolating paramagnetic [Ni(II)$_7$] and diamagnetic [Zn(II)$_7$] members of our family of double-bowl metallocalix[6]arenes, it was hypothesised that isolation of their Co(II) analogues would also represent rare examples of Co(II) solid-state polynuclear host materials and would therefore be worth pursuing. Indeed, this theory was realised in the isolation of the heptanuclear Co(II) species [Co(II)$_7$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (7) and [(MeOH)$_2$Co(II)$_7$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (8) via an analogous synthetic route to that of 1 and 2, respectively. Complexes 7 and 8 both crystallise as dark purple-brown hexagons in the trigonal P-3c1 space group in 30 % yield (Figure 87). Complete X-ray structural details for both analogues are given in Table 7 (Section 2.5).
The core structural features of the [Co(II)$_7$] architectures of 7 and 8 are analogous to those of 1-6, thus a brief discussion of their structural characteristics will be given here. While the cavity exhibited by 7 is void of guest species, guest inclusion was successfully effected in the generation of 8, where MeOH molecules take up residence within the molecular cavities formed by the stacking of individual [Co(II)$_7$] units. Both complexes comprise a central Co(II) ion (Co1) surrounded by six outer-ring Co(II) ions (Co2 and s.e.), which are linked to one another via $\mu_3$-bridging OH$^-$ anions (O1 and s.e.). This bridging topology results in a planar core comprising a hexagonal, disc-like array of Co(II) metal centres as observed previously in 1-6 (Figure 88).

**Fig. 87** (left) Image of crystal used in the X-ray data collection of 7. (right) Scanning Electron Microscope (SEM) image of the same crystals of 7.

**Fig. 88** Crystal structure of 7-8 as viewed perpendicular (a) and parallel (b) to the planar {Co(II)$_7$} core. Colour code: Co = purple, N = blue, O = red, C = grey. (c) Schematic representation of the double-bowl topology in 7-8. Hydrogen atoms have been omitted for clarity.
Such heptanuclear Co(II) based cores have been previously reported in the literature, however no solid state host-guest behaviour had been shown prior to this work.\textsuperscript{32,37} The six singly deprotonated \( {\text{L}}_1^- \) ligands bridge the six outer Co(II) ions via an \( \eta^1: \eta^2: \eta^1: \mu \) coordination motif. These ligands sit alternately above and below the \( \{ \text{Co(II)}_7(\text{OH})_6 \}^{8+} \) plane to form a pseudo-metallocalix[6]arene double-bowl architecture (Figure 88). The [Co(II)\(_7\)] systems 7-8 exhibit double-bowl dimensions similar to those of their Ni(II) analogues 1-2: (base x depth x rim diameter, in Å: 6.27 x 3.96 x 12.89 (7) and 6.25 x 4.08 x 12.12 (8)). The molecular cavities formed by the 1D pseudo-superimposable columns in the crystal of 8 act as molecular hosts by encapsulating two disordered MeOH guest molecules (the same as those observed in 2) which are drawn from the solvent media. The first methanol guest is disordered over three sites and lies on the three-fold axis that runs perpendicular to the [Co(II)\(_7\)] plane through the central Co(II) centre (as observed in [Ni(II)\(_7\)] 2). The second MeOH guest has two-fold disorder and lies at the boundary of the molecular cavity in 8, sitting perpendicular to the [Co(II)\(_7\)] plane, as observed in 2 (Figure 89).

![Figure 89](image)

**Fig. 89** Space-fill representations of the two crystallographically unique MeOH guests within molecular cavities formed by two double-bowl [Co(II)\(_7\)] units in complex 8. Colour code: Co = purple, C = light grey, O = red, N = blue. Hydrogen atoms have been omitted for clarity.

Interestingly the molecular cavities in 7 remain guest free, choosing not to accommodate EtOH solvent molecules – presumably due to steric effects and / or crystallographic restraints (i.e. perhaps the kinked nature of the EtOH molecules cannot satisfy the three-fold symmetry pattern shown by the linear MeOH guests in 8, as dictated by their identical P-3c1 space groups). This is consistent with that observed for the Ni(II) and Zn(II) analogues described previously (Section 2.2).\textsuperscript{22,23} The polynuclear systems of 7-8 both crystallise in the trigonal P-3c1 space group and only differ in terms of their guest occupancy and therefore are analogous with respect to their packing arrangement (Figure 90).
The 1D \([\text{Co(II)}_7]\) columns in the unit cells of 7 and 8 are connected via H-bonds to adjacent \([\text{Co(II)}_7]\) 1D assemblies (\([\text{Co(II)}_7]\)_{\text{plane}}-\([\text{Co(II)}_7]\)_{\text{plane}} distances (Å): 11.39 (7) and 11.52 (8)), which are propagated by multiple interactions between the \(\text{NO}_3^\text{-}\) counter ions and the individual \([\text{Co(II)}_7]\) moieties (e.g. \(\text{O4} \cdots \text{H5(C5)} = 2.406\) Å in 7 while \(\text{O4} \cdots \text{H7(C7)} = 2.431\) Å in 8). Specifically, the 3D connectivity identified in complexes 7-8 comprises H-bonding between twelve \(\text{NO}_3^\text{-}\) anions and each \([\text{Co(II)}_7]\) double-bowl, with each \(\text{NO}_3^\text{-}\) linked to six other \([\text{Co(II)}_7]\) units, resulting in the generation of (6,12)-connected nets with \(4^{15}_2(4^{18})\)-\text{alb}\) topologies, analogous to the connectivity exhibited by complexes 1-3, 5 and 6 (Section 2.2.4).

2.3.1. Functionalisation of \(L_1H\) Towards Selective Guest Inclusion

It was postulated that by functionalising the Schiff base ligand \(L_1H\), encapsulation of a variety of different guest species within \([\text{Co(II)}_7]\) double-bowl molecular cavities could be effected. To this end, \(L_1H\) was modified at the imino-N atom position (to afford \(L_3H\)) via introduction of a phenyl group, in order to modulate its second-order coordination sphere behaviour upon primary \(\{\text{M(II)}_7(\text{OH})_6(L)_6\}^{2+}\) planar disc formation (Figure 66). Indeed, it was believed that by functionalising at the imino-N atom position, the dimensions of the
molecular cavities formed in such [M(II)$_7$] species could be modified towards encapsulation of larger guest species; analogous to cavity modification techniques in the isolation of complex 4. The ligand 2-iminophenyl-6-methoxyphenol (L$_3$H) can be readily prepared via the Schiff base condensation reaction of o-vanillin with aniline in ethanol (see Section 2.5.3.1.3). L$_3$H crystallises in the orthorhombic P2$_1$2$_1$2$_1$ space group (Z = 4) and possesses an intramolecular H-bond between the phenolic proton (H1A) and the imine nitrogen atom (N1), giving a distance of O1A(H1A)···N1 = 1.880 Å and hydrogen-bond angle of 144.9° (Figure 91). Complete X-ray structural details for L$_3$H are given in Table 5 (Section 2.5). Furthermore, the imine-phenyl and phenol rings of L$_3$H twist away from one another via the imine bridge, to give a staggered conformation with a torsion angle (C10-C8-N1-C8) of ~30°. This situation is to be expected given the strain which would be associated in maintaining both aromatic moieties in a common plane. A review of the CCDC database highlights the existence of structural analogues to L$_3$H with various substituents on the imino-phenyl ring, however isolation of this ligand marks the first report (and corresponding crystal structure) of the core framework of L$_3$H.$^{38,39}$

![Fig. 91](image_url) (top): Schematic of 2-iminophenyl-6-methoxyphenol (L$_3$H). (bottom): Crystal structure of L$_3$H as viewed perpendicular (left) and along the plane (right) of the phenolic ring. Dashed line represents the intramolecular H-bonding interaction in L$_2$H, measured at O1A(H1A)···N1 = 1.880 Å. Colour code: C = grey, O = red, N = blue, H = black. The majority of the hydrogen atoms have been omitted for clarity.
2.3.1.1 Isolating a $\text{NO}_3^-$-Encapsulated $[\text{Co}(\text{III})_1\text{Co}(\text{II})_6]$ Species

Incorporation of $\text{L}_3\text{H}$ into the reaction system utilised in the isolation of our previously described $[\text{Co}($II$)_7]$ complexes 7-8 was thus proposed as a viable route towards novel guest inclusion. To this end, the reaction of $\text{Co}($NO$_3$)$_2$.6$H$_2$O, $\text{L}_3\text{H}$ and NaOH in methanol followed by evaporation and recrystallisation of the reaction mixture (from MeCN) resulted in the first example of a mixed-valence analogue of our $[\text{M}($II$)_7]$ double-bowl pseudo metallocalix[6]arenes. The complex obtained has the formula $[(\text{NO}_3)_2\subset\text{Co}($III$)_1\text{Co}($II$)_6(\text{OH})_6(\text{L}_3)_6](\text{NO}_3).3$MeCN (9). Complex 9 crystallises in the monoclinic space group C2/c in 15% yield (Figure 92) and complete X-ray structural details for this complex are given in Table 7 (Section 2.5).

![Figure 92](image)

**Figure 92** Crystal structure of the mixed-valent complex $[(\text{NO}_3)_2\subset\text{Co}($III$)_1\text{Co}($II$)_6(\text{OH})_6(\text{L}_3)_6](\text{NO}_3).3$MeCN (9) as viewed parallel (left) and perpendicular (right) to the $\{\text{Co}($III$)_1\text{Co}($II$)_6\}$ plane. Guest $\text{NO}_3^-$ anions are space-fill represented. Colour code: Co = purple, O = red, N = blue, C = grey. Hydrogen atoms have been omitted for clarity.

Complex 9 differs to that of its $[\text{M}($II$)_7]$ counterparts in that its central Co ion is in the +3 oxidation state as confirmed from charge balance considerations and Bond Valence Sum (BVS) and bond length analyses (Table 3: Section 2.5). In contrast to complexes 7-8, the polynuclear, mixed-valence system 9 comprises a $\{\text{Co}($III$)_1\text{Co}($II$)_6(\text{OH})_6\}^{9+}$ core and is thus (as a result of the extra +1 charge) able to accommodate two of the three $\text{NO}_3^-$ counter ions as guests within each $[\text{Co}($III$)_1\text{Co}($II$)_6]$ double-bowl unit. Guest inclusion here is driven by the resultant $\{\text{Co}($III$)_1\text{Co}($II$)_6(\text{OH})_6(\text{L}_3)_6\}^{3+}\cdot\text{NO}_3^-$ electrostatic interactions. It should also be
noted here that 9 represents the only polymetallic complex isolated using L₃H as synthon; previous work using this ligand has yielded solely mononuclear Re, Ru and Co species.\textsuperscript{43-45}

The two symmetry equivalent NO₃⁻ guests are held in place via their oxygen atoms (O10-O12) by four interactions in the form of two long C-H···O contacts from the imine-phenyl ring of the L₃⁻ ligands (C28(H28)···O11 = 2.969 Å, C38(H38)···O10 = 2.653 Å) and three H-bonds formed with donor protons (H1, H2 and H3H) of the bridging μ₃-OH⁻ ions within the \{Co(III)₁Co(II)₆\} core (O1(H1)···O11 = 2.280 Å, O2(H2)···O11 = 1.916 Å and O3(H3H)···O10 = 1.802 Å). These three H-bond interactions have associated H-bonding angles of 123.60 °, 146.98 ° and 170.50 °, respectively (Figure 93).

**Fig. 93** View of a NO₃⁻ anion occupying one half of a double-bowl [Co(III)₁Co(II)₆] unit in 9. Intermolecular interactions between the host and guest are represented as dashed lines. Actual distances are given in the main text.

The C-H···O interactions described here are made possible by the staggered conformation of the two aromatic rings (phenolic vs. imine-phenyl) of each L₃⁻ ligand upon metallation (torsion angles now ranging from 49-76 ° compared with 30 ° for the free L₃H ligand), thus giving rise to a more distorted double-bowl shape compared to its [Co(II)₇] analogues 7-8 (Figure 94).
Fig. 94 Crystal packing observed for 9 as viewed across the \( ab \)-plane (left) and down the \( a \)-axis (right) of the unit cell. Only guest NO\(_3^-\) anions are shown here (in space-fill mode).

In terms of intermolecular connectivity between the individual \([\text{Co(III)}_1\text{Co(II)}_6]\) units in 9, the oxygen atoms (O12 and s.e.) of the guest NO\(_3^-\) anions form close contacts with aromatic (H10) and aliphatic (H29C) ligand protons (C10(H10)···O12 = 2.439 Å, C29(H29C)···O12 = 2.627 Å). The third NO\(_3^-\) counter ion lies at the exterior of the double-bowl enclosure and acts as an additional connector of multiple \([\text{Co(III)}_1\text{Co(II)}_6]\) units via C-H···O interactions, through the aromatic ligand protons (H3, H4 and H21) at distances of: C3(H3)···O14′ = 2.449 Å, C4(H4)···O14 = 2.564 Å and C21(H21)···O13 = 2.357 Å. Interestingly, the individual double-bowl \([\text{Co(III)}_1\text{Co(II)}_6]\) units in 9 do not stack upon one another to form the enclosed molecular cavities observed in the related \([\text{M(II)}_7]\) host-guest analogues. Instead, these units lie perpendicular to one another within the unit cell and pack in wave-like rows along the \( c \)-axis.\(^{22,23,40}\) The individual rows in 9 arrange in a parallel fashion along the \( a \)-direction of the unit cell with alternating wave phases (Figure 94). The heptanuclear species 9 represents only the second such \([\text{Co(III)}_1\text{Co(II)}_6]\) mixed-valence species in the literature\(^{46}\) and is the first to show such solid-state host-guest behaviour. Indeed, the successful isolation of 9 marks the first instance whereby such oxidation of a constituent metal centre [i.e. oxidation of the central Co(II)→Co(III)] has been observed, while still maintaining the overall heptanuclear topology.
2.3.2 UV-vis and ESI-MS Studies of [Co(II)$_7$] and [Co(III)$_1$Co(II)$_6$] Complexes

Investigations into the UV-vis absorption characteristics of complexes 8 and 9 were performed for MeOH solutions of these complexes. $\pi$-$\pi^*$ excitations are identified by absorptions at wavelengths of 260, 230 and 200 nm respectively, while those absorptions occurring at wavelengths between 350 and 365 nm are indicative of strong n-$\pi^*$ excitations. ESI-MS measurements on a MeOH solution of 8 gave a parent peak at m/z = 777.80 and is indicative of the [Co(II)$_7$(OH)$_2$(OMe)$_4$(L$_1$)$_6$]$^{2+}$ fragment, where some OH$^-$ bridges have been replaced with MeO$^-$ units originating from the solvent media (Figure 95). Indeed similar bridging ligand substitutions have been previously reported in the literature.$^{37}$ Quite interesting though was the data obtained from analysis of a MeOH solution of 9. This spectrum gave rise to major fragments at (m/z) 623.70, 966.60 and 1995.15 which are attributed to the presence of the species detailed in Figure 96 and Table 1. As with previously isolated [Ni(II)$_7$] and [Zn(II)$_7$] species, host-guest characterisation via NMR titration was precluded by the poor solubility of 8 and 9 at larger concentrations in conventional NMR solvent media.

![Fig. 95 ESI-MS spectrum of a solution of 8 in MeOH with the major peak at m/z 777.80 attributed to [Co(II)$_7$(OH)$_2$(OMe)$_4$(L$_1$)$_6$]$^{2+}$.](image)

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Fig. 96 ESI-MS spectrum of a solution of 9 in MeOH with the major peaks at m/z 623.70, 966.60 and 1995.15 attributed to the 3+, 2+ and 1+ species respectively. Peaks at m/z 511.13 and 228.13 are attributed to \([\text{Co(III)}_1\text{Co(II)}_6(\text{OH})_6(L_3)_6]^{3+}\) and \([\text{Co(III)}_1\text{Co(II)}_6(\text{OMe})_1(\text{H}_2\text{O})_1(L_3)_6]^{8+}\), respectively.

Table 1 MS Analysis of 9 showing three distinct host-guest adducts.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>623.70</td>
<td>([\text{Co(III)}_1\text{Co(II)}_6(\text{OH})_6(L_3)_6]^{3+})</td>
</tr>
<tr>
<td>966.60</td>
<td>([[\text{Co(III)}_1\text{Co(II)}_6(\text{OH})_6(L_3)_6] + \text{NO}_3^-]^{2+})</td>
</tr>
<tr>
<td>1995.15</td>
<td>([([\text{Co(III)}_1\text{Co(II)}_6(\text{OH})_6(L_3)_6]+(\text{NO}_3)_2]^{+})</td>
</tr>
</tbody>
</table>

2.3.3 Switching the Anion / Switching the Guest

Stemming from the success in generating host-guest complexes involving the \(\text{NO}_3^-\) counterion in 9, we wanted to see if we could replace the \(\text{NO}_3^-\) anion with other anions of differing shapes and sizes. The first candidate was the highly symmetrical, O-rich \(\text{ClO}_4^-\) anion in the hope that these donor atoms would interact with the H-rich planar \([\text{Co(II/III)}_7(\text{OH})_6]^{9+}\) core during the course of complex formation. To this end we isolated the heptanuclear, mixed-valent complex \([\text{ClO}_4]_2\subset\text{Co(III)}_1\text{Co(II)}_6(\text{OH})_6(L_3)_6]\)(\text{ClO}_4) (10) via the reaction of \(\text{Co(ClO}_4)_2.6\text{H}_2\text{O}\) with \(L_3\text{H}\) using NaOH as a base / oxidising agent. Recrystallisation of the above reaction mixture from MeCN yielded 10 in 35 % yield. Complex 10 crystallises in the
same monoclinic C2/c space group as 9 and exhibits an analogous topology to that of its NO$_3^-$ sibling. Complete X-ray structural details for 10 are given in Table 7 (Section 2.5). Like 9 complex 10 is mixed-valent with a central Co(III) ion encircled by six Co(II) metal centres, with the alternating arrangement of μ$_3$-OH$^-$ ions and L$_3^-$ species generating the now familiar double-bowl topology (see Section 2.2). In addition, three ClO$_4^-$ ions crystallise in the structure; two unique to each [Co(III)$_1$Co(II)$_6$] unit and a third derived from a neighbouring [Co(III)$_1$Co(II)$_6$] moiety (Figure 97).

![Fig. 97 Double-bowl host-guest architecture exhibited by 10 as viewed parallel (left) and perpendicular (right) to the [Co(III)$_1$Co(II)$_6$] plane. ClO$_4^-$ depicted in space-fill mode. Colour code: Co = purple, O = red, N = blue, Cl = yellow, C = grey. Hydrogen atoms have been omitted for clarity.](image)

H-bonding interactions which exist between the μ$_3$-OH$^-$ protons (H1-H3) (lining the basal plane of the double-bowl) and the oxygen atoms of ClO$_4^-$ (O10, O12 and O13) are considerable and evidenced by relatively short distances: Cl1(O10)···H3 = 1.918 Å, Cl1(O13)···H2 = 1.929 Å, Cl1(O12)···H1 = 2.036 Å (and s.e.). As observed for complex 9, species 10 exhibits an orthogonal arrangement of double-bowl units with each unit oriented at ~90° to one another. This orthogonality is realised as wave-like rows which propagate along the c-axis of the unit cell (Figure 98). As a result of this packing arrangement, there is no molecular cavity formation in the unit cell of 10.
Fig. 98 Crystal packing observed in 10 as viewed down the $a$-axis, illustrating wave-like rows of [Co(III)$_1$Co(II)$_6$] units. ClO$_4^-$ represented as space-filled spheres. Hydrogen atoms have been omitted for clarity.

2.3.3.1 Utility of Tetrafluoroborate (BF$_4^-$)

Following successful isolation of the heptanuclear complex $[(\text{ClO}_4)_2\subset\text{Co(III)}_1\text{Co(II)}_6(\text{OH})_6(\text{L}_3)_6]\text{(ClO}_4)$ (10), it was proposed that by replacing the tetrahedral ClO$_4^-$ with the BF$_4^-$ ion a family of such mixed-valence complexes may be generated. However, this particular synthetic route using L$_3$H did not lead to analogues of 9-10, but did result in the generation of two structurally interesting complexes: [Co(III)$_2$Na$_1$(L$_2$)$_6$](BF$_4$) (11) and [Co(III)$_3$Na$_3$(L$_1$)$_6$(N$_3$)$_6$]$_n$ (12), using L$_2$H and L$_1$H, respectively (L$_3$H proved not to make any discernable products upon reaction with Co(BF$_4$)$_2$.6H$_2$O). Complex 11 is formed by initial reaction of Co(BF$_4$)$_2$.6H$_2$O with L$_2$H and NaOH in ethanol, followed by redissolution of the reaction mixture in MeCN. Subsequent filtration and Et$_2$O diffusion of the mother liquor afforded 11 as red-brown blocks, which crystallise in the monoclinic space group C2/c in 25 % yield. Complete X-ray structural details for 11 are given in Table 8 (Section 2.5). The core in 11 is V-shaped whereby a central Na(I) ion (Na1) sits in between two Co(III) centres (Co1 and s.e.) (Figure 99). BVS calculations, bond length analyses and charge-balancing considerations confirmed the oxidation state of the cobalt centres (Table 3: Section 2.5).
Fig. 99 Crystal structures of [Co(III)$_2$Na(I)$_1$(L$_2$)$_6$](BF$_4$)$_7$ (11) as viewed perpendicular (left) and parallel (right) to the V-shaped plane of the molecule. Colour code: Co = purple, Na = yellow, O = red, N = blue, Br = green, C = grey. Hydrogen atoms have been omitted for clarity.

Six L$_2^-$ ligand moieties bridge the {Co(III)$_2$Na$_1$} core in 11, two of which chelate the Co(III) ions (bite angle: N2-Co1-O4 = 91.36 °); one per crystallographically unique ion. The remaining four deprotonated L$_2^-$ species bridge the Co(III)-Na(I) vertices, two via the η$_{1}$:η$_{2}$-η$_{1}$-µ coordination motif previously observed for [M(II/III)$_7$] species and two via the η$_{1}$:η$_{2}$-µ bonding mode (Figure 99). The BF$_4^-$ anions in the unit cell of 11 sit above the central Na(I) centres (B1···Na1 = 4.537 Å) and partake in hydrogen bonding via the ligand protons (H18B and H8) and the F-atoms (F1 and F2) with distances of (Å): F1···H18B(C18) = 2.915; F2···H8(C8) = 2.442. These interactions along with their symmetry equivalents effectively connect the individual {Co(III)$_2$Na(I)} units in 11, which pack in the common brick-wall fashion along the ab-plane of the unit cell. These 2D sheets then lie parallel to one another along the c-axis and each are inverted with respect to their neighbouring wall (Figure 100).

Although complex 11 does not possess hosting abilities, its isolation represents yet another example of the utility of this class of Schiff base ligand in encouraging the generation of systems possessing interesting and varying topologies.
Fig. 100 Crystal packing observed in 11 as viewed along the c-axis. Colour code: Co = purple, O = red, N = dark blue, Na = yellow, C = grey, Br = green, B = dark green, F = light blue. Hydrogen atoms have been omitted for clarity.

As previously discussed reaction of L₁H with Co(NO₃)₂.6H₂O resulted in the formation of the heptanuclear [M(II)₇], double-bowl pseudo metallocalix[6]arene disc species 7-8. Similarly the reaction of Co(BF₄)₂.6H₂O with L₂H afforded the trinuclear [Co(III)₂Na₁] species 11. However, the incorporation of the often ferromagnetic-exchange-inducing azide (N₃⁻) bridging anion into the reaction of Co(BF₄)₂.6H₂O with L₁H and NaOH in methanol generated an entirely different breed of complex; namely the 1D chain [Co(III)₃Na(I)₃(L₁)₆(N₃)₆]ₙ (12) (Figure 101). Complex 12 crystallises as dark red-brown blocks in moderate yield (30 %), in the monoclinic space group C2/c. Complete X-ray structural details for 12 are given in Table 8 (Section 2.5).

Fig. 101 1D [Co(III)₃Na(I)₃] chain structure of 12. Colour code: Co = purple, Na = yellow, N = blue, O = red, C = grey. Hydrogen atoms have been omitted for clarity.
It is interesting to note that, unlike with 11, the BF\(_4^-\) anion does not actually crystallise in the structure of 12, but its presence seems to be a requirement shown by lack of crystallisation in the absence of BF\(_4^-\) in the mother liquor. The azide ion \([N_3^-]\) (N4, N5, N6) added in the reaction bridges each pair of Co(III) and Na(I) ions (Co1 and Na1) in a \(\mu\)-1,1 fashion: Co1-N4 = 1.952 Å, Na1-N4 = 2.479 Å (Figure 101). The hexanuclear unit which propagates along the \(a\)-axis of the unit cell consists of three Co(III) ions, three Na(I) ions and six \(L_1^+\) moieties, deprotonated at the phenolate site. BVS calculations and charge-balancing considerations confirmed the oxidation state of the cobalt centres. \(L_1H\) coordinates via an \(\eta^1:\eta^2:\eta^1\)-\(\mu\) bonding motif via the methoxy (O3), phenolate (O4) and imino-nitrogen (N2) sites respectively: Co2-O4 = 1.892 Å, Co2-N2 = 1.935 Å, Na1-O4 = 2.318 Å, Na1-O3 = 2.420 Å. Investigations into whether or not the Br-analogue to the \([Co(III)\_3Na(I)\_3]\) chain could be produced were unsuccessful. One possible reason for this becomes apparent upon examination of the packing arrangement in 12. The polymeric chains propagating along the \(a\)-axis pack very close to one another with the 4-positions of the aromatic moieties on one chain coming in close contact with the \(\mu\)-N\(_3^-\) species of its neighbouring chain: N6···H(4-position) = 2.670 Å. Not only would the production of the Br-analogue introduce considerable steric strain into the system, but the presence of a large, nucleophilic Br-atom next to a nucleophilic N\(_3^-\) ion would introduce significant electrostatic repulsion into the highly ordered polymeric array. Thus, utilisation of the Br-analogue, or indeed any analogue in which the Schiff base is functionalised at the 4-position (para with respect to OH) of the phenoxide, is unviable towards the production of this particular chain system.

Fig. 102 (left) Crystal packing observed in 12 as viewed down \(c\)-axis of cell. (right) 1D chains of 12 as viewed down \(a\)-axis of cell showing close proximity of N\(_3^-\) species on one
chain and 4-positions on aromatic rings of neighbouring-chain ligand moieties. Colour code: Co = purple, Na = yellow, N = blue, O = red, C = grey. Hydrogen atoms have been omitted for clarity.

2.3.3.2 Docking Potential of the Sulfate $SO_4^{2-}$ Anion

The production of $\text{[(NO}_3\text{)}_2\subset\text{Co(III)Co(II)}_6\text{(OH)}_b\text{(L}_2\text{)}_6\text{](NO}_3\text{)}_3\cdot3\text{MeCN}}$ (9) and $\text{[(ClO}_4\text{)}_2\subset\text{Co(III)Co(II)}_6\text{(OH)}_b\text{(L}_3\text{)}_6\text{](ClO}_4\text{)}\text{}}$ (10) prompted our focus to shift towards solid state guest inclusion of other counter anions using our $\text{[Co(III)1Co(II)6(L}_2\text{)}_6\text{]+}$ vessel. The first candidate was the O-rich $SO_4^{2-}$ anion in the hope of interaction with our H-rich planar core (containing six OH bridges). We were also curious to know what would occur when we added a doubly negative anion. However, $SO_4^{2-}$ cavity ingress was not observed. The mononuclear complex $\text{[Co(II)(L}_3\text{)}_2\text{]}$ (13) which crystallises in the monoclinic $P2_1/c$ space group (upon reaction of $\text{CoSO}_4\cdot7\text{H}_2\text{O}$, $\text{L}_3\text{H}$ and $\text{NaOH}$ in methanol) does not contain our anion and instead comprises a single distorted tetrahedral Co(II) ion (Co1) bound by two crystallographically unique $\text{L}_3^-$ ligands (Figure 103). Complete X-ray structural details for 13 are given in Table 8 (Section 2.5).

![Figure 103](image)

Fig. 103 Crystal structure of $\text{[Co(II)(L}_3\text{)}_2\text{]}$ (13) highlighting the close proximity of neighbouring monomers within the H-bonded chains (left) and between the chains (right). H-bonding shown using dashed lines. Colour code: Co = purple, O = red, N = blue, C = grey, H = light blue.

The deprotonated ligands in 13 chelate the Co(II) ion via their imine N atoms (N1 and N2) and Ophen atoms (O2 and O4) ($\eta^1:\eta^1$ mode) with bite angles of 94.32° (N1-Co1-O2) and 96.51° (N2-Co1-O4) (Figure 103). The Co(II)(L$_3$)$_2$ units in 13 are arranged into
superimposable rows along the c-axis of the unit cell and are held together via numerous H-bonding interactions. These comprise H-bonds between aromatic protons and $O_{\text{phen}}$ (H11 and H12 from same $L_3^-$) and $O_{\text{phen}}$ (O2) and OMe (O3) oxygen atoms: (O2···H11′(C11′) = 2.660 Å; O3···H12′(C12′) = 2.568 Å) (Figure 103). Indeed H-bonding interactions in 13 are extensive with each monomeric unit interacting with its four nearest monomeric neighbours. The superimposable rows in 13 also partake in interchain H-bonding (along the $ab$-cell plane), again using aromatic $L_3^-$ protons (H18, H8) and $O_{\text{phen}}$ (O2) and OMe (O4) donor atoms (C18(H18)···O2′ = 2.571 Å; C8(H8)···O3′ = 2.491 Å) (Figure 104).

![Figure 104](image)

Fig. 104 Crystal packing shown in polyhedral form highlighting the 1D superimposable H-bonded chains of $[\text{Co(II)}(L_3)_2]$ (13) propagating along the c-direction. Hydrogen atoms have been omitted for clarity.

### 2.3.4 Magnetic Susceptibility Studies of $[\text{Co(II)}_7]$ and $[\text{Co(III)}_1\text{Co(II)}_6]$ Discs

Magnetic susceptibility measurements were performed on crystalline samples of $[(\text{MeOH})_2\subset\text{Co(II)}_7(\text{OH})_6(L_1)_6](\text{NO}_3)_2$ (8) and the mixed-valent $[\text{Co(III)}_1\text{Co(II)}_6]$ complex (9) in the 300 to 5 K temperature range with an external magnetic field of 0.1 T. Both complexes exhibit similar behaviour at high temperatures with broad maxima (at ~100 K) indicative of spin-orbit coupling (see Section 1.5.3.8). At ~40 K the data points corresponding to both species diverge with ferromagnetic coupling observed for 8 indicated by an increase in $\chi_M$ with decreasing temperature reaching a maximum value of ~20.2 cm$^3$ K mol$^{-1}$ at 5 K (Figure...
The magnetic behaviour exhibited by 9 varies considerably from that of 8 however, with a decrease in $\chi_M T$ observed as the temperature is decreased reaching a minimum of ~13.9 cm$^3$ K mol$^{-1}$ at 5 K, indicating weak antiferromagnetic exchange.

![Fig. 105 Plots of $\chi_m T$ vs. T obtained from polycrystalline samples of 8 (o) and 9 (Δ) respectively measured in an applied field of 0.1 T and 5-300 K temperature range. Solid lines are for visual purposes only.](image)

2.3.4.1 Magnetisation vs. Field Studies on [Co(II)$_7$] (8) and [Co(III)$_4$Co(II)$_6$] (9)

Confirmation of ferromagnetic and antiferromagnetic exchange in complexes 8 and 9 respectively was made from analysis of the magnetization (M) vs. field (H) data for these systems (Figure 106). The M vs. H data corroborates the exchange described above and shows that for the same temperature and field, the magnetization value of complex 8 is always larger than that of complex 9. Additional evidence to support the above magnetic exchange is made from a study of the Co-O-Co bonding angles in the crystal structures of both 8 and 9. An examination of the crystal structure of 9 reveals that the Co-O-Co angles in the magnetic [Co(II)$_8$] wheel fall into two distinct categories: those on the outer rim (OR) are in the range 105.5-107.4 ° and those on the inner rim (OH) are in the range 95.5-96.3 °. The former are expected to propagate antiferromagnetic interactions and the latter ferromagnetic interactions.
interactions.\textsuperscript{47-49} On moving from complex 9 to complex 8, the inner rim $\mu_3$-bridging OH$^-$ ions now also bridge to the paramagnetic central ion and these Co-O-Co angles are also in the range (94.0-98.0 °) expected for ferromagnetic exchange. The conclusion therefore is that the larger outer rim angles dominate the exchange in 9 leading to overall weak antiferromagnetic exchange but the larger number of smaller inner rim angles present in 8 result in global ferromagnetic exchange.

![Fig. 106 Plots of M vs. H data for 8 (black) and 9 (red) at three different temperatures (2, 4 and 7 K) in 0.5-7.0 T applied magnetic fields.]

**2.4 Concluding Remarks**

Initial synthetic success using L$_x$H (x= 1, 2, 3) was realised in the isolation of a family of heptanuclear [M(II)$_7$] complexes 1-8 of general formula [M$_7$(OH)$_6$(L$_x$)$_6$(NO$_3$)$_2$; where M = Ni(II), Co(II/III), Zn(II)]. These complexes are best described as pseudo metallocalix[6]arene discs stemming from both their resemblance to macrocyclic calix[6]arene species and their possession of disc-like arrays of M(II) and M(II/III) ions in the solid state. These [M(II)$_7$] units stack one on top of another in the solid state to generate molecular cavities large enough to allow for encapsulation of a variety of guest molecules such as MeOH and NO$_2$Me. Indeed by functionalisation of the ligand employed it was possible to target specific structural distortions in the molecular cavities thus formed, thereby allowing for the isolation of a new
range of polymetallic host-guest architectures comprising both homovalent species 1-8 and mixed valence Co(II/III) anion-encapsulated systems 9-10. It is also particularly interesting that even on proceeding across the 1\textsuperscript{st} row transition metals (Co(II)→Zn(II)) the same core topology is maintained; an extremely rare characteristic with respect to polynuclear assemblies.\textsuperscript{48,49} Attempts at replacing the guest ClO$_4^-$ anion in 10 with BF$_4^-$ failed, and instead gave rise to the very different complexes 11-13. These latter findings highlight the fine balance that exists between the formation of different complexes and how the identity of the product is dependent upon 1) the starting materials present (the type and the number) 2) the reaction conditions and 3) the crystallisation methods. In the case of the Co(II) / Co(III) systems 9-10, it is apparent that the presence of the NO$_3^-$ and ClO$_4^-$ anions have a significant bearing on [Co(II/III)$_7$] double-bowl pseudo metallocalix[6]arene formation.

In addition to solid-state host-guest characterisation of heptanuclear species, magnetic characterisation of these double-bowl architectures was also undertaken in keeping with our original goal of employing magnetically interesting host units towards multifunctional materials. The magnetic behaviour of these assemblies was complicated by the presence of numerous, relatively strong intermolecular interactions (facilitated by guest molecules) and weak intramolecular exchange. In addition, the isolation of the mixed-valence species 9 led to dramatically different magnetic properties between 9 and the homovalent analogue 8; switching from antiferromagnetic exchange in the former to ferromagnetic exchange in the latter system. Undoubtedly, the polynuclear complex assemblies described by this chapter have revealed a novel route towards solid state host-guest materials. Such systems are increasingly used towards a myriad of applications such as drug delivery, chemical sensing and gas storage (see Section 1.2.5). What is even more striking is the fact that unlike the quite common organic host systems, complexes 2-4 and 8-10 are rare examples of large paramagnetic solid state host architectures that mimic classic calix[n]arene behaviour. These heptanuclear species will thus serve as a basis towards the isolation of multifunctional materials and encapsulation of more complex guest species such as organic radicals (Chapter 3).
2.5 Experimental

2.5.1 Instrumentation

Instrumentation utilised in the analysis of Schiff bases $L_xH$ (x=1, 2, 3) and complexes 1-13, contained in this chapter are detailed below.

2.5.1.1 Carbon, Hydrogen and Nitrogen Micro-analysis

Carbon, Hydrogen and Nitrogen elemental analyses were performed using a Perkin Elmer Series II CHNS / O Analyzer (2400 Series).

2.5.1.2 $^1$H and $^{13}$C NMR Spectroscopy

Nuclear Magnetic Resonance (NMR) Spectroscopic analyses were performed using a JEOL ECX-400 $^1$H NMR spectrometer and also using a Varian 500 MHz AR Premium Shielded spectrometer (where applicable). NMR spectra were recorded at room temperature in CDCl$_3$ and DMSO (d$_6$) (where applicable). Chemical shifts (δ) are indicated in ppm.

2.5.1.3 Infrared Spectroscopy

Infrared analyses were performed in the 4000 – 650 cm$^{-1}$ range (resolution = 8 cm$^{-1}$) using a Perkin Elmer Spectrum One FT-IR spectrometer equipped with a Universal ATR Sampling Accessory (ZnSe diamond).

2.5.1.4 Magnetic Susceptibility Measurements

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

High resolution mass spectrometry (HRMS) analyses were performed using a Waters LCT Premier XE system (Micromass® MS Technologies) with a Waters e2795 Separations Module.

2.5.1.6 **Single-Crystal X-ray Diffraction**

X-ray diffraction studies were performed using an Oxford Diffraction XCalibur S Kappa CCD System using an enhanced Mo source. Data collection / reduction were facilitated via use of the CrysAlisPro software package. The structures were solved by direct methods (SHELXS-97)\(^{50}\) and refined by full matrix least squares using SHELXL-97.\(^{51}\) SHELX operations were automated using the XSEED and OSCAIL software packages.\(^{52,53}\) All hydrogen atoms were placed in calculated positions. The non hydrogen atoms were refined anisotropic except for the disordered guest solvent (NO\(_2\)Me, MeCN and MeOH) molecules which were left isotropic. DFIX and restraints were required on the disordered NO\(_2\)Me (in 3 and 6), and MeOH (in 2, 5 and 8) guest molecules as a result of high isotropic thermal parameters upon refinement. The FLAT restraint was also imposed on the disordered NO\(_2\)Me guests in complexes 3 and 6. DFIX and restraints were required on the disordered MeOH guest solvent molecules in 8 as a result of high isotropic thermal parameters upon refinement.

All Crystallographic Information Files (CIFs) are located on a writeable CD, included at the end of this thesis.

2.5.1.7 **UV-visible Spectroscopy**

UV-vis measurements were performed using a Cary 100 scan (Varian) spectrophotometer. Solutions were analyses using quartz cuvettes in MeOH and MeCN solutions unless otherwise indicated.

2.5.1.8 **Scanning Electron Microscopy (SEM)**

SEM images were obtained using a Hitachi 4700 Scanning Electron Microscope with samples loaded onto conductive graphite films. Non-conducting organic ligands were pre-coated with gold prior to SEM imaging.
2.5.2. Crystallisation Techniques

Crystallisation is very sensitive to factors such as solvent, temperature, number of nucleation sites and time. A number of specific techniques have been utilised in this thesis in attempts to grow good-quality single crystals suitable for X-ray analysis. These include slow solvent evaporation and slow Et₂O diffusion. Slow solvent evaporation simply involves the gradual evaporation of solvent from a given vessel, resulting in the crystallisation of product from the saturated solution. The Et₂O diffusion crystallisation technique is described below.

2.5.2.1 Towards Crystallisation: Slow Diethyl Ether Diffusion

Diethyl ether diffusion techniques were utilised, whereby a small sample vial, half-filled with reaction solution, was placed inside a larger sample vial containing a small amount of Et₂O (higher vapour pressure). In principle, the ether slowly diffuses into the sample mother liquor forcing the product to crystallise out as the ether concentration in the inner vial increases; the compound of interest being less soluble in ether (Figure 107). The technique only works if the reaction solution is less volatile than the Et₂O (diffusing solvent) so that the Et₂O diffuses into the reaction solution.

![Diagram of crystallisation](image)

*Fig. 107* Slow Et₂O diffusion method of crystallisation.

2.5.3 Synthetic Procedures

Unless otherwise stated all materials (solvents and reagents) were purchased commercially and used as supplied without further purification. Caution: Although no difficulties were
encountered in this work, great care must be taken when working with the potentially explosive nitrate salts.

2.5.3.1 Synthesis of Schiff Base Ligands

2.5.3.1.1 Synthesis of 2-iminomethyl-6-methoxyphenol ($L_1H$)

Scheme 2.1 Reaction scheme for the synthesis of 2-iminomethyl-6-methoxyphenol ($L_1H$).

To a solution of $o$-vanillin (4.00 g, 26.3 mmol, 1.0 eq.) in EtOH (60 cm$^3$) was added an equimolar volume MeNH$_2$ (0.807 g, 2.0 cm$^3$, 41 % w/v, 26.3 mmol, 1.0 eq.) (Scheme 2.1). The solution rapidly adopted an intense yellow colour following addition of the amine. The solution was stirred under ambient conditions for a further 24 hours following which the solvent was evaporated to dryness in vacuo to afford $L_1H$ as a bright yellow solid in 80 % yield (3.46 g obtained) which was used in complex synthesis without further purification.

C, H, N Elemental Analysis

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

Theory (%): C (65.43), H (6.71), N (8.47).

Found (%): C (65.10), H (6.35), N (8.10).

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

2942 (w), 1630 (m), 1463 (m), 1392 (m), 1251 (s), 1165 (w), 1077 (m), 1005 (w), 962 (m), 868 (m), 836 (m), 779 (m), 736 (s).

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

$\delta$ 3.47 (s, 3H, N-CH$_3$), 3.89 (s, 3H, O-CH$_3$), 6.75-6.90 (m, 3H, Ar-H), 8.30 (s, 1H, N=CH).
\[ ^{13}C \text{ NMR} (400 \text{ MHz}, \text{CDCl}_3) \]
\[ \delta \ 166.34 \ (\text{N}=\text{CH}), \ 122.74 \ (\text{C}-\text{OH}), \ 121.03, \ 120.70, \ 117.73, \ 113.74 \ (\text{Ar-H}), \ 56.14 \ (\text{CH}_3-\text{O}), \ 45.65 \ (\text{CH}_3-\text{N}). \]

Melting Point (MP) Range

82.5-83.5 °C.

UV/vis Analysis (Spectra shown in Figure 108)

MeOH: \( \lambda_{\text{max}} \ [\text{nm}] \ (\epsilon_{\text{max}} \ 10^3 \ \text{dm}^3 \ \text{mol}^{-1} \ \text{cm}^{-1}): \ 202.0 \ (11.5), \ 221.0 \ (14.6), \ 242.0 \ (9.7), \ 258 \ (7.3), \ 290.0 \ (5.9), \ 328 \ (1.5), \ 415.1 \ (2.4). \) MeCN: \( \lambda_{\text{max}} \ [\text{nm}] \ (\epsilon_{\text{max}} \ 10^3 \ \text{dm}^3 \ \text{mol}^{-1} \ \text{cm}^{-1}): \ 221.0 \ (18.3), \ 257.1 \ (7.9), \ 295.0 \ (1.6), \ 323.1 \ (2.0). \)
**Fig. 108** (top) UV-vis spectra obtained from MeOH and (bottom) MeCN solutions of L₁H. UV-vis spectra were obtained from multiple solvents to see if absorptions were affected by the choice of solvent.

### 2.5.3.1.2. Synthesis of 4-bromo-2-iminomethyl-6-methoxyphenol (L₂H)

![Scheme 2.2](image)

**Scheme 2.2** Reaction scheme for the synthesis of 4-bromo-2-iminomethyl-6-methoxyphenol (L₂H).

To a stirring solution of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (2.0 g, 8.66 mmol, 1.0 eq.) in a mixed solvent system of CH₂Cl₂ (40 cm³), MeOH (10 cm³) and EtOH (60 cm³) was added an aqueous solution (1.31 cm³) of MeNH₂ (0.538 g, 17.32 mmol, 2.0 eq.) which afforded a very bright yellow and transparent solution (Scheme 2.2). The solution was stirred for a further 24 hours, after which time the solvents were evaporated in vacuo to afford L₂H as a hair-like, bright yellow solid in 96 % yield (2.03 g obtained) which was used in complex synthesis without further purification.

**C, H, N Elemental Analysis**

Calculated for: C₉H₁₀N₁O₂Br

Theory (%): C (44.44), H (4.14), N (5.76).

Found (%): C (44.20), H (3.85), N (5.35).

**Infrared Spectroscopy (cm⁻¹)**

3002 (w), 2926 (w), 2830 (w), 1634 (m), 1470 (m), 1438 (m), 1397 (m), 1241 (s), 1142 (w), 1104 (w), 1003 (w), 961 (m), 860 (m), 826 (m), 758 (m), 673 (w).

**¹H NMR (400 MHz, CDCl₃)**

δ 3.47 (s, 3H, N-CH₃), 3.86 (s, 3H, O-CH₃), 6.93-6.95 (m, 3H, Ar-H), 8.19 (s, 1H, N=CH).
$^{13}$C NMR (400 MHz, CDCl$_3$)

δ 165.17 (N=CH), 124.65 (C-OH), 119.10, 116.74, 108.81 (Ar-H), 56.33 (CH$_3$-O), 45.29 (CH$_3$-N).

Melting Point (MP) Range

86.8-87.7 °C.

UV/vis Analysis (Spectra shown in Figure 109)

MeOH: $\lambda_{\text{max}}$, nm ($\varepsilon_m$, 10$^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$): 203.1 (16.1), 228.0 (19.0), 244.0 (15.3), 288.0 (5.5), 334 (1.4), 422.0 (3.3). MeCN: $\lambda_{\text{max}}$, nm ($\varepsilon_m$, 10$^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$): 226.0 (26.4), 251.0 (shoulder), 291.0 (3.8), 332.0 (2.5), 421.0 (0.9).

Fig. 109 UV-vis spectra obtained from MeOH (top) and MeCN (bottom) solutions of L$_2$H.
2.5.3.1.3 Synthesis of 2-iminophenyl-6-methoxyphenol (L₃H)

![Scheme 2.3](image)

Scheme 2.3 Reaction scheme for the synthesis of 2-iminophenyl-6-methoxyphenol L₃H.

(Modified from published methods): To a solution of o-vanillin (2.0 g, 13.14 mmol, 1.0 eq.) in EtOH (40 cm³) was added distilled aniline (2.0 cm³, 21.94 mmol, 1.67 eq.), yielding a bright orange solution (Scheme 2.3). The solution was refluxed for 2 hours, after which the solvent was removed in vacuo to give a dark orange oil. To the oil was added a 1:1 Et₂O / Acetone mixture (total volume of 50 cm³) and the solvent was again removed in vacuo. The dark orange oil persisted and thus Et₂O (50 cm³) was added to the oil yielding a golden orange solution. The desired solid product (bright orange) soon began to crystallize out of solution. The mixture was placed in a fridge overnight (at a temperature of ~2-3°C) to encourage further crystallization of the desired product. The solid was isolated via filtration over a sintered glass frit and washed with the minimum volume of cold Et₂O. L₃H was isolated as bright orange crystalline blocks in 83 % yield (2.47 g obtained) which was used in complex synthesis without further purification (Figure 110).

![Fig. 110](image)

Fig. 110 (left) Microscope image of L₃H. (right) SEM image of L₃H.

C, H, N Elemental Analysis

Calculated for: C₁₄H₁₃N₁O₂

Theory (%): C (73.98), H (5.77), N (6.17).
Found (%): C (73.64), H (5.36), N (5.77).

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

2955 (w), 2909 (w), 2837 (w), 1612 (s), 1586 (m), 1462 (s), 1409 (w), 1250 (s), 1194 (s), 1075 (m), 999 (w), 966 (s), 832 (w), 810 (m), 781 (s), 765 (s), 735 (s), 724 (s), 689 (s).

**\(^1\)H NMR (500 MHz, CDCl\(_3\))**

\( \delta \) 13.60 (s, 1H, OH), 8.62 (s, 1H, N=CH) 7.66 (m, 8H, Ar.), 2.95 (s, 3H, O-CH\(_3\)).

**\(^{13}\)C NMR (400 MHz, CDCl\(_3\))**

\( \delta \) 162.71 (N=CH), 129.51 (C-OH), 127.09, 123.87, 121.26, 119.18, 118.63, 114.81 (Ar-H), 56.27 (CH\(_3\)-O).

**Melting Point (MP) Range**

83.5-84.5 °C.

**UV/vis Analysis (Spectra shown in Figure 111)**

MeOH: \( \lambda_{\text{max}}, \text{nm} (\varepsilon_m, 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}): \) 312 (16.8), 278 (13.2), 225 (25.5). MeCN: \( \lambda_{\text{max}}, \text{nm} (\varepsilon_m, 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}): \) 309 (17.6), 277 (17.5), 226 (30.7), 207 (25.1).
Fig. 111 UV-vis spectra obtained from MeOH (top) and MeCN (bottom) solutions of L₃H.

2.5.3.2 Synthesis of \([\text{Ni(II)}_7(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2\) (1)

\(\text{Ni(NO}_3\_2\_6\text{H}_2\text{O} (0.25\ g, 0.859\ mmol, 1.0\ eq.), L_1\text{H} (0.142, 0.859\ mmol, 1.0\ eq.)}\) and solid \(\text{NaOH} (0.034\ g, 0.859\ mmol, 1.0\ eq.)\) were dissolved in EtOH (30 cm³). The solution was stirred for a further 4 hours, after which time the solution had adopted a transparent, dark green appearance. X-ray quality crystals of 1 were obtained, over two weeks, in 30% yield upon slow evaporation of the mother liquor.

\textit{C, H, N Elemental Analysis}

Calculated for: \(\text{C}_{54}\text{H}_{66}\text{N}_8\text{O}_{24}\text{Ni}_7\)

Theory (%): C (40.09), H (4.11), N (6.93).

Found (%): C (39.76), H (4.18), N (6.85).

\textit{Infrared Spectroscopy (cm}⁻¹\)

3415 (w), 2968 (w), 2932 (w), 1627 (s), 1602 (w), 1559 (w), 1459 (m), 1406 (w), 1315 (s), 1221 (s), 1072 (m), 963 (m), 864 (m), 828 (w), 793 (m), 743 (s).
2.5.3.3 Synthesis of [(MeOH)$_2$\textsuperscript{2}<Ni(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (2)

To a solution of Ni(NO$_3$)$_2$.6H$_2$O (0.25 g, 0.859 mmol, 1.0 eq.) in MeOH (30 cm$^3$) were added (1) (0.142 g, 0.859 mmol, 1.0 eq.) and solid NaOH (0.034 g, 0.859 mmol, 1.0 eq.). The solution was stirred for 3 hours, at ambient temperature and resultant green mother liquor, following filtration, was allowed to concentrate via slow evaporation of the methanol solvent. X-ray quality, hexagonal crystals of 2 were harvested from the mother liquor after ~2 days in 40% yield (Figure 112).

Fig. 112 Microscope images showing the hexagonal crystalline structure of complex 2.

C, H, N Elemental Analysis

Calculated as C$_{56}$H$_{74}$N$_8$O$_{26}$Ni$_7$ i.e. [(MeOH)$_2$\textsuperscript{2}<Ni(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$

Theory (%): C (39.99), H (4.43), N (6.66).

Found (%): C (40.21), H (4.43), N (7.15).

After vacuum drying for two hours:

Calculated as: C$_{54}$H$_{66}$N$_8$O$_{24}$Ni$_7$ i.e [Ni(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$

Theory (%): C (40.09), H (4.11), N (6.93).

Found (%): C (39.69), H (4.43), N (7.15).

Infrared Spectroscopy (cm$^{-1}$) (Spectra shown in Figure 113)

3402 (b), 2932 (w), 2817 (w), 1627 (s), 1603 (w), 1459 (m), 1436 (m), 1407 (w), 1338 (m), 1314 (s), 1222 (s), 1073 (m), 965 (m), 864 (m), 789 (m), 741 (s).
Fig. 113 Infrared spectrum obtained from [(MeOH)$_2$\(\subset\)Ni(II)$\gamma$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (2): (top) pre-vacuum drying, (bottom) following 3 hour vacuum drying.

_Uv/vis Analysis_

MeOH: $\lambda_{\text{max}}$, nm ($\varepsilon_m$, 10$^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$): 205 (84.6), 231 (108.5), 268 (46.3), 356 (21.4).
MeCN: $\lambda_{\text{max}}$, nm ($\varepsilon_m$, 10$^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$): 230 (110.2), 268 (42.8), 356 (15.8).

2.5.3.4 Synthesis of [(NO$_2$Me)$_3$\(\subset\)Ni(II)$\gamma$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (3)

To a solution of Ni(NO$_3$)$_2$\cdot$6$H$_2$O (0.25 g, 0.859 mmol, 1.0 eq.) in EtOH (30 cm$^3$) were added L$_1$H (0.142 g, 0.859 mmol, 1.0 eq.) and solid NaOH (0.034 g, 0.859 mmol, 1.0 eq.) and the solution stirred for 4 hours at ambient temperature. The resulting bright green, opaque solution was filtered and the mother liquor allowed to evaporate to dryness. The residue was redissolved, as much as possible, in NO$_2$Me (10 cm$^3$) and, following filtration, the mother liquor was slowly diffused with Et$_2$O resulting in the growth of green hexagonal-shaped crystals of 3 in relatively low yield (10%).

_C, H, N Elemental Analysis_

Calculated for: C$_{53}$H$_{75}$N$_{11}$O$_{30}$Ni$_7$ i.e. [(NO$_2$Me)$_3$\(\subset\)Ni(II)$\gamma$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$

Theory (%): C (38.02), H (4.20), N (8.56).
Found (%): C (38.31), H (4.59), N (8.29).
Infrared Spectroscopy (cm$^{-1}$)

3625 (w), 2931 (w), 1628 (s), 1555 (s), 1476 (s), 1460 (s), 1433 (m), 1407 (m), 1337 (m), 1316 (m), 1221 (m),

2.5.3.5 Synthesis of [(MeCN)$_2$$\subset$Ni(II)$_7$(OH)$_6$(L$_2$)$_6$](NO$_3$)$_2$ (4)

To a solution of Ni(NO$_3$)$_2$.6H$_2$O (0.25 g, 0.859 mmol, 1.0 eq.) in EtOH (30 cm$^3$) were added L$_2$H (0.21g, 0.859 mmol, 1.0 eq.) and NaOH (0.034 g, 0.859 mmol, 1.0 eq.) and the solution stirred to afford dissolution of the solid reagents. The solution was stirred for a further 4 hours at ambient temperature, after which time it had adopted a green precipitous appearance. The solution was filtered and the mother liquor evaporated to dryness (fume hood). The dark green residue was redissolved in MeCN (25 cm$^3$) and the solution stirred for ~1 hour to afford, as much as possible, dissolution of the solid, green residue. The solution was then filtered and the mother liquor diffused with Et$_2$O which yielded 4 as dark green hexagons in 23 % yield.

C, H, N Elemental Analysis

Calculated for: C$_{58}$H$_{66}$N$_{10}$O$_{24}$Br$_6$Ni$_7$ i.e. [(MeCN)$_2$$\subset$Ni(II)$_7$(OH)$_6$(L$_2$)$_6$](NO$_3$)$_2$

Theory (%): C (31.99), H (3.06), N (6.43).

Found (%): (31.77), H (3.28), N (6.56).

Infrared Spectroscopy (cm$^{-1}$) (Spectra shown in Figure 114)

3620 (w), 3261 (w), 2927 (w), 2256 (w), 1629 (s), 1592 (w), 1543 (w), 1457 (m), 1393 (m), 1352 (m), 1306 (s), 1236 (m), 1212 (m).
Fig. 114 Infrared spectra of complex 4: (top) pre-vacuum drying, (bottom) post-vacuum drying.

2.5.3.6 Synthesis of [(MeOH)$_2$(H$_2$O)⊂Zn(II)$_7$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (5)

To a solution of Zn(NO$_3$)$_2$.6H$_2$O (0.25 g, 0.859 mmol, 1.0 eq.) in MeOH (30 cm$^3$) was added L$_1$H (0.142 g, 0.859 mmol, 1.0 eq.) and the solution stirred to dissolve the solid. Solid NaOH (0.034 g, 0.859 mmol, 1.0 eq.) was then added to the bright yellow solution. Stirring, at ambient temperature, was continued for a further 2 hours following which the solution was filtered to yield a bright yellow mother liquor. X-ray quality hexagonal crystals of 5 were obtained in 35 % yield upon slow evaporation of the mother liquor (Figure 115).

Fig. 115 Microscope image showing the hexagonal nature of the crystals of complex 5.
C, H, N Elemental Analysis

Calculated for: C_{56}H_{74}N_{8}O_{26}Zn_{7} i.e. [(MeOH)_2(H_2O)\subset\text{Zn(II)}_7(OH)_6(L_1)_6](NO_3)_2

Theory (%): C (38.81), H (4.30), N (6.47).
Found (%): C (38.87), H (4.65), N (6.61).

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

3406 (b), 2931 (w), 2823 (w), 1636 (s), 1602 (w), 1561 (m), 1368 (m), 1330 (m), 1308 (s), 1212 (s), 1093 (m), 967 (m), 869 (m), 743 (s).

UV/vis Analysis

MeOH: \(\lambda_{\text{max}}, \text{nm (}\varepsilon_{\text{m}}, 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})\): 202 (108.3), 226.9 (146.4), 267 (71.1), 350 (27.9).
MeCN: \(\lambda_{\text{max}}, \text{nm (}\varepsilon_{\text{m}}, 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})\): 227 (242.6), 267 (103.6), 350 (44.0).

2.5.3.7 Synthesis of [(NO_2Me)_3\subset\text{Zn(II)}_7(OH)_6(L_1)_6](NO_3)_2 (6)

To a solution of Zn(NO_3)_2.6H_2O (0.25 g, 0.859 mmol, 1.0 eq.) in EtOH (30 cm\(^3\)) were added successively L_1H (0.142 g, 0.859 mmol, 1.0 eq.) and NaOH (0.034 g, 0.859 mmol, 1.0 eq.) and the solution stirred to afford dissolution (as much as possible) of the solid reagents. The cloudy / opaque, yellow solution was stirred for a further 3 hours at ambient temperature, following which the reaction solution was filtered, transferred to a beaker and the mother liquor allowed to evaporate to dryness. The bright yellow residue was then redissolved in NO_2Me from which X-ray quality crystals of 6 were collected in 10 % yield.

C, H, N Elemental Analysis

Calculated for: C_{57}H_{75}N_{11}O_{30}Zn_{7} i.e. [(NO_2Me)_3\subset\text{Zn(II)}_7(OH)_6(L_1)_6](NO_3)_2

Theory (%): C (36.97), H (4.08), N (8.32).
Found (%): C (37.02), H (4.17), N (8.44).

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

3418 (w), 2967 (w), 2930 (w), 1625 (s), 1601 (w), 1561 (m), 1459 (m), 1405 (w), 1319 (s), 1220 (s), 1072 (m), 960 (m), 860 (m), 789 (m), 743 (s).
2.5.3.8 *Synthesis of [Co(II)(OH)₆(L₁)₆](NO₃)₂ (7)*

To a solution of Co(NO₃)₂.6H₂O (0.25 g, 0.859 mmol, 1.0 eq.) in MeOH (30 cm³) were added L₁H (0.142 g, 0.859 mmol, 1.0 eq.) and solid NaOH (0.034 g, 0.859 mmol, 1.0 eq.) and the solution stirred to gradually afford a dark red-brown solution. Stirring was continued for a further 3 hours after which time the solution was filtered to afford a dark purple-brown mother liquor. Diffusion of the mother liquor with Et₂O resulted in the growth of dark purple, hexagonal-shaped blocks of 7, which were harvested after 1 week in 30 % yield.

*C, H, N Elemental Analysis*

Calculated for C₅₆H₆₆N₈O₂₆Co₇

Theory (%): C (40.04), H (3.96), N (6.67).

Found (%): C (40.22), H (3.68), N (6.95).

*Infrared Spectroscopy (cm⁻¹)*

3622 (w), 3427 (w), 2911 (w), 2812 (w), 1626 (m), 1603 (w), 1561 (w), 1561 (w), 1457 (m), 1438 (m), 1334 (m), 1304 (m), 1241 (m), 1221 (s), 1073 (m), 1032 (m), 1012 (m), 959 (m), 743 (s).

2.5.3.9 *Synthesis of [(MeOH)₂Co(II)(OH)₆(L₁)₆](NO₃)₂ (8)*

To a solution of Co(NO₃)₂.6H₂O (0.25 g, 0.859 mmol, 1.0 eq.) in MeOH (30 cm³) was added L₁H (0.195 g, 0.859 mmol, 1.0 eq.) initially affording a dark red-coloured, transparent solution, gradually adopting a darker colour as stirring was continued. Solid NaOH (0.034 g, 0.859 mmol, 1.0 eq.) was then added resulting in the solution adopting a golden red-brown appearance. The solution was stirred for a further 5 hours, after which it was filtered, to yield a very dark red-brown mother liquor, and the product allowed to crystallise from the mother liquor via slow solvent evaporation and Et₂O diffusion. Complex 8 was isolated as dark red-brown crystalline blocks with a combined yield of 30 % (Figure 116).
**Fig. 116** Microscope images showing the hexagonal structure of crystals of 8.

_C, H, N Elemental Analysis_

Calculated for C$_{56}$H$_{66}$N$_8$O$_{26}$Co$_7$

Theory (%): C (40.04), H (3.96), N (6.67).

Found (%): C (40.22), H (3.68), N (6.95).

_Infrared Spectroscopy (cm$^{-1}$)_

1626 (m), 1603 (w), 1561 (m), 1457 (m), 1438 (m), 1407 (w), 1334 (m), 1304 (m), 1241 (m), 1221 (s), 1073 (m), 1032 (m), 1012 (m), 959 (m), 743 (s).

_UV/vis Analysis_

MeOH: $\lambda_{\text{max}}$, nm ($\varepsilon_m$, 10$^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$): 352 (20.4), 262 (44.6), 233 (90.8). MeCN: $\lambda_{\text{max}}$, nm ($\varepsilon_m$, 10$^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$): 352 (20.3), 262 (48.8), 230 (107.3), 200 (107.7).

_Mass Spectrometry (MS) Analysis_

ESI-MS measurements on a MeOH solution of 8 (Section 2.3.2) gave a parent peak at m/z = 777.8 indicative of the [Co(II)$_7$(OH)$_2$(OMe)$_4$(L$_3$)$_6$]$^{2+}$ fragment (Figure 95).

2.5.3.10 [(NO$_3$)$_2$Co(III)$_1$Co(II)$_6$(OH)$_6$(L$_3$)$_6$](NO$_3$)$_3$MeCN (9)

To a solution of Co(NO$_3$)$_2$.6H$_2$O (0.25 g, 0.859 mmol, 1.0 eq.) in MeOH (30 cm$^3$) was added L$_3$H (0.195 g, 0.859 mmol, 1.0 eq.) to give an initial dark red solution, which gradually adopted a darker colour as stirring was continued. Solid NaOH (0.034 g, 0.859 mmol, 1.0 eq.) was then added resulting in the solution adopting a golden red-brown appearance. The solution was stirred for a further 5 hours, after which it was filtered, to yield a very dark red-
brown mother liquor, and the product allowed to crystallise from the mother liquor via slow solvent evaporation and Et$_2$O diffusion. Complex 9 was isolated as dark red-brown crystalline blocks with a combined yield of 15%.

**C, H, N Elemental Analysis**

Calculated for C$_{84}$H$_{78}$N$_9$O$_7$Co$_7$ i.e. [(NO$_3$)$_2$][Co(III)$_1$Co(II)$_6$(OH)$_6$(L$_3$)$_6$](NO$_3$) (loss of all MeCN).

Theory (%): C (40.04), H (3.96), N (6.67).

Found (%): C (40.22), H (3.68), N (6.95).

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

1626 (m), 1603 (w), 1561 (m), 1457 (m), 1438 (m), 1407 (w), 1334 (m), 1304 (m), 1241 (m), 1221 (s), 1073 (m), 1032 (m), 1012 (m), 959 (m), 743 (s).

**UV/vis Analysis**

MeOH: $\lambda_{\text{max}}$, nm $(\varepsilon_m$, $10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$): 364 (27.6), 276 (97.4), 226 (122.9), 204 (149.6).

MeCN: $\lambda_{\text{max}}$, nm $(\varepsilon_m$, $10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$): 360 (32.2), 273 (97.4), 224 (164.5), 200 (226.4).

**Mass Spectrometry (MS) Analysis**

ESI-MS analysis of an MeCN solution of 9 identified sequential loss of the NO$_3^-$ species on going from m/z 1995.1 to 623.7 i.e. m/z 1995.1, 966.6 and 623.7. The MS analysis of 9 is summarized in Table 2 below.

**Table 2** MS analysis of complex 9 identifying molecular adducts formed via TOF-ESI

<table>
<thead>
<tr>
<th>m/z</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>623.70</td>
<td>[Co(III)$_1$Co(II)$_6$(OH)$_6$(L$_3$)$_6$]$^{3+}$</td>
</tr>
<tr>
<td>966.60</td>
<td>{[Co(III)$_1$Co(II)$_6$(OH)$_6$(L$_3$)$_6$] + NO$_3^-$}$^{2+}$</td>
</tr>
<tr>
<td>1995.15</td>
<td>{[Co(III)$_1$Co(II)$_6$(OH)$_6$(L$_3$)$_6$] + (NO$_3$)$_2$}$^+$</td>
</tr>
</tbody>
</table>
2.5.3.11 Synthesis of $[(\text{ClO}_4)_2\text{Co(III)}_1\text{Co(II)}_6(\text{OH})_6(\text{L}_3)_6](\text{ClO}_4)$ (10)

To a solution of Co(ClO$_4$)$_2$.6H$_2$O (0.25 g, 0.683 mmol, 1.0 eq.) in MeOH (20 cm$^3$) was added L$_3$H (0.155 g, 0.683 mmol, 1.0 eq.) and the solution stirred to afford complete dissolution of both the salt and L$_3$H. Solid NaOH pellets (0.027 g, 0.683 mmol, 1.0 eq.) were then added and the transparent, dark red-brown solution stirred for a further 6 hours. The solution was then filtered to afford a mother liquor of similar appearance. Following failure to isolate suitably crystalline material from this MeOH mother liquor, the solution was allowed to evaporate to dryness. The solid residue was recrystallised from MeCN (25 cm$^3$) (after stirring for 1 hour), which afforded dark red-brown plates of 10 in 35 % yield after 1 week, which were analysed via X-ray diffraction.

C, H, N Elemental Analysis

Calculated for: C$_{84}$H$_{78}$N$_6$Cl$_3$O$_{30}$Co$_7$ i.e. $[(\text{ClO}_4)_2\text{Co(III)}_1\text{Co(II)}_6(\text{OH})_6(\text{L}_3)_6](\text{ClO}_4)$

Theory (%): C (46.49), H (3.62), N (3.87).

Found (%): C (46.81), H (3.74), N (4.15).

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

1611 (s), 1590 (m), 1559 (m), 1487 (w), 1466 (s), 1392 (w), 1301 (m), 1235 (s), 1214 (m), 1190 (s), 1071 (s), 973 (s), 954 (m), 908 (w), 850 (s), 777 (s), 735 (s), 696 (s).

2.5.3.12 Synthesis of $[\text{Co(III)}_2\text{Na(I)}_1(\text{L}_2)_6](\text{BF}_4)$ (11)

To a solution of Co(BF$_4$)$_2$.6H$_2$O (0.25 g, 0.734 mmol, 1.0 eq.) in EtOH (25 cm$^3$) were added L$_2$H (0.179 g, 0.734 mmol, 1.0 eq.) and solid NaOH (0.0293 g, 0.734 mmol, 1.0 eq.) and the solution stirred to allow for complete dissociation of the solid reactants. The opaque brown solution was stirred at ambient temperature for a further 5 hours, after which it was filtered to afford a dark purple-brown mother liquor. Slow evaporation of the mother liquor afforded 11 as dark purple parallelepiped crystals in 25 % yield.

C, H, N Elemental Analysis

Calculated for C$_{54}$H$_{54}$N$_6$O$_{12}$B$_1$Br$_6$F$_{14}$Na$_1$Co$_2$
Theory (%): C (38.47), H (3.23), N (4.98).

Found (%): C (38.26), H (3.44), N (5.03).

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

1628 (s), 1463 (m), 1452 (m), 1435 (s), 1238 (s), 1217 (m), 1098 (m), 1080 (m), 1052 (m), 1027 (m), 1018 (m), 978 (m), 874 (m), 824 (m), 825 (m), 787 (m), 689 (s).

2.5.3.13 Synthesis of \([\text{Co(III)}_3\text{Na(I)}_3(L_1)_6(N_3)_6]_n\) (12)

To a solution of Co(BF\(_4\))\(_2\).6H\(_2\)O (0.25 g, 0.734 mmol, 1.0 eq.) in MeOH (25 cm\(^3\)) was added L\(_1\)H (0.121 g, 0.734 mmol, 1.0 eq.) and the solution stirred to afford complete dissolution of the reactants. Sodium azide (NaN\(_3\)) (0.095 g, 1.468 mmol, 2.0 eq.) was then added, which afforded a solution colour change from golden-brown (transparent) to green-brown (opaque). NaOH (0.059 g, 1.468 mmol, 2.0 eq.) was then added and the solution was stirred for a further 4 hours under ambient conditions. The solution was filtered to afford a dark red-brown mother liquor from which complex 12 was isolated after five days as dark red-brown blocks via slow evaporation of the solvent in 30 % yield.

C, H, N Elemental Analysis

Calculated for: C\(_{54}\)H\(_{60}\)N\(_{24}\)O\(_{12}\)Na\(_3\)Co

Theory (%): C (43.71), H (4.07), N (22.67).

Found (%): C (43.50), H (4.12), N (22.98).

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

2028 (s) (N\(_3\)), 1631 (m), 1601 (m), 1478 (m), 1453 (m), 1441 (m), 1313 (m), 1295 (m), 1241 (m), 1224 (s), 1195 (m), 1173 (m), 1095 (m), 1081 (s), 1020 (m), 972 (m), 862 (m), 736 (s).

2.5.3.14 Synthesis of \([\text{Co(II)}_1(L_3)_2]\) (13)

To a solution of CoSO\(_4\).7H\(_2\)O (0.25 g, 0.89 mmol, 1.0 eq.) in MeOH (25 cm\(^3\)) was added L\(_3\)H (0.202 g, 0.89 mmol, 1.0 eq.). The solution was stirred to afford complete dissolution of the reactants. Solid NaOH (0.036 g, 0.89 mmol, 1.0 eq.) was then added, which resulted in a dark red-brown solution. This solution was then stirred for a further 3 hours under ambient conditions, after which it was filtered to yield a dark red-brown mother liquor. The sample
vial (containing mother liquor) was then placed in a fridge (at ~ 4°C). Dark red-brown crystalline blocks of 13 suitable for X-ray diffraction analysis were isolated from the mother liquor in moderate yield (20%) after 4 days.

*C, H, N Elemental Analysis*

Calculated for: C$_{28}$H$_{24}$N$_{2}$O$_{4}$Co$_{1}$

Theory (%): C (65.73), H (4.73), N (5.47).

Found (%): C (65.71), H (4.64), N (5.68).

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

1602 (s), 1578 (s), 1539 (m), 1487 (m), 1463 (m), 1431 (s), 1386 (m), 1356 (w), 1323 (m), 1228 (s), 1186 (s), 1106 (m), 1076 (m), 980 (m), 852 (m), 786 (m), 773 (m), 762 (m), 743 (s), 691 (s).
**Table 3** Bond Valence Sum (BVS) results for Co(II)/Co(III) Complexes 7-13.

<table>
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<tr>
<th>Complex</th>
<th>Atom label and BVS result</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7)</td>
<td>Co1 (central) 1.98</td>
</tr>
<tr>
<td></td>
<td>Co2 (outer ring) 2.05</td>
</tr>
<tr>
<td>(8)</td>
<td>Co1 (central) 1.92</td>
</tr>
<tr>
<td></td>
<td>Co2 (outer ring) 2.01</td>
</tr>
<tr>
<td>(9)</td>
<td>Co1 (central) 3.37</td>
</tr>
<tr>
<td></td>
<td>Co2 (outer ring) 2.06</td>
</tr>
<tr>
<td></td>
<td>Co3 (outer ring) 1.99</td>
</tr>
<tr>
<td></td>
<td>Co4 (outer ring) 1.98</td>
</tr>
<tr>
<td>(10)</td>
<td>Co1 (central) 3.25</td>
</tr>
<tr>
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<td>Co2 (outer ring) 1.99</td>
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<td>Co4 (outer ring) 2.01</td>
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<td>(11)</td>
<td>Co1 3.3</td>
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<td>(12)</td>
<td>Co1 3.19</td>
</tr>
<tr>
<td>(13)</td>
<td>Co2 3.12</td>
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Table 4 Molecular cavity dimensions observed in the crystals of 1-6.

<table>
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<tr>
<th>Complex / Bowl</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
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<tbody>
<tr>
<td>Cavity Volume (Å³)</td>
<td>265.9</td>
<td>293.7</td>
<td>283.8</td>
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<tr>
<td>Cavity Dimensions (Å) (base x depth x rim)</td>
<td>6.20 x 4.21 x 11.70</td>
<td>6.20 x 4.16 x 11.81</td>
<td>6.20 x 4.08 x 11.90</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex / Bowl</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cavity Volume (Å³)</td>
<td>155.9</td>
<td>280.40</td>
<td>280.40</td>
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<tr>
<td>Cavity Dimensions (Å) (base x depth x rim)</td>
<td>6.28 x 6.18 x 11.90</td>
<td>6.23 x 4.15 x 11.84</td>
<td>6.26 x 4.07 x 12.12</td>
</tr>
</tbody>
</table>
Tables of Crystallographic Data
Table 5 Crystallographic data for 2-iminophenyl-6-methoxyphenol (L₃H).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Formula</td>
<td>C₁₄H₁₃N₁O₂</td>
</tr>
<tr>
<td>Mᵣ (g mol⁻¹)</td>
<td>227.25</td>
</tr>
<tr>
<td>Crystal Appearance</td>
<td>Orange Parallelpiped</td>
</tr>
<tr>
<td>Crystal Dimensions (mm x mm x mm)</td>
<td>0.50 x 0.10 x 0.02</td>
</tr>
<tr>
<td>Crystal system</td>
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</tr>
<tr>
<td>Space group</td>
<td>P₂₁₂₁₂₁</td>
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<td>a / Å</td>
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</tr>
<tr>
<td>b / Å</td>
<td>9.0763(12)</td>
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<td>c / Å</td>
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<td>V / Å³</td>
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<tr>
<td>λ² / Å</td>
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</tr>
<tr>
<td>Dᵇ / g cm⁻³</td>
<td>1.314</td>
</tr>
<tr>
<td>μ (Mo-Kα) / mm⁻¹</td>
<td>0.088</td>
</tr>
<tr>
<td>Meas. / Indep. (R_m) reflections</td>
<td>2000 / 1347 (0.0486)</td>
</tr>
<tr>
<td>wRᵡᵇ (all data)</td>
<td>0.1604 (2000)</td>
</tr>
<tr>
<td>R₁ᵇᵈ (reflections)</td>
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<td>Goodness of fit (GOOF) on F²</td>
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</table>

ᵃMo-Kα radiation, graphite monochromator. ᵇ
wR₂ = [Σ w(IF₀²I) / Σ wIF₀²I]⁰.⁵, ᶜ For observed data. ᵈ
R₁ = [Σ I²F₀I - IFᵣI² / Σ IF₀I]
Table 6 Crystallographic data for complexes 1-6.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$C_{54}H_{66}N_8O_{24}Ni_7$</td>
<td>$C_{56}H_{72}N_8O_{26}Ni_7$</td>
<td>$C_{57}H_{66}N_{11}O_{30}Ni_7$</td>
<td>$C_{58}H_{66}N_{10}O_{24}Br_6Ni_7$</td>
<td>$C_{56}H_{66}N_8O_{27}Zn_7$</td>
<td>$C_{57}H_{66}N_{11}O_{30}Zn_7$</td>
</tr>
<tr>
<td>$M_R$ (g mol$^{-1}$)</td>
<td>1622.12</td>
<td>1678.14</td>
<td>1796.18</td>
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<td>1740.76</td>
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</tr>
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<td>Green</td>
<td>Green Parallelepiped</td>
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<td>Pale Yellow</td>
</tr>
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<td>0.40 x 0.20 x 0.15</td>
</tr>
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<td>Trigonal</td>
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<td>P-3c1</td>
<td>Trigonal</td>
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<td>Space group</td>
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<td>P-3c1</td>
<td>P-3c1</td>
<td>C2/c</td>
<td>P-3c1</td>
<td>P-3c1</td>
</tr>
<tr>
<td>a / Å</td>
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<td>13.913(2)</td>
<td>13.933(2)</td>
<td>28.8575(14)</td>
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<td>14.082(2)</td>
</tr>
<tr>
<td>b / Å</td>
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<td>13.913(2)</td>
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<td>11.1352(3)</td>
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<td>c / Å</td>
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<td>23.141(5)</td>
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<td>23.353(5)</td>
<td>22.759(5)</td>
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<td>90</td>
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<td>90</td>
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<td>γ (°)</td>
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<td>90</td>
</tr>
<tr>
<td>V / Å$^3$</td>
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<td>3879.6(11)</td>
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<td>8296.6(6)</td>
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<td>3908.2(11)</td>
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<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>T / K</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>$\lambda$ / Å</td>
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<td>0.71070</td>
<td>0.71070</td>
<td>0.71070</td>
<td>0.71070</td>
<td>0.71070</td>
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<td>$D^b / g$ cm$^{-3}$</td>
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<td>1.437</td>
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</tr>
<tr>
<td>$\mu$ (Mo-Kα) / mm$^{-1}$</td>
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<td>2.187</td>
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<td>Meas. / Indep. (Rint$^c$) reflections</td>
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<td>2306 / 1376</td>
<td>2174 / 1743</td>
<td>6608 / 3625</td>
<td>2361 / 1766</td>
<td>2338 / 2059</td>
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<td>wR$_2$ (all data)</td>
<td>0.2452 (2153)</td>
<td>0.2446 (2306)</td>
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<td>0.1307 (6608)</td>
<td>0.2107 (2361)</td>
<td>0.2079 (2338)</td>
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<tr>
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<td>0.0802 (1376)</td>
<td>0.0505 (1743)</td>
<td>0.0502 (3625)</td>
<td>0.0628 (1766)</td>
<td>0.0713 (2059)</td>
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<tr>
<td>Goodness of fit (GOOF) on F$^2$</td>
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<td>1.047</td>
<td>1.224</td>
<td>0.886</td>
<td>1.139</td>
<td>1.119</td>
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</tbody>
</table>

$^a$Mo-Kα radiation, graphite monochromator. $^b$wR$_2$ = [$\sum w(\bar{F}_o^2 I - \bar{F}_c^2 I)^2 / \sum w\bar{F}_o^2 I^2$]$^{1/2}$. $^c$For observed data. $^d$R$_1$ = [$\sum I^2 F_o^2 I - \bar{F}_c^2 I^2 / \sum I F_o I$]
## Table 7 Crystallographic data for complexes 7-10.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(7) $\text{C}<em>{54}\text{H}</em>{66}\text{N}<em>{8}\text{O}</em>{24}\text{Co}_{7}$</th>
<th>(8) $\text{C}<em>{56}\text{H}</em>{68}\text{N}<em>{8}\text{O}</em>{26}\text{Co}_{7}$</th>
<th>(9) $\text{C}<em>{90}\text{H}</em>{57}\text{N}<em>{2}/\text{O}</em>{27}\text{Co}_{7}$</th>
<th>(10) $\text{C}<em>{84}\text{H}</em>{78}\text{N}<em>{6}\text{O}</em>{30}\text{Cl}<em>{3}\text{Co}</em>{7}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$\text{C}<em>{54}\text{H}</em>{66}\text{N}<em>{8}\text{O}</em>{24}\text{Co}_{7}$</td>
<td>$\text{C}<em>{56}\text{H}</em>{68}\text{N}<em>{8}\text{O}</em>{26}\text{Co}_{7}$</td>
<td>$\text{C}<em>{90}\text{H}</em>{57}\text{N}<em>{2}/\text{O}</em>{27}\text{Co}_{7}$</td>
<td>$\text{C}<em>{84}\text{H}</em>{78}\text{N}<em>{6}\text{O}</em>{30}\text{Cl}<em>{3}\text{Co}</em>{7}$</td>
</tr>
<tr>
<td>$M_R$ (g mol$\text{ }^{-1}$)</td>
<td>1623.66</td>
<td>1679.68</td>
<td>2181.23</td>
<td>2170.38</td>
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<td>Crystal Appearance</td>
<td>Purple-Brown Hexagon</td>
<td>Purple Parallepipiped</td>
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<td>Purple-Brown Parallepipiped</td>
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<td>Crystal Dimensions (mm x mm x mm)</td>
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<td>Monoclinic</td>
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<td>P-3c1</td>
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<td>C2/c</td>
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<td>14.041(2)</td>
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<td>30.4457(14)</td>
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<tr>
<td>$b$ / Å</td>
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<td>14.041(2)</td>
<td>12.9879(5)</td>
<td>13.4369(5)</td>
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<tr>
<td>$c$ / Å</td>
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<td>24.4043(9)</td>
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<td>90</td>
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<td>$\gamma$ (°)</td>
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<tr>
<td>$V$ / Å$^3$</td>
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<td>9470.7(7)</td>
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<td>$Z$</td>
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<td>4</td>
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<tr>
<td>$T$ / K</td>
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<td>0.71070</td>
<td>0.71070</td>
<td>0.7107</td>
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<td>1.513</td>
<td>1.306</td>
<td>1.360</td>
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<td>2362 / 2188 (0.0184)</td>
<td>8489 / 5388 (0.0684)</td>
<td>8660 / 5356 (0.0472)</td>
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<td>0.2548 (8660)</td>
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<td>1.052</td>
<td>1.096</td>
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</table>

$^a$Mo-Kα radiation, graphite monochromator. $^b\text{wR}_2 = [\sum w(IF_o^2 - IF_e^2)^2 / \sum wIF_o^2]^1/2$. $^c$ For observed data. $^dR_1 = [\sum I^2F_oI - IIF_e^2I^2 / \sum IF_oI]$
Table 8 Crystallographic data for complexes 11-13.

<table>
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<tr>
<th>Complex</th>
<th>(11)</th>
<th>(12)</th>
<th>(13)</th>
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<td>Formula</td>
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<td>$C_{28}H_{24}N_2O_4Co_1$</td>
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<td>$M_R$ (g mol$^{-1}$)</td>
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<td>1483.02</td>
<td>511.42</td>
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<td>Crystal Appearance</td>
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<td>Red-Brown Block</td>
<td>Purple-Brown Block</td>
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<td>0.50 x 0.30 x 0.20</td>
<td>0.20 x 0.15 x 0.10</td>
</tr>
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<td>Crystal system</td>
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<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C 2/c</td>
<td>C2/c</td>
<td>P2$_1$/c</td>
</tr>
<tr>
<td>a / Å</td>
<td>24.774(5)</td>
<td>17.9060(6)</td>
<td>11.6622(8)</td>
</tr>
<tr>
<td>b / Å</td>
<td>15.542(3)</td>
<td>23.6320(8)</td>
<td>23.9507(13)</td>
</tr>
<tr>
<td>c / Å</td>
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<td>9.2521(6)</td>
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<td>γ (°)</td>
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<td>Z</td>
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<td>4</td>
<td>4</td>
</tr>
<tr>
<td>T / K</td>
<td>150(2)</td>
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<td>150</td>
</tr>
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<td>$λ^a$ / Å</td>
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<td>0.7107</td>
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<td>1.891</td>
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<td>μ (Mo-Kα) / mm$^{-1}$</td>
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<td>Meas. / Indep. (R$_{int}$) reflections</td>
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<td>5945 / 4026 (0.0455)</td>
<td>4448 / 3291 (0.0341)</td>
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<td>wR$_2$ (all data)</td>
<td>0.0713 (5423)</td>
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</tr>
<tr>
<td>R$_1$ (reflections)</td>
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<td>Goodness of fit (GOOF) on F$^2$</td>
<td>1.039</td>
<td>1.019</td>
<td>1.139</td>
</tr>
</tbody>
</table>

$^a$Mo-Kα radiation, graphite monochromator. $^b$ wR$_2$=[∑$w[IF_0^2-I-F_0^2I]^2/∑wIF_0^2I^2]^{1/2}$, $^c$ For observed data. $^d$ $R_r=[∑I^2F_0-I-F_r^2/I^2F_0I]$
2.6 References


(18) Kahn, O. Magnetism: A Supramolecular Function (NATO Science series) and references therein.


(33) Barbour, L. J. *MC AVITY: Program for calculating the molecular volume of closed capsules* 2006, University of Missouri-Colombia, Colombia, MO, USA, 2003, http://www.x-seed.net/cavity.html. The free volume within the cavities of 1-4 was calculated in the absence of guests.

(34) Blatov, V. A. *IUCr CompComm Newsletter* 2006, 4-38.


(51) Sheldrick, G. M. *A Computer program for crystal structure determination* **1997**, *University of Göttingen*.


Chapter Three

3.1 Introduction

A newly-emerging research field in supramolecular chemistry is that of encapsulation and separation of reactive functional group substituted aromatic species within host Metal-Organic frameworks (MOFs), arising from the use of these reactive organic species in the production of dyes, pharmaceuticals and perfumes. The use of discrete molecular hosts offers a novel and facile alternative to traditional separation methods including chromatography and distillation. With respect to our own work, we believed that the cavities present in our [M(II)₇] complexes (Chapter Two) could act as discrete hosts for the encapsulation of such reactive aromatic molecules towards dual functional materials (i.e. light-induced magnetic perturbations). To this end, 2-Furaldehyde and its isomeric analogue 3-Furaldehyde were chosen as potential guest species stemming from previously reported Cd(II) and Zn(II) MOF encapsulation studies involving these organic molecules (Figure 117).

![Fig. 117 Isomers 2-Furaldehyde (left) and 3-Furaldehyde (right), utilised in the generation of their acyl radical species when enclosed within our double-bowl pseudo [M(II)₇] metallocalix[6]arene complexes.](image)

More specifically, Liu and co-workers utilised a Cd(II)-triazole MOF for both the trapping of these highly reactive aromatic molecules and the subsequent generation of their acyl radical guest species within the porous environment of the host. Radical generation within the MOF was evidenced from luminescence and EPR spectroscopic measurements (for background to the EPR technique, see Appendix: Section B). It was found that luminescence intensity could be tuned via encapsulation of different guests, while ESR measurements of the host-guest complexes showed broad signals (the empty host showing no signal), indicative of radical generation. Arising from the biological and chemical significance of radicals is the desire to prolong the existence of these highly reactive, short-lived species. We believed that our double-bowl pseudo [M₇] metallocalix[6]arene complexes (M = Ni(II), Co(II), Zn(II)),
previously utilised for encapsulation of solvent molecules and anions might be able to accommodate 2-Furaldehyde and its isomers as guests within the confines of the molecular cavities present therein. Successful inclusion of furaldehyde isomers and subsequent generation of radicals within the [M(II)$_7$] host framework would 1) alter the magnetic properties of the complex and 2) introduce a duality into the pseudo calix[6]arene framework, whereby light-induced radical guests modify the spin magnetic moment of the system. Indeed, our aim of encapsulating furaldehyde species within the double-bowl architecture was successful. In addition, we report in this chapter the extension of the [M(II)$_7$] double-bowl topology via further functionalisation of the Schiff base ligand, towards further selective guest encapsulation studies.

3.2 Isolation of [M(II)$_7$] Systems containing Radical Guests

The first host-guest architectures to be obtained containing 2-Furaldehyde as our organic guest were the heptanuclear [Zn(II)$_7$] complexes [(2-Fur)$\subset$Zn(II)$_7$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (14) and [(2-Fur)$\subset$Zn(II)$_7$(OMe)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (15) (where 2-Fur is the 2-Furaldehyde guest). The principal disc-like topological features associated with this breed of host architecture were discussed previously (see Section 2.2). However to briefly review, the complexes exhibit molecular cavities formed via the stacking of the [M(II)$_7$] double-bowl units in the solid state. To this end we were successful in encapsulating one molecule of 2-Furaldehyde within each molecular cavity present in both 14 and 15 (Figures 118 and 119). Complexes 14-15 form following the reaction of Zn(NO$_3$)$_2$.6H$_2$O with L$_1$H, NaOH and 2-Furaldehyde (10 eq.) and crystallise as pale yellow-orange hexagonal blocks in the same trigonal P-3c1 space group as complexes [(MeOH)$_2$(H$_2$O)$\subset$Zn(II)$_7$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (5) and [(NO$_2$Me)$_3$$\subset$Zn(II)$_7$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (6) (Chapter Two), with analogous unit cell parameters. The only difference between the two complexes is the solvent used in their production. Utilising MeOH in place of EtOH affords 15 which contains $\mu_3$-bridging MeO$^-$ groups in place of the more common $\mu_3$-OH bridging sites observed in 14. The water content in the solvent used may also play a role in complex formation. Complete X-ray structural details for 14-15 are given in Table 11 (Section 3.7).
**Fig. 118** Crystal structure of 14 as viewed perpendicular (left) and parallel (right) to the planar [Zn(II)$_7$] core. Colour code: Zn = blue, O = red, N = dark blue, C = grey. Hydrogen atoms have been omitted for clarity.

**Fig. 119** Crystal structure of [(2-Fur)$\subset$Zn(II)$_7$(OMe)$_6$(L$_1$)$_6$(NO$_3$)$_2$] (15) as viewed parallel to the planar [Zn(II)$_7$] core. Colour code: as in Figure 118. Hydrogen atoms have been included for the bridging $\mu_3$-bridging MeO$^-$ groups [O1-Me and symmetry equivalent (s.e.,)] only.

**Fig. 120** Crystals showing the colour difference when the molecular cavities in our [Zn(II)$_7$] disc complexes are empty (left) and when occupied by 2-Furaldehyde guests (centre = 14, right = 15).
3.2.1 IR Evidence for Guest Encapsulation

Initial evidence of 2-Furaldehyde encapsulation came from a comparison of the single crystals of the vacuum-dried empty [Zn(II)$_7$] complex 5, with those of [(2-Fur)$\subseteq$Zn(II)$_7$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (14) and [(2-Fur)$\subseteq$Zn(II)$_7$(OMe)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (15), the latter crystals exhibiting pale orange and bright orange appearances respectively with respect to the colourless empty host complex 5 (Figure 120). Infrared analyses of 14-15 also highlighted the C=O aldehyde stretches (1667-1675 cm$^{-1}$) of the 2-Furaldehyde guests (Figures 122 and 123). Although encapsulation of 2-Furaldehyde was achieved it was not possible to present a crystallographic representation of the guest due to the large disorder associated with this encapsulated organic molecule; thus the guests are not visible in Figures 118 and 119. Arising from this disorder, it was necessary to employ a crystallographic technique known as SQUEEZE to assess guest presence; essentially involving a determination of the electron density / count within the molecular cavities in the unit cell.$^2$ The results obtained from this procedure were consistent with the encapsulation of one furaldehyde molecule within each molecular cavity present in 14-15 (see Section 3.7: Table 10 for details). More specifically, the 2-Furaldehyde molecules are found to be disordered over three sites along the three-fold rotation axis (TFA in Figure 121). This three-fold axis lies perpendicular to the [Zn(II)$_7$] plane and therefore the disordered 2-Furaldehyde guest lies in the same plane as the [Zn(II)$_7$] motif.

**Fig. 121** Schematic highlighting the disordered 2-Furaldehyde guests in 14 which lie perpendicular to the three-fold axis (TFA) inherent to the unit cell.

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Fig. 122 Infrared spectrum of 2-Furaldehyde used as a guest in this work. The C=O stretch of 2-Furaldehyde can be seen at 1667 cm$^{-1}$.

Fig. 123 (Main) Infrared spectra overlay of vacuum-dried [Zn(II)$_7$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (5) (black line) and the 2-Furaldehyde accommodated complex [(2-Fur)$_2$Zn(II)$_7$(OH)$_6$(L$_1$)$_6$](NO$_3$)$_2$ (14) (blue line). (Inset) Expansion of the 1685-1580 cm$^{-1}$
region of the spectra highlighting the C=O aldehyde stretches (within box) of the 2-Furaldehyde guests in 14.

3.2.2 Isolating the Ni(II) and Co(II) Analogue

We were also able to produce the 3-Furaldehyde containing Ni(II) analogue to 14 in the form of [(3-Fur)\(\text{Ni}(\text{II})\)\(\gamma(\text{OH})_6(\text{L}_1)_6\)(NO\(_3\))\(_2\)] (16) (Figure 124). Likewise, the [Co(II)\(\gamma\)] analogues to 14 were obtained incorporating both the 2- and 3-Furaldehyde guests with general formulae [(Fur)\(\text{Co}(\text{II})\)\(\gamma(\text{OH})_6(\text{L}_1)_6\)(NO\(_3\))\(_2\)] (Fur = 2-Furaldehyde (17) and 3-Furaldehyde (18)) (Figure 124). While both 17 and 18 crystallise as purple-brown blocks in the same trigonal P-3c1 space group as 14 and 16, it was observed that complex 18 could only be isolated via microwave synthesis (see Section 3.7.2.7 for details). Complete X-ray structural details for complexes 16-18 are given in Table 11 (Section 3.7). Overlay infrared spectra for complexes 14 and 16-18 are illustrated in Figures 125-129, while the characteristic vibrational stretches for the imine (C=N) and carbonyl (C=O) functional groups are detailed in Table 9 below.

Fig. 124 Crystal structure of 16 (left) and 17-18 (right) as viewed perpendicular to the planar [Ni(II)\(\gamma\)] and [Co(II)\(\gamma\)] planes respectively. Colour code: Co = purple, Ni = green, O = red, N = blue, C = grey. Hydrogen atoms have been omitted for clarity.
Fig. 125 (Main) IR spectra overlay of $[\text{Co(II)}_7\text{(OH)}_6\text{(L}_1)_6]\text{(NO}_3)_2$ (7) (black line) and the 2-Furaldehyde accommodated complex $[(2-\text{Fur})\text{Co(II)}_7\text{(OH)}_6\text{(L}_1)_6]\text{(NO}_3)_2$ (14) (red line). (Inset) Expansion of the 1685-1580 cm$^{-1}$ region of the spectra highlighting the C=O aldehyde stretches (within dashed box) of the 2-Furaldehyde guests in 14.

Fig. 126 (Main) IR spectra overlay of $[\text{Co(II)}_7\text{(OH)}_6\text{(L}_1)_6]\text{(NO}_3)_2$ (7) (black line) and the 3-Furaldehyde accommodated complex $[(3-\text{Fur})\text{Co(II)}_7\text{(OH)}_6\text{(L}_1)_6]\text{(NO}_3)_2$ (18) (red line). (Inset) Expansion of the 1685-1580 cm$^{-1}$ region of the spectra highlighting the C=O aldehyde stretches (within dashed box) of the 3-Furaldehyde guests in 18.
**Fig. 127** (Main) Infrared spectra overlay of 2-Furaldehyde (black line) and the 2-Furaldehyde accommodated complexes [(2-Fur)Co(II)_{7}(OH)_{6}(L_{1})_{6}](NO_{3})_{2} (17) (red line) and [(2-Fur)Zn(II)_{7}(OH)_{6}(L_{1})_{6}](NO_{3})_{2} (14) (green line). (Inset) Expansion of the 1685-1580 cm\(^{-1}\) region of the spectra highlighting the C=O aldehyde stretches (within dashed box) of the 2-Furaldehyde solvent and guests (in 14 and 17).

**Fig. 128** (Main): IR spectra overlay of [Ni(II)_{7}(OH)_{6}(L_{1})_{6}](NO_{3})_{2} (1) (black line) and the 3-Furaldehyde accommodated complex [(3-Fur)Ni(II)_{7}(OH)_{6}(L_{1})_{6}](NO_{3})_{2} (green line). (Inset) Expansion of the 1685-1580 cm\(^{-1}\) region of the spectra highlighting the C=O aldehyde stretches (within dashed box) of the 3-Furaldehyde guests in 16.
Fig. 129 (Main) IR spectra overlay of 3-Furaldehyde (black line) and the 3-Furaldehyde accommodated complexes \([(3\text{-Fur})\subset\text{Co(II)}\eta(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2\) (18) (red line) and \([(3\text{-Fur})\subset\text{Ni(II)}\eta(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2\) (16) (green line). (Inset) Expansion of the 1685-1580 cm\(^{-1}\) region of the spectra highlighting the C=O aldehyde stretches (within dashed box) of the 3-Furaldehyde solvent and guests (in 16 and 18).

Table 9 Summary of infrared data for complexes 14-18 highlighting the C=N and C=O stretches of the imine and carbonyl functional groups respectively.

<table>
<thead>
<tr>
<th>Complex / Bowl</th>
<th>C=N (cm(^{-1}))</th>
<th>C=O (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">(2\text{-Fur})\subset\text{Zn(II)}\eta(\text{OH})_6(\text{L}_1)_6</a>_2) (14)</td>
<td>1636</td>
<td>1669</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">(2\text{-Fur})\subset\text{Zn(II)}\eta(\text{OMe})_6(\text{L}_1)_6</a>_2) (15)</td>
<td>1636</td>
<td>1671</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">(3\text{-Fur})\subset\text{Ni(II)}\eta(\text{OH})_6(\text{L}_1)_6</a>_2) (16)</td>
<td>1629</td>
<td>1671</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">(2\text{-Fur})\subset\text{Co(II)}\eta(\text{OH})_6(\text{L}_1)_6</a>_2) (17)</td>
<td>1632</td>
<td>1678</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">(3\text{-Fur})\subset\text{Co(II)}\eta(\text{OH})_6(\text{L}_1)_6</a>_2) (18)</td>
<td>1627</td>
<td>1679</td>
</tr>
</tbody>
</table>
3.3 EPR Measurements of Host-Guest Complexes

Additional evidence for guest encapsulation came from electron paramagnetic resonance (EPR) measurements of complexes 14 and 17 (for background to the EPR technique, see Appendix: Section B). The EPR spectrum obtained from a crystalline sample of [(2-fur)⊂Zn(II)7(OH)6(L1)6](NO3)2 (14) gave a single sharp resonance centred at \( g = 2.006 \), which is consistent with that expected for an acyl radical species (Figure 130 (a)).\(^1\)\(^,\)\(^3\) As illustrated in Figure 130 (b) no discernible resonances were observed upon analysis of [(2-fur)⊂Co(II)7(OH)6(L1)6](NO3)2 (17), giving an identical spectra to the background collection. Moreover no signals were observed at lower temperatures (5 K) at either X- or Q-band for 17. Such an observation is common for complexes comprising distorted octahedral Co(II) ions, arising due to crystal field and spin-orbit coupling effects and does not necessarily indicate lack of formation of acyl radical species.\(^4\) Additionally (while not direct evidence for guest encapsulation in 17) absence of signals above the background for 17 highlights the variation in EPR response between compounds containing different 3d metal ions.

Fig. 130 (a) Room temperature X-band (9.867 GHz) EPR spectra (red lines) obtained on polycrystalline samples of [(2-fur)⊂Zn(II)7(OH)6(L1)6](NO3)2 (14) and (b) [(2-fur)⊂Co(II)7(OH)6(L1)6](NO3)2 (17).
fur)\(\text{\textsubscript{CO}}(\text{II})_7\text{OH}_6(L_1)_6\text{(NO}_3\text{)}_2\) (17) respectively. The green lines represent a background collection.

**3.4 Extending the \([M(\text{II})_7]\) Framework towards Selective Guest Encapsulation**

Given our desire to encapsulate ever larger and / or chemically interesting guests within our \([M(\text{II/III})_7]\)-based molecular cavities, it was believed that by further functionalising \(L_1\)H at the 4-position of the phenol ring (the upper rim of the pseudo calix[6]arene), a *cavity-wall extension* would aid molecular guest encapsulation. In pursuit of this goal, the Schiff base ligand 4-phenyl-2-iminomethyl-6-methoxyphenol (\(L_4\)H) was synthesised via a Suzuki coupling reaction (see Section 3.7.2.1 for details).\(^5\) \(L_4\)H possesses a phenyl group (Ph) at the 4-position of the phenol ring thus we believed that potential guests possessing a high degree of aromatic (\(\pi\)) character may be readily encapsulated, through edge-to-face \(\pi\cdots\pi\) stacking and C-H-\(\pi\) interactions within the host framework (Figure 131).

![Fig. 131](image)

*Fig. 131* (left) Structure of 2-iminomethyl-6-methoxyphenol (\(L_1\)H) and (right) its functionalised Schiff base analogue 4-phenyl-2-iminomethyl-6-methoxyphenol (\(L_4\)H) used towards extension of the \([M(\text{II})_7]\) double-bowl metallodicalix[6]arene framework.

To this end the heptanuclear complex \([\text{Co(II)}_7\text{(OMe)}_4\text{(OEt)}_2\text{(L}_4\text{)}_6\text{(NO}_3\text{)}_2\) (19) was isolated via the reaction of \(\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\) with \(L_4\)H and \(\text{NaOH}\) in methanol. Complex 19 crystallises as purple-brown plates in the monoclinic C2/c space group and complete X-ray structural details for 19 are given in Table 12 (Section 3.7). Similar to previously described \([M(\text{II})_7]\) systems, the asymmetric unit of 19 comprises four Co(II) ions (Co1-Co4) (oxidation states of which were confirmed via BVS and charge-balancing analyses). Three of the Co(II) ions
(Co2-Co4) have ligating L₄⁻ ligands which chelate in the familiar η¹⁻η²⁻η¹⁻μ fashion via the methoxide-oxygen, phenolate and imino-nitrogen atom sites respectively, which affords a double-bowl topology to the [Co(II)₇] system (Figure 132). Complex 19 exhibits bowl dimensions which exceed those of its siblings [Co(II)₇(OH)₆(L₁)₆](NO₃)₂ (7) and [(MeOH)₂Co(II)₇(OH)₆(L₁)₆](NO₃)₂ (8) (Chapter Two): (base x depth x rim diameter, in Å 6.27 x 4.01 x 12.32 (7) vs. 6.25 x 7.13 x 18.0 (19)), a feature which highlights the influence that functionalisation has on the topology of the [M(II)₇] framework. It was not possible to isolate crystals of L₄H suitable for X-ray analysis and therefore it was only during isolation of 19 that we observed the considerable out-of-plane bend associated with the Ph-group (4-position) on the phenol ring of L₄⁻: (torsion angle = C3-C4-C5-C6 = 23.10°). The core topology of 19 differs to that of complexes 7-8, specifically MeO⁻ groups (from the solvent media) have replaced the μ₃-OH⁻ species which lined the core of complexes 7-8 (Co1-O2(Me) = 2.092 Å, Co4-O2(Me) = 2.170 Å, Co3-O2(Me) = 2.025 Å) (Figure 133). Additionally the μ₃-junction which bridges Co1, Co2 and Co4 (and s.e.) possesses an EtO⁻ moiety in place of MeO⁻, possibly arising as a result of trace amounts of EtOH in the MeOH solvent utilised in its production (Co1-O3(Et) = 2.088 Å, Co4-O3(Et) = 2.032 Å, Co2-O3(Et) = 2.181 Å). These types of observations are common in order to fill the void space within crystal systems.

Fig. 132 Crystal structure of 19 as viewed perpendicular (left) and parallel (right) to the planar [Co(II)₇] core. Colour code: Co = purple, O = red, N = blue, C = grey. Hydrogen atoms have been omitted for clarity.
Fig. 133 Crystal structure of 19 highlighting the [Co(II)$_7$] core which possesses bridging $\mu$-OMe and $\mu_3$-OEt groups. Colour code: as in Figure 132. Hydrogen atoms have been omitted for clarity.

The crystal packing arrangement in 9 is considerably different to those of its [M(II)$_7$] siblings 7-8 (Chapter Two), being more akin to that observed in the mixed-valence [Co(III)$_1$Co(II)$_6$] complexes 9-10. Looking down the $c$-axis of the unit cell in 19, each [Co(II)$_7$] unit is oriented diagonally with respect to the $bc$-plane with each [Co(II)$_7$] pair off-set against one another (Figure 134). The crystal packing arrangement in 19 is facilitated by multiple intermolecular C-H···π interactions between the Ph-groups at the upper-rim positions of the pseudo calix[6]arene of neighbouring [Co(II)$_7$] units: C38'(H38')···C18 = 2.800 Å. The result is that there are no molecular capsules observed for this complex. Instead, interdigitation of the [Co(II)$_7$] units is observed, with ligand moieties from pairs of heptanuclear units penetrating into a third [Co(II)$_7$] assembly via edge-to-face $\pi$···$\pi$ stacking and C-H···π interactions between the Ph-groups of the L$_4$H ligands in each pair. Specifically, two ligand Ph-groups (one from each independent [Co(II)$_7$] unit) penetrates into a third [Co(II)$_7$] assembly (C25···C38' = 3.965 Å, C38'(H38')···C18 = 2.800 Å) (Figure 134). Finally unlike in the mixed-valence [Co(III)$_1$Co(II)$_6$] complexes 9-10 (isolated using L$_3$H), the docking of NO$_3^-$ counter anions within each double-bowl unit is not observed here and instead are located at the periphery of the [Co(II)$_7$] molecules.
Fig. 134 (left) Interdigitation of the individual [Co(II)$_7$] units in 19 facilitated via π···π stacking interactions between ligand moieties on pairs of [Co(II)$_7$] units (yellow and purple units) and a third [Co(II)$_7$] assembly (red unit). (right) Polyhedral representation of the packing in 19 as viewed along the c-axis. Hydrogen atoms have been omitted for clarity.

Attempts at encapsulating amino acids (e.g. tyrosine and β-alanine) as well as Buckminsterfullerene (C$_{60}$) (stemming from the spherical nature and complementary ~ 11 Å diameter of C$_{60}$ with respect to the bowl dimensions exhibited by 19 (rim diameter = 18 Å)), within the extended double-bowl units of 19 were unsuccessful. It was hoped that C$_{60}$ and the aforementioned amino acids would sit into the approximately spherical molecular cavity of 19 and template pairs of [Co(II)$_7$] units. Indeed, all such attempts at their encapsulation simply resulted in recrystallisation of the empty [Co(II)$_7$] species [Co(II)$_7$(OMe)$_4$(OEt)$_2$(L$_4$)$_6$](NO$_3$)$_2$ (19). Analogues to complex 19 have also been obtained in the form of the [Ni(II)$_7$] and [Zn(II)$_7$] analogues [Ni(II)$_7$(OMe)$_4$(OEt)$_2$(L$_4$)$_6$](NO$_3$)$_2$ (20) and [Zn(II)$_7$(OMe)$_4$(OEt)$_2$(L$_4$)$_6$](NO$_3$)$_2$ (21). Complexes 20-21 are isolated via a similar synthetic route to that of 19 (see Section 3.7 for details) and both crystallise in the monoclinic P2$_1$/n space group (with analogous packing arrangements) as green and pale yellow blocks, respectively. Despite numerous data collections, however, the crystals of 20-21 still gave extensive disorder in their structures; thus pictorial representations of the complexes have not been given here.
3.5 Isolation of Homo- and Hetero-valent 3d Systems via Modification of the \([M(II)_7]\) Synthesis

Chapter Two described the mixed-metal complexes \([\text{Co}(\text{III})_2\text{Na(I)}_1(\text{L}_2)_6](\text{BF}_4)\) (11) and \([\text{Co}(\text{III})_3\text{Na(I)}_3(\text{L}_1)_6(\text{N}_3)_6]_n\) (12), whose isolation demonstrated how a modest change to reaction conditions / reagents can have a pronounced impact on the topology of the resultant complex. To this end, we postulated that replacing the base used in the production of 19-21 with a ‘softer’ base (such as replacing NaOH with NaOMe) may afford the traditional crystal packing arrangement of previously discussed [Co(II)\(_7\)] systems and hence molecular cavities allowing guest encapsulation. In addition, it was thought that adding more MeO\(^-\) (via NaOMe) may encourage \(\mu_3\)-OME bridging at all three-fold symmetry sites which line the complex core. To our surprise however, reaction of \(\text{Co(NO}_3\text{)}_2.6\text{H}_2\text{O}\) with \(\text{L}_4\text{H}\) and NaOMe yielded the mononuclear complex \([\text{Co}(\text{III})_1(\text{L}_4)_3]\) (22) (Figure 135). Complex 22 is isolated as purple-brown blocks which crystallise in the triclinic space group \(P-1\). Complete X-ray structural details for 22 are given in Table 12 (Section 3.7). The complex comprises a central Co(III) ion to which three singly deprotonated \(\text{L}_4^-\) ligands coordinate in a chelating manner via O\(_{\text{phen}}\) (O2) and imino-nitrogen (N2) atom sites, respectively (O\(_{\text{phen}}\)···Co1 = 1.88-1.89 Å, N2-Co1 = 1.91-1.94 Å). There are no intra- or intermolecular H-bonding interactions observed for 22, rather the crystal packing is afforded as a result of long C-H···O contacts between imine C-H protons and Me-O groups of neighbouring mononuclear units: (N2=C29)H29···O1 = 2.716 Å. It is quite remarkable how the simple replacement of NaOH with NaOMe in the reaction of Co(II) with \(\text{L}_4\text{H}\) could reduce the nuclearity of the system from seven to one, an observation which again highlights the sensitivity of the crystallisation process in inorganic chemistry.
In attempts to further elucidate whether the crystal packing arrangement in 19 could be altered, the empty host complex 19 (described above) was dissolved in toluene at ~100 °C. It was hoped that the toluene molecules would template pairs of [Co(II)₇] units to afford crystal packing akin to complexes 1-8 (Chapter Two). However the result was the entirely new, mixed-valent dinuclear complex [Co(III)₂Co(II)₂(L₄)₃(NO₃)₂].H₂O (23), afforded as rhomb-like blocks which crystallise in the triclinic P-1 space group. Complete X-ray structural details for 23 are given in Table 12 (Section 3.7). Complex 23 consists of two distinct Co centres. Two L₄⁻ ligands bridge Co1 (Co(III)) and Co2 (Co(II)) via η¹:η²:η²⁻μ and η¹:η²⁻μ bonding modes, respectively (Co1-O2 = 1.904 Å, Co2-O10 = 2.150 Å) (Figure 136). Coordination to Co2 is completed by two NO₃⁻ anions (O3-Co2 = 2.101 Å, O4-Co2 = 2.157 Å). It is interesting to note that, similar to the [Co(II)₇] complex [Co(II)₇(OMe)₄(OEt)₂(L₄)₆](NO₃)₂ (19), the Ph-group at the 4-positions of the phenol rings are non-planar with respect to the phenol ring, a feature which highlights the complex’s efforts to minimise strain in the system (which would exist if the Ph / PhO⁻ groups were co-planar). The third L₄⁻ ligand coordinates solely to the Co(III) metal centre (Co1) and does so via an η¹⁻ bonding mode (Co1-N5 = 1.946 Å, Co1-O11 = 1.870 Å). In terms of intermolecular connectivity, long C-H…O contacts exist between imine C-H protons of one molecule and the coordinated NO₃⁻ group of a neighbouring dimeric unit ((N₅-C₄₄)H₄₄…O3 = 2.531 Å) (Figure 136). The molecules in 23 pack in interlocking rows, which propagate along the c-axis, facilitated by face-to-face π…π stacking interactions between neighbouring
[Co(III)$_3$Co(II)$_3$] units (π···π = 3.70 Å). These π···π stacking interactions are readily identified along the $b$-axis of the unit cell of 23 (Figure 137).

**Fig. 136** Crystal structure of the dinuclear complex [Co(III)$_3$Co(II)$_3$(L)$_3$(NO$_3$)$_2$].H$_2$O (23). Colour code: Co = purple, O = red, N = blue, C = grey. Hydrogen atoms have been omitted for clarity.

**Fig. 137** Crystal packing illustration of 23 as viewed along the $a$-axis of the unit cell. Colour code as in Figure 136. Hydrogen atoms have been omitted for clarity.
3.6 Concluding Remarks

This chapter has described the expansion of our family of double-bowl pseudo metallocalix[6]arene discs with the isolation of the furaldehyde encapsulated species 14-18 of general formulae [(Fur)⊂M(II)⊂(OH)6(L-1)6](NO3)2 (Fur = 2- or 3-Furaldehyde and M = Ni, Co or Zn) (14 and 16-18) and [(2-Fur)⊂Zn(II)⊂(OMe)6(L-1)6](NO3)2 (15). Infrared and EPR spectroscopic measurements were employed to confirm guest furaldehyde presence. Moreover, EPR spectroscopy was utilised to identify acyl radical generation (originating from the guest) within the double-bowl cavities present in complex [(2-Fur)⊂Zn(II)⊂(OH)6(L-1)6](NO3)2 (14). Future work in this area will concentrate on measuring EPR data at various frequencies (i.e. X- and Q-band) on our analogous radical host complexes [(2-fur)⊂Zn(II)⊂(OMe)6(L-1)6](NO3)2 (15) and [(3-fur)⊂Ni(II)⊂(OMe)6(L-1)6](NO3)2 (16). Furthermore, in order to further probe the radical generation and storage of our 2- and 3-Furaldehyde guests (complexes 14-18), in situ photolysis EPR measurements will be carried out at the University of Manchester, using a 350 nm optical probe. This wavelength of light is known to promote homolytic cleavage of such guests to form σ-type radicals.

Furthermore we proposed that a cavity wall extension may be effected within our double-bowl complexes via functionalisation of the Schiff base ligand utilised. To this end, we were successful in the isolation of the heptanuclear species of general formulae [M(II)⊂(OMe)4(OEt)2(L-4)6](NO3)2 (M = Co (19), Ni (20), Zn (21) and L-4 = deprotonated L-4H Schiff base ligand). Though complexes 19-21 exhibited bowl dimensions which exceeded those of its siblings [Co(II)⊂(OH)6(L-1)6](NO3)2 (7) and [(MeOH)2⊂Co(II)⊂(OH)6(L-1)6](NO3)2 (8) (Chapter Two), molecular cavity formation was not observed in 19-21. Molecular cavity generation relies on the ability of [M(II)⊂] units to rest one on top of the other or, as observed in the study of the functionalised [Ni(II)⊂] complex 4, in their ability to interlock one another (Chapter Two). Due to the out-of-plane bending associated with the Ph-functionalised sites in 19-21, such stacking is likely to be impracticable in these particular systems. Indeed the drive for the complex to achieve a state of reduced strain by means of this out-of-plane puckering likely overcomes any potential C-H...π / π...π interactions towards molecular cavity formation.
3.7 Experimental

3.7.1 Instrumentation

Instrumentation utilised in analyses of complexes 14-23 are as detailed in Chapter Two (Section 2.5.1).

3.7.1.1 X-ray Diffraction

The crystallographic technique SQUEEZE was used to model / detect guest presence in complexes 14-18. Due to the large disorder present in the crystal structures of complexes 20 and 21, the structures (and corresponding CIF files) for these complexes are not included here and will be completed at a later date. All other Crystallographic Information Files (CIFs) are located on a writeable CD, included at the end of this thesis.

3.7.1.2 Electron Paramagnetic Resonance (EPR) Spectroscopy

All Electron Paramagnetic Resonance (EPR) studies detailed in this chapter were carried out at the EPSRC National EPR Center situated at the Photon Science Institute, University of Manchester, UK. The EPR spectra obtained on complexes 14 and 17 were collected on a continuous wave Bruker EMX Micro X-band spectrometer comprising a 1.0 T electromagnet.

3.7.2 Synthetic Procedures

Unless otherwise stated all materials (solvents and reagents) were purchased commercially and used as supplied without further purification. Caution: Although no difficulties were encountered in this work, great care must be taken when working with the potentially explosive nitrate, azide and perchlorate salts..

3.7.2.1 Synthesis of 5-phenyl-2-hydroxy-3-methoxybenzaldehyde

The first step in the synthesis of the Schiff base ligand 4-phenyl-2-iminomethyl-6-methoxyphenol (L4H) involves the synthesis of 5-phenyl-2-hydroxy-3-methoxybenzaldehyde (Scheme 3.1) from its Br-precursor (5-bromo-2-hydroxy-3-methoxybenzaldehyde) via a Suzuki coupling reaction. The synthesis is a modification of a literature procedure. The reaction was performed under a N2 atmosphere and the reaction solvent (Millipore H2O) was degassed via the freeze-pump-thaw technique.
Scheme 3.1 Reaction scheme for the synthesis of 5-phenyl-2-hydroxy-3-methoxybenzaldehyde.

To a solid mixture of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (2.30 g, 9.95 mmol, 1.0 eq.), phenylboronic acid (1.58 g, 12.92 mmol, 1.30 eq.) and finely ground potassium carbonate (K₂CO₃) (13.75 g, 99.5 mmol, 10 eq.) in a 3-neck round-bottomed flask (250 cm³), was added palladium acetate (0.50 g, 2.23 mmol, ~20 mol %) via a solid-addition ‘fish-hook’ adapter. Degassed millipore H₂O (~150 cm³) was then added via cannula to the now evacuated reaction vessel (Scheme 3.1). The resultant dirty yellow suspension was stirred under high agitation to afford maximum dissolution of the solid reactants. After 4 hours stirring the suspension had adopted a brown appearance and was stirred for a further 2 days under N₂. The pH of the mixture was subsequently adjusted (pH = 7 using 6M HCl). Dichloromethane (CH₂Cl₂) (50 cm³) was added and the mixture stirred for ~5 minutes. Two distinct phases were observed with the organic phase exhibiting a very dark red-brown appearance. The mixture was filtered over Celite to remove the palladium catalyst and the mother liquor transferred to a 500 cm³ separation funnel. The organic layer was extracted with CH₂Cl₂ (3 x 50 cm³) as an opaque red-orange solution. The aqueous layer was separated off as a sludge-like residue. The organic phase was further filtered over Celite to yield a transparent red mother liquor which was evaporated in vacuo. Dichloromethane (~50 cm³) was then added to the resultant oil and the solution pre-adsorbed onto a small quantity of silica gel. The product was purified via Dry-Column-Vacuum-Chromatography using an 80:20 CH₂Cl₂: Petroleum Ether solvent system, while the separation itself was monitored via TLC. The resultant bright yellow transparent solution was evaporated in vacuo to yield a bright yellow solid (5-phenyl-2-hydroxy-3-methoxybenzaldehyde) in 74 % yield (1.68 g).
C, H, N Elemental Analysis

Calculated for: C_{14}H_{12}O_3

Theory (%): C (73.65), H (5.30).

Found (%): C (73.73), H (5.17).

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

1644 (s), 1591 (m), 1471 (m), 1456 (w), 1443 (s), 1390 (m), 1323 (m), 1297 (m), 1273 (s), 1231 (m), 1202 (s), 1184 (m), 1103 (m), 1069 (m), 963 (s), 887 (m), 870 (m), 765 (s), 746 (m), 722 (s), 696 (s).

3.7.2.2 Synthesis of 4-phenyl-2-iminomethyl-6-methoxyphenol ($L_4H$)

The second step in the synthesis of $L_4H$ involves the Schiff base condensation reaction of 5-phenyl-2-hydroxy-3-methoxybenzaldehyde (Synthesis 3.7.2.1 above) with methylamine (MeNH$_2$).

![Scheme 3.2 Reaction scheme for the synthesis of 4-phenyl-2-iminomethyl-6-methoxyphenol ($L_4H$).](image)

5-phenyl-2-hydroxy-3-methoxybenzaldehyde (1.68 g, 7.37 mmol, 1.0 eq.) was dissolved in CH$_2$Cl$_2$ (40 cm$^3$). MeNH$_2$ (0.229 g, 7.37 mmol, 1.0 eq.) was then added resulting in the precipitation of a yellow solid. EtOH (40 cm$^3$) and MeOH (10 cm$^3$) were added to the mixture resulting in dissolution of the solid material and formation of a bright yellow-orange solution. This solution was subsequently stirred for a further 24 hours under ambient
conditions after which time the solvent was evaporated in vacuo to yield a dark red-orange, viscous oil. This oil was dissolved in Et$_2$O (40 cm$^3$) to yield a bright orange solution. This was then placed in the fridge at ~4°C for 48 hours after which time L$_4$H recrystallised as bright yellow needles in 80 % yield (1.42 g).

$C, H, N$ Elemental Analysis

Calculated for: C$_{15}$H$_{15}$N$_1$O$_2$

Theory (%): C (74.68), H (6.22), N (5.81).

Found (%): C (74.34), H (6.47), N (5.23).

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

1630 (m), 1596 (w), 1463 (m), 1441 (m), 1397 (m), 1271 (m), 1229 (w), 1208 (s), 1190 (m), 1104 (m), 1070 (m), 1005 (w), 969 (m), 853 (m), 779 (m), 758 (m), 716 (m), 696 (s).

$^1$H NMR (500 MHz, CDCl$_3$) (Spectrum shown in Figure 138)

δ 3.51 (s, 3H, N-CH$_3$), 3.97 (s, 3H, O-CH$_3$), 7.07-7.55 (m, 7H, Ar-H), 8.36 (s, 1H, N=CH).

$^{13}$C NMR (400 MHz, CDCl$_3$)

δ 166.37 (N=CH), 128.89 (C-OH), 126.92, 126.74, 121.16, 112.89 (Ar-H), 56.27 (CH$_3$-O), 45.57 (CH$_3$-N).

Melting Point (MP) Range

128.6-129.6 °C
**Fig. 138** $^1$H NMR spectrum (in CDCl$_3$) of 4-phenyl-2-iminomethyl-6-methoxyphenol (L$_4$H).

**UV/vis Analysis (Spectra shown in Figure 139)**

MeOH: $\lambda_{\text{max}}$ [nm] ($\varepsilon_{\text{max}}$ $10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$): 224 (6980), 273 (13113), 434 (1346)

MeCN: $\lambda_{\text{max}}$ [nm] ($\varepsilon_{\text{max}}$ $10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$): 208 (6828), 256 (12203), 339 (1128).
Fig. 139 UV-vis spectra obtained from MeOH (top) and MeCN (bottom) solutions of \( \text{L}_4\text{H} \).

3.7.2.3 Synthesis of \([\text{2-Fur})\text{Zn(II)}_7\text{OH}_6\text{(L}_1\text{)}_6\text{}\text{(NO}_3\text{)}_2\) (14)

To a stirring solution of \( \text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) (0.25 g, 0.842 mmol, 1.0 eq.) in EtOH (25 cm\(^3\)) was added \( \text{L}_1\text{H} \) (0.139 g, 0.842 mmol, 1.0 eq.) and the solution stirred further to afford complete dissolution of the solid material. Solid NaOH (0.034 g, 0.842 mmol, 1.0 eq.) was then added without pronounced colour change. 2-Furaldehyde (0.700 cm\(^3\), 10 eq.) was then added resulting in an opaque yellow-orange solution, which was stirred for a further 3 hours. The solution was then filtered affording a dark yellow transparent mother liquor from which dark yellow-orange blocks of 14 were harvested directly after \( \text{}\text{}\text{}\) month in low yield (10 %).

\textit{C, H, N Elemental Analysis}

Calculated for: \( \text{C}_{59}\text{H}_{70}\text{N}_8\text{O}_{26}\text{Zn}_7 \)

Theory (%): C (40.36), H (4.02), N (6.38)

Found (%): C (40.68), H (4.57), N (5.90)

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

1669 (m), 1636 (m), 1601 (w), 1559 (w), 1459 (m), 1436 (w), 1408 (w), 1338 (m), 1312 (m), 1240 (m), 1211 (s), 1174 (w), 1149 (w), 1092 (w), 1075 (m), 1015 (m), 745 (s).
### 3.7.2.4 Synthesis of [(2-Fur)\(\overset{\gamma}{\subset}\)Zn(II)\(\gamma\)(OME)\(_6\)(L\(_1\))\(_6\)](NO\(_3\))\(_2\) (15)

To a solution of Zn(NO\(_3\))\(_2\).6H\(_2\)O (0.25 g, 0.842 mmol, 1.0 eq.) in MeOH (25 cm\(^3\)) was added L\(_1\)H (0.139 g, 0.842 mmol, 1.0 eq.) and solid NaOH (0.034 g, 0.842 mmol, 1.0 eq.). The resultant solution was stirred under ambient conditions to afford complete dissolution of the solid reactants. 2-Furaldehyde (0.81 g, 0.842 mmol, 10.0 eq.) was then added affording an opaque yellow-orange solution which was stirred for a further 3 hours. The solution was subsequently filtered to afford a transparent dark yellow mother liquor, which was allowed to concentrate via slow solvent evaporation. Light orange hexagonal blocks of 15 were harvested directly from the mother liquor after one week in ~18 % yield.

**C, H, N Elemental Analysis:**

Calculated for: C\(_{65}\)H\(_{82}\)N\(_8\)O\(_{26}\)Zn\(_7\)

Theory (%): C (42.43), H (4.49), N (6.09)

Found (%): C (41.80), H (4.10), N (5.65)

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

3419 (b), 1636 (s), 1602 (m), 1560 (w), 1458 (s), 1435 (m), 1408 (m), 1335 (s), 1309 (s), 1240 (m), 1221 (s), 1174 (w), 1148 (w), 1092 (m), 1076 (m), 1013 (s), 967 (m), 860 (m), 791 (m), 744 (s).

### 3.7.2.5 Synthesis of [(3-Fur)\(\overset{\gamma}{\subset}\)Ni(II)\(\gamma\)(OH)\(_6\)(L\(_1\))\(_6\)](NO\(_3\))\(_2\) (16)

To a 25 cm\(^3\) ethanolic solution of Ni(NO\(_3\))\(_2\).6H\(_2\)O (0.25 g, 0.859 mmol, 1.0 eq.) in a Teflon microwave reaction vessel was added L\(_1\)H (0.142 g, 0.859 mmol, 1.0 eq.) and solid NaOH (0.034 g, 0.859 mmol, 1.0 eq.). The mixture was then stirred to afford complete dissolution of the solid reactants. 3-Furaldehyde (0.83 g, 8.59 mmol, 10.0 eq.) was then added neat and the solution stirred under microwave conditions (110 °C, 110 psi, 200 W, 10 mins). The resultant golden-green solution was allowed to cool and then filtered to afford a similarly-coloured mother liquor. Et\(_2\)O was allowed to slowly diffuse into samples of the mother liquor which ultimately yielded green hair-like crystals of 16 after 1 month in ~12 % yield.

**C, H, N Elemental Analysis**

Calculated for: C\(_{59}\)H\(_{70}\)N\(_8\)O\(_{26}\)Ni\(_7\)
Theory (%): C (40.15), H (4.12), N (6.54)

Found (%): C (40.68), H (3.78), N (6.82)

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

1679 (m), 1627 (s), 1603 (w), 1549 (w), 1460 (m), 1403 (s), 1336 (s), 1315 (s), 1240 (m), 1224 (s), 1210 (s), 1170 (m), 1154 (m), 1089 (m), 1072 (m), 1017 (m), 957 (m), 871 (m), 792 (m), 740 (s), 727 (m).

### 3.7.2.6 Synthesis of [(2-Fur)\(\subset\)Co(II)\(_7\)(OH)\(_6\)(L\(_1\))\(_6\)](NO\(_3\))\(_2\) (17)

A mixture of Co(NO\(_3\))\(_2\).6H\(_2\)O (0.25 g, 0.859 mmol, 1.0 eq.) and L\(_1\)H (0.142 g, 0.859 mmol, 1.0 eq.) were stirred in EtOH (25 cm\(^3\)) until complete dissolution of solid material was achieved. NaOH (0.034 g, 0.859 mmol, 1.0 eq.) was then added effecting a colour change from purple-red to dark red-brown. 2-Furaldehyde (0.715 cm\(^3\), 10 eq.) was then added and the red-brown opaque solution stirred for a further 4 hours following which it was filtered to afford a transparent, purple-brown mother liquor. Purple-brown blocks of 17 were harvested both from the mother liquor and Et\(_2\)O diffused samples of the mother liquor with a combined yield of 22% after 2 weeks.

**C, H, N Elemental Analysis**

Calculated for: C\(_{59}\)H\(_{70}\)N\(_8\)O\(_{26}\)Co\(_7\)

Theory (%): C (41.18), H (4.10), N (6.51)

Found (%): C (41.68), H (3.78), N (6.27)

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

1671 (m), 1629 (m), 1602 (w), 1560 (w), 1474 (m), 1459 (m), 1436 (m), 1339 (m), 1306 (m), 1240 (m), 1221 (s), 1090 (m), 1076 (m), 1015 (m), 964 (m), 860 (m), 788 (m), 744 (s).

### 3.7.2.7 Synthesis of [(3-Fur)\(\subset\)Co(II)\(_7\)(OH)\(_6\)(L\(_1\))\(_6\)](NO\(_3\))\(_2\) (18)

A solution of Co(NO\(_3\))\(_2\).6H\(_2\)O (0.25 g, 0.859 mmol, 1.0 eq.) and L\(_1\)H (0.142 g, 0.859 mmol, 1.0 eq.) were stirred in EtOH (25 cm\(^3\)) and placed in a glass-lined microwave reaction vessel, adopting a purple-red colour in the process. Solid NaOH (0.034 g, 0.859 mmol, 1.0 eq.) and
3-Furaldehyde (3-Fur) (0.83 g / 0.74 cm$^3$, 10 eq.) were then added neat and the system isolated from its surroundings by capping with a Teflon seal. The solution was heated under microwave conditions (110°C, 110 psi, 200 W, 20 mins) affording a dark, red-brown solution, which was filtered to afford a similarly-coloured mother liquor. Et$_2$O diffusion of the mother liquor afforded purple-brown blocks of 18 after 1 week which were harvested with a combined yield of ~10%.

**C, H, N Elemental Analysis**

Calculated for: C$_{59}$H$_{70}$N$_8$O$_{26}$Co$_7$

Theory (%): C (41.18), H (4.10), N (6.51)

Found (%): C (41.53), H (4.58), N (6.93)

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

1678 (m), 1632 (s), 1601 (m), 1459 (s), 1436 (m), 1407 (m), 1345 (s), 1306 (s), 1239 (m), 1221 (s), 1171 (m), 1149 (m), 1089 (m), 1078 (s), 1011 (m), 968 (m), 858 (m), 796 (m), 744 (s).

### 3.7.2.8 Synthesis of [Co(II)$_7$(OMe)$_4$(OEt)$_2$(L$_4$)$_6$](NO$_3$)$_2$ (19)

A solution of Co(NO$_3$)$_2$.6H$_2$O (0.10 g, 0.344 mmol, 1.0 eq.) in MeOH (25 cm$^3$) was mixed with L$_4$H (0.083 g, 0.344 mmol, 1.0 eq.) affording a dark purple-brown solution. NaOH (0.014 g, 0.344 mmol, 1.0 eq.) was then added affording a much darker-coloured solution. The mixture was then stirred for a further 6 hours and subsequently filtered to afford a transparent purple-brown mother liquor, which was allowed to slowly concentrate via slow solvent evaporation. Purple-brown plate-like crystals of 19 were harvested directly from the mother liquor after 6 days in 16%.

**C, H, N Elemental Analysis**

Calculated for: C$_{98}$H$_{106}$N$_8$O$_{25}$Co$_7$

Theory (%): C (53.27), H (4.83), N (5.07).

Found (%): C (53.21), H (4.75), N (4.98).
Infrared Spectroscopy ($cm^{-1}$)

3417 (b), 1627 (s), 1560 (w), 1460 (s), 1393 (s), 1311 (s), 1267 (s), 1202 (s), 1095 (m), 1032 (s), 966 (s), 865 (m), 804 (s), 765 (s), 757 (s), 724 (m), 697 (m).

3.7.2.9 Synthesis of [Ni(II)$_7$(OMe)$_4$(OEt)$_2$(L$_4$)$_6$](NO$_3$)$_2$ (20)

To a solution of Ni(NO$_3$)$_2$.6H$_2$O (0.10 g, 0.343 mmol, 1.0 eq.) in MeOH (20 cm$^3$) were added L$_4$H (0.083 g, 0.343 mmol, 1.0 eq.) and solid NaOH (0.014 g, 0.343 mmol, 1.0 eq.) and the mixture stirred to afford an opaque bright green solution. The solution was stirred for a further 3 hours, following which it was filtered to afford a bright green mother liquor. The mother liquor was diffused with Et$_2$O which afforded green needles of 20 in low yield (5 %).

C, H, N Elemental Analysis

Calculated for: C$_{98}$H$_{106}$N$_8$O$_{25}$Ni$_7$

Theory (%): C (53.44), H (4.85), N (5.09)

Found (%): C (53.2), H (4.38), N (5.49)

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

3395 (b), 1639 (s), 1548 (w), 1472 (s), 1393 (s), 1312 (s), 1258 (s), 1207 (s), 1095 (s), 848 (m), 837 (w), 825 (w), 760 (s), 720 (s).

3.7.2.10 Synthesis of [Zn(II)$_7$(OMe)$_4$(OEt)$_2$(L$_4$)$_6$](NO$_3$)$_2$ (21)

A solution of Zn(NO$_3$)$_2$.6H$_2$O (0.10 g, 0.33 mmol, 1.0 eq.) in MeOH (20 cm$^3$) was mixed with L$_4$H (0.081 g, 0.33 mmol, 1.0 eq.) and solid NaOH (0.013 g, 0.33 mmol, 1.0 eq.) and the mixture stirred to afford complete dissolution of the solids. The resultant yellow solution was stirred for a further 3 hours, after which time it was filtered to afford a bright yellow mother liquor. The mother liquor was allowed to slowly concentrate via slow evaporation of the solvent to yield 21 as pale yellow blocks in low yield (8 %).

C, H, N Elemental Analysis

Calculated for: C$_{98}$H$_{106}$N$_8$O$_{25}$Zn$_7$

Theory (%): C (52.44), H (4.76), N (4.99)
Infrared Spectroscopy \((cm^{-1})\)

3390 (b), 2932 (b), 1631 (s), 1599 (m), 1476 (s), 1458 (s), 1398 (m), 1313 (s), 1268 (s), 1203 (s), 1100 (m), 1073 (w), 970 (m), 862 (m), 803 (m), 759 (s), 724 (m), 697 (m).

3.7.2.11 Synthesis of \([\text{Co(III)}_1\text{(L}_4)_3] (22)\)

To a stirring solution of \(\text{Co(NO}_3)_2\cdot6\text{H}_2\text{O} (0.10 \text{ g}, 0.344 \text{ mmol, 1.0 eq.})\) in MeOH (15 cm \(^3\)) was added \(\text{L}_4\text{H} (0.083 \text{ g}, 0.344 \text{ mmol, 1.0 eq.})\) and \(\text{NaOMe} (0.019 \text{ g}, 0.344 \text{ mmol, 1.0 eq.})\). The solution was stirred for 15 minutes, after which time it had adopted a dark red-brown transparent appearance. The solution was stirred for a further 3 hours and then filtered to yield a red-brown mother liquor. Dark purple-brown blocks of 22 were isolated directly from the mother liquor after 1 week of slow solvent evaporation in low yield (5 %).

\(\text{C, H, N Elemental Analysis}\)

Calculated for: \(\text{C}_{45}\text{H}_{42}\text{N}_3\text{O}_6\text{Co}_1\)

Theory (%): C (69.29), H (5.43), N (5.39).

Found (%): C (68.90), H (5.29), N (4.90).

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

1626 (s), 1598 (m), 1537 (w), 1450 (s), 1318 (s), 1271 (s), 1205 (s), 1103 (m), 1082 (m), 1058 (m), 1024 (m), 982 (m), 973 (w), 894 (m), 879 (m), 795 (m), 757 (s), 718 (m), 694 (s).

3.7.2.12 Synthesis of \([\text{Co(III)}_1\text{Co(II)}_1\text{(L}_4)_3(\text{NO}_3)_2]\cdot\text{H}_2\text{O} (23)\)

To a transparent purple solution of \(\text{Co(NO}_3)_2\cdot6\text{H}_2\text{O} (0.10 \text{ g}, 0.344 \text{ mmol, 1.0 eq.})\) in MeOH (20 cm \(^3\)) was added \(\text{L}_4\text{H} (0.083 \text{ g}, 0.344 \text{ mmol, 1.0 eq.})\) and solid \(\text{NaOH} (0.014 \text{ g}, 0.344 \text{ mmol, 1.0 eq.})\) and the mixture stirred to afford complete dissolution of the solid reactants. The solution was stirred for a further 4 hours and then filtered to afford a red-brown mother liquor. The mother liquor was allowed to concentrate via slow solvent evaporation in attempts to induce crystallisation. However, following lack of crystallisation from the MeOH mother liquor, the fully-evaporated crystallisation residue was redissolved in Toluene (in attempts to afford guest inclusion); facilitated by heating the mixture at ~90-100 °C.
Filtration of this solution, after cooling, afforded a very dark red-brown mother liquor from which samples were Et₂O diffused to afford rhombic-like blocks of 23 in moderate yield (15%).

_C, H, N Elemental Analysis_

Calculated for: C₄₅H₄₂N₅O₁₃Co₂

Theory (%): C (55.20), H (4.32), N (7.15).

Found (%): C (54.85), H (4.01), N (7.04).

_Infrared Spectroscopy (cm⁻¹)_

1627 (m), 1559 (m), 1536 (w), 1469 (m), 1450 (s), 1410 (w), 1321 (m), 1271 (s), 1205 (s), 1176 (m), 1080 (m), 1057 (m), 1019 (m), 977 (m), 761 (s), 736 (m), 718 (m), 695 (s).

**Table 10** Void and electron count values for complexes 14-18 accommodating 2-Furaldehyde and 3-Furaldehyde guests. The electron counts confirm the presence of one Furaldehyde molecule.

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<th>Complex / Bowl</th>
<th>Void</th>
<th>Electron Count</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="NO%E2%82%83">(2-Fur)⊂Zn(II)₇(OH)₆(L₁)₂</a>₂ (14)</td>
<td>403</td>
<td>85</td>
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<tr>
<td><a href="NO%E2%82%83">(2-Fur)⊂Zn(II)₇(OMe)₆(L₁)₂</a>₂ (15)</td>
<td>403</td>
<td>85</td>
</tr>
<tr>
<td><a href="NO%E2%82%83">(3-Fur)⊂Ni(II)₇(OH)₆(L₁)₂</a>₂ (16)</td>
<td>481</td>
<td>82</td>
</tr>
<tr>
<td><a href="NO%E2%82%83">(2-Fur)⊂Co(II)₇(OH)₆(L₁)₂</a>₂ (17)</td>
<td>477</td>
<td>83</td>
</tr>
<tr>
<td><a href="NO%E2%82%83">(3-Fur)⊂Co(II)₇(OH)₆(L₁)₂</a>₂ (18)</td>
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<td>98</td>
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Tables of Crystallographic Data
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<td>Mₐ (g mol⁻¹)</td>
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<td>14.064(2)</td>
<td>13.8183(5)</td>
<td>14.100(2)</td>
<td>14.098(2)</td>
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<tr>
<td>b / Å</td>
<td>13.928(2)</td>
<td>14.064(2)</td>
<td>13.8183(5)</td>
<td>14.100(2)</td>
<td>14.098(2)</td>
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<td>23.056(5)</td>
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<tr>
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<td>3908.7(11)</td>
<td>3909.5(11)</td>
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</tr>
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<td>150.1</td>
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<td>D² / g cm⁻³</td>
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<td>1.474</td>
<td>1.405</td>
<td>1.380</td>
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<tr>
<td>μ (Mo-Kα) / mm⁻¹</td>
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<td>2.162</td>
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<td>Meas. / Indep. (Rint) reflections</td>
<td>2388 / 1830 (0.0396)</td>
<td>2416 / 1718 (0.0598)</td>
<td>2344 / 1771 (0.0380)</td>
<td>2388 / 1897 (0.0409)</td>
<td>2388 / 1561 (0.0760)</td>
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<td>wR²</td>
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<td>1.066</td>
<td>1.178</td>
<td>1.149</td>
<td>1.188</td>
</tr>
</tbody>
</table>

*Mo-Kα radiation, graphite monochromator.  
²wR² = \[\sum w(I_F^2 - I_E^2)^2 / \sum wI_F^2I_E^2\]⁻¹/².  
³For observed data.  
⁴Ri = [\sum I^2F_0^2 - I_F^2I_E^2 / \sum I_F^2I_E^2]
### Table 12 Crystallographic data for complexes 19 and 22-23.

<table>
<thead>
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<th>Complex</th>
<th>(19)</th>
<th>(22)</th>
<th>(23)</th>
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<tbody>
<tr>
<td>Formula</td>
<td>C_{98}H_{106}N_{8}O_{25}Co_{7}</td>
<td>C_{45}H_{42}N_{3}O_{6}Co_{1}</td>
<td>C_{45}H_{42}N_{5}O_{13}Co_{2}</td>
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<td>M_{R} (g mol(^{-1}))</td>
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<td>779.75</td>
<td>978.70</td>
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<td>Purple-Brown Block</td>
<td>Purple-Brown Parallelepiped</td>
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<td>Crystal Dimensions (mm x mm x mm)</td>
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<tr>
<td>Crystal system</td>
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<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>P-I</td>
<td>P-I</td>
</tr>
<tr>
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<td>26.7878(12)</td>
<td>10.6963(8)</td>
<td>9.5986(3)</td>
</tr>
<tr>
<td>b / Å</td>
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<td>c / Å</td>
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<td>λ / Å</td>
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<td>D(^b) / g cm(^{-3})</td>
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<td>6918 / 4295 (0.0615)</td>
<td>8758 / 6031 (0.0386)</td>
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<td>wR(_{2})(^{b}) (all data)</td>
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<td>R(_{1})(^{cd}) (reflections)</td>
<td>0.0901 (6301)</td>
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<td>Goodness of fit (GOOF) on F(^{2})</td>
<td>1.077</td>
<td>1.043</td>
<td>1.071</td>
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</table>

\(^{a}\)Mo-Kα radiation, graphite monochromator. \(^{b}\)wR\(_{2}\) = \(\sum w(I_{F_0}^2 - I_{F}^2)/\sum wI_{F_0}^2\)^1/2, \(^{c}\)For observed data. \(^{d}\)R\(_{1}\) = \(\sum I^2/F_0^2 - I/F_0^2 / \sum IF_0^2\)
3.8 References


(4) Mabbs, F. E., Collison, D. *Electron Paramagnetic Resonance of Transition Metal Compounds (Studies in Inorganic Chemistry)*, Elsevier, **1992**.

Chapter Four

Mixing It Up: Exploring the Utility of Schiff Base Ligands in the Synthesis of Homo- and Heterometallic Planes, Chains and Cubanes
4.1 Introduction

Chapters Two and Three described the use of the Schiff base ligand 2-iminomethyl-6-methoxyphenol (L₁H) and its analogues (L₂H and L₃H) in the development of a family of heptanuclear, pseudo [M₇] (where M = Ni(II), Zn(II), Co(II/III)) metallocalix[6]arene disc-like complexes. As well as exhibiting interesting magnetic properties (when M = Ni(II), Co(II/III)), these complexes were also shown to exhibit solid-state host-guest characteristics with the ability to encapsulate a variety of different guest species within the double-bowl cavities formed therein.¹² In attempts to probe the feasibility of extending this family of complexes, L₁H and its analogue 2-imino-6-methoxyphenol (L₅H) (Figure 140) were combined with other first-row transition metal ions. Moreover, modification to the reaction conditions (e.g. change of solvent, base, reagent ratios etc.), previously used in the synthesis of our [M(II/III)₇] species were also executed in efforts to afford novel polynuclear architectures, perhaps themselves exhibiting interesting inclusion and / or magnetic properties. However, when such modifications to reaction conditions were performed, no systems exhibiting host-guest characteristics were isolated. Instead, we were successful in producing a wide range of polynuclear transition metal complexes exhibiting interesting structural and magnetic characteristics. These include mixed-metal [M(II/III)₂Na(I)₂] butterfly systems, tetranuclear [M₄] cubanes (where M = Ni(II), Mn(III/IV)) and 1D chain systems.

![Fig. 140 The Schiff base ligands 2-iminomethyl-6-methoxyphenol (L₁H) (left) and 2-imino-6-methoxyphenol (L₅H) (right) utilised towards extension of our previously described family of pseudo [M(II/III)₇] metallocalix[6]arene solid-state host-guest complexes.](image)
4.1.1 Exploring Mixed-Metal Systems

Homo- and heterometallic polynuclear complexes have been exploited for a variety of applications in a diverse range of fields. In the field of bio-inorganic chemistry, for example, coordination chemistry has been shown to play a vital role in gleaning a thorough understanding of the photosynthetic process; specifically in the development of heterometallic manganese complexes for use as biomimetic models for energy and electron transfer processes. A prime example of such biomimetic species is that of the proposed bimetallic [Mn₄CaO₄] cubane-like catalytic unit within photosystem II (PSII).³⁻⁷ As well as biological systems, heterometallic species have also been utilised for a variety of modern applications, not least of which being the field of molecular magnetism. One of the most widely exploited first-row transition metal ions in the development of such systems is the Mn(III) ion which is regularly utilised in the generation of Single-Molecule Magnets (SMMs)⁸,⁹ and Single-Chain Magnets,¹⁰⁻¹³ while the isotropic Mn(II) ion is regularly employed in the construction of molecular magnetic refrigerants.¹⁴,¹⁵ Increasingly, lanthanoid ions such as Gd(III), Dy(III) and Tb(III) have been incorporated into Mn(II/III/IV) and other 3d transition metal-based complexes to generate heterometallic 3d/4f systems exhibiting tuneable anisotropy of the lanthanide ions.¹⁶⁻¹⁹ Commensurate with this, alkali and alkaline earth metals of groups I and II, such as Na(I), Ca(II) and Mg(II), as well as other diamagnetic metal centres (e.g. Zn(II) (3d) or La(III) (4f)) are also being increasingly incorporated into such heterometallic architectures in attempts to elucidate specific and individual M-L-M magnetic exchange pathways within such polynuclear systems, when directly compared to their paramagnetic counterparts.²⁰

4.2 Flying High: Isolation of Mixed-Metal Butterflies

Pilot investigations involving the Schiff base ligand 2-iminomethyl-6-methoxyphenol (L₁H, Figure 140) afforded a family of heptanuclear pseudo metallocalix[6]arene disc-like complexes ([M₇] where M = Ni(II), Co(II)/(III), Zn(II)) (Chapter Two). These heptanuclear species stack on top of one another in the solid state to generate molecular cavities within which can be accommodated a wide variety of guest molecules (Figure 141).¹²
Fig. 141 The ligands LₙH (x= 1, 2, 3) were previously used to generate host [M(II/III)₇] architectures capable of accommodating a variety of guest species. Above is the heptanuclear host-guest complex 10 containing two ClO₄⁻ anions per double-bowl unit.

Building on this work and diversifying towards other 1ˢᵗ row transition metals, we have found that the reaction of an Fe(III) or Ni(II) salt [Fe(NO₃)₃.9H₂O or [Fe(III)₃O(O₂CPh)₆(MeOH)₃](NO₃) in 24 and Ni(NO₃)₂·6H₂O in 25] with L₁H produces the butterfly complexes [Na(I)₂Fe(III)₂(OMe)₂(L₁)₄(NO₃)₂]·2MeOH (24) and [Na(I)₂Ni(II)₂(µ₃-N₃)₂(L₁)₄(MeCN)₂] (25), respectively. Complexes exhibiting butterfly topologies are frequently encountered in the literature (Figure 142).

Fig. 142 Schematic representation of a typical butterfly topology as observed regularly in the literature. M = 1ˢᵗ row transition metal, X = µ₃-bridging donor atom / group (e.g. MeO⁻, N₃⁻, OH⁻).

4.3 Probing the Topology of the Butterfly Core

Given the similarity of the core framework of 24 and 25, a general description of their topology will first be given, followed by an analysis of the characteristic features unique to each system. Both butterfly complexes 24 and 25 exhibit an identical skeletal core, with key structural variations arising from the choice of metal starting material and base used in their
production. The planar diamond or butterfly-like core of complexes 24-25 is comprised of first row transition metal centres situated at the central or body position connected to two outer or wing-tip Na(I) ions, to form a near planar rhombic core. The unique, relative positions of the alkali- and transition metal ions combined with the coordination motif of the deprotonated $L_1^-$ ligand affords the widely acknowledged butterfly topology (Figure 143).

Fig. 143 Characteristic topological features exhibited by butterfly complexes (24-25).

4.4 Exploring the Topologies of $[\text{Na(I)}_2\text{Fe(III)}_2(\text{OMe})_2(L_1)_4(\text{NO}_3)_2.2\text{MeOH}]$ (24) and $[\text{Na(I)}_2\text{Ni(II)}_2(\mu_3-\text{N}_3)_2(L_1)_4(\text{MeCN})_2]$ (25)

The first butterfly complex that we isolated was the heterometallic complex $[\text{Na(I)}_2\text{Fe(III)}_2(\text{OMe})_2(L_1)_4(\text{NO}_3)_2.2\text{MeOH}]$ (24) formed following the reaction of $[\text{Fe(III)}_3\text{O(O}_2\text{CPh})_6(\text{MeOH})_3](\text{NO}_3)$ with $L_1\text{H}$ and NaOMe in MeOH. Filtration and subsequent Et$_2$O diffusion of the mother liquor afforded 24 as dark purple blocks (in 23 % yield) in the monoclinic $P2_1/n$ space group (Figure 144). Complex 24 was also isolated in slightly lower yield (20 %) via the reaction of Fe(NO$_3$)$_3.9$H$_2$O with $L_1\text{H}$ and NaOMe. Complete X-ray structural details for 24 are given in Table 14 (Section 4.10).
Fig. 144 Crystal structure of 24. The bonding motif of L₁⁻ affords a butterfly topology and O-rich core in 24. Selected bond angles and distances (Å) in 24: Fe1-O5-Fe1’ = 101.41°, Fe⁻⁻Fe⁻ = 3.133 Å. Colour code: Na = yellow, Fe = orange, N = blue, O = red, C = grey. Hydrogen atoms have been omitted for clarity.

The heterometallic complex [Na(I)₂Ni(II)₂(μ₃-N₃)₂(L₁)₄(MeCN)₂] (25) was isolated following the reaction of Ni(NO₃)₂.6H₂O with L₁H, sodium azide (N₃⁻) and NaOH in MeOH affording green rhomb-shaped crystals of 25, which crystallise in the monoclinic space group P2₁/n, in 10 % yield (Figures 145 and 146). Complete X-ray structural details for 25 are given in Table 14 (Section 4.10).

Fig. 145 (left) Microscope image of rhomb-shaped crystals of 25 used for magnetic measurements. (right) Crystal of 25 used in X-ray data collection.
Fig. 146 The Butterfly core of 25 exhibits $\mu_3$-1,1,1 $N_3^-$ bridges with terminally bonded MeCN molecules. Selected distances (Å) and bond angles in 25: Ni1-N1-Ni1 = 99.75°, Ni$^+$-Ni = 3.352 Å. Colour code: Ni = green, Na = yellow, N = blue, O = red, C = grey. Hydrogen atoms have been omitted for clarity.

In both 24 and 25 an inversion centre is located at the midway point between the two paramagnetic centres occupying the central body positions. In each case the four metal centres are linked by $\mu_3$-bridging ions, MeO$^-$ in 24 and end-on (EO) $\mu_3$-1,1,1-$N_3^-$ ions in 25. The $L_1^-$ ligands are singly deprotonated (via loss of the phenolic proton) and link the wing-tip ions to the central body metal ions, bridging in a $\eta^1:\eta^2:\eta^1$-$\mu$ fashion (Figure 146). The four $L_1^-$ ligands lie alternately above and below the near planar core formed by the four metal centres. The central $\mu_3$-bridging ions lie out of the [Na(I)$_2$M$_2$($\mu_3$-$L$)$_2$] plane (Figure 147).

Fig. 147 A Closer look at the $\mu_3$-bridging MeO$^-$ (left) and $\mu_3$-$N_3^-$ (right) sites in 24 and 25 respectively. Colour code as in Figures 144 and 146.
The coordination spheres of the wing-tip metals are completed by chelating \( \text{NO}_3^- \) ions in 24 and neutral MeCN solvent molecules in 25. Each butterfly complex possesses Na(I) ions at the wing-tip positions of their \([\text{Na}_2\text{M}_2(\mu_3-L)_2]\) cores (where \( L = \text{MeO}^- (24) \) and \( \text{N}_3^- (25) \)); those in 25 exhibit a six coordinate octahedral geometry, while those in 24 are seven coordinate with the additional bond arising from the chelating \( \text{NO}_3^- \) ions (Figure 148). The distorted octahedral Fe(III) and Ni(II) ions in 24 and 25 possess \( \{\text{N}_2\text{O}_4\} \) and \( \{\text{N}_4\text{O}_2\} \) coordination spheres respectively, with bond length ranges of 1.944 – 2.156 Å in 24 and 2.004 – 2.176 Å in 25. The formation of complex 25 represents only the second example of an end-on (EO) \( \mu_3\text{-}1,1,1 \text{N}_3^- \) bridged 2p/3d butterfly complex (Figure 149).²⁴

**Fig. 148** (left) Seven-coordinate and (right) six-coordinate Na(I) sites of 24 and 25 respectively. Bond lengths in (Å) (24): O6-Na1 = 2.545, O8-Na1 = 2.374, O3-Na1 = 2.399, O2-Na1 = 2.351, O1-Na1 = 2.426. Bond lengths in (Å) (25): N6-Na1 = 2.456, N1-Na1 = 2.579, O3-Na1 = 2.461, O1-Na1 = 2.447, O2-Na1 = 2.250, O4-Na1 = 2.264, N1-Na1 = 2.579.

**Fig. 149** Characteristic bridging modes exhibited by the \( \text{N}_3^- \) anion. The \( \mu_3\text{-}1,1,1 \) bridging motif is observed in the core of 25.
On close scrutiny of the crystal structure of 24 it becomes apparent that there are numerous intermolecular H-bonding interactions. The non-bonded O-atom (O7, Figure 144) of the chelating NO$_3^-$ anion partakes in H-bonding with protons of neighbouring L$_1^-$ ligands belonging to three separate units of 24; O7$^-$-H17(C17) = 2.545 Å, O7$^-$-H8(C8) = 2.464 Å, O7$^-$-H3(C3) = 2.559 Å. Further contacts occur between the bonded NO$_3^-$ O-atoms with juxtaposed L$_1^-$ ligands; O6$^-$-H18A(C18) = 2.542 Å and O8$^-$-H17A(C17) = 2.545 Å. These multiple intermolecular interactions link individual units of 24 into superimposable chains which traverse the bc-plane of the unit cell (via the acceptor atoms O6, O7 and O8) (Figure 150). These individual hydrogen bonded chains are then linked via the aforementioned O7$^-$-H-C interactions in both the two remaining directions (Figure 144). In the crystals of 25 there are no intra- or intermolecular H-bonding interactions but there are numerous intermolecular short contacts. For example, the bridging azides interact with –Me-protons (H10B and H20C) belonging to the L$_1^-$ ligands of an adjacent {Na(I)$_2$Ni(II)$_2$} cluster (N3$^-$-H10B = 2.611 Å, N3$^-$-H20C = 2.655 Å). Long contacts are also observed between the six coordinate body Na(I) ions (Na1 and s.e) and nearby –Me protons (H1A and s.e) on adjacent cluster units at a distance of 3.192 Å. These intermolecular interactions occur in all three directions to give the brickwork packing motif shown in Figure 150.

![Fig. 150](image-url) Ball and stick (left) and polyhedral (right) crystal packing schematics of 24 as viewed along the (010) face of the cell. Complex 25 packs in the same way. Hydrogen atoms have been omitted for clarity.

Complexes exhibiting the butterfly topology have been widely reported in the literature whereby all four metal sites are occupied by transition metal ions (i.e. [M$_4$] species where M = 1$^\text{st}$ row transition metal ion). These systems have also been widely studied in terms of Mn and Fe chemistry stemming from the magnetic utility and synthetic facility of these ions.$^{25-30}$
As well as Mn- and Fe-based complexes, a variety of other metal ions have been utilised in generating such polynuclear systems. Far rarer though are heterometallic, tetranuclear systems which incorporate both alkali- and transition metal ions into the same complex architecture as observed here (i.e. 2p/3d systems). Some notable exceptions reported on the Cambridge Structural Database (CSD) include [Na(I)_2Fe(II)_2(t-BuO)_6(thf)_2] and [{(tmeda)Na(R)(BuO)(o-C_6H_4OMe)Mn(II)}_2] (where tmeda = N,N,N’,N’-tetramethylethylenediamine and thf = tetrahydrofuran), as well as complexes comprising [Na(I)_2Zn(II)]^{31} and [Na(I)_2Ru(III)] cores. There are, however, no such butterfly species reported which utilise the Schiff base ligand L_1H and which also incorporate the particular combinations of hetero-ions observed in 24-25. There have also been a number of butterfly systems only recently reported, whereby lanthanide ions (4f) have been incorporated, along with Co(II) (3d) ions, to generate 3d/4f butterfly species of general formula [Co(II)_2Ln(III)]_2. Within this new 3d/4f family of complexes, the [Co(II)_2Gd(III)] member has exhibited Single-Molecule Magnet (SMM) behaviour.  

4.4.1 Isolation of the Homometallic Complex [Ni(II)_3(OH)_2(L_1)_2(L_1H)_2(H_2O)_2](NO_3)_2 (26)

The isolation of butterfly species 24-25 led us to investigate the effect of base selection on parameters such as complex topology. To this end, the homo-metallic trinuclear complex [Ni(II)_3(OH)_2(L_1)_2(L_1H)_2(H_2O)_2](NO_3)_2 (26) was generated. Following the reaction of Ni(NO_3)_2.6H_2O with L_1H and NaOMe and redissolution of the reaction residue in MeCN, 26 crystallised after Et_2O diffusion as dark green blocks which form in the monoclinic space group C2/c in 40 % yield. Complete X-ray structural details for 26 are given in Table 14 (Section 4.10). The crystal structure of 26 comprises a trinuclear assembly of octahedral Ni(II) ions (Ni1, Ni2 and s.e.) linked by two pairs of oxo-bridges (O4, O5 and s.e.) (Figure 151). Overall, the {Ni(II)_3} assembly is coordinated by four L_1^{-} species: L_1H x 2, L_1^{-} x 2. Each L_1^{-} ligand (deprotonated at the phenolate site) comprises one half of the above oxo-bridges (O4-Ni1 = 1.952 Å, O4-Ni2 = 2.012 Å, Ni2-O4-Ni1 = 107.38 °), with the other half completed by OH moieties (O5-Ni1 = 2.205 Å, O5-Ni2 = 2.129 Å, Ni2-O5-Ni1 = 94.93 °). As intimated from this bridging topology the L_1^{-} ligands engage in the familiar η^1:η^2:η^1-µ coordination motif involving each Ni1/Ni2 pair while each L_1H species coordinates to a single Ni2 metal centre via an η^1:η^1 bonding mode. A single bonding H_2O molecule

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completes the coordination sphere of Ni2 (and s.e.) with charge balancing arising from the two NO$_3^-$ counter anions.

**Fig. 151** The trinuclear assembly of 26 generated by replacing NaOH with NaOMe in the synthesis of butterfly complex 25. Colour code: Ni = green, N = blue, O = red, C = grey. Hydrogen atoms have been omitted for clarity.

Each [Ni(II)$_3$] unit is non-covalently linked to its neighbour via favourable C-H···O and H-bonding interactions (Figure 152). The NO$_3^-$ counter ion (bisecting each [Ni(II)$_3$] pair) acts as a bridge to facilitate interaction between each unit. The intermolecular association comprises C-H···O interactions (C8(H8)···O9 = 2.420 Å, C3(H3)···O7 = 2.610 Å) and relatively weak H-bonding interactions (O5(H5)···O8 = 2.275 Å). This intermolecular bridging arrangement generates a zig-zag array of [Ni(II)$_3$] units assembled into 1D chains which propagate across the c-axis of the unit cell (Figure 153).
Fig. 152 Pairs of [Ni(II)$_3$] units in 26 linked by intermolecular H-bonding (O5(H5)···O8 = 2.275 Å) and C-H···O (C8(H8)···O9 = 2.420 Å, C3(H3)···O7 = 2.610 Å) interactions. Intermolecular interactions are depicted as dashed lines.

Fig. 153 (left) Crystal packing in 26 (viewed down along the $a$-axis) and (right) crystal packing in 26 identifying wave-like rows which propagate across the $c$-axis.

Similar [Ni(II)$_3$] Schiff-base assemblies have previously been reported including [Ni(II)$_3$L(O$_2$CPh)$_4$] (where LH = 2-[(3-methylamino-propylimino)-methyl]-phenol) developed by Mukherjee and co-workers,$^{34}$ however complex 26 represents the first example of such a trinuclear architecture obtained using L$_1$H.
4.5 Anion Substitution leads to Topology Modification

4.5.1 The Role of the Cl\(^{-}\) Anion

Aspirations of generating a family of butterfly species spurred investigations into replacing the counter anion in the synthesis with other anions analogous to synthetic modifications performed in isolating families of [M(II/III)] complexes (Chapters Two and Three). The NO\(_3\)\(^{-}\) anion used in the synthesis of 25 was replaced with Cl\(^{-}\) which resulted in the formation of the mononuclear complex [Ni(II)(L\(_1\))]\(_2\) (27). Complex 27 crystallises in the monoclinic space group P2\(_1\)/c in 15 % yield. The Ni(II) centre is coordinated by two L\(_1\)\(^{-}\) ligands (deprotonated at the phenolate site), which bind in an \(\eta^1:\eta^1\) mode via the O\(_{\text{phen}}\) and imino N donor atoms (O2 and N1 respectively) (Figure 154). Complete X-ray structural details for 27 are given in Table 14 (Section 4.10). Complex 27 packs in pairs along the \(c\)-axis of the unit cell facilitated by intra- and intermolecular short contacts comprising C-H\(^{+}\)-O interactions between O\(_{\text{phen}}\) (O2) atoms and imine Me-protons in one molecule of 27, as well as C-H\(^{+}\)-O interactions between Me-O groups on adjacent mononuclear assemblies (O2-H1(C1) = 2.368 Å, O1-H9'(C9') = 2.723 Å, respectively) (Figures 154 and 155).

**Fig. 154** Mononuclear complex 27 isolated using NiCl\(_2\).6H\(_2\)O as the starting salt. Colour code: Ni = green, O = red, N = blue, C = grey. Hydrogen atoms have been omitted for clarity.
4.5.2 The Role of ClO$_4^-$

Replacement of NO$_3^-$ with ClO$_4^-$ in the Ni(II) / L$_1$H / base synthesis generated the very different species [Na(I)$_3$Ni(II)$_2$(L$_1$)$_6$](ClO$_4$) (28), which crystallises as green crystalline blocks in 30% yield in the trigonal P-3 space group. Complete X-ray structural details for 28 are given in Table 14 (Section 4.10). The structure of 28 comprises a trigonal bipyramidal core of metal ions in which the three six-coordinate Na(I) ions (Na1 and s.e.), possessing a distorted octahedral geometry, occupy the equatorial positions while the two Ni(II) metal centres are located at the two axial positions (Figures 156 and 157). The six L$_1$- anions each span one of the six axial Ni$^{2+}$Na vertices comprising the trigonal bipyramidal core, employing the rather unusual η$^1$:η$^3$:η$^1$-µ$_3$ bonding mode. More specifically, the phenoxide O-atoms (O1 and O4) link the axial Ni(II) centres to the equatorial Na(I) ions as well as forming bridges between the Na(I) ions around the equatorial plane of the molecule (Figure 157). An inversion centre lies within the molecule located at the centre of the triangle formed by the three equatorial Na(I) ions. The Na-O bond distances lie in the 2.26-2.69 Å range, while a sole ClO$_4^-$ counter anion balances the charge of the [Na(I)$_3$Ni(II)$_2$(L$_1$)$_6$]$^+$ unit.
Fig. 156 Trigonal bipyramidal core observed in 28. Selected bond lengths (Å) and bond angles in 28: Ni1-O1 = 2.057 Å, O1-Na1 = 2.266 Å, O4-Na1 = 2.618 Å, Ni2-O4 = 2.044 Å. Colour code: Ni = green, O = red, Na = yellow.

Fig. 157 (left) The molecular structure of 28. (right) The molecular structure of 28 viewed along the Ni−Ni vector of the [Na(I)3Ni(II)2] trigonal bipyramidal core, highlighting the pseudo 3-fold symmetry. Selected bond lengths (in Å) in 28: Ni1-O1 = 2.058, O2-Na1 = 2.330, O3-Na1 = 2.344, Ni2-N2 = 2.104, Ni1-N1 = 2.106. Selected bond angles in 28: Na1-O1-Na1 = 81.72°, Na1-O4-Na1 = 83.34°, Ni1-O1-Na1 = 109.51° Ni2-O4-Na1 = 96.68°. Colour code: Ni = light green, Na = yellow, O = red, N = blue, C = grey. Hydrogen atoms have been omitted for clarity.
The ClO$_4^-$ anions lie on a pseudo C$_3$ axis (D$_{3h}$ symmetry of core when L$_1^-$ ligands are ignored) directly above the Ni(II) ions and are positioned alternately in between the individual [Na(I)$_3$Ni(II)$_2$] moieties propagating -[Na(I)$_3$Ni(II)$_2$]-[ClO$_4$]-[Na(I)$_3$Ni(II)$_2$]- 1D chains along the c-axis of the unit cell (Figures 158 and 159). These chains are stabilised by numerous hydrogen bonding interactions between the perchlorate O-atoms (O5, O6 and s.e) and the –Me protons of four nearby L$_1^-$ ligands (two from each [Na(I)$_3$Ni(II)$_2$], unit sandwiching the ClO$_4^-$ anions (Figure 159)). Complex 28 represents the first example of a trigonal bipyramidal [Na(I)$_3$Ni(II)$_2$] species, although a similar La(III) complex, [La(III)$_2$Na(I)$_3$(µ$_4$-OR)$_3$(µ-OR)$_6$(THF)$_5$] is known in the literature.  

**Fig. 158** Crystal packing observed in 28, viewed along the c-axis, showing 1D rows of [Na(I)$_3$Ni(II)$_2$]-[ClO$_4$]-[Na(I)$_3$Ni(II)$_2$] which propagate in that direction.

**Fig. 159** Section of the [Na(I)$_3$Ni(II)$_2$]−[ClO$_4$]−[Na(I)$_3$Ni(II)$_2$] 1D chains observed in the crystal structure of 28. Dashed lines represent H-bonds at distances (Å): H1C−O6 = 2.349 Å, H18C−O5 = 2.520 Å.
4.6 Homometallic \([M_4]\) Cubanes (\(M = \text{Mn(III/IV), Ni(II)}\)) and a Mn(III) 1D Coordination Polymer

A host of first-row transition metal ions were surveyed towards potential, novel complex formation with \(L_1H\) and its analogues. Interestingly, the employment of the Mn(III) ion via the oxidation of a Mn(II) precursor (MnCl\(_2\).4H\(_2\)O) \([\text{using NaOH}]\) in the presence of \(L_1H\) and NaOH, gives rise to the homometallic 1D coordination polymer \([\text{Mn(III)}(L_1)_2(\text{Cl})]_n(29)\), which crystallises in the monoclinic space group C2/c. Complete X-ray structural details for 29 are given in Table 15 (Section 4.10). In this species, two singly deprotonated \(L_1^-\) ligands (deprotonated at the phenolate site) chelate a central Mn(III) ion at its equatorial positions while its Jahn-Teller elongated bonds are provided by two symmetry equivalent Cl\(^-\) ions (Mn1–Cl1 = 2.676 Å) (Figure 160). The above chloride ions act as linker ligands between pairs of \([\text{Mn(III)}(L_1)_2]^+\) units to form a covalent zig-zag chain structure (Figure 161). The \(L_1^-\) ligands coordinate in the familiar \(\eta^1:\eta^2:\eta^1\)-\(\mu\) binding motif. We do not see participation of the methoxy oxygen (O2) in metal coordination here (Mn1–O2 = 4.359 Å), unlike with our \([\text{M}(\text{II/III})_7]\) complexes discussed in Chapters Two and Three. Additionally, the adjacent ligand moieties are oriented in a staggered conformation with respect to one another, thus reducing any erroneous steric effects associated with the coordination of such bulky Ph-containing units (Figure 161). Such 1D coordination polymers are a well known class of compound with numerous examples to be found in the literature. For instance, Yang and co-workers described isomerism in Cu(II) based 1D coordination polymers incorporating N-(2-Hydroxybenzyl)-L-valine building blocks.\(^{45}\) Porous frameworks developed by Wu and co-workers were formed via the assembly of individual Cd(II) based 1D coordination polymers, for potential applications in chiral separations and asymmetric catalysis.\(^{46}\) Also, the normally ferromagnetic inducing azide (N\(_3^-\)) species was utilised by Tommasino and co-workers in the synthesis of an azide-bridged Cu(II) 1D coordination polymer, with the structure and observed antiferromagnetic properties arising from the unusual asymmetric \(\mu_{1,1,3}\) coordination mode of N\(_3^-\).\(^{47}\)
Fig. 160 Two \{\text{Mn(III)(L}_1\text{)}_2\text{(Cl)\}} \text{ units within the 1D chain in 29. Selected bond lengths and distances (in Å): Mn1-Cl1 = 2.678 Å, Mn1-O1 = 1.854 Å, Mn1-N1 = 2.030 Å, Mn1-O2 = 4.359 Å. Colour code: Mn = pink, Cl = green, O = red, N = blue, C = grey. Hydrogen atoms have been omitted for clarity.}

Fig. 161 Crystal packing in 29 as observed down the \(c\)-axis (left) and \(a\)-axis (right) of the unit cell respectively. Hydrogen atoms have been omitted for clarity.

In the synthesis of complexes 24, 25, 28 and 29, a strong base (NaOH) was utilised. Since the phenol moiety of \(L_1\text{H}\) is inherently acidic, we postulated what the effect might be of utilising a base of lower strength or even eliminating the addition of the base from these reaction
media. To this end we found that the oxidation of Mn(OAc)$_2$·4H$_2$O via reaction with L$_1$H in EtOH (no base) produced black X-ray quality crystals of the tetrametallic complex [Mn(III)$_3$Mn(IV)$_1$(O)$_3$(OEt)(OAc)$_3$(L$_1$)$_3$] (30) in 20 % yield. Complex 30 crystallizes in the orthorhombic space group P2$_1$2$_1$2$_1$. Complete X-ray structural details for 30 are given in Table 15 (Section 4.10). The core in 30 can be described as a highly distorted {Mn$_4$O$_4$} cubane which, when viewed along the Mn1-O13 vertex, exhibits pseudo three-fold symmetry with Mn centres occupying alternate corners of the cube (Figure 162). Mn-O bond length considerations, Bond valence sum (BVS) calculations as well as charge-balance considerations reveal that Mn1 possesses an oxidation state of (+4) while Mn ions 2-4 exhibit an oxidation state of +3 (see Section 4.10: Table 13). The latter display the expected Jahn–Teller elongations (2.182(3) – 2.250(4) Å), which all lie perpendicular to each other (Figure 163).

Fig. 162 Crystal structure of 30. Dashed lines represent the intra-molecular H-bonds at distances (Å): H19B···O4 = 2.375, H19B···O3 = 2.516, H10B···O2 = 2.547, H10B···O1 =
2.414, H1B···O5 = 2.497, H1B···O6 = 2.660. Colour code: Mn = pink, O = red, N = blue, C = grey. Hydrogen atoms have been omitted for clarity.

**Fig. 163** (left) View of the pseudo C₄ axis exhibited in complex 30. (right) The cubane core in 30 highlighting (dark lines) the mutually orthogonal Jahn-Teller elongation axes.

The Mn centres of 30 are linked into the cubane topology via three μ₃-O²⁻ anions (O14, O15 and O16) and one μ₃-bridging EtO⁻ ligand (O13). The three AcO⁻ ligands each bridge two Mn centres across one face of the cubane in the common η¹⁻:η¹⁻:μ bonding motif. The three L₁⁻ ligands are singly deprotonated at the phenolate site and simply chelate Mn2, Mn3 and Mn4 at three of the four corners of the cube. By chelating to the Mn(III) ions Mn2, Mn3 and Mn4, the three L₁⁻ ligands form a shallow cavity of approximate dimensions 3.72 x 9.90 x 4.33 Å (base x rim x height) of which the Mn2 / Mn3 / Mn4 plane forms its triangular base. The μ₃-EtO⁻ bridging moiety sits inside this cavity (Figure 164).

**Fig. 164** Space-fill representation of the μ₃-bridging EtO⁻ ligand which sits within a molecular cavity forged by the three L₁⁻ ligands in 30.
Close inspection of the crystal structure in 30 shows evidence of multiple intramolecular H-bonding interactions involving the three L₁⁻ ligands. More specifically, each ligand forms four H-bonds with its nearest neighbour via their N–Me methyl protons and juxtaposed Me-O and Ophen sites; illustrated by dashed lines in Figure 162. The [Mn₄O₄] cubane units arrange into superimposable 1D rows down the a-axis which, in the bc-plane, are assembled in the common brick-wall motif (Figure 165). The tetranuclear complex 30 joins a small family of analogous mixed-valence [Mn(III)₃Mn(IV)] cubanes which include the previously reported Single-Molecule Magnets [Mn(III)₃Mn(IV)₁O₂X(OAc)₃(dbm)₃] (where X = Cl⁻, Br⁻, dbm = dibenzoylmethane) and [Mn(III)₃Mn(IV)₁O₃(O₂CR)₃(dbm)₃] (R = Me, Ph).

![Fig. 165 Polyhedral representation of the crystal packing in 30 observed down the a-axis. Hydrogen atoms have been omitted for clarity.](image)

4.7 The Quest for Analogues to [Mn(III)₃Mn(IV)₁] (30)

Numerous attempts at producing analogues to 30 were made using other first-row transition metals. With this in mind, it was hoped that generating the analogous [Fe₄] cubane would lead to a system with interesting magnetic properties. However the mixed-valence (or otherwise) analogue to 30 could not be isolated; instead reaction of FeCl₂·4H₂O with L₁H and NaOAc afforded the mononuclear species [Fe(III)(L₁)₂Cl] (31), which crystallises in the orthorhombic Pbcn space group (Figure 166). Complete X-ray structural details for 31 are
given in Table 15 (Section 4.10). \( \text{L}_1^- \) chelates the square-based pyramidal Fe(III) core (formed \textit{in situ} via oxidation of FeCl\(_2\).4H\(_2\)O) in an \( \eta^1:\eta^1 \) bonding mode via \text{O}_{\text{phen}} \ (O1) and imino nitrogen donor atoms (O1-Fe1 = 1.877 Å, N1-Fe1 = 2.115 Å). Coordination to the Fe(III) centre is completed by the terminally-bonded Cl1 (Cl1-Fe1 = 2.257 Å), whose terminal bonding mode means that 1D covalent chains of mononuclear units in 31 are not observed as they were in 29 (Figure 161). Instead, the individual [Fe(III)\(_1\)(L\(_1\))\(_2\)Cl] units pack in a zig-zag fashion along the \( a \)-axis of the unit cell with neighbouring Fe-Cl moieties oriented in opposite directions along the \( b \)-axis of the unit cell (Figure 167). There is no intra- or intermolecular H-bonding instead the packing arrangement is facilitated by intermolecular short contacts between neighbouring [Fe(III)\(_1\)(L\(_1\))\(_2\)Cl] units: O2⋯H8A(C8) = 2.701 Å, O2⋯H5(C5) = 2.615 Å and symmetry equivalent. These interactions are bolstered by longer intermolecular contacts between terminal Cl1 atoms and imine C-H protons (N1=C2)H2⋯Cl1 = 2.996Å).

**Fig. 166** Fe(III) mononuclear complex 31 with terminally-bonded Cl\(^-\) species. Colour code: Fe = orange, Cl = green, N = blue, O = red, C = grey. Hydrogen atoms have been omitted for clarity.
Fig. 167 Mononuclear units of 31 pack in an up-down-up arrangement in the unit cell (viewed down the c-axis of the unit cell).

The formation of complexes 30-31 illustrates that the addition of a relatively strong base in such reactions is not imperative, but a base of some sort – even the acetate present in the starting material of [Mn(III)₃Mn(IV)₃(O)(OEt)(OAc)₃(L₄)₃] (30) – appears to be required in order to produce a polymetallic complex. Reactions in the absence of base produced no isolable products for any other 1st row transition metal. Previous work employing strong bases in Ni(II)/L₁H chemistry led to the formation of a family of heptanuclear pseudo metallocalix[6]arene complexes.¹² Use of NaOMe in place of NaOH in the reaction of Ni(NO₃)₂·6H₂O with the Schiff base analogue to L₁H₂-imino-6-methoxyphenol (L₅H, Figure 140), produces the tetranuclear Ni(II) cubane [Ni(II)₄(μ₃-OMe)₄(L₅)₄(MeOH)₄] (32). Alkoxide-bridged Ni(II) cubanes are a well-known class of compound.³⁷-³⁹ Crystals of 32 form in the tetragonal I₄₁/a space group and its cationic {Ni(II)₄(μ₃-OMe)₄}⁴⁺ core is comparable to that in [Mn₄] (30), comprising a distorted cubane core topology with the Ni(II) centres (Ni1 and s.e) occupying alternate corners of the cube (Figure 168). Complete X-ray structural details for 32 are given in Table 15 (Section 4.10). The six-coordinate, octahedral Ni(II) centres are connected via four μ₃-bridging MeO⁻ ions (O1 and s.e), with the four singly deprotonated L₅⁻ ligands chelating to the four metal centres (through N1, O3 and s.e.). The internuclear separations between each Ni(II) centre in 32 is represented schematically by Figure 169. The distorted octahedral geometries of the metal ions are completed by terminal MeOH solvent molecules.
Fig. 168 Crystal structure of 32 as viewed off-set (top) and aligned (bottom) with one of the cube faces. Ni = green, O = red, N = blue, C = grey. Hydrogen atoms have been omitted for clarity.
Fig. 169 Schematic representation of the [Ni(II)$_4$] core in 32 identifying the internuclear Ni···Ni separations.

The aforementioned MeOH solvent molecules partake in intramolecular H-bonding with O$_{\text{phen}}$ atoms (O3) of a nearby L$_5$ ligand at a distance of O1(H1)$^\cdots$O3 = 1.896 Å (Figure 168). The individual [Ni(II)$_4$] units in 32 form superimposable 1D rows along the c-axis of the cell, which are packed into a grid-like arrangement when viewed in the ab-plane (Figure 170). This packing motif is propagated by numerous crystallographically equivalent intermolecular interactions. More specifically each [Ni(II)$_4$] moiety has eight C-H$^\cdots$O interactions via the aromatic protons (H3) and methoxy oxygen atoms (O4) of the four symmetry equivalent L$_1^{-}$ ligands (C3(H3)$^\cdots$O4 = 2.447 Å). Interestingly, [Ni(II)$_4$(µ$_3$-OMe)$_4$(L)$_4$(MeOH)$_4$], despite much effort, cannot be made. A probable reason for this apparent anomaly soon becomes clear on close scrutiny of the structure of 32. The only difference between ligands L$_1$H and L$_5$H is the absence of a –Me imine group on the latter. This C=NH imine group (N1-H1 on L$_5$H) lies in close proximity to the adjacent bridging µ$_3$-OMe ligand (denoted C10-O2) at a distance of only N1(H1)$^\cdots$H10A(C10) = 2.329 Å. Thus the replacement of L$_5$H with L$_1$H in 32 is likely implausible due to the steric constraints the C=N-Me methyl group would impose on the system.
Fig. 170 Crystal packing diagrams of 32 viewed along the c-axis (left) and along the b-axis (right) of the unit cell respectively.

4.8 Magnetic Susceptibility Measurements

DC magnetic susceptibility measurements were prioritised and performed on powdered microcrystalline samples of complexes 24, 25, 29, 30, and 31 in the 300-5 K temperature range and in an applied field of 0.1 T. See Section 2.5.1.4 for details of instrumentation utilised in magnetic susceptibility measurements.

4.8.1 [Na(I)$_2$Fe(III)$_2$(OMe)$_2$(L$_1$)$_4$(NO$_3$)$_2$.2MeOH (24)

The $\chi_M T$ product of 24 at room temperature is 6.36 cm$^3$ K mol$^{-1}$, slightly lower than the expected value of 8.75 cm$^3$ K mol$^{-1}$ (assuming $g = 2.0$) (Figure 171). The value drops sharply with temperature, reaching a $\chi_M T$ value close to zero (0.11 cm$^3$ K mol$^{-1}$) at 5 K. This is clearly indicative of antiferromagnetic exchange between the Fe(III) centres in 24. The data can be fitted with the simple isotropic Hamiltonian 4.1 to afford $J = -6.7$ cm$^{-1}$ and $g = 2.0$.

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_1') \quad (4.1)$$

Fitting of the $1/\chi_M$ versus $T$ data to the Curie-Weiss law affords a Weiss constant ($\theta$) of -85.25 K, indicative of antiferromagnetic exchange in 24 (Figure 172). These values are
comparable with previously reported alkoxide-bridged Fe(III) dimers containing similar Fe-O-Fe angles and Fe···Fe distances.\textsuperscript{40}

**Fig. 171** Plot of $\chi_M T$ vs. $T$ obtained for 24. (inset) The magnetic coupling scheme employed in fitting magnetic data for 24. $J$ is the magnetic exchange coupling parameter. The solid red lines represent a best fit to the experimental data.

**Fig. 172** Fitting of the $1/\chi$ vs. $T$ data to the Curie-Weiss law confirms antiferromagnetic exchange between Fe(III) centres in 24.
4.8.2 [Na(I)$_2$Ni(II)$_2$(μ$_3$-N$_3$)$_2$(L$_1$)$_4$(MeCN)$_2$] (25)

The susceptibility data obtained from complex [Na(I)$_2$Ni(II)$_2$(μ$_3$-N$_3$)$_2$(L$_1$)$_4$(MeCN)$_2$] (25) is shown in Figure 173. The room temperature $\chi_M T$ value of 2.10 cm$^3$ K mol$^{-1}$ is consistent with that expected for two non interacting Ni(II) centres (2.0 cm$^3$ K mol$^{-1}$, assuming $g = 2$). This value rapidly rises to reach a maximum $\chi_M T$ product of 3.74 cm$^3$ K mol$^{-1}$ at 17 K, before rapidly decreasing to a final value of 3.61 cm$^3$ K mol$^{-1}$. This is indicative of ferromagnetic exchange with the low temperature decrease due to zero-field splitting (zfs) and/or intermolecular exchange. Ferromagnetic exchange here is facilitated by the inclusion of the ferromagnetic exchange inducing μ$_3$-N$_3$ bridging groups. For the interpretation of the magnetic properties of 25 we employed the following spin-Hamiltonian 4.2:

\[
\hat{H} = -2 J \hat{S}_1 \cdot \hat{S}_2 + \mu_B B g \sum_{1,2} \hat{S}_i + D \sum_{1,2} \hat{S}_{i,z} - S(S+1)/3 \quad (4.2)
\]

where $J$ is the isotropic exchange interaction parameter, $\hat{S}$ is a spin-operator, $i$ runs from 1 to 2, $\mu_B$ is the Bohr magneton, $B$ is the applied magnetic field, $g = 2$ is the $g$-factor, $D$ is the uniaxial anisotropy parameter of Ni(II) and $S = 1$ is the electronic spin of Ni(II) in octahedral geometry.\cite{41} Intermolecular interactions were taken into account in the frame of mean-field theory, by use of the Curie-Weiss temperature, $\theta$. This produces an excellent fit of the experimental data with $J = +9.35$ cm$^{-1}$, $g = 2.18$ and a Curie-Weiss (CW) constant $\theta = -0.4$ K. The inclusion of the latter parameter is consistent with the significant intermolecular interactions observed in the crystals of 25. Magnetisation versus field data confirm the $S = 2$ ground state (Figure 174). In order to determine the sign and magnitude of D, we have numerically fitted the magnetisation data collected using the spin-Hamiltonian 4.1, at temperatures between 2 and 7 K in magnetic fields ranging from 1 to 7 T, keeping $J = +9.35$ cm$^{-1}$ and $g = 2.18$ as determined by fitting the $\chi_M T$ product. The obtained best-fit parameters are $D$(Ni(II)) = -3.96 cm$^{-1}$ and $\theta = +0.01$ K. The smaller CW constant obtained here is due to higher field intermolecular exchange quenching. Additionally, no out-of-phase ac ($\chi''$) peaks were observed in 25 indicating that it is not a SMM.
Fig. 173 Plot of $\chi_M T$ vs. $T$ obtained for \([\text{Na(I)}_2\text{Ni(II)}_2(\mu_3-N_3)_2(L_1)_4(\text{MeCN})_2] \) (25). The solid red line represents a best fit to the experimental data.

Fig. 174 Reduced magnetisation ($M/N\mu_B$) vs. field for \([\text{Na(I)}_2\text{Ni(II)}_2(\mu_3-N_3)_2(L_1)_4(\text{MeCN})_2] \) (25) in the range 0.5-7.0 T. The solid red lines represent a best fit to the experimental data.

**4.8.3 Magnetic Characterisation of \([\text{Mn(III)}(L_1)_2\text{Cl}])_n \) (29)**

Magnetic susceptibility measurements obtained from the Cl-bridged 1D Mn(III) chain \([\text{Mn(III)}(L_1)_2\text{Cl}])_n \) (29) shows typical antiferromagnetic behaviour with decreasing temperature (Figure 175). The kink at low temperature (~20K) is suggestive of the onset of
spin-canting, as reported previously in related structures.\textsuperscript{42} No frequency dependent ac signals were observed in \textbf{29}, ruling out Single-Chain Magnet classification.

\textbf{Fig. 175} Plots of $\chi_m T$ vs. $T$ and $\chi_m$ vs $T$ (inset) obtained from a polycrystalline sample of \textbf{29} in an external field of 0.1 T and scanned along the 300-5 K temperature range.

\textbf{4.8.4 Magnetic Characterisation of [M$_4$] Cubanes}

\textbf{4.8.4.1 Magnetic Characterisation of [Mn(III)$_3$Mn(IV)$_1$] (30)}

Complex \textbf{30} exhibits a room-temperature $\chi_M T$ value of 9.21 cm$^3$ K mol$^{-1}$ which indicates the presence of antiferromagnetic exchange within \textbf{30}, since the expected 300 K value is approximately 10.88 cm$^3$ K mol$^{-1}$ (assuming $g = 2.0$). The $\chi_M T$ product gradually rises with decreasing temperature to a maximum value of 11.52 cm$^3$ K mol$^{-1}$ at 70 K, before decreasing to a minimum of 9.70 cm$^3$ K mol$^{-1}$ at 5 K (Figure 176).
Fig. 176 Plot of $\chi_M T$ vs. $T$ data for 30 identifying antiferromagnetic exchange between Mn-centres with sharp drop below $\sim 70$ K attributed to zero-field splitting (black line represents simulated data).

The $T < 70$ K decrease is assigned to a combination of intermolecular interactions, zero-field splitting and/or the Zeeman effect of the applied field. The data is thus indicative of ferrimagnetic behaviour (exchange) with the low temperature $\chi_M T$ value suggestive of a $S = \frac{9}{2}$ ground spin state, as expected for this class of compound. The data can be fitted using the Hamiltonian (4.3) assuming two different exchange interactions (i.e. a 2-J model shown in Figure 177) ($J_1 = \text{Mn(III)} - \text{Mn(IV)} = -25.97$ cm$^{-1}$, $J_2 = \text{Mn(III)} - \text{Mn(III)} = + 8.97$ cm$^{-1}$) and a Curie-Weiss term ($\theta = -1.84$ K) to account for the intermolecular interactions.

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_1 \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \hat{S}_4 + \hat{S}_2 \hat{S}_4) \quad (4.3)$$

This results in a $S = \frac{9}{2}$ ground spin state with $g = 1.97$. In order to confirm this proposed ground state magnetization vs. field (M vs. H) measurements were obtained in the 10 to 2 K and 0.5 to 7 T temperature and external magnetic field ranges respectively. Magnetic saturation of the sample occurred at a value of 8.80 Nμβ and pointed to the hypothesized $S = \frac{9}{2}$ ground state (assuming $g \sim 2$). This was confirmed via simulation of these data as shown by the solid red lines in Figure 177, to give the spin Hamiltonian parameters $S = \frac{9}{2}$, $D(\text{IV}) = -0.66$ cm$^{-1}$, $D(\text{III}) = -1.63$ cm$^{-1}$, $g = 1.97$ and a Curie-Weiss Constant ($\theta$) of 0.06 cm$^{-1}$.
Fig. 177 Reduced magnetization (M/NμB) vs. field (B) data for 30. The solid red lines represent simulated data while black lines are experimental data. (inset) Schematic representing 2-J model utilised to fit data for 30 (solid lines = J₁, dashed lines = J₂). Specific spin Hamiltonian parameters corresponding to this model are described in the main text.

4.8.4.2 Magnetic Characterisation of [Ni(II)₄] (32)

The room temperature χ_M T value in 32 of 5.08 cm³ K mol⁻¹ is larger than expected for four non-interacting Ni(II) centres (4.88 cm³ K mol⁻¹ assuming g ~ 2.2) and points to ferromagnetic exchange within the metal centres. As illustrated in Figure 178 the χ_M T product rises gradually with decreasing temperature before increasing more rapidly at around 60 K, whereby a maxima of 13.06 cm³ K mol⁻¹ is attained at 14 K. The χ_M T value then decreases slightly before reaching a resting value of 12.34 cm³ K mol⁻¹. Fitting of the magnetic data using a 1-J model (coupling is equivalent between all Ni(II) ions) described by the Hamiltonian 4.3 gave the spin Hamiltonian parameters S = 4, g = 2.25 and J = + 7.0 cm⁻¹, with the S = 3 spin state lying 61 cm⁻¹ above the well isolated ground spin state (Figure 179). Fitting the 1/χ_M vs. T data to the Curie-Weiss law using the 300–100 K data affords a Weiss constant (θ) of + 29.06 K and thus supports ferromagnetic exchange in 32 (Figure 180).
Fig. 178 Magnetic susceptibility curve obtained for 32. (inset) Reduced magnetisation ($M/N\mu_B$) vs. Field (H) data for 32 in the 7-2K temperature range at magnetic fields of 3, 4, 5, 6 and 7 T.

Fig. 179 1-J model adopted for 32 (dashed line = $J_1$). Specific spin Hamiltonian parameters corresponding to this model are described in the main text.
Fig. 180 Plot of $1/\chi_M$ vs. $T$ data for 32 confirming strong ferromagnetic exchange due to a positive Weiss constant ($\theta$).

In order to verify the ground-state of 32, we performed variable temperature and variable field dc magnetisation experiments in the ranges 1.8 to 6 K and 0.5 to 7 T, these data are presented as reduced magnetisation ($M/N\mu_B$) vs. $H/T$ in Figure 178 (inset). We were able to fit the data employing a matrix diagonalisation method to a model that assumes only the ground state is populated, includes axial zero-field splitting ($D\hat{S}_z^2$) and the Zeeman interaction, and carries out a full powder average. The corresponding Hamiltonian is:

$$\hat{H} = D\hat{S}_z^2 + g\mu_B\mu_0\hat{S} \cdot H \quad (4.4)$$

where $D$ is the axial anisotropy, $\mu_B$ is the Bohr magneton, $\mu_0$ is the vacuum permeability, $\hat{S}_z$ is the easy-axis spin operator and $H$ is the applied field. This model gave: $S = 4$, $g = 2.22$ and $D_{\text{cluster}} = -0.40 \text{ cm}^{-1}$. Indeed, such parameters are in line with previously reported [Ni(II)$_4$] cubane species.$^{37-39}$ Ac magnetisation studies showed no out-of-phase signals, indicating that 32 does not possess SMM properties above 2 K.

4.9 Concluding Remarks

This chapter has described the synthesis, structural and magnetic characterization of a wide variety of polymeric complexes isolated using the Schiff base ligands 2-iminomethyl-6-methoxyphenol (L$_1$H) and 2-imino-6-methoxyphenol (L$_2$H). Previous work using these Schiff
base ligands and their analogues (L₂H, L₃H, L₄H) afforded a family of double-bowl pseudo metallocalix[6]arene disc complexes as described in Chapters 2 and 3. We have shown here that by altering the reaction conditions and reagents used to generate these heptanuclear systems, we have produced a myriad of novel polynuclear architectures with interesting structural and magnetic characteristics. These include the heterometallic tetrانuclear complexes [Na(I)₂Fe(III)₂(OMe)₂(L₁)₄(NO₃)₂] (24) and [Na(I)₂Ni(II)₂(μ₃-N₃)₂(L₁)₄(MeCN)₂] (25) which each exhibit a unique butterfly-like topology (Figure 181). Magnetic characterisation of these complexes identified antiferromagnetic exchange in 24 and ferromagnetic exchange in 25.

![Fig. 181 Crystal structure of the butterfly complex 24; a breed of complex isolated using L₁H.](image)

Although butterfly systems are known in the literature, complexes 24-25 are the first examples of such heterometallic systems to incorporate these particular pairs of ions (Na(I) / Fe(III) and Na(I) / Ni(II)). By varying the employed synthetic parameters we have produced the trinuclear [Ni(II)₃] complex 26 and pentanuclear [Na(I)₃Ni(II)₂] complex 28; isolated via substitution of base and counter anion respectively. Utilisation of an alternative magnetic core, in the form of Mn(III), led to the generation of the 1D chain assembly 29 comprising {Mn-Cl} monomeric units and exhibiting antiferromagnetic exchange between Mn(III) centres. Finally by further synthetic manipulation (including replacement of L₁H with L₃H), we were successful in obtaining the homometallic, tetrarnuclear cubane complexes [Mn(III)₃Mn(IV)₁] (30) and [Ni(II)₄] (34). Complexes 30 and 31, though possessing analogous tetrarnuclear cores, exhibit starkly different magnetic properties stemming from
their differing metal centres and mixed-valence nature of the former; complex 30 exhibiting antiferromagnetic exchange while magnetic coupling in 31 is found to be ferromagnetic in origin.

4.10 Experimental

4.10.1 Instrumentation

Instrumentation utilised in analyses of L$_5$H and complexes 24-31 are as detailed in Chapter Two (Section 2.5.1).

4.10.1.1 X-ray Diffraction

All hydrogen atoms in all complexes were placed in calculated positions. All non-hydrogen atoms were refined anisotropically. In complex 24, the MeOH solvent molecules were modelled to be disordered over two sites at 50:50 occupancy. DFIX restraints were also put in place between the C and O atoms in both disordered MeOH solvent molecules. The collection for complex 28 gave the rather large $R_{int}$ value of 0.25 and R factor of 13 %. Numerous other collections on this set of crystals (and others) gave even poorer data and was assumed to be down to the weakly diffracting nature of these crystals. All Crystallographic Information Files (CIFs) are located on a writeable CD, included at the end of this thesis.

4.10.2 Synthetic Procedures

Unless otherwise stated, all materials (solvents and reagents) were purchased commercially and used as supplied without further purification. In addition, though no difficulties were encountered in this work, great care must be taken when working with the potentially explosive perchlorate, nitrate and azide salts. The trinuclear complex [Fe(III)$_3$O(O$_2$CPh)$_6$(MeOH)$_3$](NO$_3$)$_2$ was synthesised according to a literature procedure. 43

4.10.2.1 Synthesis of 2-imino-6-methoxyphenol (L$_5$H)

The procedure described overleaf (Scheme 4.1) is a modification to a previously reported method towards production of the Schiff base ligand 2-imino-6-methoxyphenol (L$_5$H). 44
Scheme 4.1 Reaction scheme for the synthesis of 2-imino-6-methoxyphenol (L₅H).

To a transparent, yellow solution of 2-hydroxy-3-methoxybenzaldehyde (o-Vanillin) (3.0 g, 19.7 mmol, 1.0 eq.) in MeOH (100 cm³) was added a slight excess of an aqueous solution of NH₃ (25 % in H₂O) (0.35 g, 20.48 mmol, 1.04 eq.) (Scheme 4.1). A bright yellow opaque viscous mixture was afforded following addition of NH₃. A further aliquot of MeOH (50 cm³) was then added to afford a transparent golden-yellow solution. The reaction vessel was covered with parafilm (to limit loss of NH₃) and the solution stirred for a further 24 hours, after which time a yellow precipitate had formed in the flask. This yellow solid was removed by filtration (crop 1) and the bright yellow mother liquor evaporated in vacuo to afford crop 2 as a bright yellow solid. Infrared analyses of both crops were consistent with one another and both microanalyses were also consistent with the Schiff base ligand 2-imino-6-methoxyphenol (L₅H). The combined yield of L₅H was 87 % (2.633 g). NMR and MP data were in line with literature results.

C, H, N Elemental Analysis

Calculated for: C₈H₉N₁O₂

Theory (%): C (63.54), H (6.00), N (9.26).

Found (%): C (63.92), H (6.41), N (9.58).

Infrared Spectroscopy (cm⁻¹)

1621 (m), 1462 (s), 1417 (m), 1248 (s), 1221 (s), 1168 (m), 1075 (s), 1053 (s), 1024 (m), 963 (m), 831 (m), 784 (s), 735 (s), 684 (m).

¹H NMR (400 MHz, CDCl₃)

δ 3.86 (s, 3H, O-CH₃), 6.74-6.95 (m, 3H, Ar-H), 7.19 (s, 1H, N=CH), 11.05 (C=NH).
$^{13}$C NMR (400 MHz, CDCl$_3$)

$\delta$ 164.90 (N=CH), 123.68, 118.31, 114.54 (Ar-H), 56.13 (CH$_3$-O)

Melting Point (MP) Range

151.0-152.5 °C.

**4.10.2.2 Synthesis of [Na(I)$_2$Fe(III)$_2$(μ$_3$-OMe)$_2$(L$_1$)$_4$(NO$_3$)$_2$.2MeOH (24)**

The tetranuclear, butterfly complex 24 was isolated via two synthetic routes (detailed below) with comparable yields. The infrared and elemental analyses of products yielded from both routes were consistent with 24.

**4.10.2.2.1 Method A:**

To a dark orange solution of [Fe(III)$_3$O(O$_2$CPh)$_6$(MeOH)$_3$](NO$_3$) (0.50 g, 0.47 mmol, 1.0 eq.) in MeOH (30 cm$^3$) was added the Schiff base ligand L$_1$H (0.08 g, 0.47 mmol, 1.0 eq.) and the solution stirred magnetically to afford complete dissolution of the solid reactants. The addition of L$_1$H resulted in a colour change from dark orange to deep purple. Sodium methoxide (NaOMe) (0.025 g, 0.47 mmol, 1.0 eq.) was then added to the solution and magnetic agitation was continued for a further 2 hours. The solution was subsequently filtered to yield a deep purple mother liquor which, upon diffusion with Et$_2$O, resulted in the growth of dark purple crystalline blocks of 24 in 23 % yield.

**4.10.2.2.2 Method B:**

To a pale orange solution of Fe(NO$_3$)$_3$.9H$_2$O (0.25 g, 0.63 mmol, 1.0 eq.) in MeOH (30 cm$^3$) was added L$_1$H (0.102 g, 0.63 mmol, 1.0 eq.) and NaOMe (0.066 g, 1.23 mmol, 2.0 eq.). The now deep purple-black solution was stirred for a further 4 hours and subsequently filtered to yield a deep purple-black mother liquor. Et$_2$O diffusion of the mother liquor afforded dark purple crystalline blocks of 24 (as in Method A), suitable for X-ray analysis, in 20 % yield.

**C, H, N Elemental Analysis**

Calculated for: C$_{38}$H$_{46}$N$_6$O$_{16}$Na$_2$Fe$_2$

Theory (%): C (45.21), H (4.63), N (8.40).
Found (%): C (45.21), H (4.38), N (8.87).

_Infrared Spectroscopy (cm\textsuperscript{-1})_

1621 (vs), 1600 (s), 1559 (m), 1454 (m), 1405 (m), 1371 (s), 1344 (vs), 1303 (s), 1248 (s), 1198 (m), 1172 (m), 1076 (m), 1017 (m), 999 (m), 971 (m), 860 (m), 781 (m), 752 (m), 737 (m).

4.10.2.3 Synthesis of [Na(I)\textsubscript{2}Ni(II)\textsubscript{2}(\mu\textsubscript{3}-N\textsubscript{3})\textsubscript{2}(L\textsubscript{1})\textsubscript{4}(MeCN)\textsubscript{2}] (25)

To a solution of Ni(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O (0.25 g, 0.859 mmol, 1.0 eq.) in methanol (MeOH) (25 cm\textsuperscript{3}) was added L\textsubscript{1}H (0.142 g, 0.859 mmol, 1.0 eq.). NaN\textsubscript{3} (0.112 g, 1.718 mmol, 2.0 eq.) was then added to the transparent light green solution resulting in the solution gradually adopting a cloudy-green appearance. Solid NaOH (0.068 g, 1.718 mmol, 2.0 eq.) was then added to the solution with no immediate colour change. The solution was stirred at ambient temperature for a further 4 hours, after which time the solvent (MeOH) was evaporated to dryness. The light green residue was redissolved in MeCN (25 cm\textsuperscript{3}) and the solution stirred for ~1 hour at ambient temperature. The solution was then filtered and the light green mother liquor diffused with Et\textsubscript{2}O from which green rhombic crystals of 25 were harvested after ~1 week in 10 % yield (Figure 182).

Fig. 182 Rhomb-shaped crystals of 25 used for magnetic measurements (see Section 4.8.2 for magnetic data).

_C, H, N Elemental Analysis_

Calculated for: C\textsubscript{40}H\textsubscript{46}N\textsubscript{12}O\textsubscript{8}Na\textsubscript{2}Ni\textsubscript{2}

Theory (%): C (48.71), H (4.70), N (17.04).

Found (%): C (48.43), H (4.47), N (17.44).

_Infrared Spectroscopy (cm\textsuperscript{-1})_
4.10.2.4 Synthesis of $[\text{Ni(II)}_3(\mu-\text{OH})_2(L_1)_2(L_1\text{H})_2(H_2\text{O})_2](\text{NO}_3)_2$ (26)

To a solution of Ni(NO$_3$)$_2$.6H$_2$O (0.25 g, 0.859 mmol, 1.0 eq.) in MeOH (25 cm$^3$) was added L$_1$H (0.142 g, 0.859 mmol, 1.0 eq.) and the solution stirred to afford complete dissolution of the solid material. Solid sodium methoxide (NaOMe) (0.092 g, 1.70 mmol, 2.0 eq.) was then added which resulted in a change from a bright transparent yellow-green solution to a very slightly opaque dark green solution after ~20 minutes stirring under ambient conditions. Stirring was continued for a further 4 hours, after which time the solution was evaporated to dryness in vacuo. The resultant solid residue was redissolved in MeCN, filtered and aliquots of the resultant mother liquor diffused with Et$_2$O. Dark green X-ray quality crystalline blocks of 26 were isolated after ~ 1 week in very good yield (40 %).

$C, H, N$ Elemental Analysis

Calculated for: C$_{36}$H$_{48}$N$_6$O$_{20}$Ni$_3$

Theory (%): C (40.82), H (4.57), H (7.94).

Found (%): C (40.68), H (4.21), H (7.68).

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

3215 (b), 1629 (m), 1454 (m), 1440 (w), 1413 (w), 1391 (m), 1352 (w), 1300 (s), 1245 (m), 1218 (s), 1081 (m), 1043 (w), 1014 (m), 963 (m), 730 (s).

4.10.2.5 Synthesis of $[\text{Ni(II)}(L_1)_2]$ (27)

To a solution of NiCl$_2$.6H$_2$O (0.238 g, 1.0 mmol, 1.0 eq.) in MeOH (30 cm$^3$) was added L$_1$H (0.330 g, 2.0 mmol, 2.0 eq). The solution was stirred to dissolve the solid after which tetraethylammonium hydroxide (NEt$_4$OH) (1.47 cm$^3$ of a 40 % aq. Solution) (0.588 g, 4.0 mmol, 4.0 eq.) was added imparting a very dark red-brown colour to the solution. This solution gradually adopted a dirty-brown opaque appearance. The solution was stirred for a further 3 hours under ambient conditions and was subsequently filtered. Slow evaporation of
the filtered brown-black mother liquor afforded 27 as dark green crystalline blocks in 15 % yield.

*C, H, N Elemental Analysis*

Calculated for: C\textsubscript{18}H\textsubscript{20}N\textsubscript{2}O\textsubscript{4}Ni\textsubscript{1}

Theory (%): C (55.94), H (5.22), N (7.25).

Found (%): C (56.12), H (5.40), N (7.55).

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

3373 (b), 1616 (m), 1600 (m), 1547 (w), 1478 (m), 1449 (s), 1410 (m), 1334 (m), 1241 (s), 1228 (s), 1194 (m), 1171 (m), 1100 (m), 1076 (m), 1014 (m), 983 (m), 753 (m), 726 (s).

**4.10.2.6 Synthesis of [Na(I)\textsubscript{3}Ni(II)\textsubscript{2}(L\textsubscript{1})\textsubscript{6}](ClO\textsubscript{4}) (28)**

To a solution of Ni(ClO\textsubscript{4})\textsubscript{2}.6H\textsubscript{2}O (0.25 g, 0.68 mmol, 1.0 eq.) in MeOH (30 cm\textsuperscript{3}) was added L\textsubscript{1}H (0.112 g, 0.68 mmol, 1.0 eq.) and the solution stirred to afford complete dissolution of the solid material. Solid NaOH (0.04 g, 1.0 mmol, 1.5 eq.) was then added which afforded a lime-green solution. Stirring was continued for a further 4 hours after which time the solution was filtered and the mother liquor allowed to concentrate via slow solvent evaporation. Following a lack of crystallisation from the MeOH mother liquor, the evaporated residue was redissolved in CH\textsubscript{2}Cl\textsubscript{2} (10 cm\textsuperscript{3}). The resultant solution was again filtered and samples of this mother liquor were diffused with Et\textsubscript{2}O. Green, crystalline blocks of 28 suitable for X-ray analysis, were obtained via this route in 30 % yield.

*C, H, N Elemental Analysis*

Calculated for: C\textsubscript{54}H\textsubscript{60}N\textsubscript{6}O\textsubscript{16}Cl\textsubscript{1}Na\textsubscript{3}Ni\textsubscript{2}

Theory (%): C (51.03), H(4.76), N(6.61).

Found (%): C (50.45), H(4.80), N(7.02).

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

3063 (w), 2894 (w), 2850 (s), 2789 (w), 1631 (s), 1595 (s), 1547 (w), 1453 (s), 1396 (s), 1319 (w), 1213 (s), 1168 (w), 1142 (w), 1077 (s), 967 (s), 872 (w), 851 (m), 778 (w), 728 (s).
4.10.2.7 Synthesis of $[\text{Mn(III)}_1(L_1)_2\text{Cl}]_n$ (29)

To a solution of $\text{MnCl}_2.4\text{H}_2\text{O}$ (0.25 g, 1.26 mmol, 1.0 eq.) in MeOH (25 cm$^3$) was added $L_1\text{H}$ (0.208 g, 1.26 mmol, 1.0 eq.). Solid NaOH (0.050 g, 1.26 mmol, 1.0 eq.) was then added affording a very dark brown solution over the course of ~10 minutes. The solution was stirred for a further 3 hours after which it was filtered to afford a dark red-brown mother liquor. Et$_2$O diffusion of this mother liquor yielded 29 as reddish brown crystalline tabloid-shaped blocks in 35-40% yield.

$C, H, N$ Elemental Analysis

Calculated for: $C_{18}H_{20}N_2O_4\text{Cl}_1\text{Mn}_1$

Theory (%): C (51.61), H (4.78), N (6.69).

Found (%): C (51.30), H (4.74), N (6.40).

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

1618 (s), 1595 (s), 1551 (m), 1472 (w), 1445 (s), 1434 (s), 1401 (m), 1382 (w), 1306 (s), 1254 (s), 1220 (s), 1101 (m), 1078 (s), 1007 (m), 973 (m), 960 (m), 738 (s).

4.10.2.8 Synthesis of $[\text{Mn(III)}_3\text{Mn(IV)}_1(\mu_3-O)_3(\mu_3-O\text{Et})(L_1)_3(\text{OAc})_3]$ (30)

To a solution of $\text{Mn(OAc)}_2.4\text{H}_2\text{O}$ (0.25 g, 1.02 mmol, 1.0 eq.) in EtOH (25 cm$^3$) was added $L_1\text{H}$ (0.168 g, 1.02 mmol, 1.0 eq.). The addition of $L_1\text{H}$ gradually afforded a dark red-brown solution after ~10 minutes stirring under ambient conditions. The solution was stirred for a further 24 hours and subsequently filtered to afford a brown-black mother liquor. Et$_2$O diffusion of the mother liquor afforded 30 as dark brown-black blocks in 20% yield after 7 days.

$C, H, N$ Elemental Analysis

Calculated for: $C_{35}H_{44}N_3O_{16}\text{Mn}_4$

Theory (%): C (42.79), H (4.51), N (4.28).

Found (%): C (42.59), H (4.33), N (4.20).
**Infrared Spectroscopy (cm$^{-1}$)**

1630 (m), 1595 (w), 1551 (s), 1440 (s), 1408 (m), 1385 (w), 1336 (w), 1298 (s), 1238 (s), 1225 (s), 1081 (m), 1056 (w), 1017 (m), 972 (m), 861 (s), 787 (w), 738 (s).

**Table 13** BVS results for Mn(III)/Mn(IV) centres in complex 30.

<table>
<thead>
<tr>
<th>Calculated as:</th>
<th>Mn1</th>
<th>Mn2</th>
<th>Mn3</th>
<th>Mn4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(III)</td>
<td>3.99</td>
<td>3.01</td>
<td>2.99</td>
<td>3.09</td>
</tr>
<tr>
<td>Mn(IV)</td>
<td>3.91</td>
<td>2.96</td>
<td>2.94</td>
<td>3.03</td>
</tr>
</tbody>
</table>

**4.10.2.9 Synthesis of [Fe(III)$_4$(L)$_2$Cl] (31)**

To a solution of FeCl$_2$.4H$_2$O (0.25 g, 1.26 mmol, 1.0 eq.) in EtOH (25 cm$^3$) were added L$_1$H (0.208 g, 1.26 mmol, 1.0 eq.) and NaOAc (0.207 g, 2.52 mmol, 2.0 eq.). The resultant opaque red-black solution was stirred for a further 24 hours under ambient conditions. The solution was subsequently filtered and the mother liquor allowed to concentrate to encourage crystallisation. The mononuclear product 31 was isolated as X-ray quality red-brown blocks, suitable for X-ray analysis in low yield (10%) after ~2 weeks.

*C, H, N Elemental Analysis*

Calculated for: C$_{18}$H$_{20}$N$_2$O$_4$Cl$_1$Fe$_1$

Theory (%): C (51.54), H (4.81), N (6.68).

Found (%): C (51.50), H (4.45), N (6.50).

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

1624 (s), 1594 (m), 1556 (m), 1479 (w), 1448 (s), 1431 (m), 1407 (m), 1395 (m), 1300 (s), 1249 (s), 1222 (s), 1193 (m), 1172 (m), 1098 (m), 1078 (m), 1006 (m), 968 (m), 862 (m), 785 (m), 744 (s).

**4.10.2.10 Synthesis of [Ni(II)$_4$(μ$_3$-OMe)$_4$(L)$_5$]$_4$(MeOH)$_4$ (32)**

To a solution of Ni(NO$_3$)$_2$.6H$_2$O (0.25g, 0.859 mmol, 1.0 eq.) in MeOH (30 cm$^3$) was added L$_5$H (0.21 g, 1.37 mmol, 1.6 eq.) and NaOMe (0.046 g, 0.859 mmol, 1.0 eq.) to afford a dark
green transparent solution. The solution was stirred for a further 5 hours under ambient conditions and was subsequently filtered. The product was allowed to crystallise from the mother liquor via slow solvent evaporation. Dark green X-ray quality plate-like crystals of 32 were harvested directly from the mother liquor in good yield (30 %) after ~ 1 month.

**C, H, N Elemental Analysis**

Calculated for C$_{40}$H$_{60}$N$_{4}$O$_{16}$Ni$_{4}$

Theory (%): C (42.79), H (4.51), N (4.28).

Found (%): C (42.59), H (4.33), N (4.20).

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

1626 (s), 1607 (m), 1539 (m), 1468 (m), 1444 (w), 1434 (w), 1239 (m), 1202 (m), 1055 (m), 1037 (m), 961 (m), 943 (w), 746 (m), 726 (m).

**Uv-vis Analysis**

UV-vis analyses of 32 identifies similar absorption behaviour to those of its [M$_{7}$] counterparts, with ligand-centric absorptions much more pronounced here due to the system’s less symmetrical nature with respect to the heptanuclear disc topology (Figure 183). Characteristic $\pi\rightarrow\pi^*$ transitions are evidenced by absorptions at 220 and 264 nm (with $\varepsilon$ values 81.99 and 50.00 dm$^3$ mol$^{-1}$ cm$^{-1}$ respectively) while the absorption at 336 nm ($\varepsilon$ of 16.15 dm$^3$ mol$^{-1}$ cm$^{-1}$) is representative of a $n\rightarrow\pi^*$ excitation.

MeCN: $\lambda_{max}$, nm ($\varepsilon_{max}$, 10$^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$): 336 (16.15), 264 (50.00), 220 (81.99).

---

**Fig. 183** UV-vis spectrum for a solution of 32 in MeCN showing significant $\pi\rightarrow\pi^*$ excitations at 220 / 264 nm and a $n\rightarrow\pi^*$ excitation at 336 nm.
Tables of Crystallographic Data
Table 14 Crystallographic data for complexes 24-28.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(24)</th>
<th>(25)</th>
<th>(26)</th>
<th>(27)</th>
<th>(28)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{39}H_{49}N_{6}O_{17}Na_{2}Fe_{2}</td>
<td>C_{40}H_{46}N_{12}O_{8}Na_{2}Ni_{2}</td>
<td>C_{44}H_{50}N_{6}O_{17}Ni_{3}</td>
<td>C_{18}H_{30}N_{6}O_{4}Ni_{2}</td>
<td>C_{54}H_{60}N_{6}O_{1}Cl_{16}Na_{3}Ni_{2}</td>
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<tr>
<td>M_r (g mol^{-1})</td>
<td>1031.52</td>
<td>986.29</td>
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<tr>
<td>Crystal Appearance</td>
<td>Dark red parallelepiped</td>
<td>Green Parallelepiped</td>
<td>Green Block</td>
<td>Green Parallelepiped</td>
<td>Green Block</td>
</tr>
<tr>
<td>Crystal Dimensions (mm x mm x mm)</td>
<td>0.25 x 0.15 x 0.15</td>
<td>0.25 x 0.20 x 0.15</td>
<td>0.30 x 0.20 x 0.10</td>
<td>0.25 x 0.10 x 0.10</td>
<td>0.50 x 0.40 x 0.20</td>
</tr>
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<td>Crystal system</td>
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<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Trigonal</td>
</tr>
<tr>
<td>Space group</td>
<td>P 21/n</td>
<td>P21/n</td>
<td>C2/c</td>
<td>P 21/c</td>
<td>P 3</td>
</tr>
<tr>
<td>a / Å</td>
<td>11.6905(5)</td>
<td>11.663(2)</td>
<td>21.427(2)</td>
<td>9.942(2)</td>
<td>13.808(2)</td>
</tr>
<tr>
<td>b / Å</td>
<td>11.1560(5)</td>
<td>11.884(2)</td>
<td>12.4420(3)</td>
<td>5.3344(11)</td>
<td>13.808(2)</td>
</tr>
<tr>
<td>c / Å</td>
<td>19.0629(9)</td>
<td>15.975(3)</td>
<td>21.3877(7)</td>
<td>15.923(3)</td>
<td>90</td>
</tr>
<tr>
<td>α (°)</td>
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<td>90</td>
<td>90.00</td>
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<tr>
<td>β (°)</td>
<td>93.391(4)</td>
<td>98.72(3)</td>
<td>90.00</td>
<td>105.71(3)</td>
<td>120.00</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V / Å^3</td>
<td>2481.82(19)</td>
<td>2188.5(8)</td>
<td>4903.9(3)</td>
<td>812.9(3)</td>
<td>2857.8(8)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>T / K</td>
<td>150 (2)</td>
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<td>149.9</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>λ^2 / Å</td>
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<td>0.71070</td>
<td>0.7107</td>
<td>0.7107</td>
<td>0.7107</td>
</tr>
<tr>
<td>D^2 / g cm^{-3}</td>
<td>1.380</td>
<td>1.497</td>
<td>1.437</td>
<td>1.581</td>
<td>1.477</td>
</tr>
<tr>
<td>μ (Mo-Kα) / mm^{-1}</td>
<td>0.674</td>
<td>0.946</td>
<td>1.217</td>
<td>1.220</td>
<td>0.802</td>
</tr>
<tr>
<td>Meas. / Indep. (R_{m}) reflections</td>
<td>4336 / 2737 (0.0956)</td>
<td>3991 / 3584 (0.0171)</td>
<td>4475 / 3785 (0.0252)</td>
<td>1491 / 1341 (0.0164)</td>
<td>2834 / 2239 (0.0267)</td>
</tr>
<tr>
<td>wR_2 (\text{all data})</td>
<td>0.3012 (4336)</td>
<td>0.0674 (3991)</td>
<td>0.2416 (4475)</td>
<td>0.0634 (1491)</td>
<td>0.2481 (2834)</td>
</tr>
<tr>
<td>R_{w}^{a,b} (reflections)</td>
<td>0.1086 (2737)</td>
<td>0.0255 (3584)</td>
<td>0.0736 (3785)</td>
<td>0.0228 (1341)</td>
<td>0.1108 (2239)</td>
</tr>
<tr>
<td>Goodness of fit (GOOF) on F^2</td>
<td>1.145</td>
<td>1.108</td>
<td>1.167</td>
<td>1.097</td>
<td>1.254</td>
</tr>
</tbody>
</table>

*a Mo-Kα radiation, graphite monochromator. b wR_2 = \[ \sum w(IF_0^2 - IF_c^2)^2 / \sum wIF_0^2 I^2 \]^{1/2}, c For observed data.

d \(R_i = \sum I_c^2 F_0 - IF_c I^2 / \sum IF_c I\)
Table 15 Crystallographic data for complexes 29-32.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(29)</th>
<th>(30)</th>
<th>(31)</th>
<th>(32)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{18}H_{20}N_{2}O_{4}Cl_{1}Mn_{1}</td>
<td>C_{18}H_{20}N_{2}O_{4}Cl_{1}Mn_{4}</td>
<td>C_{18}H_{20}N_{2}O_{4}Cl_{1}Fe_{1}</td>
<td>C_{30}H_{60}N_{4}O_{16}Ni_{4}</td>
</tr>
<tr>
<td>( M_r ) (g mol(^{-1}))</td>
<td>418.75</td>
<td>982.49</td>
<td>419.66</td>
<td>1087.76</td>
</tr>
<tr>
<td>Crystal Appearance</td>
<td>Brown Tabloid</td>
<td>Black Block</td>
<td>Red Irregular Crystal</td>
<td>Green Parallelpiped</td>
</tr>
<tr>
<td>Crystal Dimensions (mm x mm x mm)</td>
<td>0.15 x 0.10 x 0.08</td>
<td>0.50 x 0.40 x 0.20</td>
<td>0.10 x 0.08 x 0.04</td>
<td>0.15 x 0.10 x 0.08</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>C 2/c</td>
<td>P 21 21 21</td>
<td>Pbcn</td>
<td>I ( 4_1 /a )</td>
</tr>
<tr>
<td>( a / \AA )</td>
<td>14.731(3)</td>
<td>11.6508(4)</td>
<td>18.7892(17)</td>
<td>22.187(3)</td>
</tr>
<tr>
<td>( b / \AA )</td>
<td>12.851(3)</td>
<td>16.9627(6)</td>
<td>7.3665(7)</td>
<td>22.187(3)</td>
</tr>
<tr>
<td>( c / \AA )</td>
<td>9.6901(19)</td>
<td>20.6910(7)</td>
<td>13.2831(11)</td>
<td>9.5524(19)</td>
</tr>
<tr>
<td>( \alpha (^\circ) )</td>
<td>90</td>
<td>90</td>
<td>90.00</td>
<td>90</td>
</tr>
<tr>
<td>( \beta (^\circ) )</td>
<td>106.66(3)</td>
<td>90</td>
<td>90.00</td>
<td>90</td>
</tr>
<tr>
<td>( \gamma (^\circ) )</td>
<td>90</td>
<td>90</td>
<td>90.00</td>
<td>90</td>
</tr>
<tr>
<td>( V / \AA^3 )</td>
<td>1757.3(6)</td>
<td>4089.1(2)</td>
<td>1838.5(3)</td>
<td>4702.1(13)</td>
</tr>
<tr>
<td>( Z )</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>( T / K )</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>( \lambda / \AA )</td>
<td>0.71070</td>
<td>0.71070</td>
<td>0.7107</td>
<td>0.71070</td>
</tr>
<tr>
<td>( D^\circ / g \text{ cm}^{-3} )</td>
<td>1.583</td>
<td>1.596</td>
<td>1.516</td>
<td>1.537</td>
</tr>
<tr>
<td>( \mu (\text{Mo-K}\alpha) / \text{mm}^{-1} )</td>
<td>0.930</td>
<td>1.280</td>
<td>0.991</td>
<td>1.648</td>
</tr>
<tr>
<td>Meas. / Indep. (( R_{int} )) reflections</td>
<td>1610 / 1374 (0.0657)</td>
<td>6272 / 4611 (0.0599)</td>
<td>1676 / 1257 (0.0346)</td>
<td>2060 / 1134 (0.5545)</td>
</tr>
<tr>
<td>( wR^2 ) (all data)</td>
<td>0.176 (1610)</td>
<td>0.0946 (6272)</td>
<td>0.1311 (1676)</td>
<td>0.1161 (2060)</td>
</tr>
<tr>
<td>( R_{int}^{a,b} ) (reflections)</td>
<td>0.0665 (1374)</td>
<td>0.0544 (4611)</td>
<td>0.0377 (1257)</td>
<td>0.0574 (1134)</td>
</tr>
<tr>
<td>Goodness of fit (GOOF) on ( F^2 )</td>
<td>1.067</td>
<td>1.001</td>
<td>1.176</td>
<td>0.818</td>
</tr>
</tbody>
</table>

\(^{a}\)Mo-K\(\alpha\) radiation, graphite monochromator. \(^{b}\) \( wR^2 = \left[ \sum w(I_F^2 - I_{\text{c}}^2 I)^2 / \sum wIF_i^2 I^2 \right]^{1/2} \). \(^{c}\) For observed data.

\( d \) \( R_i = \left[ \sum I_i^2 F_i^0 / \text{IF}_{\text{c}}^2 \right] / \sum I_{\text{c}}^2 \).
4.11 References


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Chapter Five

Concluding Remarks and Future Outlook
5.1 Introduction

This section discusses whether the aims of the thesis were met, answering the questions posed at the start of the thesis: Do the Schiff base ligands 2-iminomethyl-6-methoxyphenol (L₁H) and analogues thereof (Figure 184) allow for the synthesis of self-assembled molecular flasks capable of encapsulating smaller guest molecules? Additionally, do the self-assembled architectures (if isolated) incorporate magnetically interesting host units when L₁H and its analogues are combined with 1st row (3d) transition metal ions? As well as reviewing the utility of L₁H and its analogues in the synthesis of polymetallic cluster complexes described in this thesis, the potential applications of these clusters in the fields of host-guest chemistry and molecular magnetism have been discussed.

Fig. 184 (a) o-Vanillin precursor, (b) the Schiff base ligand L₁H and (c) functionalised Schiff base analogues: R = Br, R' = Me (L₂H); R = H, R' = Ph (L₃H); R = Ph, R' = Me (L₄H), R = H, R' = H (L₅H).

5.2 Local Conclusions

5.2.1 Novel host-guest architectures containing L₁H (or its analogues)

Chapter Two introduced the first Schiff base ligand to be used in this research towards molecular capsule generation; that of 2-iminomethyl-6-methoxyphenol (L₁H). Inspection of the structure of L₁H readily identifies it as effectively ¼ of the common cyclophane calix[4]arene (Figure 185). Calix[4]arene and its derivatives have been widely utilised in host-guest chemical sensing, as highlighted in a recent review by Kim and co-workers, for the
detection of cations, anions and hydrocarbons.\(^1\) \(L_1H\) also has numerous donor sites for potential coordination to metal ions (Figure 185). It was thus believed that using highly paramagnetic 3d metal ions as a platform for cluster growth calixarene complex architectures could be generated \textit{in situ}, towards potential host-guest applications. We were successful in this regard and reported the synthesis and characterisation of a family of ferromagnetic planar disc-like \(\text{[Ni(II)}_7\) complexes (1-4), which possess double-bowl pseudo metallocalix[6]arene topologies. These double-bowl units are templated by \(\text{NO}_3^-\) counter anions, generating molecular cavities that allow for encapsulation of a wide variety of guest molecules (\(\text{NO}_2\text{Me}, \text{MeCN}, \text{MeOH}, 2\)-Furaldehyde, 3-Furaldehyde); in turn allowing for direct comparison to supramolecular calix[n]arene behaviour (Figures 185 and 186).

**Fig. 185** (left) Structure of calix[4]arene (exhibiting the cone conformation in this case) and (right) structure of \(L_1H\); effectively one-quarter of a calix[4]arene molecule.

We showed how functionalisation of \(L_1H\) at the imino nitrogen atom site and also at the 4-position of the phenol ring (Figure 184) allowed for alteration of cavity size and shape towards selective guest encapsulation. For instance, complex 4 isolated using \(L_2H\) exhibited a crystal packing arrangement whereby the individual \([\text{Ni(II)}_7]\) units interlocked one another thus affording a more tightly-enclosed cavity which allowed for encapsulation of two \(\text{MeCN}\) molecules. In contrast complex 2 exhibited a packing arrangement whereby the heptanuclear \([\text{Ni(II)}_7]\) units simply rested one on top of the other forming a less tightly bound molecular capsule.

Additionally we synthesised the Zn(II) and Co(II/III) analogues to complexes 1-4 by simply employing a different transition metal salt in the synthon, affording the polynuclear systems 5-6 and 7-10 respectively. Reproducibility, stability and retainment of the core topology in this manner, despite moving across the 1\(^{\text{st}}\) row of the \(d\)-block, is extremely rare with respect to polynuclear assemblies. Cooper and co-workers have reported the synthesis of \([M_{12}] (M =\)
Co, Ni) polymetallic clusters using \textit{trans}-1,3,5-triaminocyclohexane exhibiting similar coordination behaviour.\(^2\) Additionally, the ferromagnetic Ni(II) and Co(II) hexamers incorporating azide- (\(\text{N}_3^–\)) and oxo-bridges reported by Wang and co-workers retain a common core topology even on moving from Co(II) to Ni(II).\(^3\) The heptanuclear disc-like clusters (\textbf{1-10}) represent additional members of this family of compounds exhibiting such coordination behaviour and contribute to the knowledge-base required towards fully directing the synthesis of large polymetallic complexes.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig186.png}
\caption{(left) Generation of molecular cavities via templation of NO\(_3^–\) anions (represented as space-filled spheres) between pairs of [M(II)\(_7^\)] double-bowl units. (right) Schematic of molecular cavities formed via stacking of individual double-bowl units and which allow for encapsulation of a variety of molecular guests. Colour code: Ni = green, O = red, N = blue, C = grey. Hydrogen atoms have been omitted for clarity.}
\end{figure}

The isolation of our pseudo metallocalix[6]arene double-bowl complexes spurred investigations into whether or not we could alter the magnetic characteristics of these systems and / or introduce a duality into the calix[6]arene framework, via the inclusion of an alternative guest in the molecular cavities formed therein. A recent report by Liu and co-workers described the encapsulation of 2-Furaldehyde and 3-Furaldehyde isomers within a porous Cd(II)-triazole metal-organic framework (MOF) with subsequent alteration of the spectral and magnetic properties therein (arising from radical generation).\(^4\) We thus believed that these molecules would be ideal candidates towards encapsulation within the molecular cavities of our double-bowl systems (Figure 186). We were successful in this regard with the isolation of the [Zn(II)\(_7^\)]-based furaldehyde encapsulated complexes \textbf{14, 16-18} of general formula \([(\text{Fur})\subset\text{M(II)}\subset(\text{OH})\subset(\text{L}_1\subset)(\text{NO}_3)\subset2\text{ (Fur = 2- or 3-Furaldehyde and M = Ni, Co, Zn)}\)
and the complex [(2-Fur)⊂Zn(II)₇(OMe)₆(L₁)₆](NO₃)₂ (15). Infrared and EPR spectroscopic measurements were utilised to detect the presence of acyl radical species (originating from furaldehyde guests) (Figure 187) generated within the molecular cavities of our double-bowl complexes. Future work will encompass in situ photolysis EPR measurements using a 350 nm optical probe (a wavelength known to promote homolytic cleavage of furaldehyde guests to form σ-type radicals). This work may lead to further investigations in which we perform radical reactions within the confines of our double-bowl pseudo metallocalix[6]arene cavities (see Section 1.2.4.1).

**Fig. 187** (left) 2-Furaldehyde and (right) 3-Furaldehyde isomers utilised in attempts to generate radical species within the double-bowl molecular cavities of [M(II)₇] metallocalix[6]arenes.

In addition, we were successful in significantly altering the bowl dimensions of our double-bowl complexes via functionalisation of the Schiff base ligand used. The complexes of general formulae [M(II)₇(OMe)₄(OEt)₂(L₄)₆](NO₃)₂ (M = Co (19), Ni (20), Zn (21) and L₄ = deprotonated L₄H Schiff base ligand) exhibited bowl dimensions which exceeded those of its siblings [Co(II)₇(OH)₆(L₁)₆](NO₃)₂ (7) and [(MeOH)₂⊂Co(II)₇(OH)₆(L₁)₆](NO₃)₂ (8) (Chapter Two). Future work in this regard will involve further functionalisation of the Schiff base ligand utilised towards templation of individual double-bowl units and thus molecular cavity generation and encapsulation of larger guest molecules such as amino acids. The work described in Chapters Two and Three of this thesis which involved the synthesis and characterisation of [M₇] pseudo metallocalix[6]arene discs (M = Ni(II), Zn(II), Co(II/III)) is summarised in Figure 188.
Fig. 188 Summary of complexes reported in Chapter Two and Chapter Three of this thesis.
5.2.2 Modification of the general \([\text{M(II/III)}_7]\) Synthesis leads to a New Family of Homo- and Heterometallic 3d Complexes

In attempts to extend our family of pseudo metallocalix[6]arene host-guest complexes, we proposed that modification of the reaction conditions used in their synthesis may allow for encapsulation of guest molecules of varying size and / or shape. Such modifications instead yielded a large collection of homo- and heterometallic planar, cubane and chain-like complexes (24-32), themselves exhibiting interesting structural and magnetic characteristics. Of these, the tetranuclear cubane species \([\text{Mn(III)}_3\text{Mn(IV)}_1(\text{O})(\text{OEt})(\text{OAc})_3(\text{L}_1)_3]\) (30) and \([\text{Ni(II)}_4(\mu_3-\text{OMe})_4(\text{L}_5)_4(\text{MeOH})_4]\) (32) are attracting ever-increasing interest across a broad range of research fields from both a structural and magnetochemistry viewpoint, as well as for host-guest and catalysis applications. Leeland et al recently reported the synthesis of a magnesium hydroxide cubane complex, which was shown to exhibit guest characteristics within its bowl-shaped macrocyclic host via supramolecular interactions and metal-ligand bond formation.\(^5\) They elegantly showed that by hydrolysis of the bimetallic magnesium-based precursor a novel tetranuclear cubane species could be generated. Interest in cubane species is not restricted to the study of host-guest systems, with recent attention being afforded to their use as catalysts in the oxidation of hydrocarbons and other organic molecules. For instance, Thakurta et al recently reported the catalytic activity of a tetranuclear \([\text{Cu}_4]\) Schiff base complex towards the oxidation of a variety of hydrocarbons including cyclohexane and cycloheptane by \(\text{H}_2\text{O}_2\).\(^6\) Results from this research (Thakurta et al) have shown that the tetranuclear topology is exceedingly important since, in contrast, simple copper salts like \(\text{Cu(NO}_3)_2.3\text{H}_2\text{O}\) exhibit far less catalytic activity towards the same oxidisable, hydrocarbon precursors. Indeed, it is readily apparent that \([\text{M}_4]\) cubane systems are drawing the attention of research clusters in disparate fields with \([\text{M}_4]\) systems reported in this thesis adding greatly to the knowledge-base in this branch of coordination chemistry. The work described in Chapter Four of this thesis which involved the synthesis and characterisation of a variety of homo- and heterometallic planes, chains and cubanes is summarized in Figure 189.
Fig. 189 Summary of complexes reported in Chapter Four of this thesis.
5.3 Global Conclusions

5.3.1 Future Work

This section details the future course of research involving the double-bowl pseudo metallocalix[6]arene disc complexes discussed in Chapter Two and Chapter Three.

5.3.1.1 Solid-State NMR and Doping Studies

As previously described (Section 2.2.8), the fitting or simulation of magnetic data for complexes 1 and 4 is problematic, primarily as a result of the presence of numerous different exchange interactions and the presence of relatively strong intermolecular interactions. The first step employed in this thesis towards resolving this difficulty lay in the isolation of the diamagnetic [Zn(II)₇] analogues 5 and 6. It was additionally hoped that, being diamagnetic, NMR titrations of 5 and 6 incorporating a variety of different guests would allow for characterisation of guest behaviour within the host framework. However, the poor solubility of these [Zn(II)₇] heptanuclear complexes at concentrations sufficient for NMR meant that solution state host-guest measurements were not feasible. Solid-state NMR spectroscopy is therefore proposed as a viable tool for confirming loss or residency of guests. Additionally, it is hoped that doping [Zn(II)₇] with small amounts of Co(II) or Ni(II) ions may afford magnetically dilute systems which can be analysed via EPR spectroscopy (Figure 190). Isolation of magnetically dilute systems (thus elimination of erroneous intermolecular interactions) means that the magnetic coupling parameter J may be obtained. EPR measurements would then allow us to determine the exact ratio of Zn(II):Ni(II) or Co(II) in the [M(II)₇] array. Inductively coupled plasma mass spectrometry (ICP-MS) would also facilitate such measurements. Doping studies have already been initiated, with crystals of doped [Zn(II)₇] awaiting analysis via EPR spectroscopy (Figure 191).
Fig. 190 Schematic representation of the doping process showing (left) the undoped \([\text{Zn(II)}_7]\) system and (right) the \([\text{M(II)}_7]\) array after doping with Ni(II). The location of the Ni(II) ion in the doped system shown is for illustration purposes only. The position of the dopant in the real system will be governed by a statistical distribution. Colour code: Zn = blue, Ni = green, O = red. Hydrogen atoms have been omitted for clarity.

Fig. 191 (left) Microscope image of a crystal of the undoped \([\text{Zn(II)}_7]\) system. (right) Microscope image of the doped Zn(II)-Co(II) analogue (concentration of Co(II) = 10% by mass).

5.3.1.2 Gas Storage

Industrial application of macrocyclic compounds is being increasingly focused on the development of porous materials towards gas storage and sequestration, stemming from the widening scarcity of fossil fuels and associated environmental pollution. At the forefront of this research are macrocyclic calixarene systems which may be readily functionalised towards selective gas adsorption.\(^8\)-\(^{10}\) It is believed that the molecular cavities generated in the empty heptanuclear \([\text{M(II)}_7]\) complexes \([\text{Ni(II)}_7(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2\) (1) and \([\text{Co(II)}_7(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2\) (7) may allow for the storage of CO\(_2\) and / or H\(_2\) (cavity volume in
1 = 265.9 Å³). To this end, future work will involve gas storage in 1 and 7 and the alteration of the size and/or shape of the molecular cavities therein, towards tailored storage materials.

5.3.1.3 Functionalisation of Schiff base: Towards Aqueous Solubility

It is our enduring goal to encapsulate ever more interesting guests of varying size and shape towards potential useful applications. With this in mind, we believe that further functionalisation at the upper-rim position of our pseudo metallocalix[6]arenes (specifically the 4-position of the phenol ring of the Schiff base) may afford a much larger double-bowl molecular cavity towards encapsulation of a wider range of guest molecules. There have been several reports to date describing the use of polyether linkages in the generation of macromolecular species including amphiphilic cavitands.11,12 We propose a similar synthetic route in attempts to solubilize our [M(II)₇] systems. Synthesis will initially involve catalytic hydrogenation of commercially available 3-methoxy-5-nitrosalicylaldehyde 1 at the 5-position of the aldehyde to form the corresponding amine 2 (Figure 192). The next step will involve the extension of a tetraethylene glycol species via reaction with ethyl acrylate which will subsequently be converted to the acid chloride 3 (Figure 192).11,12 Reaction of 2 and 3 then yields the aldehyde 4, functionalised at the upper-rim position. The Schiff base will then be isolated via reaction of 4 with MeNH₂, as in the synthesis of L₁H, L₂H and L₄H. The potential aqueous solubility imparted onto our [M(II)₇] systems via functionalization of the Schiff base employed may allow for sequestration of toxic industrial chemicals (TICs) such as thiols, H₂S and NOₓ gases. Additionally, aqueous solubility of our [M(II)₇] systems may potentially allow for their use as imaging agents.
Fig. 192 Synthetic route describing the functionalisation of the Schiff base towards aqueous solubility of our [M(II)] systems.

5.3.1.4 Chemical Sensor Materials

The ability to selectively encapsulate guest molecules within molecular cavities generated in our double-bowl pseudo metallocalix[6]arene complexes discussed in this thesis posed the question: can these macrocyclic compounds act as hosts for fluorophore / quencher species and thus behave as chemical sensors? (Section 1.2.5.1). Our work in this area has already begun, as described in Chapter Three, with the encapsulation of 2-Furaldehyde species. Future work will involve further functionalisation of templating Schiff base ligands towards cavity size / shape alteration. With this, it may be possible to encapsulate highly fluorescent fluorophores such as quantum dots (QDs) within the cavities generated in the empty complexes 1 and 7 (i.e. no guests). Success in this field has been recently reported using CdSe/ZnS QDs and the smaller calix[4]arene species.\(^1\) In addition to novel optical and
electrical properties quantum dots also have the added advantages of extreme brightness and high photostability.

5.4 Final remarks

This thesis has described a broad range of 3d transition metal complexes based on Ni(II), Co(II/III), Zn(II), Mn(III/IV) and Fe(III), incorporating L1H and its Schiff base ligand analogues (LxH; x = 2-5). Isolation of these structures has not only addressed the question posed at the start of the thesis regarding the potential of complexes incorporating these ligands towards molecular capsule generation, but they have also highlighted the sensitivity of the crystallisation process. For instance, anion substitution reduces the nuclearity of the complex isolated from seven ([NO3]2Co(III)1Co(II)b(OH)6(L3)6(NO3)3MeCN (9)) to one ([Co(II)1(L3)2] (13)). Indeed, by utilisation of additional bridging species such as MeO⁻ and azide (N3⁻), we were able to isolate polynuclear architectures exhibiting different complex structures exemplified by [Na(I)2Fe(III)2(OMe)2(L1)4(NO3)2.2MeOH (24) and [Na(I)2Ni(II)2(µ3-N3)2(L1)4(MeCN)]2 (25), each comprising the molecular butterfly topology. While supramolecular solid-state host-guest encapsulation involving polynuclear clusters has been a research field of increasing interest over the last twenty years, it has witnessed a pronounced resurgence in recent times, due to its many and varied applications such as gas storage, chemical sensing, drug delivery and medical imaging. While difficulties remain in terms of controlling and directing the synthesis of large polynuclear clusters, it is paramount that research continues into the development of such compounds and that novel synthetic strategies are conceived to allow academic research to be translated into functional materials for a rapidly changing society.
5.5 References

(10) Zyryanov, G. V.; Kang, Y.; Rudkevich, D. M. J. Am. Chem. Soc. 2003, 125, 2997-3007.
Appendix
Section A: Magnetic Resonance Imaging (MRI) Contrast Agents

Initial discussions focused on the development of supramolecular host-guest systems for applications including catalysis, sensing and drug delivery (see Section 1.2 for further details). There has, however, been a growing desire to combine the inclusion characteristics of host-guest complexes with those of molecular magnetism to aid in the isolation of multifunctional materials; a concept illustrated in greater detail in the examples which follow. While most of the above examples, as well as most host-guest systems in general, involve host-guest interactions between organic moieties and diamagnetic species such as Zn(II) or purely organic molecular containers with diamagnetic molecular organic guests, a field of host-guest chemistry still in its infancy involves the development of magnetically interesting host-units. One may ask the question: Why should the development of such ‘magnetically interesting’ host species be of any importance? One of the most apparent answers to this question is in the field of medical imaging and biology. Originally, magnetic resonance imaging (MRI) contrast agents were host-guest systems comprised of a highly paramagnetic metal ion docked within the cavity of a macrocyclic, species (Figure 193). The metal ion utilised is usually a lanthanoid (more specifically Gd(III)) stemming from the large ground spin state (large S: many unpaired electrons) observed for such species. More recently, however, encapsulated iron-oxide nano particles within an organic host framework have demonstrated exceptional utility as MRI agents. Commercial names for some well-known contrast agents include Dotarem (Gd(III)), Magnevist (Gd(III)) and Lumirem (Fe-oxide) (Figure 194). The use of MRI contrast agents alters the relaxation rates of tissue protons, ultimately allowing for enhanced selectivity and tissue specificity in the MRI technique; thus affording a more effective diagnostic procedure for detection of cancerous growths and tumors.
Fig. 193 (left) Schematic of a Host-Guest complex. (right) Crystal structure of a Gd(III)-based contrast agent.¹

Fig. 194 Structures of two common Gd(III)-based contrast agents (left = Dotarem, right = Magnevist).

A.1 Recent Developments in MRI Contrast Agent Synthesis

The discussion above highlighted some of the principal contrast agents in use at present, however there are many newly emerging architectures under investigation as potential MRI probes of biological systems. Iron-oxide (Fe₂O₃) nanoparticles are increasingly used as contrast agents in MRI imaging procedures, to this end Gao and co-workers have developed a nanoparticle-based system consisting of an Fe₂O₃ core encapsulated within an FePt capsule / shell (Figure 195).² As was evident in Chapter Two of this thesis, multifunctional materials are an enduring pursuit of researchers as they allow for multiple functions to be effected from a single supramolecular assembly. In the above assembly, the Fe₂O₃ allows for enhanced contrast in MRI while incorporation of an FePt core, as reported, affords anticancer characteristics to the host-guest system. For instance, Gao and co-workers reported significant cytotoxicity in their host-guest system towards HeLa cells. Stemming from the latter point, this FePt-Fe₂O₃ dual system allows for ‘anchoring’ of targeted cancer cells on the
capsule surface, which may be functionalised via the inclusion of various molecular anchors such as dopamine.

Fig. 195 (left) FePt nanoparticle imaging agent developed by Gao and co-workers. (right) HeLa cells towards which the FePt imaging agent showed significant cytotoxicity.  

Similar nanoparticle, host-guest architectures towards imaging have been developed by Chou and co-workers with emphasis again been placed on multifunctionality in terms of the applications of isolated supramolecular assemblies. Different from the work of Gao and co-workers, the systems developed here involve FePt cores which are only functionalised on the surface with cysteamine to allow for biocompatibility and grafting of (for example) antibodies (Figure 196). It is reported that synthesis of the nanoparticles is feasible with controllable size and shape which, combined with the observed pronounced superparamagnetic characteristics and significant X-ray absorption, presents these compounds as exemplary candidates of dual imaging agents in both MRI and CT (computerised tomography).

Fig. 196 Antibody-functionalised FePt nanoparticle imaging agents developed by Chou and co-workers.
Additionally, a recent report by Valero and co-workers described the combination of iron-oxide nanoparticles with the protein apoferritin (and subsequent functionalisation with carbohydrate species), resulting in nanoparticle-encapsulated protein assemblies towards functional MRI materials. Indeed the effective functionalisation of the nanoparticle with both protein and carbohydrate imparts such systems with an inherent biocompatibility placing them as viable candidates towards commercial MRI agents. There have also been reports of non-Fe transition metal imaging agents, such as the Mn(II) chelate macrocycles developed by Tan and co-workers. This breed of nanoglobular clusters, as they are called, are shown in Figure 197, and consist of a micelle-like assembly of Mn(II) ions enclosing a lysine-based core. Tan and co-workers highlight that, due to the reported renal-toxicity of Gd(III) imaging species, the evolution of this new class of non-toxic Mn(II) system promises to afford great potential in diagnostic imaging techniques.

![Fig. 197 Lysine-encapsulated Mn(II)-based MRI contrast agent developed by Tan et al.](image)

Finally, a novel breed of MRI contrast agent developed by Mikawa and co-workers involves the encapsulation of Gd(III) ions within fullerene (C_{82}) cage assemblies. The pronounced H_{2}O-solubility of these particular host-guest architectures enabled them to out-perform commercially-available contrast agents in in vivo and in vitro studies. The extensive water solubility combined with signal-enhancement ability of the contrast agents discussed above presents this newly-emerging family of compounds as viable candidates for replacement of many commercially available imaging agents utilised at present.
Section B: EPR Spectroscopy and its Application in Host-Guest Chemistry

Before concluding with a discussion of the aims and objectives of the research detailed in this thesis, a brief case study will be described on the application of Electron Paramagnetic Resonance (EPR) spectroscopy in elucidating host-guest relationships in supramolecular systems; a technique of particular relevance to the present doctoral thesis. The study will involve a brief description of the technique and subsequently its direct application in the characterisation of host-guest systems.

B.1 EPR Spectroscopy: Basic Theory

Resonance is now a widely known phenomenon, with early examples including Barton’s pendulums (where one or more vertical weights attached separately to a horizontal string could be set into vibration following an initial oscillation of one of its neighbours). This resonance is caused by energy transfer from one oscillator to another and is most frequently observed in the routine analytical technique of Nuclear Magnetic Resonance (NMR) spectroscopy.

In NMR spectroscopy protons are exposed to electromagnetic radiation in the radiofrequency (RF) range (commonly 300-600 MHz) in the presence of extremely strong magnetic fields (some as high as 20 T). The protons are moving charged particles with corresponding spin moments \(M_s = +/- \frac{1}{2}\) and these states correspond to the allowed orientations of the moments with respect to the external magnetic field. As was noted in the preceding sections, these spin states are not of the same energy: spin moments aligned with H are lower in energy than those opposing H. When the system containing these protons is exposed to RF radiation, the absorption of energy causes the spin moments to switch direction: \(M_s = +1/2 \rightarrow M_s = -1/2, M_s = -1/2 \rightarrow M_s = +1/2\) (Figure 198). These resonances are the origins of the signals on an NMR spectrum.
Like NMR, EPR spectroscopy is based on the excitation of spin moments by electromagnetic radiation in the presence of strong magnetic fields. The technique, however, involves energy absorption by the electrons in a given system as opposed to protons (for $^1$H NMR). Indeed, the energy required to effect resonance between the electrons and the applied radiation is much higher than that for nuclei, stemming from the fact that electron magnetic moments are considerably larger than those of nuclei. Thus, it is found that microwave radiation (GHz) is required to effect resonance, while lower fields relative to NMR are utilised (e.g. 9 T in NMR vs. 1 T in EPR). Unlike NMR, EPR is particularly suited to the study of transition metal complexes since it is based on resonance with unpaired electrons. It may also be used to study radical species (Chapter Three) and biological processes (such as the uptake of oxygen by haemoglobin).\(^7\) A schematic of a typical continuous-wave spectrometer is shown in Figure 199. The EPR spectrum is collected by monitoring the absorption of microwave radiation as the field is swept from X-band (0.3 T) to Q-band (1 T).
One of the great applications of the EPR technique, particularly in the field of supramolecular chemistry, is the characterisation of host-guest inclusion complexes by virtue of its ability to detect the presence of unpaired electrons. EPR is therefore most commonly used in the detection and characterisation of host-guest inclusion complexes involving a radical species as guest. One of the most commonly utilised radical guests are those based on nitroxide (NO$^\cdot$), largely due to the reported high sensitivity of this species to its surroundings.$^8$ To this end inclusion complexes in which it is incorporated have garnered widespread appeal in recent years, evidenced by a review of the literature on this subject. For instance, recent reports (Jayaraj et al.) involving the encapsulation of nitroxide include the self-assembly of cationic nitroxides within the cavities of cucurbit[8]uril species; systems proposed as candidates for use in drug delivery, gas storage and chemical sensing (Figure 200).$^9$
There have been separate reports by Mileo and Franchi (and co-workers) involving the EPR study of inclusion architectures involving nitroxide as guest and resorcinarene and β-cyclodextrin as host frameworks respectively.\textsuperscript{8,10} The latter (Franchi et al) highlight the utility of EPR in monitoring reaction kinetics within such supramolecular systems. Additionally, EPR studies of nitroxide guest rotations in cavitands\textsuperscript{11} as well as adamantine radical behaviour within an octahedral cage\textsuperscript{12} (Capsule A discussed in Section 1.2.3) reported by Kulasekharan and Furutani respectively, have afforded greater insight into the self-assembly process and stability of host-guest systems. It is evident that EPR spectroscopy will continue to play an increasingly important role in the structural and magnetic characterisation of supramolecular host-guest species, particularly as the impetus grows towards the development of miniaturised and multifunctional materials towards useful applications; including their use as chemical reactors and in drug delivery.\textsuperscript{13-15}
References