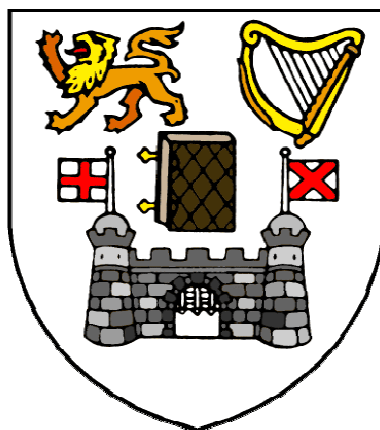


The self-assembly of polynuclear transition metal complexes, metallo-helicates and extended coordination assemblies

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A thesis submitted to the University of Dublin for the degree of Doctor of
Philosophy.

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Declaration

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Summary

The research presented in this thesis focuses on the exploitation of self-assembly approaches to generate hybrid organic-inorganic materials. More specifically, the project involves the synthesis and structural characterisation of a variety of metallo-supramolecular assemblies including molecular helicates, coordination clusters and coordination networks. These assemblies are stabilised by either Schiff base ligands, carboxylic acid substituted aromatic ligands or iminodiacetic acid substituted phenol ligands. The physical properties (magnetism, surface-area and thermal-stability) of these compounds have also been studied with the goal of exploiting them for future device fabrication.

Chapter 1 introduces the reader to the research area described in this thesis. It puts the work into context and discusses appropriate literature references. Chapter 2 details the aims of the work and provides a brief outline of the thesis.

Chapter 3 details the synthesis of a series of bis-bidentate Schiff base ligands, N,N-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-4-diamine (**L1**), N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-3-diamine (**L2**) and N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-2-diamine (**L3**), which consist of two imine-methyl-imidazole binding units linked by a benzene backbone. In attempts to understand the transition metal directed self-assembly of these ligands they were reacted with a variety of transition metal salts. Upon complexation the relative conformation of the ligand's imine-imidazole bidentate binding sites influences the topology of the resultant species. For example, upon reaction with $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, the ligand, **L2**, adopts a *cis-trans* confirmation resulting in the formation of a tetranuclear iron(III) compound, $[\text{Fe}_4(\mu\text{-O})_2(\text{L2})_2\text{Cl}_8] \cdot 2\text{THF}$ (**1**). **L2** was also applied in the formation of the dinuclear complexes in $[\text{Co}_2(\text{L2})_2(\text{MeOH})_2(\text{H}_2\text{O})_2]\text{Cl}_4 \cdot 4\text{MeOH} \cdot 3\text{H}_2\text{O}$ (**2**) and $[\text{Ni}_2(\text{L2})_3](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ (**3**). In attempts to generate coordination clusters **L2** was reacted with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, resulting in the formation of two coordination compounds $[\text{Cu}_4(\text{L2})_2(\text{EMM})_4](\text{CH}_3\text{COO})_4 \cdot \text{H}_2\text{O}$ (**4**) (where **EMM** = ethoxy(1-methylimidazol-2-yl)methanolate) and $[\text{Cu}^{\text{II}}_9(\mu_3\text{-O})_2(\text{O-L2-O})_2(\text{CH}_3\text{COO})_{10}] \cdot 2\text{THF} \cdot 2\text{H}_2\text{O}$ (**5**). The nonanuclear coordination cluster in **5** is stabilised by two carbinolamine ligands which result from the *in-situ* partial hydrolysis of the imine ligand **L2** under the applied reaction conditions. An

arsonate analogue of these ligands, 4-[(pyridin-2-ylmethylene)-amino]-arsonic acid (**H₂L4**), was also employed in the generation of the coordination compound [Co(**HL4**)₂]·MeOH·2H₂O (**6**).

In chapter 4, the synthesis of a series of molecular helicates, [Co₂(**L5**)₃](NO₃)₄·2MeOH (**8**), [Co₂(**L6**)₃](ClO₄)₄·MeCN (**9**), [Mn₂(**L6**)₃](ClO₄)₄·2MeOH (**10**), [Ni₂(**L5**)₃](PF₆)₄·2MeCN (**11**), [Fe₂(**L6**)₃](PF₆)₄·4MeCN·H₂O (**12**), [Fe₂(**L6**)₃](BF₄)₄·H₂O (**13**), [Fe₂(**L5**)₃](PF₆)₄·4MeCN·H₂O (**14**) and [Fe₂(**L5**)₃](BF₄)₄·2MeCN (**15**), is discussed. These complexes are stabilised by flexible Schiff base ligands N,N'-bis-(1-methyl-1-H-imidazol-2-yl-methylene)-4,4'-diaminodiphenylmethane (**L5**) and N,N'-bis-(1-methyl-1-H-imidazol-2-yl-methylene)-4,4'-oxydianiline (**L6**) which contain two imine-methyl-imidazole head groups linked by a flexible diamine linker. The Fe^{II} helicates **12** - **15** were shown to exhibit spin crossover (SCO) transitions which can be induced thermally and by light irradiation. It was demonstrated that the counterion used in these compounds can have a dramatic impact on the SCO properties leading to the formation of compounds that display SCO transitions in the room temperature range. It has also been shown that subtle changes to the structure of the organic ligand employed also influence the SCO behaviour of these helicates. The variation in SCO behaviour may be attributable to the different ligand types but could also be the result of packing effects in the crystal structure.

In Chapter 5, the coordination chemistry of a series of extended Schiff base ligands N,N',N''-tris-(4-H-imidazol-2-ylmethylene)-1-3-5-triphenylbenzene (**L8**), N,N',N''-tris-(1-methyl-1-H-imidazol-2-ylmethylene)-1-3-5-triphenylbenzene (**L9**), N,N',N''-tris-(4-pyridin-2-ylmethylene)-1-3-5-triphenylbenzene (**L10**), N,N',N''-tris-(4-phen-2-ol-2-ylmethylene)-1-3-5-triphenylbenzene (**L11**) and N,N',N''-tris-(2-benzoic acid-2-ylmethylene)-1-3-5-triphenylbenzene (**L12**) is discussed. These tris-bidentate ligands consist of imine binding groups linked by a tri-phenyl benzene core. This work yielded the trinuclear Co^{II} complexes in [Co₃(**L8**)₂(H₂O)₆]·Cl₆·DMF·9H₂O (**16**) and [Co₃(**L9**)₂(H₂O)₆]Cl₆·DMF·9H₂O (**17**). In the solid state, these Co^{II} complexes arrange into hexagonally packed network structures, which contain large solvent filled channels. The Brunauer Emmet Teller (BET) surface area of **16** was found to be 87 m² g⁻¹.

Chapter 6 presents a variety of lithium-based coordination networks, [Li₂(C₈H₄O₄)] (**18**), [Li₂(C₁₄H₈O₄)] (**19**), [Li₂(C₁₂H₆O₄)] (**20**) and

(NH₂Me₂)[Li₂(C₉H₃O₆)]·H₂O (**21**), that are stabilised by terephthalic acid, 4,4'-biphenyl dicarboxylic, 2,6'-naphthalene dicarboxylic acid and 1,3,5-benzenetricarboxylic acid, respectively. These framework structures are densely packed and contain limited accessible void space.

Chapter 7 describes a variety of mononuclear Fe^{III} complexes, [Fe(**Bc₂hda**)(H₂O)(EtOH)]·3H₂O (**22**), [Fe(**tBu₂hda**)(H₂O)₂]·4H₂O (**23**), [Fe(**p-C₁₂Mehda**)(H₂O)₂]·nH₂O (**24**) and [Fe(**o-C₁₂Mehda**)(H₂O)₂]·nH₂O (**25**) which are stabilised by iminodiacetic acid substituted phenol ligands. The ligands used in this study are N-[3,5-bis(α,α-dimethylbenzyl-2-hydroxy-benzyl)] iminodiacetic acid (**Bc₂hda**), N-[3,5-bis(tertbutyl-2-hydroxy-benzyl)] iminodiacetic acid (**t-Bu₂hda**), N-[3-methyl-5-dodecyl-2-hydroxy-benzyl)] iminodiacetic acid (**p-C₁₂Mehda**) and N-[3-dodecyl-5-methyl-2-hydroxy-benzyl)] iminodiacetic acid (**o-C₁₂Mehda**), respectively. In the solid state, the Fe^{III} complexes are linked *via* hydrogen bonding, involving constitutional water molecules, resulting in the formation of amphiphilic coordination assemblies. H-bonded networks of water molecules which show some similarities to solid ice polymorphs are contained within the Fe^{III} coordination assemblies. The amphiphilic nature of the coordination assemblies can be exploited to assemble hierarchical, non-crystalline nanostructures. For example, **24** can be used to prepare nanosized spherical vesicles which were imaged by SEM and TEM. These techniques demonstrate that these vesicles have similar layered lamellar structures to the parent crystalline materials.

Chapter 8 provides an account of the experimental details for this work.

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List of compounds

- 1 $[\text{Fe}_4(\mu\text{-O})_2(\text{L2})_2\text{Cl}_8] \cdot 2\text{THF}$
- 2 $[\text{Co}_2(\text{L2})_2(\text{MeOH})_2(\text{H}_2\text{O})_2]\text{Cl}_4 \cdot 4\text{MeOH} \cdot 3\text{H}_2\text{O}$
- 3 $[\text{Ni}_2(\text{L2})_3](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$
- 4 $[\text{Cu}_4(\text{L2})_2(\text{EMM})_4](\text{CH}_3\text{COO})_4 \cdot \text{H}_2\text{O}$
- 5 $[\text{Cu}_9(\mu_3\text{-O})_2(\text{O-L2-O})_2(\text{CH}_3\text{COO})_{10}] \cdot 2\text{THF} \cdot 2\text{H}_2\text{O}$
- 6 $[\text{Co}(\text{HL4})_2] \cdot \text{MeOH} \cdot 2\text{H}_2\text{O}$
- 7 $[\text{Fe}_2(\text{L6})_3](\text{ClO}_4)_4 \cdot 2\text{MeCN}$
- 8 $[\text{Co}_2(\text{L5})_3](\text{NO}_3)_4 \cdot 2\text{MeOH}$
- 9 $[\text{Co}_2(\text{L6})_3](\text{ClO}_4)_4 \cdot \text{MeCN}$
- 10 $[\text{Mn}_2(\text{L6})_3](\text{ClO}_4)_4 \cdot 2\text{MeOH}$
- 11 $[\text{Ni}_2(\text{L5})_3](\text{PF}_6)_4 \cdot 2\text{MeCN}$
- 12 $[\text{Fe}_2(\text{L6})_3](\text{PF}_6)_4 \cdot 4\text{MeCN} \cdot \text{H}_2\text{O}$
- 13 $[\text{Fe}_2(\text{L6})_3](\text{BF}_4)_4 \cdot \text{H}_2\text{O}$
- 14 $[\text{Fe}_2(\text{L5})_3](\text{PF}_6)_4 \cdot 4\text{MeCN} \cdot \text{H}_2\text{O}$
- 15 $[\text{Fe}_2(\text{L5})_3](\text{BF}_4)_4 \cdot 2\text{MeCN}$
- 16 $[\text{Co}_3(\text{L8})_2(\text{H}_2\text{O})_6] \cdot \text{Cl}_6 \cdot \text{DMF} \cdot 9\text{H}_2\text{O}$
- 17 $[\text{Co}_3(\text{L9})_2(\text{H}_2\text{O})_6] \cdot \text{Cl}_6 \cdot \text{DMF} \cdot 9\text{H}_2\text{O}$
- 18 $[\text{Li}_2(\text{C}_8\text{H}_4\text{O}_4)]$
- 19 $[\text{Li}_2(\text{C}_{14}\text{H}_8\text{O}_4)]$
- 20 $[\text{Li}_2(\text{C}_{12}\text{H}_6\text{O}_4)]$
- 21 $(\text{NH}_2\text{Me}_2)[\text{Li}_2(\text{C}_9\text{H}_3\text{O}_6)]$
- 22 $[\text{Fe}(\text{Bc}_2\text{hda})(\text{H}_2\text{O})(\text{EtOH})] \cdot 3\text{H}_2\text{O}$
- 23 $[\text{Fe}(\text{tBu}_2\text{hda})(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$
- 24 $[\text{Fe}(\textit{o}\text{-C}_{12}\text{Mehda})(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$
- 25 $[\text{Fe}(\textit{p}\text{-C}_{12}\text{Mehda})(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$

List of ligands

BC₂hda	N-[3,5-bis(α,α -dimethylbenzyl-2-hydroxy-benzyl)] iminodiacetic acid
BDCA	4,4'-biphenyl dicarboxylic acid
BTCA	1,3,4-benzenetricarboxylic acid
BTPA	1,3,5 benzenetri-(phenylacetic acid)
EMM	ethoxy(1-methylimidazol-2-yl) methanolate
L1	N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-4-diamine
L2	N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-3-diamine
L3	N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-2-diamine
H₂L4	4-[(Pyridin-2-ylmethylene)-amino]-arsonic acid
L5	N,N'-bis-(1-methyl-1-H-imidazol-2-yl-methylene)- 4,4'-diaminodiphenylmethane
L6	N,N'-bis-(1-methyl-1-H-imidazol-2-yl-methylene)-4,4'-oxydianiline
L7	N,N'-bis-(1-methyl-1-H-imidazol-2-yl-methylene)-4,4'- diaminodiphenylamine
L8	N,N',N''-tris-(4-H-imidazol-2-ylmethylene)-1-3-5-triphenyl(benzene)
L9	N,N',N''-tris-(1-methyl-1-H-imidazol-2-ylmethylene)-1-3-5- triphenyl(benzene)
L10	N,N',N''-tris-(4-pyridin-2-ylmethylene)-1-3-5-triphenyl(benzene)
L11	N,N',N''-tris-(4-phen-2-ol-2-ylmethylene)-1-3-5-triphenylbenzene
L12	N,N',N''-tris-(2-benzoic acid-2-ylmethylene)-1-3-5-triphenylbenzene
NDCA	2,6-napthalene dicarboxylic acid
<i>o</i>-C₁₂Mehda	N-[3- dodecyl-5-methyl-2-hydroxy-benzyl)] iminodiacetic acid
<i>p</i>-C₁₂Mehda	N-[3-methyl-5-dodecyl-2-hydroxy-benzyl)] iminodiacetic acid
TA	Terephthalic acid
tBu₂hda	N-[3,5-bis(tertbutyl-2-hydroxy-benzyl)] iminodiacetic acid

Abbreviations

1D:	one dimensional
2D:	two dimensional
3D:	three dimensional
a/c:	alternating current
ATR:	attenuated total reflectance
au.:	arbitrary units
BET:	Brunauer Emmet Teller
C:	Currie constant
CHN:	carbon hydrogen nitrogen elemental analysis
D:	zero-field splitting
d/c:	direct current
DNA:	deoxyribonucleic acid
DMA:	dimethylacetamide
DMF:	dimethylformamide
DMSO:	dimethyl sulfoxide
ESI:	electron spray ionisation
FTIR:	Fourier-transform infrared
HPLC:	high performance liquid chromatography
HS:	high spin
<i>g</i> :	Landé <i>g</i> -factor
IR:	infrared
J:	coupling constant
LIESST:	light induced electronic spin state trapping
LITH:	light induced thermal hysteresis
LS:	low spin
M:	magnetisation
min:	minutes
Me:	methyl
MOF:	metal-organic framework
MRI:	magnetic resonance imaging

NMR:	nuclear magnetic resonance
NLDFT:	non-linear density functional theory
Oe:	Oersted
S:	spin quantum number
SBU:	secondary building unit
SCM:	single chain magnet
SCO:	spin crossover
SCOF:	spin crossover metal-organic framework
SEM:	scanning electron microscopy
SMM:	single molecule magnet
SQUID:	superconducting quantum interference device
ST:	spin transition
T:	temperature
T _{1/2} :	SCO temperature
TEM:	transmission electron microscopy
TGA:	thermogravimetric analysis
THF:	tetrahydrofuran
U:	Spin reversal barrier
UV-vis:	ultraviolet visible
wt:	weight
XRD:	X-ray diffraction
γ :	mole fraction
δ :	chemical shift
χ :	magnetic susceptibility
λ :	wavelength

Chapter One



Introduction

1.1 Supramolecular chemistry: An overview

Over recent decades the desire to develop new functional materials has led to a rejuvenation of research into supramolecular chemistry approaches. Supramolecular chemistry was defined by Lehn as “chemistry beyond the molecule”^{1,2} and involves the utilisation of weaker non-covalent interactions such as hydrogen bonding, π - π stacking and van der Waals forces as a means to assemble molecules into predetermined molecular structures. Supramolecular architectures have been shown to exhibit a wide range of applicable properties that can be exploited in areas such as gas storage,³ catalysis,⁴ data storage and processing⁵ and in molecular sensing.⁶

We are particularly interested in the development of metallo-supramolecular compounds as these materials have displayed the capacity to possess desirable physico-chemical properties.⁷ Work in this area has led to the synthesis of a diverse range of supramolecular structures that incorporate transition metal ions stabilised by organic ligand moieties.⁷ These materials may combine the advantageous properties of organic and inorganic components, thus allowing for their potential application in the areas of electrochemistry,⁸ photophysics,⁹ molecular recognition¹⁰ and catalysis.¹¹

The goal of this progressive and evolving area of chemistry is to conceive and synthesise novel compounds whose molecular topology and chemical properties are pre-determined by the designer. The achievement of this objective has been largely made possible due to the groundbreaking work of scientists, such as Lehn,^{1,2} Yaghi,^{3,12} and Stoddart^{13,14} who have made a substantial contribution to increasing the understanding of the interactions that are employed in the formation of supramolecular structures. This knowledge has enabled the discovery of a series of synthetic approaches for the formation of desirable supramolecular compounds e.g. metal-organic frameworks,¹⁵ molecular helicates^{16,17} and molecular cages.¹⁸

1.2 Reticular synthesis concept and metal-organic frameworks

A prominent example of a synthetic approach for the generation of metallo-supramolecular compounds is the reticular synthesis concept developed by Yaghi *et al.*^{12,15} This concept “requires the use of secondary building units to direct the assembly of ordered frameworks” (Figure 1.1).¹² Secondary building units (SBUs) are defined as “molecular complexes and cluster entities in which ligand coordination

modes and metal coordination environments can be utilised in the transformation of these fragments into extended porous networks using polytopic linkers”.¹⁵ These SBUs are held together by coordination bonds throughout the framework, allowing for the formation of new materials with pre-desired structure, composition and properties.

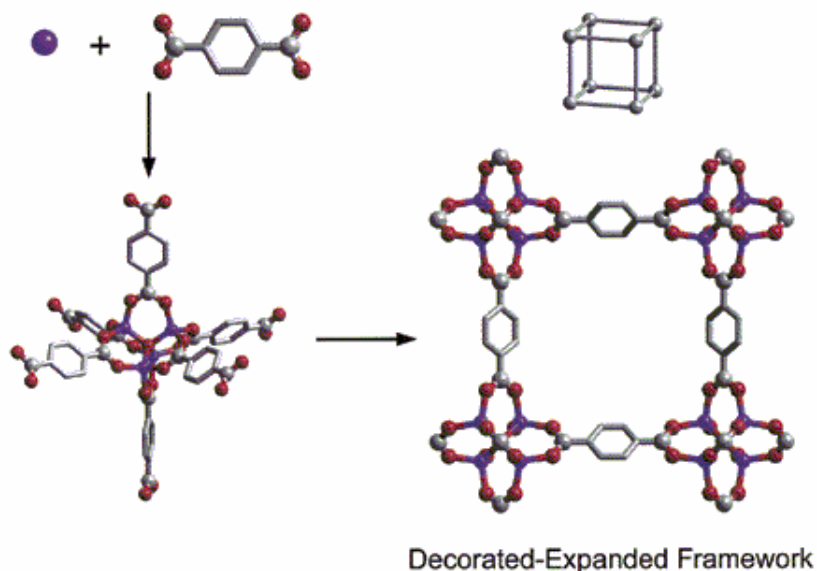


Figure 1.1: Carboxylate-stabilised coordination clusters with tetrahedral arrangements of Zn^{II} centres, that can be linked by dicarboxylate “struts” to form rigid frameworks, in which the M-O-C core (SBU) of each cluster acts as a large octahedron decorating a 6-connected vertex in a cube. All hydrogen atoms are omitted for clarity. M, purple; O, red; C, grey.¹⁵

Yaghi and co-workers have demonstrated how powerful a technique the reticular synthetic concept can be by using it to produce expanded metal-organic frameworks (MOFs) with noteworthy molecular architectures and unprecedented porosities.¹² MOFs are defined as metal ions or clusters linked *via* organic linkers resulting in the formation of 2D or 3D molecular structures.^{19,20}

Inspired by Yaghi’s success, a large number of metal-organic frameworks have been formed and these materials have the potential to be used as catalysts,²¹ gas storage materials^{3, 22,23} and as magnetic materials.²⁴

MOFs have the potential to be exploited for catalysis as they contain accessible metal sites and large pores which can be utilised to instigate a specific chemical process.²¹ The pores can also act as an effective host for catalytic species giving rise to shape and size selectivity, thereby allowing the catalytic process to proceed efficiently within the framework. The combination of all these properties

means catalysis is one of the most promising applications for MOFs, however to date only a few examples have been reported.²¹ It has been shown that the copper containing metal-organic framework, $[\text{Cu}_3(\text{btc})_2(\text{H}_2\text{O})_3]_n$ (Figure 1.2), developed by Williams and co-workers can be employed as a Lewis acid catalyst.^{25,26} This compound is an effective catalyst as it contains large pores and has easily accessible catalytically active Cu^{II} sites.

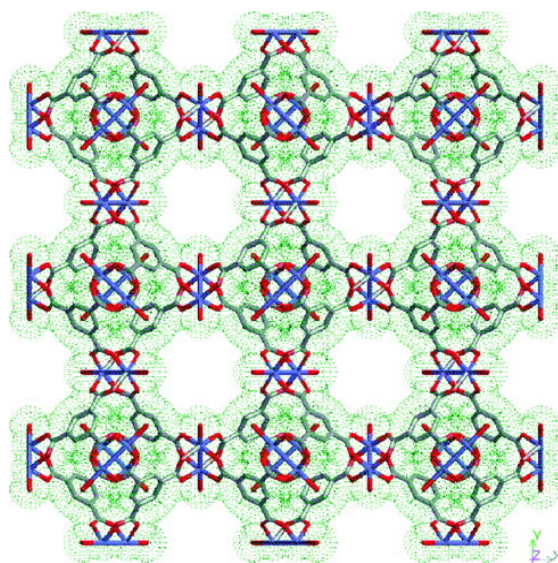


Figure 1.2: The molecular structure of $[\text{Cu}_3(\text{btc})_2(\text{H}_2\text{O})_3]_n$ which has shown activity as a Lewis acid catalyst.²⁵

Another promising application displayed by metal-organic frameworks is their ability to store gas molecules such as hydrogen and carbon dioxide.^{3,22,23} The need to develop a safe storage media for hydrogen gas is of particular importance as it is considered to be a promising future fuel source.^{27,28} The use of hydrogen as a fuel source is desirable as it has a high gravimetric heat of combustion and the only combustion bi-product it produces is water.²⁸ However, there are enormous difficulties in providing a safe method for the storage of gaseous hydrogen. Current storage techniques involve the use of high pressure tanks, cryoscopic tanks and chemisorption approaches.²⁹ The use of these tanks is hampered by safety concerns and the irreversibility of chemisorption methods and their high temperature requirements make these storage techniques problematic.²⁹ Therefore, intense research activities in this area focus on the development of highly porous solid materials which can utilise physisorption to store hydrogen gas molecules.³⁰ For example, the ability of zeolitic materials to store hydrogen gas has been widely

investigated.^{31,32} However, it was shown that these materials only show a maximum hydrogen storage capacity of 1-2 wt %.³²

The unprecedented porosity of metal-organic frameworks (MOFs) can also be utilised to store hydrogen molecules through physisorption processes.³ The ability of a MOF to uptake hydrogen directly correlates with the surface area of the material, thus when designing a hydrogen storage system using a MOF a large surface area is desirable.³³

Yaghi *et al.* have developed a synthetic methodology for the generation of high surface area MOFs (Figure 1.3). This involves the use of polyaromatic carboxylate ligands to assemble $\{\text{Zn}_4\text{O}(\text{CO}_2)_6\}$ units into extended network structures.^{3,22} These materials possess a high surface area and display a permanent porosity. These materials have shown the propensity to uptake a variety of gases including hydrogen. For example, the compound $[\text{Zn}_4\text{O}(\text{BTB})_2]$ where BTB is 1,3,5-benzenetribenzoate, shows a surface area of $4500 \text{ m}^2 \text{ g}^{-1}$ and has a hydrogen gas uptake capacity of 7.5 wt % at 77 K (Figure 1.3 b).³⁴ Recently, Yaghi and co-workers have reported a series of augmented frameworks which have surface areas in excess of $6000 \text{ m}^2 \text{ g}^{-1}$ and which display hydrogen storage capacity above 10 wt%.²² However, the uptake capacity of MOFs is significantly reduced at ambient temperature and pressure, thus diminishing the ability of current framework materials to be exploited for hydrogen storage.²⁷

Current research therefore centres on the attempt to develop novel MOFs that display enhanced hydrogen uptake at room temperature. One potential way to achieve this is by increasing the interactions between the hydrogen molecules and the framework. This can be achieved by tailoring the pore size of the framework so the hydrogen molecules ‘fit’ better³⁵ or by using unsaturated metal centres to bind the hydrogen molecules.³⁶ It has been proposed that the design of cage like frameworks could also be used to ‘trap’ the hydrogen molecules, thus increasing the uptake of hydrogen.³⁷ The potential for MOFs to safely and efficiently store molecular hydrogen underlines their importance in future ‘green’ technologies.²⁸

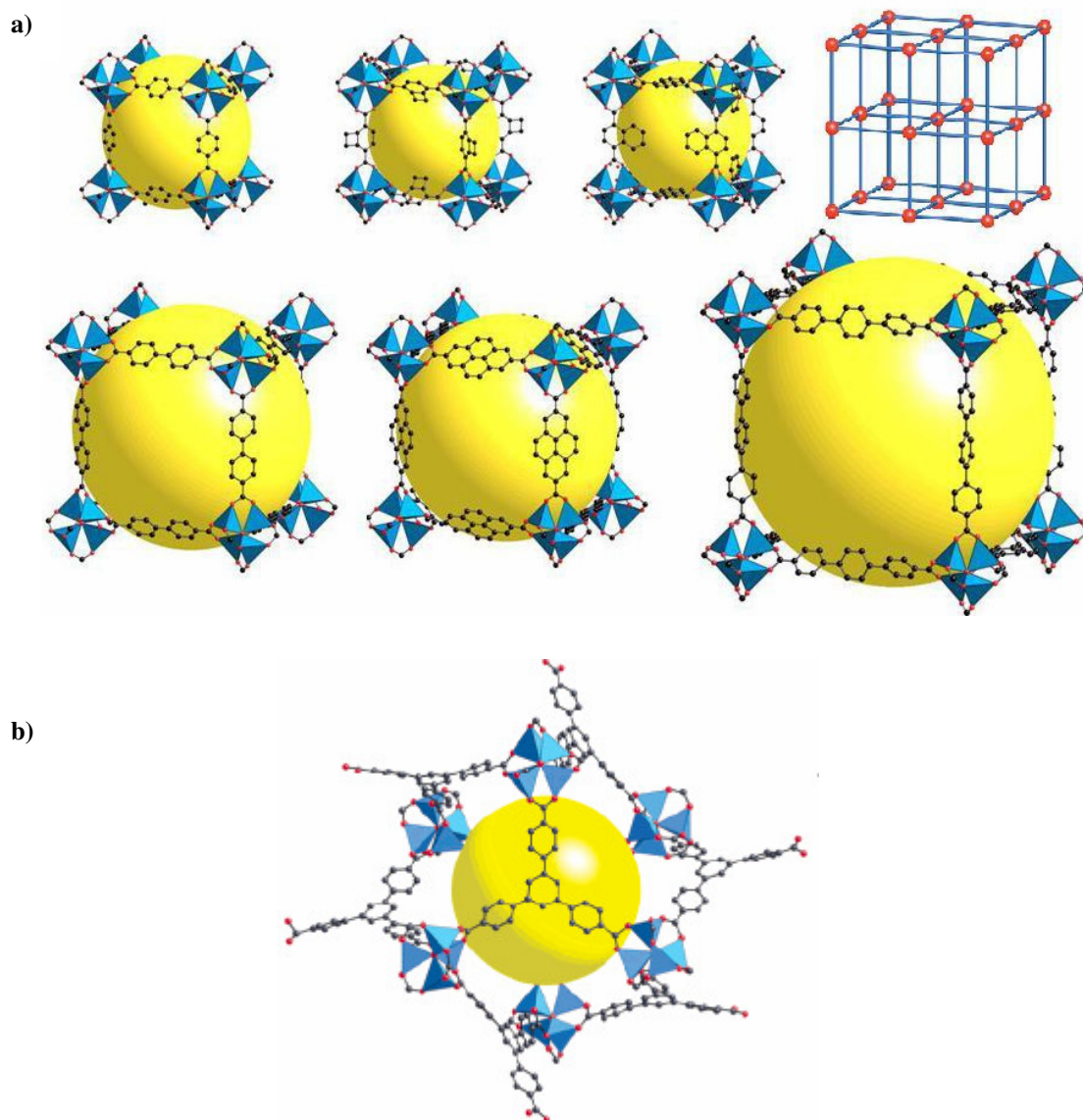


Figure 1.3: **a)** Examples of metal-organic frameworks, developed by Yaghi and co-workers, that consist of $\{\text{Zn}_4\text{O}(\text{CO}_2)_6\}$ tetrahedra (blue polyhedra) linked by rigid di-carboxylate linkers (O red and C black). The extended 3D cubic framework structures of these compounds contain interconnected pores (yellow spheres) which can be exploited for gas storage.³ **b)** The structure of $[\text{Zn}_4\text{O}(\text{BTB})_2]$ which shows a hydrogen uptake capacity of 7.5 wt%.³³

Metal-organic frameworks also possess interesting magnetic properties that can be exploited for potential device applications.²⁴ The choice of ligand and the arrangement of the metal ions within the framework have a major influence on the magnetic properties of the resultant material. Metal-organic frameworks have been shown to display ferromagnetic,³⁸ antiferromagnetic³⁹ and spin crossover properties,⁴⁰ thus indicating that these materials could have future utilisation in the areas of data storage and molecular sensing.

The reticular synthesis concept has also aided research in other areas of supramolecular chemistry thus leading to the discovery of a variety of synthetic

approaches for the formation of novel applicable materials such as molecular cages⁴¹ and molecular helicates.^{16,17}

1.3 Amphiphilic coordination networks and their use in the self-assembly of nanostructures

Another class of hybrid organic-inorganic materials are amphiphilic coordination networks and molecular coordination assemblies. These result from the self-assembly of amphiphilic transition metal complexes into extended networked structures.⁴² The complexes are held together throughout the frameworks *via* weaker interactions such as dipole-cation interactions, hydrogen bonding, π - π stacking and van derWaals forces. The utilisation of these supramolecular interactions allows for the formation of complicated structural topologies with well defined hydrophobic and hydrophilic regions. These advantageous structural properties can be exploited to develop new materials which have shown potential applications in the areas of magnetism,^{7,43} catalysis⁴⁴ and nanotechnology.⁴⁵

The advent of nanotechnology has meant that there is now significant attention focused on attempts to control the size and morphology of coordination compounds in the hope of generating nanosized materials that can be used for many applications in catalysis, optics, electronics and biosensing.^{46,47} The knowledge about structurally determining intermolecular forces, garnered in the formation of crystalline hybrid inorganic-organic materials such as coordination networks, can be exploited in the self-assembly of desirable non-crystalline nanomaterials.⁴⁸ In addition, coordination compounds can be used as solid state precursors for the preparation of nanoscale semi-conducting materials and metal oxides and for the formation of hybrid carbonous materials, that are formed *via* thermolysis or pyrolysis.⁴⁹

There are two main approaches applied in the synthesis of nanomaterials. They are known as the 'top down' and 'bottom up' approach, respectively.⁴⁸ The 'top down' approach implies that one uses a bulk material and exploits techniques such as lithography to slowly remove parts of the substance, thus revealing the desired nanomaterial. The 'bottom up' method involves the use of subtle molecular forces to assemble molecules into the desired nano-structure.⁵⁰ One such 'bottom up' approach involves the application of amphiphilic molecules to self-assemble nanomaterials in

solution.^{51,52} In solution, these amphiphilic molecules orientate the moiety with the highest affinity for the solvent, towards the solvent, while the other part orientates away from the solvent. In this way, these molecules align in a well defined way that gives rise to the formation of nano-sized aggregates.⁵² There are a variety of potential aggregate types (Figure 1.4) that could be formed using molecular assembly approaches, including tubular and spherical vesicles, bilayer arrangements and fibrous materials.⁵³ The shape of these aggregates is determined by the size ratio of the hydrophilic and hydrophobic parts of the molecular entities.⁵² The nature of the solvent used in the assembly process also plays a key role in determining the topology of the aggregates.⁵² Therefore, coordination compounds that display amphiphilic character, are considered to be ideal candidates for the ‘bottom up’ synthesis of nanostructures using self-assembly approaches.⁴²

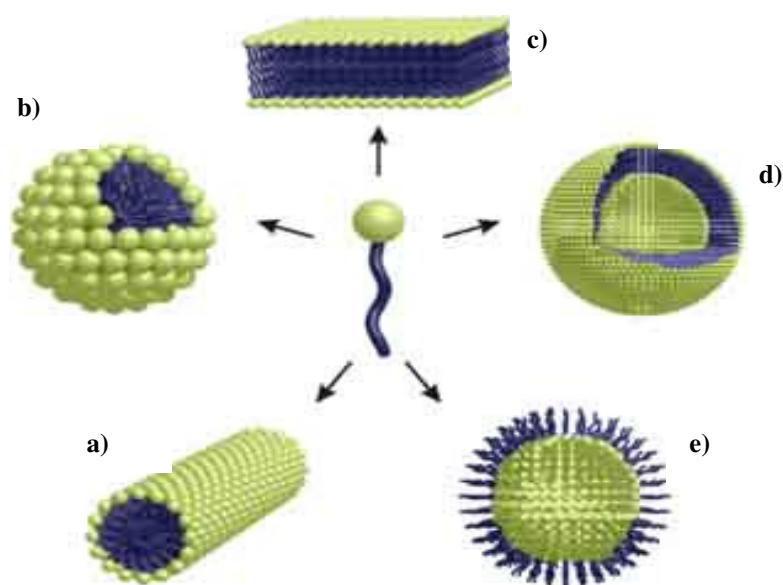


Figure 1.4: Schematic representation showing the potential nano-structures that can be formed *via* the self-assembly of amphiphilic molecules.⁵³ a) Tubular aggregate b), d) and e) spherical vesicle and c) bi-layer arrangement.

A synthetic approach for the generation of amphiphilic coordination networks was previously developed within the group of Dr. Wolfgang Schmitt.^{54,55} This approach involves the use of iminodiacetic acid substituted naphthol and phenol ligands to assemble amphiphilic coordination networks.^{54,55} Iminodiacetic acid type ligands were chosen as they have been shown to be useful chelating agents for the formation of a variety of metallo-supramolecular assemblies.⁵⁶ For example, the tetradentate ligand ethylenediaminetetraacetic acid (EDTA) has been widely exploited

in coordination chemistry.⁵⁷ EDTA has been shown to be a very useful chelation agent due to its high affinity for metal ions.⁵⁷ This property has led EDTA to be used in the practice of chelation therapy as means to treat mercury and lead poisoning.^{56,57} EDTA and related ligands have also been used to stabilise coordination complexes that display interesting magnetic properties. In particular, EDTA has been used to form a series of 1D coordination polymers that can act as ferromagnets.^{58,59,60} The iminodiacetic acid functionality can also be attached to aromatic moieties through the use of the Mannich reaction. The resultant iminodiacetic substituted aromatic ligands have been used to stabilise a range of coordination networks exhibiting lamellar, double-helical or chiral structures, dense hexagonal arrays or open-framework networks.^{55,61}

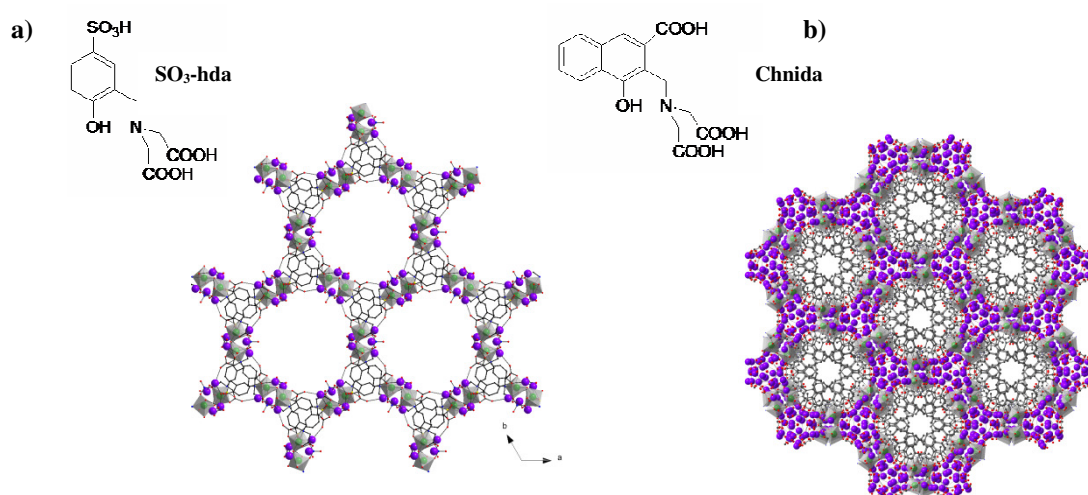


Figure 1.5: Coordination networks formed using iminodiacetic acid substituted ligands **a)** Open-framework structure in $K_6[Fe_2(\mu-O)(\mu-CO_3)(SO_3-hda)_2] \cdot 11H_2O \cdot 9MeOH$, and **b)** honeycomb structure in $K_6[Fe_2(\mu-O)(\mu-CO_3)(Chnida)_2] \cdot 13.5H_2O$.⁵⁵

For example, Schmitt and co-workers have reacted a variety of iminodiacetic acid substituted phenol and naphthol ligands with Fe^{III} salts. This approach has yielded dinuclear complexes with the general formulae $[Fe_2(\mu-OH)(\mu-CO_3)L_2]^{3-}$ or $[Fe_2(\mu-O)(\mu-CO_3)L_2]^{4-/6-}$ where L is the iminodiacetic acid substituted phenol or naphthol ligand.⁵⁵ In these compounds alkali metal counterions are linked to the negatively charged Fe^{III} complexes through the O-donors and are further networked to each other forming coordination assemblies where self-assembling processes organise vast areas of different polarities (Figure 1.5).⁵⁵ The obtained topologies are controlled by the additional functionalities attached to the aromatic ring moieties of the ligands used. For example, the incorporation of O-donating groups *para* to the hydroxyl

functionality of the phenol or naphthol ligand generally promotes the formation of open-framework structures.⁵⁵ However, when the O-donor group is positioned elsewhere on the aromatic ligand moiety, densely packed arrangements are normally generated.⁵⁵ This effect was demonstrated by $K_6[Fe_2(\mu-O)(\mu-CO_3)(SO_3-hda)_2] \cdot 11H_2O \cdot 9MeOH$ which displays an open hexagonal packing structure whereas $K_6[Fe_2(\mu-O)(\mu-CO_3)(Chnida)_2] \cdot 13.5H_2O$ has a corresponding densely packed structure (Figure 1.5).⁵⁵

The latter densely packed hexagonal structure types have also been used as templates for the formation of nanomaterials. This template approach was investigated using the coordination compound $Na_6[Fe_2(\mu-O)(\mu-CO_3)(Chnida)_2] \cdot 13.5H_2O$ which is isostructural with its potassium analogue shown in Figure 1.5b. Single crystals of the compound transformed into aligned hybrid organic-inorganic nanofibres and intersected Na_2CO_3/Fe_2O_3 fibres upon heating.⁶²

1.4 Molecular helicates: Nature's “supra”molecules

The inspiration for research into supramolecular chemistry is often found in the natural world as nature employs a variety of weaker interactions to assemble molecules into complex molecular structures. One of the most important examples of this behaviour is provided by deoxyribonucleic acid (DNA), a polymeric nucleic acid that contains all the genetic information required for organisms and some viruses to function. DNA generally takes up a double helix structure (Figure 1.6) where two strands are linked together *via* hydrogen bonding between the base pairs on the strands.⁶³

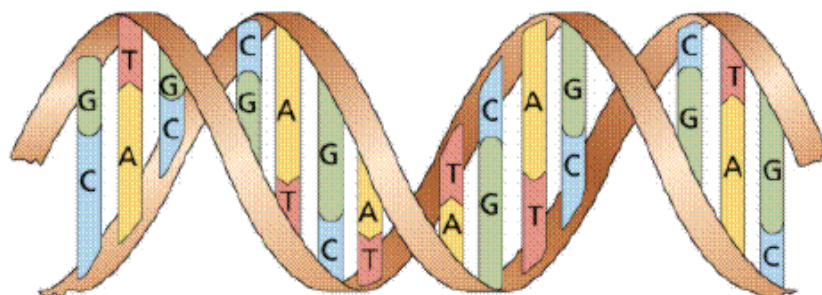


Figure 1.6: Schematic of the *B*-DNA helical structure.⁶³

Since the publication of Lehn's influential work on the formation of inorganic helicates in 1987,⁶⁴ chemists have sought to develop molecular architectures that

display a helical structure as these complexes can be applied for a variety of purposes. For example, helicates contain large inner cavities which can be used to trap guest molecules.⁶⁵ Helicates have also been studied as building blocks for the formation of macromolecular assemblies such as catenates and molecular knots.⁶⁶ The helical topology of these complexes may also be applied as a means to interact with DNA molecules.⁶⁷

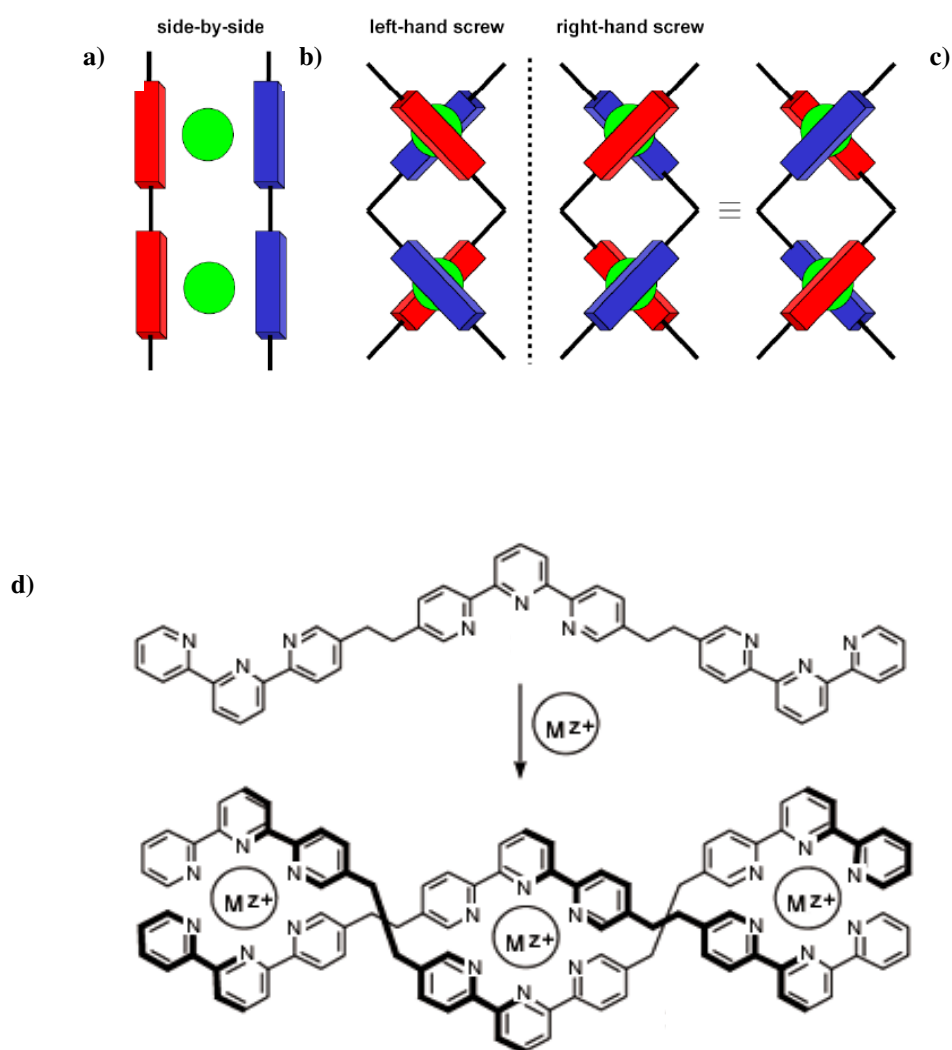


Figure 1.7: Schematic representation of **a)** non-helical structure. **b)** left-handed helicate. **c)** right-handed helicate⁶⁸ and **d)** an example of a helical structure synthesised by Lehn *et al.*⁶⁹

Helicity can be induced by various factors including conformational restrictions, inter- or intra-molecular hydrogen bonding or by metal ions coordination.⁷⁰ In particular there has been a lot of effort to generate molecular helicates. These are defined as coordination compounds consisting of two or more metal centres, where the ligand strands connecting the two metal centres intersect the metal - metal axis.⁷¹

As helicity is a special form of chirality, helicates can therefore be right-handed or left-handed according to whether the helical rotation occurs clockwise or anticlockwise (Figure 1.7).⁶⁸ The formation of metal helicates generally prevails *via* a ‘strict’ self-assembly process whereby the reaction of metal ions with two or more ligand strands produce a helical molecule, as the most stable thermodynamic product.⁷²

A variety of ligand types have been used in the formation of metallo-helicates. Initially, Lehn and co-workers exploited a series of flexible ligands, which consist of a number of 2-2'-2'' terpyridine moieties linked *via* bridging groups, for the synthesis of polynuclear double helicates (Figure 1.7d).⁶⁹ Due to their ability to act as excellent electron pair donors linear Schiff base ligands containing heterocyclic nitrogen functionalities (such as pyridine, pyrrole, imidazole and bipyridine moieties) have also been utilised extensively in the development of helicates.⁷³

As these imine ligands have the advantage of being easily and inexpensively synthesised, there are numerous examples of these ligands reported in the topical literature.^{73,74,75} For example the flexible imine ligand N,N'-bis-(2-pyridine-2-yl-methylene)-4,4'-diaminodiphenylmethane has been exploited widely in the formation of molecular helicates.⁷⁶ This work led to the formation of the complexes $[\text{Ru}_2\text{L}_3]^{4+}$ and $[\text{Fe}_2\text{L}_3]^{4+}$ where L is N,N'-bis-(2-pyridine-2-yl-methylene)-4,4'-diaminodiphenylmethane. These complexes have been shown to bind selectively to DNA.^{77,78}

Not only do molecular helicates have the ability to produce unique and aesthetically pleasing supramolecular architectures, but more importantly, these helicates display appealing physicochemical properties⁷⁰ (e.g. magnetism,^{75,79} molecular recognition⁸⁰ and photochemical properties^{81,82}) that can be exploited for applications. Molecular helicates possess a large inner cavity and current research focuses on the attempt to encapsulate desirable guest molecules within the cavity.^{65,80} The presence of these guest molecules could be determined by a change in the physical properties of the helicate compound, allowing these materials to be useable for molecular recognition purposes.

There has also been a lot of interest in the use of metallo-helicates as building blocks for the formation of helical macromolecular structures such as catenates and molecular knots (Figure 1.8).⁶⁶ This work enables complex architectures to be synthesised using simple helicate starting materials. This synthetic approach was

demonstrated for instance, by Sauvage and co-workers⁸³ whereby a double stranded copper helicate, $[\text{Cu}_2\text{L}_2]^{2+}$ ($\text{L} = 4,4'-(1,4\text{-butanediyl-di-1,10-phenanthroline-9,2-diyl})\text{bis-phenol}$), was utilised to prepare catenate structures using intramolecular crown ether linkers (Figure 1.8).⁸³ It has also been demonstrated that the copper ions within these macromolecular complexes can be removed upon reaction with KCN or NH_4OH , allowing for the formation of complex organic structures.^{84,85}

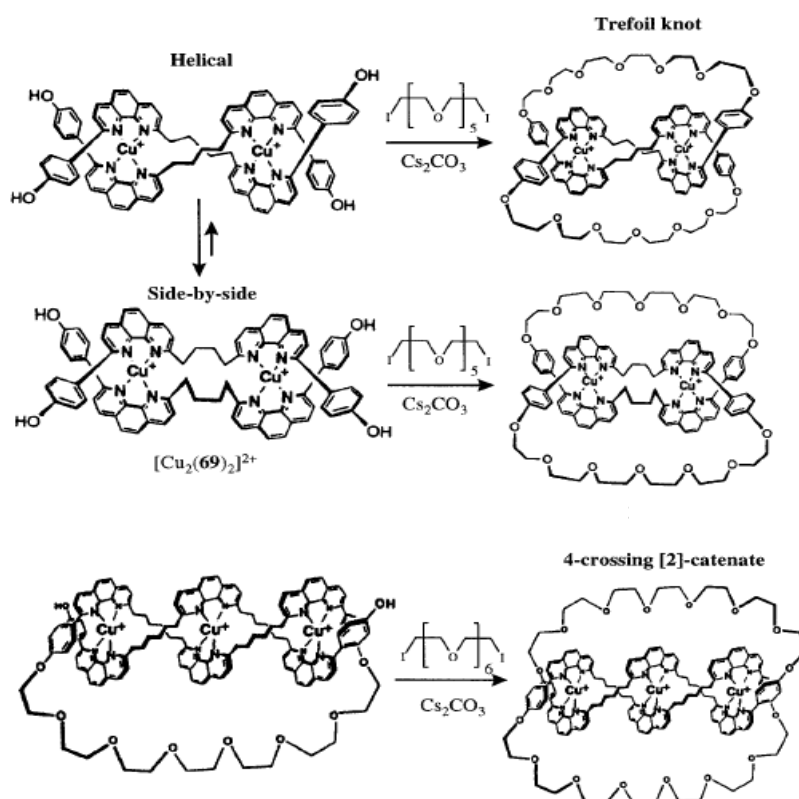


Figure 1.8: Schematic representation of the work conducted by Sauvage and co-workers whereby molecular helicates were used as building blocks for the formation of catenates and molecular knots.⁸³

Another aspect of helicate research involves their use for medicinal purposes. Given their shape and structure they were considered as ideal candidates for use as DNA intercalators thus allowing them to be used as potential drug molecules.⁶⁷ Although, it is believed that helicates interact with DNA at different sites they are considered most likely to engage in major groove binding interactions. Most promisingly of all it has been shown that helicates initiate single strand DNA cleavage upon light irradiation making them candidates for selective recognition binding and cleavage of oligonucleotides.⁸⁶ This research underlines the important role molecular helicates can play in the development of modern functional materials.

1.5 Molecular cages

Molecular cages are another class of supramolecular compound that has benefited from the greater understanding of self-assembly garnered in recent decades.¹⁰ These fascinating architectures often contain large inner cavities that can potentially be applied for molecular recognition purposes or as ‘molecular flasks’ (which enable chemical reactions to occur inside these cavities).⁴¹ These materials are normally formed by exploiting non-covalent forces such as hydrogen bonding and coordination bonds resulting in cage-like supramolecular architectures built from simple components.⁴¹

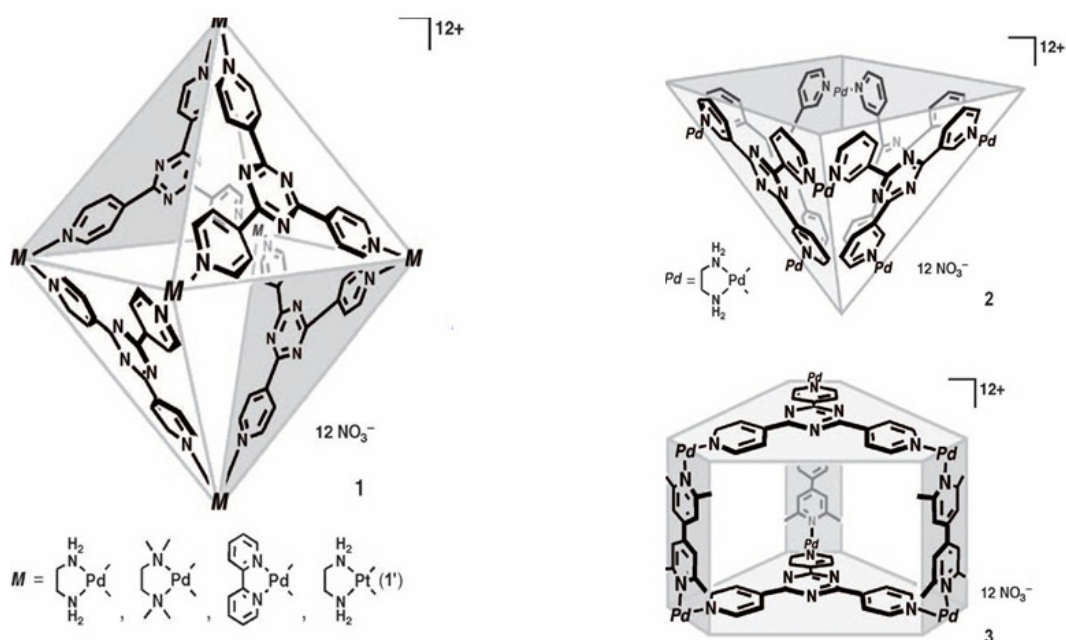


Figure 1.9: Examples of molecular cages developed by Fujita and co-workers.⁴¹

A synthetic approach for the synthesis of these molecular cages has been developed by Fujita and co-workers (Figure 1.9).⁸⁷ Their method employs a series of nitrogen donating organic ligands to link Pd^{II} or Pt^{II} ions into cage-like supramolecular structures. Ethylenediamine ‘capping’ ligands have been utilised as a means to enforce the square planar coordinated metal ions into a 90° *cis* conformation.⁸⁷ This system has led to the development of a variety of new supramolecular compounds which contain large cavities that could be used as a means to controllably trap and release guest molecules.⁸⁸ In conjunction with the potential use of these compounds for molecular recognition, it has also been shown that the

metal ion which they contain can be exploited for catalysis which can occur efficiently inside the cavity.⁸⁹

1.6 Molecular Magnetism

The desire to develop new materials with applicable magnetic properties has instigated renewed focus on metallo-supramolecular compounds. These compounds allow for the linking of spin centres, which can interact resulting in substances which exhibit interesting magnetic behaviour.⁹⁰ Innovative synthetic approaches have led to the design and synthesis of a variety of compounds such as spin crossover materials,⁹¹ single molecule magnets⁹² and spin chains.⁹³ It has been suggested that these magnetic materials could in future be applied in the formation of data storage or switching devices.⁹⁰

1.6.1 Spin crossover compounds

The desire to develop new data storage and information processing devices has led to an interest in materials that exhibit bistability. This has rejuvenated efforts to generate spin crossover (SCO) compounds.^{91,94}

Spin crossover is a phenomenon of transition metal complexes with an electronic configuration between d^4 and d^7 .^{91,94} The metal ions within these complexes can be in a high spin (HS) or low spin (LS) state depending on the field strength of the ligand that binds to the metal centre (Figure 1.10).⁹⁴ For an intermediate ligand field the energy gap (ΔE_{HL}^0) between the lowest vibronic level of the two states (HS and LS) can be sufficiently small that an external perturbation such as the application of light, heat or pressure can instigate a change in state.⁹⁴ This process is known as a spin transition (ST) or spin crossover (SCO) and is usually accompanied by a change in the physical properties (colour, magnetism and bond lengths) of the material. If there is a high degree of cooperativity between the metal ions of SCO materials, the transition can occur abruptly or *via* a hysteresis loop.⁹⁴ SCO compounds are therefore ideal candidates for application in memory storage devices as they may exhibit bistability.

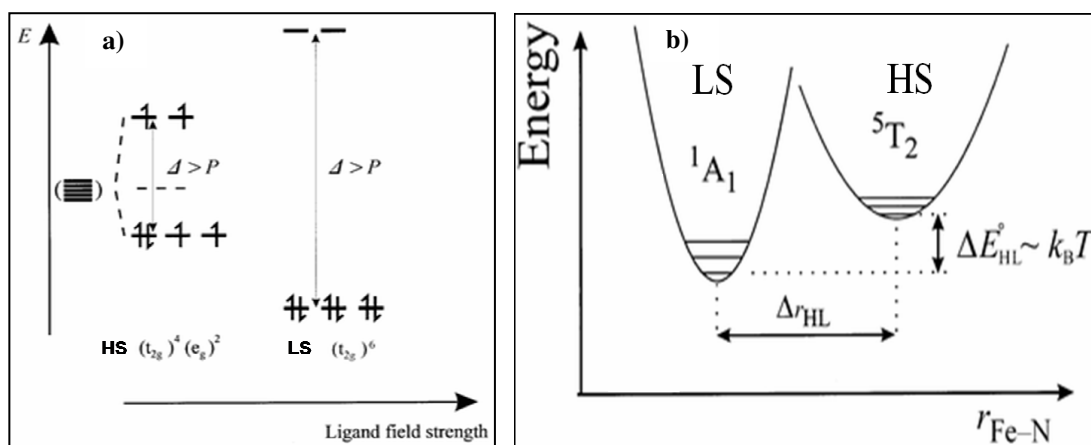


Figure 1.10: a) Electronic configuration for a d^6 Fe^{II} ion in the LS and HS states. Equilibrium between these two states exists in the case of spin crossover. b) Representation of the potential well for 1A_1 (LS) and 5T_2 (HS) states in a Fe^{II} SCO system.⁹⁴

Within the literature, Fe^{II} complexes have shown the greatest propensity to display SCO properties. The use of nitrogen donor ligands to generate complexes with a $\{\text{FeN}_6\}$ coordination sphere has proved particularly successful in the production of SCO materials.^{91,94} Predominantly, work in this area focuses on the formation of supramolecular arrays which contain SCO centres linked *via* weaker interactions, such as π - π stacking, hydrogen bonding or coordination bonds.^{95,96} These intermolecular forces result in a high degree of cooperativity between the metal centres enabling the SCO to occur through a hysteresis loop.

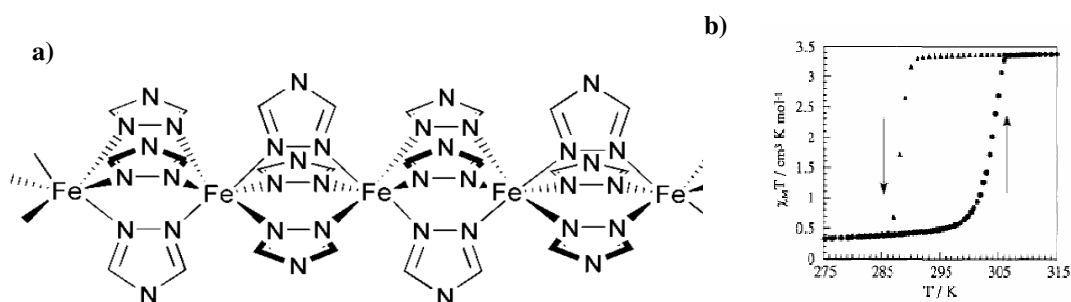


Figure 1.11: a) The structure of $[\text{Fe}(\text{Htrz})_3]^{2+}$ (H atoms have been removed for clarity).⁹⁷ b) The temperature dependent magnetic susceptibility measurement for $[\text{Fe}(\text{Htrz})_3]^{2+}$ revealing a broad hysteresis loop.⁹⁸

Kahn and co-workers have developed a synthetic approach for the formation of Fe^{II} coordination polymers (Figure 1.11) that display fascinating SCO properties.⁹⁷ These compounds consist of Fe^{II} ions linked in 1D polymeric chains composed of $[\text{Fe}(\text{Rtrz})_3]^{2+}$ sub-units ($\text{Rtrz} = 4\text{-R-1,2,4-triazole}$ where $\text{R} = \text{H}$ or NH_2)^{97,98} The covalent linking of the Fe^{II} ions within the polymeric chains gives rise to strong

cooperativity.⁹⁰ These cooperative effects result in abrupt spin crossover transitions which occur in the room temperature range.⁹⁷ These polymeric species also reveal broad thermal hysteresis loops of between 5 K and 20 K in width.⁹⁷ For example, Figure 1.11 shows the structure of the $[\text{Fe}(\text{Htrz})_3]^{2+}$ complex which has two characteristic spin crossover temperatures at 285 K and 305 K.⁹⁷

Recently there has also been an endeavour to utilise SCO behaviour for molecular recognition purposes.^{40,99,100} These approaches involve the recognition of a guest molecule within a host through a change in the magnetic and/or optical properties of the material. It has previously been shown that the magnetic properties of metal-organic frameworks can be alerted dramatically through the presence of guest molecules such as solvent molecules.²⁴ This work led researchers to investigate if SCO centres could be incorporated within framework structures. Examples of such systems have been reported by Kepert *et al.* and are known as spin crossover metal-organic frameworks (SCOFs).^{99,100,101,102} Within these frameworks, the Fe^{II} ions centres are linked by rigid pyridyl ligands.¹⁰¹ These frameworks were shown to contain large 1D channels which can incorporate guest solvent molecules.^{100,101} The presence of the guest molecules was recognised by a change in the spin crossover temperature of the material.^{100,101}

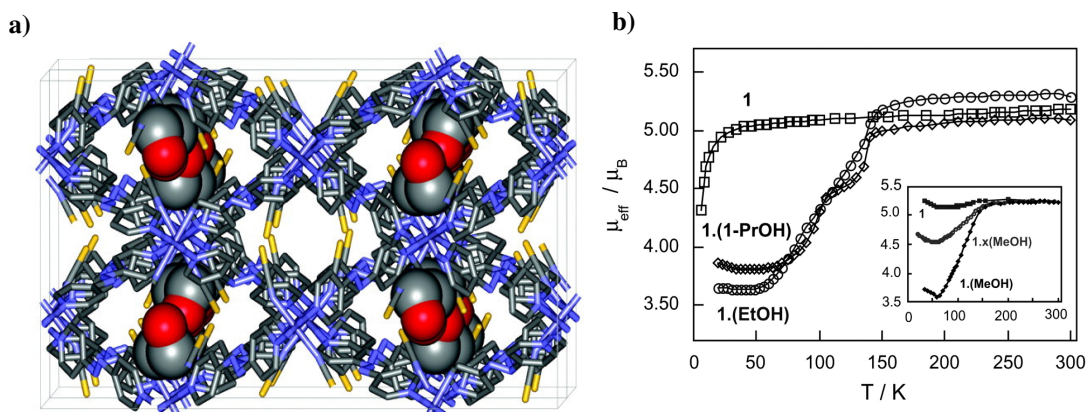


Figure 1.12: **a)** The X-ray crystal structure of the spin crossover metal-organic framework (SCOF), $\text{Fe}_2(\text{azpy})_4(\text{NCS})_4 \cdot (\text{EtOH})$ viewed approximately down the 1-D channels (c axis). Framework atoms are represented as sticks and atoms of the ethanol guests as spheres. In the framework the ethanol guests occupy every second 1-D channel in a "chessboard" arrangement.⁹⁹ **b)** Temperature dependent magnetic susceptibility measurements showing the change in SCO properties upon the absorption of guest solvent molecules.⁹⁹

A relevant compound is the highly cited SCOF, $[\text{Fe}_2(\text{azpy})_4(\text{NCS})_4] \cdot \text{EtOH}$ (azpy = *trans*-4,4'-azopyridine), which undergoes a spin crossover transition at 150 K

(Figure 1.12).⁹⁹ However, when the ethanol molecules are removed the compound no longer displays a SCO transition and it remains in the HS state at all measured temperatures.⁹⁹ It was shown that $[\text{Fe}_2(\text{azpy})_4(\text{NCS})_4] \cdot \text{EtOH}$ could absorb other guest molecules such as methanol and propanol molecules.⁹⁹ The presence of these guest molecules were recognised by a change in the SCO behaviour of the compound. When methanol molecules are absorbed by the compound it exhibits a one step SCO transition at 140 K, however the propanol containing analogue displays a two step SCO transition with a plateau centered at 120 K.⁹⁹

For spin crossover materials to be applicable for future devices the spin crossover transition must occur within an appropriate temperature range.¹⁰³ Therefore, there is an ongoing effort to understand the factors which induce and influence spin crossover behaviour.¹⁰⁴ It has been demonstrated that molecular shape has an important influence on spin crossover in Fe^{II} and Fe^{III} complexes.^{104,105} A HS molecule will not undergo a spin transition if its shape differs too strongly from that preferred by its LS form.¹⁰⁶ The molecular rearrangement that would be required in such a case can not be accommodated by a rigid solid lattice and the molecule remains trapped in its HS.¹⁰⁶ This suggests that the structure of the organic ligand used in SCO complexes can have a dramatic impact on their SCO properties. This effect was exemplified by Halcrow and co-workers who have investigated the SCO behaviour of a series of Fe^{III} saltrien complexes (Figure 1.13a).¹⁰⁵ The spin-state behaviour (Figure 1.13b) of these complexes is influenced by two factors.¹⁰⁵ Firstly, the HS and LS forms of the complexes may co-exist in solution at ambient temperatures. Therefore, the least soluble form of the complex is likely to crystallise.¹⁰⁵ The second factor is the shape of the molecules, which is highly non-spherical with two phenoxy “arms” projecting from the same face of the molecule.¹⁰⁵ The relative orientations of these arms, α differs substantially between the compounds ($61.8^\circ \leq \alpha \leq 125.0^\circ$), demonstrating a substantial degree of flexibility in the saltrien ligand framework.¹⁰⁵ It was concluded that only HS $[\text{Fe}(\text{saltrien})]^+$ complexes whose ligand conformations resemble those adopted by the LS species, can undergo spin-crossover.¹⁰⁵ Therefore, only species with α values less than 90° should display SCO behaviour.¹⁰⁵ This was demonstrated by the coordination compound $[\text{FeL}^5]\text{PF}_6$ ($\text{L}^5 = 1,8\text{-diamino-3,6-diazaoctane}$) which has an α value of 100.94° and does not exhibit any SCO behaviour (Figure 1.13a and b).¹⁰⁵

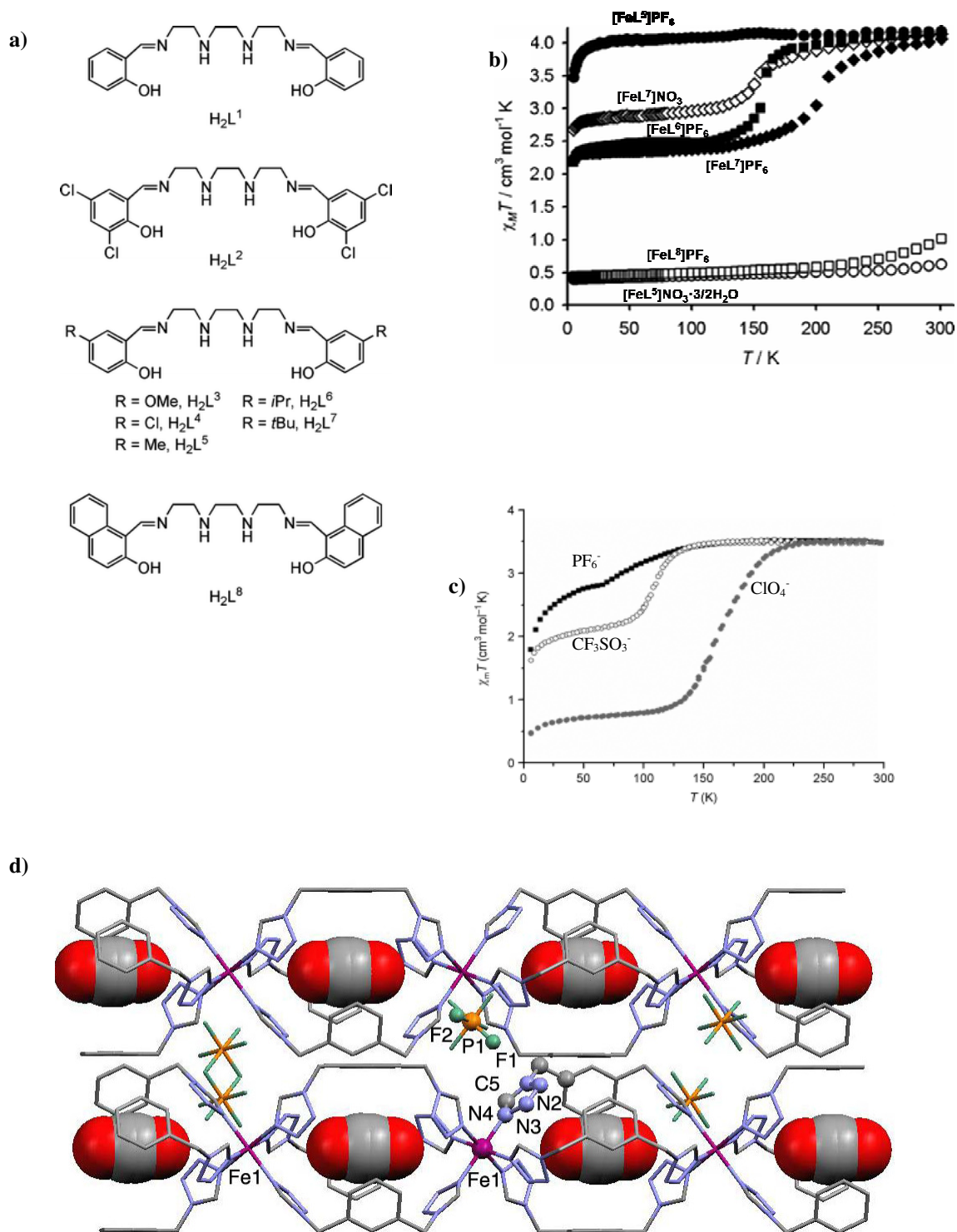


Figure 1.13: a) The ligands used in the formation of the Fe^{III} salttrien complexes developed by Halcrow and co-workers and b) the temperature dependent magnetic susceptibility measurements of these complexes showing the influence of ligand conformation on the spin transition process.¹⁰⁵ c) the magnetic properties of the $[\text{Fe}(\text{btzx})_3]^{2+}$ complexes demonstrating the effect the counterion has on the spin crossover properties of these materials.¹⁰⁷ d) The structure of the $[\text{Fe}(\text{btzx})_3]^{2+}$ complexes synthesised by Quesada *et. al.*¹⁰⁷

The counterion employed in spin crossover systems also influences their SCO behaviour.^{104,108} Quesda *et al.* have investigated this effect for a series polymeric $[\text{Fe}(\text{btzx})_3]^{2+}$ complexes (where $\text{btzx} = m\text{-xylene}(\text{bis})\text{tetrazole}$) (Figure 1.13d).¹⁰⁷ In this study PF_6^- , ClO_4^- and CF_3SO_3^- were selected as the counterions.¹⁰⁷ Figure 1.13c shows the temperature dependent magnetic susceptibility for each compound and demonstrates the effect counterions have on the transition temperatures of these complexes. When PF_6^- is employed as the counterion the compound undergoes a one step SCO transition with a transition temperature of 160 K but for the analogous ClO_4^- and CF_3SO_3^- compounds the transition temperatures are lowered to 130 K and 110 K, respectively.¹⁰⁷ Quesda *et al.* suggest that the variation in distances between the counterion and the Fe^{II} centre within the compound is the reason for this change in transition temperature.¹⁰⁷ Short counterion to metal distance leads to a distortion of the Fe^{II} octahedral coordination environment.¹⁰⁷ This distortion limits the freedom of the compound's tetrazole rings to move, thus stabilising the HS state.¹⁰⁷ This effect gives rise to the lower transition temperatures observed for $[\text{Fe}(\text{btzx})_3](\text{ClO}_4)_2$ and $[\text{Fe}(\text{btzx})_3](\text{CF}_3\text{SO}_2)_2$.¹⁰⁷

Since 1984, when Decurtins *et al.* discovered the phenomenon of light-induced $^1\text{A}_1$ (LS) $\rightarrow$ $^5\text{T}_2$ (HS) transitions in Fe^{II} complexes¹⁰⁹ a significant part of the research in the field of Fe^{II} spin crossover has focused on the use of light as a means of instigating spin crossover.^{91,108} This photo-induced transition (Figure 1.14a) involves the excitation of the $^1\text{A}_1$ (LS) state to the $^1\text{T}_1$ state.⁹¹ This is followed by two successive inter-systems crossing (ISC) steps ($^1\text{T}_1 \rightarrow ^3\text{T}_1 \rightarrow ^5\text{T}_2$), resulting in the population of the metastable $^5\text{T}_2$ (HS) state.⁹¹ The energy barrier between the two states ($^1\text{A}_1$ and $^5\text{T}_2$) is large enough to 'trap' the system in the HS state at low temperatures.¹⁰⁸ This phenomenon is known as light induced excited spin state trapping or LIESST and has been investigated for a wide variety of Fe^{II} complexes.^{110,111,112} The LIESST behaviour is only observed at very low temperatures because above a certain critical temperature defined as $T(\text{LIESST})$, the system clears the energy barrier between the two spin states and relaxes to the LS state.¹¹²

An example of a Fe^{II} compound that displays LIESST behaviour is the highly cited $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ (PM-BiA = *N*-(2-pyridylmethylene)aminobiphenyl) complex synthesised by Kahn and his co-workers (Figure 1.14b).¹¹³ This compound has a $T(\text{LIESST})$ of 80 K and was the first to display a phenomenon known as light induced thermal hysteresis (LITH).¹¹³ This behaviour occurs when the temperature

dependence of the magnetic susceptibility is not the same in the cooling and warming modes when the compound is irradiated at temperatures below $T(\text{LIESST})$.¹¹³

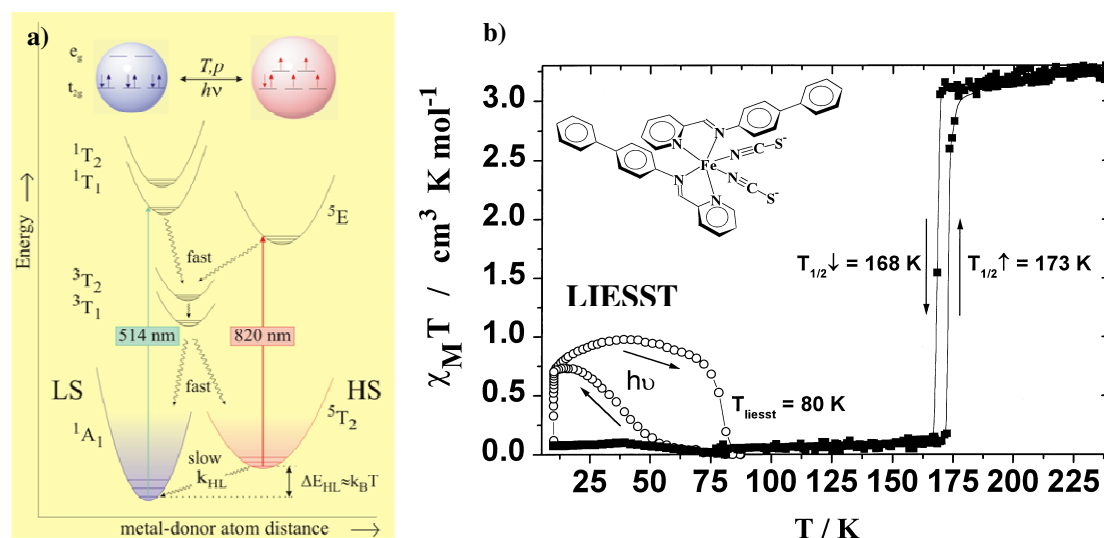


Figure 1.14: a) The Jablonski diagram highlighting the LIESST process.⁹⁴ b) The LIESST behaviour of the complex $\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2$ (inset: the structure of the complex.)¹¹³

1.6.2 Single molecule magnets

The desire to develop new magnetic materials has prompted research into single molecule magnets (SMM).^{92,114} These are, as the name suggests, single molecules that display bulk magnetic properties.¹¹⁵ Single molecule magnets are large and often complex coordination clusters that possess a combination of high spin (S), and axial anisotropy (D) in their ground state.¹¹⁶ This combination results in a significant barrier (U) to magnetisation reversal which leads to slow relaxation of magnetisation and hysteresis effects.¹¹⁶

The first compound to display this fascinating behaviour, $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 2\text{H}_2\text{O}$ (Figure 1.15a), was synthesised by Lis in 1980.¹¹⁷ This compound contains an unprecedented dodecanuclear mixed valent Mn cluster core with a disc shaped geometry. Its structure features a central $\text{Mn}^{\text{IV}}_4\text{O}_4$ cubane connected to a non-planar ring of eight Mn^{III} atoms by eight bridging μ_3 -oxide atoms.¹¹⁷ Bridging acetate and terminal water ligands passivate the surface of the cluster, such that each Mn ion displays a distorted octahedral coordination environment.^{116,117}

Magnetisation data for this compound collected at high magnetic field strengths and low temperatures indicate that the compound has a $S = 10$ ground state

and a large axial anisotropy. The total spin of the ground state arises from a situation where the spins of the four central Mn^{IV} ions ($S = 3/2$) are all aligned antiparallel to the spins of the eight outer Mn^{III} ions ($S = 2$), giving a total spin of $S = [(4 \times 3/2) - (8 \times 2)] = 10$.¹¹⁸ This Mn_{12} cluster also displays slow relaxation of magnetisation at low temperatures and this results in hysteresis effects (Figure 1.15a).¹¹⁹ The Mn_{12} cluster exhibits a magnetisation relaxation half-life of more than 2 months at 2 K. However, above 4 K this half-life is dramatically reduced and magnetic hysteresis is no longer observed.¹²⁰ Therefore, a lot of research has focused on the development of related coordination clusters that display large spin reversal barriers U and thus exhibit magnetic hysteresis effects at higher temperatures.¹²¹

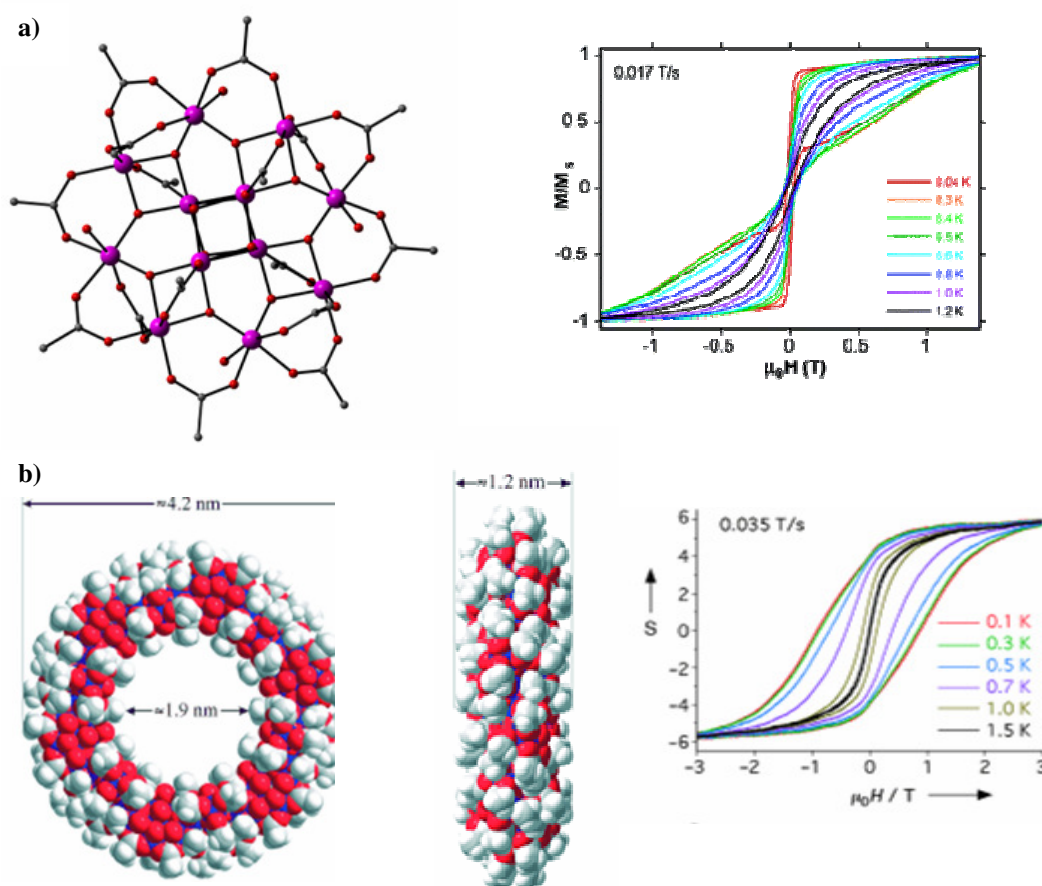


Figure 1.15: a) The classical $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 2\text{H}_2\text{O}$ cluster and a plot of its magnetisation versus applied d/c magnetic field, showing hysteresis effects at temperatures below 4 K.^{117,118} b) The Mn_{84} cluster and a plot of its magnetisation versus applied d/c magnetic field (The magnetisation has been plotted as spin (S) per $\{\text{Mn}_{84}\}$ molecule).¹²²

Investigations using this cluster type have primarily focused on the modification of the original Mn_{12} structure. One such approach, developed by

Christou and co-workers, has focused on exchanging the bridging acetate ligands for other carboxylate type ligands.^{123,124} The ability to synthesise reduced species has also been investigated by varying the $\text{Mn}^{\text{II}}:\text{Mn}^{\text{VII}}$ ratio used in the formation of the cluster species.^{125,126} This approach is known as ‘reductive aggregation’,¹¹⁴ and was exploited in the formation of the fascinating Mn_{84} cluster, $[\text{Mn}_{84}\text{O}_{72}(\text{O}_2\text{CMe})_{78}(\text{OMe})_{24}(\text{MeOH})_{12}(\text{H}_2\text{O})_{42}(\text{OH})_6]$, shown in Figure 1.15b.¹²² Within this coordination cluster, the Mn ions are arranged into a circular torus motif.¹²² This compound displays magnetic hysteresis at temperatures below 1.5 K (Figure 1.15b).¹²²

Iron coordination clusters have also been studied with the desire to develop SMMs. For instance, the compound $[\text{Fe}_{19}\text{O}_6(\text{OH})_{14}(\text{metheidi})_{10}(\text{H}_2\text{O})_{12}]$ (metheidi = N-(1-hydroxynethylethyl)iminodiacetic acid), developed by Heath and co-workers shows a large spin ground state of $S = 33/2$.¹²⁷

Another potential way to alter the magnetic properties of these cluster species is the incorporation of heteroatoms within the cluster core.¹²¹ Lanthanide ions are ideal candidates for this purpose as they possess a large magnetic anisotropy.¹²⁸ Powell *et al.* have developed a synthetic approach for the formation of large coordination clusters that contain both transition metal and lanthanide ions.¹²⁹ This approach involves the reaction of preformed 3d carboxylate aggregates with simple lanthanide salts in the presence of N-substituted diethanolamine ligands. This synthetic methodology has led to the generation of a variety of 3d-4f clusters which exhibit SMM behaviour.¹³⁰

1.6.3 Single chain magnets

Another class of compounds that are of interest to magneto-chemists are single chain magnets (SCM).⁹³ These are 1D polymeric materials which display slow relaxation of magnetisation and can show some hysteresis behaviour at low temperature.^{93,131} In 2001, Sessoli and co-workers reported the first example of SCM behaviour within a 1D polymer chain, $[\text{Co}(\text{hfac})_2(\text{NITPhOMe})]$ (hfac = hexafluoroacetylacetonate, NITPhOMe = 4'-methoxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide), that consist of alternating Co^{II} centres and organic radical moieties.¹³² This compound reveals a magnetic hysteresis below 4 K and the

1D chains behave as superparamagnetic nanowires.¹³² Since the publication of this seminal work, numerous synthetic approaches have been developed for the generation of SCMs.^{131,133,134} To achieve SCM behaviour a number of criteria must be met.¹³¹ Firstly, The 1D chains must possess a strong uniaxial anisotropy (D) together with a net spin magnitude ($S > 0$) along the chain. This means it is preferable that the spin centres of the chains are ferro- or ferrimagnetically coupled.¹³¹ However, spin canted antiferromagnetic interactions may also be employed in the formation of SCMs.¹³¹ The generation of SCM systems also requires that the inter-chain interactions must be much smaller than the intra-chain ones.¹³¹ This requirement can be overcome by the use of extended organic linkers that act as spacers between the 1D chains.^{135,136}

Liu and co-workers have utilised a series of azido bridges to link Co^{II} ions into homonuclear chains, $[\text{Co}(2\text{-}2'\text{-bithazoline})(\text{N}_3)_2]_n$ (Figure 1.16a).¹³⁷ Within these 1D polymer chains, bithazoline ligands are also employed as peripheral spacers which are required to reduce the inter-chain magnetic interactions.¹³⁷ This compound shows intriguing magnetic behaviour with a large hysteresis cycle at temperatures below 1.85 K (Figure 1.16b).¹³⁷

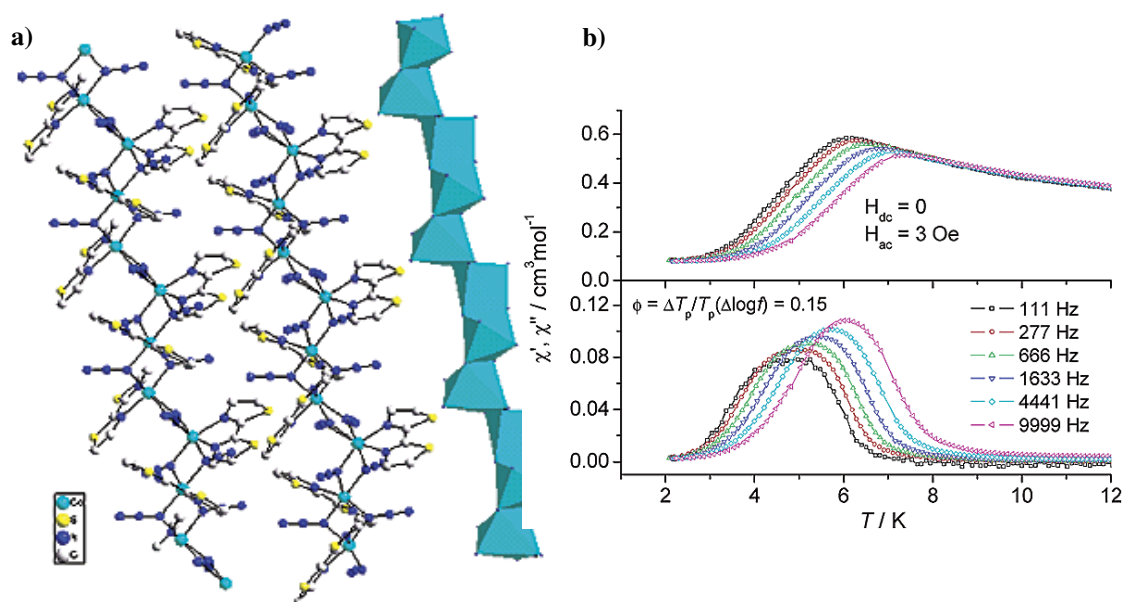


Figure 1.16: a) The coordination polymer $[\text{Co}(2\text{-}2'\text{-bithazoline})(\text{N}_3)_2]_n$ and b) its temperature dependent magnetic susceptibility displaying single chain magnet behaviour.¹³⁷

Although the development of these SCM materials has progressed rapidly there remains one major flaw with regard to the potential application of these compounds for device purposes: As with SMMs, SCMs only display bistability at

very low temperatures.^{93,131} However, it is thought that the coupling of the 1D magnetic properties of SCMs with other physical phenomenon such as spin crossover or photo-magnetism could in future produce desirable multifunctional devices.^{113,138}

1.7 Schiff base ligands in supramolecular chemistry

Since they were first discovered by Hugo Schiff in 1864,¹³⁹ Schiff base ligands have become one of the most widely used ligand type in coordination chemistry.^{140,141} The predictable binding modes of these imine type ligands can be exploited in transition metal directed self-assembly to produce a variety of metallo-supramolecular architectures such as macrocycles,^{142,143} grid structures,¹⁴⁴ metallohelicates^{145,146} and coordination cages.¹⁴⁷

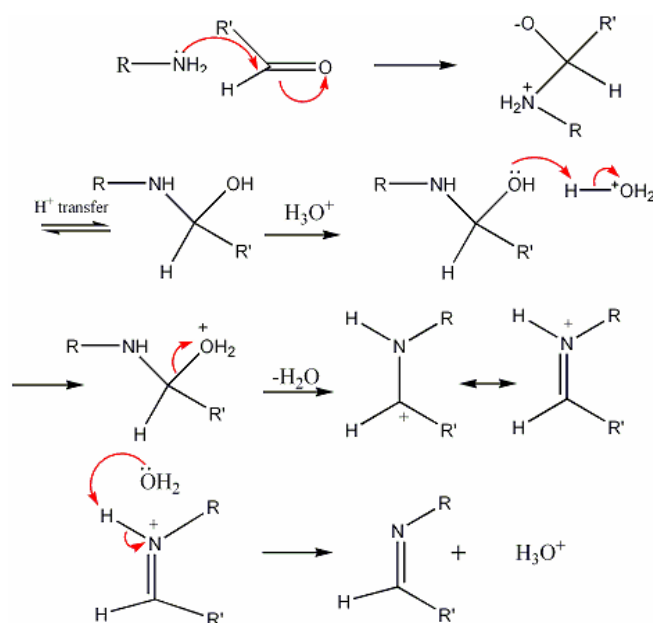


Figure 1.17: The reaction mechanism for the formation of Schiff bases (R and R' represent various aryl and alkyl groups).^{140,148}

Schiff base ligands are easily prepared *via* a nucleophilic addition reaction between a primary amine and a carbonyl compound. The reaction are usually carried out in alcoholic solutions.¹⁴⁰ The mechanism of the imine formation (Figure 1.17) involves a nucleophilic attack on the carbonyl functionality by the lone pair electrons of the amine, yielding a tetrahedral intermediate.¹⁴⁹ Proton transfer from the nitrogen atom to the oxygen atom then occurs, resulting in the formation of a neutral carbinolamine species. The hydroxyl group is then protonated by an acid catalyst

followed by the expulsion of water to give an iminium ion. Subsequent loss of a proton from the nitrogen atom gives the neutral Schiff base product.^{148,149}

Owing to their ease of formation, a large variety of Schiff base ligands, ranging from monodentate species¹⁵⁰ to large macrocyclic moieties,¹⁴² have been described in the literature.^{140,141} One of the most prominent examples are the so called salen-type ligands.¹⁵¹ These tetradentate ligands exhibit a {N₂O₂} binding mode and result from a condensation reaction between a salicylaldehyde derivative and a diamine.¹⁵¹ Salen derivatives have been used in the formation of polynuclear transition metal complexes that display appealing catalytic and magnetic properties.^{104,152} For example, Jacobsen and co-workers have developed a chiral salen-type ligand, (R,R)-N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, which was used to form a mononuclear Mn^{II} complex that displays activity as an epoxidation catalyst.¹⁵³

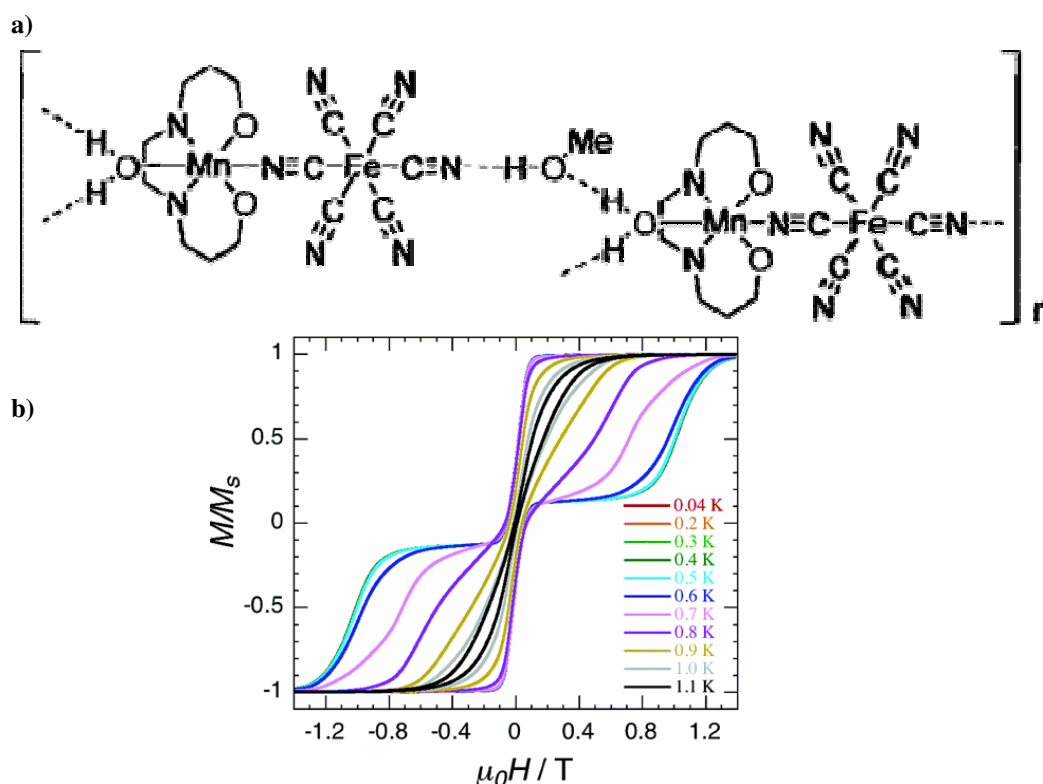


Figure 1.18: a) Schematic representation of the 1D polymer chain in (NEt₄)[Mn₂(salmen)₂(MeOH)₂Fe(CN)₆].¹⁵⁶ b) Field dependence of the magnetisation of (NEt₄)[Mn₂(salmen)₂(MeOH)₂Fe(CN)₆] below 1.1 K.¹⁵⁷

Salen-type ligands have also been utilised for the synthesis of coordination compounds that display fascinating magnetic properties.^{154,105} It was demonstrated that the [Mn^{III}(salen)]⁺ complex exhibits axial elongated Jan-Teller distortion which

results in a large uniaxial anisotropy (D).¹⁵⁵ For this reason, $[\text{Mn}^{\text{III}}(\text{salen})]^+$ and derivative complexes have recently been attracting much attention as a source of uniaxial magnetic anisotropy for the design of molecular superparamagnets such as SMMs or SCMs.¹⁵⁴ Miyasaka and co-workers have developed the compound $(\text{NEt}_4)[\text{Mn}_2(\text{salmen})_2(\text{MeOH})_2\text{Fe}(\text{CN})_6]$ (salmen = *rac-N,N'*-(1-methylethylene)bis(salicylideneimine)) (Figure 1.18a) which consists of a network of discrete dinuclear $[\text{Mn}_2(\text{salmen})_2(\text{MeOH})_2\text{Fe}(\text{CN})_6]$ complexes linked by H-bonding.¹⁵⁶ It was shown that this compound behaves as a SMM at temperatures below 1.1 K, with a $S = 9/2$ ground state (Figure 1.18b).¹⁵⁷

Macrocyclic Schiff base complexes have also attracted much attention as they can be used as model systems for complicated metalloproteins, such as haemoglobin.^{141,158} Many macrocyclic complexes have been prepared using template synthesis.^{140,141} This synthetic approach involves the condensation of a dicarbonyl precursor with an appropriate polyamine in the presence of a metal ion.^{141,159} This template effect has been known since 1964 when Curry and Busch reported the Fe^{II} -templated condensation of 2,6-diacetylpyridine with triethylenetetramine to give a Fe^{III} pentaazadiimino macrocycle. Since then researchers have developed synthetic approaches for the generation of complex macrocycles that can be applied as biological models.¹⁶⁰ For instance, McKee and co-workers have developed a series of dinuclear Cu^{II} macrocycles derived from the condensation of 2,6-diacetylpyridine and 1,*n*-diamino-*n'*-hydroxyalkanes (where *n,n'* = 3,2; 4,2; and 5,3).¹⁶¹ These dinuclear Cu^{II} macrocyclic compounds are used as model systems for haemocyanin which is the dioxygen-carrying metalloprotein found in arthropods and molluscs.¹⁶¹

Schiff bases have also shown the ability to self-assemble into molecular helicates in the presence of transition metal ions.^{73,145,146} A series of ligands which consist of two imine binding groups linked by a diaminophenylmethane core have been extensively exploited for this purpose (Figure 1.19).^{75,76} As discussed in section 1.4, Hannon and co-workers have used these diimine ligands to develop a series of dinuclear helicates that were shown to bind and coil with DNA.^{76,77,78} They have also reported the Ru^{II} helicate, $[\text{Ru}_2\text{L}_3]^{4+}$ (where $\text{L} = \text{N,N'}$ -bis-(2-pyridine-2-yl-methylene)-4,4'-diaminodiphenylmethane), which displays some cytotoxic activity against the human breast cancer cells HBL-100 and T47D.⁷⁷

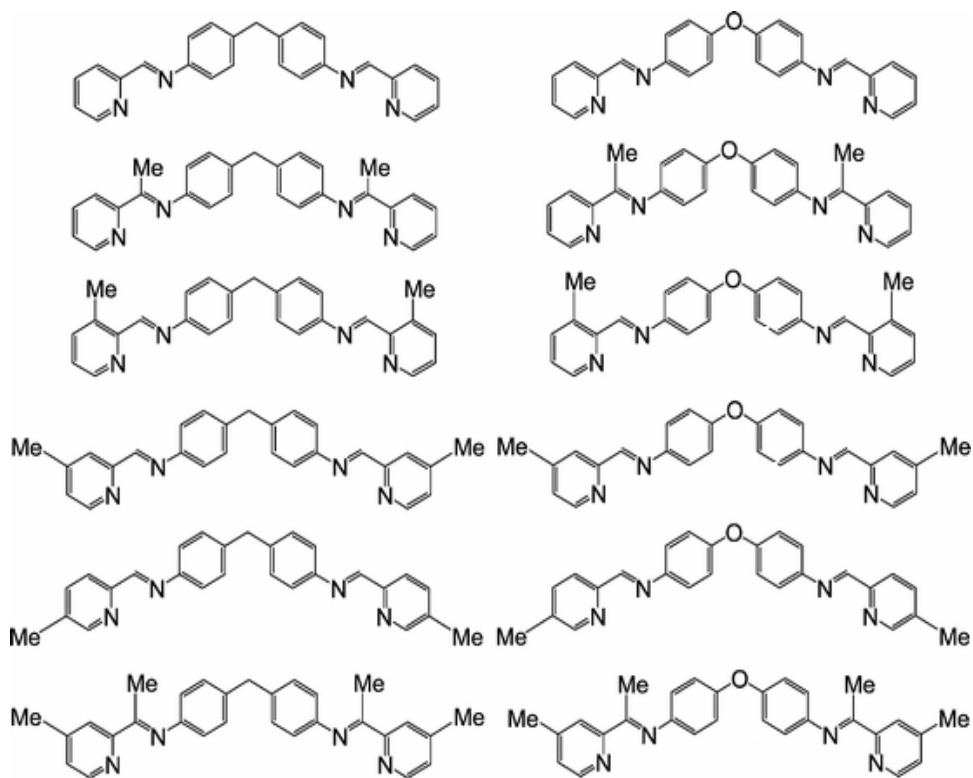


Figure 1.19: Examples of flexible Schiff base ligands that have been used in the self-assembly of molecular helicates.⁷⁶

Chapter Two



Objectives and thesis outline

2.1 Aims and objectives of present study

The aim of this study is to exploit transition metal directed self-assembly approaches to generate hybrid inorganic-organic materials that display appealing physical properties. Particular attention is focused on the development of metallo-supramolecular assemblies such as molecular helicates and coordination clusters that may exhibit interesting magnetic properties such as spin crossover and superparamagnetism. We further aim to modify our reaction systems to obtain supramolecular architectures with open-framework topologies that may give rise to a degree of porosity that could potentially be exploited for molecular recognition or gas storage purposes. In order to synthesise these metallo-supramolecular assemblies three main types of ligands are employed, bis-bidentate and tris-bidentate Schiff base ligands (Figure 2.1), carboxylic acid substituted aromatic ligands (Figure 2.2a) and iminodiacetic acid substituted phenol ligands (Figure 2.2b).

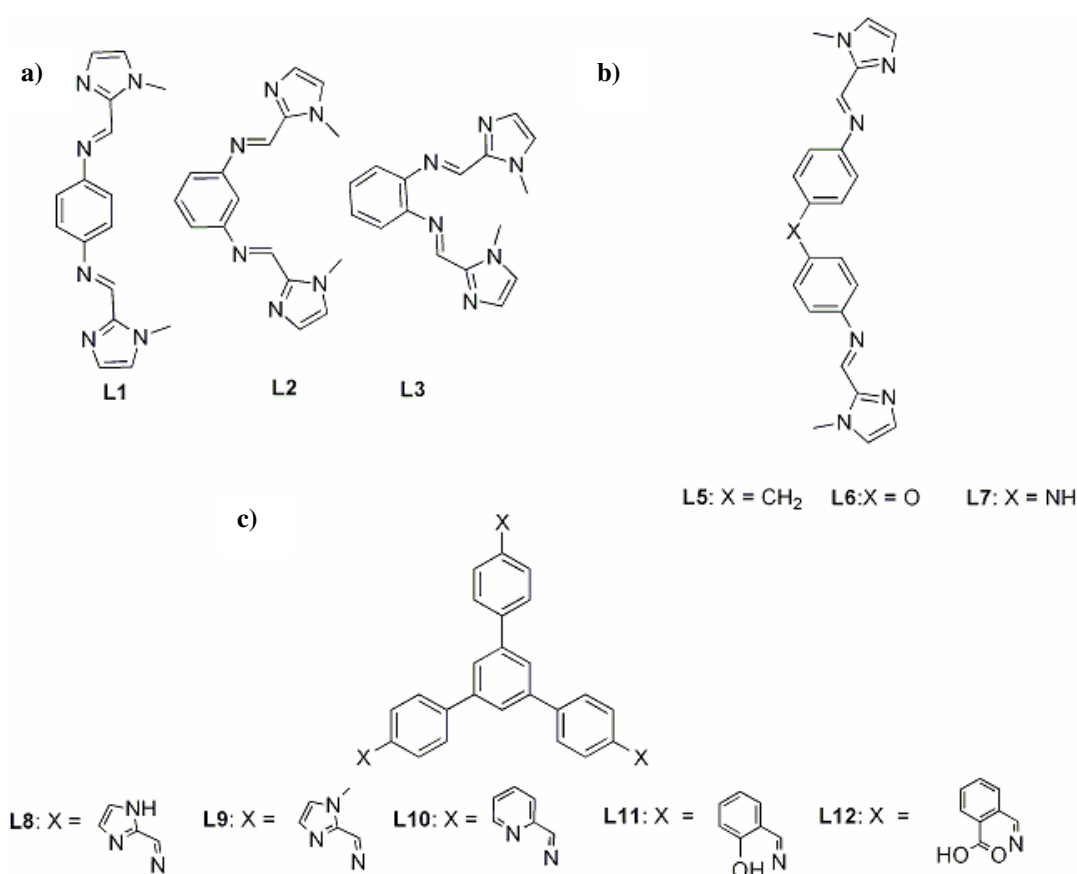


Figure 2.1: Structure of bis-bidentate and tris-bidentate ligands used in this study.

2.2 Thesis outline

This thesis mainly concentrates on the transition metal directed self-assembly of a series of bis-bidentate and tris-bidentate Schiff base ligands shown in Figure 2.1 (Chapters 3-5). Imine ligands are employed in this study as their modular nature and bidentate binding mode could potentially give rise to the generation of a diverse range of metallo-supramolecular assemblies. These Schiff base ligands are also useful for the formation of transition metal complexes that display interesting magnetic properties. For example, upon complexation with Fe^{II} ions these imine ligands produce an intermediate ligand field which may allow the resultant complexes to exhibit spin crossover behaviour.

In Chapter 3, the coordination chemistry of a series of novel bis-bidentate Schiff base ligands (Figure 2.1a) is investigated. These ligands consist of two methyl-imine-imidazole functionalities linked *via* a benzene ring. Upon complexation with transition metal ions, the relative orientation of the imine-imidazole bidentate binding sites influence the topology of the resultant species. We obtain dinuclear Co^{II} and Ni^{II} complexes and tetranuclear Fe^{III} and Cu^{II} complexes. Attention is also focused on using these imine ligands to stabilise coordination clusters. The applied synthetic approach results in the formation of a nonanuclear Cu oxo-cluster that is stabilised by two carbinolamine ligands. The carbinolamine ligands arise from the partial hydrolysis of the Schiff base ligands under the applied reaction conditions.

Chapter 4 presents a synthetic strategy for the formation of metallo-helicates. The applied approach involves the use of flexible bis-bidentate ligands (Figure 2.1b). These ligands consist of imine-imidazole binding sites linked by 4-4'-diaminodiphenylmethane, 4-4' oxydianiline or 4-4' diaminodiphenylamine linkers. The flexible nature of the amine linkers gives rise to the formation of helical architectures upon reaction with transition metal ions. The reaction of the flexible Schiff base ligands with Fe^{II} salts is of particular interest as helicate species that display spin crossover behaviour can be generated. The counterions used or the structure of the organic ligand employed in the formation of the Fe^{II} helicate play a significant role in determining the SCO properties of the resultant compound.

In Chapter 5, the coordination chemistry of related tris-bidentate Schiff base ligands is discussed (Figure 2.1c). In this case the imine binding sites are connected by a tri-phenyl benzene backbone. The ligands generate trinuclear Co^{II} complexes that

are stabilised by two Schiff base ligands. These molecular entities further pack in the solid state into a hexagonal network structure which is stabilised by weak H-bonding and CH-halogen bonding interactions. The hexagonally packed coordination assembly contains solvent filled channels.

A further aspect of the presented research project is concerned with the formation of Li coordination networks as these materials have recently been shown to display enhanced hydrogen storage capabilities.^{162,163} Surprisingly, carboxylic acid substituted aromatic ligands have rarely been employed for the formation of Li-based network structures. In Chapter 6, a synthetic approach for the formation of Li coordination networks that are stabilised by simple carboxylic acid substituted aromatic ligands (Figure 2.2a), is described.

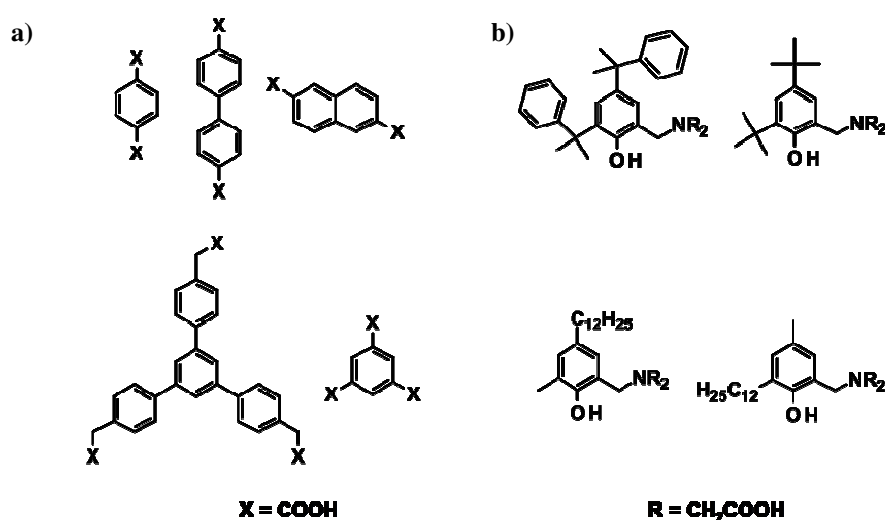


Figure 2.2: a) Structure of carboxylic acid substituted aromatic ligands used in the formation of Li coordination networks. b) The structure of the iminodiacetic acid substituted phenol ligands used in the generation of amphiphilic Fe^{III} coordination assemblies.

Chapter 7 outlines the use of iminodiacetic acid substituted phenol ligands (Figure 2.2b) for the formation of amphiphilic Fe^{III} coordination assemblies. The resulting architectures originate from the self-assembly of mononuclear Fe^{III} complexes that network *via* hydrogen bonds involving constitutional water molecules. The amphiphilic nature of the coordination assemblies that contain well defined hydrophobic organic and hydrophilic inorganic areas, can be exploited for molecular self-assembly purposes to generate non-crystalline, hierarchical nanomaterials, e.g. spherical vesicles. Electron microscopy was employed to characterise the self-assembled materials suggesting that they consist of layered lamellar structural motifs similar to the parent crystalline materials.

2.3 Specific aims of this study

In order to accomplish our objectives we initially set out to attain the following:

- a) Synthesise and fully characterise assorted organic ligands.
- b) Obtain an understanding of the structural directing influences of these ligands in order to generate metallo-helicates, metal-organic frameworks, coordination compounds and oxo-cluster compounds upon complexation with transition metals.
- c) Utilise single crystal X-ray diffraction to structurally characterise the compounds.
- d) Determine the physiochemical properties (photochemical properties, thermal stability, etc.) of all the compounds.
- e) Monitor the formation of these compounds *via* spectroscopic methods.
- f) Investigate the magnetic properties of all relevant compounds with particular emphasis on the study of the Fe^{II} complexes that may display SCO behaviour. The temperature dependent magnetic susceptibility of oxo coordination clusters and other molecular species will also be examined where appropriate.
- g) Gain an insight into the effect of ligand functionality, on both the SCO behaviour of the Fe^{II} complexes and on the inter-atomic coupling and spin ground state of potential cluster compounds.
- h) Determine the surface area of all relevant compounds.
- i) Investigate if molecular self-assembly can be employed to synthesise hierarchical nanomaterials using H-bonded Fe^{III} coordination networks.
- j) Utilise electron microscopy techniques (TEM and SEM) to monitor the morphology of the nanomaterials.

Chapter Three

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The self-assembly of bis-bidentate Schiff base

ligands: from dinuclear complexes to

coordination clusters

3.1 Introduction

As discussed in Section 1.7, Schiff base ligands have been shown to be useful chelating agents for the formation of a variety of metallo-supramolecular compounds. Their predictable bidentate binding mode can be exploited in transition metal directed self-assembly processes to generate molecular assemblies such as macrocycles, grid structures, metallohelicates and coordination cages.¹⁴⁰ Therefore, we set out to investigate the coordination chemistry of a series of novel bis-bidentate imine ligands N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-4-diamine (**L1**), N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-3-diamine (**L2**) and N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-2-diamine (**L3**) (Figure 3.1) with the aim of developing metallo-supramolecular compounds that may display interesting magnetic properties such as spin crossover and superparamagnetic effects.

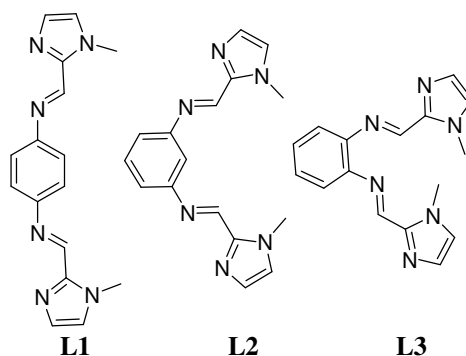


Figure 3.1: Structure of the bis-bidentate Schiff base ligands to be used in this study.

These imine ligands were considered good candidates for the formation of spin crossover compounds, as after complexation with Fe^{II} ions, the resultant complexes would contain Fe^{II} ions with six nitrogen atoms in their coordination sphere. Thus, one of the requirements for SCO to occur would be fulfilled.⁹¹ Also the use of Schiff base chemistry could easily allow for subtle ligand variation which would enable the SCO properties of these materials to be varied in a controllable manner.

In addition, we set out to investigate if we could exploit these chelating agents for the synthesis of high nuclearity coordination clusters that could potentially display superparamagnetic effects and quantum behaviour. These fascinating properties may in future be exploited for the formation of data storage or switching devices.

3.2 Ligand Synthesis

A series of bis-bidentate Schiff base ligands (Figure 3.1) were designed and successfully synthesised. These ligands are characterised by the presence of two imine functionalities linked *via* a benzene ring. Within these ligands, the imine carbon atom is attached to a methyl-imidazole functional group. These versatile ligands are easily prepared by a nucleophilic addition reaction between the relevant phenyldiamine and two equivalents of 1-methyl-2-imidazolcarboxyaldehyde in methanol solution. Subtle changes in the positions of the imine functionalities gave rise to a family of bis-bidentate imine ligands with the functionalities situated *ortho*, *meta* and *para* to each other (Figure 3.1).

3.2.1 N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-4-diamine (L1)

The novel imine ligand N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-4-diamine (**L1**) (Figure 3.2) was prepared *via* the reaction of *p*-phenyldiamine with two equivalents of 1-methyl-2-imidazolcarboxyaldehyde in methanol solution. The ligand forms in good yield (84%) and the elemental analysis (CHN) is consistent with the proposed formulation. The FT-IR spectrum of **L1** indicates the presence of the imine groups as it shows a strong asymmetric C=N bond stretch at 1619 cm^{-1} .¹⁶⁴ The ESI mass spectrum of **L1** in methanol solution shows a molecular ion peak at 293.1 m/z and there are no other species observed. The 400 MHz ^1H NMR spectrum of **L1** is shown together with its assignment in Figure 3.2.

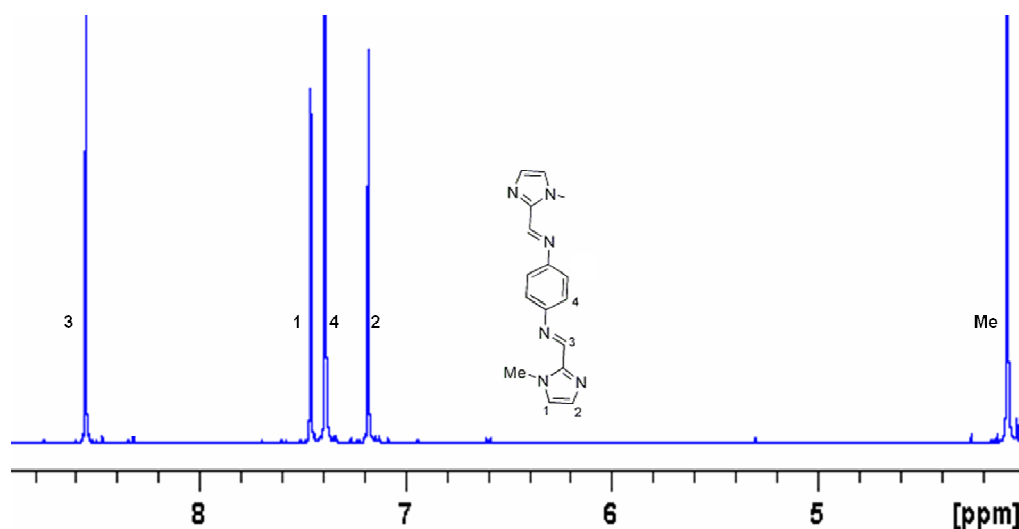


Figure 3.2: The 400 MHz ^1H NMR ($\text{D}_6\text{-DMSO}$) spectrum and assignment for **L1**.

3.2.2 N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-3-diamine (L2)

A similar Schiff base condensation to that used in the synthesis of **L1** was employed in the formation of the novel ligand N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-3-diamine (**L2**) (Figure 3.3). In this case *m*-phenyldiamine was utilised as the starting material. FT-IR analysis of the compound shows the presence of the asymmetric C=N imine bond (1628 cm^{-1})¹⁶⁴ and ESI mass spectrometry shows a molecular ion peak corresponding to **L2** at 293.0 m/z. The formation of **L2** was also confirmed by elemental analysis. The 400 MHz ¹H NMR spectra of **L2** and its assignment is displayed in Figure 3.3.

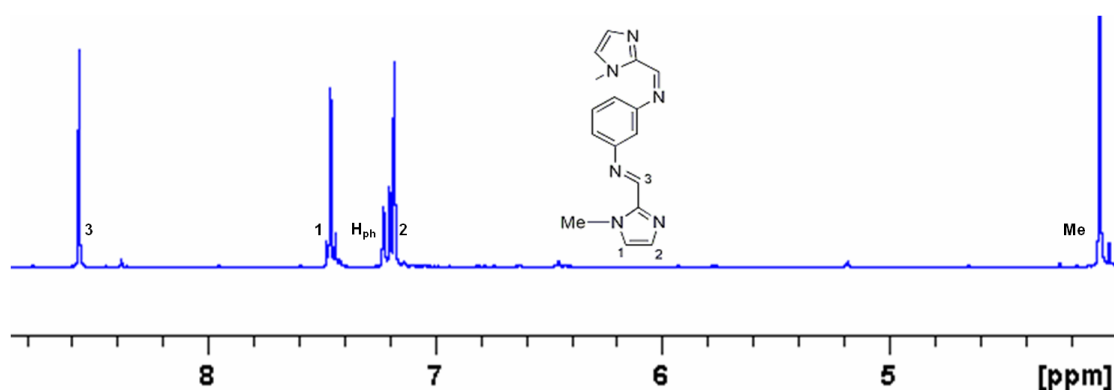


Figure 3.3: The 400 MHz ¹H NMR (D₆-DMSO) spectrum and assignment for **L2**.

3.2.3 N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-2-diamine (L3)

The Schiff base reaction involving *o*-phenyldiamine and 1-methyl-2-imidazolcarboxyaldehyde yielded N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-2-diamine (**L3**) (Figure 3.4). This compound formed in a lower yield (24 %) and was characterised using ¹H NMR spectroscopy (Figure 3.4). FT-IR analysis of **L3** verifies the formation of the imine bonds with a asymmetric C=N bond stretch seen at 1630 cm^{-1} ¹⁶⁴ and the mass spectrum of **L3** in methanol reveals a molecular ion peak of 293.2 m/z.

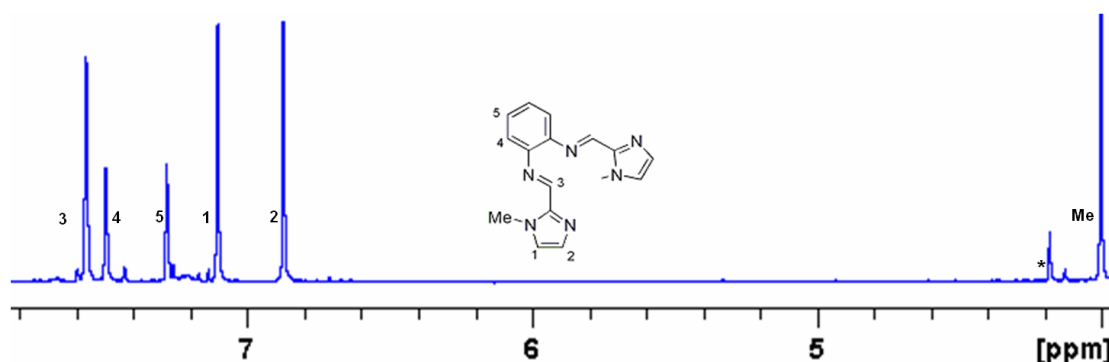


Figure 3.4: The 400 MHz ^1H NMR (D_6 -DMSO) spectrum and assignment for **L3**. * denotes residual solvent MeOH.

3.3 Coordination chemistry of **L1**, **L2** and **L3**

L1, **L2** and **L3** were first reacted with a variety of Fe^{II} salts with the aim of generating spin crossover compounds. The resultant complex species were subject to oxidation and phase pure Fe^{II} complexes were not obtained. However, the reaction of **L2** with $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ yielded a tetranuclear Fe^{III} complex *via* an oxidative process (Section 3.4).

To investigate further the transition metal directed self-assembly of these imine ligands they were systematically reacted with various transition metal salts. In the case of **L1** and **L3**, these reactions often yielded precipitates and insoluble materials that proved difficult to structurally characterise.

In contrast **L2**, the ligand with the imine-imidazole binding sites positioned *meta* to each other, proved to be a useful chelating agent for the stabilisation of dinuclear complexes (Section 3.5), tetranuclear complexes (Section 3.4 and 3.6) and coordination clusters (Section 3.6).

3.4 $[\text{Fe}_4(\mu\text{-O})_2(\text{L2})_2\text{Cl}_8] \cdot 2\text{THF}$ (**1**)

3.4.1 Synthesis and structural characterisation of compound **1**

Initially, the imine ligands **L1**, **L2** and **L3** were reacted with a series of Fe^{II} salts in the hope of generate spin crossover (SCO) compounds. This work led to the formation of $[\text{Fe}_4(\mu\text{-O})_2(\text{L2})_2\text{Cl}_8] \cdot 2\text{THF}$ (**1**) *via* a redox process whereby the Fe^{II} ions are oxidised to Fe^{III} by O_2 from the atmosphere. This oxidative process is a well known phenomenon in related reaction systems.^{165,166} Compound **1** results from the reaction of $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ with **L2** in methanol. This reaction yielded a red solution

which was evaporated to dryness resulting in a red powder, which was then dissolved in acetonitrile. Slow diffusion of tetrahydrofuran into this acetonitrile solution yielded orange plate like crystals of **1** which were characterised using single crystal X-ray diffraction.

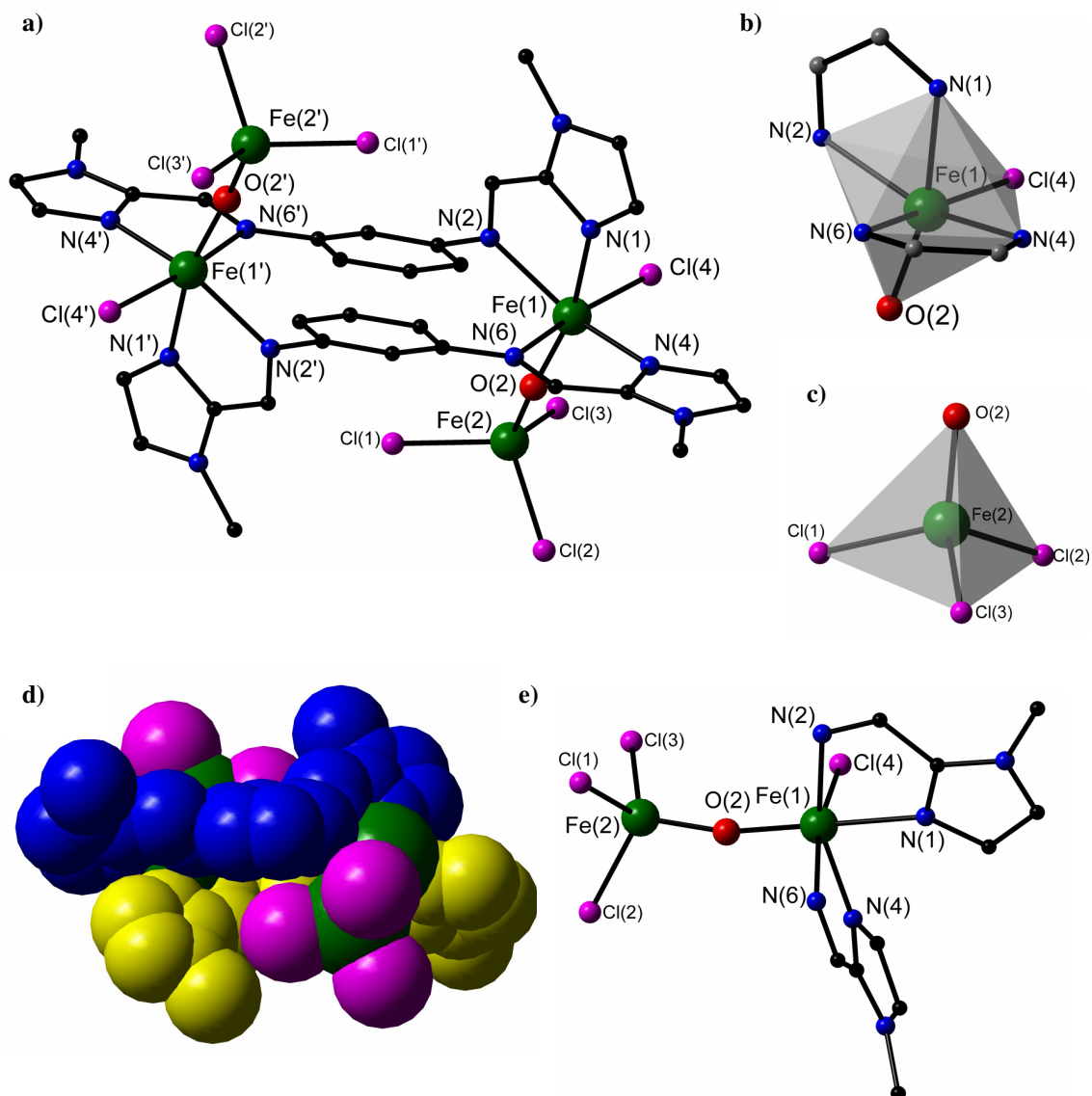


Figure 3.5: **a)** The structure of the tetranuclear Fe^{III} complex found in **1** (H atoms and solvent THF molecules have been removed for clarity). **b)** The coordination environment of Fe(1). **c)** The coordination environment of Fe(2). **d)** Space filling representation of the tetranuclear complex in **1**. **e)** The dinuclear subunit contained within **1**. Fe dark green, C grey, N blue, O red, H white and Cl purple. ' corresponds to the 2-x, 2-y, -z positions.

Compound **1** crystallises in the triclinic crystal system in the space group $P-1$ and contains a tetranuclear Fe^{III} complex. The structure of the tetranuclear complex in **1** consists of two oxo-bridged dinuclear Fe^{III} subunits linked through two **L2** ligands (Figure 3.5). The asymmetric unit of **1** contains half the tetranuclear complex with the

remainder generated by symmetry operations with an inversion centre situated in the centre of the complex.

Within the dinuclear subunit (Figure 3.5c) one of the Fe^{III} atoms, Fe(2), binds to three Cl⁻ ions and one O²⁻ ligand resulting in a distorted tetrahedral coordination environment. The bridging oxo ligand links Fe(2) to the other Fe^{III} site, Fe(1), which also binds to four N atoms from two different Schiff base ligands and a Cl⁻ ion resulting in a distorted octahedral coordination environment. The N donor atoms of one **L2** ligand N(6) and N(4), along with the bridging oxo ligand O(2) arrange in a *facial* manner. The N donors of the other **L2** ligand N(1) and N(5) along with the terminal chloride Cl(4), also adopt a *facial* arrangement. The distorted nature of this octahedron is exemplified by viewing some of the bond angles of the Fe^{III} metal centre. The bond angles of atoms that are *trans* to each other, N(4)-Fe(1)-N(5), N(1)-Fe(1)-O(2) and N(6)-Fe(1)-Cl(4) of 156.62(2)°, 164.72(2)° and 167.37(2)° deviate from the ideal octahedral angle of 180°. The distortion in geometry is caused by the rigid nature of the Schiff base ligands; this can be clearly demonstrated by viewing the bond angles between the various N donor atoms. The following bond angles: N(1)-Fe(1)-N(4) and N(1)-Fe(1)-N(5) and N(4)-Fe(1)-N(6) of 83.53(2)°, 74.38(2)° and 74.67(1)° all involve just Schiff base N atoms and all deviate significantly from the ideal octahedral angle of 90°. The distorted nature of the tetrahedral coordination environment of Fe(2) can be seen by examining the following bond angles O(2)-Fe(2)-Cl(3), Cl(1)-Fe(2)-Cl(3) and Cl(2)-Fe(2)-Cl(3) of 112.30(2)°, 106.07(2)° and 106.86(2)° which deviate from the ideal tetrahedral angle of 109.5°. These bond angles are summarised in Table 3.1.

The Fe-N bond distances between the N donor atoms and the Fe(1) atom confirm that the oxidation state of the iron centre is +III. The Fe-N_{imidazole} bond lengths are 2.175(5) Å and 2.114(9) Å, respectively for N(1) and N(4) whereas the Fe-N_{imine} bond distances are 2.301(8) Å and 2.223(9) Å for N(2) and N(5). The Fe(2)-Cl bond lengths range from 2.219(3) Å to 2.230(7) Å and are consistent with previously reported Fe^{III}-Cl bond distances.^{166,167,168} The oxygen atom, O(2), that bridges both Fe atoms reveals Fe-O bond lengths of 1.754(2) Å and 1.793(3) Å. These very short bonds are evidence that O(2) is indeed an oxo ligand and confirm the assignment of the oxidation states of the tetranuclear complex. The most important bond lengths are presented in Table 3.2. The oxidation states of the Fe ions and the O(2) ligand were confirmed by bond valence sum analysis which is presented in Table 3.3.

Table 3.1: Selected bond angles for **1**

Bond Angle		Bond Angle	
N(1)-Fe(1)-N(4)	88.55(2)°	N(5)-Fe(1)-Cl(4)	94.43 (1)°
N(1)-Fe(1)-N(5)	74.38 (2)°	N(5)-Fe(1)-O(2)	96.60 (2)°
N(1)-Fe(1)-N(6)	80.65 (1)°	N(6)-Fe(1)-Cl(4)	167.37 (2)°
N(1)-Fe(1)-Cl(4)	92.60 (2)°	N(6)-Fe(1)-O(2)	87.85(2)°
N(1)-Fe(1)-O(2)	166.74(2)°	Cl(4)-Fe(1)-O(2)	100.48(1)°
N(4)-Fe(1)-N(5)	155.66(2)°	O(2)-Fe(2)-Cl(1)	111.96(2)°
N(4)-Fe(1)-N(6)	74.67(1)°	O(2)-Fe(2)-Cl(2)	109.32(2)°
N(4)-Fe(1)-Cl(4)	94.06(2)°	O(2)-Fe(2)-Cl(3)	112.30(2)°
N(4)-Fe(1)-O(2)	103.17(2)°	Cl(1)-Fe(2)-Cl(2)	110.15(1)°
N(5)-Fe(1)-N(6)	94.02(2)°	Cl(1)-Fe(2)-Cl(3)	106.07(2)°
		Cl(2)-Fe(2)-Cl(3)	106.86(2)°

Table 3.2: Selected bond lengths for **1**

Bond	Bond Length	Bond	Bond Length
Fe(1)-N(1)	2.175(5) Å	Fe(2)-O(2)	1.754(3) Å
Fe(1)-N(4)	2.114(9) Å	Fe(2)-Cl(1)	2.227(7) Å
Fe(1)-N(5)	2.223(5) Å	Fe(2)-Cl(2)	2.223(7) Å
Fe(1)-Cl(4)	2.301(8) Å	Fe(2)-Cl(3)	2.219(3) Å
Fe(1)-O(2)	1.793(3) Å		

Table 3.3: Bond valence sum analysis for **1**

Fe or O site	Bond Valence Sum (BVS)	Assigned Oxidation State
Fe(1)	3.132	+III
Fe(2)	3.213	+III
O(2)	2.436	-II

In the solid state the Fe^{III} complexes and the constitutional tetrahydrofuran molecules are linked by weak dipole-dipole interactions resulting in the densely

packed structure presented in Figure 3.6. The closest contact of 3.6 Å involves the chloride ligand Cl(1) and the hydrogen atom of the tetrahydrofuran molecule.

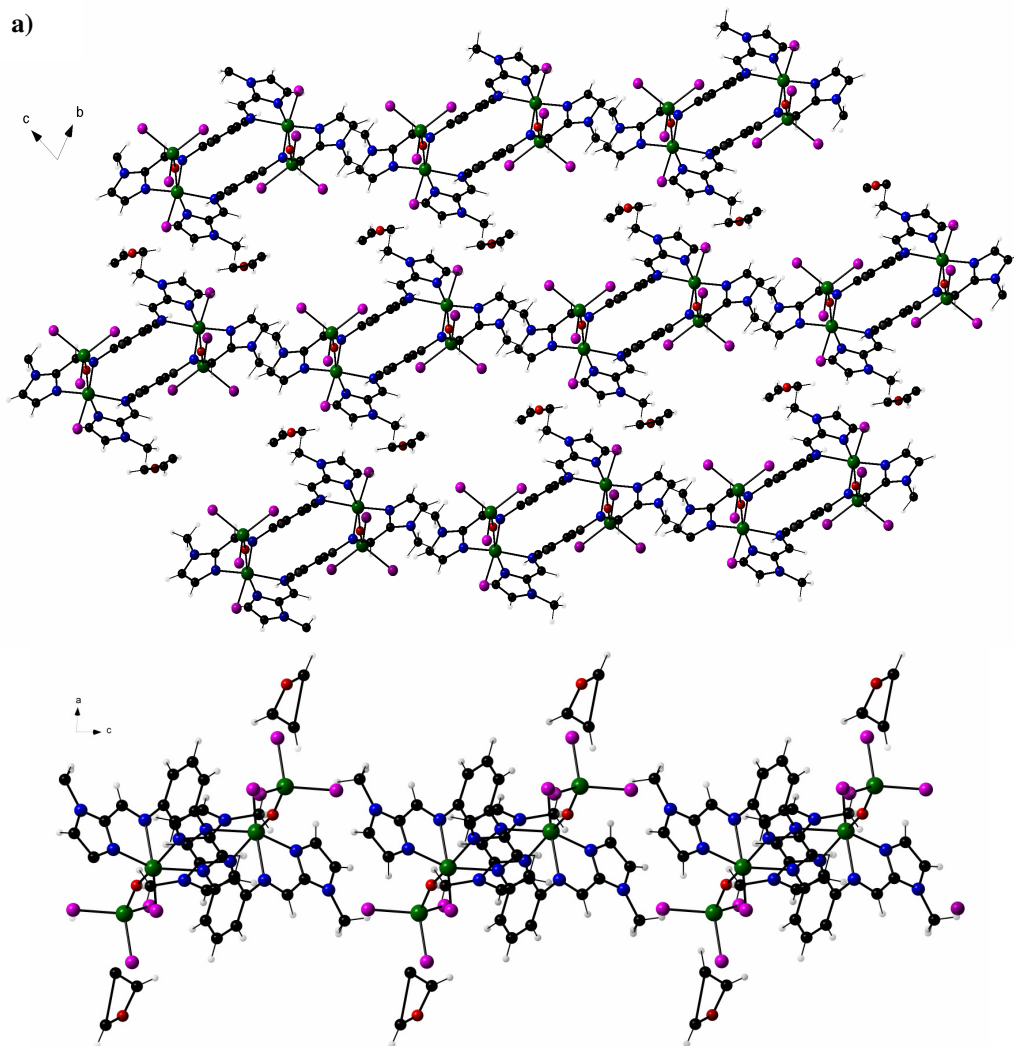


Figure 3.6: The packing of the tetranuclear complexes in **1**, as viewed in the direction of **a)** the crystallographic *a*-axis and **b)** the crystallographic *b*-axis. Fe dark green, C grey, N blue, O red, H white and Cl purple.

3.4.2 Magnetic properties of compound **1**

Within **1** the Fe^{III} ions Fe(1) and Fe(2) are linked *via* a bridging oxo ligand O(2) which displays short Fe-O bond lengths of 1.754(3) and 1.793(3) and a Fe-O-Fe bond angle of 161.14(2)°. As these Fe^{III}-O bond distances are very short we expected very strong magnetic interactions between the Fe^{III} ions within the dimer. Therefore, the temperature dependence of the magnetic susceptibility of **1** was measured between 300 K and 1.8 K at 1000 Oe.

At room temperature, the χT product is $2.61 \text{ cm}^3 \text{ K mol}^{-1}$. This χT value is significantly lower than the expected value ($17.5 \text{ cm}^3 \text{ K mol}^{-1}$) for four uncoupled high spin $S = 5/2$ Fe^{III} ions indicating the presence of strong antiferromagnetic interactions between the Fe^{III} ions in the dimeric subunits in **1**. At 30 K, the χT product begins to decrease reducing to a value of $1.2 \text{ cm}^3 \text{ K mol}^{-1}$, at temperatures below 4 K. These measurements suggest unusual spin state interactions involving the Fe^{III} ions and further experiments would be required to understand the interesting magnetic behaviour.

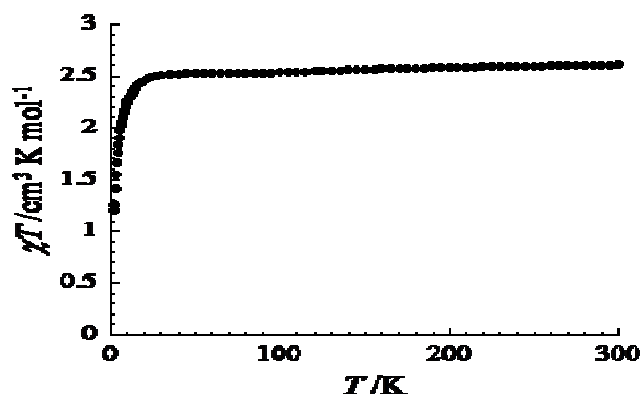


Figure 3.7: The temperature dependence of the magnetic susceptibility at 1000 Oe for **1**.

3.4.3 Characterisation of compound **1**

Compound **1** was further characterised by FT-IR spectroscopy. The presence of the oxo-bridge is confirmed by the asymmetric Fe-O-Fe bond stretch at 861 cm^{-1} .¹⁶⁴ Sanders-Loehr *et al.* have demonstrated that this stretching frequency can be used to calculate the expected value of the Fe-O-Fe angle within similar oxo-bridged Fe systems.¹⁶⁹ The predicted value for **1** is *ca.* 160° which was in good agreement with the value obtained from crystallography. Finally, elemental analysis (CHN) verifies the molecular formula that was determined by X-ray diffraction.

Table 3.4: Crystal data and structure refinement for **1**

Identification code	1	
Empirical formula	Fe ₄ C ₄₀ H ₄₈ N ₁₂ O ₄ Cl ₈	
Formula weight	1267.90 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 9.816(4) Å b = 12.802(5) Å c = 13.529(5) Å	α = 67.47(6)° β = 79.03(6)° γ = 68.41(6)°
Volume	1457.7(9) Å ³	
Z	1	
Density (calculated)	1.547 Mg/m ³	
Absorption coefficient	1.394 mm ⁻¹	
F(000)	686	
Crystal size	0.3 x 0.05 x 0.6 mm ³	
Theta range for data collection	1.63 to 25.11°	
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16	
Reflections collected	12333	
Independent reflections	5168 [R(int) = 0.1579]	
Completeness to theta = 25.11°	99.1 %	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5168 / 0 / 345	
Goodness-of-fit on F ²	0.905	
Final R indices [I > 2σ(I)]	R1 = 0.0850, wR2 = 0.1760	
R indices (all data)	R1 = 0.1761, wR2 = 0.2024	
Largest diff. peak and hole	0.766 and -0.487 e.Å ⁻³	

3.5 Co^{II} and Ni^{II} Coordination Compounds Containing L2

Following on from the successful synthesis of compound **1** we decided to gain further insight in to the binding ability of the bis-bidentate ligand **L2** by reacting it with a series of transition metal salts. We expected that the relative conformations of the functional groups of this bis-bidentate ligand could give rise to a variety of supramolecular topologies within oligonuclear metal complexes. We also sought to exploit UV-vis spectroscopy to rationalise the formation of the resultant species in solution.

3.5.1 [Co₂(L2)₂(MeOH)₂(H₂O)₂]Cl₄·4MeOH·3H₂O (**2**)

3.5.1.1 The synthesis and structural characterisation of compound **2**

The coordination compound [Co₂(L2)₂(MeOH)₂(H₂O)₂]Cl₄·4MeOH·3H₂O (**2**) was formed by the reaction of CoCl₂·6H₂O with the ligand **L2** in a methanol solution. This synthetic approach yielded a clear orange solution. After 5 days yellow plate shaped crystals suitable for single crystal X-ray diffraction formed from solution.

2 crystallises in the triclinic system in the space group of *P*-1 and is composed of a dinuclear Co^{II} complex (Figure 3.8) in which the Co^{II} centres are bridged by two **L2** ligands. Each metal centre is coordinated by four N donor atoms from the two **L2** ligands, one H₂O ligand and one MeOH ligand. The Co atoms are separated within the dinuclear complex by a distance of 7.35(4) Å.

Both Co^{II} centres in the dinuclear complex contained in **2** are crystallographically equivalent. The asymmetric unit contains half of the dinuclear complex which is generated by inversion symmetry with the inversion centre situated in the middle of the metal-metal axis.

Two imine N atoms, two imidazole N atoms and two O atoms (one water O atom and one methanol O atom) bind to each Co^{II} metal centre. The imine N donors N(2) and N(3), display Co-N bond lengths of 2.17(1) Å and 2.15(1) Å. The imidazole moieties that bind to the metal centres show Co-N bond distances of 2.10(2) Å and 2.10(1) Å for Co(1)-N(1) and Co(1)-N(4), respectively. The Co-O bond distances are 2.06(1) Å for the Co-O(2)_{water} bond and 2.14(3) Å for the Co-O(1)_{methanol} bond. These bond lengths are summarised in Table 3.5.

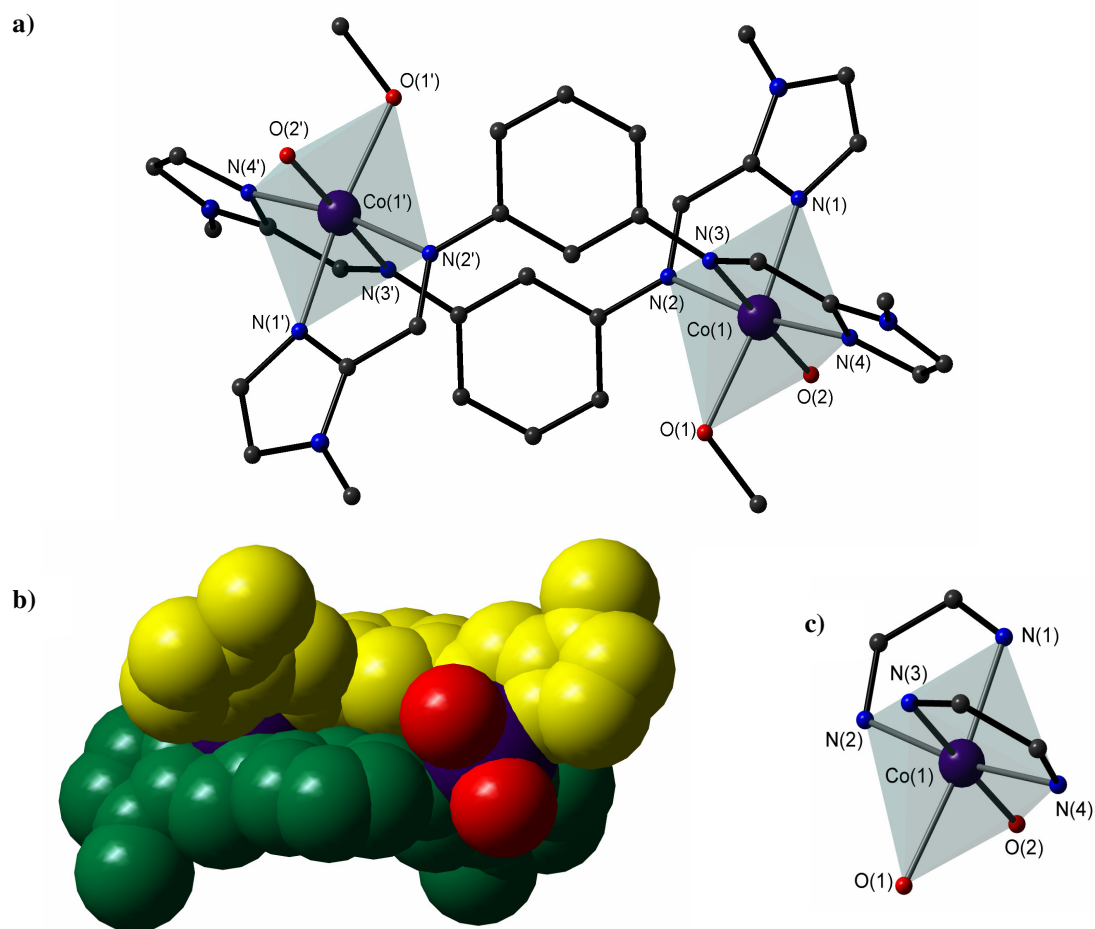


Figure 3.8: **a)** The structure of the dinuclear Co^{II} complex contained in **2** (H atoms, counterions and constitutional solvent molecules have been omitted for clarity). **b)** Space filling representation of Co^{II} complex in **2**. **c)** The coordination environment of the Co^{II} metal centres. Co purple, O red, N blue and C black, ' corresponds to the 1-x, 1-y, 1-z positions.

Table 3.5: Selected bond lengths for **2**

Bond	Bond Length	Bond	Bond Length
Co(1)-N(1)	2.10(2) Å	Co(1)-N(4)	2.10(1) Å
Co(1)-N(2)	2.17(1) Å	Co(1)-O(1)	2.14(3) Å
Co(1)-N(3)	2.15 (1) Å	Co(1)-O(2)	2.06(1) Å

The overall coordination geometry of each Co^{II} centre is distorted octahedral (Figure 3.8c) with the N donor atoms of one Schiff base ligand N(1) and N(2) and the *aqua* O atom O(2) exhibiting a *facial* arrangement. In addition to this, the N donor atoms of the other ligand N(3) and N(4) in conjunction with the methanol O atom O(1) also arrange in a *facial* manner. This distorted octahedral geometry is clearly demonstrated by examining some of the bond angles in the Co^{II} coordination

environment. For example the bond angles between N(1)-Co(1)-N(2), N(3)-Co(1)-N(4) and N(2)-Co(1)-N(4) of 77.61(2)°, 78.79(2)° and 171.09(2)° deviate significantly from the ideal octahedral angles of 90° and 180°. However, the bond angles involving the less sterically restrained O donor atoms (MeOH and H₂O) depart less from the ideal octahedral bond angles. This is evident by considering the following angles O(2)-Co(1)-N(3), O(1)-Co(1)-N(1), O(1)-Co(1)-N(4) and O(1)-Co(1)-O(2) of 176.77(2)°, 172.77(2)°, 91.78(2)° and 86.71(2)° which are much closer to ideal octahedral bond angles. This emphasises that it is the rigidity of the Schiff base ligand that causes the distortion in geometry upon coordination. The bond angles of the Co^{II} centre are further summarised in Table 3.6.

In the solid state the dinuclear Co^{II} complexes, solvent molecules and chloride ions in **2** are held together by weak van der Waals interactions and dispersion forces.

Table 3.6: Selected bond angles for **2**

Bond Angle		Bond Angle	
N(1)-Co(1)-N(2)	77.61(2)°	N(3)-Co(1)-N(4)	78.79(2)°
N(1)-Co(1)-N(3)	86.50(2)°	N(3)-Co(1)-O(2)	176.77(2)°
N(1)-Co(1)-O(1)	172.77(2)°	N(4)-Co(1)-O(1)	91.78(2)°
N(2)-Co(1)-N(4)	171.09(2)°	O(1)-Co(1)-O(2)	88.71(2)°
N(2)-Co(1)-O(2)	86.47 (2)°		

3.5.1.2 Characterisation of compound **2**

Compound **2** was further characterised by FT-IR spectroscopy. The moderately intense asymmetric C=N bond stretch seen at 1616 cm⁻¹ is characteristic of the imine functionality of the **L2** ligand.¹⁶⁴ The ESI mass spectrum of **2** displays a molecular ion peak at 200.7 m/z which corresponds to the [Co₂(**L2**)₂(MeOH)₂(H₂O)₂]⁴⁺ species.

In order to determine the composition of **2**, thermogravimetric analysis (TGA) (Figure 3.9) was carried out on a freshly filtered sample of **2**. The sample was heated to ~900 °C under an air atmosphere at a heating rate of 10 °C min⁻¹. The compound undergoes a weight loss of *ca.* 24% between 30 °C and 125 °C. The compound then undergoes a gradual thermal decomposition between 125 °C and 900 °C resulting in the probable formation of metal oxide materials, which were not further characterised.

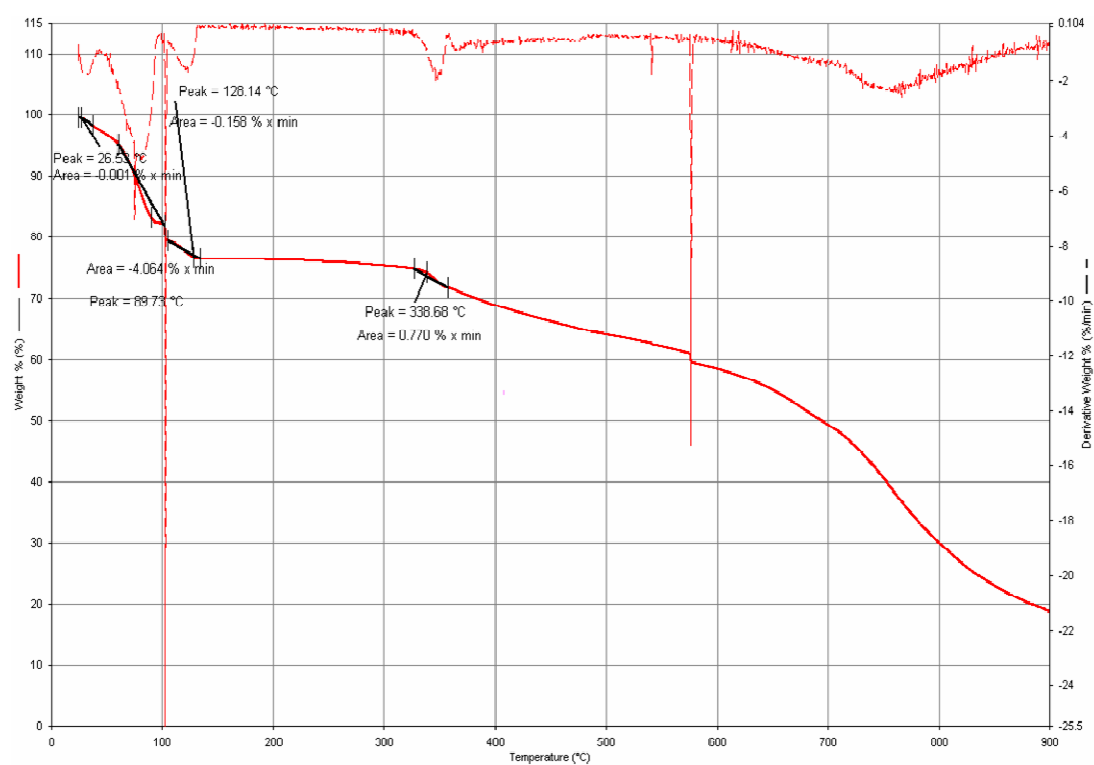


Figure 3.9: Thermogravimetric analysis (TGA) for 1.

Table 3.7: Crystal data and structure refinement for **2**

Identification code	2	
Empirical formula	Co ₂ C ₃₈ H ₆₆ N ₁₂ O ₁₁ Cl ₄	
Formula weight	1012.55 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 8.310(4) Å b = 11.536(5) Å c = 13.102(5) Å	α=91.167(13)° β= 107.75(2)° γ= 106.715(9)°
Volume	1137.6(9) Å ³	
Z	1	
Density (calculated)	1.452 Mg/m ³	
Absorption coefficient	1.021 mm ⁻¹	
F(000)	506	
Crystal size	0.12x 0.08 x 0.07 mm ³	
Theta range for data collection	2.33 to 25.23°	
Index ranges	-9<=h<=9, -13<=k<=13, -15<=l<=15	
Reflections collected	12014	
Independent reflections	4047 [R(int) = 0.1484]	
Completeness to theta = 25.23°	99.5 %	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4047 / 0 / 267	
Goodness-of-fit on F ²	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0873, wR2 = 0.2773	
R indices (all data)	R1 = 0.1196, wR2 = 0.2462	
Largest diff. peak and hole	0.951 and -0.741 e.Å ⁻³	

3.5.2 [Ni₂(L2)₃](ClO₄)₄·H₂O (**3**)

3.5.2.1 The synthesis and structural characterisation of compound **3**

The compound [Ni₂(L2)₃](ClO₄)₄·H₂O (**3**) was synthesised by the reaction of the Schiff base ligand **L2** and Ni(ClO₄)₂·4H₂O in methanol. This reaction results in the formation of a yellow powder. Yellow plate like crystals of **3** suitable for single crystal X-ray diffraction were obtained *via* the slow diffusion of tetrahydrofuran into acetonitrile solutions of this powder.

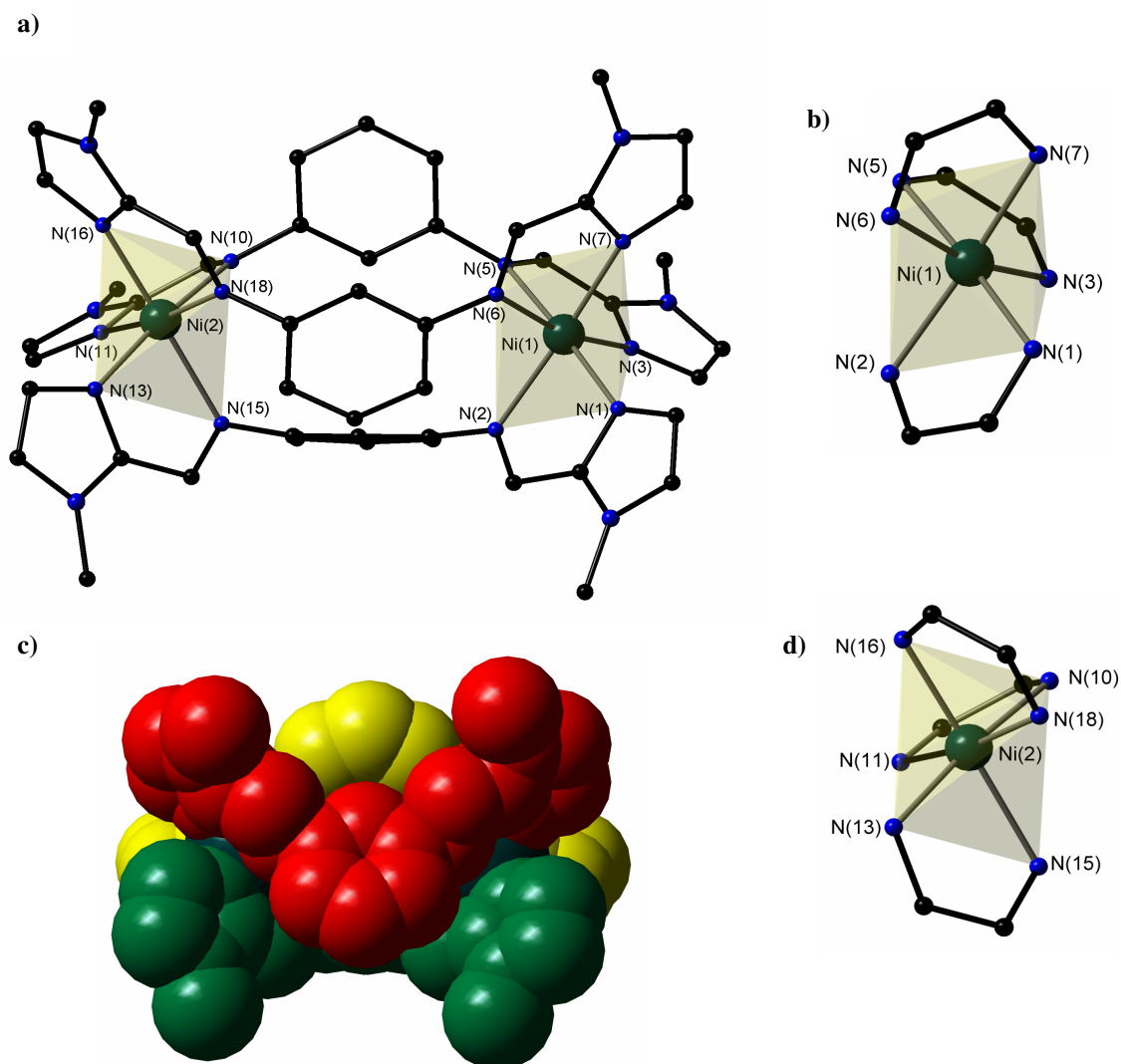


Figure 3.10: a) The crystal structure of the dinuclear Ni^{II} complex contained in **3** (H atoms, counterions and constitutional solvent molecules have been omitted for clarity). b) The coordination environment of Ni(1) in **3**. c) Space filling representation of the Ni^{II} complex in **3**. d) The coordination environment of Ni(2) in **3**. Ni green, O red, N blue and C black.

The refinement R values for compound **3** are R1 = 0.0884 and wR2 = 0.2780. These remain relatively high due to positional disorder demonstrated by the ClO₄⁻ counterions. This occurs when an atom or group of atoms is statistically distributed over two or more points in space. This effect is particularly common for highly

symmetric ions such as ClO_4^- as these anions are frequently found on points which have symmetries inconsistent with their own.¹⁷⁰

Compound **3** crystallises in the triclinic crystal system in the space group $P-1$. In contrast to the Co^{II} complex in **2**, the dinuclear complex in **3** (Figure 3.10) is stabilised by three Schiff base **L2** ligands. The intramolecular distance between the two nickel ions is 7.12(2) Å. The coordination about each Ni^{II} centre is of opposite handedness, Δ or Λ , yielding the meso-helical structure in **3**. The packing of the complexes in the crystal structure presents no evidence of strong supramolecular interactions between the individual complexes.

Each Ni ion in **3** binds to three imine N atoms and three imidazole N atoms. The Ni(1)-N_{imine} bond lengths in **3** range from 2.13(2) Å to 2.20(5) Å and the Ni(1)-N_{imidazole} bond lengths vary between 2.06(3) Å and 2.07(2) Å and are detailed in Table 3.8.

Table 3.8: Selected bond lengths for **3**

Bond	Bond Length	Bond	Bond Length
Ni(1)-N(1)	2.07(2) Å	Ni(2)-N(10)	2.13(1) Å
Ni(1)-N(2)	2.13(2) Å	Ni(2)-N(11)	2.04(3) Å
Ni(1)-N(3)	2.06(3) Å	Ni(2)-N(13)	2.02(2) Å
Ni(1)-N(5)	2.19(1) Å	Ni(2)-N(15)	2.19(7) Å
Ni(1)-N(6)	2.20(5) Å	Ni(2)-N(16)	2.10(7) Å
Ni(1)-N(7)	2.06(9) Å	Ni(2)-N(18)	2.16(3) Å

The asymmetric unit of **3** contains one dinuclear complex and both Ni^{II} centres Ni(1) and Ni(2) have slightly different coordination environments. However both metal centres display distorted octahedral coordination environments, with the imine N atoms arranging in a *facial* manner. In addition to this, the imidazole donor N atoms also form *facial* arrangements. The deviation from ideal octahedral coordination is best exemplified by examining some bond angles of Ni(1) (Table 3.9), which depart noticeably from the ideal octahedral angles of 90° and 180°. The distortion is evident from the N(1)-Ni(1)-N(2), N(3)-Ni(1)-N(5) and N(6)-Ni(1)-N(7) bond angles of 79.22(2)°, 78.33(2)° and 78.07(2)° respectively, which deviate significantly from those of an ideal octahedron. This distortion is further underlined by examining the

N(1)-Ni(1)-N(5), N(2)-Ni(1)-N(7) and N(6)-Ni(1)-N(3) angles of 173.83(2)°, 171.17(2)° and 167.26(2)°. These bond angles depart from the ideal 180° angle expected from atoms *trans* to each other in an octahedral coordination arrangement. The bond angles of the Ni(2) centre are similar and are presented in Table 3.9.

Table 3.9: Selected bond angles for **3**

Bond Angle		Bond Angle	
N(1)-Ni(1)-N(2)	79.22(2)°	N(10)-Ni(2)-N(11)	78.5(2)°
N(1)-Ni(1)-N(3)	97.82(2)°	N(10)-Ni(2)-N(13)	169.68(2)°
N(1)-Ni(1)-N(5)	173.89(2)	N(10)-Ni(2)-N(16)	94.44(2)°
N(1)-Ni(1)-N(7)	97.30(2)°	N(10)-Ni(2)-N(18)	97.69(2)
N(2)-Ni(1)-N(7)	171.17(2)°	N(11)-Ni(2)-N(15)	93.74(2)°
N(3)-Ni(1)-N(5)	78.33(2)°	N(11)-Ni(2)-N(16)	96.22(2)°
N(3)-Ni(1)-N(7)	91.68(2)°	N(13)-Ni(2)-N(15)	78.03(2)°
N(5)-Ni(1)-N(7)	87.61(2)°	N(13)-Ni(2)-N(16)	94.22(2)°
N(6)-Ni(1)-N(3)	167.26(2)°	N(15)-Ni(2)-N(16)	167.86(2)°
N(6)-Ni(1)-N(7)	78.07(2)°	N(15)-Ni(2)-N(18)	92.14(2)°

3.5.2.2 Characterisation of compound **3**

Compound **3** was further analysed by FT-IR spectroscopy. The asymmetric C=N bond stretch observed at 1618 cm⁻¹ is the typical stretch associated with the imine functionality of **L2**.¹⁶⁴ To further characterise the molecular composition of **3** thermogravimetric analysis (Figure 3.11) was performed on a freshly filtered sample of **3**. The compound was heated to 900 °C at a heating rate of 10 °C min⁻¹. The compound undergoes a weight loss of *ca.* 1.8% between 30 °C and 70 °C. This corresponds to the loss of one solvent water molecule from **3** (calculated weight 1.3%). The compound then undergoes thermal decomposition with two thermogravimetric events centred at 380 °C and at 415 °C, respectively. The TGA suggests the molecular formulae of **3** is [Ni₂(**L2**)₃](ClO₄)₄·H₂O.

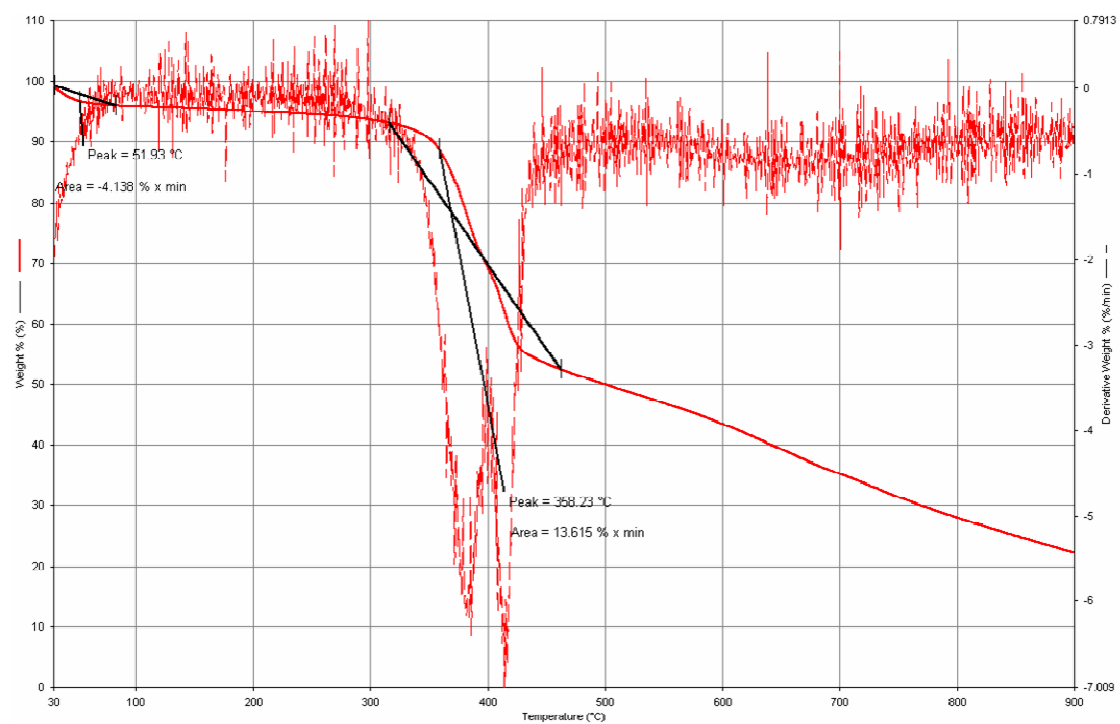


Figure 3.11: Thermogravimetric analysis (TGA) for **3**.

Table 3.10: Crystal data and structure refinement for **3**

Identification code	3	
Empirical formula	Ni ₄ C ₉₆ H ₁₀₀ N ₃₆ O ₃₄ Cl ₈	
Formula weight	2820.46 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 14.224(3) Å b = 14.253(3) Å c = 17.950(4) Å	α = 104.99(3)° β = 93.04(3)° γ = 117.19(3)°
Volume	3064.0(11) Å ³	
Z	1	
Density (calculated)	1.526 Mg/m ³	
Absorption coefficient	0.870 mm ⁻¹	
F(000)	1444	
Crystal size	0.14 x 0.22 x 0.05 mm ³	
Theta range for data collection	2.46 to 25.00°	
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21	
Reflections collected	46629	
Independent reflections	10666 [R(int) = 0.0646]	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10666 / 0 / 859	
Goodness-of-fit on F ²	1.093	
Final R indices [I > 2σ(I)]	R1 = 0.0884, wR2 = 0.2773	
R indices (all data)	R1 = 0.1146 wR2 = 0.3310	
Largest diff. peak and hole	1.322 and -1.633 e. Å ⁻³	

3.5.3 UV-vis compleximetric titration studies to characterise the formation of the coordination complexes **2** and **3**

3.5.3.1 UV-vis titration study of **L2** with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

From the crystal structures of **2** and **3**, it is clearly demonstrated that the dinuclear complex in **2** shows a 1:1 ligand to metal ratio, with the ligands' imine-imidazole binding groups adopting a *cis-trans* arrangement, whereas in **3** these head groups orientate in a *cis-cis* manner stabilising a dinuclear complex with a ligand to metal ratio of 3:2. To further rationalise the formation of the complex species in solution UV-vis compleximetric titrations were carried out.

Firstly, methanol solutions of **L2** and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were prepared. Figure 3.12 shows the UV-vis spectral changes upon addition of sub-stoichiometric quantities of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ to an **L2** solution. Spectra were recorded after each addition and additions were continued until super-imposable spectra were obtained. It is evident that the spectrum of **L2** changes upon addition of Co^{II} .

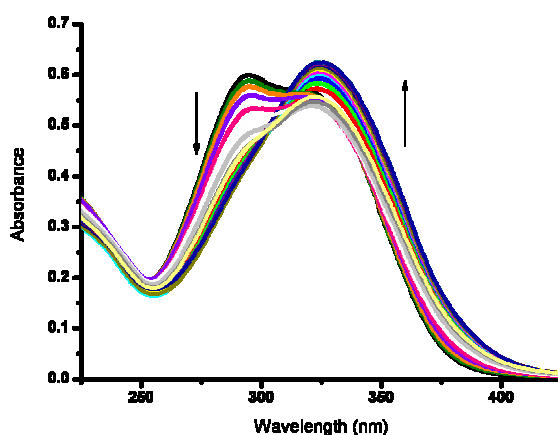


Figure 3.12: UV-vis spectral changes of a methanol solution of **L2** upon addition of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in methanol. $[\text{L2}] = 8 \times 10^{-6} \text{ mol L}^{-1}$ and $[\text{Co}^{\text{II}}] = 8 \times 10^{-5} \text{ mol L}^{-1}$.

There is a decrease in the absorbance of the ligand $\pi\text{-}\pi^*$ band at 295 nm and the emergence of a new band at 320 nm. A molar ratio plot (Figure 3.13) showing the change in absorbance of the 295 nm and 320 nm bands as a function of equivalents of Co^{II} added to the **L2** solution, indicates the formation of a 1:1 metal to ligand complex. The titration profile reaches a maximum after one equivalent of Co^{II} is added and no further significant changes are observed upon the addition of excess

metal. This data may indicate the formation of a $[\text{Co}^{\text{II}}_2\text{L2}_2]^{4+}$ species in solution, thus supporting the X-ray crystallographic results.

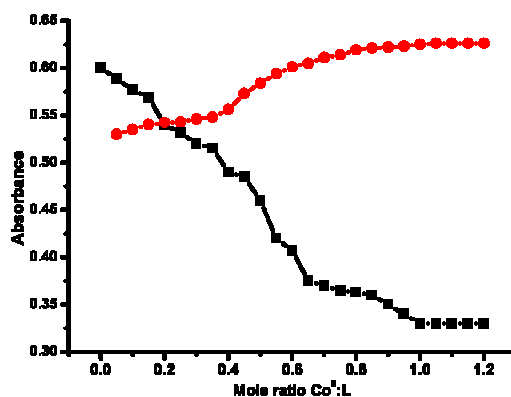


Figure 3.13: Mole ratio plot showing the change in absorbance at 293 nm (black) and at 320 nm (red) as a function of equivalents of Co^{II} added to the **L2** solution.

3.5.3.2 UV-vis titration study of **L2** with $\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$

A similar study was carried out using **L2** and $\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ to monitor the formation of the $[\text{Ni}_2(\text{L2})_3]^{4+}$ species in solution. The spectra were recorded in methanol solution.

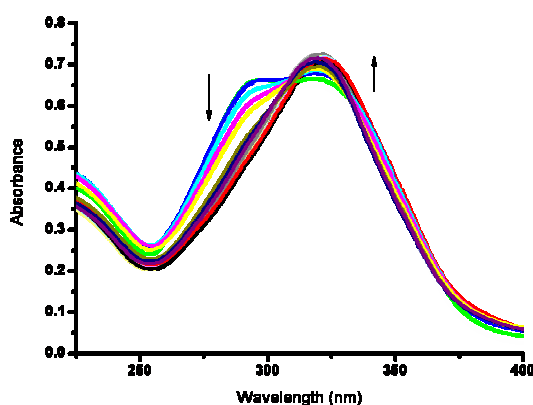


Figure 3.14: UV-vis spectral changes of a methanol solution of **L2** upon the addition of $\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ in methanol. $[\text{L2}] = 8 \times 10^{-6} \text{ mol L}^{-1}$ and $[\text{Ni}^{\text{II}}] = 8 \times 10^{-5} \text{ mol L}^{-1}$.

Again there are clear changes in the spectra of **L2** upon the addition of the Ni^{II} (Figure 3.14). The absorbance due to the ligand $\pi\text{-}\pi^*$ transition at 296 nm decreases and a new band at 318 nm emerges upon each subsequent addition of nickel(II). A plot that shows the change in absorbance as a function of Ni^{II} equivalents added

(Figure 3.15) results in a titration profile which reaches a maximum at molar ratios between 0.5 and 0.65. The experimental data indicates the formation of a 3:2 ligand: Ni^{II} complex in solution. This is in agreement with the crystallographic studies. However, for a detailed solution speciation analysis further experiments would be necessary.

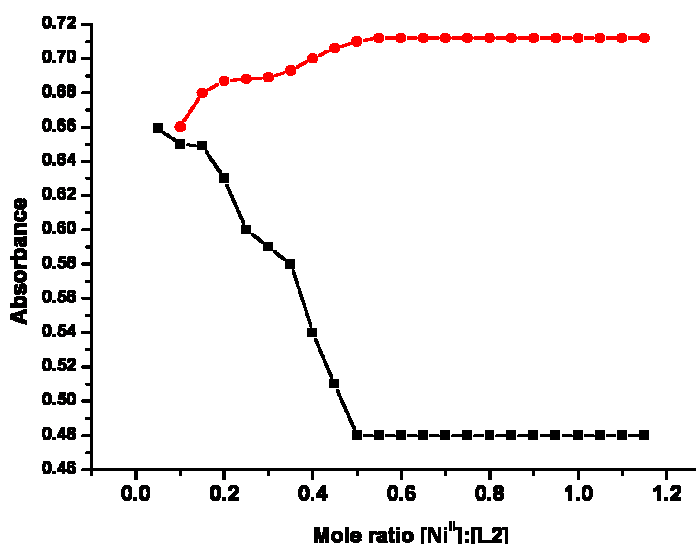


Figure 3.15: Mole ratio plot showing the change in absorbance at 296 nm (blue) and at 318 nm (violet) as a function of equivalents of Ni^{II} added to the **L2** solution.

3.6 Copper coordination compounds containing **L2**

Two interesting coordination compounds $[\text{Cu}_4(\text{L2})_2(\text{EMM})_4](\text{CH}_3\text{COO})_4 \cdot \text{H}_2\text{O}$ (**4**) and $[\text{Cu}_9(\mu_3\text{-O})(\text{O-L2-O})_2(\text{CH}_3\text{COO})_{10}] \cdot 2\text{THF} \cdot 2\text{H}_2\text{O}$ (**5**) have been formed by the reaction of Cu^{II} acetate monohydrate with the bis-bidentate Schiff base ligand **L2**. The structure of the product that forms is governed by the ligand to metal ratio and the solvents used in the crystallisation process.

3.6.1 $\text{Cu}_4(\text{L2})_2(\text{EMM})_4](\text{CH}_3\text{COO})_4 \cdot \text{H}_2\text{O}$ (**4**)

3.6.1.1 Synthesis and structural characterisation of compound **4**

The reaction of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ with 1.5 equivalents of **L2** in methanol yielded a green solution. This solution was evaporated to dryness yielding a green oil, which was dissolved in acetonitrile. The subsequent addition of ethanol to this solution yielded blue/green single crystals of the coordination compound $\text{Cu}_4(\text{L2})_2(\text{EMM})_4](\text{CH}_3\text{COO})_4 \cdot \text{H}_2\text{O}$ (**4**) in low yields (< 10 %) after five days. These

crystals were characterised *via* single crystal X-ray diffraction and this analysis demonstrated that the compound contains a tetranuclear Cu^{II} complex (Figure 3.16) which is stabilised by two neutral **L2** ligands and four negatively charged ethoxy(1-methylimidazol-2-yl) methanolate (**EMM**) ligands. The positive charge of the tetraanuclear complex is balanced by four acetate counterions. The crystals of **4** were small and weakly diffracting which led to the poor quality of the refinement parameters.

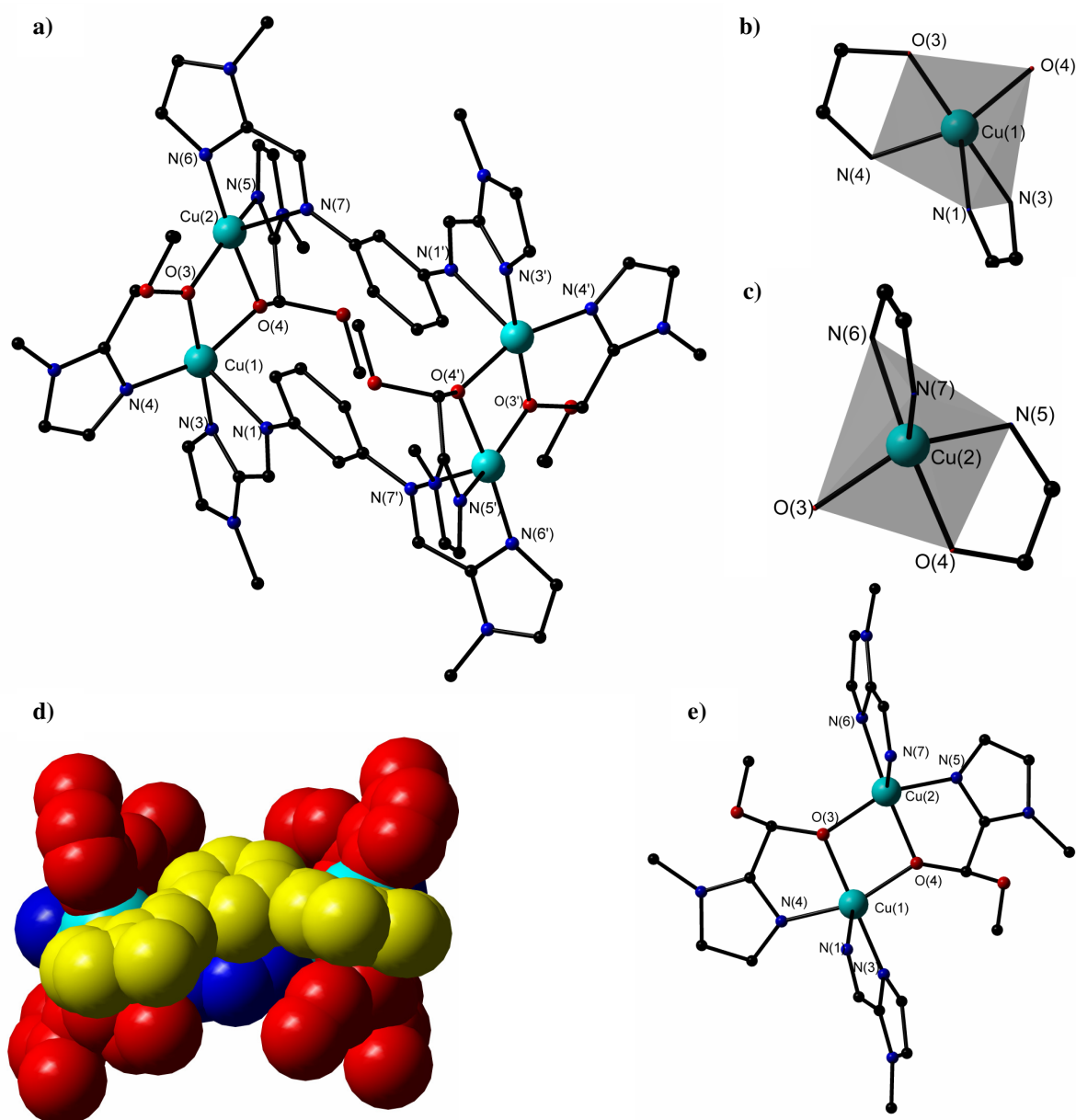


Figure 3.16: **a)** The structure of the tetranuclear complex contained in **4** (H atoms, counterions and constitutional H_2O molecule have been removed for clarity). **b)** The coordination environment of Cu(1). **c)** The coordination environment of Cu(2). **d)** Space filling representation of the tetranuclear complex in **4**. **e)** The dinuclear subunit contained in **4**. Cu cyan, O red, N blue and C black. ' ' corresponds to the -x, 1-y, 2-z positions.

The **EMM** ligands result from the decomposition of **L2** under the applied reaction conditions. This process may involve the imine hydrolysis of **L2**, which leads to the formation of an aldehyde that undergoes nucleophilic attack from an ethanol solvent molecule thus yielding the **EMM** ligand (Figure 3.17).

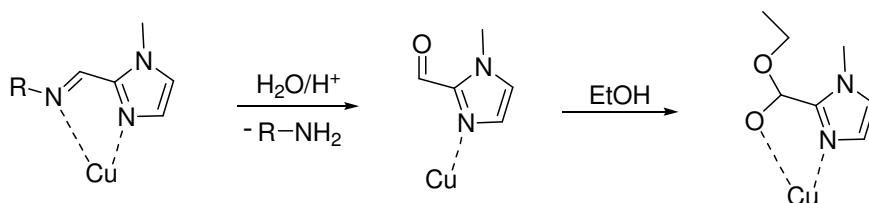


Figure 3.17: Schematic representation of the formation of the **EMM** ligand.

Compound **4** crystallises in the triclinic system with the space group of *P*-1. The asymmetric unit of **4** contains half the tetranuclear complex with the remainder generated through symmetry operations, with an inversion centre situated in the centre of the complex. The overall architecture of the tetranuclear Cu^{II} complex, [Cu₄(**L2**)₂(**EMM**)₄]⁴⁺, can be considered as two dinuclear Cu^{II} subunits (Figure 3.16e) linked through two **L2** ligands. Within the dinuclear subunit, each Cu^{II} ion binds to one **L2** ligand, one **EMM** ligand and is linked to the other Cu^{II} ion through the oxygen donor atoms of the **EMM** ligand. The complex displays Cu-N_{imine} bond lengths which range between 2.143(5) Å and 2.149(2) Å and has Cu-N_{imidazole} bonds which vary in length from 1.994(7) Å to 2.023(9) Å. The complex also demonstrates Cu-O bonds; their bond distances range from 1.985(6) Å to 2.023(6) Å and are summarised in Table 3.11.

Table 3.11: Selected bond lengths for **4**

Bond	Bond Length	Bond	Bond Length
Cu(1)-N(1)	2.149(2) Å	Cu(2)-N(2)	2.143(5) Å
Cu(1)-N(3)	1.996(7) Å	Cu(2)-N(5)	1.995(8) Å
Cu(1)-N(4)	1.994(7) Å	Cu(2)-N(6)	2.023(9) Å
Cu(1)-O(3)	1.987(6) Å	Cu(2)-O(3)	1.985(6) Å
Cu(1)-O(4)	1.977(3) Å	Cu(2)-O(4)	2.023(6) Å

The two types of Cu^{II} ions within the complex, Cu(1) and Cu(2) both display similar distorted square pyramidal coordination geometries, with the imidazole nitrogen donor atoms and the oxygen donor atoms situated in the square plane of the pyramid. The bond angles involving the metal centres are outlined in Table 3.12.

Table 3.12: Selected bond angles for **4**

Bond Angle		Bond Angle	
N(1)-Cu(1)-N(3)	75.41(3)°	N(2)-Cu(2)-N(5)	104.29 (3)°
N(1)-Cu(1)-N(4)	95.91 (3)°	N(2)-Cu(2)-N(6)	75.38 (3)°
N(1)-Cu(1)-O(3)	106.14(3)°	N(2)-Cu(2)-O(3)	98.83(3)°
N(1)-Cu(1)-O(4)	99.42(3)°	N(2)-Cu(2)-O(4)	102.04(3)°
N(3)-Cu(1)-N(4)	96.47(3)°	N(5)-Cu(2)-N(6)	94.36(3)°
N(3)-Cu(1)-O(3)	178.48(3)°	N(5)-Cu(2)-O(6)	152.28(3)°
N(3)-Cu(1)-O(4)	101.02(3)°	N(5)-Cu(2)-O(4)	82.14(3)°
N(4)-Cu(1)-O(3)	82.99(3)°	N(6)-Cu(2)-O(3)	106.22(3)°
N(4)-Cu(1)-O(4)	159.36(3)°	N(6)-Cu(2)-O(4)	175.07(3)°
O(3)-Cu(1)-O(4)	79.23(3)°	O(3)-Cu(2)-O(4)	78.22(3)°

3.6.1.2 Characterisation of compound **4**

Compound **4** was also characterised by FT-IR spectroscopy. The bond stretch at 1620 cm⁻¹ is the typical asymmetric C=N stretch associated with the imine functionality of **L2**.¹⁶⁴ The band observed at 1343 cm⁻¹ originates from the symmetric C-O stretch of the ester moiety of the **EMM** ligand.¹⁶⁴ The bands at 1560 cm⁻¹ and at 1421 cm⁻¹ are the asymmetric and symmetric COO stretches of the ester moiety, respectively.¹⁶⁴

Table 3.13: Crystal data and structure refinement for **4**

Identification code	4	
Empirical formula	$\text{Cu}_4\text{C}_{68}\text{H}_{90}\text{N}_{20}\text{O}_{11}$	
Formula weight	1617.97 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	$a = 11.070(17)$ Å $b = 13.21(2)$ Å $c = 16.49(3)$ Å	$\alpha = 110.13(3)^\circ$ $\beta = 104.061(17)^\circ$ $\gamma = 91.279(7)^\circ$
Volume	2181(6) Å ³	
Z	1	
Density (calculated)	1.429 Mg/m ³	
Absorption coefficient	1.045 mm ⁻¹	
F(000)	976	
Crystal size	0.2 x 0.05 x 0.025 mm ³	
Theta range for data collection	3.31 to 25.00°	
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -19 ≤ l ≤ 19	
Reflections collected	32118	
Independent reflections	7649 [R(int) = 0.0907]	
Completeness to theta = 25.00°	99.5 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7649 / 0 / 544	
Goodness-of-fit on F ²	1.127	
Final R indices [I > 2σ(I)]	R1 = 0.1108, wR2 = 0.2984	
R indices (all data)	R1 = 0.1404, wR2 = 0.3364	
Largest diff. peak and hole	2.025 and -0.739 e.Å ⁻³	

3.6.2 [Cu₉(μ₃-O)₂(O-L2-O)₂(CH₃COO)₁₀].2THF.2H₂O (**5**)

3.6.2.1 Synthesis and characterisation of compound **5**

When the ratio of Cu(CH₃COO)₂·H₂O to **L2** was increased to 4:1, a compound which contains a nonanuclear copper coordination cluster, [Cu₉(μ₃-O)₂(O-L2-O)₂(CH₃COO)₁₀].2THF.2H₂O (**5**), results. Compound **5** forms after the reaction of **L2** with Cu(CH₃COO)₂·H₂O in methanol. The resultant green solution is evaporated to dryness under vacuum yielding an oil. Green rectangular crystals of this compound were grown *via* the slow diffusion of tetrahydrofuran into an acetonitrile solution of the oil.

The structure of the resultant nonanuclear complex contained in **5** was determined by single crystal X-ray diffraction and is displayed in Figure 3.18.

Compound **5** crystallises in the monoclinic crystal system in the space group of *C2/c*. The asymmetric unit of **5** contains half of the nonanuclear coordination cluster with the remainder generated by symmetry operations, with a two-fold axis involving the central Cu atom Cu(5).

The structure of the coordination cluster in **5** is comprised of nine square planar coordinated Cu^{II} ions linked *via* a combination of ligands ({O-L2-O}²⁻, acetate and oxo ligands). The {O-L2-O}²⁻ ligand arises from the partial hydrolysis of the Schiff base ligand **L2** under the applied reaction conditions. The *in-situ* partial hydrolysis of imine ligands has previously been shown to occur in the formation of a variety of macrocyclic Schiff base complexes^{171,172} and recently a number of oligonuclear Schiff base complexes that also display this behaviour have been reported.^{173,174} The oxidation state of each copper ion was confirmed by bond valence sum analysis (Table 3.14).

Table 3.14: Bond valence sum analysis for **5**

Cu or O site	Bond Valence Sum (BVS)	Assigned Oxidation State
Cu(1)	1.981	+II
Cu(2)	1.980	+II
Cu(3)	2.005	+II
Cu(4)	2.187	+II
Cu(5)	2.090	+II
O(11)	1.873	-II

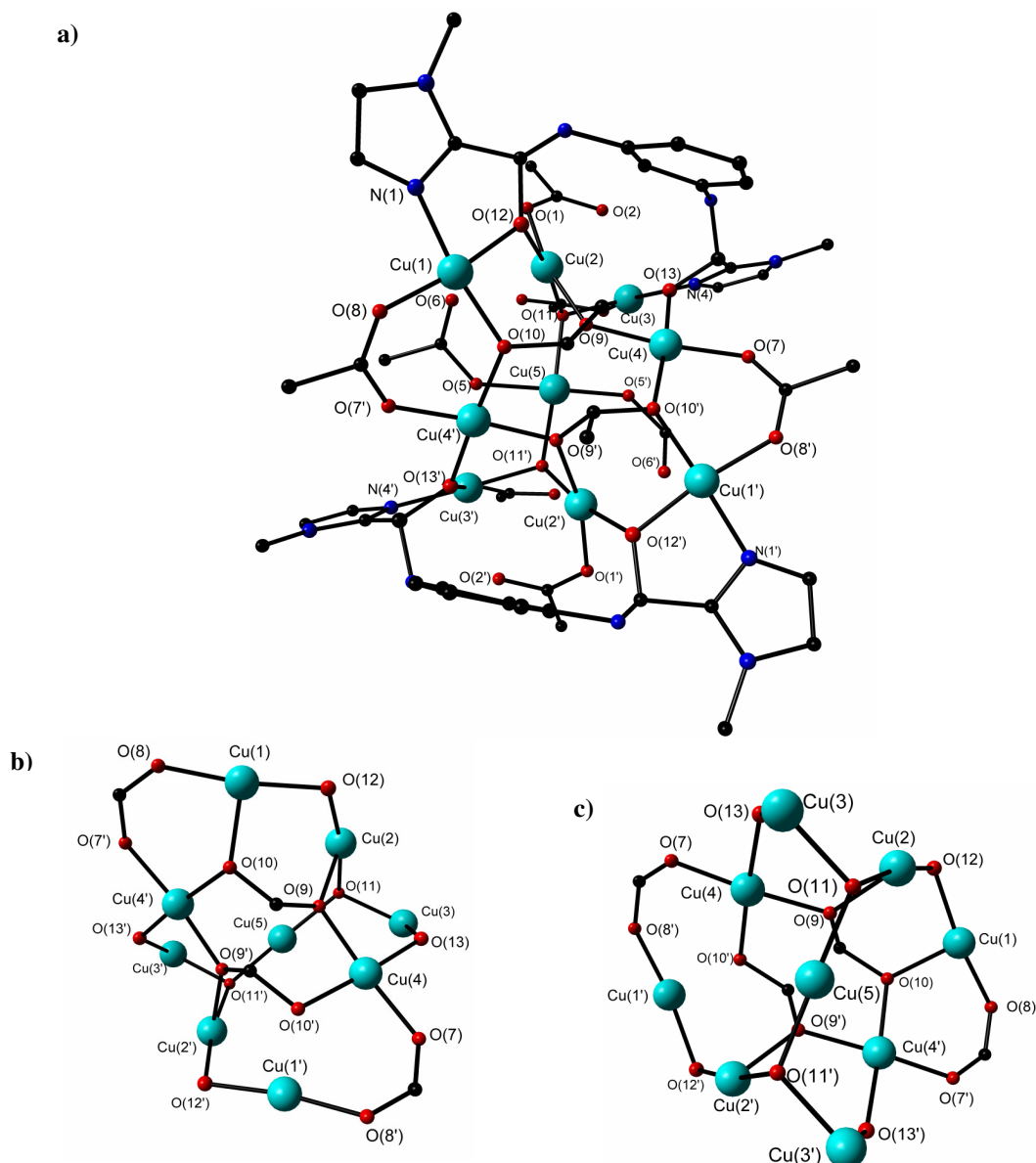


Figure 3.18: **a)** The structure of the nonanuclear Cu coordination cluster contained in **5** (H atoms and constitutional solvent molecules have been omitted for clarity). **b)** and **c)** The core structure of the cluster contained in **5**. Cu cyan, O red, N blue and C black. ' corresponds to the 1-x, y, 0.5-z positions.

The nonanuclear Cu coordination cluster contains a central Cu^{II} atom Cu(5) which is linked to Cu(2) and Cu(3) and their symmetry equivalents by two μ_3 -O oxo ligands O(11) and O(11'), resulting in a highly distorted 'butterfly' arrangement. This core is further linked through a series of bridging acetate ligands to Cu(1) and Cu(4) and their symmetry equivalents. Two partially hydrolysed Schiff base $\{\text{O-L2-O}\}^{2-}$ ligands stabilise the coordination complex and bridge between Cu(1), Cu(2), Cu(3) and Cu(4) and their symmetry equivalents. The O donor atoms of the $\{\text{O-L2-O}\}^{2-}$ ligand bridge between two Cu^{II} ions. The square planar coordination environments of Cu(2), Cu(3) and Cu(5) and their symmetry equivalents are completed by binding to

terminal acetate ligands. Further acetate O donor atoms reside 2.42(1) - 2.66(1) Å from the Cu centre and formally increase the coordination number of the Cu centres to five and six. The bond angles characterising the Cu coordination environments are presented in Table 3.15.

The Cu-O_{acetate} bonds in **5** reveal bond distances of between 1.88(2) Å and 1.99(1) Å and the O donor atoms of the {O-L2-O}²⁻ ligand show Cu-O bond lengths that range between 1.90(1) and 2.00(1). The Cu-N_{imidazole} bonds Cu(1)-N(1) and Cu(3)-N(4) have bond lengths of 1.98(1) Å and 1.98(2), respectively. These bond distances are summarised in Table 3.16.

Table 3.15: Selected bond angles for **5**

Bond Angle		Bond Angle	
N(1)-Cu(1)-O(8)	89.67(6)°	O(11)-Cu(2)-O(12)	170.03(5)°
N(1)-Cu(1)-O(10)	165.41(5)°	N(4)-Cu(3)-O(3)	91.24(6)°
N(1)-Cu(1)-O(12)	82.10(5)°	N(4)-Cu(3)-O(11)	174.32(6)°
O(8)-Cu(1)-O(10)	92.83(6)°	N(4)-Cu(3)-O(13)	81.70(6)°
O(8)-Cu(1)-O(12)	171.63(6)°	O(3)-Cu(3)-O(11)	93.96(5)°
O(10)-Cu(1)-O(12)	92.52(5)°	O(3)-Cu(3)-O(13)	171.27(6)°
O(1)-Cu(2)-O(9)	166.76(5)°	O(11)-Cu(3)-O(13)	92.91(5)°
O(1)-Cu(2)-O(12)	93.67(5)°	O(9)-Cu(4)-O(13)	92.24(5)°
O(9)-Cu(2)-O(12)	91.71(5)°	O(9)-Cu(4)-O(10')	83.58(4)°
O(9)-Cu(2)-O(11)	83.95(5)°	O(5)Cu(5)-O(11)	93.53(5)°

Table 3.16: Selected bond lengths for **5**

Bond	Bond Length	Bond	Bond Length
Cu(1)-N(1)	1.98(1) Å	Cu(3)-N(4)	1.98(2) Å
Cu(1)-O(8)	1.88(2) Å	Cu(3)-O(3)	1.92(2) Å
Cu(1)-O(10)	1.95(1) Å	Cu(3)-O(11)	1.95(1) Å
Cu(1)-O(12)	1.95(1) Å	Cu(3)-O(13)	2.00(1) Å
Cu(2)-O(1)	1.99(1) Å	Cu(4)-O(9)	1.91(1) Å
Cu(2)-O(9)	1.93(1) Å	Cu(4)-O(13)	1.91(1) Å
Cu(2)-O(11)	1.93(1) Å	Cu(5)-O(5)	1.94(1) Å
Cu(2)-O(12)	1.95(1) Å	Cu(5)-O(11)	1.95(1) Å

The single crystals of **5** are small. The small crystal size and the low intensity of the resulting X-ray data are reflected in the low quality refinement values of the structure. However, the analysis of the dataset and X-ray powder diffraction (Figure 3.19) measurements clearly established the structure of the cluster compound and verifies the space group assignment.

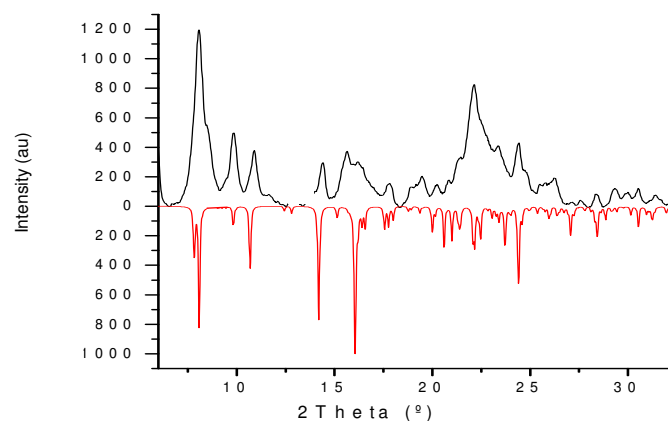


Figure 3.19: The XRD powder pattern of **5** (black) and the simulated XRD pattern (red) based on the single crystal X-ray diffraction data.

Compound **5** was further analysed by FT-IR spectroscopy. The strong bands at 1548 cm^{-1} and 1401 cm^{-1} arise from the asymmetric and symmetric carboxylate stretch of the acetate ligands.¹⁶⁴ It has been demonstrated by Deacon and Phillips, that the value of $\Delta = [\nu_{\text{asymmetric}}(\text{CO}_2^-) - \nu_{\text{symmetric}}(\text{CO}_2^-)]$ can be used to determine the binding mode of carboxylic acid ligands such as acetates.¹⁷⁵ In the case of **5**, Δ value of 205 cm^{-1} suggests that **5** contains bridging acetate ligands. This result is consistent with the structure of **5** obtained from single crystal X-ray diffraction measurements.

To investigate the composition of **5** thermogravimetric analysis (Figure 3.20) was carried out on a freshly filtered sample of **5**. The sample was heated to $900\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The compound undergoes a weight loss of 9% between $30\text{ }^{\circ}\text{C}$ and $130\text{ }^{\circ}\text{C}$. This accounts for the loss of the two solvent tetrahydrofuran molecules and the two solvent water molecules (calculated weight of 8.9%) from **5**. Elemental analysis (CHN) further supports the constitutional assignment of **5**.

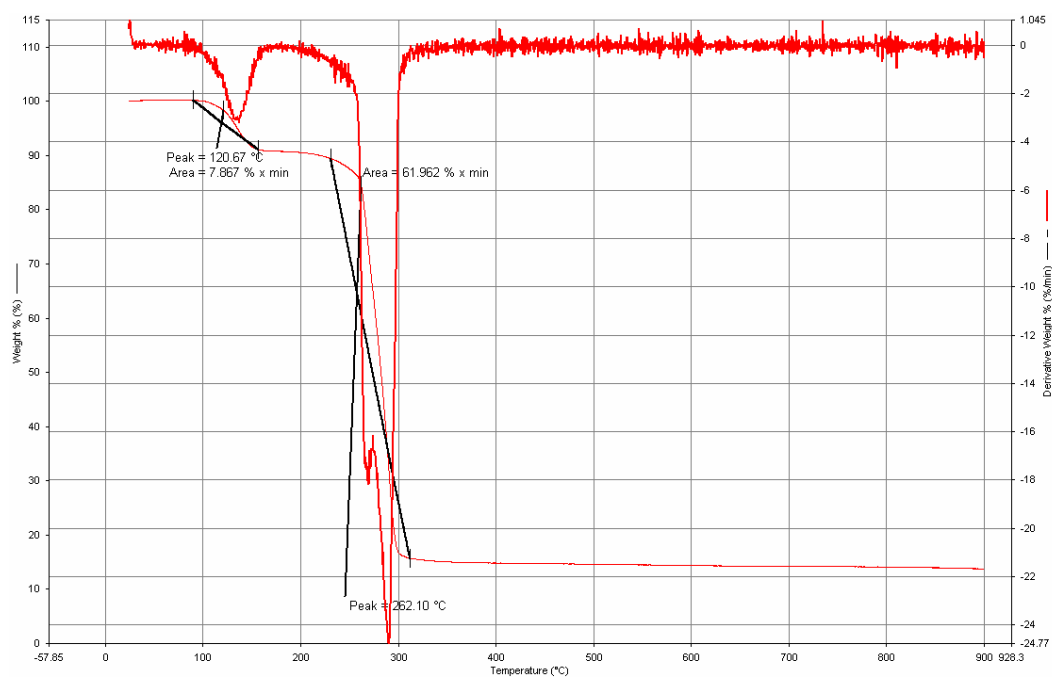


Figure 3.20: Thermogravimetric analysis (TGA) for 5.

Table 3.17: Crystal data and structure refinement for **5**

Identification code	5	
Empirical formula	Cu ₉ C ₆₀ H ₈₂ N ₁₂ O ₃₀	
Formula weight	2023.29 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.094(7) Å b = 20.925(7) Å c = 19.087(7) Å	α = 90° β = 95.176(5)° γ = 90°
Volume	9186(5) Å ³	
Z	4	
Density (calculated)	1.456 Mg/m ³	
Absorption coefficient	2.120 mm ⁻¹	
F(000)	4067	
Crystal size	0.09 x 0.07 x 0.05 mm ³	
Theta range for data collection	1.32 to 22.50°	
Index ranges	-24 ≤ h ≤ 24, -22 ≤ k ≤ 22, -20 ≤ l ≤ 20	
Reflections collected	38152	
Independent reflections	6007 [R(int) = 0.2942]	
Completeness to theta = 22.50°	99.9 %	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6007 / 0 / 472	
Goodness-of-fit on F ²	0.999	
Final R indices [I > 2σ(I)]	R1 = 0.0947, wR2 = 0.2143	
R indices (all data)	R1 = 0.1960, wR2 = 0.2429	
Largest diff. peak and hole	1.306 and -0.670 e.Å ⁻³	

3.7 [Co(HL4)₂] $\cdot$ MeOH $\cdot$ 2H₂O (6)

3.7.1 Synthesis of H₂L4

In an attempt to further explore the coordination chemistry of related ligand systems, we decided to modify **L2** by substituting one of the imine functionalities for an arsonate moiety and by exchanging the methyl-imidazole head group for a pyridine ring, to give **H₂L4** (Figure 3.22). The arsonate moiety was introduced to the ligand system as these oxygen donating ligands have been shown to stabilise a variety of desirable hybrid inorganic-organic materials such as molecular cages,¹⁷⁸ coordination clusters¹⁷⁹ and coordination networks.¹⁸⁰

The novel ligand 4-[(pyridin-2-ylmethylene)-amino]-arsonic acid (**H₂L4**) was obtained in high yields (85 %) from the reaction of 2-aminophenyl arsonic acid with 1-methyl-2-imidazolcarboxyaldehyde in methanol solution. FT-IR analysis of **H₂L4** verifies the formation of the imine bond and reveals a strong asymmetric C=N bond stretch at 1618 cm⁻¹.¹⁶⁴ The bands at 885 cm⁻¹ and 785 cm⁻¹ arise from the asymmetric and symmetric stretches of the As-O bonds of the **H₂L4** ligand.¹⁸¹ The ESI mass spectrum shows a molecular ion peak corresponding to **H₂L4** at 307.1 m/z and elemental analysis (CHN) confirms its purity. The 400 MHz ¹H NMR spectrum of **H₂L4** together with its assignment is presented in Figure 3.22.

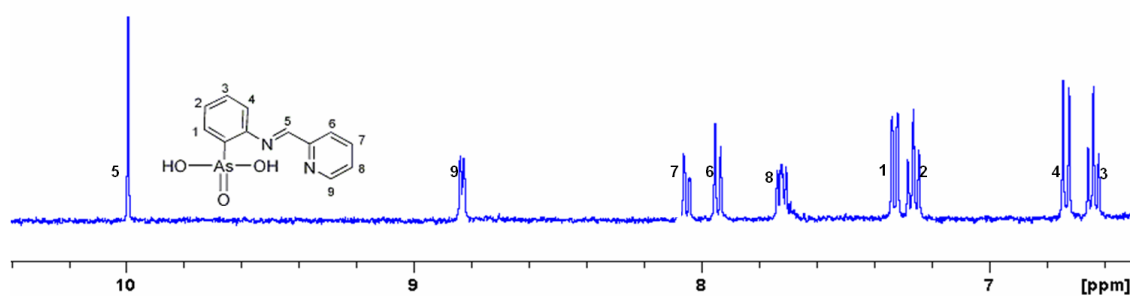


Figure 3.22: The 400 MHz ¹H NMR (D₆-DMSO) spectrum and assignment for **H₂L4**.

3.7.2 Coordination chemistry of H₂L4

H₂L4 was then reacted with a series of transition metal ions (Fe^{II}, Fe^{III}, Co^{II}, Ni^{II} and Cu^{II}) using various ligand to metal ratios in the hope of generating high nuclearity coordination compounds that would display appealing magnetic properties such as superparamagnetic effects and quantum behaviour. This synthetic approach

proved to have limited success, and often lead to the formation of insoluble precipitates and non-crystalline materials that proved difficult to characterise. However, **H₂L4** was used to form [Co(**HL4**)₂]·MeOH·2H₂O (**6**).

3.7.3 Synthesis and structural characterisation of [Co(**HL4**)₂]·MeOH·2H₂O (**6**)

The reaction of **H₂L4** with one equivalent of CoCl₂·6H₂O in methanol yielded an orange solution. The slow evaporation of this solution generated orange plate like crystals of [Co(**HL4**)₂]·MeOH·2H₂O (**6**), which were analysed using single crystal X-ray diffraction.

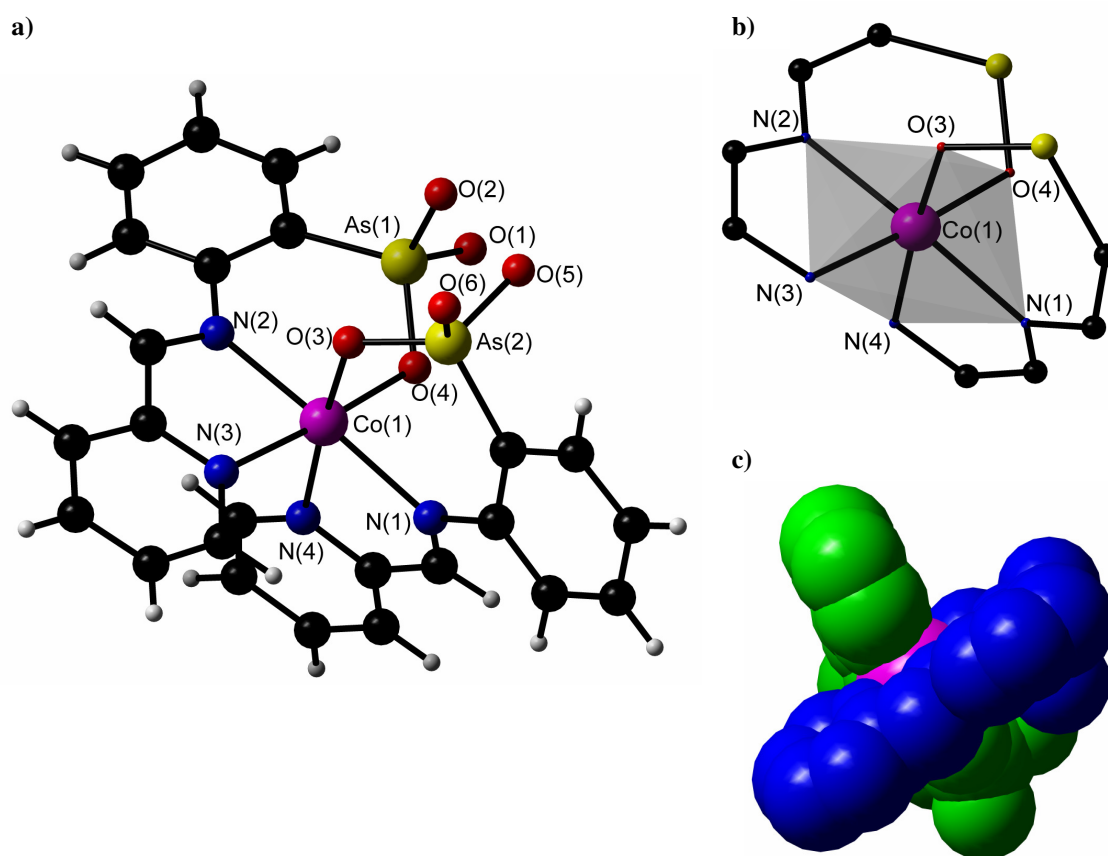


Figure 3.23: a) The structure of the mononuclear Co^{II} complex contained in **6** (arsonic acid protons and solvent molecules have been removed for clarity). b) The coordination environment of the Co^{II} metal centre. c) Space filling representation of the Co^{II} complex. Co purple, As yellow, O red, N blue, C black and H white.

Compound **6** crystallises in the triclinic system in the *P*-1 space group. The asymmetric unit of **6** contains the complete mononuclear Co^{II} complex [Co(**HL4**)₂] which is displayed in Figure 3.23. The mononuclear Co^{II} complex is stabilised by two monodeprotonated **H₂L4** ligands (**HL4**). Within the mononuclear complex, the Co^{II}

ion binds to two imine N atoms N(1) and N(2), two pyridine N atoms N(3) and N(4) and two arsonate O atoms O(4) and O(3). The imine N donors N(1) and N(2) display Co-N bond lengths of 2.230(8) Å and 2.204(8) Å, respectively. The pyridine moieties that bind to the metal centre show Co-N bond distances of 2.083(8) Å and 2.121(8) Å for Co(1)-N(3) and Co(1)-N(4), respectively. The Co-O bond distances are 2.040(6) Å for the Co(1)-O(3) bond and 2.058(6) Å for the Co(1)-O(4) bond. These bond lengths are further summarised in Table 3.18. The two protonated O atoms of the arsonate groups O(2) and O(5) display As-O bond lengths of 1.730(2) Å and 1.722(9) Å. These As-O bond lengths are as expected longer than those involving the deprotonated O atoms O(3) and O(4) which display bond lengths of 1.661(2) Å and 1.672(6) Å, respectively. The protons of O(2) and O(5) could not be found crystallographically and this O atoms were assigned as protonated based on the bond lengths and charge considerations.

Table 3.18: Selected bond lengths for **6**

Bond	Bond Length	Bond	Bond Length
Co(1)-N(1)	2.230(8) Å	As(1)-O(3)	1.661(2) Å
Co(1)-N(2)	2.204(8) Å	As(1)-O(5)	1.722(9) Å
Co(1)-N(3)	2.083(8) Å	As(1)-O(6)	1.718(3) Å
Co(1)-N(4)	2.121(8) Å	As(2)-O(1)	1.710(2) Å
Co(1)-O(3)	2.040(6) Å	As(2)-O(2)	1.730(2) Å
Co(1)-O(4)	2.058(6) Å	As(2)-O(4)	1.672(6) Å

The Co^{II} ion displays distorted octahedral coordination geometry (Figure 3.23b) with the donor atoms of each **HL4** ligand adopting a *meridional* arrangement. The distortion from ideal octahedral coordination geometry is best exemplified by examining some of the bond angles of Co(1) (Table 3.19), which depart noticeably from the ideal octahedral angles of 90° and 180°. The deviation is evident from the N(1)-Co(1)-N(4), N(2)-Co(1)-N(3) and N(1)-Co(1)-O(4) bond angles of 78.12(2)°, 79.53(2)° and 83.40(2)° respectively, which deviate significantly from those of an ideal octahedron. This distortion is further underlined by examining the N(1)-Co(1)-N(2), N(3)-Co(1)-O(4) and N(4)-Co(1)-O(3) angles of 174.78(3)°, 174.30(3)° and 172.74(3)°. These bond angles depart from the ideal 180° angle expected from atoms

trans to each other in an octahedral coordination arrangement.

Table 3.19: Selected bond angles for **6**

Bond Angle		Bond Angle	
N(1)-Co(1)-N(2)	174.78(3)°	N(2)-Co(1)-O(4)	95.24(2)°
N(1)-Co(1)-N(3)	101.61(2)°	N(3)-Co(1)-N(4)	91.13(2)°
N(1)-Co(1)-N(4)	78.12(2)°	N(3)-Co(1)-O(3)	86.83(2)°
N(1)-Co(1)-O(3)	95.73(2)°	N(3)-Co(1)-O(4)	174.30(3)°
N(1)-Co(1)-O(4)	83.40(2)°	N(4)-Co(1)-O(3)	172.74(3)°
N(2)-Co(1)-N(3)	79.53(2)°	N(4)-Co(1)-O(4)	87.21(2)°
N(2)-Co(1)-N(4)	96.80(2)°	O(3)-Co(1)-O(4)	95.98(2)°

Upon viewing the packing structure of the molecular entities in **6** (Figure 3.24), it is noticeable that Co^{II} complexes, the constitutional water and methanol molecules in **6** are held together by weak van der Waals forces resulting in a densely packed structure.

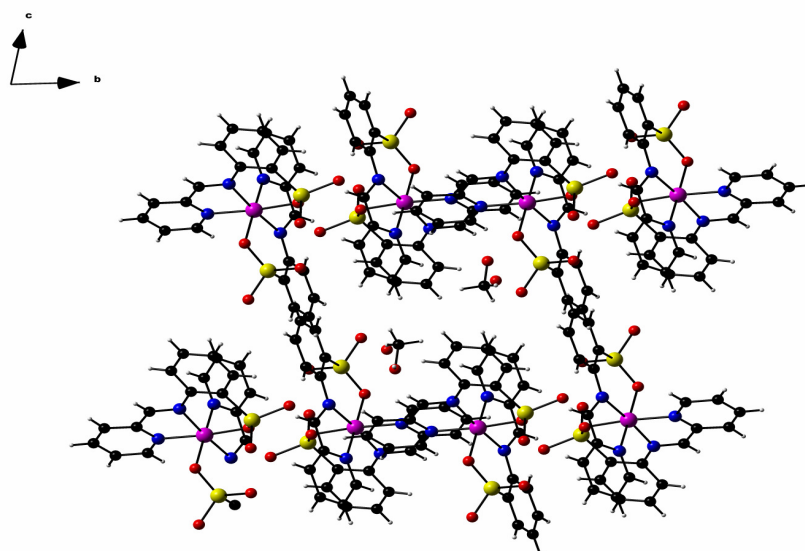


Figure 3.24: The packing of the Co^{II} complexes found in **6** viewed in the direction of the crystallographic *c*-axis.

Compound **6** was further analysed by FT-IR spectroscopy. The strong asymmetric C=N bond stretch at 1608 cm⁻¹ is characteristic of the imine functionality in **HL4**.¹⁶⁴ CHN microanalysis helped to confirm the composition of compound **6**.

Table 3.20: Crystal data and structure refinement for **6**

Identification code	6	
Empirical formula	CoAs ₂ C ₂₅ H ₂₈ N ₄ O ₉	
Formula weight	737.30 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 11.401(2) Å b = 12.097(2) Å c = 12.513 (2) Å	α = 71.51(3)° β = 63.49(3)° γ = 72.90(3)°
Volume	1440.80(5) Å ³	
Z	2	
Density (calculated)	1.686 Mg/m ³	
Absorption coefficient	2.933 mm ⁻¹	
F(000)	736	
Crystal size	0.5 x 0.4 x 0.05 mm ³	
Theta range for data collection	1.80 to 25.00°	
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14	
Reflections collected	22691	
Independent reflections	5075 [R(int) = 0.1042]	
Completeness to theta = 25.00°	99.9%	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5075 / 0 / 358	
Goodness-of-fit on F ²	1.281	
Final R indices [I > 2σ(I)]	R1 = 0.0853, wR2 = 0.2323	
R indices (all data)	R1 = 0.1105, wR2 = 0.2647	
Largest diff. peak and hole	1.296 and -1.472-e.Å ⁻³	

3.8 Conclusion

A series of versatile bis-bidentate Schiff base ligands were designed, synthesised and fully characterised. One of these novel ligands **L2** was shown to stabilise a series of coordination compounds **1**, **2**, **3**, **4** and **5**.

L2 was exploited in transition metal directed self-assembly to produce a variety of coordination compounds. Upon complexation the relative conformation of the ligands imine-imidazole functionalities influence the topology of the resultant species (Figure 3.25).

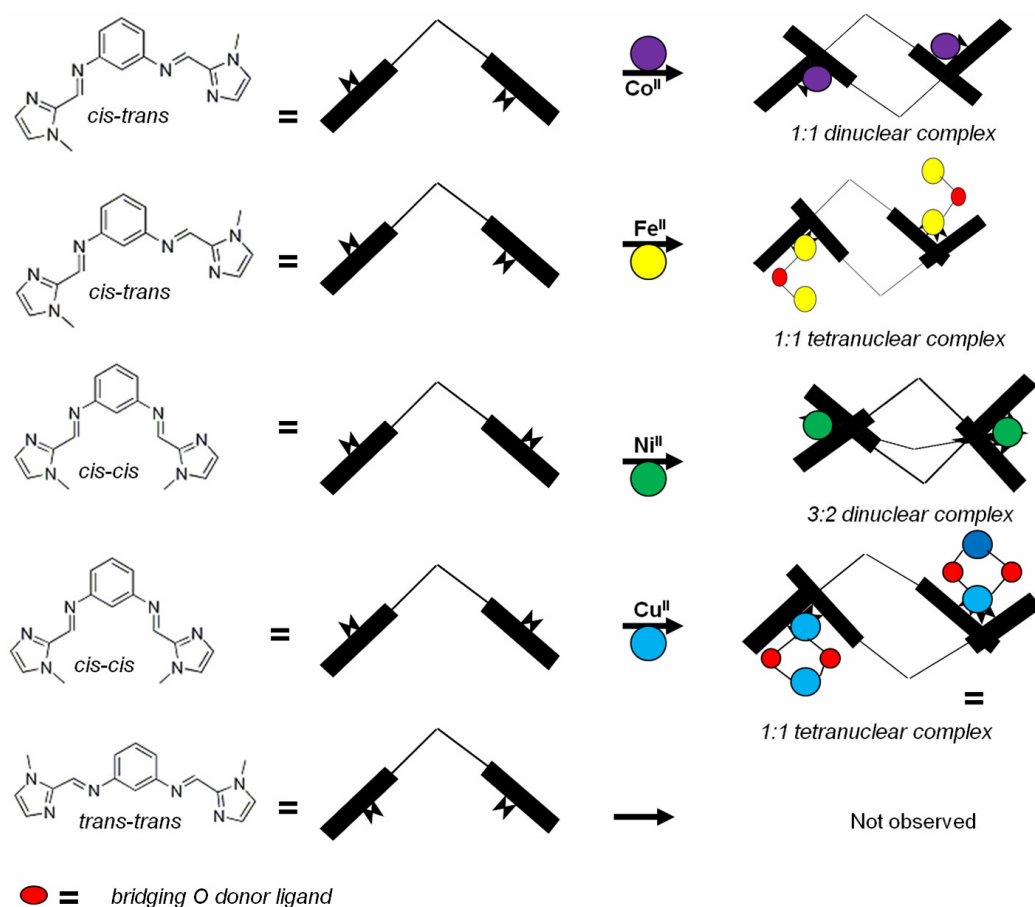


Figure 3.25: Schematic representation of the transition metal directed self-assembly of **L2**, demonstrating the various conformations adopted by **L2** upon complexation.

For example, upon reaction with $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, **L2** adopts a *cis-trans* conformation resulting in the formation of a tetranuclear iron(III) compound (**1**). This compound contains two dinuclear Fe^{III} subunits linked by two **L2** ligands.

In the case of **2**, the ligand adopts a *cis-trans* conformation resulting in a dinuclear complex with a 1:1 ligand to metal ratio. However, in **3** when **L2** was reacted with Ni^{II} a 3:2 complex results, whereby the Schiff base ligands adopt a *cis-cis*

arrangement. UV-vis titration studies were used to investigate the formation of these 1:1 and 3:2 species in solution.

In the hope of generating coordination clusters, the reaction of **L2** with Cu^{II} acetate monohydrate was investigated. Our applied synthetic approach yielded a tetranuclear complex **4** and a coordination compound **5** which contains an interesting Cu^{II} nonanuclear coordination cluster. It is worth noting that the nonanuclear coordination cluster in **5** is stabilised by two carbinolamine ligands {O-**L2**-O}²⁻. These ligands result from the *in-situ* partial hydrolysis of the Schiff base **L2** ligand under applied reaction conditions. In contrast to **L2**, the {O-**L2**-O}²⁻ ligand contains O donor atoms which can bridge between the Cu centres giving rise to the formation of the cluster species.

We have also introduced arsonate groups into our ligand systems as these O donating ligands have been applied in the stabilisation of large coordination clusters.¹⁷⁹ This approach led to the synthesis of the novel Schiff base ligand **H₂L4**. Attempts to utilise this ligand for the formation of polynuclear complexes proved unsuccessful. However **H₂L4** was employed in the formation of the coordination compound **6**, which contains a mononuclear Co^{II} complex.

The synthetic approach discussed in this chapter demonstrates that bis-bidentate ligands can be applied to assemble a diverse range of metallo-supramolecular architectures ranging from dinuclear complexes to coordination clusters. Given these results it has been speculated that the synthetic approach used in the formation of **5** could potentially be generalised to a variety of Schiff base ligands which could give rise to coordination clusters with variable nuclearities and topologies.

Chapter Four

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Twist and spin: The synthesis, structural characterisation and spin crossover behaviour of a series of Schiff base-stabilised molecular helicates

4.1 Introduction

Recently there has been an endeavour to utilise SCO for molecular recognition purposes^{99,100} and it has been suggested that molecular helicates are ideal candidates for such behaviour since they may contain large inter-helical cavities that could potentially recognise a guest molecule through a change in their magnetic properties.^{81,182,183} We therefore set out to design a series of Fe^{II} metallo-helicates, whereby SCO behaviour could potentially be utilised to identify the presence of guest molecules.

It has been shown that the predictable binding modes of flexible Schiff base ligands can be exploited in transition metal directed self-assembly to produce metallo-helicates.^{73,74} So, we designed a series of ligands (Figure 4.1) that consist of imine-imidazole binding groups linked *via* 4-4'-diaminodiphenylmethane, 4-4' oxydianiline or 4-4' diaminodiphenylamine linkers. The flexible nature of these bis-bidentate imine ligands is expected to generate molecular helicates upon reaction with various Fe^{II} salts whilst the imine-imidazole moieties should produce an intermediate ligand field which might enable these supramolecular assemblies to undergo SCO transitions.

Previous work carried out within the group yielded the helical dinuclear complex in [Fe₂(**L6**)₃](ClO₄)₄·2MeCN (**7**).¹⁸⁴ This compound was shown to undergo a SCO transition at a temperature of 150 K. Based on this result, we sought to investigate if the SCO behaviour of these helicate compounds could be modified by subtle changes in the ligand structure or through altering the counterions.

4.2 Synthesis and characterisation of Schiff base ligands

A series of bis-bidentate Schiff base ligands were proposed for exploitation in the formation of Fe^{II} molecular helicates. The ligand types used are characterised by the presence of two imine-imidazole functionalities linked through a flexible organic linker. Within these ligands, the imine carbon atoms are attached to methyl-imidazole moieties. These versatile ligands are easily prepared *via* nucleophilic addition reactions between the relevant diamine and two equivalents of 1-methyl-2-imidazolcarboxyaldehyde in methanol solution. Subtle changes of the amine backbone may give rise to a family of flexible ligands (Figure 4.1), that could be exploited in the formation of Fe^{II} molecular helicates. The alteration of the organic

linker was expected to impact on the arrangement of the ligand strands within the resultant molecular helicate which might affect the SCO properties of the material. Alternatively, the variation of the N-heterocyclic head groups could also allow the SCO behaviour of the molecular helicates to be tuned.

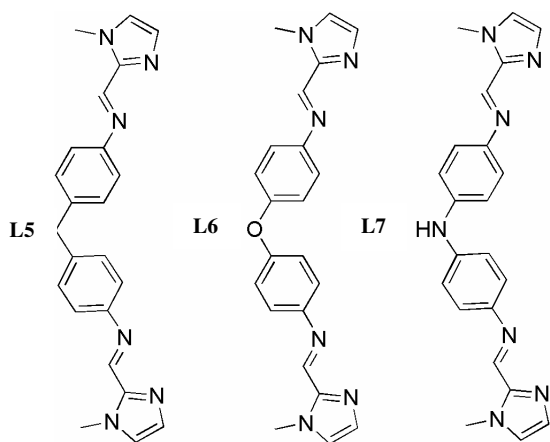


Figure 4.1: Structure of the flexible Schiff base ligands to be used in the formation of molecular helicates.

4.2.1 Synthesis of N,N'-bis-(1-methyl-1H-imidazol-2-yl-methylene)-4,4'-diaminodiphenylmethane (**L5**)

The novel ligand N,N'-bis-(1-methyl-1H-imidazol-2-yl-methylene)-4,4'-diaminodiphenylmethane (**L5**) was prepared *via* the reaction of two equivalents of 1-methyl-2-imidazolecarboxaldehyde with 4-4'-diaminodiphenylmethane in methanol. The ligand formed in a reasonable yield (60%) and the elemental analysis (CHN) is consistent with the expected composition. The 400 MHz ^1H NMR spectrum of **L5** is shown together with the peak assignment in Figure 4.2.

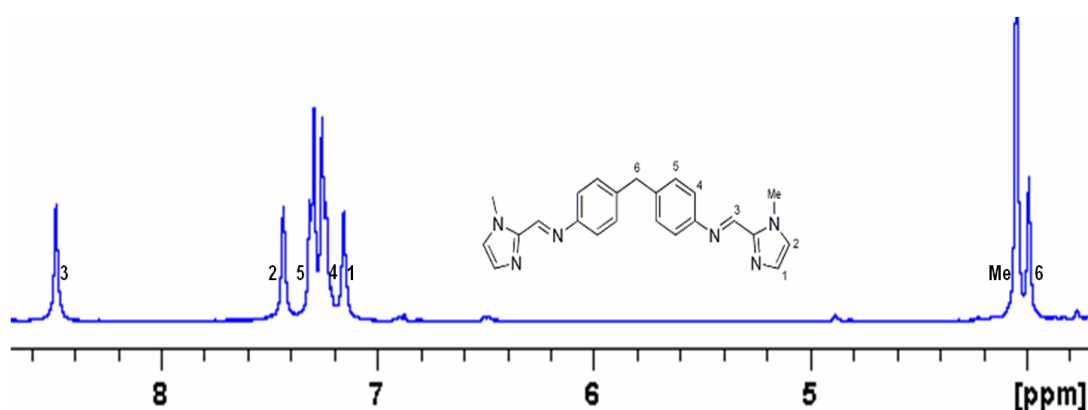


Figure 4.2: The 400 MHz ^1H NMR ($\text{D}_6\text{-DMSO}$) spectrum and assignment for **L5**.

The FT-IR spectrum of **L5** confirms the presence of the imine groups, as it shows a strong asymmetric C=N bond stretch at 1627 cm^{-1} .¹⁶⁴ The ESI mass spectrum of **L5** dissolved in methanol shows a molecular ion peak at 383.1 m/z and there are no other species observed in solution.

4.2.2 Synthesis of N,N'-bis-(1-methyl-1-H-imidazol-2-yl-methylene)-4,4'-oxydianiline (**L6**)

The Schiff base ligand N,N'-bis-(1-methyl-1-H-imidazol-2-yl-methylene)-4,4'-oxydianiline (**L6**) was synthesised in a similar manner to **L5** except that 4-4' oxydianiline is used instead of 4-4' diminodiphenylmethane. This reaction yielded a cream powder (58 %) and the elemental analysis is consistent with the constitution of **L6**. The FT-IR spectrum of **L6** also shows a strong asymmetric C=N imine bond stretch at 1629 cm^{-1} .¹⁶⁴ The ESI mass spectrum reveals the presence of the appropriate molecular ion at 385.3 m/z . The 400 MHz ^1H NMR spectrum of **L6** together with its assignment is presented in Figure 4.3.

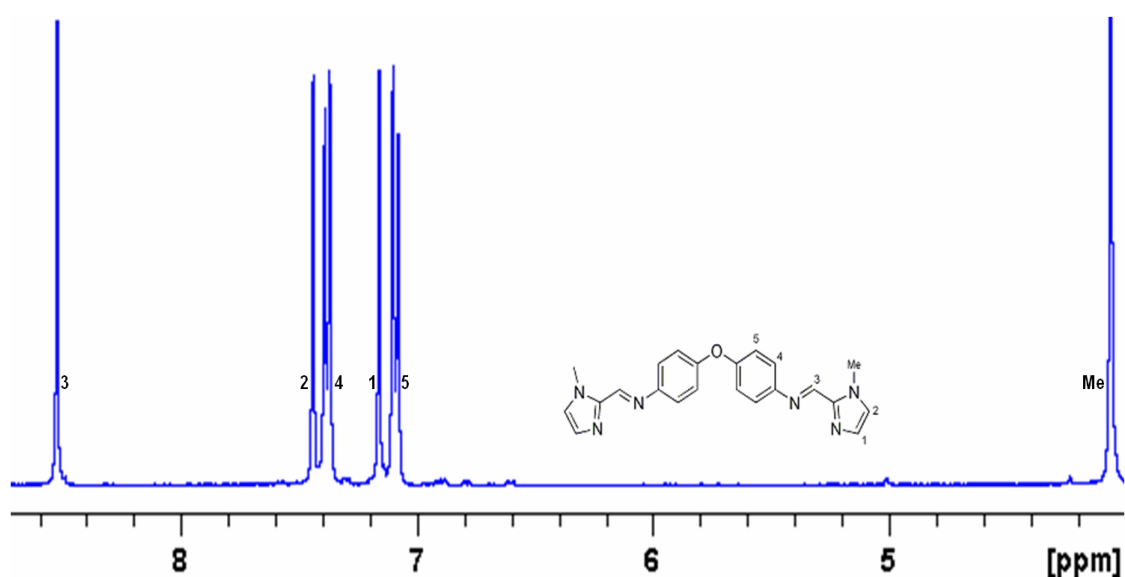


Figure 4.3: The 400 MHz ^1H NMR ($\text{D}_6\text{-DMSO}$) spectrum and assignment for **L6**.

4.2.3 Synthesis of N,N'-bis-(1-methyl-1-H-imidazol-2-yl-methylene)-4,4'-diaminodiphenylamine (**L7**)

The novel ligand N,N'-bis-(1-methyl-1-H-imidazol-2-yl-methylene)-4,4'-diaminodiphenylamine (**L7**) was synthesised in a similar manner to **L5** except that

4-4' diaminodiphenylamine was employed as the amine in the Schiff base reaction. This produced **L7** in a reasonable yield (62 %). **L7** was characterised using ^1H NMR spectroscopy (Figure 4.4) and by ESI mass spectrometry which confirms the presence of the appropriate molecular ion at 384.1 m/z. FT-IR spectroscopy verifies the formation of the C=N bond with a band at 1620 cm^{-1} .¹⁶⁴

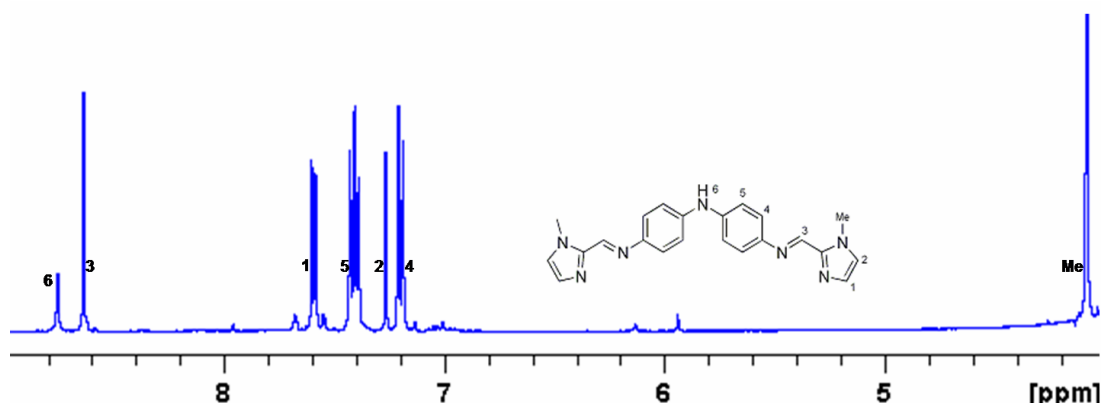


Figure 4.4: The 400 MHz ^1H NMR (D_6 -DMSO) spectrum and assignment for **L7**.

4.3 Synthesis of Co^{II} , Mn^{II} and Ni^{II} helicates using flexible Schiff base ligands

4.3.1 Synthesis and structural characterisation of $[\text{Co}_2(\text{L5})_3](\text{NO}_3)_4 \cdot 2\text{MeOH}$ (**8**)

In an effort to understand the coordination chemistry of these flexible Schiff base ligands they were reacted with a series of transition metal salts with the aim of synthesising novel metallo-helicates. This work resulted in the coordination compound $[\text{Co}_2(\text{L5})_3](\text{NO}_3)_4 \cdot 2\text{MeOH}$ (**8**). Compound **8** forms from the reaction of three equivalents of **L5** and with two equivalents of $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in methanol. This reaction yields an orange solution. Slow evaporation of the solution at room temperature resulted in the formation of light orange crystals after 1 week.

These crystals were characterised using single crystal X-ray diffraction and the measurements show that **8** crystallises in the orthorhombic crystal system in the space group $Pna2_1$. The overall structure of the Co^{II} complex contained within **8** can best be described as a dinuclear triple helicate (Figure 4.5) with two Co^{II} ions linked *via* three Schiff base ligands. The Co^{II} ions are separated by a distance of $11.54(3)\text{ \AA}$ and the ligands wrap around the metal-metal axis giving rise to the helical arrangement. The asymmetric unit of **8** contains one complete dinuclear Co^{II} complex. It also worth

noting that there is no evidence of direct interactions between the individual helicates in the solid state.

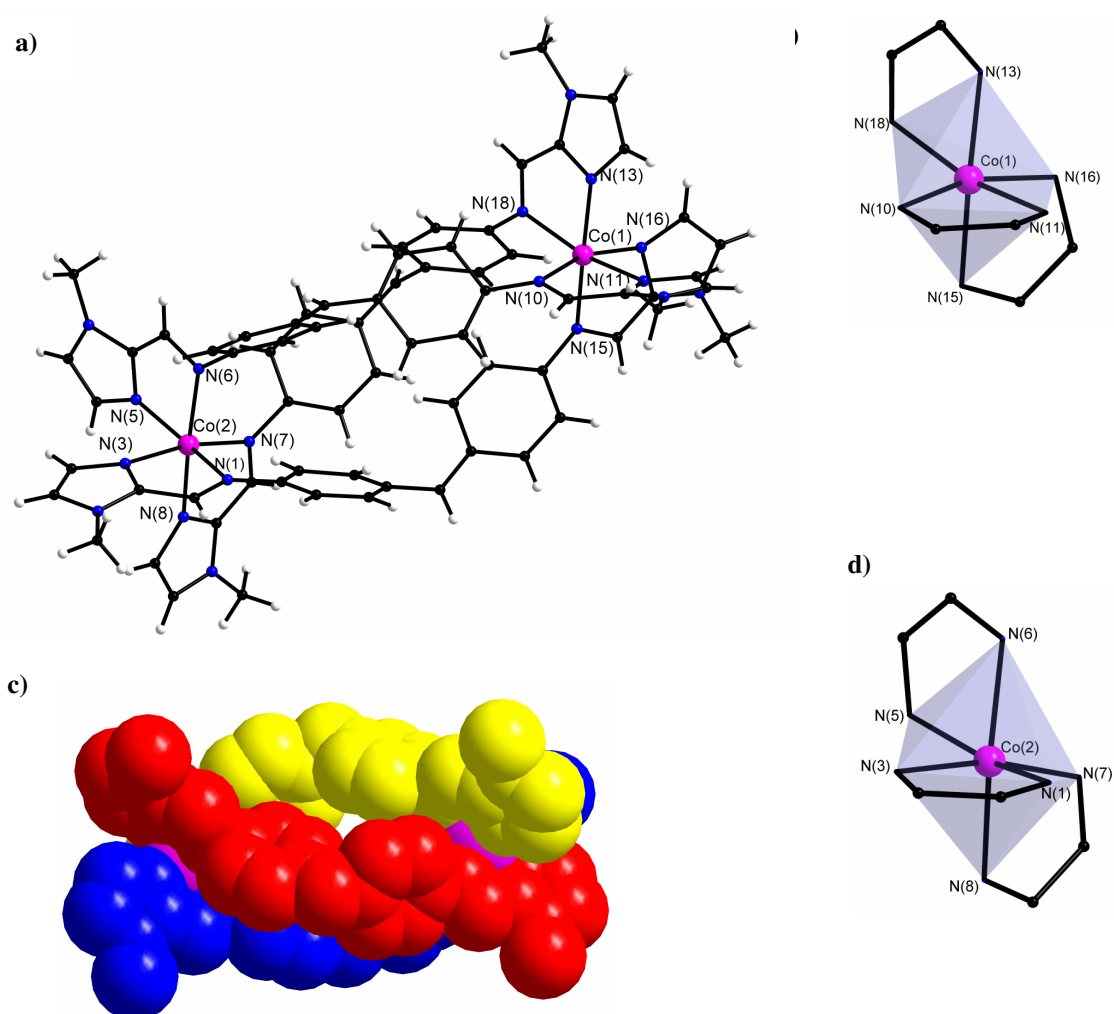


Figure 4.5: **a)** The structure of the dinuclear triple helicate in **8** (counterions and constitutional solvent molecules have been removed for clarity). **b)** The coordination environment of Co(1). **c)** Space filling representation of the helicate complex in **8**. **d)** The coordination environment of Co(2). Co purple, N blue, C black and H white.

Within the dinuclear complex, each Co atom binds to six N atoms (three imine N atoms and three imidazole N atoms) from three individual **L5** ligands. The imine N atoms that bind to the Co^{II} ions have Co-N_{imine} bond lengths that range in length from 2.153(8) Å to 2.267(9) Å. The Co-N_{imidazole} bonds have distances of between 2.076(8) Å and 2.130(8) Å. These bond lengths are summarised further in Table 4.1.

Table 4.1: Selected bond lengths for **8**

Bond	Bond Length	Bond	Bond Length
Co(1)-N(10)	2.198(7) Å	Co(2)-N(1)	2.267(9) Å
Co(1)-N(11)	2.130(8) Å	Co(2)-N(3)	2.084(9) Å
Co(1)-N(13)	2.124(9) Å	Co(2)-N(5)	2.128(9) Å
Co(1)-N(15)	2.181(8) Å	Co(2)-N(6)	2.153(8) Å
Co(1)-N(16)	2.076(8) Å	Co(2)-N(7)	2.199(9) Å
Co(1)-N(18)	2.212(8) Å	Co(2)-N(8)	2.109(9) Å

Both Co^{II} centres within the dinuclear complex display distorted octahedral geometries (Figure 4.5) with the imine N atoms arranged in a *facial* manner. The imidazole donor atoms also adopt a *fac* orientation within the coordination sphere of the Co^{II} ions. The deviation from ideal octahedral coordination is best exemplified by examining some of bond angles involving Co(1) (Table 4.2), which depart noticeably from the ideal octahedral angles of 90° and 180°. The distortion is evident from the N(13)-Co(1)-N(18), N(10)-Co(1)-N(11) and N(11)-Co(1)-N(16) bond angles of 77.48(3)°, 76.46(3)° and 86.70(3)°, respectively which deviate significantly from those of an ideal octahedron. This distortion is further underlined by examining the N(13)-Co(1)-N(15), N(10)-Co(1)-N(16) and N(11)-Co(1)-N(18) angles of 171.20(3)°, 160.98(3)° and 167.61(3)°. These bond angles depart from the ideal 180° angle expected from atoms in *trans* positions to each other in an octahedral coordination arrangement. The bond angles of the Co(2) centre are closely related to those involving Co(1) and are presented in Table 4.2.

Table 4.2: Selected bond angles for **8**

Bond Angle		Bond Angle	
N(10)-Co(1)-N(11)	76.46(3)°	N(1)-Co(2)-N(3)	77.31(3)°
N(10)-Co(1)-N(13)	93.72(3)°	N(1)-Co(2)-N(5)	159.90(3)°
N(10)-Co(1)-N(15)	94.56(3)°	N(1)-Co(2)-N(6)	89.42(3)°
N(10)-Co(1)-N(16)	160.98(3)°	N(1)-Co(2)-N(7)	104.76(3)°
N(10)-Co(1)-N(18)	102.58(3)°	N(1)-Co(2)-N(8)	92.26(3)°
N(11)-Co(1)-N(13)	90.22(3)°	N(3)-Co(2)-N(5)	87.93(4)°
N(11)-Co(1)-N(15)	94.61(3)°	N(3)-Co(2)-N(6)	95.10(3)°
N(11)-Co(1)-N(16)	86.70(3)°	N(3)-Co(2)-N(7)	166.14(3)°
N(11)-Co(1)-N(18)	167.61(3)°	N(3)-Co(2)-N(8)	90.89(3)°
N(13)-Co(1)-N(15)	171.20(3)°	N(5)-Co(2)-N(6)	78.24(3)°
N(13)-Co(1)-N(16)	95.16(3)°	N(5)-Co(2)-N(7)	92.85(3)°
N(13)-Co(1)-N(18)	77.48(3)°	N(5)-Co(2)-N(8)	101.66(3)°
N(15)-Co(1)-N(16)	77.81(3)°	N(6)-Co(2)-N(7)	98.61(3)°
N(15)-Co(1)-N(18)	97.78(3)°	N(6)-Co(2)-N(8)	174.00(4)°
N(16)-Co(1)-N(18)	95.76(3)°	N(7)-Co(2)-N(8)	75.39(3)°

Table 4.3: Crystal data and structure refinement for **8**

Identification code	8	
Empirical formula	$\text{Co}_2\text{C}_{71}\text{H}_{74}\text{N}_{22}\text{O}_{14}$	
Formula weight	1577.36 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71070 Å	
Crystal system	Orthorhombic	
Space group	<i>Pna</i> 2 ₁	
Unit cell dimensions	<i>a</i> = 39.366 (9) Å	$\alpha = 90^\circ$
	<i>b</i> = 10.529 (2) Å	$\beta = 90^\circ$
	<i>c</i> = 17.878 (4) Å	$\gamma = 90^\circ$
Volume	7410 (3) Å ³	
<i>Z</i>	2	
Density (calculated)	1.461 Mg/m ³	
Absorption coefficient	0.532 mm ⁻¹	
<i>F</i> (000)	3399	
Crystal size	0.1 x 0.5 x 0.4 mm ³	
Theta range for data collection	1.03 to 25.00°	
Index ranges	-37 ≤ <i>h</i> ≤ 46, -12 ≤ <i>k</i> ≤ 12, -21 ≤ <i>l</i> ≤ 20	
Reflections collected	12062	
Independent reflections	7472 [<i>R</i> (int) = 0.1846]	
Completeness to theta = 25.00°	99.8 %	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	7472 / 0 / 1059	
Goodness-of-fit on <i>F</i> ²	1.032	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0947, <i>wR</i> 2 = 0.2102	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1339, <i>wR</i> 2 = 0.2285	
Largest diff. peak and hole	0.970 and - 0.751 e.Å ⁻³	

4.3.2 Synthesis and structural characterisation of $[\text{Co}_2(\text{L6})_3](\text{ClO}_4)_4 \cdot \text{MeCN}$ (**9**)

In the hope of generating a metallo-helicate similar to that in **8**, three equivalents of the structurally modified ligand **L6** was reacted with two equivalents of $\text{Co}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ in methanol. This approach resulted in the precipitation of an orange powder which was dissolved in acetonitrile. The slow diffusion of methanol into this solution yielded large orange crystals of $[\text{Co}_2(\text{L6})_3](\text{ClO}_4)_4 \cdot \text{MeCN}$ (**9**) after 5 days.

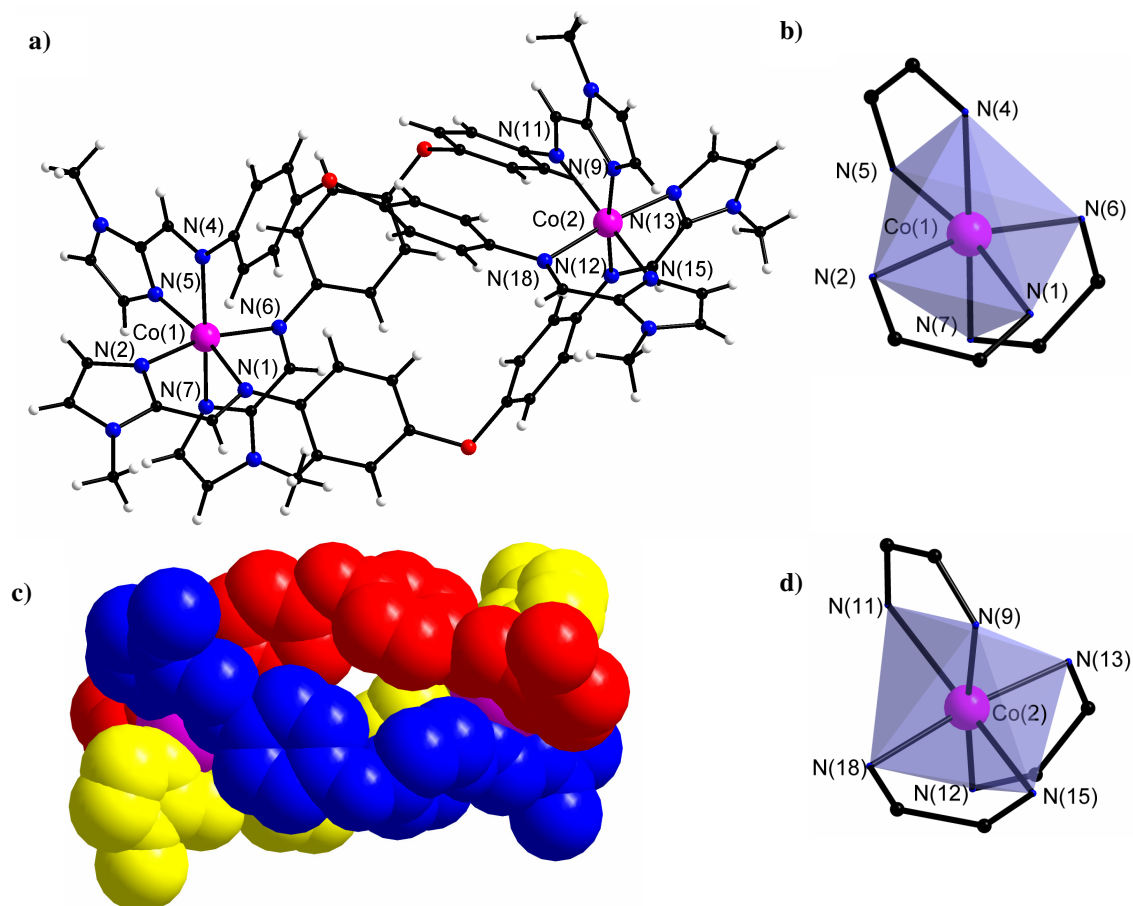


Figure 4.6: a) The structure of the dinuclear triple helicate in **9** (counterions and constitutional solvent molecules have been removed for clarity). b) The coordination environment of Co(1). c) The space filling representation of the helicate complex in **9**. d) The coordination environment of Co(2). Co purple, N blue, C black, O red and H white.

Compound **9** crystallises in the monoclinic crystal system in the space group $P2_1/n$. **9** contains a triple stranded dinuclear Co^{II} helicate (Figure 4.6) closely related to that in **8**. In this case, the Co^{II} ions are separated by a distance of $11.377(2) \text{ \AA}$.

The Co^{II} ions in **9** also display distorted octahedral coordination geometries by binding to the N donor atoms of three **L6** ligands. The distorted nature of the coordination geometry is underlined by examining the bond angles of the Co(1) coordination sphere. For example, the bond angles $\text{N}(1)\text{-Co}(1)\text{-N}(5)$, $\text{N}(2)\text{-Co}(1)\text{-}$

N(6), N(4)-Co(1)-N(7), N(1)-Co(1)-N(2), N(1)-Co(1)-N(4), N(4)-Co(1)-N(5), and N(6)-Co(1)-N(7) of 169.87(1)°, 166.10(1)°, 170.19(1)°, 76.53(1)°, 105.78(1)°, 76.98(1)° and 77.16(1)° all diverge significantly from the ideal octahedral angles of 90° and 180°. The bond angles of the Co(1) and Co(2) centres are further summarised in Table 4.4.

The Co-N bond lengths in **9** are similar to those in **8**. The Co-N_{imine} bonds display bond distances that range between 2.174(4) Å and 2.214(3) Å whereas the Co-N_{imidazole} bonds reveal bond lengths that range from 2.079(3) Å to 2.112(3) Å. Important bond lengths are summarised in Table 4.5.

Table 4.4: Selected bond angles for **9**

Bond Angle		Bond Angle	
N(1)-Co(1)-N(2)	76.53(1)°	N(9)-Co(2)-N(11)	76.97(1)°
N(1)-Co(1)-N(4)	105.78(1)°	N(9)-Co(2)-N(12)	173.32(1)°
N(1)-Co(1)-N(5)	169.87(1)°	N(9)-Co(2)-N(13)	95.72(1)°
N(1)-Co(1)-N(7)	83.46(1)°	N(9)-Co(2)-N(15)	87.97(1)°
N(2)-Co(1)-N(4)	92.61(1)°	N(11)-Co(2)-N(12)	104.38(1)°
N(2)-Co(1)-N(5)	93.70(1)°	N(11)-Co(2)-N(13)	92.65(1)°
N(2)-Co(1)-N(7)	92.79(1)°	N(11)-Co(2)-N(15)	163.13(1)°
N(2)-Co(1)-N(6)	166.10(1)°	N(11)-Co(2)-N(18)	93.61(1)°
N(4)-Co(1)-N(5)	76.98(1)°	N(12)-Co(2)-N(13)	77.73(1)°
N(4)-Co(1)-N(7)	170.19(1)°	N(12)-Co(2)-N(15)	91.45(1)°
N(4)-Co(1)-N(6)	98.78(1)°	N(12)-Co(2)-N(18)	100.73(1)°
N(5)-Co(1)-N(7)	94.50(1)°	N(13)-Co(2)-N(15)	96.44(1)°
N(6)-Co(1)-N(7)	77.16(1)°	N(13)-Co(2)-N(18)	173.74(1)°

Table 4.5: Selected bond lengths for **9**

Bond	Bond Length	Bond	Bond Length
Co(1)-N(1)	2.214(1) Å	Co(2)-N(9)	2.111(2) Å
Co(1)-N(2)	2.104(1) Å	Co(2)-N(11)	2.201(3) Å
Co(1)-N(4)	2.212(3) Å	Co(2)-N(12)	2.192(3) Å
Co(1)-N(5)	2.082(3) Å	Co(2)-N(13)	2.079(3) Å
Co(1)-N(7)	2.105(3) Å	Co(2)-N(15)	2.112(3) Å
Co(1)-N(6)	2.200(3) Å	Co(2)-N(18)	2.174(4) Å

Table 4.6: Crystal data and structure refinement for **9**

Identification code	9	
Empirical formula	$\text{Co}_2\text{C}_{68}\text{H}_{63}\text{N}_{19}\text{O}_{19}\text{Cl}_4$	
Formula weight	1716.08 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$.	
Unit cell dimensions	a = 19.366(2) Å	$\alpha = 90^\circ$
	b = 18.186(2) Å	$\beta = 108.443(2)^\circ$
	c = 23.954(2) Å	$\gamma = 90^\circ$
Volume	8003(1) Å ³	
Z	2	
Density (calculated)	1.412 Mg/m ³	
Absorption coefficient	0.755 mm ⁻¹	
F(000)	3460	
Crystal size	0.2 x 0.5 x 0.075 mm ³	
Theta range for data collection	1.18 to 25.00°	
Index ranges	-23 ≤ h ≤ 23, -21 ≤ k ≤ 21, -28 ≤ l ≤ 28	
Reflections collected	85963	
Independent reflections	14091 [R(int) = 0.0830]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14091 / 0 / 1207	
Goodness-of-fit on F ²	0.955	
Final R indices [I > 2σ(I)]	R1 = 0.0579, wR2 = 0.1532	
R indices (all data)	R1 = 0.0906, wR2 = 0.1665	
Largest diff. peak and hole	0.654 and -0.482 e.Å ⁻³	

4.3.3 Synthesis and structural characterisation of $[\text{Mn}_2(\text{L6})_3](\text{ClO}_4)_4 \cdot 2\text{MeOH}$ (**10**)

The reaction of $\text{Mn}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ with a slight excess of **L6** in methanol yielded a yellow powder. This powder was dissolved in acetonitrile resulting in a clear yellow solution. The slow diffusion of methanol into this solution produces large orange crystals of $[\text{Mn}_2(\text{L6})_3](\text{ClO}_4)_4 \cdot 2\text{MeOH}$ (**10**) after 2 weeks.

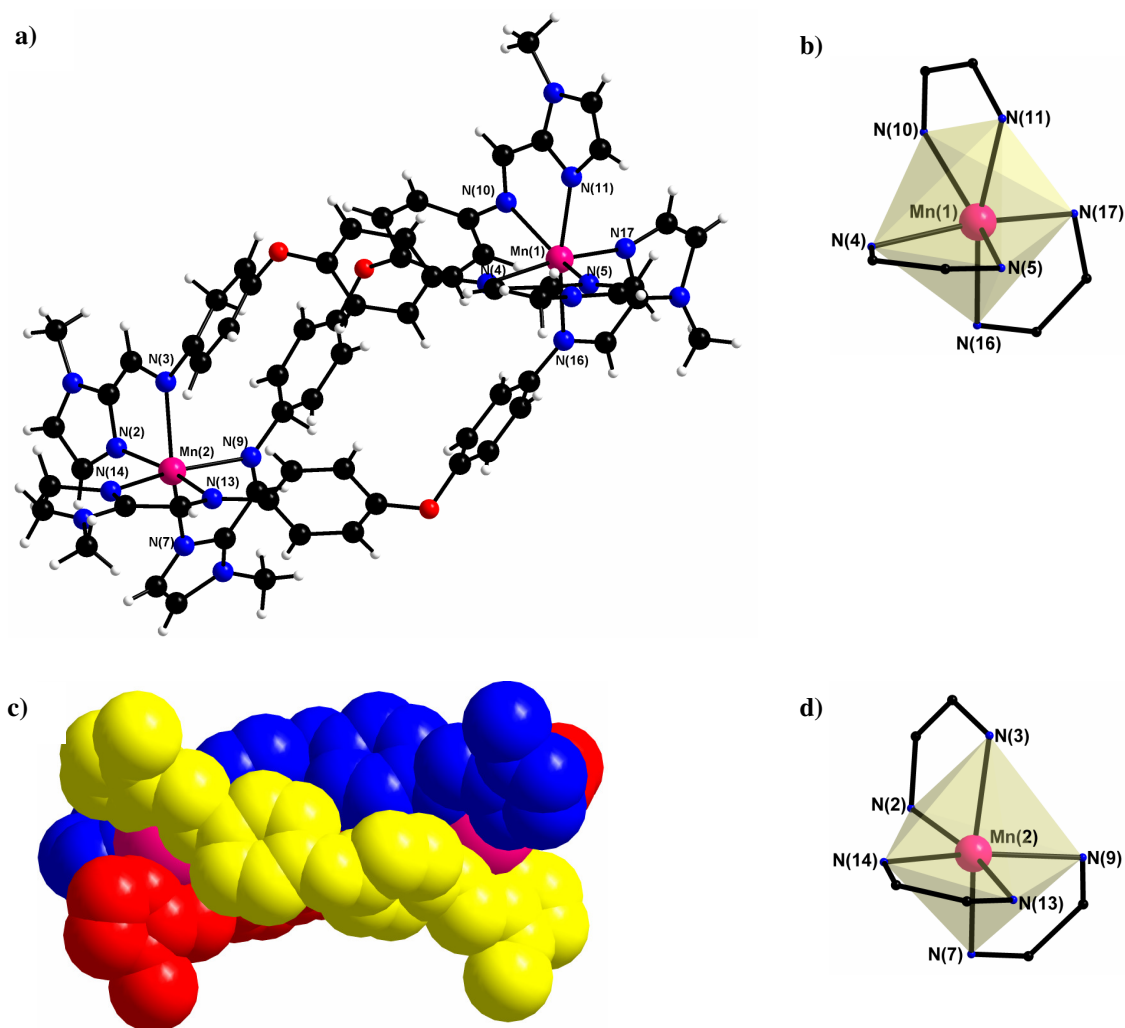


Figure 4.7: **a)** The structure of the dinuclear triple helicate in **10** (counterions and constitutional solvent molecules have been removed for clarity). **b)** The coordination environment of Mn(1). **c)** The space filling representation of the helicate complex in **10**. **d)** The coordination environment of Mn(2). Mn pink, N blue, C black and H white.

10 crystallises in the monoclinic system in the space group *Cc*. **10** consists of dinuclear Mn^{II} helicates separated by their perchlorate counterions and solvent molecules. The structural assignment and refinement of the disordered perchlorate ions led to relatively high X-ray diffraction quality values and resulted in a $R1[I > 2\sigma I]$ value of 0.0832. The asymmetric unit of **10** contains one complete dinuclear complex.

The architecture of the triple stranded molecular helicate in **10** (Figure 4.7) is similar to those of **8** and **9**. The Mn^{II} ions are separated by a distance of 11.914(3) Å and each ion binds to three different **L6** ligands.

In an identical manner to **8** and **9**, each Mn^{II} ion in **10** binds to the six N donor atoms of three Schiff base ligands. The imine functionalities that bind to the Mn^{II} ions display Mn-N_{imine} bond lengths that range between 2.241(3) Å and 2.379(3) Å whereas the imidazole moieties exhibit Mn-N_{imidazole} bond lengths that range from 2.128(2) Å to 2.307(1) Å. These observed Mn-N bond lengths (Table 4.7) confirm the +II oxidation state of the Mn ions.

Table 4.7: Selected bond lengths for **10**

Bond	Bond Length	Bond	Bond Length
Mn(1)-N(4)	2.276(5) Å	Mn(2)-N(2)	2.181(4) Å
Mn(1)-N(5)	2.128(2) Å	Mn(2)-N(3)	2.276 (2) Å
Mn(1)-N(10)	2.377(1) Å	Mn(2)-N(7)	2.307(1) Å
Mn(1)-N(11)	2.248(2) Å	Mn(2)-N(9)	2.337(5) Å
Mn(1)-N(16)	2.379(2) Å	Mn(2)-N(13)	2.241(3) Å
Mn(1)-N(17)	2.154(4) Å	Mn(2)-N(14)	2.257(4) Å

As in **8** and **9**, the Mn ions in **10** display distorted octahedral coordination geometries (Figure 4.7) with the imine N donor atoms arranging in a *facial* manner and with the imidazole N atoms also exhibiting a *facial* arrangement. The distortion in coordination geometry is clearly demonstrated by examining the bonding angles involving Mn(1) and Mn(2) which are presented in Table 4.8. These bond angles depart in varying degrees from the ideal octahedral angles of 90° and 180°. For instance, the bond angles N(4)-Mn(1)-N(17), N(5)-Mn(1)-N(10) and N(11)-Mn(1)-N(16) of 169.77(1)°, 150.39(1)° and 166.06(1)° deviate significantly from the ideal angle of 180°.

Table 4.8: Selected bond angles for **10**

Bond Angle		Bond Angle	
N(4)-Mn(1)-N(5)	74.66(1)°	N(2)-Mn(2)-N(3)	73.69(1)°
N(4)-Mn(1)-N(10)	89.43(1)°	N(2)-Mn(2)-N(7)	84.93(1)°
N(4)-Mn(1)-N(11)	100.49(1)°	N(2)-Mn(2)-N(9)	99.53(1)°
N(4)-Mn(1)-N(16)	93.36(1)°	N(2)-Mn(2)-N(13)	166.47(1)°
N(4)-Mn(1)-N(17)	169.77(1)°	N(2)-Mn(2)-N(14)	70.12(1)°
N(5)-Mn(1)-N(10)	150.39(1)°	N(3)-Mn(2)-N(7)	148.69(1)°
N(5)-Mn(1)-N(11)	85.71(1)°	N(3)-Mn(2)-N(9)	86.25(1)°
N(5)-Mn(1)-N(16)	95.59(1)°	N(3)-Mn(2)-N(13)	167.45(1)°
N(5)-Mn(1)-N(17)	108.60(1)°	N(3)-Mn(2)-N(14)	97.92(1)°
N(10)-Mn(1)-N(11)	72.61(1)°	N(7)-Mn(2)-N(9)	79.84(1)°
N(10)-Mn(1)-N(16)	106.24(1)°	N(7)-Mn(2)-N(13)	98.69(1)°
N(10)-Mn(1)-N(17)	91.49(1)°	N(7)-Mn(2)-N(14)	107.12(1)°
N(11)-Mn(1)-N(16)	166.06(1)°	N(9)-Mn(2)-N(13)	94.00(1)°
N(11)-Mn(1)-N(17)	89.50(1)°	N(9)-Mn(2)-N(14)	164.11(1)°

Table 4.9: Crystal data and structure refinement for **10**

Identification code	10	
Empirical formula	Mn ₂ C ₆₈ H ₆₈ N ₁₈ O ₂₁ Cl ₄	
Formula weight	1725.07 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>Cc</i>	
Unit cell dimensions	a = 19.441(4) Å b = 10.578(2) Å c = 39.748(8) Å	α = 90° β = 95.547(4)° γ = 90°
Volume	8136(3) Å ³	
Z	4	
Density (calculated)	1.275 Mg/m ³	
Absorption coefficient	0.451 mm ⁻¹	
F(000)	3216	
Crystal size	0.18 x 0.14 x 0.08 mm ³	
Theta range for data collection	1.03 to 25.00°	
Index ranges	-23 ≤ h ≤ 22, -7 ≤ k ≤ 12, -47 ≤ l ≤ 47	
Reflections collected	22635	
Independent reflections	13919 [R(int) = 0.0965]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9648 and 0.9233	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13919 / 2 / 1038	
Goodness-of-fit on F ²	0.898	
Final R indices [I > 2σ(I)]	R1 = 0.0832, wR2 = 0.2038	
R indices (all data)	R1 = 0.1924, wR2 = 0.2604	
Largest diff. peak and hole	0.785 and -0.387 e.Å ⁻³	

4.3.4 Synthesis and structural characterisation of $[\text{Ni}_2(\text{L5})_3](\text{PF}_6)_4 \cdot 2\text{MeCN}$ (**11**)

The reaction of three equivalents of **L5** with two equivalents of $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ in methanol yielded a clear yellow solution. The addition of NH_4PF_6 to this methanol solution produced a yellow precipitate which was dissolved in acetonitrile. The slow diffusion of methanol into this solution generated yellow crystals of the coordination compound, $[\text{Ni}_2(\text{L5})_3](\text{PF}_6)_4 \cdot 2\text{MeCN}$ (**11**) after 3 weeks.

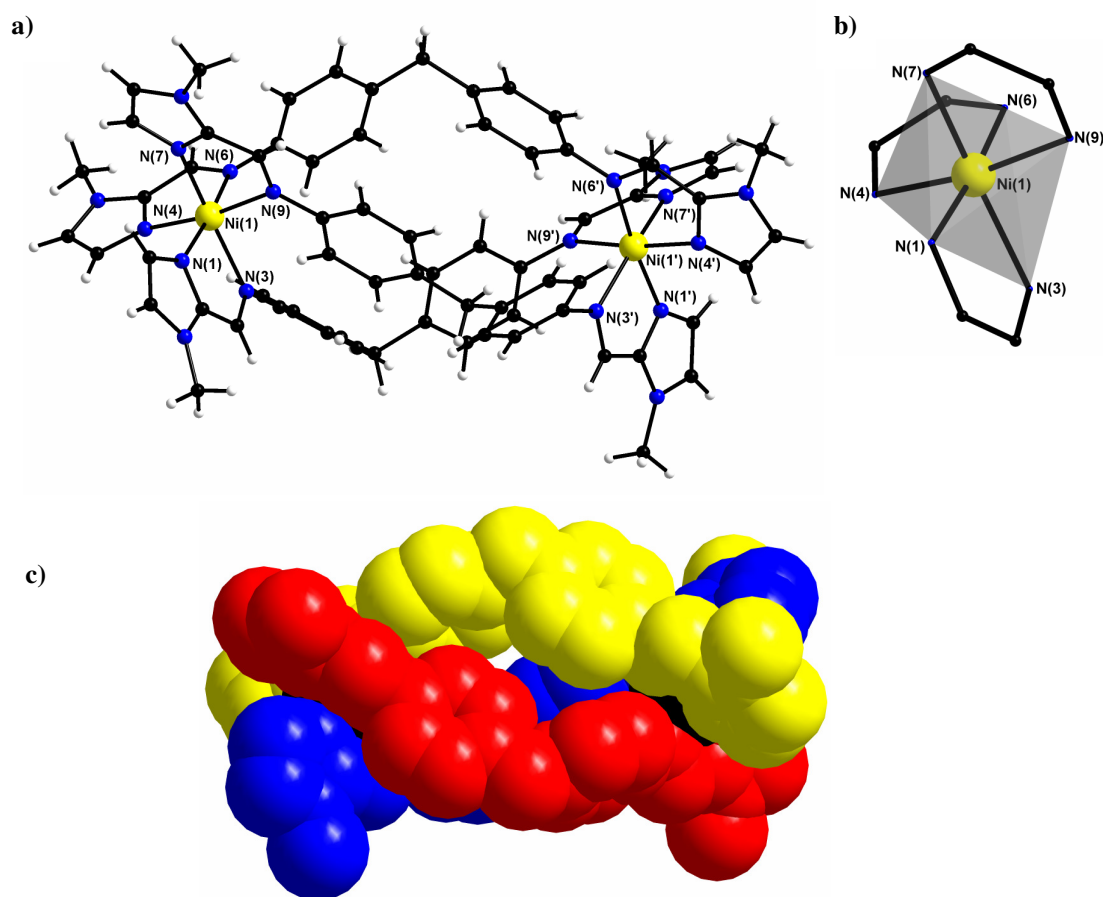


Figure 4.8: **a)** The structure of the dinuclear Ni^{II} complex in **11** (counterions and constitutional solvent molecules have been removed for clarity). **b)** The coordination environment of the Ni^{II} metal centres. **c)** The space filling representation of the helicate in **11**. Ni yellow, O red, N blue and C black. ' corresponds to the $-x, y, 0.5-z$ positions.

These crystals were analysed by single crystal X-ray diffraction which showed that compound **11** contains a triple stranded dinuclear Ni^{II} helicate (Figure 4.8) which has a closely related structure to those in **8**, **9** and **10**. **11** crystallises in the monoclinic crystal system in the space group $P2_1/c$. In contrast to **8**, **9** and **10**, the asymmetric unit of **11** contains half the dinuclear complex with the remainder generated by symmetry operations.

The Ni atoms in **11** are crystallographically equivalent and are separated by a distance of 11.43(1) Å. Each Ni ion in **11** binds to N donor atoms of three **L5** ligands. The imine N donors, N(3), N(6) and N(9), display Ni-N bond lengths of 2.154(5) Å, 2.147(6) Å and 2.146(2) Å, respectively. The imidazole functionalities that bind to the metal centres show Ni-N bond distances of 2.047(5) Å, 2.052(2) Å and 2.076(4) Å for Ni(1)-N(1), Ni(1)-N(4) and Ni(1)-N(7). These bond lengths are summarised in Table 4.10.

Table 4.10: Selected bond lengths for **11**

Bond	Bond Length	Bond	Bond Length
Ni(1)-N(1)	2.047(5) Å	Ni(1)-N(6)	2.147(6) Å
Ni(1)-N(3)	2.154(5) Å	Ni(1)-N(7)	2.076(4) Å
Ni(1)-N(4)	2.052(5) Å	Ni(1)-N(9)	2.146(2) Å

The distorted octahedral coordination environment (Figure 4.8b) of each Ni centre in **11** is similar to those of **8**, **9** and **10**. The distortion of the octahedral geometry is clearly demonstrated by examining some of the bond angles of the Ni^{II} coordination environment. For example, the bond angles between N(1)-Ni(1)-N(3), N(3)-Ni(1)-N(6), N(3)-Ni(1)-N(7), N(4)-Ni(1)-N(9) and N(7)-Ni(1)-N(9) of 78.36(1)°, 101.98(1)°, 169.92(1)°, 172.14(1)° and 78.05(1)° deviate significantly from the ideal octahedral angles of 90° and 180°. Some of the bond angles of the Ni(1) centre are summarised in Table 4.11.

Table 4.11: Selected bond angles for **11**

Bond Angle		Bond Angle	
N(1)-Ni(1)-N(3)	78.36(1)°	N(3)-Ni(1)-N(9)	92.18(1)°
N(1)-Ni(1)-N(4)	94.48(1)°	N(4)-Ni(1)-N(6)	76.44(1)°
N(1)-Ni(1)-N(6)	172.92(1)°	N(4)-Ni(1)-N(7)	94.44(1)°
N(1)-Ni(1)-N(7)	89.69(1)°	N(4)-Ni(1)-N(9)	172.14(1)°
N(1)-Ni(1)-N(9)	87.86(1)°	N(6)-Ni(1)-N(7)	91.01(1)°
N(3)-Ni(1)-N(4)	95.64(1)°	N(6)-Ni(1)-N(9)	99.17(1)°
N(3)-Ni(1)-N(6)	101.98(1)°	N(7)-Ni(1)-N(9)	78.05(1)°
N(3)-Ni(1)-N(7)	169.92(1)°		

Table 4.12: Crystal data and structure refinement for **11**

Identification code	11	
Empirical formula	Ni ₂ C ₇₃ H ₇₂ N ₂₀ P ₄ F ₂₄	
Formula weight	1926.74 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 19.306(2) Å	<i>α</i> = 90°
	<i>b</i> = 10.7108(12) Å	<i>β</i> = 130.804(5)°
	<i>c</i> = 26.661(2) Å	<i>γ</i> = 90°
Volume	4173.1(7) Å ³	
<i>Z</i>	1	
Density (calculated)	1.423 Mg/m ³	
Absorption coefficient	0.633 mm ⁻¹	
<i>F</i> (000)	1903	
Crystal size	0.18 x 0.14 x 0.08 mm ³	
Theta range for data collection	1.39 to 25.00°	
Index ranges	-13 ≤ <i>h</i> ≤ 22, -12 ≤ <i>k</i> ≤ 12, -31 ≤ <i>l</i> ≤ 26	
Reflections collected	24003	
Independent reflections	7356 [<i>R</i> (int) = 0.0729]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	7356 / 0 / 693	
Goodness-of-fit on <i>F</i> ²	0.985	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0580, <i>wR</i> 2 = 0.1580	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0842, <i>wR</i> 2 = 0.1624	
Largest diff. peak and hole	0.642 and -0.477 e.Å ⁻³	

4.3.5 Characterisation of compounds 8, 9, 10 and 11

8, 9, 10 and **11** were further characterised by FT-IR spectroscopy and ESI mass spectrometry. The results are summarised in Table 4.13.

The FT-IR spectrum of each compound shows a strong asymmetric C=N bond stretch that occurs between 1615 cm⁻¹ and 1618 cm⁻¹.¹⁶⁴ This bond stretch is the characteristic signature of the imine ligands used in this study.¹⁶⁴ An ESI-mass spectrum was recorded for each compound dissolved in acetonitrile. A molecular ion peak corresponding to the [M₂L₃]⁴⁺ (M = Co^{II}, Mn^{II} or Ni^{II} and L = **L5** or **L6**) species is observed in each case. CHN microanalysis was also applied to confirm the composition of each compound.

Table 4.13: Summary of FT-IR spectroscopic and ESI mass spectrometric data

Compound	Asymmetric C=N vibration	Molecular ion peak
8	1615 cm ⁻¹	[Co ₂ (L5) ₃] ⁴⁺ at 316.3 m/z
9	1618 cm ⁻¹	[Co ₂ (L6) ₃] ⁴⁺ at 317.8 m/z
10	1617 cm ⁻¹	[Mn ₂ (L6) ₃] ⁴⁺ at 315.5 m/z
11	1617 cm ⁻¹	[Ni ₂ (L5) ₃] ⁴⁺ at 315.9 m/z

4.4 Formation and structural characterisation of Fe^{II} molecular helicates

4.4.1 Synthesis and structural characterisation of [Fe₂(**L6**)₃](PF₆)₄·4MeCN·H₂O (**12**)

Inspired by the successful synthesis of the metallo-helicate species, [Fe₂(**L6**)₃](ClO₄)₄·2MeCN (**7**),¹⁸⁴ we attempted to modify the SCO behaviour of this material through simple counterion exchange. This work resulted in the formation of a related coordination compound [Fe₂(**L6**)₃](PF₆)₄·4MeCN·H₂O (**12**). The compound was prepared by the reaction of the Schiff base ligand **L6** with FeCl₂·6H₂O, followed by the addition of NH₄PF₆ resulting in the formation of a red powder. Dark red hexagonal shaped crystals of **12**, suitable for single crystal X-ray diffraction, were obtained by the slow diffusion of methanol into an acetonitrile solution of this powder.

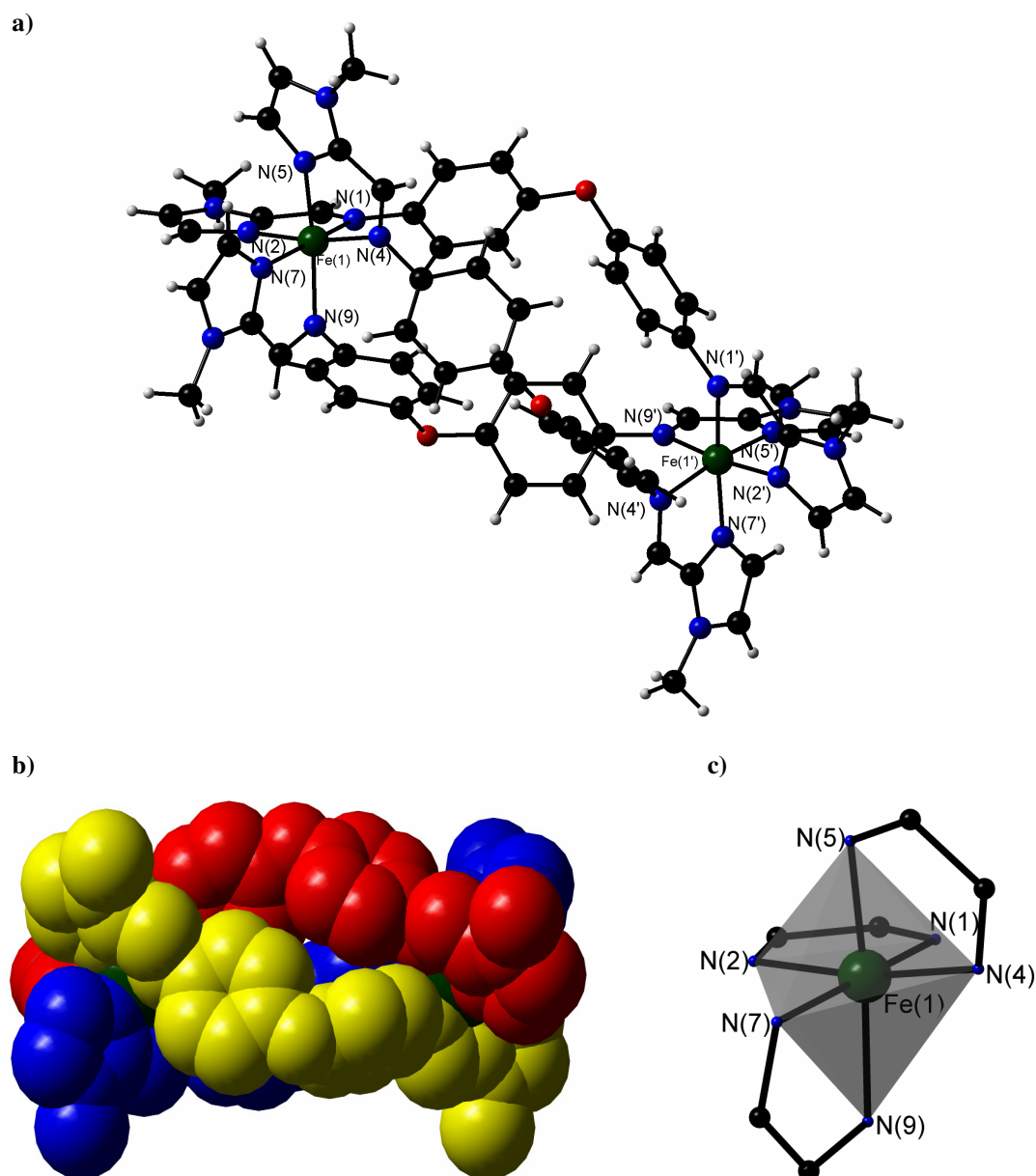


Figure 4.9: a) The structure of the triple helical complex in **12**. b) Space filling representation of the helicate complex in **12** (counterions and constitutional solvent molecules have been removed for clarity). c) The coordination environment of Fe(1). Fe green, O red, N blue, C black and H white. ' corresponds to the $-x, y, 0.5-z$ positions.

The X-ray quality factors of **12** ($R1 = 0.0924$ and $wR2 = 0.2359$) still remain quite high after refinement of the structure. This is mainly due to the positional disorder of the PF_6^- counter ions whose atoms are statistically distributed over several points in space.¹⁷² **12** also contains some constitutional acetonitrile molecules that display disorder, further contributing to the relatively high R values.

The coordination compound **12** crystallises in the monoclinic crystal system in the space group $C2/c$. The overall structure of the complex (Figure 4.9) in **12** is closely related to those of **8** - **11** and is that of a dinuclear triple helicate with two

metal centres bound to three **L6** ligands. The two Fe atoms are separated by a distance of 11.36(3) Å. The asymmetric unit of **12** contains half the dinuclear coordination complex. The complete triple metallo-helicate is generated by symmetry operations.

In a similar manner to **8**, **9**, **10** and **11**, each Fe^{II} centre in **12** binds to six N atoms (three imine N atoms and three imidazole N atoms). In this case, the imine functionalities that bind to the Fe^{II} centres display Fe-N bond lengths varying between 2.030(4) Å and 2.039(3) Å. The imidazole moieties that bind to the metal centres reveal Fe-N bond distances ranging from 1.954(3) Å to 1.978(1) Å. These Fe-N bond lengths are summarised in Table 4.14 and indicate that the two Fe^{II} metal centres are in a low spin state at 150 K, as they are consistent with those previously reported in the literature for low spin Fe^{II} compounds.^{94,95}

Table 4.14: Selected bond lengths for **12**

Bond	Bond Length	Bond	Bond Length
Fe(1)-N(1)	2.039(3) Å	Fe(1)-N(5)	1.977(1) Å
Fe(1)-N(2)	1.954(3) Å	Fe(1)-N(7)	1.978 (1) Å
Fe(1)-N(4)	2.030(4) Å	Fe(1)-N(9)	2.036(1) Å

As is the case for the related helicate complexes **8** - **11**, the Fe^{II} ions within **12** display distorted octahedral coordination geometries (Figure 4.9c). In **12**, the imidazole N donor atoms of each Schiff base ligand N(2), N(5) and N(7) also adopt a *facial* arrangement and the imine nitrogen atoms N(1), N(4) and N(9) arrange in a *facial* manner. The bond angles involving the Fe(1) atom (Table 4.15) emphasise the distorted nature of the coordination environment. The bond angles N(1)-Fe(1)-N(7), N(2)-Fe(1)-N(4) and N(5)-Fe(1)-N(9) of 167.1(3)°, 170.97(3)° and 170.42(2)° vary significantly from the ideal octahedral angle of 180°. Also the bond angles of N(1)-Fe(1)-N(4), N(1)-Fe(1)-N(5), N(2)-Fe(1)-N(1), N(2)-Fe(1)-N(7) and N(7)-Fe(1)-N(9) of 98.71(2)°, 94.69(2)°, 80.30(2)°, 98.35(2)° and 79.94(2)° deviate to varying degrees from the 90° bond angle expected for atoms *cis* to each other in regular octahedral geometries.

Table 4.15: Selected bond angles for **12**

Bond Angle		Bond Angle	
N(1)-Fe(1)-N(2)	80.30(2)°	N(2)-Fe(1)-N(5)	90.86(2)°
N(1)-Fe(1)-N(4)	98.71(2)°	N(2)-Fe(1)-N(7)	98.35(2)°
N(1)-Fe(1)-N(5)	94.69(2)°	N(5)-Fe(1)-N(9)	170.42(2)°
N(1)-Fe(1)-N(7)	167.1(3)°	N(7)-Fe(1)-N(9)	79.94(2)°
N(2)-Fe(1)-N(4)	170.97(3)°		

The packing diagram of **12** (Figure 4.10) demonstrates that there are no noteworthy direct intermolecular contacts between adjacent helicates which are separated by their PF_6^- counterions and solvent molecules.

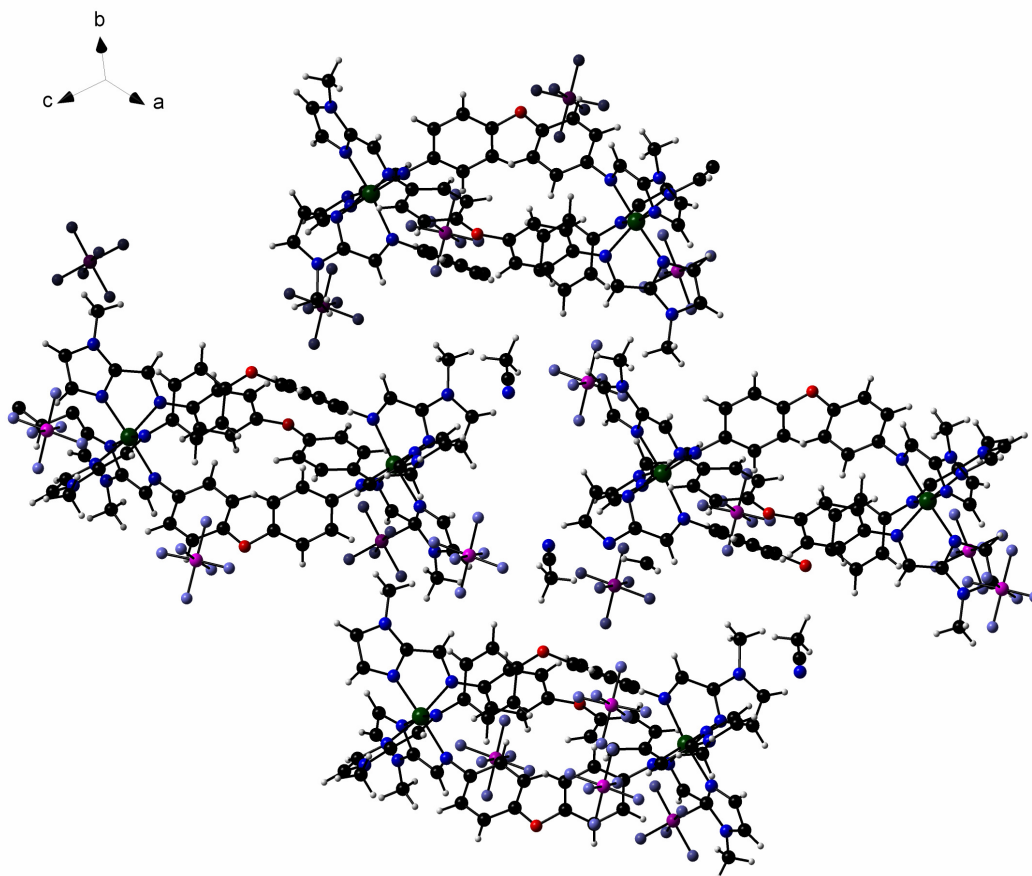


Figure 4.10: The packing of the helicates contained in **12**. There are no direct interactions between neighbouring helicates and they are separated by counterions and solvent molecules. Fe green, O red, N blue, C black, P purple and F light blue.

Elemental analysis is in agreement with the single crystal X-ray diffraction analysis and the ESI mass spectrum of **12** shows a molecular ion peak at 315.9 m/z which is characteristic of the $[\text{Fe}_2(\text{L3})_3]^{4+}$ species. The FT-IR spectrum of compound **12** shows a strong asymmetric C=N bond stretch at 1617 cm^{-1} which is characteristic of the imine functionality of the Schiff base ligand.¹⁶⁴ The shift of this bond stretch to lower frequency when compared to the free ligand (1629 cm^{-1}) confirms that the Fe^{II} ions coordinate to N donor atoms of the imine **L6** ligand.¹⁸⁵ The FT-IR spectrum also shows an asymmetric C=N stretch at 1594 cm^{-1} , an asymmetric C-C stretch at 1502 cm^{-1} and an asymmetric C-N stretch at 1367 cm^{-1} . These stretches arise from the methyl-imidazole moiety of the **L6** ligand.¹⁶⁴

Table 4.16: Crystal data and structure refinement for **12**

Identification code	12	
Empirical formula	Fe ₂ C ₇₄ H ₇₄ N ₂₂ O ₄ F ₂₄ P ₄	
Formula weight	2027.08 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71070 Å	
Crystal system	Monoclinic	
Space group	<i>C2/c</i>	
Unit cell dimensions	a = 33.116(15) Å	α = 90°
	b = 10.994(5) Å	β = 103.554(7)°
	c = 24.756(11) Å	γ = 90°
Volume	8762(7) Å ³	
Z	4	
Density (calculated)	1.535 Mg/m ³	
Absorption coefficient	0.516 mm ⁻¹	
F(000)	4119	
Crystal size	0.1 x 0.5 x 0.4 mm ³	
Theta range for data collection	2.49 to 25.00°	
Index ranges	-39 ≤ h ≤ 39, -12 ≤ k ≤ 13, -29 ≤ l ≤ 29	
Reflections collected	49956	
Independent reflections	7697 [R(int) = 0.0800]	
Completeness to theta = 25.00°	99.8 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7697 / 0 / 637	
Goodness-of-fit on F ²	1.097	
Final R indices [I > 2σ(I)]	R1 = 0.0924, wR2 = 0.2335	
R indices (all data)	R1 = 0.0956, wR2 = 0.2359	
Largest diff. peak and hole	0.908 and -0.659 e.Å ⁻³	

4.4.2 Magnetic properties of $[\text{Fe}_2(\text{L6})_3](\text{PF}_6)_4 \cdot 4\text{MeCN} \cdot \text{H}_2\text{O}$ (**12**)

Temperature dependent magnetic susceptibility measurements were carried out on a freshly filtered sample of **12** at 10000 Oe. The measurements (Figure 4.11) were performed firstly in cooling mode by reducing the temperature from 300 K to 2 K (black curve) and then in heating mode by increasing the temperature back from 2 K to 400 K (red curve). Measurements were also recorded over a second thermal cycle (blue curve) and a $d\chi T/dT$ versus T plot (Figure 4.11b) was constructed to determine the SCO temperature of **12**.

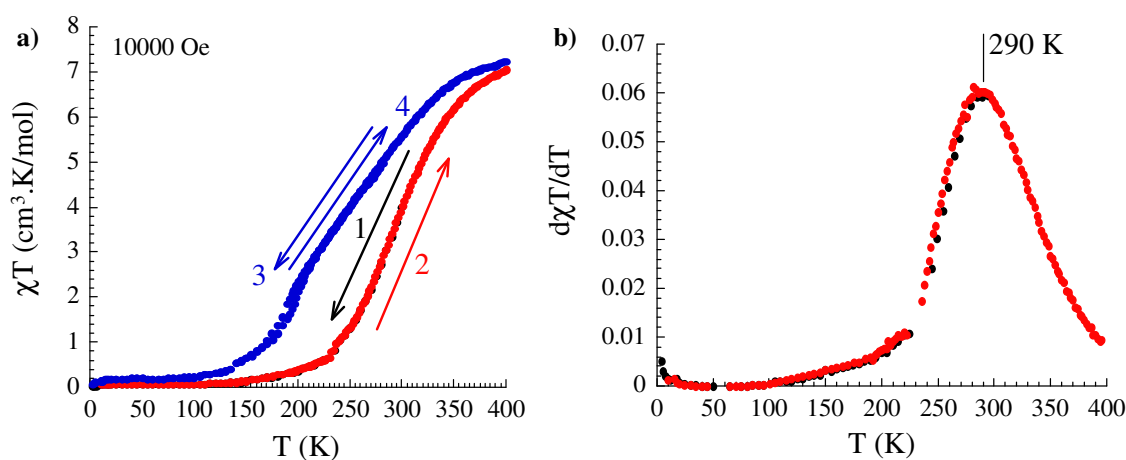


Figure 4.11: a) Temperature dependence of the χT product for **12**, the first thermal cycle between 300 K and 2 K (black curve) and then between 2 K to 400 K (red curve) and the second thermal cycle from 400 K to 2 K and back to 400 K (blue curve). b) Temperature dependence of the first derivative of χT with respect to T ($d\chi T/dT$) for **12**.

At 400 K, the observed χT value of $7.0 \text{ cm}^3 \text{ K mol}^{-1}$ is in good agreement with the presence of two $S = 2$ high spin Fe^{II} metal ions ($C = 3.5 \text{ cm}^3 \text{ K mol}^{-1}$ with $g = 2.16$). When the temperature is lowered, χT decreases with the typical S-shaped curve associated with SCO systems.⁹¹ At 150 K, almost no paramagnetic signal is seen ($\chi T = 0.6 \text{ cm}^3 \text{ K mol}^{-1}$), indicating that both Fe^{II} ions are now in the low spin $S = 0$ state, thus the SCO process is complete. It is clear that for this compound the SCO process occurs in one step suggesting that both Fe^{II} ions exhibit a simultaneous spin change.

From the plot of the first derivative of χT against the temperature (Figure 4.11b) it was found that, in contrast to the ClO_4^- analogue **7**,¹⁸⁴ the SCO temperature ($T_{1/2}$) of **12** is *ca.* 290 K. Therefore, **12** undergoes SCO in the room temperature range. This remarkable behaviour is desired by many researchers working in this field as current research activities strive for applicable material (e.g. magneto/optical

switches) that operate in a convenient and energetically high-temperature range.⁹⁴ It is also worth noting that the SCO of **12** is not associated with any significant hysteresis effects. This observation is in agreement with the packing of the helicates in the crystal structure and their negligible intermolecular interactions which give rise to a low intermolecular cooperativity.

During the magnetic measurements, when several heating and cooling cycles were applied it was found that **12** was susceptible to the loss of solvent molecules. It also appears that the loss of solvent molecules has an effect on the magnetic properties of the compound. To further investigate this behaviour, a sample of **12** was dried in an oven at 100 °C for 2 days. Thermogravimetric analysis (Figure 4.12) was then employed to determine the composition of the dried sample.

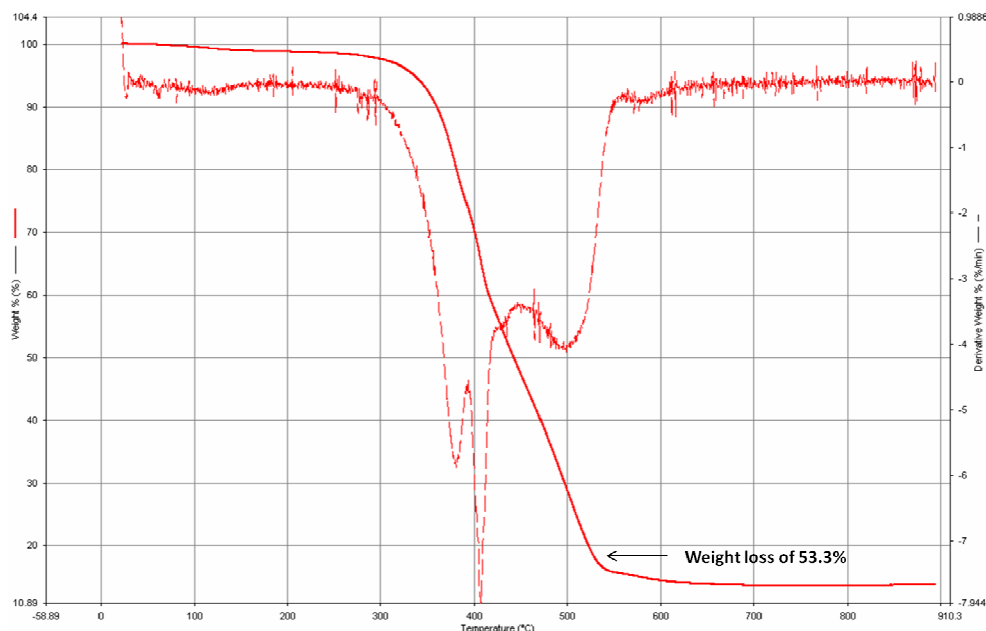


Figure 4.12: The Thermogravimetric analysis (TGA) carried out on a sample of **12** dried at 100 °C for two days.

The dried sample was heated to 900 °C under an air atmosphere at a heating rate of 10 °C min⁻¹. The composition of the dried compound remains unchanged until *ca.* 300 °C when the organic ligands in **12** undergo a step-wise oxidative degradation with a total weight loss of 53.3%. This can be assigned to the combustion of all the carbon, hydrogen and nitrogen atoms of the ligands (calculated weight 52.1%). The further combustion of the compound yields residual oxide materials that weren't further characterised. This experiment suggests that when **12** was dried in an oven at 100 °C all constitutional solvent molecules were removed. The temperature dependence of

the magnetic susceptibility of the fully desolvated compound (Figure 4.13) was then measured.

The dried compound also exhibits SCO transitions but in this case they occur over a wider temperature domain. This behaviour possibly indicates a thermal distribution of the SCO events due to reduced symmetry in the material brought about by a loss of crystallinity during the drying process. The presence of residual paramagnetic material at 110 K could be due to partial Fe^{II} oxidation occurring during the heating process or the presence of intrinsic defects in the material.⁸¹ The first derivative of χT with respect to temperature ($d\chi T/dT$) displayed in Figure 4.13b further emphasises the wide temperature range of the SCO event and in fact shows that the desolvated compound reveals two characteristic SCO temperatures ($T_{1/2} = 202$ K and 320 K). These results underline the importance of constitutional solvent molecules in SCO systems.

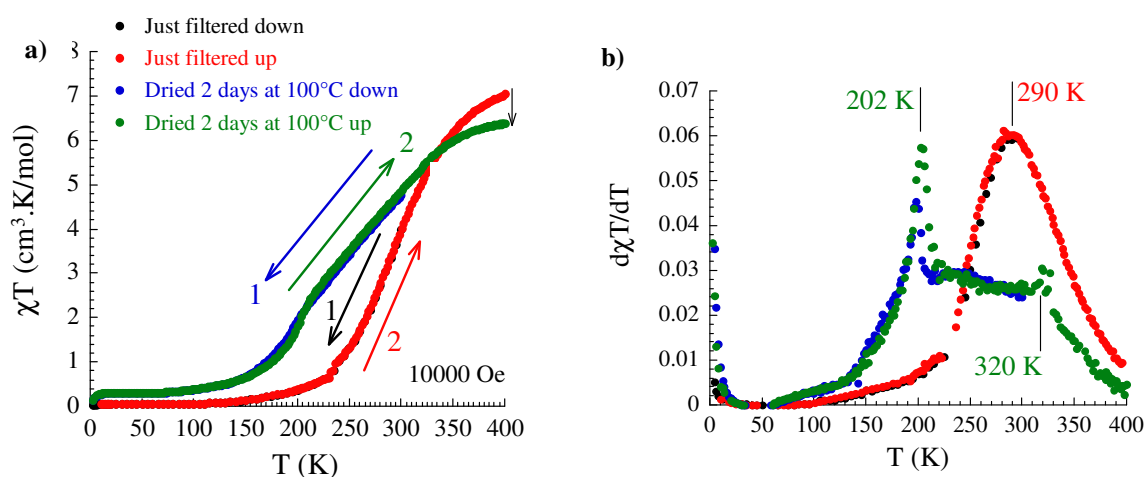


Figure 4.13: a) Temperature dependence of χT with thermal cycles between 300 K and 2 K and between 2 K and 400 K for a dried (blue and green curves) and a solvated (red and black curves) sample of **12**. b) Temperature dependence of the first derivative of χT with respect to T ($d\chi T/dT$) for the dried (green and blue curves) and solvated samples of **12** (red and black curves).

As discussed earlier, SCO transitions can also be instigated by light leading to a phenomenon known as the LIESST effect, whereby at low temperatures the high spin state can be obtained *via* light irradiation.^{109,112} In order to probe the possibility that the HS-HS phase can be recovered from the LS-LS phase at low temperatures a series of photo-magnetic measurements have been recorded on a fully solvated sample of **12**. To do this a white light source (183 mW cm^{-2} power) was applied to the sample at 10 K, followed by the measurement of the thermal dependence of the χT product

after the population of the HS state from 2 K to 300 K. The results are shown in Figure 4.14.

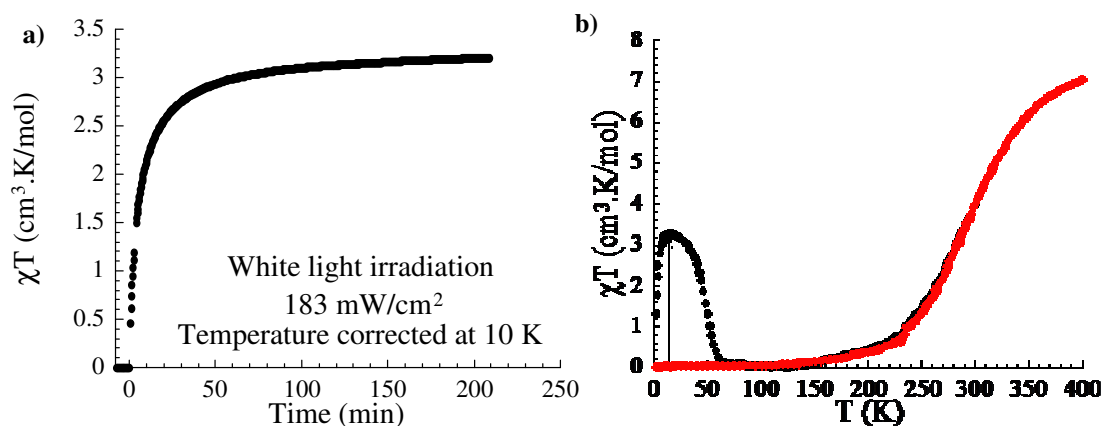


Figure 4.14: a) χT versus time plot at 10 K under white light irradiation for **12**. b) The temperature dependences of the χT product of **12** after white light irradiation at 10 K. (Temperature sweep rate of 0.4 K min⁻¹)

The χT product at 10 K has an initial value of 0.01 $\text{cm}^3 \text{K mol}^{-1}$ and increases to *ca.* 3 $\text{cm}^3 \text{K mol}^{-1}$ after 1 hour of white light irradiation and to 3.2 $\text{cm}^3 \text{K mol}^{-1}$ after an irradiation time of 4 hours. This demonstrates that white light irradiation is a very efficient means to photo-convert LS Fe^{II} species into HS species. The light irradiation was then stopped and the temperature was increased at a rate of 0.4 K min⁻¹. An increase of χT from 1.3 $\text{cm}^3 \text{K mol}^{-1}$ at 2 K, to 3.3 $\text{cm}^3 \text{K mol}^{-1}$ at 16 K is seen. This low temperature behaviour is consistent with the magnetic anisotropy of the HS Fe^{II} metal ions,¹⁸⁶ but may also be related to weak antiferromagnetic interactions between the HS Fe^{II} sites within the dinuclear complex. The temperature was then increased further and the complete relaxation of the metastable HS state to give the low spin species is observed at 60 K. From the data it was concluded that **12** has a critical LIESST temperature, $T(\text{LIESST})$ of 55 K at a heating rate of 0.4 K min⁻¹.

In consecutive experiments, the power of the white light was then increased essentially resulting in no change in the efficiency or speed of the excitation process. Next the wavelength of the irradiating light used was varied between 540 nm and 1064 nm as shown in Figure 4.15. It appears that for light with wavelengths of 1064 nm and 950 nm, the same irradiation effects seen for white light are observed. This process involves a rapid increase in χT which results in a saturation at *ca.* 3 $\text{cm}^3 \text{K mol}^{-1}$ after two hours. The use of lights with wavelengths of 850 nm and 650 nm as the irradiation source reveal a lower χT saturation value of *ca.* 2 $\text{cm}^3 \text{K mol}^{-1}$ after two

hours. This suggests that the excitation processes are less efficient and may require longer excitation times. The use of a diode with a wavelength of 540 nm provides an excitation process that is even less efficient resulting in a χT saturation value of *ca.* 1 $\text{cm}^3 \text{K mol}^{-1}$ after two hours.

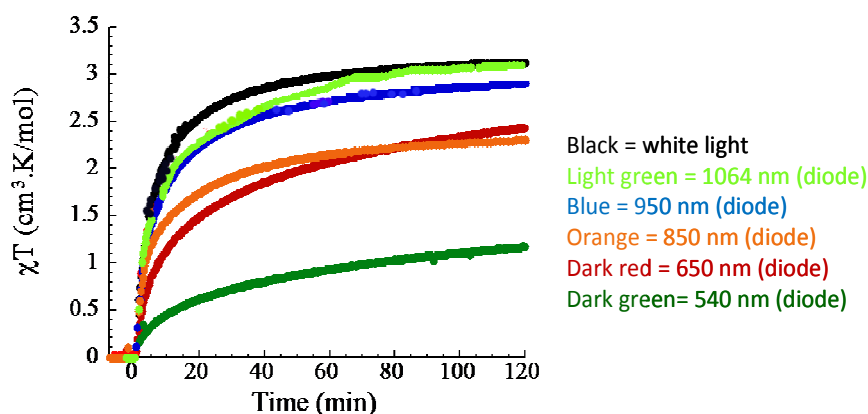


Figure 4.15: Irradiation plot at various wavelengths for **12** at 10 K: χT versus time (minutes) between 0 and 120 min.

From these results it is clear that only *ca.* 50% of the Fe^{II} LS ions can be systematically converted into the HS species upon irradiation. There are two possible explanations for this behaviour. Firstly, it is possible that the implied intensities do not allow the light to interpenetrate the crystalline material. As a result, it is predominately the Fe^{II} low spin ions at the surface of the material that are converted into HS species and the Fe^{II} LS ions further inside the material do not undergo conversion. But this explanation is unlikely as the same saturation value of around 3 $\text{cm}^3 \text{K mol}^{-1}$ (corresponding to roughly 50% of HS-HS and 50% of LS-LS species) at 10 K is obtained independently of both the power of light used and the sample preparation method applied. So the likely reason, for 50 % light induced spin state conversion, is that only one of the two Fe^{II} ions within the dinuclear complexes is converted into its high spin state generating an intermediate HS-LS species. So this suggests that compound **12** unlike its ClO_4^- analogue¹⁸⁴ only undergoes partial SCO upon light irradiation.

4.4.3 Optical properties of $[\text{Fe}_2(\text{L6})_3](\text{PF}_6)_4 \cdot 4\text{MeCN} \cdot \text{H}_2\text{O}$ (**12**)

To further investigate the LIESST phenomenon exhibited by compound **12**, solid state reflectivity measurements were recorded (Fig. 4.16) under white light

irradiation between 10 K and 295 K. At room temperature, the absorption spectrum is composed of two broad bands at *ca.* 900 nm and 560 nm. Upon cooling to 75 K, the optical spectra were modified, with an important increase in the reflectivity above 750 nm, accompanied with a small decrease of the reflectivity in the 600-750 nm region. Below 75 K, a new phenomenon results in a small decrease in the reflectivity above 750 nm, and a very minor increase of the reflectivity in the 600-750 nm region. An alternative way to visualise (Figure 4.16b) the thermal change of the optical spectra is by viewing the thermal dependence of the reflectivities at 871 nm and at 683 nm (noted hereafter R_{871} and R_{683}). The reflectivity was monitored at these wavelengths as the absorbance band at 871 nm is assigned to the ${}^5T_2 \rightarrow {}^5E$ transition seen for HS Fe^{II} ions in octahedral environments and the transition at 683 nm is characteristic of the MLCT transition associated with LS Fe^{II} ions.^{79,184}

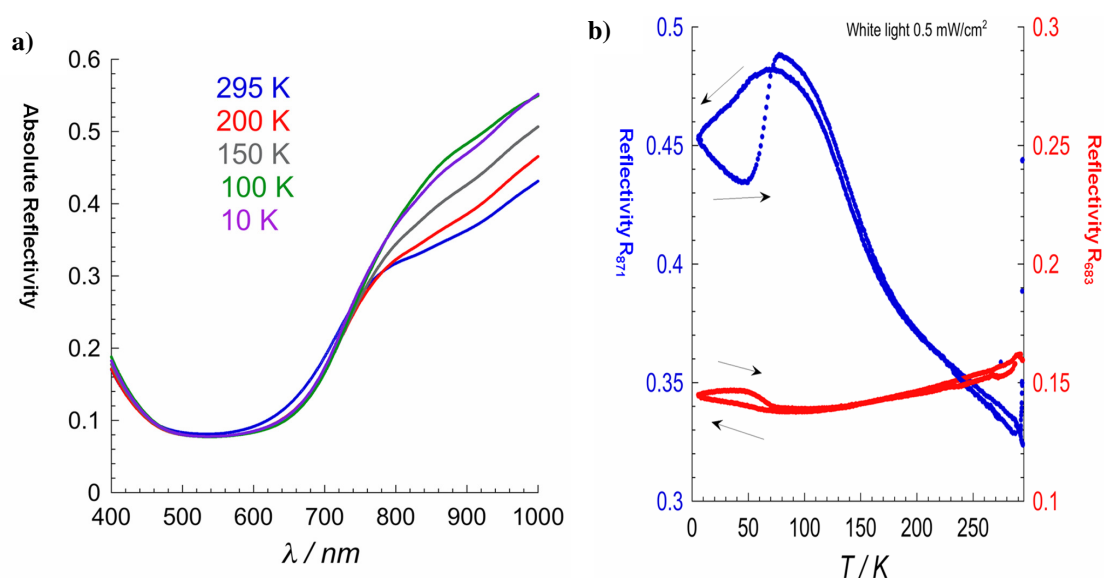


Figure 4.16: a) Selected surface absorption spectra of **12** at different temperatures and b) The temperature dependence of surface reflectivity of **12** at 871 nm and 683 nm. All data between 280 K and 100 K were collected at a cooling rate of 6 K min⁻¹.

Upon cooling from 300 K to 75 K, the R_{871} reflectivity increases from 0.13 to a maximum of 0.49. Between 75 K and 10 K, the R_{871} reflectivity decreases continuously to reach a value of 0.45 at 10 K. In the heating mode, the R_{871} reflectivity continues to decrease to reach a local minimum of 0.43 at 48 K. The R_{871} reflectivity then increases to reach a maximum of 0.49 at 75 K (with the appearance of a hysteresis loop). Upon further heating to 300 K the reflectivity R_{871} continues to decrease reaching a local minimum of 0.13. A related behaviour is observed for the R_{683} reflectivity.

To interpret these data, it is appropriate to compare the tendencies in reflectivity with the temperature dependent magnetic susceptibility results. From 295 K to 100 K, the increase of the R_{871} reflectivity (i.e. the decrease of the absorbance at 871 nm), corresponds to the conversion of the HS Fe^{II} ions within the complex into LS Fe^{II} ions. The R_{871} reflectivity continues to decrease between 100 K and 75 K even though the compound is in the LS state at these temperatures. This means that the optical reflectivities are also sensitive to thermal effects in the LS state. Below 75 K, the decrease of the R_{871} reflectivity (i.e. the increase of the absorbance at 871 nm) corresponds to the appearance of HS Fe^{II} centres in the compound. Thus, suggesting that the LS state can be photo-excited at low temperatures resulting in the regeneration of the HS state under white light irradiation.

4.4.4 Synthesis and structural characterisation of $[\text{Fe}_2(\text{L6})_3](\text{BF}_4)_4 \cdot \text{H}_2\text{O}$ (**13**)

In order to determine the counterion influence on the SCO properties of these helicates, the coordination compound $[\text{Fe}_2(\text{L6})_3](\text{BF}_4)_4 \cdot \text{H}_2\text{O}$ (**13**) was formed under similar synthetic conditions to those used in the generation of **12** except NH_4BF_4 was utilised instead of NH_4PF_6 . However, the resultant red hexagonal crystals proved difficult to analyse by single crystal X-ray diffraction methods.

Nevertheless, FT-IR and UV-vis spectroscopic methods (Figure 4.17) can be employed to characterise compound **13**. The FT-IR spectra of **12** and **13** (Figure 4.17a) are very similar. They both show a strong asymmetric $\text{C}=\text{N}$ bond stretch at 1617 cm^{-1} and 1618 cm^{-1} , respectively. These bond stretches are characteristic of the imine functionality of the Schiff base ligand.¹⁶⁴ The shift of these bond stretches to lower frequency when compared to the free ligand (1629 cm^{-1}) confirms that the Fe^{II} ions in both compounds coordinate to N donor atoms of the imines.¹⁸⁵ Both spectra also show the characteristic bond stretches associated with the methyl-imidazole moieties of the **L6** ligands. The major difference in the FT-IR spectra arises from the counterions. The FT-IR spectrum of **12** shows a strong bond stretch at 813 cm^{-1} which is characteristic of the PF_6^- counterions whereas the spectrum of **13** shows a strong bond stretch at 1055 cm^{-1} which is due to the BF_4^- ions.¹⁶⁴

The UV-vis spectra of **12** and **13** (Figure 4.17b) dissolved in acetonitrile are also very similar and both show an absorbance at 320 nm which is due to the $\pi\text{-}\pi^*$

transition of the imine ligand **L6**. Both complexes also display a weak d-d transition at *ca.* 530 nm. This transition can be assigned $^1A_1 \rightarrow ^1T_1$ transition associated with LS Fe^{II} ions in octahedral coordination environments.^{91, 94}

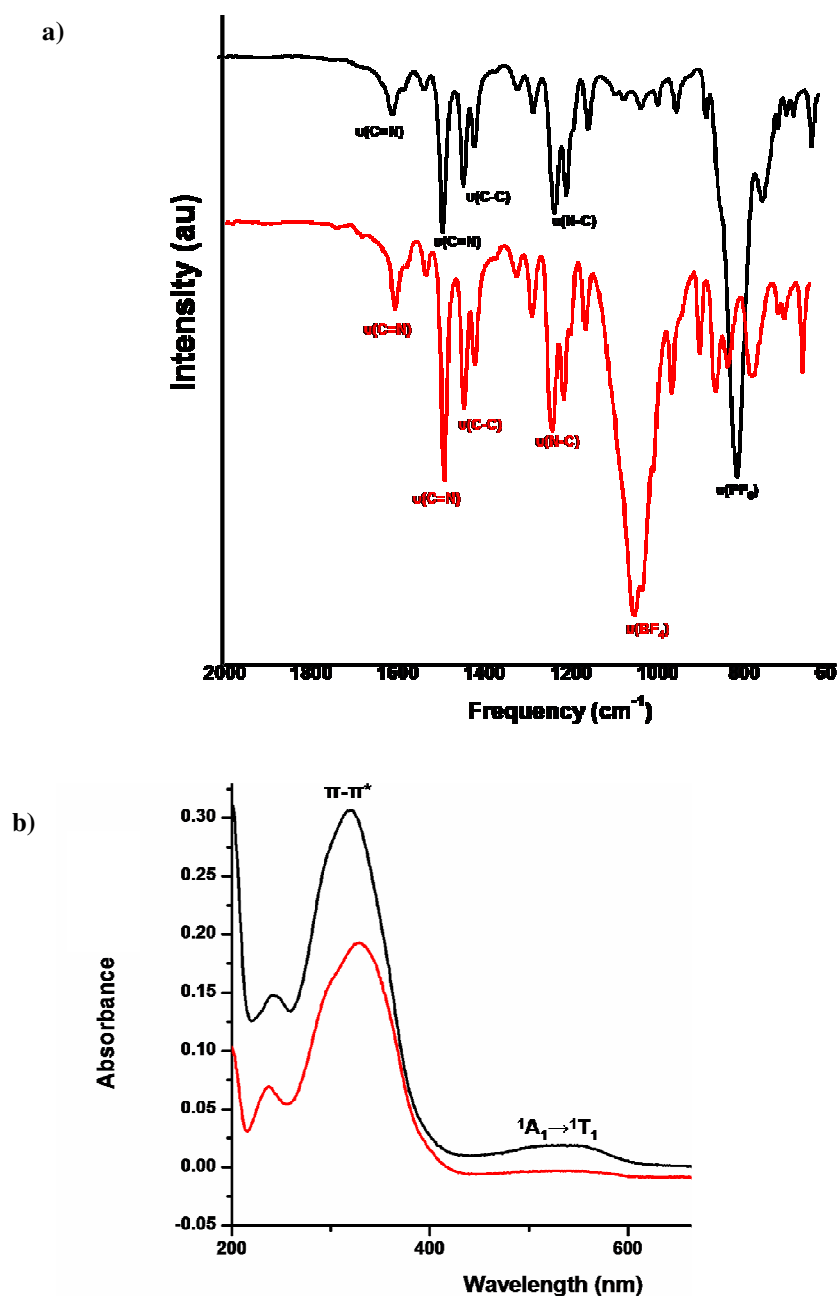


Figure 4.17: a) The FT-IR spectrum of compound **13** (red) as compared to that of compound **12** (black). b) The UV-vis spectrum of **13** in acetonitrile (red) in comparison to that of **12** (black). [**12**] = $2 \times 10^{-6} \text{ mol L}^{-1}$ [**13**] = $1.25 \times 10^{-6} \text{ mol L}^{-1}$.

The FT-IR and UV-vis spectra of **13** both indicate that **13** contains similar dinuclear Fe^{II} helicate complexes to those in **7** and **12**. This was further confirmed by

ESI mass spectrometry which shows a molecular ion peak at 316.2 m/z due to the $[\text{Fe}_2(\text{L6})_3]^{4+}$ species.

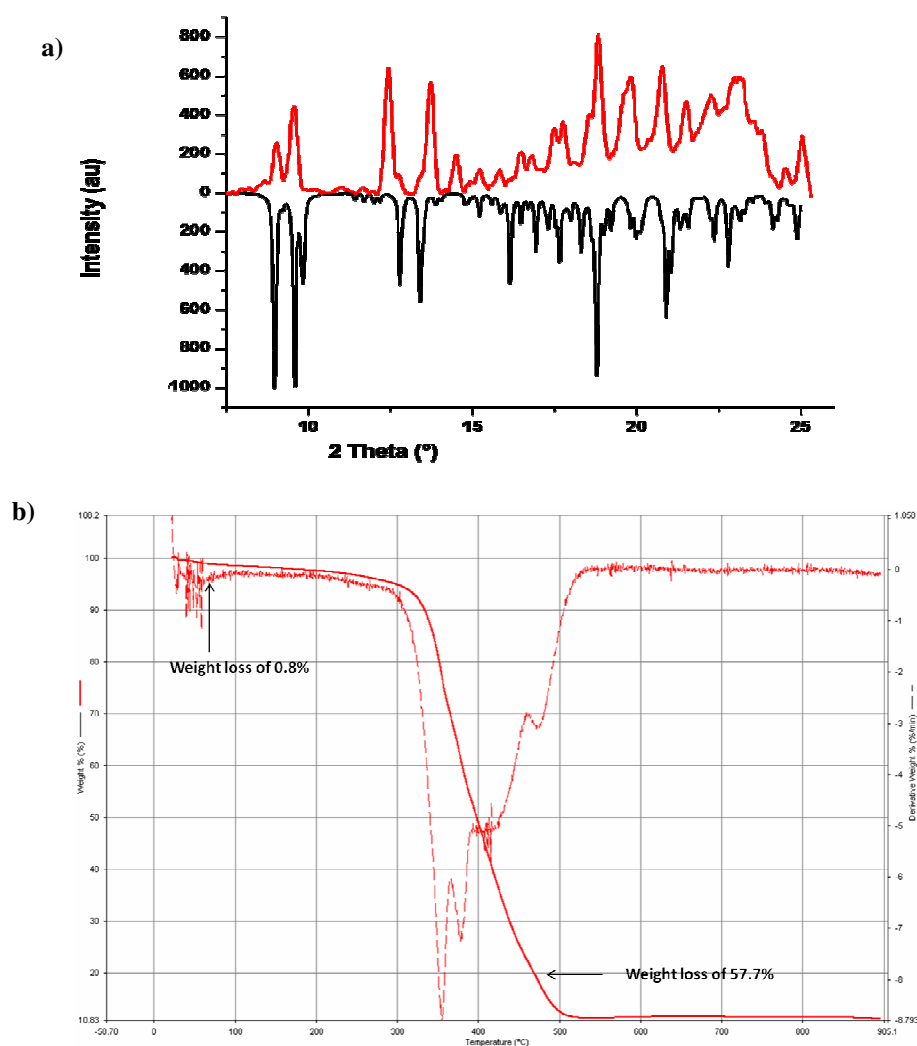


Figure 4.18: a) The XRD powder pattern of **13**. (Red: The measured pattern. Black: The simulated pattern based on the single crystal data obtained for $[\text{Fe}_2(\text{L6})_3](\text{ClO}_4) \cdot 2\text{MeCN}$ (**7**).¹⁸⁴ b) The thermogravimetric analysis (TGA) carried out on a crystalline sample of **13**.

In attempts to structurally characterise **13**, X-ray powder diffraction measurements were recorded on a freshly filtered sample of **13** (Figure 4.18a). The pattern obtained shows some similarities to that of the simulated pattern based on single crystal X-ray data obtained for **7**. However, the reflection seen in the simulated pattern at a 2θ value of 13° is shifted to 12.5° in the measured pattern. An additional reflection is also observed in the measured pattern at a 2θ value of 14.5° . This suggests that **13** does not have the same solid state structure as **7**.

To further characterise the composition of **13**, a thermogravimetric analysis (TGA) was carried out on a freshly filtered sample of **13** (Figure 4.18b). The sample was heated at a rate of 10 °C min⁻¹ to 900 °C under an air atmosphere. A weight loss of 0.8% is observed between 30 °C and 100 °C. This weight loss can be attributed to loss of one constitutional solvent water molecule (calculated weight of 0.8%) from **13**. The structure of **13** subsequently collapses with the oxidation of the remaining organic constituents commencing at *ca.* 300 °C. This process involves three thermogravimetric events centred at 360 °C, 385 °C and 415 °C, respectively. The combined weight loss observed was 57.7% which corresponds to the combustion of all the carbon, nitrogen and hydrogen atoms of the **L8** ligand (calculated weight 58.8%). The composition of [Fe₂(**L6**)₃](BF₄)₄·H₂O (**13**) was also verified by CHN microanalysis.

4.4.5 Magnetic properties of [Fe₂(**L6**)₃](BF₄)₄·H₂O (**13**)

In order to probe the possibility that compound **13** also undergoes SCO transitions, temperature dependent magnetic susceptibility measurements were performed at 1000 Oe. The magnetic measurements (Figure 4.19a) have been performed in cooling mode from 300 K to 2 K (black curve) and then in heating mode from 2 K to 400 K (red curve). As shown in Figure 4.19a the measurements result in super-imposable data indicating that the compound is stable under the examined conditions.

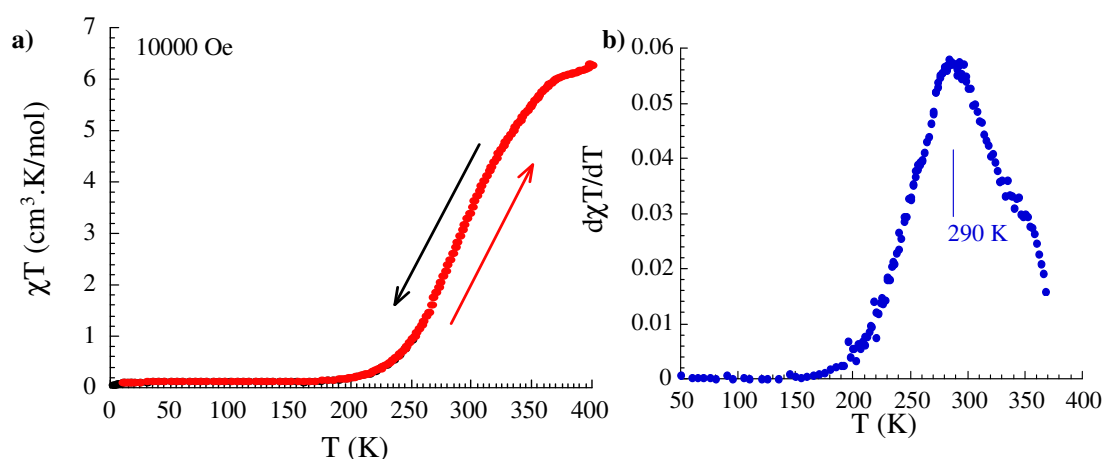


Figure 4.19: **a)** Temperature dependence of the χT product for **13**. The thermal cycles between 300 K and 2 K (black curve) and then between 2 K and 400 K (red curve). **b)** The temperature dependence of the first derivative of χT against T ($d\chi T/dT$) for **13**.

At 400 K, the χT product of *ca.* $6.3 \text{ cm}^3 \text{ K mol}^{-1}$ is in good agreement with the presence of two $S = 2$ high spin Fe^{II} metal ions ($C = 3.15 \text{ cm}^3 \text{ K mol}^{-1}$ with $g = 2.05$) and corresponds well to the SCO behaviour observed in the ClO_4^- and PF_6^- analogues **7** and **12**. When the temperature is lowered (Figure 4.19a), the χT product decreases in a typical S-shaped curve characteristic for spin-crossover systems. At 150 K, the spin crossover behavior is completed and almost no residual paramagnetism (only $0.1 \text{ cm}^3 \text{ K mol}^{-1}$) is detectable. It seems the spin-crossover process occurs here in a one step process suggesting that both Fe^{II} sites in the dinuclear complex change their spin state simultaneously. The $T_{1/2}$, as determined by the first derivative of χT against the temperature $d\chi T/dT$ (Figure 4.19b), is *ca.* 290 K. No thermal hysteresis is observed.

A similar one step spin-crossover transition is observed for the analogous ClO_4^- and PF_6^- stabilised compounds **7**¹⁸⁴ and **12** (Figure 4.20). However, it is evident that the counterion exchange has a significant effect on the transition temperature, resulting in the preparation of supramolecular systems that show SCO behaviour at room temperature

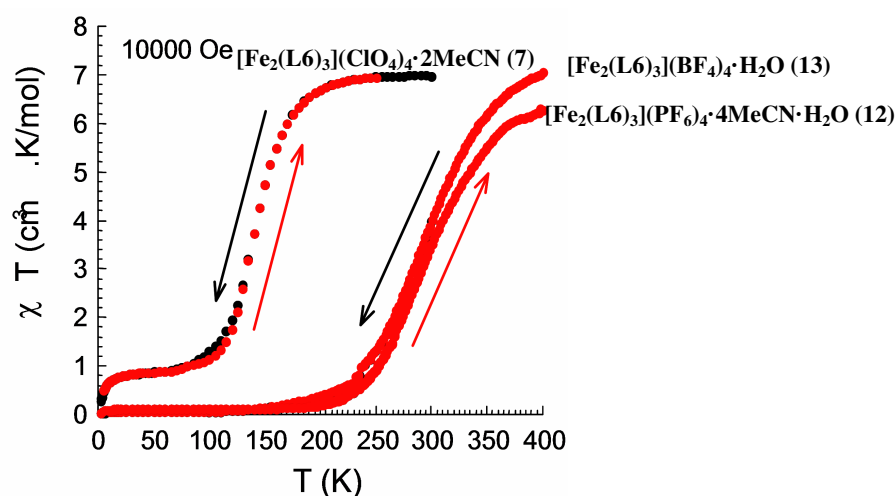


Figure 4.20: Temperature dependences of the χT product for compounds **7**, **12** and **13**.

4.4.6 Synthesis and structural characterisation of $[\text{Fe}_2(\text{L5})_3](\text{PF}_6)_4 \cdot 4\text{MeCN} \cdot \text{H}_2\text{O}$ (**14**)

We next sought to investigate what effect ligand exchange would have on the SCO properties of these Fe^{II} helicates. So we decided to employ N,N'-bis-(1-methyl-1-H-imidazol-2-yl-methylene)-4,4'-diaminodiphenylmethane (**L5**) in the formation

of related complexes. This led to the synthesis of the coordination compound $[\text{Fe}_2(\text{L5})_3](\text{PF}_6)_4 \cdot 4\text{MeCN} \cdot \text{H}_2\text{O}$ (**14**) which was formed under identical synthetic conditions to those applied in the synthesis of **12**. **14** formed as red plate like crystals which proved difficult to structurally elucidate using single crystal X-ray diffraction, as these crystals appear to be twinned. FT-IR and UV-vis spectroscopy (Figure 4.21) were employed to characterise **14**.

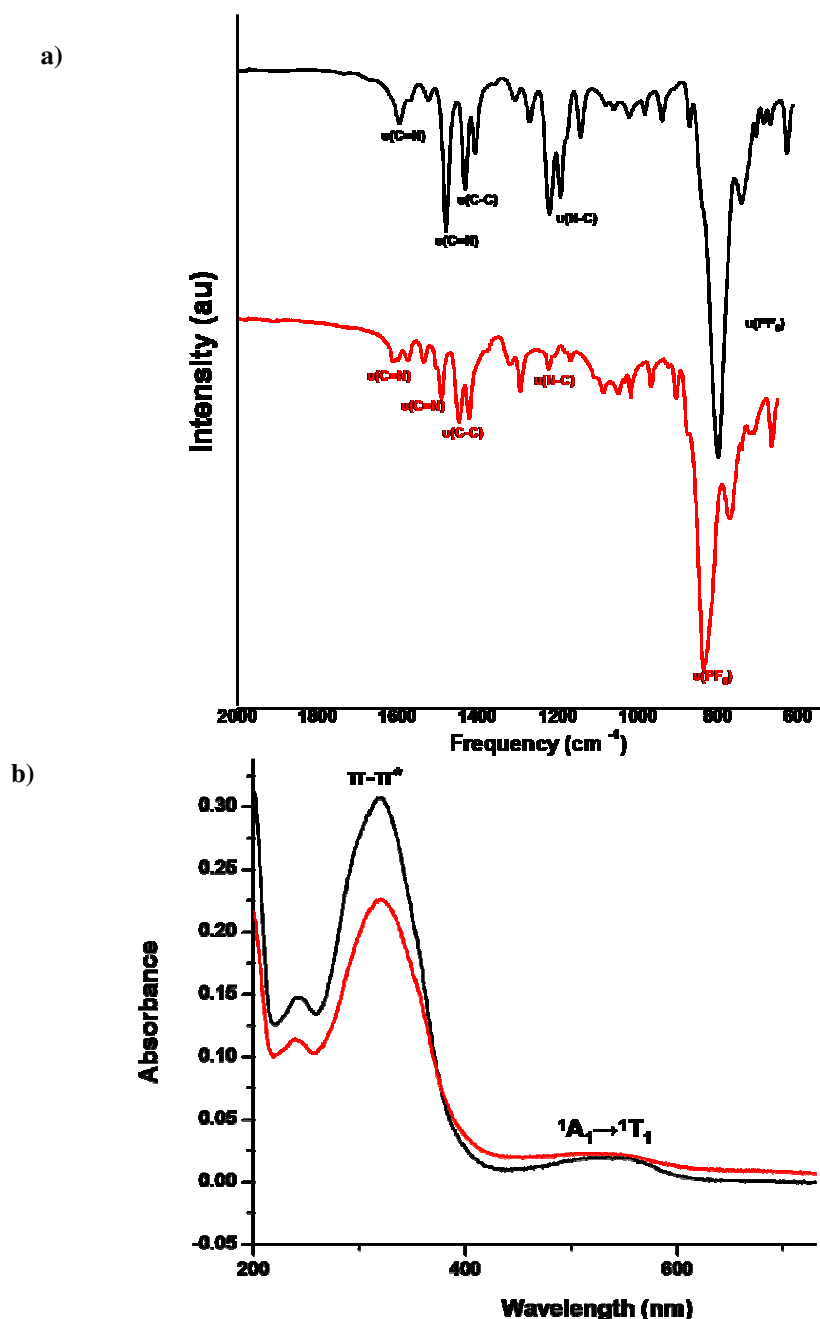


Figure 4.21: a) The FT-IR spectrum of compound **14** (red) as compared to that of compound **12** (black). b) The UV-vis spectrum of **14** in acetonitrile (red) in comparison to that of **12** (black). $[\text{12}] = 2 \times 10^{-6} \text{ mol L}^{-1}$ $[\text{14}] = 1.25 \times 10^{-6} \text{ mol L}^{-1}$.

The FT-IR spectrum of **14** is comparable to that of **12** (Figure 4.21a). Both spectra show evidence of the asymmetric C=N bond stretch that arises from the imine ligands. In **14** this bond stretch occurs at 1617 cm^{-1} .¹⁶⁴ The spectrum of **14** also shows the characteristic bond stretches of the methyl-imidazole functionalities of the **L5** Schiff base ligands.¹⁶⁴ The presence of the PF_6^- counterions was confirmed by the strong bond stretch seen in both spectra at *ca.* 810 cm^{-1} .¹⁶⁴

The UV-vis spectra of **12** and **14** in acetonitrile (Figure 4.21b) both show an absorbance at *ca.* 320 nm which is due to the $\pi\text{-}\pi^*$ transition of the Schiff base ligands. Both complexes also undergo a $^1\text{A}_1 \rightarrow ^1\text{T}_1$ transition at *ca.* 530 nm. This transition is the characteristic d-d transition seen for LS Fe^{II} ions in octahedral coordination environments.^{91,94}

The FT-IR and UV-vis spectroscopy results suggest that **14** contains related dinuclear helicates to those observed in **12**. The ESI mass spectrum of **14** in acetonitrile shows a molecular ion peak attributed to the $[\text{Fe}_2(\text{L5})_3]^{4+}$ species at 314.8 m/z.

To characterise the composition of **14**, a thermogravimetric analysis (TGA) was carried out on a freshly filtered sample of **14** (Figure 4.22a). The sample was heated to *ca.* 900 °C under an air atmosphere at a rate of $10\text{ }^\circ\text{C min}^{-1}$. A weight loss of 6.6% occurs between 30 °C and 85 °C. This weight loss can be attributed to the loss of four constitutional acetonitrile molecules (calculated weight 7.0%) from **14**. A further weight loss of 0.9% was then observed between 85 °C and 110 °C. This corresponds to the loss of one constitutional water molecule (calculated weight of 0.8%) from **14**. The compound then begins to undergo gradual thermal decomposition at *ca.* 300 °C in two successive thermogravimetric steps, centred at 330 °C and 405 °C, yielding unknown oxides which were not further characterised. The combined weight loss for these events amounts to approximately 46.8%. This can be assigned to the combustion of all the carbon, nitrogen and hydrogen atoms of the **L5** ligand, which have a calculated weight loss of 49.6%. This experiment suggests that the composition of **14** is $[\text{Fe}_2(\text{L5})_3](\text{PF}_6)_4 \cdot 4\text{MeCN} \cdot \text{H}_2\text{O}$ and this was also verified by CHN microanalysis.

In order to structurally characterise **14** further an X-ray powder diffraction measurement was recorded on a freshly filtered sample of **14**. The obtained pattern is similar to that simulated on the basis of the single crystal X-ray data obtained for $[\text{Fe}_2(\text{L6})_3](\text{PF}_6)_4 \cdot 4\text{MeCN} \cdot \text{H}_2\text{O}$ (**12**) (Figure 4.22b). The reflections seen in the

measured pattern are broadened when compared to the simulated pattern. This effect is probably due to loss of the volatile solvent molecules during the measurement which results in structural alterations. This experiment suggests that compound **12** and **14** have a related solid state structure.

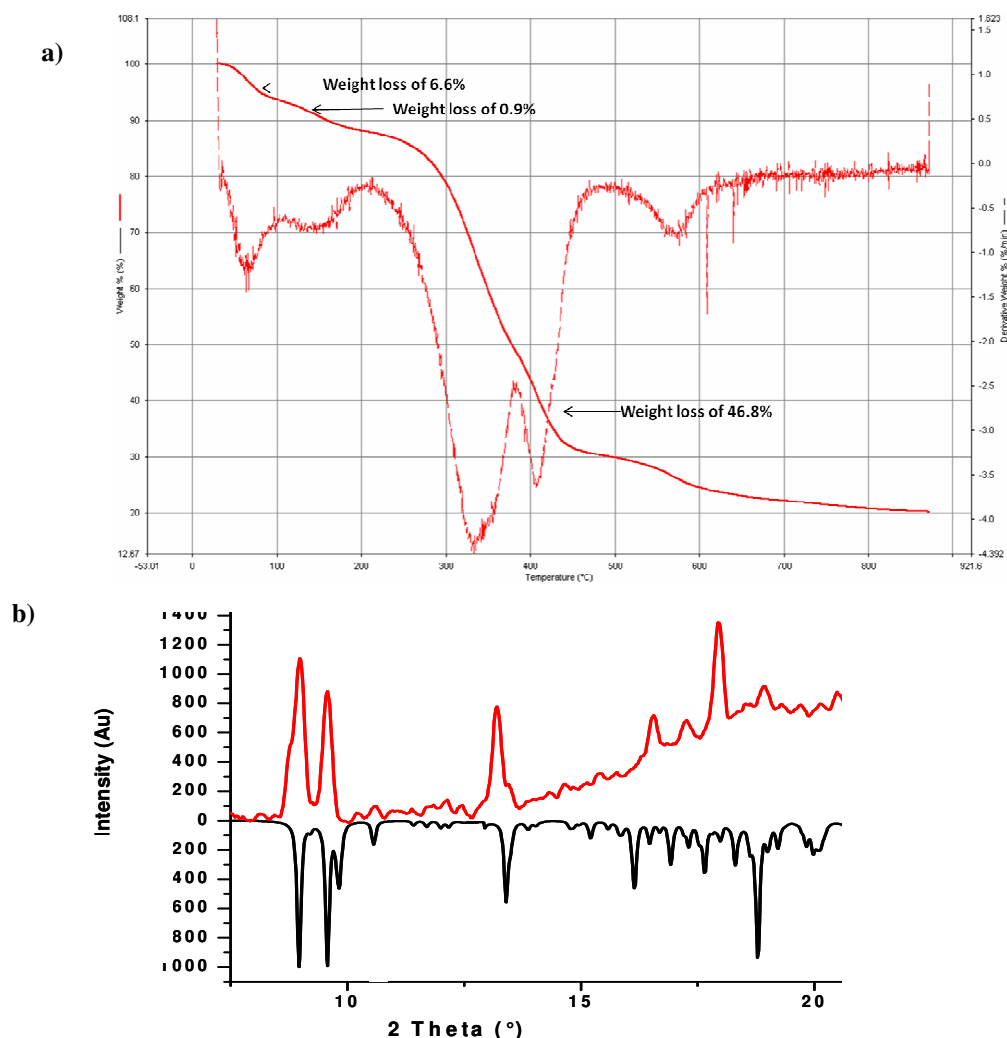


Figure 4.22: a) The thermogravimetric analysis (TGA) carried out on a crystalline sample of **14**. b) The XRD powder pattern of **14**. (Red: The measured pattern. Black: The simulated pattern based on the single crystal data obtained for [Fe₂(L6)₃](PF₆)·4MeCN·H₂O (**12**).)

4.4.7 Synthesis and structural characterisation of [Fe₂(L5)₃](BF₄)₄·2MeCN (**15**)

As part of this study, the coordination compound [Fe₂(L5)₃](BF₄)₄·2MeCN (**15**) was formed under similar synthetic conditions to those used to prepare **14**. In this case, BF₄⁻ was employed as the counterions. Compound **15** formed as plate like red crystals which proved difficult to analyse by single crystal X-ray diffraction. Therefore, FT-IR and UV-vis spectroscopy (Figure 4.23) was employed as a means to characterise **15**.

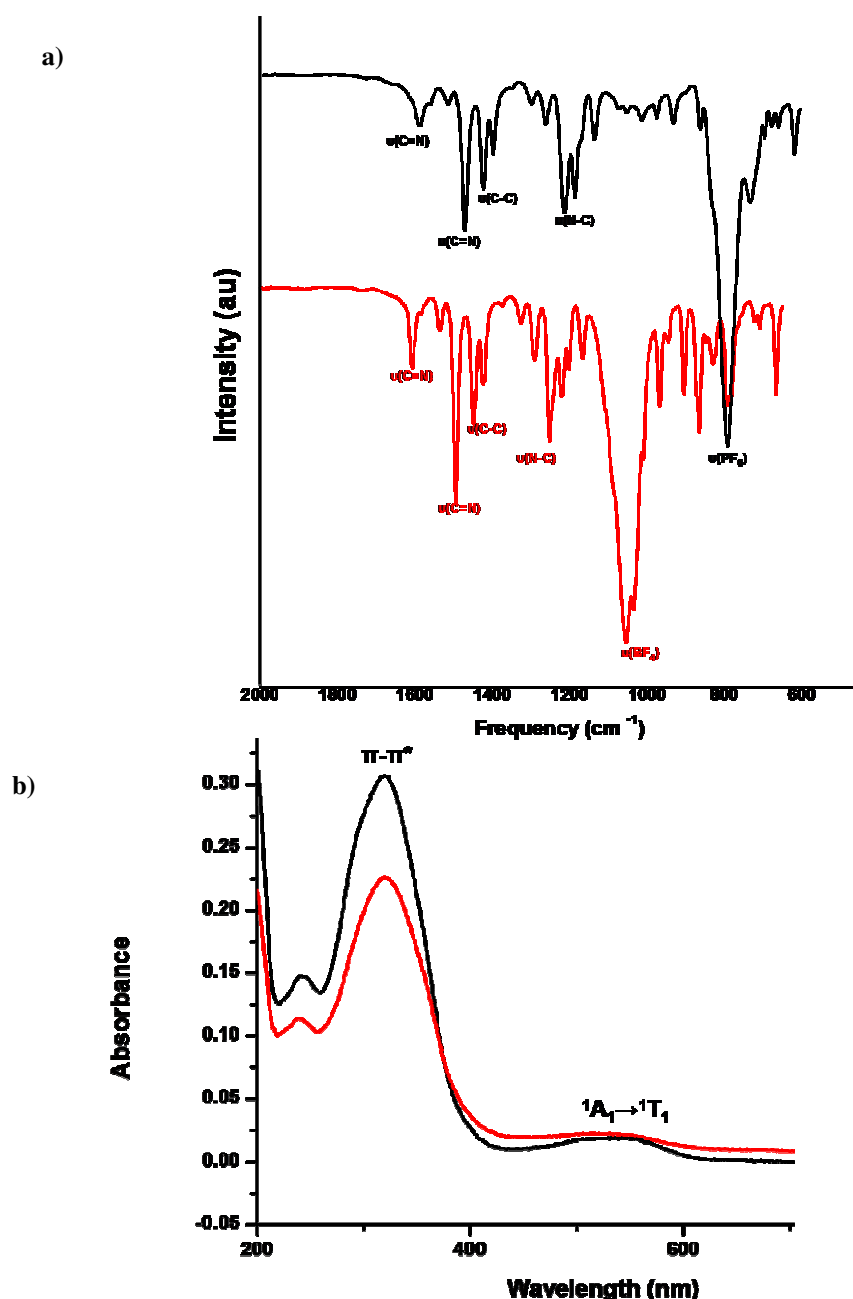


Figure 4.23: a) The FT-IR spectrum of compound **15** (red) as compared to that of compound **12** (black). b) The UV-vis spectrum of **15** in acetonitrile (red) in comparison to that of **12** (black). $[\mathbf{12}] = 2 \times 10^{-6} \text{ mol L}^{-1}$ $[\mathbf{15}] = 2 \times 10^{-6} \text{ mol L}^{-1}$.

The FT-IR spectrum of **15** was recorded and compared to that of **12** (Figure 4.23a). Both spectra show evidence of the asymmetric imine bond stretch that originates from the Schiff base ligands.¹⁶⁴ In **15**, this C=N bond stretch is observed at 1618 cm^{-1} . The spectrum of **15** also shows an asymmetric C=N bond stretch at 1582 cm^{-1} , an asymmetric C-C stretch at 1502 cm^{-1} and an asymmetric C-N stretch at 1382 cm^{-1} which arise from the methyl-imidazole functionalities of the Schiff base ligand **L5**.¹⁶⁴ The major difference between both spectra is due to the bond stretches

associated with the counterions. The spectrum of **12** shows a bond stretch at 813 cm^{-1} due to the PF_6^- ions whereas **15** shows a strong bond stretch at 1052 cm^{-1} which is characteristic of the BF_4^- ions.¹⁶⁴

The UV-vis spectrum of **15** was recorded in acetonitrile (Figure 4.23b). This spectra is similar to that obtained for **12** (Figure 4.23b). In both spectra an absorbance band is observed at *ca.* 320 nm. This arises from the $\pi\text{-}\pi^*$ transition of the imine ligands. Both complexes also show a $^1\text{A}_1 \rightarrow ^1\text{T}_1$ transition at *ca.* 530 nm.^{91,94}

The FT-IR and UV-vis spectroscopy demonstrate that **15** also contains the dinuclear Fe^{II} helicates $[\text{Fe}_2(\text{L5})_3]^{4+}$ species. The ESI mass spectrum of compound **15** in acetonitrile also confirms this by revealing a molecular ion peak at 315.1 m/z.

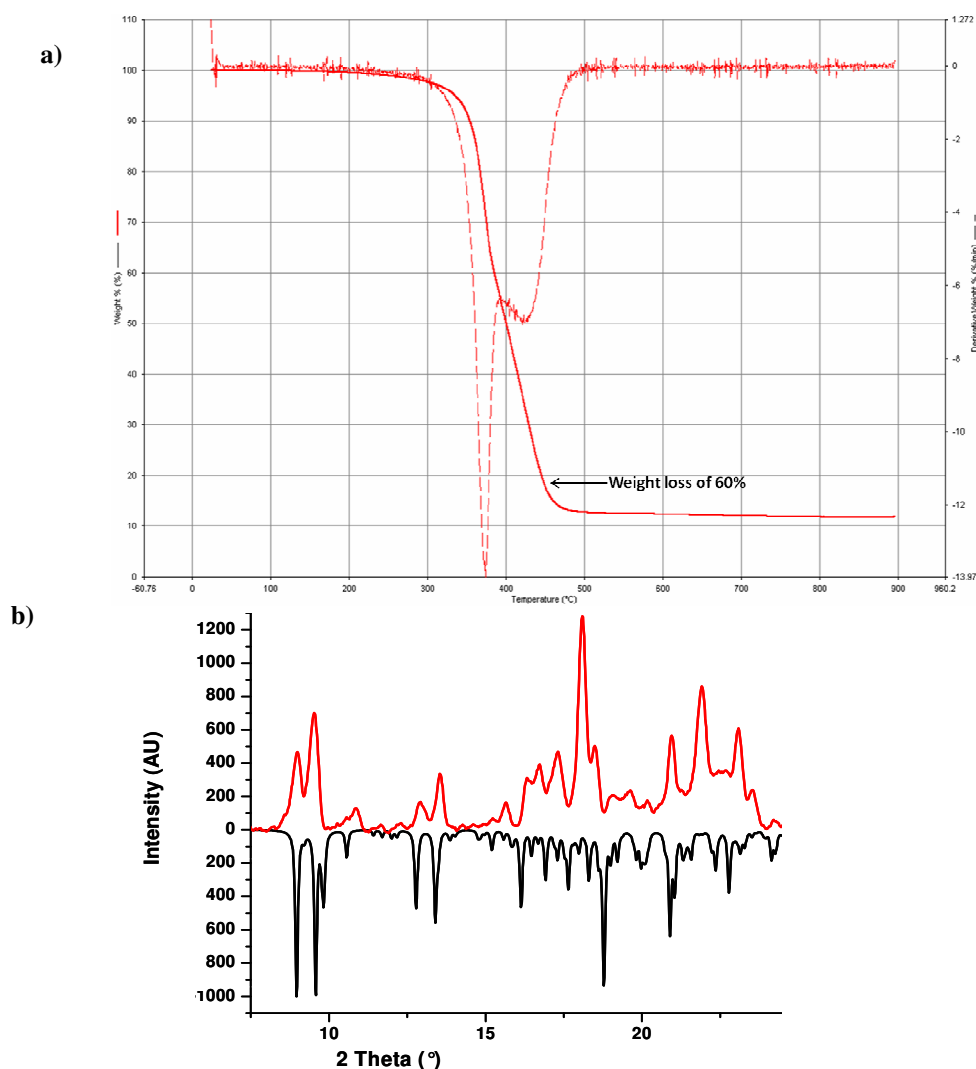


Figure 4.24: a) The thermogravimetric analysis (TGA) carried out on a crystalline sample of **15**. b) The XRD powder pattern of **15**. (Red: The measured pattern. Black: The simulated pattern based on the single crystal data obtained for $[\text{Fe}_2(\text{L6})_3](\text{ClO}_4) \cdot 2\text{MeCN}$ (7).¹⁸⁴)

To characterise the composition of **15**, a TGA experiment was carried out on a freshly filtered sample of **15** (Figure 4.24a). The sample was heated under an air atmosphere at a rate of 10 °C min⁻¹ to 900 °C. The composition of **15** remains unchanged until ca. 300 °C when the organic ligands undergo oxidative degradation. A combined weight loss of *ca.* 60% was observed, and corresponds with the combustion of all the C, H and N components of the ligand (calculated 57.9%). The volatile acetonitrile solvent molecules appear to be lost prior to the experiment. The composition of **15** as [Fe₂(**L5**)₃](BF₄)₄·2MeCN was also confirmed by CHN microanalysis.

An X-ray powder diffraction measurement was also recorded on a freshly filtered sample of **15**. The obtained pattern was compared with the pattern simulated on the basis of the single crystal X-ray data obtained for [Fe₂(**L6**)₃](ClO₄)₄·2MeCN (**7**) (Figure 4.24b). The measured and simulated patterns are similar thus suggesting that **15** and **7** are structural related. Again the broadening of the reflections observed in the measured pattern was due to structural changes occurring due to the loss of the constitutional acetonitrile molecules from **15**.

3.4.8 Magnetic properties of compounds **14** and **15**

In order to investigate the SCO properties of the compounds which contain the N,N'-bis-(1-methyl-1-H-imidazol-2-yl-methylene)-4,4'-diaminodiphenylmethane ligand (**L5**), temperature dependent magnetic susceptibility measurements were also carried out on compounds **14** and **15** at 1000 Oe. The magnetic measurements (Figure 4.25) were performed in the cooling mode from 300 K to 2 K (black curves) and then in the heating from 2 K to 400 K (red curves). As shown in Figures 4.25a and 4.25b for compound **14** and compound **15**, respectively, the data are perfectly superimposable with respect to temperature variations, confirming that the compounds are stable up to 300 K.

At 400 K, the χT products for both compounds are 6.8 and 5.7 cm³ K mol⁻¹ respectively, and are in good agreement with the presence of two *S* = 2 high spin Fe^{II} metal ions (*C* = 3 cm³ K mol⁻¹ per Fe^{II} with *g* = 2.0). It is worth mentioning that the χT products do not saturate at 400 K showing that these compounds are not completely in their high spin states at 400 K. When the temperature is lowered (Figure 4.21), the χT

product for **14** decreases in a typical S-shape curve characteristic for SCO compounds. However, for **15** a two step S-shaped curve is observed.

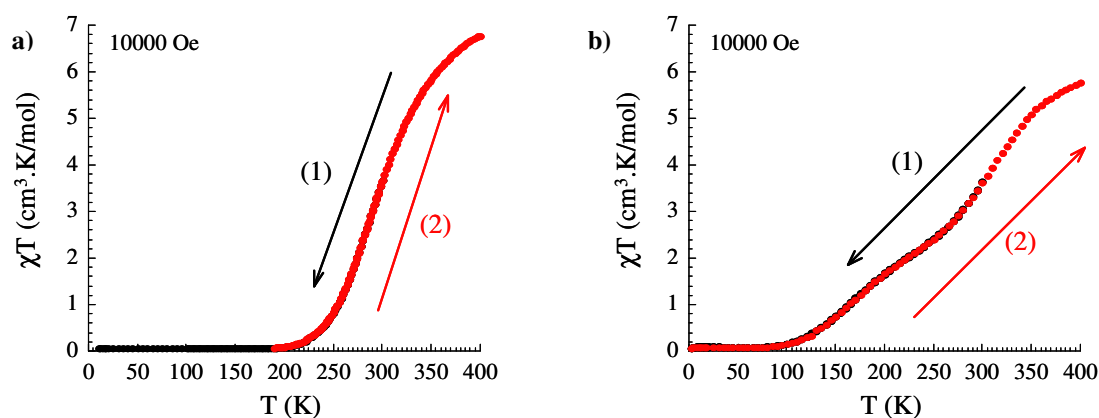


Figure 4.25: **a)** Temperature dependence of the χT product for **14**. The thermal cycles between 300 K and 2 K (black curve) and then between 2 K and 400 K (red curve). **b)** Temperature dependence of the χT product for **15**. The thermal cycles between 300 K and 2 K (black curve) and then between 2 K and 400 K (red curve).

For compound **14**, the spin crossover behavior is completed at 180 K, and at this temperature almost no residual paramagnetic signal ($0.05 \text{ cm}^3 \text{ K mol}^{-1}$) is detectable (Figure 4.25a). Clearly the spin-crossover process occurs here in one step indicating that both Fe^{II} sites in the dinuclear complex exhibit a simultaneous spin change. The $T_{1/2}$ is at *ca.* 285 K and was determined from the first derivative of χT against the temperature ($d\chi T/dT$, Figure 4.26a).

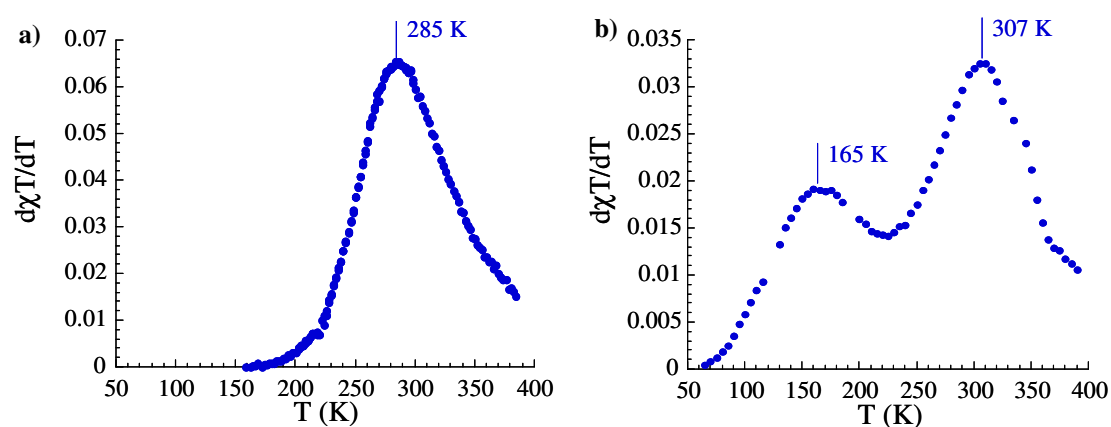


Figure 4.26: Temperature dependence of the first derivative of χT against T ($d\chi T/dT$) for **a)** compound **14** and **b)** compound **15**.

However in the case of compound **15**, the spin crossover behavior is completed only at 80 K, at which point the χT product reaches a value of $0.07 \text{ cm}^3 \text{ K}$

mol⁻¹ (Figure 4.25b). Clearly the spin-crossover process occurs here in two steps, hence indicating that the two Fe^{II} sites in the dinuclear complex undergo a spin transition at two different temperatures. The first derivative of χT against the temperature suggests that the T_{1/2} transition temperatures for **15** are 165 K and 307 K (Figure 4.26b).

This study demonstrates that the magnetic properties of the Fe^{II} helicate compounds were dramatically altered by exchanging the 4-4' oxydianiline bridging group in **L6** with the 4-4'diaminodiphenylmethane moiety in **L5** and by using different counterions to stabilise the related compounds. Structural and geometrical differences in the complexes and their packing structure may also be decisive for the SCO behaviour of the investigated compounds. As the crystal quality of **13** - **15** did not allow detailed structural analyses, further studies would be required to understand the underlying reasons for the observed changes in SCO behaviour.

4.5 Conclusion

A family of novel flexible Schiff base ligands **L5**, **L6** and **L7** have been successfully synthesised and fully characterised. These ligands have shown a propensity to undergo transition metal directed self-assembly to generate helical architectures. This synthetic approach was exploited to generate a variety of molecular helicates **8** - **15** incorporating Co^{II}, Mn^{II}, Ni^{II} and Fe^{II} ions.

Particular attention was focused on the utilisation of the bis-bidentate ligands **L5**, **L6** and **L7** for the generation of Fe^{II} complexes. This work led to the formation of a series of Fe^{II} molecular helicates present in **12** - **15**. All these compounds display spin crossover behaviour which can be induced thermally or *via* light irradiation.

It has been demonstrated that the counterions used in these compounds can have a dramatic effect on the SCO properties. In the case of **12** and **13** when PF₆⁻ or BF₄⁻ are employed as the counterions, the SCO transitions occur in the room temperature range. This remarkable behaviour is desired by many researches in this field.^{91,187}

It has also been shown that subtle changes to the structure of the organic ligand influence the SCO behaviour of these materials. For example, in **13** and **15** when the diamine backbone of the ligand is changed from an oxyaniline to a methylene aniline moiety, a different transition type is observed. A one-step SCO

process is observed in **13**, whilst **15** undergoes a two-step transition. The variation in SCO behaviour may be attributable to the different ligand types but could also be the result of packing effects in the crystal structure.

It was also noted that constitutional solvent molecules have an impact on the SCO properties of these materials. Structural effects upon de-solvation were investigated using **12**. In its fully solvated form, **12** undergoes a one step spin transition. However, when the solvent molecules were removed upon heating, the SCO occurs *via* a two step process.

The synthetic approach discussed herein results in Fe^{II} compounds that undergo SCO transitions at room temperature and the nature of the SCO behaviour seems susceptible to minor structural changes. Based on these observations it may be feasible to utilise the cavities of the helicate structures for host-guest chemistry approaches and sensing purposes. For instance, the incorporation of urea moieties within the bridging diamine ligand backbone may allow SCO behaviour to be exploited for the detection of anions. The molecular compounds **12** - **15** do not display any strong intermolecular interactions and show low cooperativity. Therefore, the SCO transitions of these compounds are not accompanied by any substantial hysteresis effects. Hence, future activities may consider the alteration of the ligand system allowing the incorporation of the SCO centres into network structures. This approach would give rise to strong cooperativity and thermal hysteresis effects which could potentially be exploited for device fabrication.

Chapter Five

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The transition metal directed self-assembly of extended Schiff base ligands

5.1 Introduction

Inspired by our previous studies of the transition metal directed self-assembly of bis-bidentate Schiff base ligands (Chapters 3 and 4), we decided to investigate the coordination chemistry of a series of extended Schiff base ligands N,N',N''-tris-(1-H-imidazol-2-ylmethylene)-1-3-5-triphenyl benzene (**L8**), N,N',N''-tris-(1-methyl-1-H-imidazol-2-ylmethylene)-1-3-5-triphenyl benzene (**L9**), N,N',N''-tris-(4-pyridin-2-ylmethylene)-1-3-5-triphenyl benzene (**L10**), N,N',N''-tris-(4-phen-2-ol-2-ylmethylene)-1-3-5-triphenyl benzene (**L11**) and N,N',N''-tris-(2-benzoic acid-2-ylmethylene)-1-3-5-triphenyl benzene (**L12**) (Figure 5.1). In these ligands the imine binding units are linked to a triphenyl-benzene backbone.

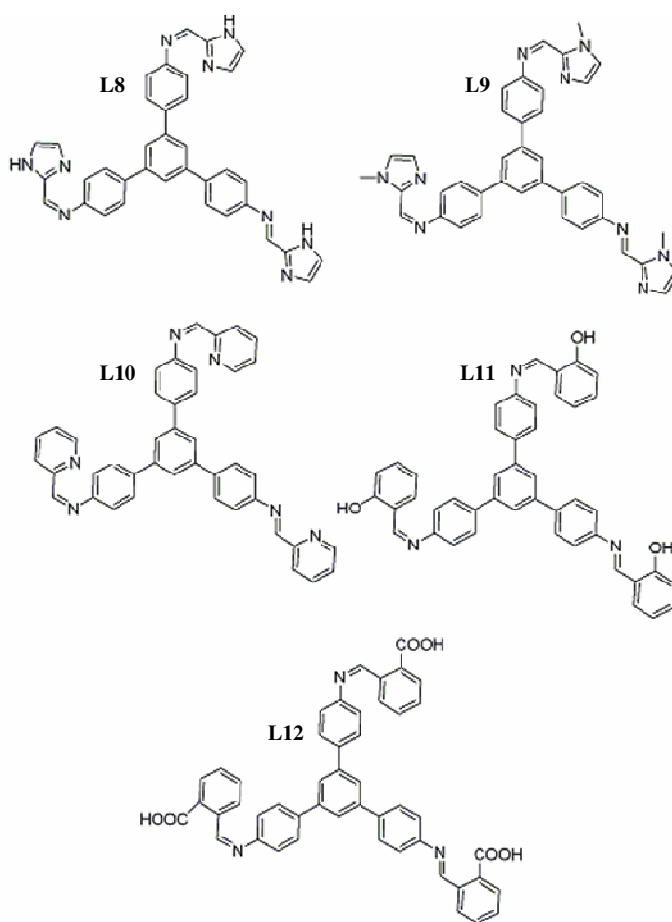


Figure 5.1: Structure of extended imine ligands **L8** - **L12**.

The imine ligands **L8** - **L12** were chosen as their tris-bidentate binding mode could be exploited to assemble a variety of supramolecular architectures such as molecular cages or coordination networks. The extended nature of the Schiff base

ligands **L8** - **L12** may also give rise to the formation of open framework structures that could display some degree of porosity that could potentially be exploited for gas storage or molecular recognition purposes. In addition, the reaction of these ligands with Fe^{II} salts would be investigated with the aim of generating metallo-supramolecular species that display spin crossover (SCO) behaviour.

5.2 Synthesis of Schiff base ligands **L8** - **L12**

5.2.1 Synthesis of 1,3,5-tri(4-aminophenyl)benzene

In order to synthesise these extended imine ligands (**L8** - **L12**), 1,3,5-tri(4-aminophenyl)benzene was required as the starting amine. This aromatic amine was synthesised according to a literature procedure, which involves the reaction of *p*-nitroacetophenone with SiCl_4 in dry ethanol to give 1,3,5-tri(4-nitrophenyl)benzene.¹⁸⁸ This aromatic nitro compound was subsequently reduced to 1,3,5-tri(4-aminophenyl)benzene using a Pd/C catalyst and hydrazine monohydrate.¹⁸⁸

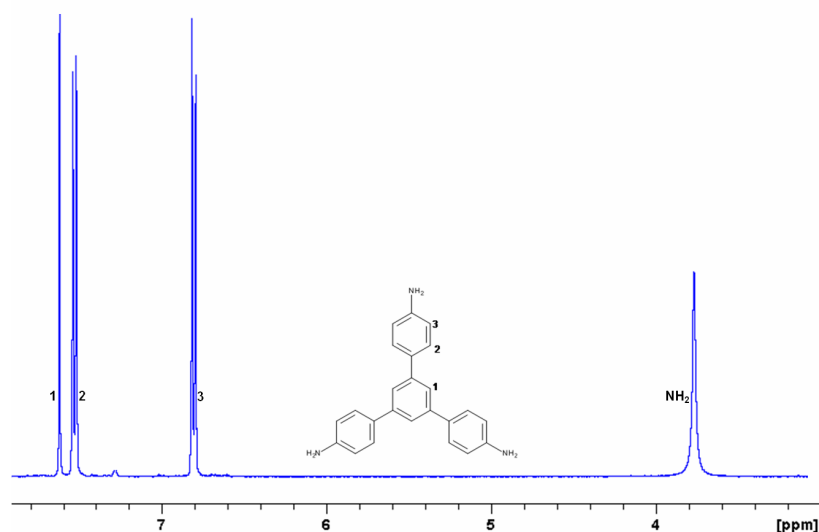


Figure 5.2: The 400 MHz ^1H NMR ($\text{D}_6\text{-DMSO}$) spectrum and assignment for 1,3,5-tri(4-aminophenyl)benzene.

The product formed in high yields (80 %) and was characterised by 400 MHz ^1H NMR spectroscopy (Figure 5.2). The FT-IR spectroscopy also verifies the formation of 1,3,5-tri(4-nitrophenyl)benzene. The FT-IR spectrum shows the N-H bond stretches at 3433 cm^{-1} and at 3346 cm^{-1} , the N-H bend vibration band at 1618 cm^{-1} , the C-N stretch at 1278 cm^{-1} and the N-H bond wagging vibration at 765 cm^{-1} .¹⁶⁴ The ESI mass spectrum of the product shows a molecular ion peak at 352.2 m/z which

was due to the $[\text{C}_{24}\text{H}_{22}\text{N}_3]^+$ species. Furthermore, elemental analysis (CHN) confirms the purity of the compound.

5.2.2 Synthesis of extended ligands **L8** - **L12**

A family of novel Schiff base ligands (Figure 5.3), N,N',N''-tris-(1-H-imidazol-2-ylmethylene)-1-3-5-triphenyl benzene (**L8**), N,N',N''-tris-(1-methyl-1-H-imidazol-2-ylmethylene)-1-3-5-triphenyl benzene (**L9**), N,N',N''-tris-(4-pyridin-2-ylmethylene)-1-3-5-triphenyl benzene (**L10**), N,N',N''-tris-(4-phen-2-ol-2-ylmethylene)-1-3-5-triphenyl benzene (**L11**) and N,N',N''-tris-(2-benzoic acid-2-ylmethylene)-1-3-5-triphenyl benzene (**L12**) were successfully synthesised. These ligands were prepared from the reaction of 1,3,5-tri(4-aminophenyl)benzene with three equivalents of the relevant aldehyde in methanol. The synthetic routes for the formation of the **L8** - **L12** ligands are summarised in Figure 5.3.

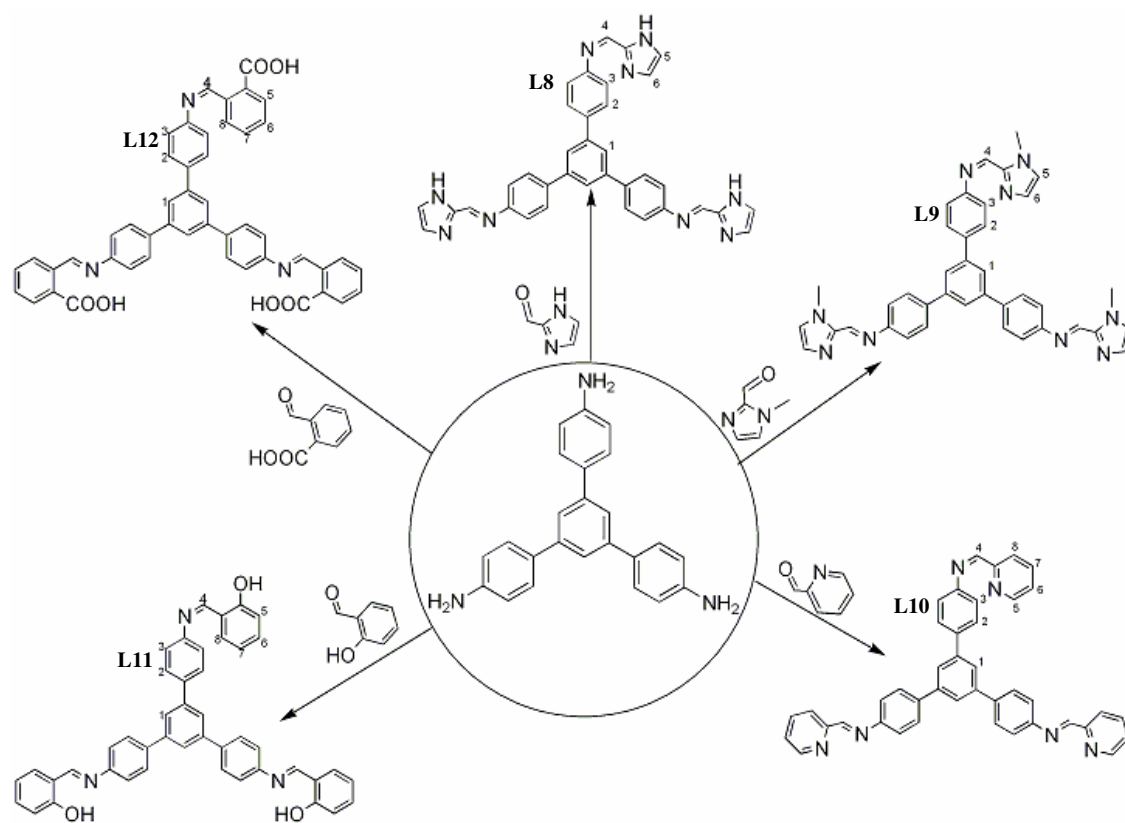


Figure 5.3: Schematic representation of the formation of the extended Schiff base ligands **L8** - **L12**.

^1H NMR spectroscopy (Table 5.1) was employed to confirm the formation of **L8** - **L12**. The spectrum of each ligand shows a highly deshielded chemical shift at *ca.*

9 ppm which arises from hydrogen atoms of the the imine functionalities. Each spectrum also shows proton signals that arise from the aromatic hydrogen atoms of the triphenyl-benzene backbone. The remaining signals observed in the spectra can be assigned to the various head groups of the extended ligands. These assignments are summarised in Table 5.1.

The compounds were also characterised by FT-IR spectroscopy (Table 5.2) which confirms the formation of the imine bonds, as the spectra show a characteristic asymmetric C=N bond stretch at *ca.* 1630 cm⁻¹ in each case.¹⁶⁴ The relevant molecular ion peak is also observed in the ESI mass spectrum of each ligand (Table 5.2) and elemental analysis (CHN) also confirms the composition of each ligand.

Table 5.1: 400 MHz ¹H NMR data for L8 - L12

Ligand	Chemical Shift and Assignment
L8	δ = 13.1 (s, 3H, H _{NH}), 8.6 (s, 3H, H ₄), 7.9 (m, 6H, H ₅ +H ₆), 7.6 (s, 3H, H ₁), 7.3 (m, 12H, H ₂ +H ₃) ppm.
L9	δ = 8.7 (s, 3H, H ₄), 8.0 (m, 6H, H ₅ +H ₆), 7.9 (s, 3H, H ₁), 7.7 (d, J = 7.6 Hz, 6H, H ₂), 7.5 (d, J = 7.6 Hz, 6H, H ₃), 4.0 (s, 9H, H _{Me}) ppm.
L10	δ = 9.5 (s, 3H, H ₄), 8.9 (d, J = 5.2 Hz, 3H, H ₅), 8.85 (d, J = 7.6 Hz, 3H, H ₈), 8.8 (dd, J = 7.6 Hz, 5.4 Hz, 3H, H ₇), 8.6 (dd, J = 5.2 Hz, 5.4 Hz, 3H, H ₆), 8.1 (d, J = 8 Hz, 6H, H ₃), 8.0 (d, J = 8 Hz, 6H, H ₂), 7.9 (s, 3H, H ₁) ppm.
L11	δ = 12.1 (s, 3H, H _{OH}), 9.1 (s, 3H, H ₄), 8.0 (m, 6H, H ₅ +H ₇), 7.7 (d, J = 8 Hz, 6H, H ₃), 7.6 (d, J = 8 Hz, 6H, H ₂), 7.5 (s, 3H, H ₁), 7.0 (m, 6H, H ₆ +H ₈) ppm.
L12	δ = 8.7 (s, 3H, H ₄), 7.6 (m, 6H, H ₅ +H ₇), 7.4 (m, 6H, H ₂ +H ₃), 7.3 (s, 3H, H ₁), 7.2 (m, 6H, H ₆ +H ₈) ppm.

Table 5.2: Summary of FT-IR spectroscopic and ESI mass spectrometric data

Ligand	Asymmetric C=N vibration	Molecular ion peak
L8	1628 cm ⁻¹	[NaC ₃₆ H ₂₇ N ₉] ⁺ at 608.2 m/z
L9	1627 cm ⁻¹	[NaC ₃₉ H ₃₃ N ₉] ⁺ at 650.3 m/z
L10	1629 cm ⁻¹	[NaC ₄₂ H ₃₀ N ₆] ⁺ at 641.1 m/z
L11	1627 cm ⁻¹	[C ₄₅ H ₃₄ N ₃ O ₃] ⁺ at 664.2 m/z
L12	1630 cm ⁻¹	[C ₄₈ H ₃₄ N ₃ O ₆] ⁺ at 748.2 m/z

5.2.3 The crystal structure of L11·2H₂O

The re-crystallisation of **L11** in acetonitrile yielded colourless single crystals suitable for single crystals X-ray diffraction. **L11**·2H₂O crystallises in the orthorhombic crystal system in the space group of *Aba2*. The structure of the ligand

(Figure 5.4) consists of a planar triphenyl-benzene unit to which three coordinating imine ‘arms’ are attached. The phenol ring of each ‘arm’ is twisted relative to the plane of the tri-phenyl benzene core in a propeller-like arrangement. The imine ‘arms’ display dihedral angles of 40.01(2)°, 31.41(2)° and 30.23(2)° with respect to the central benzene ring.

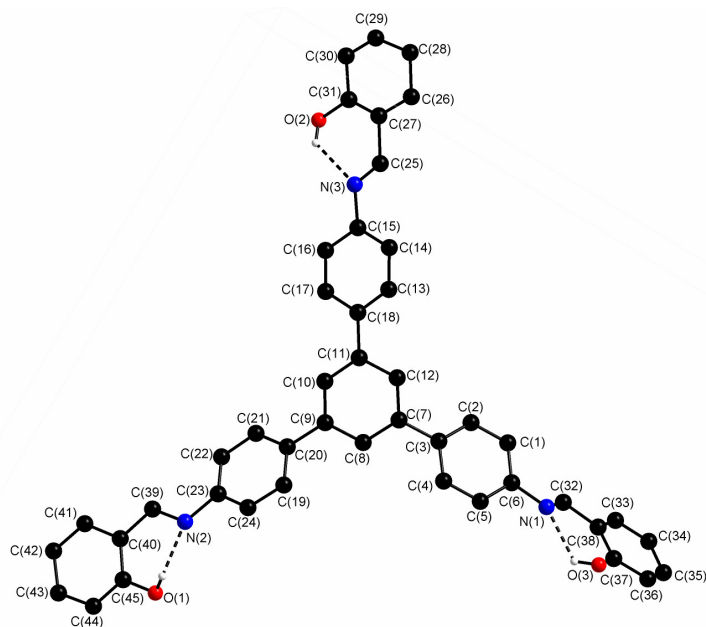


Figure 5.4: The crystal structure of **L11**. (All hydrogen atoms except phenolic H-atoms and constitutional water molecules have been removed for clarity.) C black, O red, N blue and H white. Dashed lines indicate intramolecular hydrogen bonding.

The most notable feature of the molecule is the orientation of the OH groups, which face in the direction of the imino-nitrogen atoms. This arrangement enables the phenol groups to engage in intramolecular hydrogen bonding with the imine nitrogen atoms. The N-O distances for this H-bonding interactions range from 2.546(1) Å to 2.630(1) Å. These distances and other characteristic bond lengths for **L11** are summarised in Table 5.3.

In the solid state, the **L11** molecules are linked by very weak π - π interactions and van der Waals forces resulting in a repeating *abab* stacking arrangement in the direction of the crystallographic *c*-axis (Figure 5.5a). Figure 5.5b highlights the repeating *abab* motif viewed in the crystallographic *ab*-plane. Figure 5.5c reveals the overall packing structure of **L11**·2H₂O, with the constitutional water molecules residing in the void spaces between the neighbouring stacks of **L11** molecules.

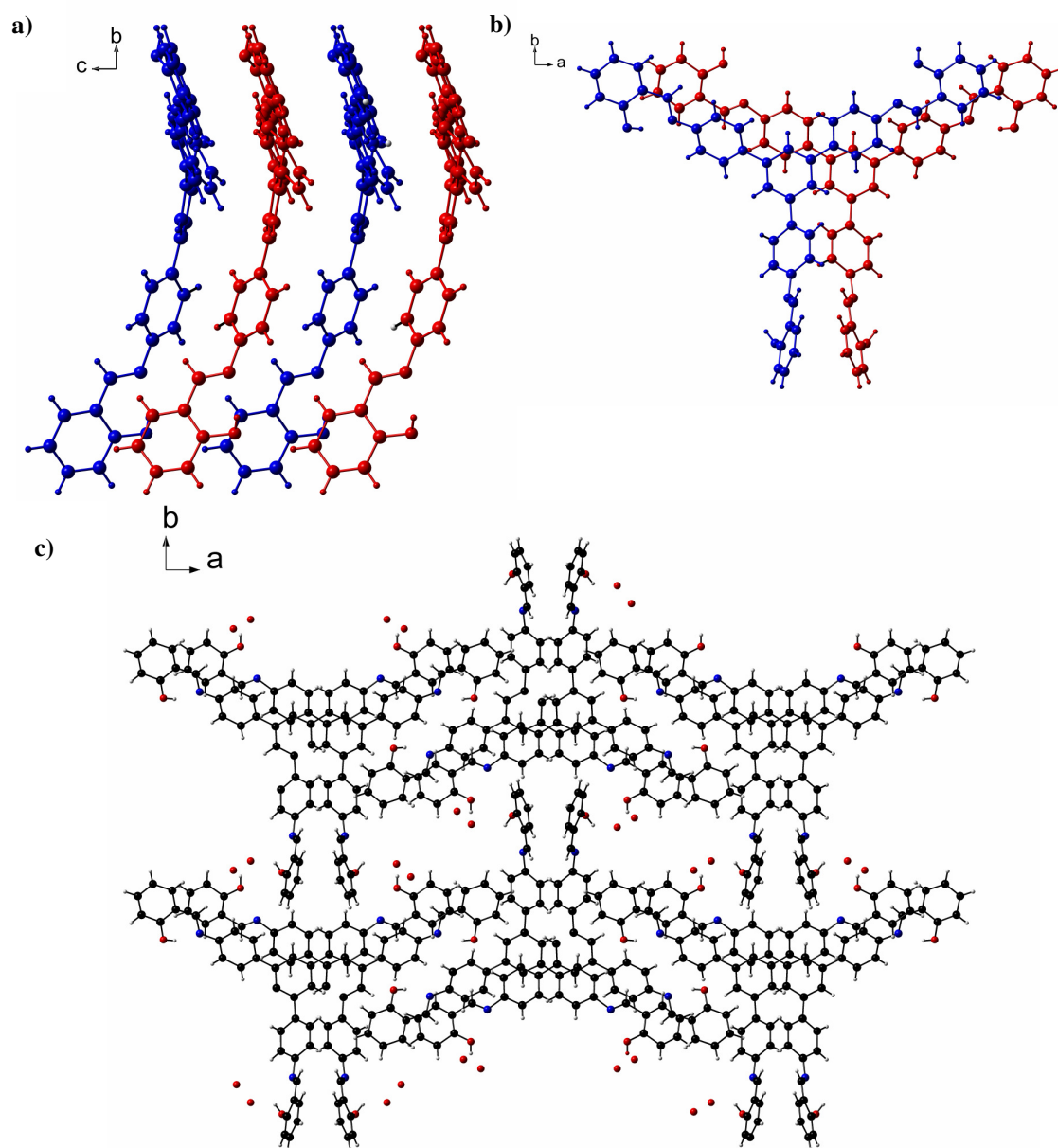


Figure 5.5: The packing arrangement adopted by the **L11** molecules as viewed along **a)** the crystallographic *a*-axis and **b)** the crystallographic *c*-axis. Alternate **L11** molecules coloured red and blue, respectively. **c)** The packing structure of **L11·2H₂O** as viewed along the crystallographic *c*-axis. C black, O red, N blue and H white.

Table 5.3: Selected bond lengths for **L11·2H₂O**

Bond	Bond Length	Bond	Bond Length
N(1)-C(32)	1.252(1) Å	O(3)-C(37)	1.312(1) Å
N(2)-C(39)	1.242(1) Å	O(1)-N(2)	2.613(1) Å
N(3)-C(25)	1.162(1) Å	O(2)-N(3)	2.630 (1) Å
O(1)-C(45)	1.317(1) Å	O(3)-N(1)	2.546(1) Å
O(2)-C(31)	1.416(1) Å		

Table 5.4: Crystal data and structure refinement for **L11·2H₂O**

Identification code	L11·2H₂O	
Empirical formula	C₄₅H₃₈N₃O₅	
Formula weight	700.80 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Ab</i> a2	
Unit cell dimensions	a = 31.576(12) Å	α = 90°
	b = 33.022(13) Å	β = 90°
	c = 7.190(3) Å	γ = 90°
Volume	7497(5) Å ³	
Z	2	
Density (calculated)	1.233 Mg/m ³	
Absorption coefficient	0.081 mm ⁻¹	
F(000)	1580	
Crystal size	0.02 x 0.05 x 0.2 mm ³	
Theta range for data collection	1.23 to 25.00°	
Index ranges	-27 ≤ h ≤ 30, -31 ≤ k ≤ 31, -6 ≤ l ≤ 6	
Reflections collected	12994	
Independent reflections	3476 [R(int) = 0.1461]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3476 / 1 / 544	
Goodness-of-fit on F ²	1.208	
Final R indices [I > 2σ(I)]	R1 = 0.0894, wR2 = 0.2304	
R indices (all data)	R1 = 0.1197, wR2 = 0.2512	
Largest diff. peak and hole	0.862 and -0.304 e.Å ⁻³	

5.2.4 Coordination chemistry of extended Schiff base ligands **L8** - **L12**

Initially, the extended imine ligands **L8** - **L12** were reacted with Fe^{II} salts with the aim of synthesising SCO coordination compounds. These reactions were carried out in dimethylformamide (DMF), dimethylacetamide (DMA) and dimethyl sulfoxide (DMSO) as the solubility of these ligands is low in other organic solvents such as alcohols. Solvothermal synthesis was also employed as a means to form Fe^{II} coordination complexes with these ligands. This synthetic approach led to the formation of insoluble products that proved difficult to structurally elucidate.

To investigate further the transition metal directed self-assembly of these extended imine ligands, they were reacted with various transition metal salts. Again, solubility constraints often led to the formation of non phase-pure products that proved difficult to characterise. However, the reaction of **L8** and **L9** with CoCl₂·6H₂O in DMF did result in the formation of the trinuclear Co^{II} complexes [Co₃(**L8**)₂(H₂O)₆]Cl₆·DMF·9H₂O (**16**) and [Co₃(**L9**)₂(H₂O)₆]Cl₆·DMF·9H₂O (**17**) (Section 5.3) that organise in the solid state to give hexagonal assemblies. The structure of **16** and **17** highlight the binding mode of the extended ligands and may provide insights into the potential of these ligands to form framework structures.

5.3 Synthesis and structural characterisation of [Co₃(**L8**)₂(H₂O)₆]Cl₆·DMF·9H₂O (**16**)

The reaction of two equivalents of **L8** with three equivalents of CoCl₂·6H₂O in dimethylformamide (DMF) yielded a green solution and the slow diffusion of tetrahydrofuran into this solution yielded orange hexagonal single crystals of **16**. These crystals were analysed *via* single crystal X-ray diffraction which showed that compound **16** crystallises in the hexagonal crystal system in the *P*6₁22 space group. This space group was assigned by solving the structure in a monoclinic, lower symmetry space group and by using the program Platon¹⁸⁹ to assign the correct space group and to find the additional symmetry elements. The SQUEEZE¹⁹⁰ routine was employed to refine the crystal structure as there are a large number of disordered solvent molecules contained within the structure. The squeezed and raw crystallographic data are presented in Tables 5.7 and 5.8, respectively.

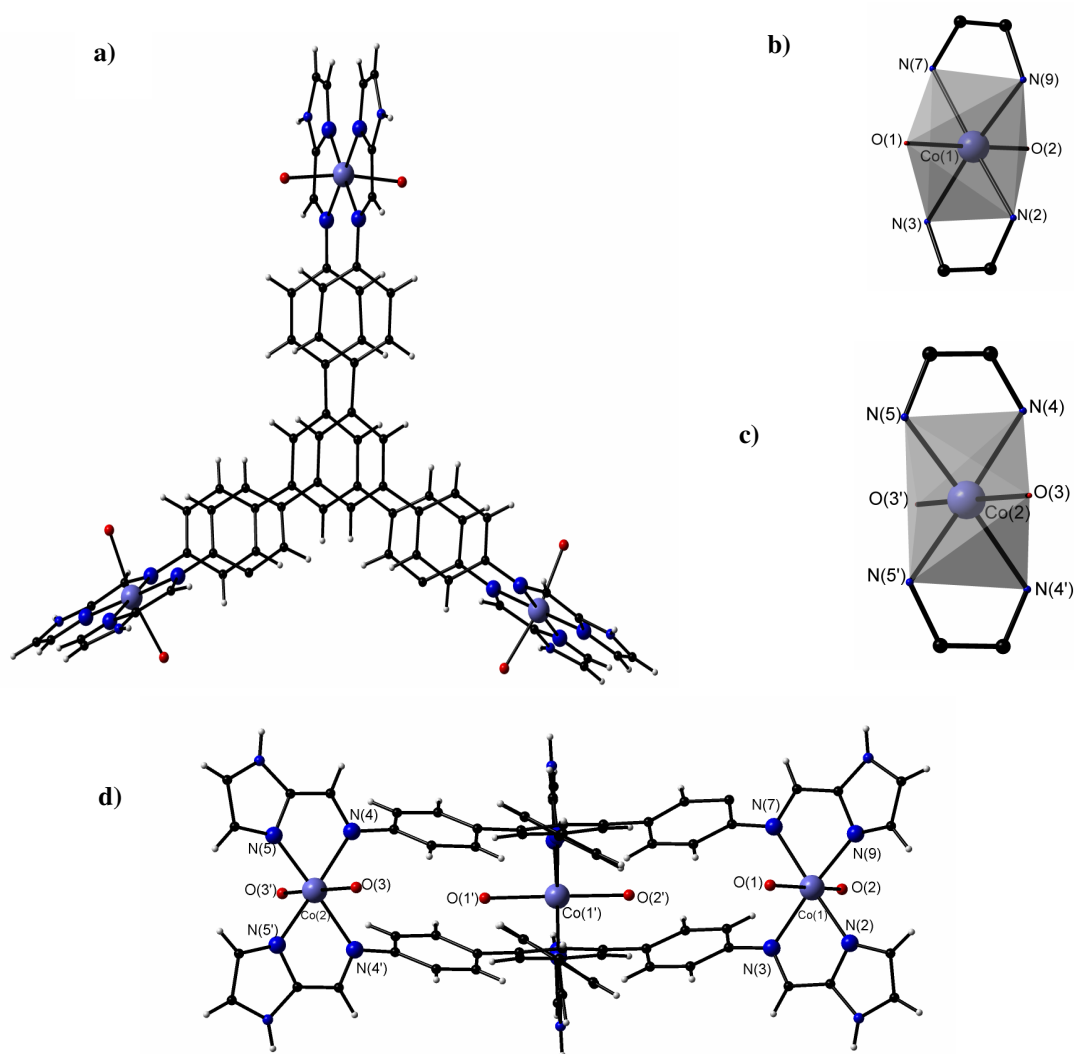


Figure 5.6: **a)** The trinuclear Co^{II} complex contained in **16** (counterions and solvent molecules have been removed for clarity). **b)** The coordination environment of Co(1). **c)** The coordination environment of Co(2). **d)** Alternative view of the trinuclear complex showing the parallel arrangement of the aromatic rings. Co purple, C black, O red, N blue and H white. ' corresponds to the $-x, x-y, 0.1667-z$ positions.

The asymmetric unit of the compound contains only half the formula unit of **16** with the remainder of the structure being generated by symmetry operations. The complex contained within **16** consists of three Co^{II} atoms, coordinated by two **L8** ligands (Figure 5.6). The aromatic ring systems of the two ligands are aligned parallel to each other (Figure 5.6d); the distances between the centroids of the aromatic rings range between 3.628(8) Å and 3.678(2) Å and are characteristic of π - π interactions.

There are two types of cobalt centres within the trinuclear complex, Co(1) and Co(2). They both display distorted octahedral coordination geometries (Figure 5.6b and c) by binding to two imine nitrogen atoms and two imidazole nitrogen atoms, as well as to two oxygen atoms originating from two coordinating water molecules. All the nitrogen donor atoms are located in the equatorial plane of the octahedral

coordination environment, whereby each imine-imidazole moiety acts as a *cis* coordinating bi-dentate functionality. The apical binding sites of the octahedral coordination polyhedra are occupied by water molecules. The bond lengths for the Co-N_{imine} bonds range between 2.179(4) Å and 2.218(5) Å and the Co-N_{imidazole} bond lengths vary between 2.088(5) Å and 2.129(4) Å. The distances for the Co-O_{water} bonds range between 2.113(4) Å and 2.136(4) Å. Selected bond lengths are summarised in Table 5.5.

Table 5.5: Selected bond lengths for **16** [squeezed data]

Bond	Bond Length	Bond	Bond Length
Co(1)-N(2)	2.089(4) Å	Co(1)-O(2)	2.113(4) Å
Co(1)-N(3)	2.218(5) Å	Co(2)-N(4)	2.179(4) Å
Co(1)-N(7)	2.205(4) Å	Co(2)-N(5)	2.088(5) Å
Co(1)-N(9)	2.129(4) Å	Co(1)-O(3)	2.113(4) Å
Co(1)-O(1)	2.136(4) Å		

The deviation of the Co^{II} ions from ideal octahedral coordination geometry can be investigated by examining the bond angles involving Co(1). Atoms that are *cis* to each other have bond angles in the range of 76.25(2)° to 106.67(2)°, deviating significantly from the ideal octahedral angle of 90°. Angles between atoms that are *trans* to each other range between 169.34(2)° and 176.83(2)° and show significant divergence from the ideal 180° angle. The bond angles involving Co(2) are similar and are presented in Table 5.6.

The trinuclear Co^{II} complex contained within **16** carries an overall charge of +6 which is compensated by six Cl⁻ counterions. The solid state packing of these trinuclear complexes and their counterions generates a hexagonal framework structure (Figure 5.7) which contains large channels that run parallel to the crystallographic *c*-axis. The channels have a diameter of *ca.* 18 Å and are filled with disordered solvent molecules.

Table 5.6: Selected bond angles for **16** [squeezed data]

	Bond Angle		Bond Angle
N(2)-Co(1)-N(3)	76.25(2)°	N(7)-Co(1)-N(9)	78.14(2)°
N(2)-Co(1)-N(7)	176.83(2)°	N(7)-Co(1)-O(1)	85.62(2)°
N(2)-Co(1)-N(9)	98.98(2)°	N(7)-Co(1)-O(2)	87.54(2)°
N(2)-Co(1)-O(1)	93.31(2)°	N(9)-Co(1)-O(1)	94.30(2)°
N(2)-Co(1)-O(2)	93.94(2)°	N(9)-Co(1)-O(2)	92.28(2)°
N(3)-Co(1)-N(7)	106.67(2)°	O(1)-Co(1)-O(2)	169.34(2)°
N(3)-Co(1)-N(9)	175.01(2)°	N(4)-Co(2)-N(5)	77.08(2)°
N(3)-Co(1)-O(1)	87.48(2)°	N(4)-Co(2)-O(3)	86.86(2)°
N(3)-Co(1)-O(2)	86.67(2)°	N(5)-Co(2)-O(3)	91.76(2)°

The hexagonal framework structure results from the linking of the $[\text{Co}_3(\text{L8})_2(\text{H}_2\text{O})_6]^{6+}$ complexes *via* weak hydrogen bonding interactions, involving the six coordinating water molecules and the constitutional solvent water molecules. The disordered nature of the constitutional water molecules does not allow a detailed analysis of these interactions. The complexes are further linked through halogen bonding interactions between the Cl^- counterions and the imidazole hydrogen atoms of the **L8** ligand. These interactions occur over distances that range between 2.58(1) Å and 2.62(2) Å. Within the crystallographic *ab*-plane the complexes in **16** arrange as shown in the Figure 5.7a and b. Rotated layers of this arrangement pack in the direction of the crystallographic *c*-axis resulting in the hexagonal packing arrangement shown in Figure 5.7c and d.

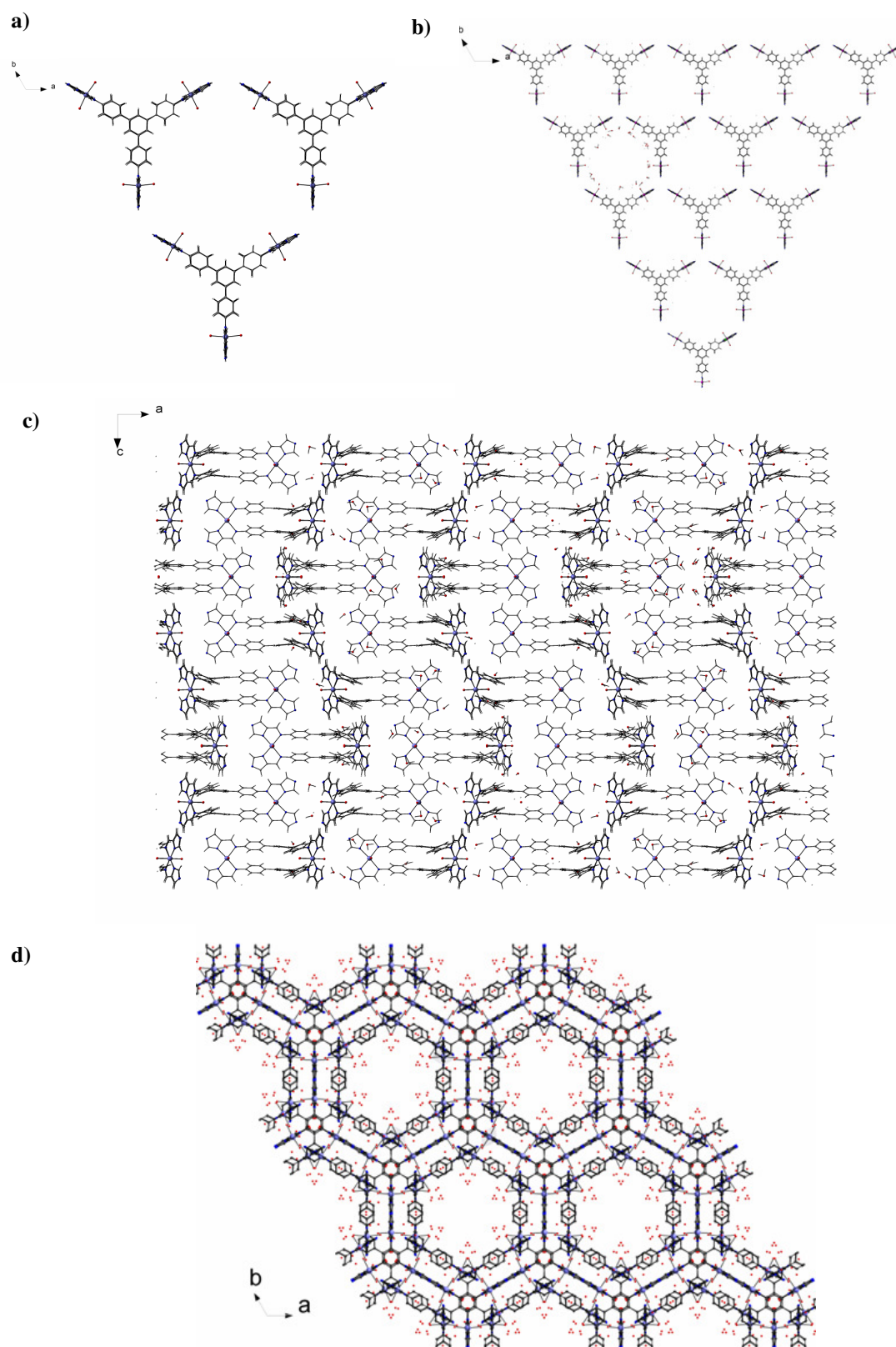


Figure 5.7: a) and b) The packing arrangement of the trinuclear Co^{II} complexes in **16** as seen in the crystallographic ab -plane. The hexagonal packing arrangement of the complexes in **16** as viewed along c) the crystallographic b -axis and d) along the crystallographic c -axis. Co purple, C black, O red, N blue and H white.

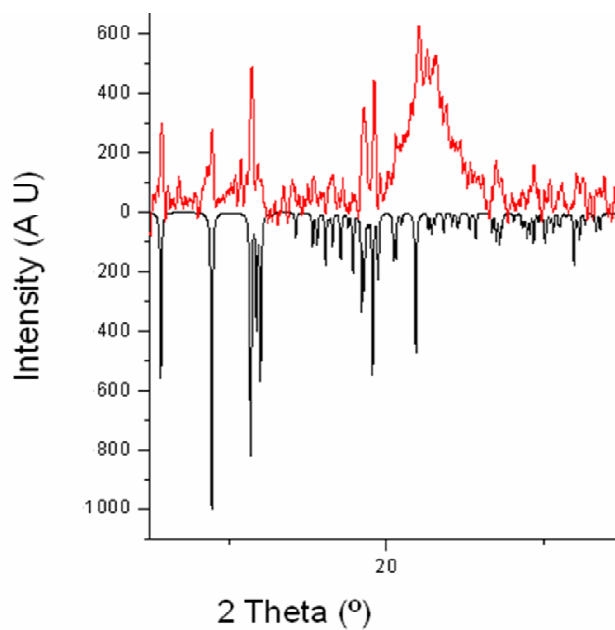
Compound **16** was further characterised by FT-IR spectroscopy revealing a strong asymmetric C=N bond vibration at 1614 cm^{-1} originating from the imine functionalities of the **L8** ligands.¹⁶⁴ The shift of this bond stretch to lower frequency when compared to the free ligand (1628 cm^{-1}) confirms that the Co^{II} ions coordinate to N donor atoms of the imine **L8** ligand.¹⁸⁵ The FT-IR spectrum also shows an asymmetric C=N stretch at 1560 cm^{-1} , an asymmetric C-C stretch at 1506 cm^{-1} and an asymmetric C-N stretch at 1367 cm^{-1} . These latter stretches arise from the methyl-imidazole moiety of the **L8** ligand.¹⁶⁴

X-ray powder diffraction analysis was performed on a microcrystalline sample of **16** (Figure 5.8a). The resultant powder pattern collates well with a pattern that was simulated based on the single crystal X-ray data. This confirms that the bulk material of **16** is phasepure.

To determine the composition of **16**, thermogravimetric analyses (TGA) were carried out on a freshly filtered sample of **16** (Figure 5.8b). The sample was heated to $900\text{ }^{\circ}\text{C}$ in an air atmosphere at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$. A weight loss 16.9% is observed between $45\text{ }^{\circ}\text{C}$ and $110\text{ }^{\circ}\text{C}$. This weight loss can be attributed to loss of six coordinating water molecules and nine constitutional water molecule (calculated weight of 16.4%) from **16**. A further weight loss of 4.3% occurs between $110\text{ }^{\circ}\text{C}$ and $146\text{ }^{\circ}\text{C}$. This weight loss arises from the loss of one dimethylformamide solvent molecule (calculated weight of 4.5%) from **16**. It was also possible that some of the solvent molecules contained in **16** were lost prior to the experiment.

The gradual step-wise oxidative degradation of the organic ligands occurs from *ca.* $200\text{ }^{\circ}\text{C}$. This process involves a total weight loss of 64.7% and involves two thermogravimetric events centred at $490\text{ }^{\circ}\text{C}$ and $555\text{ }^{\circ}\text{C}$. This weight loss corresponds to the combustion of all the carbon, nitrogen and hydrogen atoms of the **L8** ligand (calculated weight loss of 65.8%). The remaining oxide residues obtained during the TGA experiment were not further characterised. The TGA experiment suggests that the composition of **16** can be represented by the formula $[\text{Co}_3(\text{L8})_2(\text{H}_2\text{O})_6]\text{Cl}_6\cdot\text{DMF}\cdot 9\text{H}_2\text{O}$. This constitutional assignment of samples stored at room temperature was further confirmed by CHN microanalysis.

a)



b)

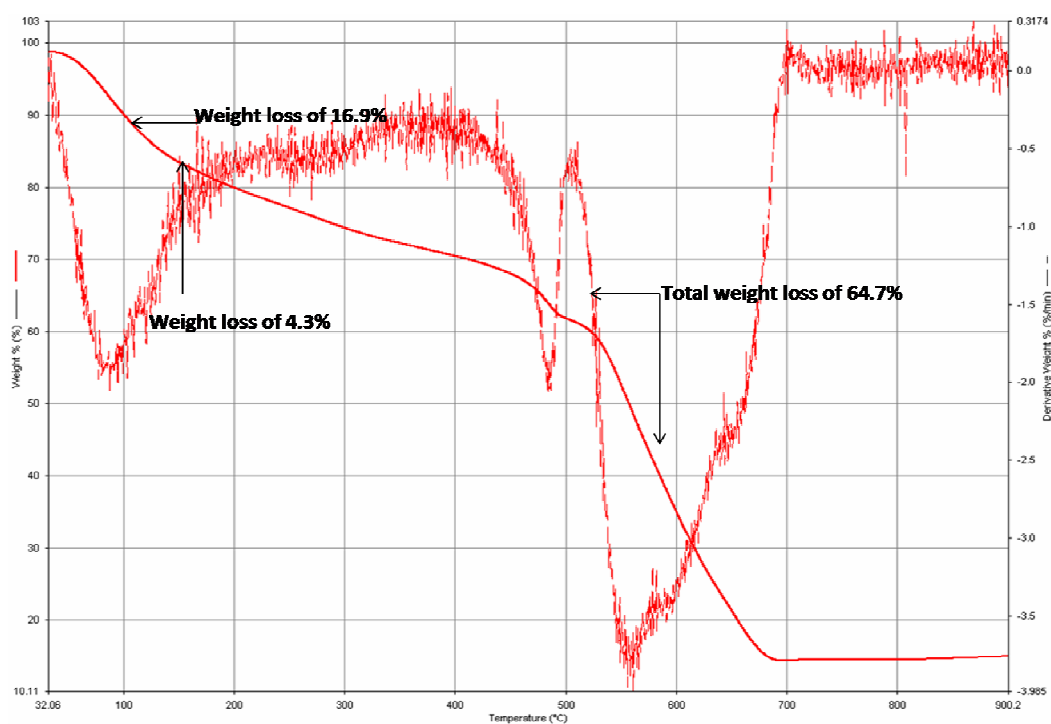


Figure 5.8: a) The X-ray powder diffraction pattern of compound **16** (Red: The measured pattern. Black: The simulated pattern based on the single crystal data for **16**.) b) The thermogravimetric analysis (TGA) carried out on a microcrystalline sample of **16**.

Table 5.7: Crystal data and structure refinement for **16** [squeezed data]

Identification code	16	
Empirical formula	$\text{Co}_3\text{C}_{75}\text{H}_{91}\text{N}_{19}\text{O}_{16}\text{Cl}_6$	
Formula weight	1904.17 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	$P6_122$	
Unit cell dimensions	$a = 24.2977(17)$ Å	$\alpha = 90^\circ$
	$b = 24.2977(17)$ Å	$\beta = 90^\circ$
	$c = 53.285(4)$ Å	$\gamma = 120^\circ$
Volume	27244(3) Å ³	
Z	6	
Density (calculated)	0.547 Mg/m ³	
Absorption coefficient	0.340 mm ⁻¹	
F(000)	4428	
Crystal size	0.25 x 0.3 x 0.05 mm ³	
Theta range for data collection	0.97 to 25.00°	
Index ranges	-28 ≤ h ≤ 28, -28 ≤ k ≤ 28, -63 ≤ l ≤ 63	
Reflections collected	296060	
Independent reflections	16106 [R(int) = 0.1981]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	16106 / 0 / 496	
Goodness-of-fit on F ²	0.943	
Final R indices [I > 2σ(I)]	R1 = 0.0735, wR2 = 0.1869	
R indices (all data)	R1 = 0.1261, wR2 = 0.2034	
Largest diff. peak and hole	0.514 and -0.385 e.Å ⁻³	

Table 5.8: Crystal data and structure refinement for **16** [raw data]

Identification code	16	
Empirical formula	$\text{Co}_3\text{C}_{75}\text{H}_{91}\text{N}_{19}\text{O}_{16}\text{Cl}_6$	
Formula weight	1904.17 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	$P6_122$	
Unit cell dimensions	a = 24.2977(17) Å	$\alpha = 90^\circ$
	b = 24.2977(17) Å	$\beta = 90^\circ$
	c = 53.285(4) Å	$\gamma = 120^\circ$
Volume	27244(3) Å ³	
Z	6	
Density (calculated)	0.547 Mg/m ³	
Absorption coefficient	0.340 mm ⁻¹	
F(000)	4428	
Crystal size	0.25 x 0.3 x 0.05 mm ³	
Theta range for data collection	0.97 to 25.00°	
Index ranges	-28 ≤ h ≤ 28, -28 ≤ k ≤ 28, -63 ≤ l ≤ 63	
Reflections collected	296060	
Independent reflections	16106 [R(int) = 0.1981]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	16106 / 0 / 592	
Goodness-of-fit on F ²	1.353	
Final R indices [I > 2σ(I)]	R1 = 0.1269, wR2 = 0.3635	
R indices (all data)	R1 = 0.1716, wR2 = 0.3877	
Largest diff. peak and hole	0.982 and -0.625 e.Å ⁻³	

5.4 UV-vis compleximetric titration studies to characterise the formation of the Co^{II} complexes in 16

In order to investigate the formation of the trinuclear Co^{II} complexes in solution, an UV-vis compleximetric titration study (Figure 5.9) was conducted. Solutions of **L8** and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were prepared in dimethylformamide (DMF). Figure 5.9 shows the UV-vis spectral changes upon addition of sub-stoichiometric quantities of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ to a solution of **L8**. Spectra were recorded after each addition and additions were continued until super-imposable spectra were obtained. It is evident that the spectrum of **L8** changes upon addition of Co^{II} .

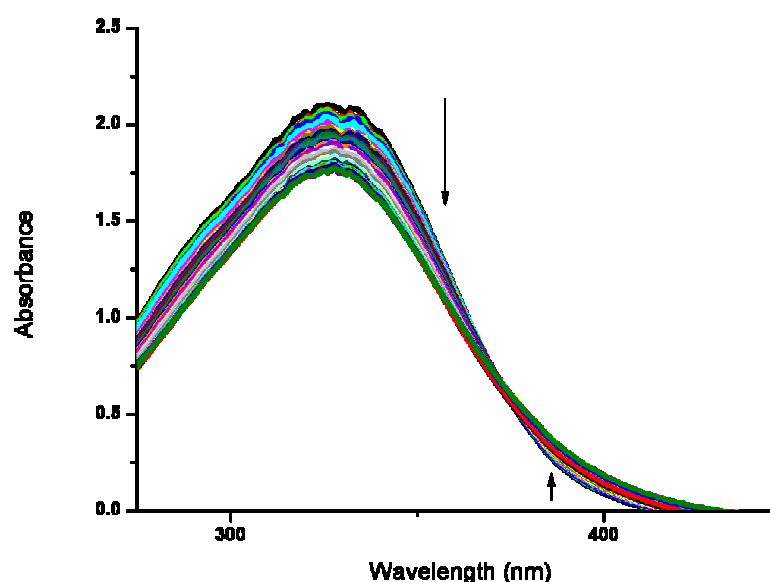


Figure 5.9: UV-vis spectral changes of a DMF solution of **L8** upon addition of a DMF solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. $[\text{L8}] = 8 \times 10^{-5} \text{ mol L}^{-1}$ and $[\text{Co}^{\text{II}}] = 8 \times 10^{-4} \text{ mol L}^{-1}$.

There is a decrease in the absorbance of the ligand $\pi\text{-}\pi^*$ band at 320 nm and the emergence of a new very weak band at 400 nm, which is characteristic of the formation of the Co^{II} complex. A molar ratio plot (Fig 5.10) showing the change in absorbance of the 320 nm band as a function of equivalents of Co^{II} added to the **L8** solution, clearly demonstrates the formation of a 3:2 metal to ligand complex in solution. The titration profile reaches a maximum after 1.5 equivalents of Co^{II} were added and no further changes are observed upon the addition of excess CoCl_2 . This data is in agreement with the formation of a $[\text{Co}^{\text{II}}_3\text{L8}_2]^{6+}$ species in solution, thus verifying the formation of the trinuclear Co^{II} complex.

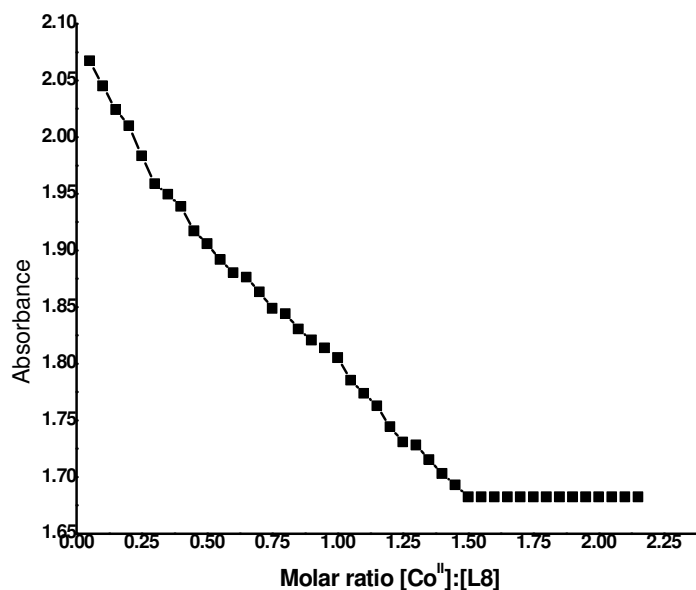


Figure 5.10: Mole ratio plot showing the change in absorbance at 320 nm as a function of Co^{II} added to the **L8** solution.

5.5 Synthesis and characterisation of $[\text{Co}_3(\text{L9})_2(\text{H}_2\text{O})_6]\text{Cl}_6 \cdot \text{DMF} \cdot 9\text{H}_2\text{O}$ (**17**)

The reaction of **L9** with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ under the same reaction conditions that produced **16**, yielded a microcrystalline green powder (**17**). The structural characterisation of this material was impossible by single crystal X-ray diffraction. However, other characterisation techniques (FT-IR spectroscopy, X-ray powder diffraction and TGA) were employed to characterise the compound. The FT-IR spectrum of **17** is similar to that of **16** (Figure 4.11a). Both spectra show evidence of asymmetric $\text{C}=\text{N}$ bond stretches that arises from the imine ligands. In **17** this characteristic vibration occurs at 1615 cm^{-1} .¹⁶⁴ The shift of this bond stretch to lower frequency when compared to the free ligand (1627 cm^{-1}) confirms the coordination of the Co^{II} ions to the **L9** ligand.¹⁸⁵ The spectrum of **17** also shows the characteristic bond vibrations associated with the methyl-imidazole functionalities of the Schiff base ligand **L9**.¹⁶⁴

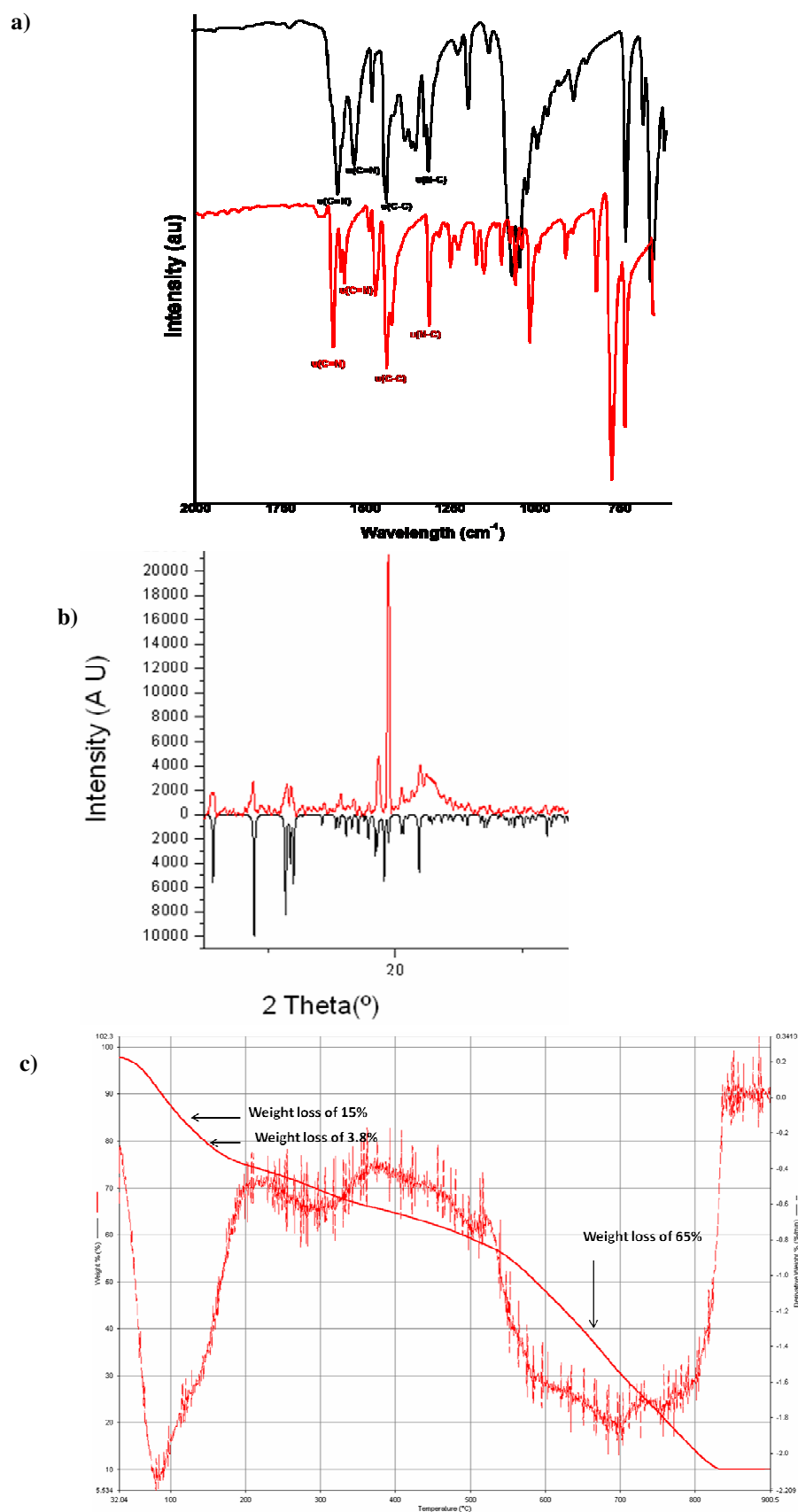


Figure 5.11: a) The FT-IR spectrum of compound **17** (red) as compared to that of compound **16** (black). b) The X-ray powder diffraction pattern of compound **17**. (Red: The measured pattern. Black: The simulated pattern based on the single crystal data for **16**.) c) The thermogravimetric analysis (TGA) carried out on a microcrystalline sample of **17**.

The powder X-ray diffraction pattern of **17** (Figure 5.11b) is very similar to that of **16** and fits well with the simulated data based on the single crystal structure of **16**. This result suggests that compounds **16** and **17** have closely related structures.

To characterise the composition of **17**, a TGA experiment was carried out using a freshly filtered sample of **16** (Figure 5.11c). The sample was heated to *ca.* 900 °C in an air atmosphere at a heating rate of 10 °C min⁻¹. Between 45 °C and 120 °C, a weight loss of 15% is observed. This weight loss can be attributed to loss of six coordinating water molecules and nine constitutional water molecule (calculate weight 15.6%) from **17**. A further weight loss of 3.8% occurs between 120 °C and 155 °C. This corresponds to the loss of one solvent DMF molecule (calculate weight of 4.2%) from **17**. The compound then begins to undergo a stepwise thermal decomposition starting at *ca.* 200 °C. This process involves two thermogravimetric events centred at 485 °C and 560 °C and accounts for an overall weight loss of 65%. This weight loss can be accounted for by the combustion of the carbon, nitrogen and hydrogen atoms of the organic ligands in **17** (calculated weight 66.5%). The remaining oxide residues of the TGA were not further characterised. The TGA experiment suggests that the composition of **17** can be described by the formula [Co₃(**L9**)₂(H₂O)₆]Cl₆·DMF·9H₂O. The CHN microanalysis further supports this assignment.

UV-vis compleximetric titrations studies monitoring the reaction of **L9** and CoCl₂·6H₂O in dimethylformamide (Figure 5.12a and b) were also carried out. Again there are clear changes in the spectra of **L9** upon the addition of the CoCl₂ (Figure 5.12a). The absorbance due to the ligand π - π^* transition at 320 nm decreases and a new band at *ca.* 400 nm emerges upon each subsequent addition of Co^{II} ions. A plot that shows the change in absorbance as a function of Co^{II} equivalents added (Figure 5.12b) gives a titration profile which reaches a maximum at a molar ratio of *ca.* 1.5. Therefore these UV-vis experiments support the formation of the [Co^{II}₃**L9**₂]⁶⁺ species in solution as a 3:2 species is observed.

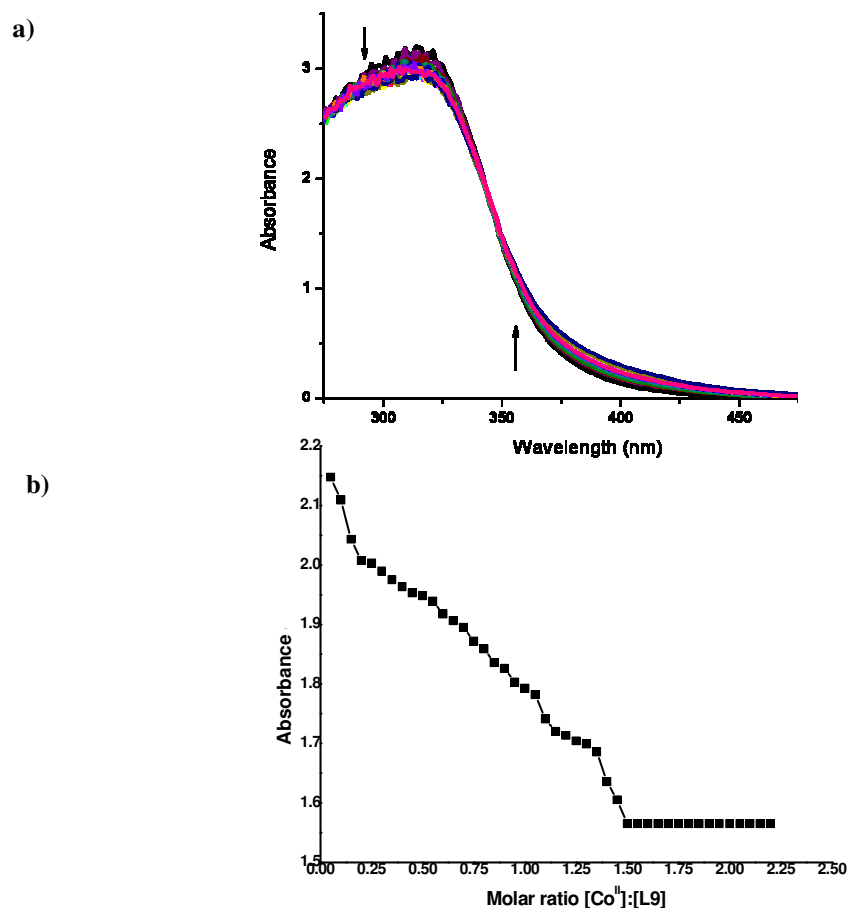


Figure 5.12: a) UV-vis spectral changes of a DMF solution of **L9** upon addition of a DMF solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. $[\text{L9}] = 8 \times 10^{-5} \text{ mol L}^{-1}$ and $[\text{Co}^{\text{II}}] = 8 \times 10^{-4} \text{ mol L}^{-1}$. b) Mole ratio plot showing the change in absorbance at 320 nm as a function of Co^{II} added to the **L9** solution.

5.6 Surface area determination for compound **16**

As compound **16** contained solvent filled channels we decided to determine the surface area of the compound and thus investigate the propensity of this material for gas storage purposes. Initially, the solvent guest molecules were removed from the channels by evacuating a sample of compound **16** at 100 °C for 24 hours. The permanent porosity of compound **16** after desolvation was demonstrated by recording N_2 absorption/desorption isotherm (Figure 5.13a) at 77K.

The BET surface area of compound **16** was estimated to be $87 \text{ m}^2 \text{ g}^{-1}$. To evaluate the pore size distribution, the N_2 isotherm was analysed using a density functional theory model (NLDTF) based on a zeolite/silica compound containing cylindrical pores (Figure 5.13b).¹⁹¹ The distribution calculated by fitting this data revealed that the average pore width is within the realm of an ultramicropore ($< 3 \text{ \AA}$). The calculated pore width is much shorter than the diameter of the channels in **16** (18

Å) determined crystallographically. This suggests that the solid state structure of **16** collapses upon desolvation.

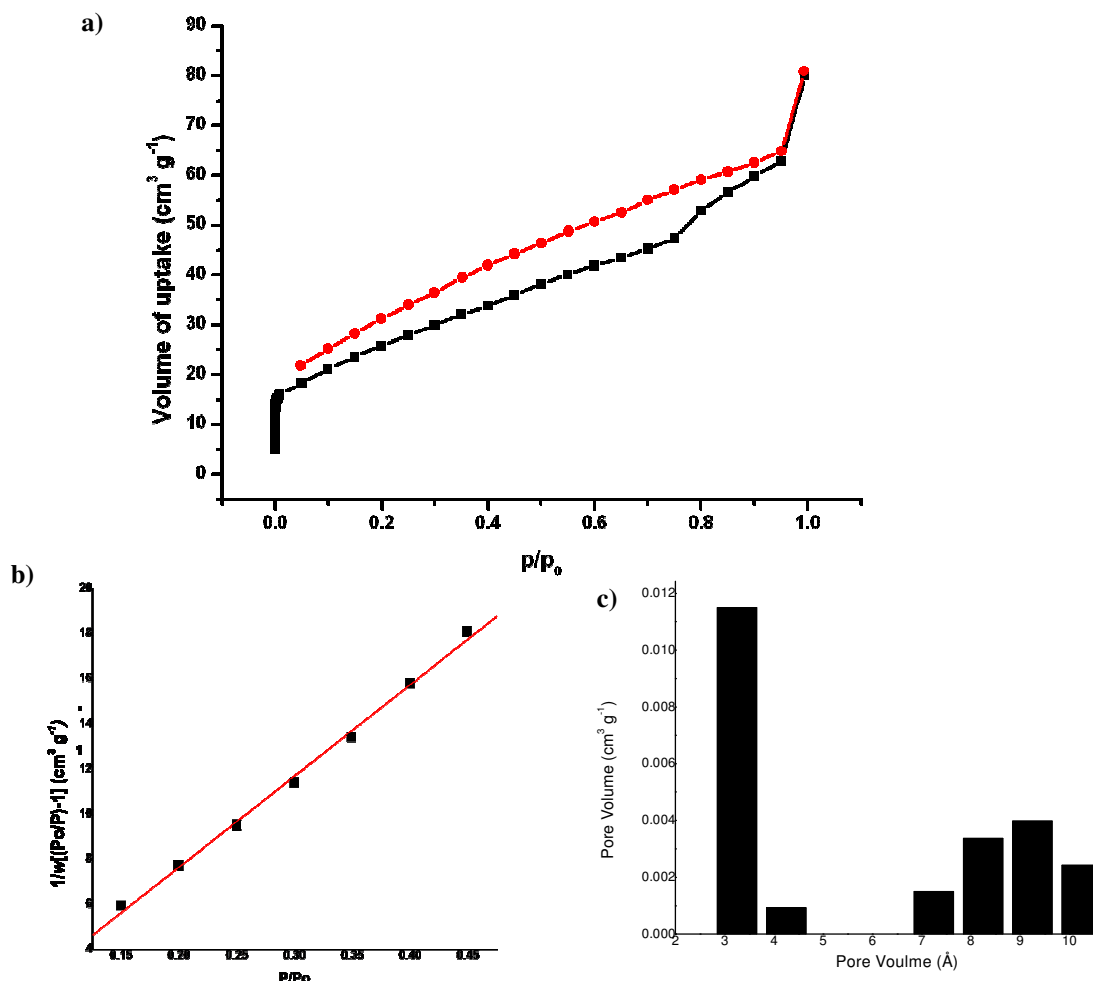


Figure 5.13: a) The N₂ isotherm for compound **16** after desolvation at 77K (black curve is adsorption and red curve is desorption). b) Plot of the linear region of the BET equation for **16**. c) Pore size distribution for **16** calculated from a NLDFT fit to the N₂ adsorption data.¹⁹¹

We also determined the H₂ absorption isotherm on a desolvated sample of compound **16** (Figure 5.14). This data suggests that the compound shows, as expected, limited H₂ uptake of 2.67 mg g⁻¹ (1.46 g L⁻¹) at 77 K and at 1 bar. This equates to a hydrogen storage capacity of 0.03 wt%. This value is low in comparison to ultra high surface area MOFs.^{192,193} These materials reveal H₂ uptake capacities of *ca.* 22-24 g L⁻¹.^{192,193} So in order to produce materials that show higher H₂ uptake it is necessary to provide higher surface area materials with robust and stable framework structures.

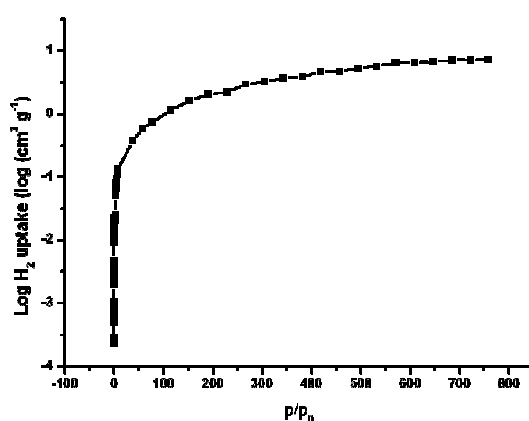


Figure 5.14: The H₂ isotherm for compound **16** after desolvation at 77K.

5.7 Conclusion

A series of novel extended Schiff base ligands (**L8** - **L12**) have been successfully synthesised. To investigate the coordination chemistry of these ligands, they were reacted with a variety of transition metal salts in dimethylformamide solutions. This work has led to the formation of the coordination compounds **16** and **17**. These compounds contain trinuclear complexes that consist of three Co^{II} atoms linked by two extended Schiff base ligands. In the solid state, the Co^{II} complexes are linked *via* weak supramolecular interactions to form packing assemblies with hexagonal topology. As these compounds also contain large solvent filled channels, the gas absorption properties of **16** were investigated. The BET surface area of **16** was estimated to be 87 m² g⁻¹. **16** was also shown to display a negligible H₂ gas storage capacity. The limited gas storage ability of **16** arises from the fact that its solid state structure collapses upon desolvation. This result underlines that high surface area materials with robust structures are required for advanced gas storage applications.

The single crystal X-ray diffraction data obtained for **16** demonstrates that each imine-imidazole head group of **L8** adopts a *cis* coordinating bidentate binding mode within the trinuclear Co^{II} complexes. It is likely that the imine groups of the other extended ligands **L9** - **L12** would adopt similar binding modes upon complexation with transition metal ions. This highlights the potential these extended ligands have for the formation of framework structures.

Chapter Six

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The self-assembly of lithium coordination networks stabilised by carboxylate ligands

6.1 Introduction

The depletion of the world's fossil fuels coupled with the effects of global warming has created a need for the development of alternative fuel sources. Hydrogen is an ideal candidate for this purpose as it has a higher energy per unit mass than the fuel sources currently employed and the only product of its combustion is water.²⁷ However, it has proven difficult to develop a safe and cost effective storage medium for hydrogen. Therefore, a lot of current research focuses on the synthesis of new materials in which hydrogen can be stored safely allowing it to be utilised for energy production.²⁸

Lithium containing materials such as Li_3N ¹⁹⁴ can be exploited in the storage of hydrogen as hydride materials. Another strategy for gas storage involves the use of porous metal-organic frameworks to trap hydrogen gas molecules *via* physisorption.²⁸ To date most attention has focused on the use of first row transition metal ions and polyaromatic carboxylate ligands to generate these metal-organic frameworks.^{15,19} Surprisingly, carboxylic acid substituted aromatic ligands have rarely been employed in attempts to form metal-organic frameworks with lightweight metals such as lithium and magnesium.^{195,196} Lithium is of particular interest as theoretical studies have shown that lithium doped frameworks display a two-fold increase in H_2 uptake capacity.^{162,163} This increase can be contributed to strong electrostatic interactions between uncoordinated lithium sites and the hydrogen gas molecules. Recently, lithium coordination frameworks have also been developed that exhibit enhanced hydrogen storage capacity.¹⁹⁵

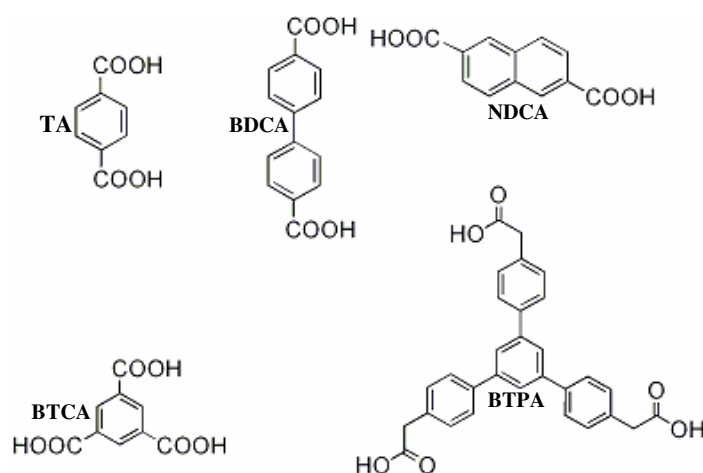


Figure 6.1: Structure of the carboxylate ligands used in the formation of lithium based coordination networks. **TA** = Terephthalic acid, **BDCA** = 4,4'-biphenyl dicarboxylic acid, **NDCA** = 2,6-naphthalene dicarboxylic acid **BTCA**= 1,3,5-benzenetricarboxylic acid and **BTPA** = 1,3,5-benzenetri(phenylacetic acid)

Inspired by these studies, terephthalic acid (**TA**), 4,4'-biphenyl dicarboxylic acid (**BDCA**), 2,6-naphthalene dicarboxylic acid (**NDCA**), 1,3,5-benzenetricarboxylic acid (**BTCA**) and 1,3,5-benzenetri-(phenylacetic acid) (**BTPA**) (Figure 6.1) would be utilised in attempts to generate lithium frameworks. It was envisaged that this synthetic approach could give rise to the formation of novel lightweight frameworks that may display increased hydrogen storage capacities.

6.2 Synthesis and characterisation of 1,3,5-benzenetri-(phenylacetic acid) (**BTPA**)

With the aim of generating porous lithium coordination networks in mind, the novel ligand 1,3,5-benzenetri-(phenylacetic acid) (**BTPA**) (Figure 6.2) was designed and successfully synthesised.

BTPA was prepared from 1,3,5-benzene-triacetophenone which was synthesised following literature procedures in moderate yields (60 %).¹⁹⁷ 1,3,5-Benzene-triacetophenone was then reacted with boron trifluoride etherate and lead tetraacetate resulting in the generation of 1,3,5 benzene-tri(methyl phenylacetate) which was subsequently treated with 2M NaOH yielding 1,3,5-benzenetri(phenylacetic acid) (**BTPA**).

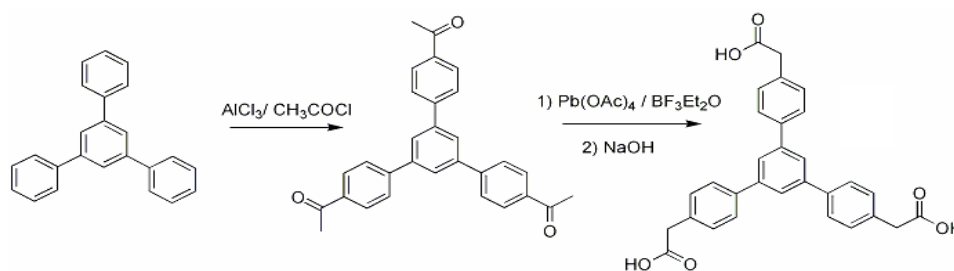


Figure 6.2: Synthetic route for the formation of 1,3,5-benzenetri-(phenylacetic acid) (**BTPA**).

BTPA was characterised by ¹H NMR spectroscopy (Figure 6.3). The ESI mass spectrum of **BTPA** shows the expected [C₂₇H₁₈O₆]⁺ molecular ion peak at 481.1 m/z and the FT-IR spectrum shows strong asymmetric and symmetric carboxylate stretches at 1671 cm⁻¹ and 1392 cm⁻¹, respectively.¹⁶⁴ Elemental analysis (CHN) also confirmed the composition of **BTPA**.

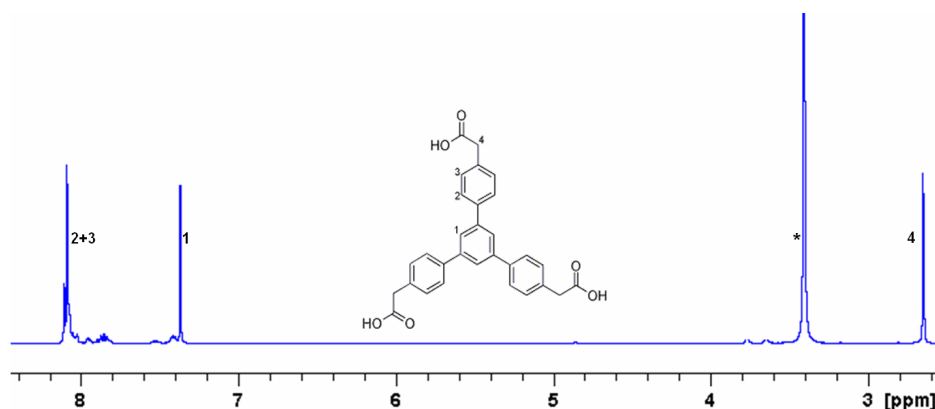


Figure 6.3: The 400 MHz ^1H NMR (D_6 -DMSO) spectrum and assignment for 1,3,5-benzenetri(phenylacetic acid) (**BTPA**). (* demotes residual solvent MeOH)

BTPA was then reacted systematically with a variety of lithium salts under solvothermal conditions. Unfortunately, the applied synthetic approach only yielded insoluble non-crystalline materials that have proved difficult to structurally characterise.

6.3 Synthesis and structural characterisation of $[\text{Li}_2(\text{C}_8\text{H}_4\text{O}_4)]$ (**18**)

The reaction of terephthalic acid (**TA**) with two equivalents of $\text{Li}(\text{OH})\cdot\text{H}_2\text{O}$ under solvothermal conditions, in methanol at 145°C , yielded colourless plate like crystals of $[\text{Li}_2(\text{C}_8\text{H}_4\text{O}_4)]$ (**18**). These crystals were characterised by single crystals X-ray diffraction. These measurements revealed that the structure of **18** consists of a densely packed 3D Li framework (Figure 6.4).

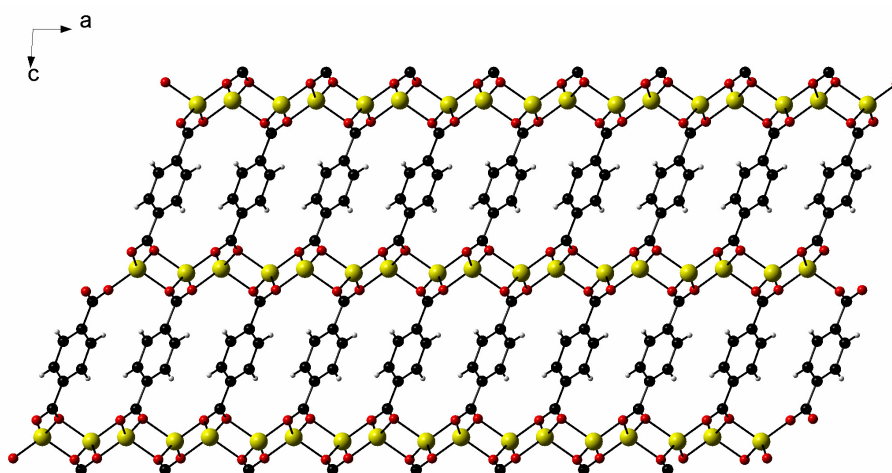


Figure 6.4: The structure of the 3D network of **18** as viewed along the crystallographic b -axis. Li yellow, C black, O red and H white.

18 crystallises in the monoclinic $P2_1/c$ space group. The asymmetric unit of **18** contains half the formula unit with the reminder of the complex being generated by symmetry operations. Each Li ion in **18** binds to four carboxylate O atoms from four different **TA** ligands (Figure 6.5). The Li-O bond lengths range between 1.909(1) Å and 1.973(3) Å. Details regarding the Li-O bond lengths are further summarised in Table 6.1.

The Li ions in **18** display distorted tetrahedral coordination geometries (Figure 6.5). The distorted nature of the tetrahedron is best illustrated by considering some of the bond angles of the coordination sphere of Li(1). These angles vary from 91.99(2)° to 123.06(2)° and all diverge significantly from the ideal tetrahedral angle of 109.5°. Important bond angles involving Li(1) are further summarised in Table 6.1.

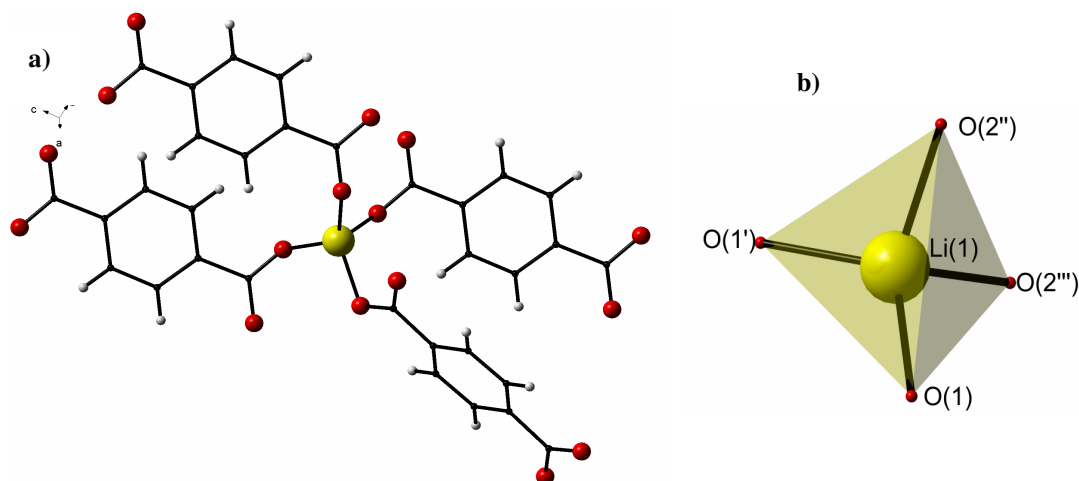


Figure 6.5: a) The binding arrangement of Li ions in **18**, each binding to four different **TA** ligands. b) The coordination environment of Li(1). Li yellow, O red, C black and H white. (' refers to the $-x$, $0.5+y$, $0.5-z$ positions, " refers to the x , $1+y$, z positions and "' refers to the $-x$, $2-y$, $-z$ positions)

Each O donor atom from the **TA** ligand binds to two separate Li ions (Figure 6.6a). The carboxylate functionalities of the ligand are also employed to further link the Li ions resulting in the formation of a 2D Li-O sheet which is displayed in Figure 6.6b. These 2D sheets are built from a series of edge sharing dimeric units (Figure 6.6c). The polyhedra of the dimer units are further connected through the vertices. This binding motif results in the generation of 2D Li-O sheets that extend in the (110) plane. Within the 2D sheets, the lithium atoms are contained within a twelve membered $\{-\text{Li-O-Li}\}$ ring-shaped arrangement (Figure 6.6d).

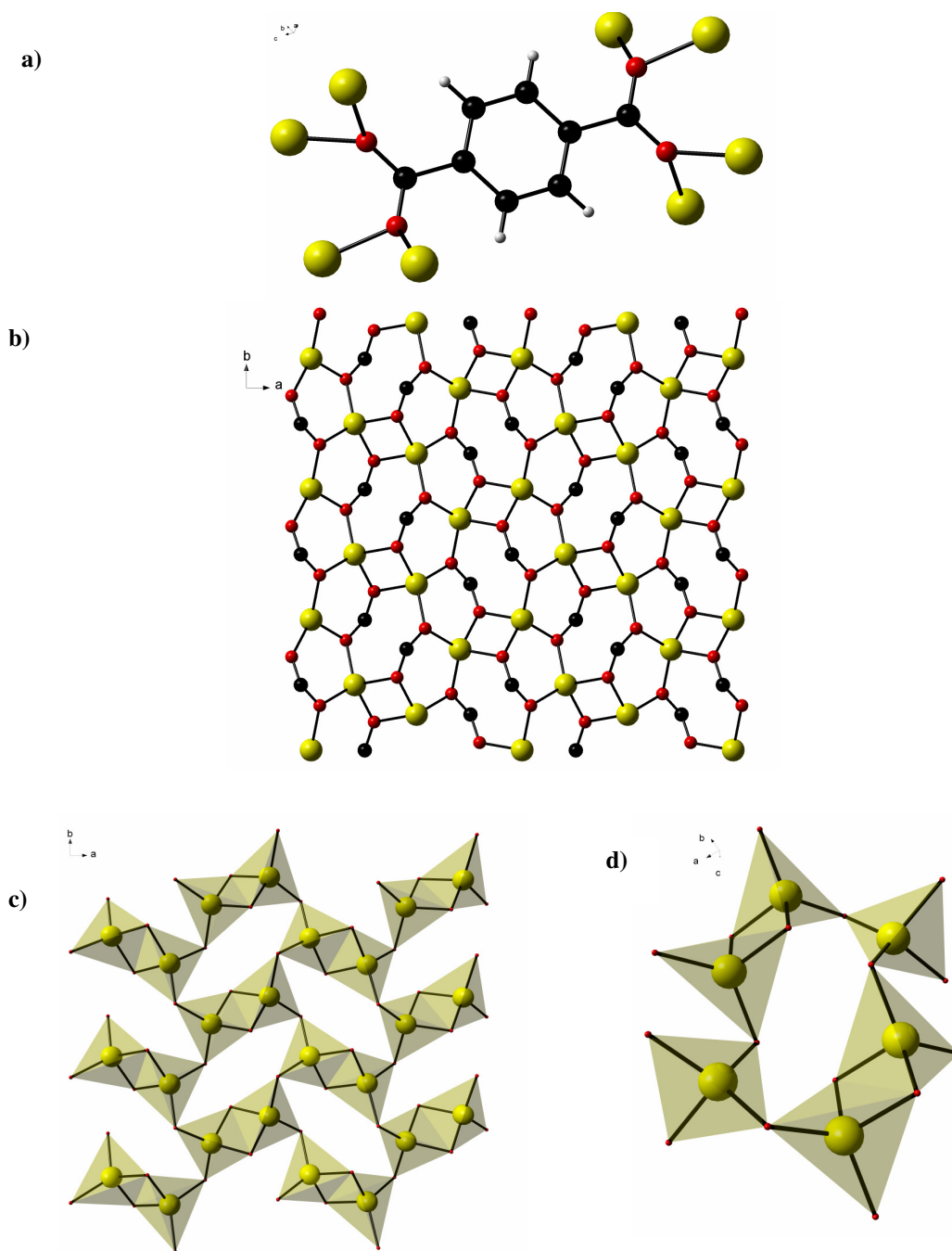


Figure 6.6: **a)** Representation of the binding mode of the **TA** ligands. **b)** The 2D Li-O sheets in **18** as viewed along the crystallographic *c*-axis. (The aromatic rings of the **TA** ligands have been removed for clarity). **c)** Polyhedral representation of the 2D Li-O sheet as seen in **18**. **d)** The twelve membered ring motif in **18**. (C and H atoms have been removed for clarity.) Li yellow, O red, C black and H white.

The 2D Li-O layers are connected by the phenyl moieties of the **TA** ligands that pillar between the sheets and link them in the direction of the crystallographic *c*-axis, resulting in the overall 3D framework structure (Figure 6.4). The Li-O layers are separated by a distance of 6.6 Å.

Table 6.1: Selected bond lengths and angles for **19**

Bond	Bond Length	Bond Angle
Li(1)-O(1)	1.962(6) Å	O(1)-Li(1)-O(1') 119.25(2)°
Li(1)-O(1')	1.969(2) Å	O(1)-Li(1)-O(2'') 123.06(2)°
Li(1)-O(2'')	1.909(1) Å	O(1)-Li(1)-O(2''') 103.19(3)°
Li(1)-O(2''')	1.973(3) Å	O(1')-Li(1)-O(2'') 104.70(2)°
		O(1')-Li(1)-O(2''') 110.85(2)°
		O(2'')-Li(1)-O(2''') 91.99(2)°

Symmetry transformations used to generate equivalent atoms:

' = - x, 0.5+y, 0.5-z, '' = x, 1+y, z and ''' = -x, 2-y, -z

Compound **18** was further characterised by FT-IR spectroscopy which showed the presence of the carboxylate ligands and revealed strong asymmetric and symmetric carboxylate bond stretches at 1611 cm⁻¹ and 1488 cm⁻¹.¹⁶⁴ CHN microanalysis was also employed to confirm the composition of **18**.

Table 6.2: Crystal data and structure refinement for **18**

Identification code	18	
Empirical formula	Li ₂ C ₈ H ₄ O ₄	
Formula weight	177.99 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 8.3220(17) Å <i>b</i> = 5.1300(10) Å <i>c</i> = 8.3600(17) Å	<i>α</i> = 90.00(3)° <i>β</i> = 93.86(3)° <i>γ</i> = 90.00(3)°
Volume	356.09(12) Å ³	
<i>Z</i>	4	
Density (calculated)	1.660 Mg/m ³	
Absorption coefficient	0.129 mm ⁻¹	
<i>F</i> (000)	180	
Crystal size	0.3 x 0.4 x 0.05 mm ³	
Theta range for data collection	2.44 to 25.00°	
Index ranges	-9 ≤ <i>h</i> ≤ 6, -4 ≤ <i>k</i> ≤ 6, -8 ≤ <i>l</i> ≤ 9	
Reflections collected	1803	
Independent reflections	1176 [<i>R</i> (int) = 0.0130]	
Completeness to theta = 25.00°	99.5 %	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	588 / 0 / 64	
Goodness-of-fit on <i>F</i> ²	0.746	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0309, <i>wR</i> 2 = 0.0811	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0367, <i>wR</i> 2 = 0.1241	
Largest diff. peak and hole	0.344 and -0.317 e.Å ⁻³	

6.4 Synthesis and structural characterisation of $[\text{Li}_2(\text{C}_{14}\text{H}_8\text{O}_4)]$ (**19**)

We decided to modify our ligand system in order to extend the distance between the Li-O sheets with the aim of generating a new compound with increased void spaces and enhanced porosity. With this in mind 4,4'-biphenyl dicarboxylic acid (**BDCA**) was reacted with two equivalents of LiCl under solvothermal conditions at 145 °C, using a 1:1 mixture of dimethylformamide and methanol as the solvent. This yielded colourless crystals of $[\text{Li}_2(\text{C}_{14}\text{H}_8\text{O}_4)]$ (**19**), which were suitable for structural analysis by single crystal X-ray diffraction.

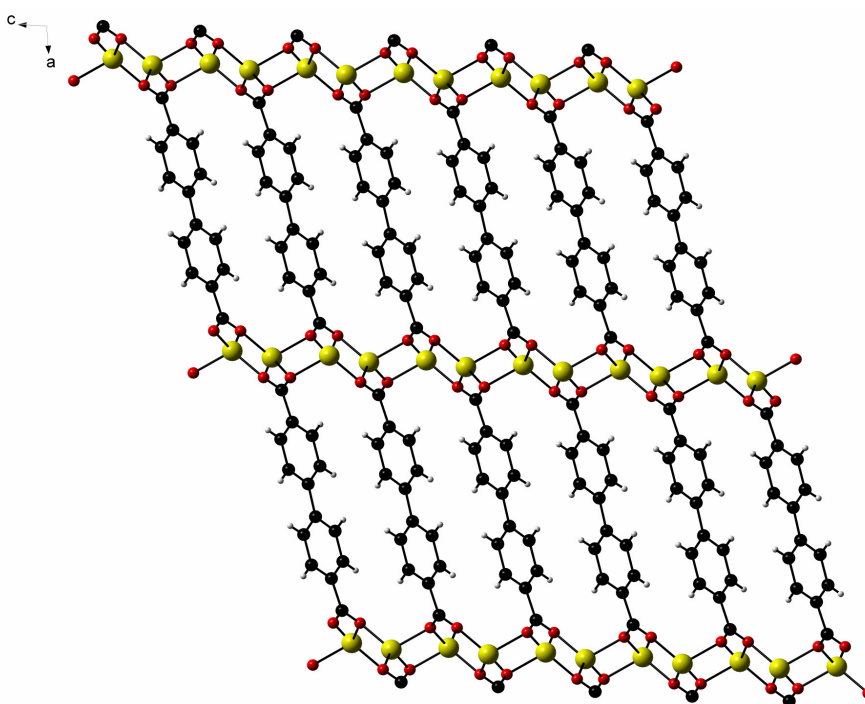


Figure 6.7: The structure of the 3D network of **19** viewed in the direction of the crystallographic *b*-axis. Li yellow, C black, O red and H white.

19 crystallises in the same monoclinic $P2_1/c$ space group as **18**. Again, the asymmetric unit of **19** contains half the formula unit with the remainder of the complex being generated by symmetry operations. The overall structure of **19** is very similar to that of compound **18** and is that of 3D Li network (Figure 6.7). Again the network consists of 2D Li-O sheets linked *via* the biphenyl moieties of the **BDCA** ligands in the direction of the crystallographic *a*-axis. In this case the Li-O sheets are separated by a distance of 11.9 Å. This shows that the use of the **BDCA** ligand has increased the distance between the Li-O 2D sheets. This augmentation also affects the unit cell

parameters as the length of the crystallographic *a*-axis increases from 8.3 Å in **18** to 12.8 Å in **19**.

As is the case of **18**, the Li ions in **19** display distorted tetrahedral coordination geometries, each binding to four different **BDCA** ligands. The Li-O bond distances range between 1.924(9) Å and 1.986(1) Å and are summarised with the relevant bond angles in Table 6.3.

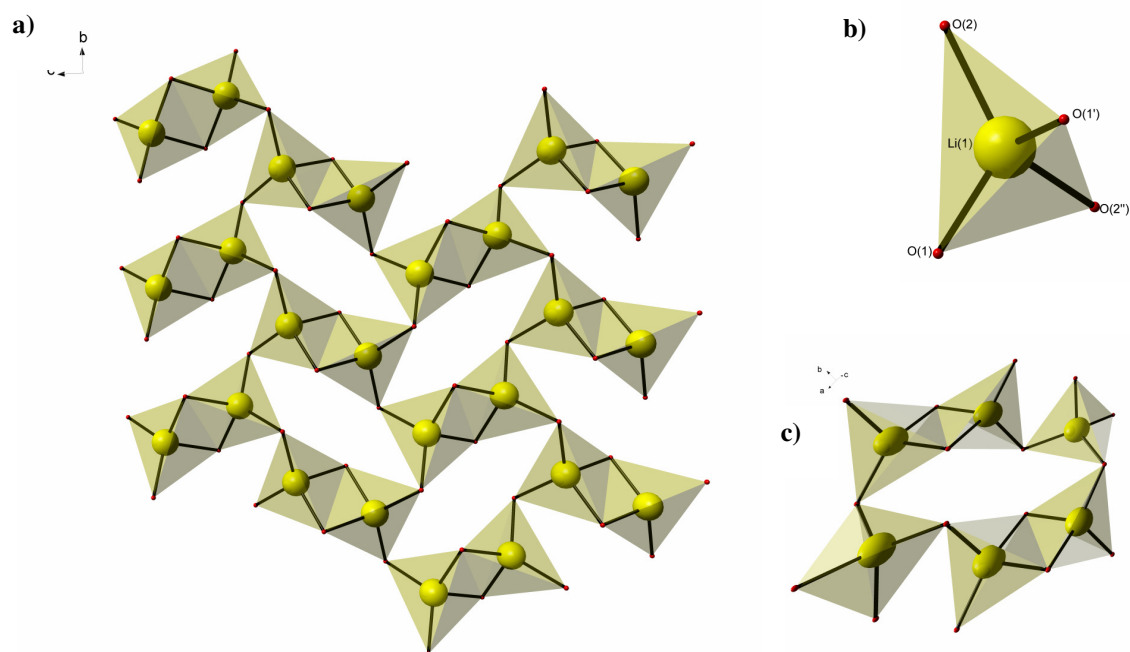


Figure 6.8: **a)** The structure (polyhedral representation) of the 2D Li-O sheet contained in **19** (C and H atoms removed for clarity). **b)** The coordination environment of the Li ions contained in **19**. **c)** The twelve membered ring motif in **19**. Li yellow and O red. (' refers to the 1- *x*, -*y*, 1-*z* positions and " refers to the 1-*x*, -0.5+*y*, 0.5-*z* positions)

As before the O donor atoms of the ligand link the Li ions into tetrahedral dimer units in which the distorted tetrahedrons share common edges. Similarly to **18**, linkage of these dimer units through four vertices generates 2D Li-O sheets that extend in (011) plane (Figure 6.8). As is the case in **18**, the Li ions in the sheets are contained within a series of twelve membered {Li-O-Li} ring shaped motifs (Figure 6.8c). The 2D Li-O sheets are connected through the **BDCA** ligand which gives rise to the overall 3D structures (Figure 6.7).

Table 6.3: Selected bond lengths and angles for **19**

Table S17. Selected bond lengths and angles for 1b			
Bond	Bond Length		Bond Angle
Li(1)-O(1)	1.924(9) Å	O(1)-Li(1)-O(2)	101.51(3)°
Li(1)-O(2)	1.971(8) Å	O(1)-Li(1)-O(1')	91.67(3)°
Li(1)-O(1')	1.986(1) Å	O(1)-Li(1)-O(2'')	103.02(3)°
Li(1)-O(2'')	1.938(1) Å	O(2)-Li(1)-O(1')	101.51(3)°
		O(2)-Li(1)-O(2'')	120.83(3)°
		O(1')-Li(1)-O(2'')	112.15(4)°

Symmetry transformations used to generate equivalent atoms:

' = 1- x, -y, 1-z and '' = 1-x, -0.5+y, 0.5-z

Compound **19** was also characterised by FT-IR spectroscopy. Its spectrum shows bands at 1609 cm⁻¹ and 1486 cm⁻¹ due to the asymmetric and symmetric carboxylate stretches of the ligand moieties.¹⁶⁴ The composition of **19** was also confirmed by microanalysis (CHN).

Table 6.4: Crystal data and structure refinement for **19**

Identification code	19	
Empirical formula	$\text{Li}_2\text{C}_{14}\text{H}_8\text{O}_4$	
Formula weight	254.04 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.70173 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 12.753(6)$ Å	$\alpha = 90^\circ$
	$b = 5.138(2)$ Å	$\beta = 97.218(13)^\circ$
	$c = 8.420(4)$ Å	$\gamma = 90^\circ$
Volume	547.4(4) Å ³	
Z	2	
Density (calculated)	1.541 Mg/m ³	
Absorption coefficient	0.027 mm ⁻¹	
F(000)	260	
Crystal size	0.08 x 0.03 x 0.01 mm ³	
Theta range for data collection	1.87 to 17.21°	
Index ranges	-18 ≤ h ≤ 18, 0 ≤ k ≤ 7, 0 ≤ l ≤ 12	
Reflections collected	1544	
Independent reflections	1544 [R(int) = 0.650]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1544 / 0 / 93	
Goodness-of-fit on F ²	0.836	
Final R indices [I > 2σ(I)]	R1 = 0.0788, wR2 = 0.1770	
R indices (all data)	R1 = 0.1302, wR2 = 0.2241	
Largest diff. peak and hole	0.605 and -0.416 e.Å ⁻³	

6.5 Synthesis and structural characterisation of $[\text{Li}_2(\text{C}_{12}\text{H}_6\text{O}_4)]$ (**20**)

As part of this study, the coordination compound $[\text{Li}_2(\text{C}_{12}\text{H}_6\text{O}_4)]$ (**20**) was synthesised under solvothermal conditions. This involved the reaction of 2,6-naphthalene dicarboxylic acid (**NDCA**) with two equivalents of LiCl in methanol. Compound **20** contains a similar 3D network (Figure 6.9) to those observed in **18** and **19**. However, in this case the 2D Li-O sheets are linked by naphthalene moieties.

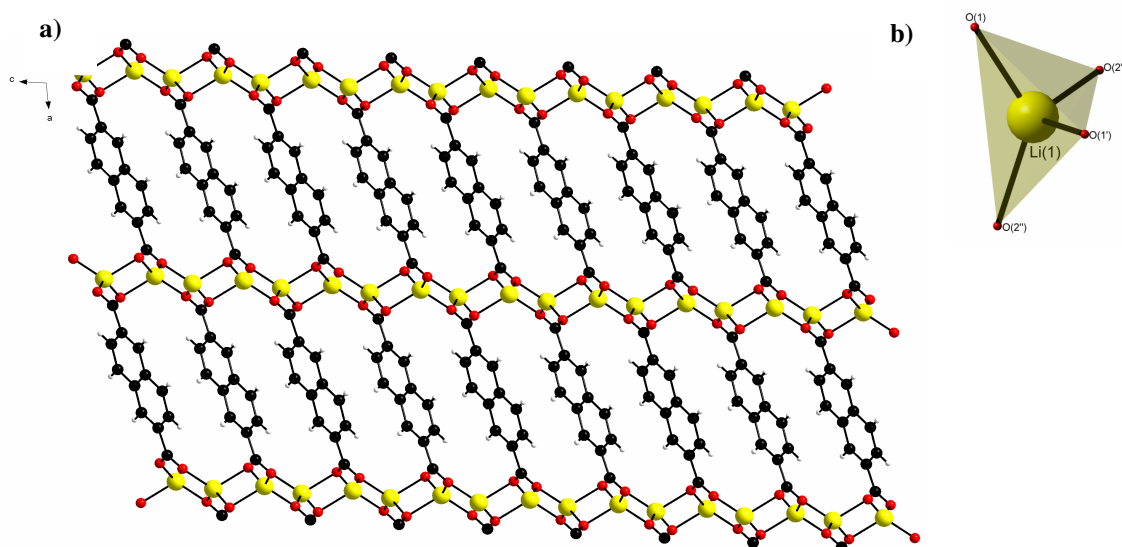


Figure 6.9: a) The structure of the 3D network contained in **20** as viewed along the crystallographic *b*-axis. b) The coordination environment of the Li ions contained in **20**. Li yellow, C black, O red and H white. (' refers to the 1- *x*, -*y*, 1-*z* positions, '' refers to the 1-*x*, -0.5+*y*, 0.5-*z* positions and ''' refers to the *x*, -1+*y*, 1-*z* positions)

20 also crystallises in the same monoclinic $P2_1/c$ space group as **18** and **19**. The asymmetric unit of **20** contains half the $[\text{Li}_2(\text{C}_{12}\text{H}_6\text{O}_4)]$ formula unit with the remainder generated by symmetry operations. Again, each Li ion binds to four different **NDCA** ligands and adopts a highly distorted coordination environment. Important bond angles and bond lengths involving the Li ions are summarised in Table 6.5. As before the Li ions are linked together *via* O donor atoms generating the afore described 2D sheets which are connected this time through the naphthalene groups of the **NDCA** ligands, producing the overall 3D framework structure (Figure 6.7). In contrast to **19**, the Li-O sheets in **20** are separated by a distance of 11.5 Å. The shortening of the inter-layer distance is also observed in the unit cell parameters, whereby the length of the crystallographic *a*-axis decreases from 12.8 Å in **19** to 10.3 Å in the case of **20**.

Table 6.5: Selected bond lengths and angles for **20**

Bond	Bond Length	Bond Angle	
Li(1)-O(1)	1.959(9) Å	O(1)-Li(1)-O(1')	91.67(1)°
Li(1)-O(1')	2.018(3) Å	O(1)-Li(1)-O(2'')	130.32(1)°
Li(1)-O(2'')	1.999(4) Å	O(1)-Li(1)-O(2''')	102.77(1)°
Li(1)-O(2''')	1.968(2) Å	O(1')-Li(1)-O(2'')	99.51(1)°
		O(1')-Li(1)-O(2''')	115.22(1)°
		O(2'')-Li(1)-O(2''')	115.09(1)°

Symmetry transformations used to generate equivalent atoms:

' = 1 - x, -y, 1 - z, '' = 1 - x, -0.5 + y, 0.5 - z and ''' = x, -1 + y, 1 - z

FT-IR spectroscopy was also used to characterise compound **20** and the spectrum shows bands at 1602 cm⁻¹ and 1497 cm⁻¹, which arise from the asymmetric and symmetric carboxylate stretches of the **NDCA** ligand.¹⁶⁴ CHN microanalysis is also consistent with the assigned molecular formula of **20** obtained from crystallography.

Table 6.6: Crystal data and structure refinement for **20**

Identification code	20	
Empirical formula	$\text{Li}_2\text{C}_{12}\text{H}_6\text{O}_4$	
Formula weight	228.06 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 10.290(2)$ Å	$\alpha = 90^\circ$
	$b = 5.3400(11)$ Å	$\beta = 98.61(3)^\circ$
	$c = 8.5700(17)$ Å	$\gamma = 90^\circ$
Volume	465.60(16) Å ³	
Z	1	
Density (calculated)	1.627 Mg/m ³	
Absorption coefficient	0.119 mm ⁻¹	
F(000)	232	
Crystal size	0.1 x 0.15 x 0.05 mm ³	
Theta range for data collection	2.00 to 24.98°	
Index ranges	-12 ≤ h ≤ 12, -6 ≤ k ≤ 6, -10 ≤ l ≤ 9	
Reflections collected	3774	
Independent reflections	808 [R(int) = 0.0541]	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	808 / 0 / 82	
Goodness-of-fit on F ²	1.179	
Final R indices [I > 2σ(I)]	R1 = 0.0569, wR2 = 0.1589	
R indices (all data)	R1 = 0.0984, wR2 = 0.2721	
Largest diff. peak and hole	0.703 and -0.746 e.Å ⁻³	

6.6 Thermal stability and gas sorption properties of **18 - 20**

6.6.1 Thermal stability of **18 - 20**

To study the thermal stability of **18 - 20**, thermogravimetric analyses (TGA) were performed (Figure 6.10). The compounds were heated to 900 °C in an air atmosphere at a heating rate of 10 °C min⁻¹. All three compounds, in general, show similar patterns of decomposition. The composition of all compounds remains stable until *ca.* 500 °C, when the compounds undergo decomposition *via* two thermogravimetric steps centred at *ca.* 600 °C and *ca.* 830 °C. The remaining residues observed are most likely due to the formation of lithium oxides.

6.6.2 Gas sorption properties of **18 - 20**

The thermogravimetric analyses for **18 - 20** demonstrate that these network structures are stable to high temperatures. Therefore, preliminary N₂ absorption studies were carried out to determine if these compounds display any degree of porosity that may be exploited for hydrogen storage purposes.

Firstly, a freshly filtered sample of each compound was desolvated under vacuum at 200 °C for 12 hours. To determine the permanent porosity of each compound, N₂ absorption /desorption isotherms (Figure 6.11) at 77K were recorded. These measurements were used to determine the BET surfaces areas of each compound. Compounds **18**, **19** and **20** have surface areas of 9.7 m² g⁻¹, 12.3 m² g⁻¹, and 10.6 m² g⁻¹, respectively. The low surface area values obtained from the N₂ absorption /desorption isotherms are in agreement with the densely packed structural motifs of **18 - 20**.

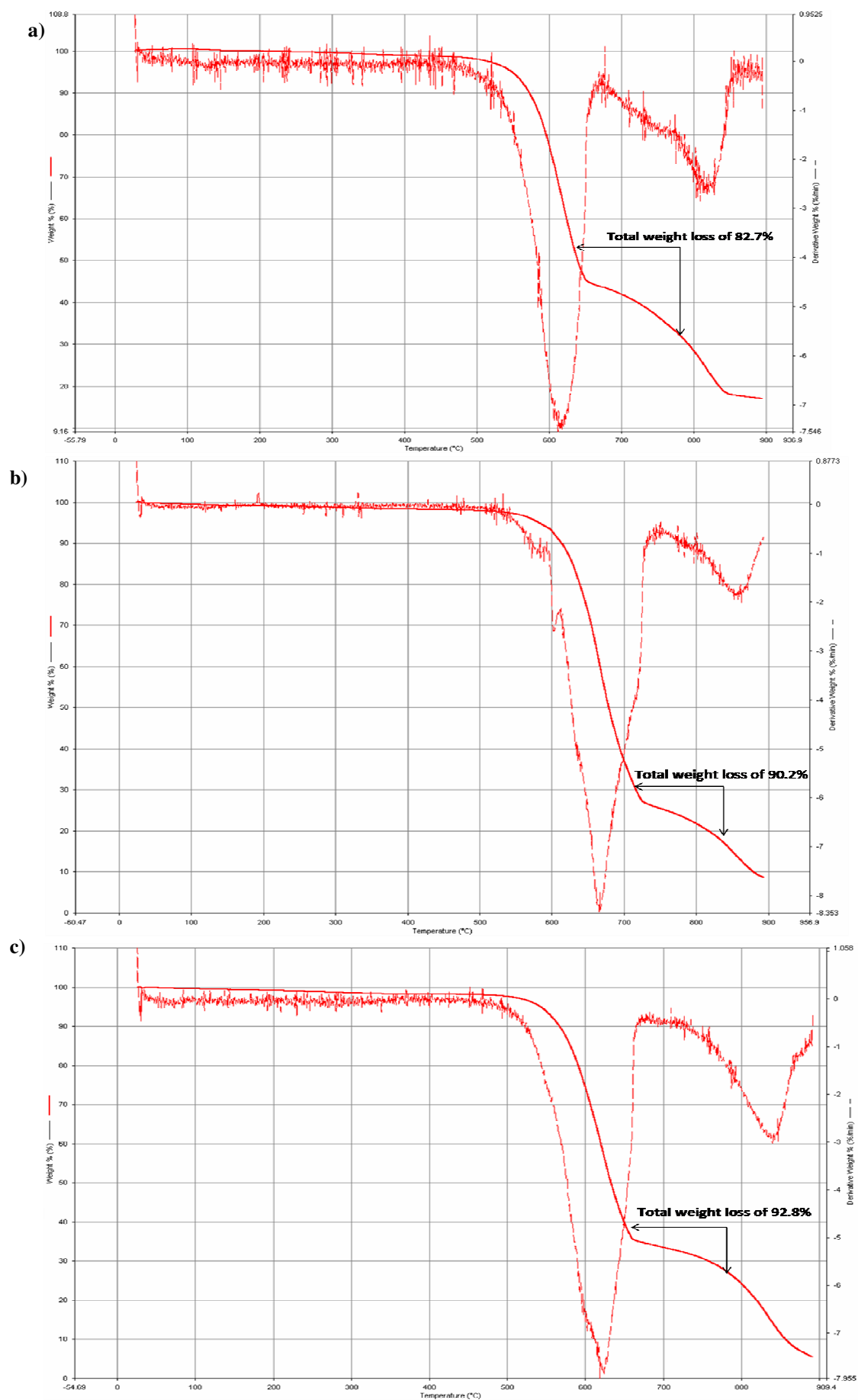


Figure 6.10: Thermogravimetric analysis (TGA) for a) 18, b) 19 and c) 20.

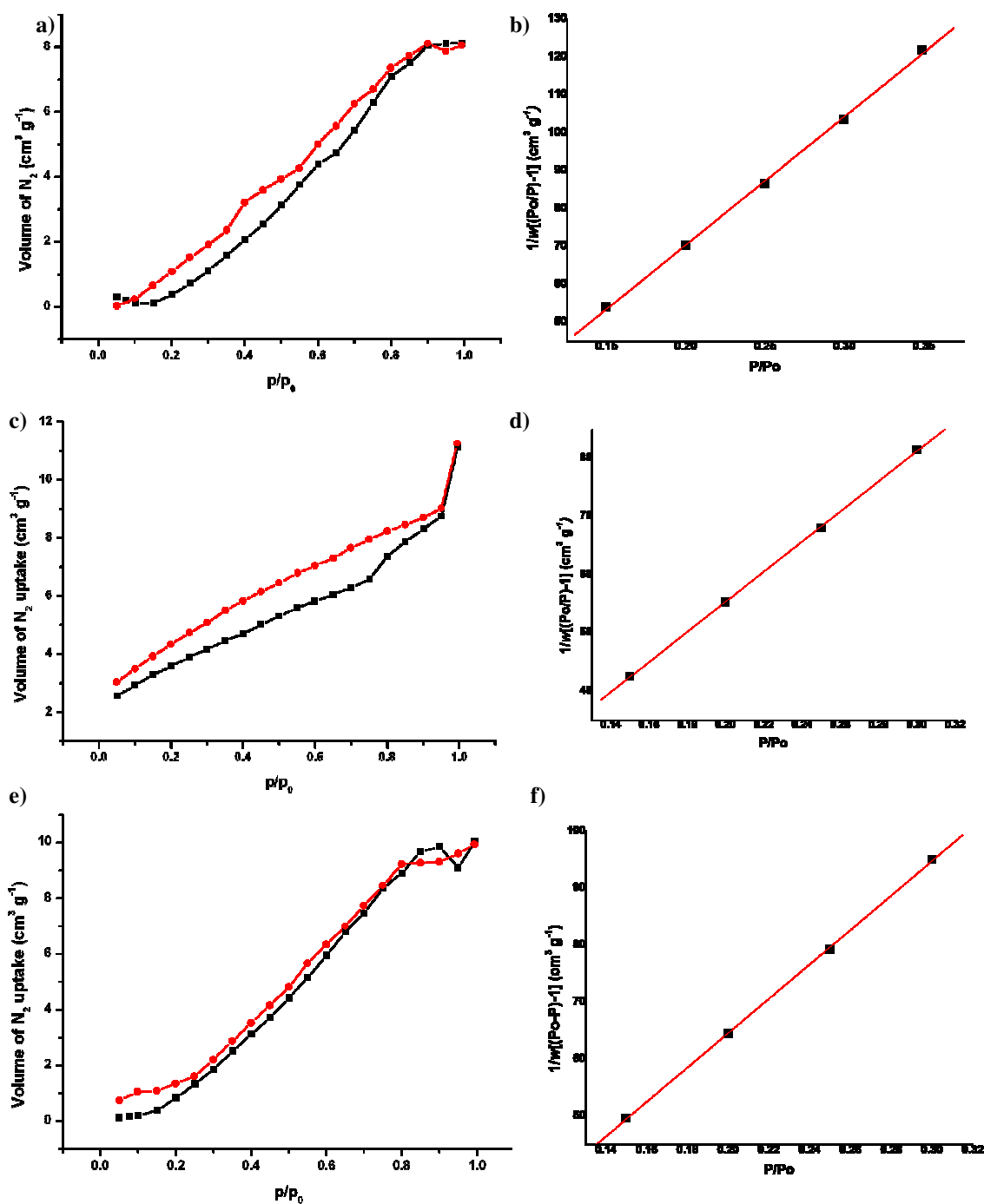


Figure 6.11: The N_2 isotherm at 77K for a) 18, c) 19 and e) 20 (The black curves are adsorption and the red curves are desorption). Plots of the linear region of the BET equation for b) 18, d) 19 and f) 20.

6.7 Synthesis and structural characterisation of $(\text{NH}_2\text{Me}_2)[\text{Li}_2(\text{C}_9\text{H}_3\text{O}_6)]\cdot\text{H}_2\text{O}$ (**21**)

The reaction of 1,3,5-benzenetricarboxylic acid (**BTCA**) with three equivalents of $\text{Li}(\text{OH})\cdot\text{H}_2\text{O}$ was carried out under solvothermal conditions in dimethylformamide (DMF) solution. This approach yielded large colourless crystals of $(\text{NH}_2\text{Me}_2)[\text{Li}_2(\text{C}_9\text{H}_3\text{O}_6)]\cdot\text{H}_2\text{O}$ (**21**).

21 crystallises in the orthorhombic crystal system in the space group of *Pnma*. The asymmetric unit of **21** contains a fully deprotonated **BTCA** ligand, two lithium ions Li(1) and Li(2), a constitutional water molecule and a dimethyl ammonium cation which acts as a charge balancing counterion. In contrast to **18**, **19** and **20**, the O donor atoms of the **BTCA** ligand display two different binding modes (Figure 6.12). The O atoms, O(1), O(2) and O(5) all bind to two different Li ions whereas the O donors O(3), O(4) and O(6) only bind to one Li ion. The Li-O bond lengths vary between 1.881(3) Å and 2.287(3) Å. Detailed bond lengths are summarised in Table 6.7.

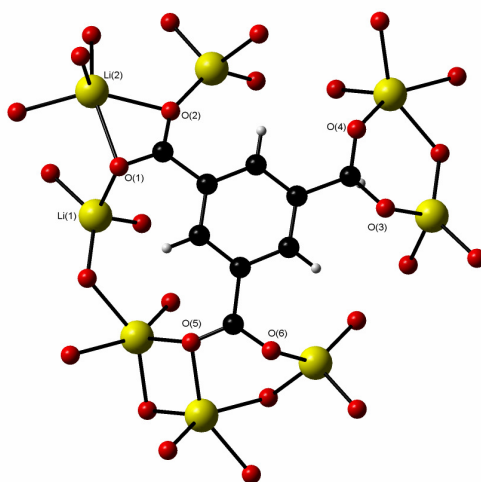


Figure 6.12: Representation of the binding mode of the **BTCA** ligands contained within **21**. Li yellow, C black, O red and H white.

The lithium ions in **21** are linked *via* the O donor atoms resulting in a 2D Li-O network (Figure 6.13). Within the network there are two types of Li ions, Li(1) and Li(2). Li(1) displays a highly distorted tetrahedral coordination geometry with relevant bond angles ranging between 59.47(8)° and 153.84(2)°, whereas Li(2) shows a distorted square pyramidal coordination environment. The bond angles involving Li(2) vary from 94.62(1)° to 149.49(1)° and are summarised in Table 6.8.

Table 6.7: Selected bond lengths for **21**

Bond	Bond Length	Bond	Bond Length
Li(1)-O(1)	1.965(3) Å	Li(2)-O(1)	2.287(3) Å
Li(1)-O(3')	1.923(3) Å	Li(2)-O(2)	2.147(3) Å
Li(1)-O(6'')	1.923(3) Å	Li(2)-O(4''')	2.017(3) Å
Li(1)-O(2''')	1.881(3) Å	Li(2)-O(5''')	2.004(3) Å
		Li(2)-O(5''')	2.076(3) Å

Symmetry transformations used to generate equivalent atoms:

' = 2-x, 2-y, 1-z, " = 1.5-x, 2-y, 0.5+z, "' = -0.5+x, y, 1.5-z, "" = 2.5-x, 2-y, 0.5+z
and "" = 0.5 +x, y, 1.5-z

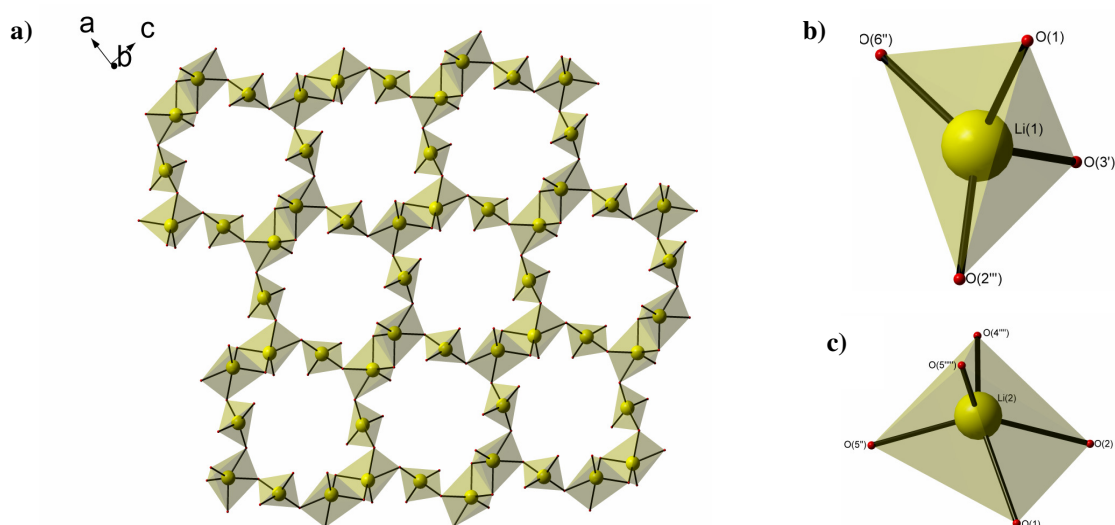


Figure 6.13: a) Polyhedral representation of the 2D Li-O network contained in **21** (C and H atoms removed for clarity). b) Highly distorted tetrahedral coordination environment of Li(1) c) distorted square pyramidal coordination environment of Li(2). Li yellow and O red. (' refers to the 2-x, 2-y, 1-z positions, " refers to the 1.5-x, 2-y, 0.5+z positions, "' refers to the -0.5+x, y, 1.5-z positions, "" refers to the 2.5-x, 2-y, 0.5+z positions and "" refers to the 0.5 +x, y, 1.5-z positions)

The Li ions with distorted square pyramidal coordination geometries, Li(2) and its symmetry equivalents, are linked together through edge sharing interactions generating dimer units. Within the dimer units the Li ions are doubly bridged by two μ_2 carboxylate oxygen atoms, O(5) and its symmetry equivalent. The dimer units are further involved in corner sharing interactions with the tetrahedral polyhedra of the Li(1) ions. The corner sharing interactions occur through two vertices of the tetrahedra and involve O(1) and O(2). The edge and corner-sharing bridging motifs result in the formation of Li-O sheets that extend in the (101) plane (Figure 6.13). Within the sheet the Li ions are arranged in a connected 20-membered {Li-O-Li} ring motif (Figure 6.14c).

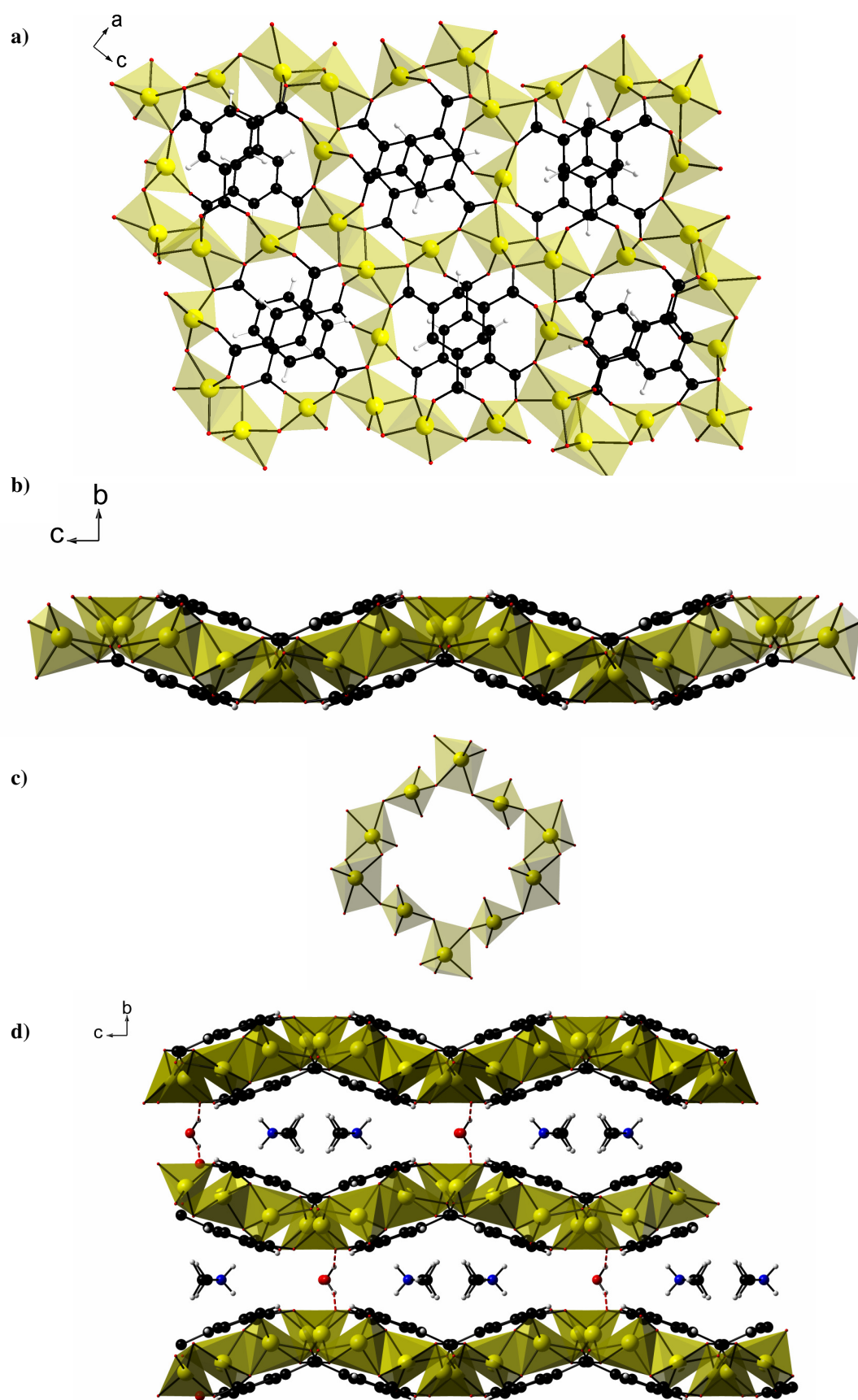


Figure 6.14: The 2D Li coordination network contained in **21** as viewed along **a)** the crystallographic *b*-axis and **b)** the crystallographic *a*-axis. **c)** The twenty membered ring motif in **21**. **d)** The coordination network in **21**. Li yellow, O red, C black N, blue and H white.

Unlike the previous compounds **18** - **20** the aromatic ligands don't further link the Li-O sheets. The ligands are contained within the Li-O sheet producing a 2D hybrid inorganic-organic network (Figure 6.14a and b). The aromatic rings of the **BTCA** ligands in **21** engage in intermolecular π - π staking interactions which occur along the crystallographic *b*-axis. The distance between the centroid of the aromatic planes is 3.638(2) Å.

The 2D Li-O networks are also linked through hydrogen bonding interactions between the constitutional water molecules and the O donor atoms from the **BTCA** ligands. The H-bonding interactions occur in the direction of the crystallographic *b*-axis and pillar the 2D sheets. The resulting void spaces that extend in the direction of the crystallographic *a*-axis are filled with the dimethyl ammonium counterions (Figure 6.14d). The O-O distance of the H-bonding interaction in **21** is 2.45 Å.

Table 6.8: Selected bond angles for **21**

Bond Angle		Bond Angle	
O(1)-Li(1)-O(3')	112.61(1)°	O(1)-Li(2)-(O5''')	97.11(1)°
O(1)-Li(1)-O(6'')	99.53(1)°	O(1)-Li(2)-O(5'')	96.53(1)°
O(1)-Li(1)-O(2''')	107.81(1)°	O(2)-Li(2)-O(4''')	99.87(1)°
O(3')-Li(1)-O(6'')	93.39(1)°	O(2)-Li(2)-O(5''')	106.14(1)°
O(3')-Li(1)-O(2''')	109.46(1)°	O(2)-Li(2)-O(5'')	149.49(1)°
O(6'')-Li(1)-O(2''')	133.08(2)°	O(4''')-Li(2)-O(5''')	104.58(1)°
O(1)-Li(2)-O(2)	59.47(8)°	O(4''')-Li(2)-O(5'')	96.13(1)°
O(1)-Li(2)-O(4''')	153.84(2)°	O(5''')-Li(2)-O(5'')	94.62(1)°

Symmetry transformations used to generate equivalent atoms:

' = 2-x, 2-y, 1-z, '' = 1.5-x, 2-y, 0.5+z, ''' = -0.5+x, y, 1.5-z, '''' = 2.5-x, 2-y, 0.5+z
and ''''' = 0.5 +x, y, 1.5-z

Compound **21** was also analysed by FT-IR spectroscopy. The spectrum reveals the presence of the **BTCA** ligand through its characteristic asymmetric and symmetric carboxylate stretches at 1611 cm⁻¹ and at 1484 cm⁻¹, respectively.¹⁶⁴ The composition of **21** was also confirmed by microanalysis (CHN).

Table 6.9: Crystal data and structure refinement for **21**

Identification code	21	
Empirical formula	Li ₂ C ₁₁ H ₁₁ O ₇ N	
Formula weight	283.09 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pnma</i>	
Unit cell dimensions	a = 9.9114(7) Å	α = 90°
	b = 14.6847(10) Å	β = 90°
	c = 13.5500(9) Å	γ = 90°
Volume	1972.1(2) Å ³	
Z	8	
Density (calculated)	1.731 Mg/m ³	
Absorption coefficient	0.143 mm ⁻¹	
F(000)	1024	
Crystal size	0.35 x 0.20 x 0.20 mm ³	
Theta range for data collection	2.05 to 28.32°	
Index ranges	-9 ≤ h ≤ 13, -18 ≤ k ≤ 19, -18 ≤ l ≤ 18	
Reflections collected	14208	
Independent reflections	2546 [R(int) = 0.0496]	
Completeness to theta = 28.32°	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2546 / 0 / 200	
Goodness-of-fit on F ²	1.052	
Final R indices [I > 2σ(I)]	R1 = 0.0416, wR2 = 0.1217	
R indices (all data)	R1 = 0.0479, wR2 = 0.1249	
Largest diff. peak and hole	0.461 and -0.698 e.Å ⁻³	

6.8 Thermal stability and gas sorption properties of **21**

Thermogravimetric analysis (TGA) was performed on **21** (Figure 6.15). A freshly filtered sample of **21** was heated to 900 °C in an air atmosphere at a rate of 10 °C min⁻¹.

The composition of **18** remained unchanged until *ca.* 135 °C. At this temperature the compound begins to undergo thermal decomposition. A weight loss of *ca.* 75 % is observed between 135 °C and 260 °C.

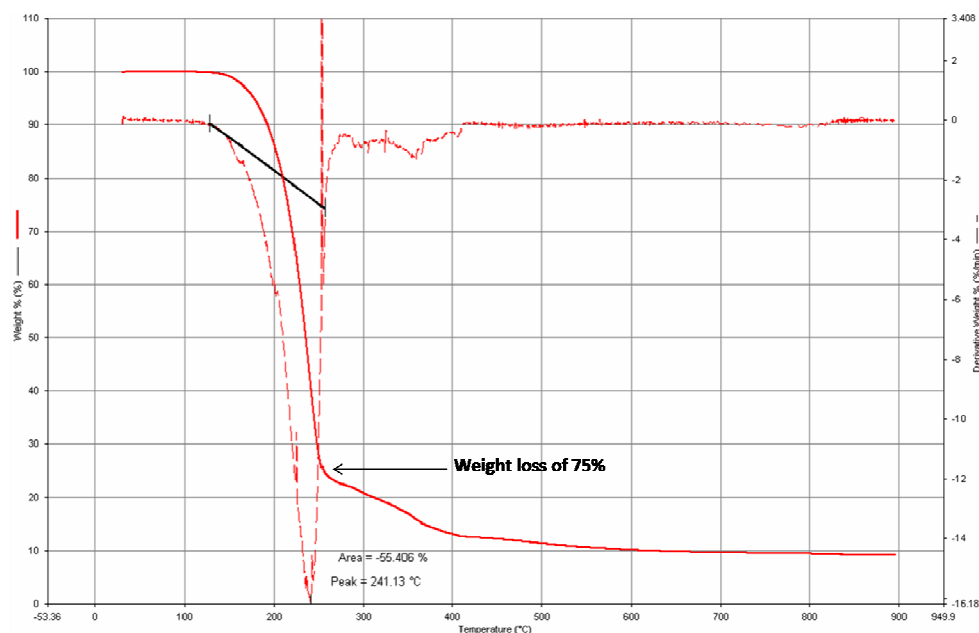


Figure 6.15: Thermogravimetric analysis (TGA) for **21**.

To determine the permanent porosity of **21** a freshly filtered sample was firstly degassed at 100 °C for 24 hours and N₂ absorption measurements were attempted. However, the compound appears to decompose during the sample preparation and consistent N₂ absorption/desorption isotherms were not obtained.

6.9 Conclusion

A synthetic approach has been developed for the generation of lithium coordination networks. These compounds are synthesised under solvothermal reaction conditions.

The reaction of dicarboxylate ligands with lithium salts resulted in the formation of 3D coordination networks **18** - **20**. Within these networks, the lithium ions are linked by the O-donor atoms of the carboxylate ligands generating 2D Li-O sheets. The Li-O sheets are connected by the aromatic moieties of the carboxylate

ligands that pillar between the sheets and link them in the direction of the crystallographic *c*-axis. This bridging arrangement results in densely packed 3D framework structures that contain limited accessible void spaces. The framework structures also show high thermal stabilities.

In **21**, a tricarboxylate ligand, 1,3,5-benzenetricarboxylic acid, was employed in the reaction system. This led to the formation of a 2D coordination network. This coordination network displays a different structure to **18** - **20**. In **21**, the lithium ions are also contained within 2D Li-O sheets. However in this case the Li-O sheets are not further linked by the organic ligands. The ligands are contained within the Li-O sheets giving the overall 2D framework structure. **21** has a lower thermal stability than **18** - **20**.

The described synthetic approach has demonstrated that carboxylic acid substituted aromatic ligands can be employed for the formation of lithium coordination networks. It is possible to imagine that this approach could be applied to more extended carboxylate ligands. This could potentially yield coordination networks that display some degree of porosity which could be employed for gas storage applications.

Chapter Seven

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Self-organisation of amphiphilic Fe^{III} complexes

and their network assemblies to form

hierarchical nanomaterials

7.1 Introduction

The ability to exploit self-assembly techniques to produce hierarchical ordered structures is one key goal of supramolecular chemistry and nanoscience.¹⁹⁸ In recent years there has been a dramatic increase in the research of nanomaterials as these materials have demonstrated great potential for utilisation in areas such as catalysis, molecular electronics and gas separation.^{46,47} Molecular self-assembly approaches provide a means to controllably assemble advanced nanostructures from simple building units.⁴⁸ A controlled assembly requires the ability to fully understand and influence the structural directing forces which give rise to the resultant nanoscopic assemblies. Structural studies of crystalline network structures that contain amphiphilic molecular subunits can help to understand the relevant intermolecular forces that may be exploited to produce related hierarchical nanoassemblies.^{50,51}

Previously within the group of Dr. Wolfgang Schmitt, a series of iminodiacetic substituted naphthol and phenol ligands have been employed in the formation of Fe^{III} coordination networks that display well defined hydrophobic and hydrophilic areas.^{54,55} So, we set out to determine whether the amphiphilic nature of these coordination networks could be exploited for the self-assembly of nanomaterials.

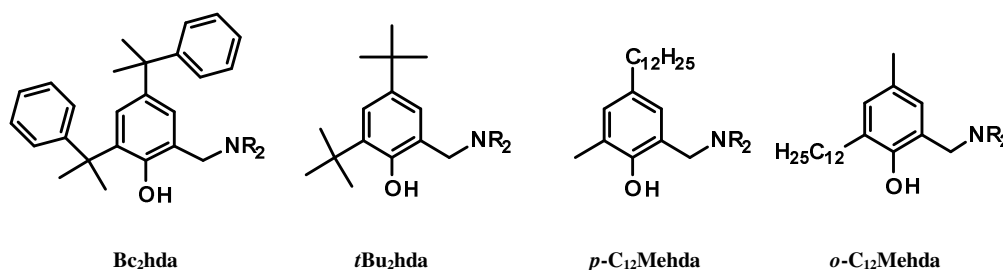


Figure 7.1: Structure of the iminodiacetic acid substituted phenol ligands used in the formation of amphiphilic coordination network structures. R = CH₂COOH

Figure 7.1 shows the ligands that were chosen for this study. Initially, we intended to react these ligands with Fe^{III} salts with the expectation of creating amphiphilic network structures in which the secondary building units are either linked through hydrogen bonding or counterion mediation. Our goal was to synthesise crystalline materials which could be structurally characterised using diffraction methods. This would allow us to gain an insight into the self-assembly process that gives rise to the generation of these coordination assemblies. We further aimed to exploit this knowledge to self-assemble these and related SBUs into nanoscopic, non-crystalline materials that display hierarchical order.

7.2 The synthesis of the iminodiacetic acid substituted phenol ligands

The iminodiacetic acid substituted phenol ligands (Figure 7.1) are prepared *via* the Mannich reaction starting with the corresponding phenol derivative, formaldehyde and iminodiacetic acid.^{199,200} An imine salt is initially formed from the reaction between formaldehyde and iminodiacetic acid.²⁰⁰ The imine salt is then attacked by the relevant phenolate ion forming the desired product.²⁰⁰ The ligands **Bc₂hda** and **tBu₂hda** had been previously synthesised and were used without further purification.^{54,55} The ligands ***p*-C₁₂Mehda** and ***o*-C₁₂Mehda** were prepared following a modified literature procedure.²⁰⁰ The applied approach involved the reaction of 4-dodecyl-2-methyl phenol or 2-dodecyl-4-methyl phenol with iminodiacetic acid and formaldehyde.

The ***p*-C₁₂Mehda** and ***o*-C₁₂Mehda** ligands were characterised by 400 MHz ¹H NMR (Table 7.1) spectroscopy. The spectrum of each ligand shows two deshielded signals that arise from their aromatic hydrogen atoms. The signals due to the aromatic hydrogen atoms occur at 6.8 ppm and 6.6 ppm for ***p*-C₁₂Mehda** and at 6.8 and 6.5 ppm for ***o*-C₁₂Mehda**. Two signals due to the methylene hydrogen atoms of the ligands are also seen in each 400 MHz ¹H NMR spectrum. For ***p*-C₁₂Mehda**, the chemical shifts arising from the methylene hydrogen atoms are observed at 3.7 ppm and 3.4 ppm whereas for ***o*-C₁₂Mehda** they occur at 3.9 and 3.5 ppm. The spectra also reveal signals due to the hydrogen atoms of the C₁₂ alkyl chain of the ligands. These signals are observed between 1.4 ppm and 1.6 ppm for ***p*-C₁₂Mehda** and between 1.5 ppm and 1.7 ppm for ***o*-C₁₂Mehda**.

Table 7.1: ¹H NMR data for iminodiacetic acid substituted phenol ligands

Ligand	Chemical Shift and Assignment
<i>p</i>-C₁₂Mehda	δ = 6.8 (s, 1H, 1 x H _{aromatic}), 6.6 (s, 1H, 1 x H _{aromatic}), 3.7 (s, 2H, 1 x CH ₂), 3.4 (s, 4H, 2 x CH ₂), 1.4-1.6 (mm, 25H, 1 x C ₁₂ H ₂₅), 0.7 (s, 3H, 1 x CH ₃) ppm
<i>o</i>-C₁₂Mehda	δ = 6.8 (s, 1H, 1 x H _{aromatic}), 6.5 (s, 1H, 1 x H _{aromatic}), 3.9 (s, 2H, 1 x CH ₂), 3.5 (s, 4H, 2 x CH ₂), 1.5-1.7 (mm, 25H, 1 x C ₁₂ H ₂₅), 0.6 (s, 3H, 1 x CH ₃) ppm

The FT-IR spectrum of each ligand reveals a characteristic carbonyl stretch at 1677 cm⁻¹ for ***p*-C₁₂Mehda** and at 1679 cm⁻¹ for ***o*-C₁₂Mehda**.¹⁶⁴ ***p*-C₁₂Mehda** and ***o*-C₁₂Mehda** were also characterised by ESI mass spectrometry. A molecular ion peak [NaC₂₄H₃₈NO₅]⁺ that arises from the Na salt of each ligand, is observed at 442.2 m/z

in both spectra. Elemental analysis (CHN) also confirms the composition of each compound.

7.3 The synthesis and structural characterisation of Fe^{III} coordination networks

The reaction of the **Bc₂hda** and **tBu₂hda** ligands with FeCl₃·6H₂O yielded the coordination compounds [Fe(**Bc₂hda**)(H₂O)(EtOH)]·3H₂O (**22**) and [Fe(**tBu₂hda**)(H₂O)₂]₂·4H₂O (**23**), respectively. These compounds crystallise in the monoclinic crystal system in the *C2/c* space group. These coordination compounds contain mononuclear Fe^{III} complexes (Figure 7.2). The structure of **23** was previously reported⁵⁴ but its supramolecular structure was further investigated as part of this study.

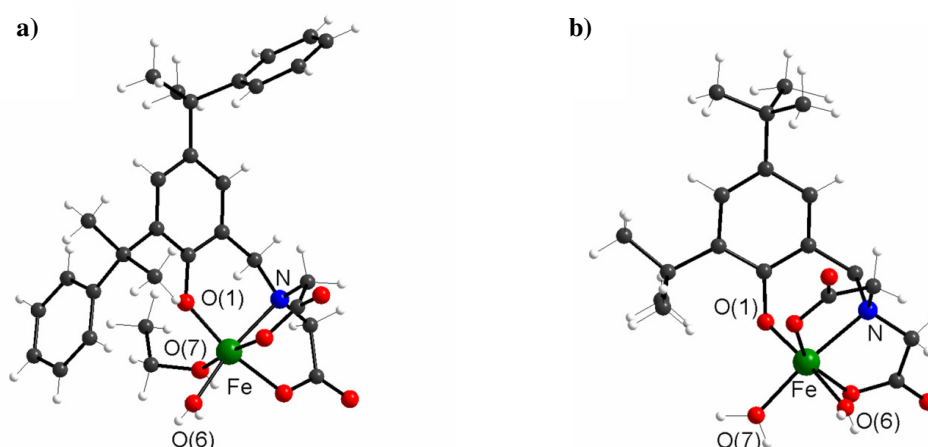


Figure 7.2: The mononuclear complexes contained in **a**) **22** and in **b**) **23** (solvent molecules removed for clarity). Fe green, C black, O red, N blue and H white.

Within these mononuclear complexes the Fe^{III} ions display similar binding modes, with two carboxylate O atoms, one phenolic O atom and one N atom from the organic ligand coordinating to the Fe^{III} ion. The distorted coordination environments of the Fe^{III} ions are completed by the presence of solvent molecules. In **22** one ethanol and one water molecule bind to the central Fe^{III} ion whereas in **23** two water molecules complete the coordination sphere. This slight modification is a consequence of the different preparation methods employed in the formation of the complexes.

The Fe^{III} ions in both complexes, display distorted octahedral coordination geometries with the O donor atoms of the organic ligands occupying *meridional*

position. The N atom of the carboxylate ligand and the O donor atoms of the solvent molecules also adopt a *meridional* arrangement. The bond angles that give rise to the coordination geometries are presented in Tables 7.2 and 7.3.

Table 7.2: Selected bond angles for **22**

Bond Angle		Bond Angle	
O(1)-Fe(1)-O(2)	94.89(2)°	O(2)-Fe(1)-N(1)	81.52(1)°
O(1)-Fe(1)-O(4)	164.65(2)°	O(4)-Fe(1)-O(6)	94.99(2)°
O(1)-Fe(1)-O(6)	99.74(2)°	O(4)-Fe(1)-O(7)	84.07(1)°
O(1)-Fe(1)-O(7)	91.42(2)°	O(4)-Fe(1)-N(1)	78.11(2)°
O(1)-Fe(1)-N(1)	87.88(2)°	O(6)-Fe(1)-O(7)	90.75(1)°
O(2)-Fe(1)-O(4)	89.29(2)°	O(6)-Fe(1)-N(1)	169.29(2)°
O(2)-Fe(1)-O(6)	90.29(1)°	O(6)-Fe(1)-N(1)	96.61(1)°
O(2)-Fe(1)-O(7)	173.34(2)°		

Table 7.3: Selected bond angles for **23**

Bond Angle		Bond Angle	
O(1)-Fe(1)-O(2)	101.69(1)°	O(2)-Fe(1)-N(1)	78.37(1)°
O(1)-Fe(1)-O(4)	95.38(1)°	O(4)-Fe(1)-O(6)	80.56(1)°
O(1)-Fe(1)-O(6)	173.37(1)°	O(4)-Fe(1)-O(7)	104.34(1)°
O(1)-Fe(1)-O(7)	91.44(1)°	O(4)-Fe(1)-N(1)	79.84(1)°
O(1)-Fe(1)-N(1)	93.53(1)°	O(6)-Fe(1)-O(7)	84.60(1)°
O(2)-Fe(1)-O(4)	152.71(1)°	O(6)-Fe(1)-N(1)	99.84(1)°
O(2)-Fe(1)-O(6)	84.08(1)°	O(6)-Fe(1)-N(1)	173.43(1)°
O(2)-Fe(1)-O(7)	96.42(1)°		

The Fe-O_{carboxylate} bonds within the complexes range from 2.002(1) Å to 2.026(3) Å. The Fe-O_{phenol} bond distances in **22** and **23** are 1.843(3) Å and 1.901(1) Å, and the Fe-N bond lengths are 2.197(2) Å and 2.180(1) Å, respectively. In **22** the Fe-O bonds involving the solvent molecules are 1.987(1) Å for the coordinating water molecule and 2.039(2) Å for the coordinating ethanol molecule. Within **23**, the bond distances involving the Fe^{III} ion and the coordination water molecules are 1.959(1) Å

and 2.180(1) Å, respectively. These bond lengths are summarised in Tables 7.4 and 7.5.

The two Fe^{III} compounds, **22** and **23**, form layered lamellar arrangements with the hydrophilic part of the monomeric Fe^{III} complexes situated in the *bc*-crystallographic plane and the hydrophobic organic moieties pointing parallel to the *a*-axis (Figure 7.3). In both compounds, hydrogen bonded constitution water molecules link the Fe^{III} complexes into network structures. Both these networks encapsulate ordered H-bonded water networks.

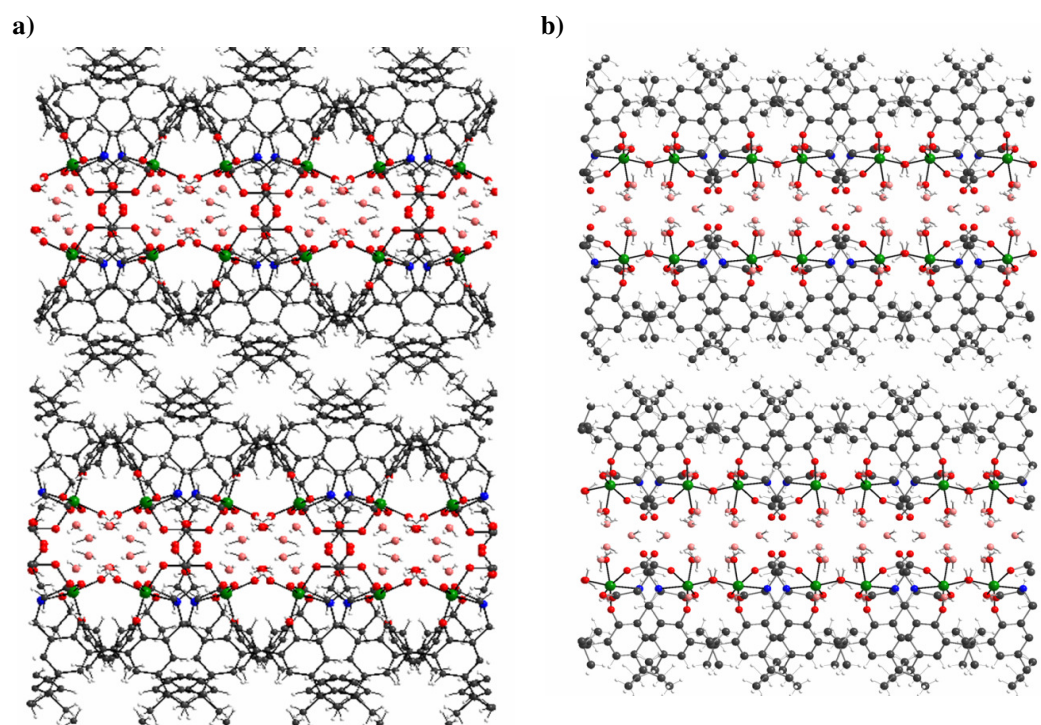


Figure 7.3: a) Layered lamellar structure of **22** viewed in the direction of the crystallographic *c*-axis. b) Layered lamellar structure of **23** viewed in the direction of the crystallographic *c*-axis. Fe green, C black, O red, N blue and H white.

In **22** the H-bonded water network (Figure 7.4a) can best be described as a tape of fused (H₂O)₁₀ rings that extends parallel to the crystallographic *c*-axis. Half of the molecular entities of the (H₂O)₁₀ ring motif are generated by symmetry operations with the inversion centre situated in the centre of the ring. The O-O distances in the hydrogen bonded water network vary between 2.64(2) Å and 2.89(2) Å and the angles between the O-atoms range between 88.1(1) ° and 117.9(1) °.

Compound **23** contains a H-bonded water network (Figure 7.4b) which consists of water molecules organised into 1D chains. The structural motif in the 1D chain reveal similarities to the crystal structure of ice I_h, in the respect that the

network displays both boat and chair conformations. The O-O distances of the network range between 2.76(3) Å and 2.87(2) Å which are comparable to those seen in the modifications of hexagonal ice I_h . However the observed O-O-O angles (74.5(1) ° - 137.2(1) °) deviate significantly from the ideal tetrahedral angle of 109.5 ° which is characteristic for the I_h ice modification.

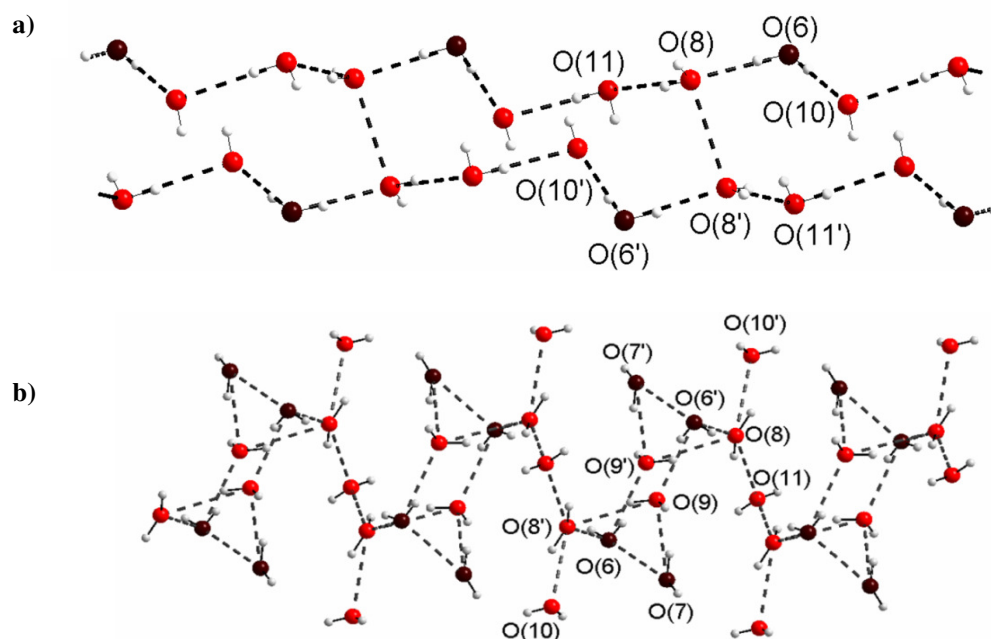


Figure 7.4: **a)** Hydrogen bonded network of constitutional (red) and coordination water (brown) molecules in **22** as viewed in the direction of the crystallographic *b*-axis. **b)** Hydrogen bonded network of constitutional (red) and coordination water (brown) molecules in **23** as viewed in the direction of the crystallographic *b*-axis.

Table 7.5: Selected bond lengths for **22**

Bond	Bond Length	Bond	Bond Length
Fe(1)-O(1)	1.863(3) Å	Fe(1)-O(6)	1.987(1) Å
Fe(1)-O(2)	2.009(4) Å	Fe(1)-O(7)	2.039(2) Å
Fe(1)-O(4)	2.026(3) Å	Fe(1)-N(1)	2.197(2) Å

Table 7.6: Selected bond lengths for **23**

Bond	Bond Length	Bond	Bond Length
Fe(1)-O(1)	1.901(1) Å	Fe(1)-O(6)	2.197(1) Å
Fe(1)-O(2)	2.020(1) Å	Fe(1)-O(7)	1.959(1) Å
Fe(1)-O(4)	2.002(1) Å	Fe(1)-N(1)	2.180(1) Å

These compounds were also characterised by FT-IR spectroscopy. Both compounds show strong asymmetric carboxylate stretches at 1573 cm⁻¹ and 1575 cm⁻¹, respectively.¹⁶⁴ They both show strong symmetric carboxylate stretches at 1362 cm⁻¹ and at 1365 cm⁻¹. The $\Delta = [\nu_{\text{asymmetric}}(\text{CO}_2^-) - \nu_{\text{symmetric}}(\text{CO}_2^-)]$ values of 211 cm⁻¹ for **22** and 210 cm⁻¹ for **23**, underline the X-ray analysis and suggest monodentate binding modes.^{164,175} The UV-vis spectra of both complexes dissolved in methanol display a phenolate LMCT band at 590 nm for **22** and at 588 nm for **23**.²⁰¹ This transition is characteristic of this type of mononuclear Fe^{III} complex.²⁰¹ CHN microanalysis was also employed to verify the composition and purity of the bulk samples of **22** and **23**.

Table 7.6: Crystal data and structure refinement for **22**

Identification code	22	
Empirical formula	FeC ₃₁ H ₄₆ NO ₁₁	
Formula weight	664.54 g mol ⁻¹	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>C2/c</i>	
Unit cell dimensions	a = 44.981(9) Å b = 9.206(4) Å c = 16.552(6) Å	α = 90° β = 108.938(7)° γ = 90°
Volume	6485(4) Å ³	
Z	8	
Density (calculated)	1.361 Mg/m ³	
Absorption coefficient	0.525 mm ⁻¹	
F(000)	2824	
Crystal size	0.1 x 0.1 x 0.08 mm ³	
Theta range for data collection	0.96 to 23.30°	
Index ranges	-47 ≤ h ≤ 50, -10 ≤ k ≤ 10, -18 ≤ l ≤ 18	
Reflections collected	21323	
Independent reflections	4667 [R(int) = 0.0224]	
Completeness to theta = 23.30°	99.6 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4667 / 0 / 581	
Goodness-of-fit on F ²	1.100	
Final R indices [I > 2σ(I)]	R1 = 0.0290, wR2 = 0.0804	
R indices (all data)	R1 = 0.0352, wR2 = 0.0902	
Largest diff. peak and hole	0.381 and -0.396 e.Å ⁻³	

7.4 The synthesis and self-assembly of [Fe(*p*-C₁₂Mehda)(H₂O)₂] nH₂O (**24**)

An important feature of **22** and **23** is that they form layered lamellar structures of an amphiphilic nature, thus making these complexes ideal candidates for self-assembly approaches to create nanomaterials. We set out to increase the amphiphilicity of our reaction system by employing an extended ligand *p*-C₁₂Mehda, which contains a C₁₂ alkyl chain *para* to the phenolic oxygen donor. The reaction of this ligand with Fe^{III} salts in water, resulted in the precipitation of the coordination compound, [Fe(*p*-C₁₂Mehda)(H₂O)₂] $\cdot$ nH₂O (**24**).

The formation of this compound was verified by the comparison of its UV-vis and FT-IR spectra with those of compound **23** (Figure 7.5a). The FT-IR spectra of **24** and **23** (Figure 7.5a) are similar and both present evidence of the asymmetric and symmetric carboxylate bond stretches.¹⁶⁴ In **24** these bond vibrations occur at 1576 cm⁻¹ and 1362cm⁻¹.¹⁶⁴ CHN analyses are also in agreement with the constitutional assignment.

Compounds **23** and **24** also have similar UV-vis spectra (Figure 7.5b). These both display a band at *ca.* 580 nm which is characteristic of a phenolate LMCT transition.²⁰¹ Transmission electron microscopy (Figure 7.6) was used to structurally characterise powered samples of **24**. Although these samples are very sensitive to electron-beam induced damage, it can be clearly observed that **24** displays a highly ordered motif resulting from the layered lamellar packing arrangement. The experiments suggest that **24** adopts a similar layered structure to **22** and **23**. The observed inter-layer distance in **24** is *ca* 3.5 nm and this is in good agreement with the expected dimension of the alkylated Fe^{III} complexes and corresponds well to the *d*-spacing determined by X-ray powder diffraction (Figure 7.5c). Energy dispersive X-ray (EDX) analysis was also used to confirm the composition of **24** (Figure 7.5c).

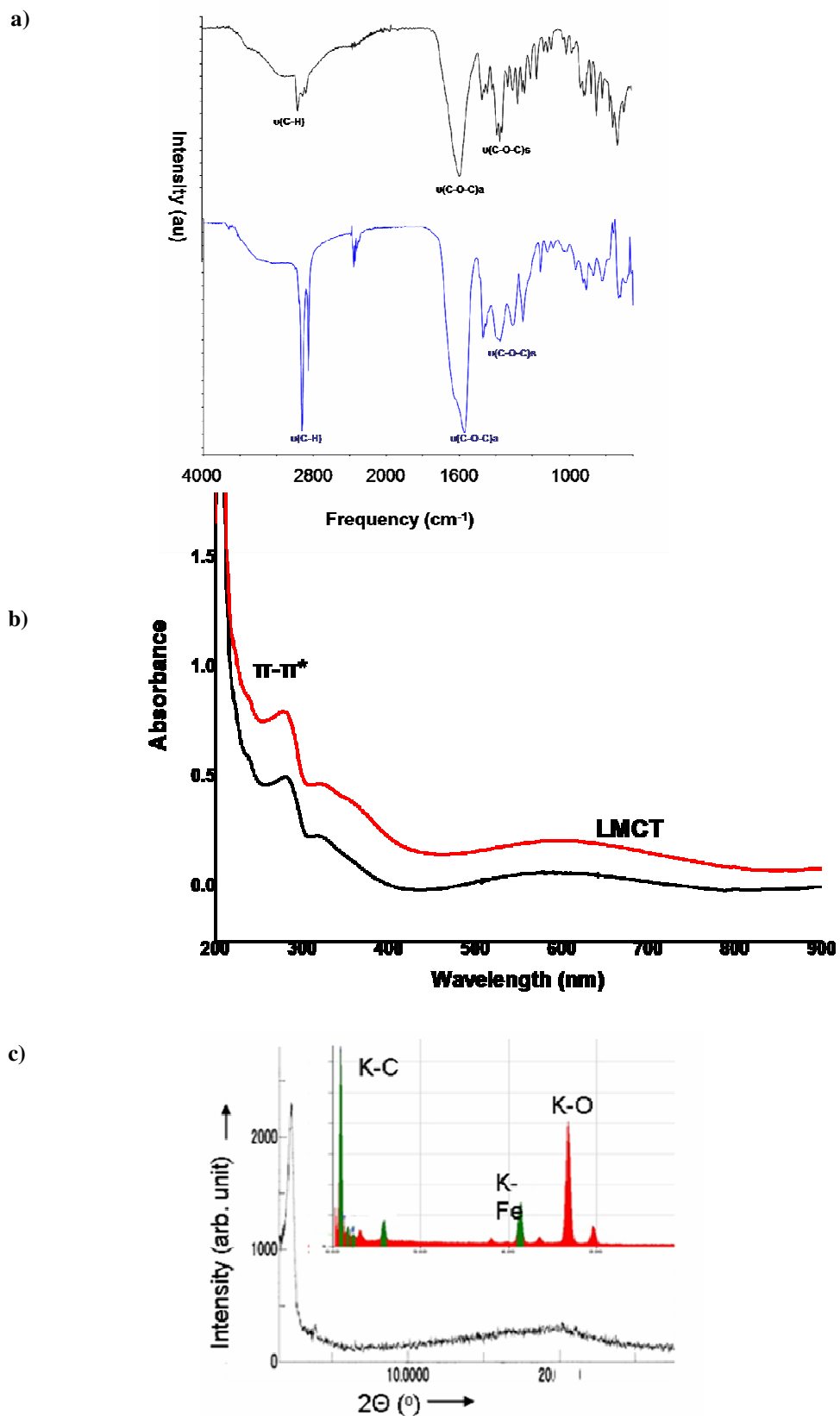


Figure 7.5: a) The FT-IR spectrum of **24** (blue) as compared to that of **23** (black). b) The UV-vis spectrum of **24** (black) as compared to that of **23** (red). [**23**] = 1×10^{-5} mol L⁻¹ and [**24**] = 1×10^{-5} mol L⁻¹. c) X-ray powder diffraction pattern of **24** reveals a signal at 2θ of 2.3° which corresponds to a d -spacing of *ca.* 3.5 nm. Inset shows EDX analyses carried out on **24**.

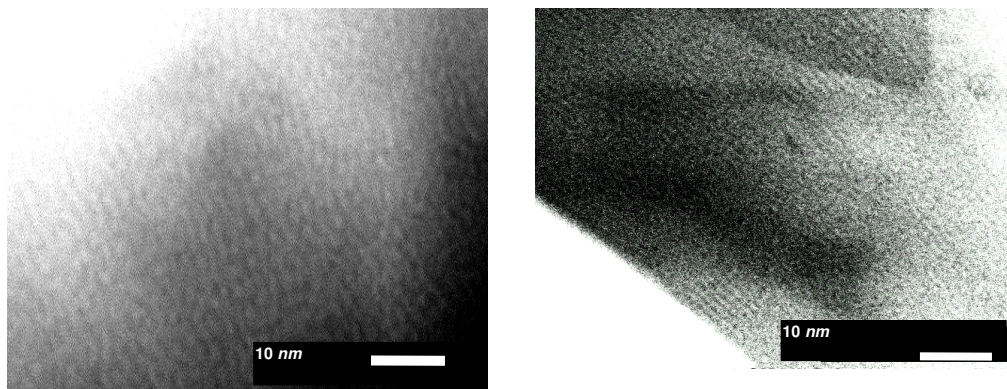


Figure 7.6: TEM micrographs suggest a layered, lamellar arrangement of the Fe^{III} complexes in **24**.

In attempts to assemble **24** into nanostructures, a solid sample was dispersed in EtOH/ H_2O solution. This solution was then heated to 80 °C and drop-cast onto a Si surface. The Si surface was then viewed using a scanning electron microscope (SEM) which revealed the formation of isolated nanosized spherical vesicles (Figure 7.7 a-f). The vesicles range in diameter from *ca.* 10 nm to *ca.* 500 nm. It was possible to obtain higher yields and separate the vesicles from the EtOH/ H_2O solution by using a 0.2 μm polycarbonate membrane. The membrane was then imaged by SEM which also showed the generation of nanosized vesicles (Figure 7.7 g-h). It is most likely that the complexes in these aggregates adopt a similar lamellar arrangement to those observed in the corresponding crystalline compounds **22** and **23**. This was verified by transmission electron microscopy (TEM) (Figure 7.8) which showed that vesicles are composed of layers that also display a highly ordered layered, endohedral packing motif. The TEM images demonstrate that the inter-layer distance within the vesicles is *ca.* 3.5 nm (Figure 7.8 g and h).

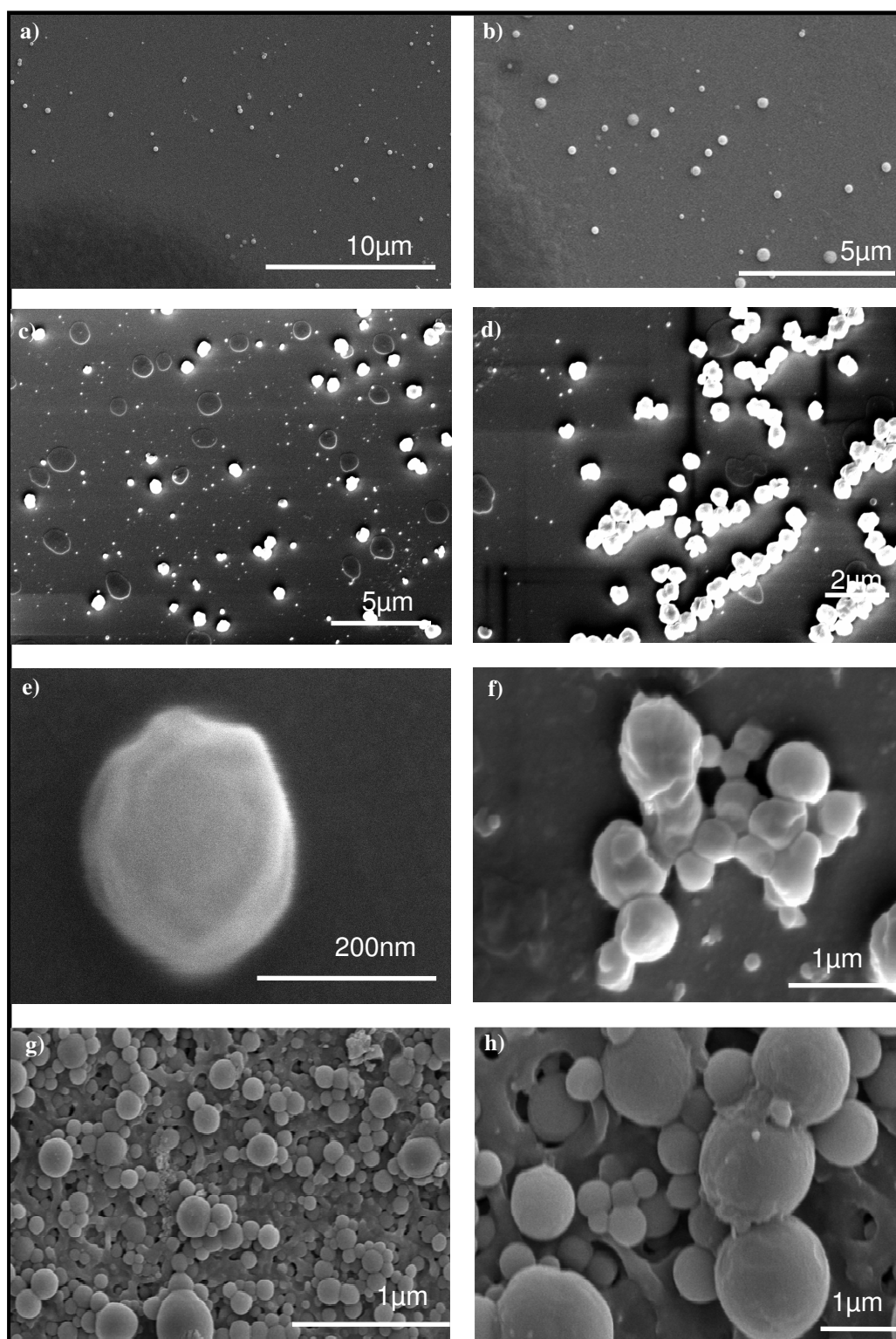


Figure 7.7: SEM micrographs of the spherical vesicles formed from the self-assembly of **24**. **a-f)** Nanosized vesicles formed by drop-casting an EtOH/H₂O solution of **24** onto a Si surface. **g)** and **h)** The spherical vesicles on a polycarbonate filter.

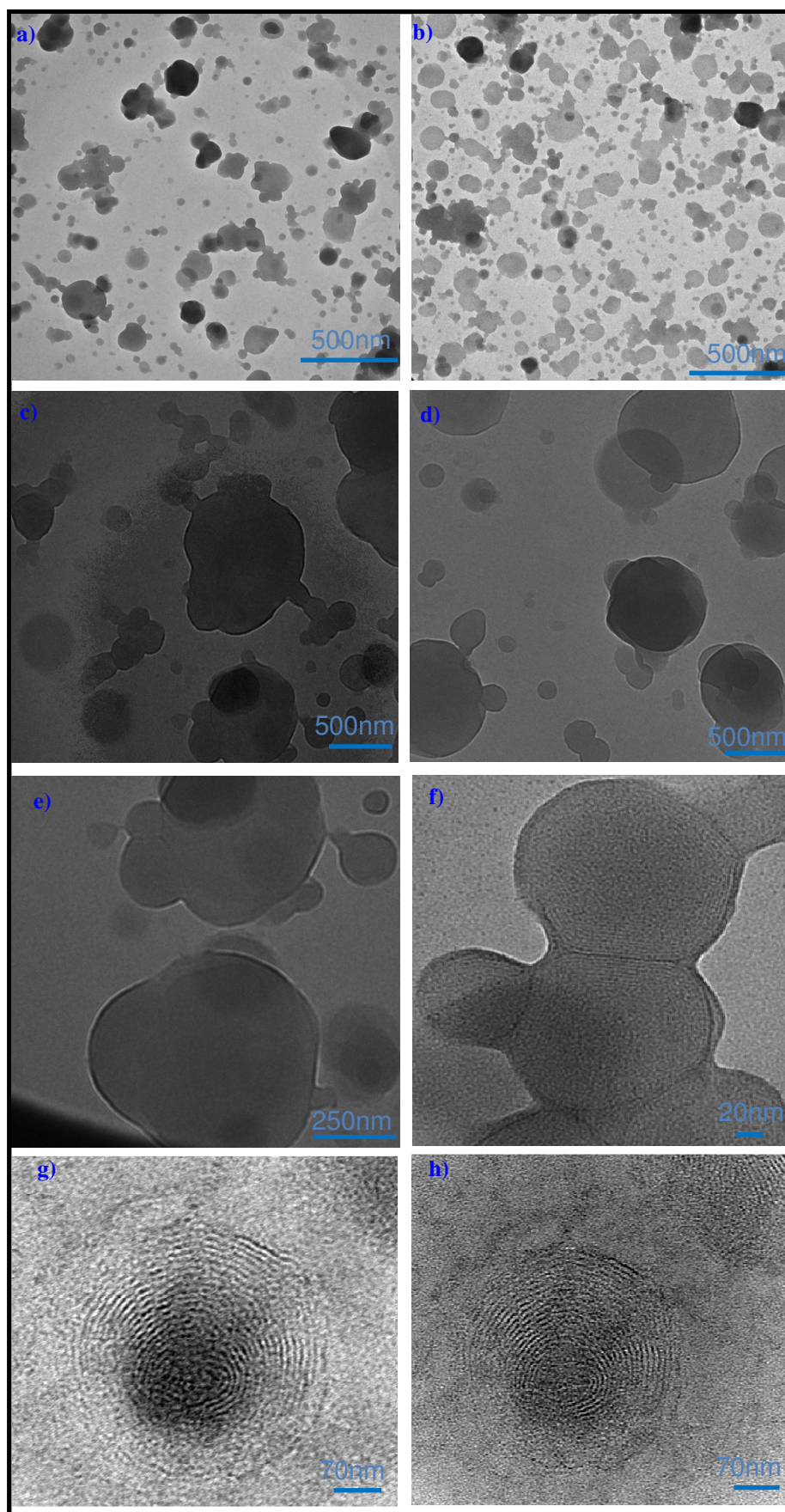


Figure 7.8: TEM micrographs of the spherical vesicles showing the layered lamellar arrangement with an inter-layer spacing of *ca.* 3.5 nm.

When the spherical vesicles were imaged using a JEOL FX 2000 operating at 200 kV at the National Institute for Material Science in Japan, an interesting phenomenon was observed. The vesicles appeared to undergo decomposition. This led to the formation of endohedral onion-type carbon structures which can be identified in high yields on the TEM grid (Figure 7.10). These endohedral carbon structures have diameters that range between *ca.* 15 nm and *ca.* 30 nm and display inter-layer distance of *ca.* 0.4 nm which is significantly smaller than that seen for the vesicles. It is likely, that the formation of the endohedral carbon structures is caused by heating effects induced by the high voltage electron beam. It has previously been reported that the irradiating effects of high voltage electron beams can instigate structural changes within a variety of different nanomaterials.^{202,203} It is also possible that the Fe contained within the vesicles may have acted as a catalyst for the formation of the endohedral onion type carbon structures as the ability of Fe to catalyse the formation of related nanomaterials is well known in the literature.^{204,205}

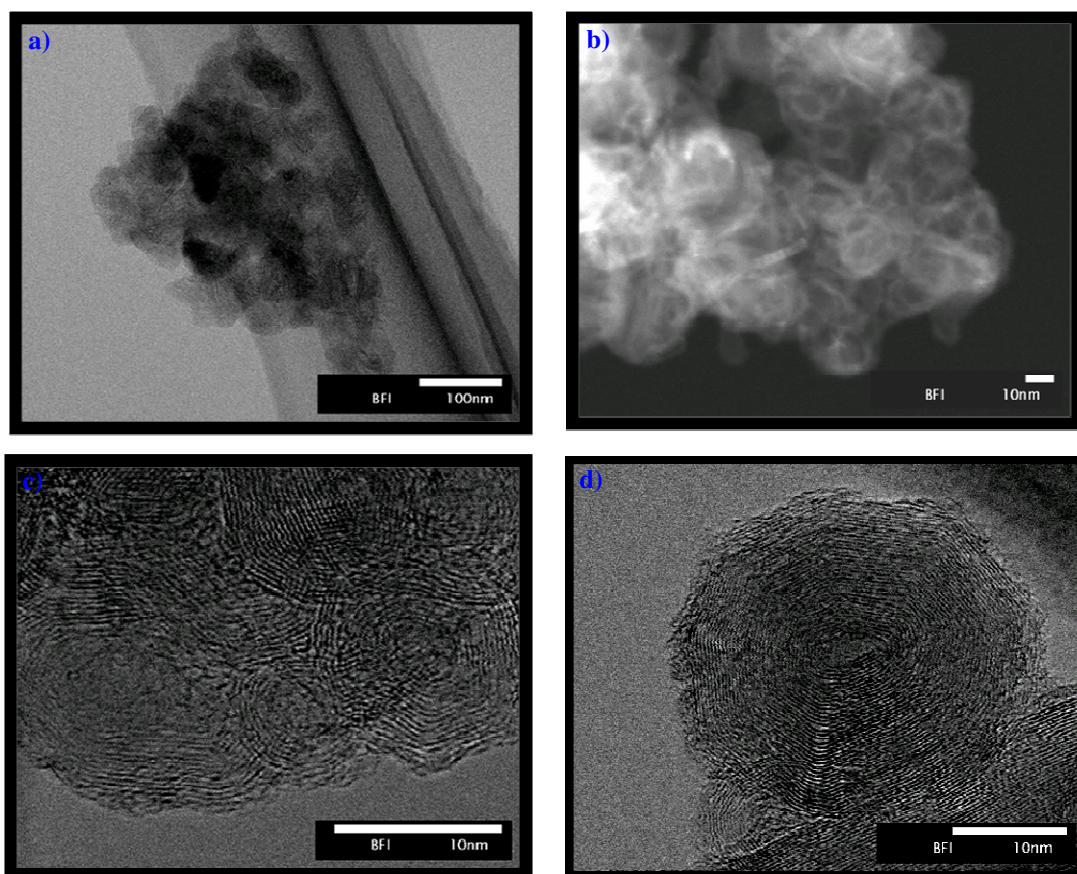


Figure 7.10: TEM micrographs of the endohedral carbon structures which result from the decomposition of the spherical vesicles.

7.5 The synthesis and self-assembly of $[\text{Fe}(\textit{o}\text{-C}_{12}\text{Mehda})(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$ (**25**)

We next set out to determine the effect of the ligand functionality on the assembly of related nanostructures. This involved the use of a similar ligand *o*-**C₁₂Mehda**, with the C₁₂ alkyl chain now *ortho*-positioned to the phenolate O donor. This ligand was reacted with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ generating the compound $[\text{Fe}(\textit{o}\text{-C}_{12}\text{Mehda})(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$ (**25**) as a blue powder. The formation of the compound was verified by FT-IR and UV-vis spectroscopy (Figure 7.11) which confirm that **25** contains similar mononuclear Fe^{III} complexes to those of **22** and **23**. CHN microanalysis also verifies the composition of **25**.

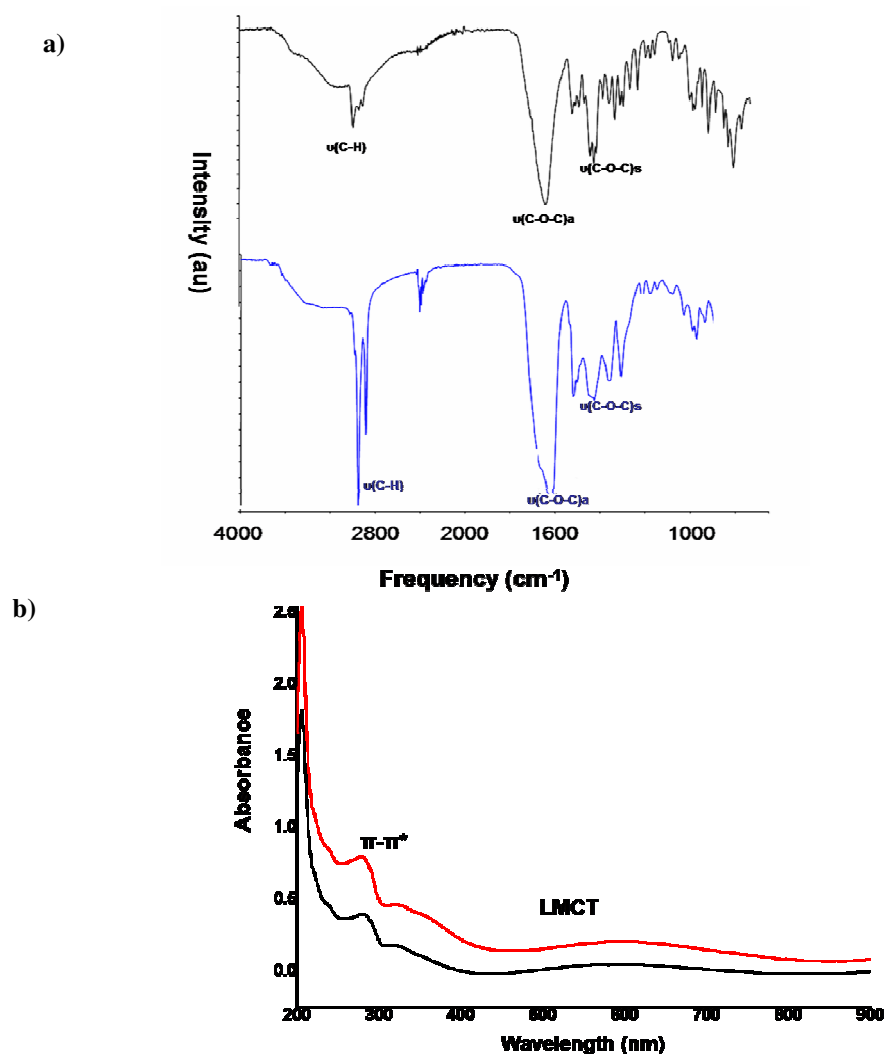


Figure 7.11: a) The FT-IR spectrum of **25** (blue) as compared to that of **23** (black). b) The UV-vis spectrum of **25** (red) as compared to that of **23** (black). $[\text{23}] = 1 \times 10^{-5} \text{ mol L}^{-1}$ and $[\text{25}] = 1 \times 10^{-5} \text{ mol L}^{-1}$.

The FT-IR spectrum of **25** shows a strong asymmetric carboxylate stretch at 1578 cm^{-1} and a symmetric carboxylate stretch at 1363 cm^{-1} .¹⁶⁴ These bond stretches arise from the *o*-C₁₂Mehda ligand. The UV-vis spectrum of **25** shows a LMCT transition at 582 nm which is characteristic of the mononuclear Fe^{III} complexes in **25**.²⁰¹

We next sought to disperse compound **25** in EtOH/H₂O solutions and explore if the molecular entities would self-organise to form hierarchical nanostructures. The resulting EtOH/H₂O solution was again drop-cast onto Si surfaces. Compound **25** self-assembles into vesicular spherical aggregates and droplets with a mean diameter of 80 nm (Figure 7.12). However, the self-assembled product of **25** is significantly less homogeneous than **24**. The SEM images reveal additionally elongated cylindrical deposits, with lengths ranging between 450 nm and 800 nm, and larger flat aggregates on the Si surface (Figure 7.12). The latter assemblies range between 150 nm and 250 nm in thickness and cover an area of several micrometers and can be considered as thin films.

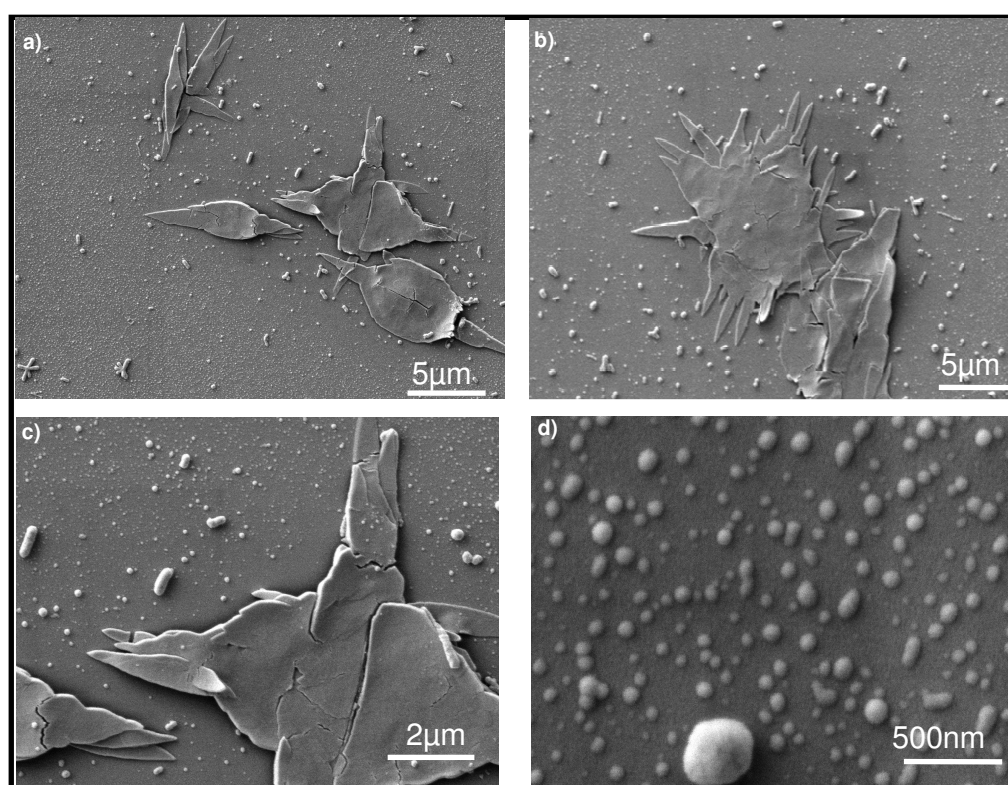


Figure 7.12: SEM micrograph of the molecular self-assembly experiments using **25**.

These electron microscopy studies demonstrate that the position of the C₁₂ alkyl chain has an impact on the topology of the resultant nanostructures that form through self-assembly approaches.

7.6 Conclusion

A series of amphiphilic coordination networks, **22** - **25**, were synthesised using Fe^{III} salts and iminodiacetic acid substituted phenol ligands. Within the network structures, Fe^{III} complexes self-assemble *via* hydrogen bonds, involving constitutional water molecules, into layered lamellar coordination assemblies with well defined hydrophilic organic and hydrophobic inorganic regions. The network structures incorporate H-bonded assemblies of water molecules that have some similarities with solid ice polymorphs.

The amphiphilicity of the reaction system allowed us to investigate if the molecular entities could be self-assembled into nanomaterials. In the case of **24**, this approach led to the generation of nanosized vesicular spheres. Even though the spherical vesicles were susceptible to electron beam induced decomposition, we were able to employ electron microscopy to characterise these materials. Transmission electron microscopy confirms that the vesicles consist of layered lamellar assemblies which are similar to the molecular structures of the parent crystalline materials. The vesicles also undergo decomposition when they are exposed to high voltage electron beams, resulting in the apparent generation of endohedral carbon structures.

Future work involving these amphiphilic Fe^{III} assemblies could involve determining if guest molecules such as fluorescent dyes could be incorporated into the spherical vesicles. This could lead to the formation of fluorescent nanoparticles which have shown applications in the area of biotechnology.²⁰⁶ It could also be possible to investigate these vesicles as a potential drug delivery system. The synthetic approach discussed in this chapter provides scope for the synthesis of related nanosized materials. For example the coordination assemblies could potentially be employed as templates for generating desirable carbonous nanomaterials.

Chapter Eight



Experimental

8.1 Materials and methods

8.1.1 Reagents

All chemicals and solvents were of reagent grade and were purchased from Sigma-Aldrich Ltd. or local solvent suppliers and were used as received, unless otherwise stated. Water was deionised before use.

8.1.2 Nuclear magnetic resonance spectroscopy

^1H NMR spectra were recorded on a Bruker DPX 400 machine operating at 400.13 MHz by either Dr. John O'Brien or Dr. Manuel Rüther. Samples were dissolved in deuterated solvents which are listed for each spectrum. Standard abbreviations for spectra: s, singlet; d, doublet; t, triplet; qt quartet; q, quaternary; m, multiplet; br, broad and J, coupling constant.

8.1.3 Infrared spectroscopy

Infrared spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer using either a universal ATR sampling accessory or a diffuse reflectance sampling accessory. Data were collected and processed using the Spectrum v5.0.1 (2002 PerkinElmer Instrument LLC) software. The scan rate was 16 scans per minute with a resolution of 4 scans in the range $4000\text{--}600\text{ cm}^{-1}$. The following abbreviations were used to describe the intensities: s, strong; m, medium; w, weak; sh, shoulder and br, broad.

8.1.4 Mass spectrometry

Electrospray ionisation mass spectrometry experiments were carried out on a Micromass LCT Electrospray mass spectrometer by Dr. Martin Feeney, Dr Dilip Rai or Dr. Bernard-Jean Denis. Samples were dissolved in HPLC grade solvents which are listed for each spectrum.

8.1.5 Elemental analysis

Elemental analysis was performed using an Exeter Analytical CE 440 housed at the analytical laboratory, UCD Belfield.

8.1.6 Single crystal X-ray diffraction

Single crystal X-ray analyses for crystals described in this report were performed by Dr. Tom McCabe, Dr Lei Zhang or Dr. Wolfgang Schmitt with a Bruker SMART APEX CCD diffractometer or a Rigaku Saturn-724 diffractometer.

Both diffractometers utilise a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$) source. The omega scan method was used to collect either a full sphere or

hemisphere of data for each crystal with a detector to crystal distance of either 5 or 6 cm. Data sets collected from the Bruker diffractometer were processed and corrected for Lorentz and polarisation effects using the SMART²⁰⁷ and SAINT-PLUS²⁰⁸ software. The structures were solved using direct methods with the SHELXTL²⁰⁹ program package.

The data sets from the Rigaku Saturn-724 diffractometer were collected using Crystalclear-SM 1.4.0 software and in each case 1680 diffraction images, of 0.5° per image, were recorded. Data integration, reduction and correction for absorption and polarisation effects were all performed using the Crystalclear-SM 1.4.0 software. Space group determination, structure solution and refinement were obtained using the Crystalstructure ver.3.8 and the Bruker SHELXTL²⁰⁹ software.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to calculated positions using a riding model with appropriately fixed isotropic thermal parameters.

8.1.7 X-ray powder diffraction

X-ray powder diffraction was performed using a Siemens D500 diffractometer with Cu-K α_1 radiation with a wavelength of $\lambda = 1.54056 \text{ \AA}$.

8.1.8 Ultraviolet-visible spectroscopy

UV-vis spectra were recorded in the range of 200-900 nm on a Cary 300 Scan spectrophotometer at 20 °C using quartz cells of 1 cm path length. Titrations were carried out on a 2 mL portion of a 10^{-6} M solution of the chosen ligand to which substoichiometric quantities of the chosen metal salts were added. The titration procedure involved recording a UV-vis spectrum of the ligand, adding an aliquot of metal salt solution to the cuvette and mixing thoroughly. A spectrum was recorded after each addition until super-imposable spectra were obtained.

8.1.9 Magnetic measurements

All magnetic measurements were recorded and modelled by Prof. Rodolphe Cl  rac at the Centre de Recherche Paul Pascal (CRPP), Pessac, France. The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer operates between 1.8 and 300 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on polycrystalline samples. The magnetic data were corrected for the sample holder and the diamagnetic contributions.

8.1.10 Photo-magnetic measurements

The photo-magnetic experiments were performed by Prof. Corine Mathonière at the Institut de Chimie de la Matière Condensée de Bordeaux with a 150 W halogen lamp (LEICA CLS 150X) coupled through an optical fibre directed into the magnetometer cavity. 2 to 3 mg of powdered samples were packed in a thermoformed SQUID straw which was maintained at about 1 mm from the optical fibre. At each temperature, data in the dark has been systematically subtracted from the raw data. The obtained difference was simply added to the dc measurements which are obtained from the standard SQUID set-up. These values were utilised in order to determine the magnetic susceptibility after irradiation. The effective power of the lamp received by the sample was measured at $200(40) \text{ m W cm}^{-2}$ under white light irradiation and at about $30(5) \text{ m W cm}^{-2}$ under 650 nm light irradiation. The recorded temperatures have been corrected to take into account the heating effect caused by the light irradiation. Systematic calibration of the temperatures has been carried out by using the data without irradiation as a reference.

8.1.11 Surface reflectivity measurements

The surface reflectivity measurements were performed, by Prof. Corine Mathonière, under white-light irradiation (90 mW cm^{-2}) using a home-built reflectivity system housed at the Institut de Chimie de la Matière Condensée de Bordeaux. It is composed of a CVI spectrometer and three optical fibres (two for incoming light which were used for white light irradiation and spectral analysis and one for out coming light which was used for spectral analysis). The reflectivity signal was compared with two standard references: barium sulphate for the white colour ($R = 1$, $Abs. = 0$) and activated charcoal for the black colour ($R = 0$, $Abs. = 1$). This experimental set-up allows the absorption spectra to be collected, within the range of 430-800 nm, between 10 and 280 K (3 K min^{-1}). The set up also enables the temperature dependence of the reflectivity signal to be determined simultaneously at two different wavelengths ($\pm 2.5 \text{ nm}$) and at different temperatures.

8.1.12 Thermogravimetric analysis

Thermogravimetric analyses were carried out using a Perkin Elmer Pyris 1TGA. The measurements unless stated, were recorded in air using a ceramic crucible (ca. 5 mg sample; heating rate of $10 \text{ }^{\circ}\text{C}$; range $25\text{-}900 \text{ }^{\circ}\text{C}$). The instrument was calibrated to In and Ni standards in air atmosphere.

8.1.13 Gas absorption measurements

Low-pressure N₂ and H₂ adsorption measurements were performed on an Autosorb-IQ (Quantachrome) volumetric analyser. The sample was outgassed at 10⁻⁶ torr. Helium was used for the estimation of the dead volume, assuming that it is not absorbed at any of the studied temperatures. A liquid N₂ bath was used for the adsorption measurements at 77 K. To provide high accuracy and precision in determining p/p_0 , the saturation pressure was measured throughout the N₂ measurement by means of a dedicated saturation pressure transducer. Ultra-high grade N₂, H₂ and He (99.999 % purity) were used throughout the experiments. Non-ideality of gases were obtained from the second virial coefficient at experimental temperature.²¹⁰ The surface area of the sample was determined from the N₂ isotherm. To estimate the pore sizes, the N₂ isotherm was analyzed using nonlocal density functional theory (NLDFT), implementing a hybrid kernel for N₂ adsorption at 77 K based on a zeolite/silica model containing cylindrical pores.¹⁹⁵

8.1.14 Scanning electron microscopy

Scanning electron micrographs were obtained using Hitachi S-3500N, Hitachi S-4800 and Tescan Mira XMU microscopes. All samples were coated with a *ca.* 4 nm thick Au layer.

8.1.15 Transmission electron microscopy

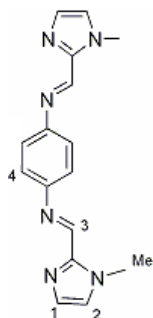
Transmission electron microscopy was carried out using JEOL FX 2000, JEOL 2100 and FEI titan microscopes. The samples for TEM analysis were placed on copper formvar 200 square mesh TEM grids which were purchased from Agar. Ltd.

8.1.16 Solvothermal synthesis

Solvothermal synthesis was carried out using a Parr Instrument Company Series 4760/4765 general-purpose digestion bomb employing a 23 ml Teflon insert. Maximum loading of the insert was dependent on reagents. The heating cycles and maximum loadings are specified for each reaction and the reactions were performed in a conventional oven.

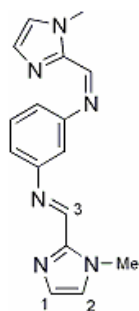
8.2 Ligand Synthesis

8.2.1 Synthesis of N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-4-diamine (L1)



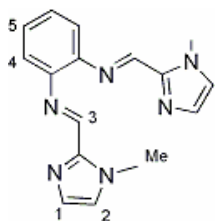
A methanol solution (30 mL) of 1-methyl-2-imidazolcarboxyaldehyde (0.53 g, 4.4 mmol) was added drop-wise to a methanol solution (30 mL) of *p*-phenyldiamine (0.22 g, 2.2 mmol). The resultant reaction mixture was stirred for 18 hours. Afterwards, the mixture was evaporated to dryness under vacuum yielding an oil, that was purified from acetonitrile yielding a yellow powder. Yield: 0.548 g (84%); ^1H NMR (D_6 -DMSO, 400 MHz): δ = 8.6 (s, 2H, H_3), 7.5 (s, 2H, H_1), 7.4 (d, J = 8 Hz, 4H, H_4), 7.2 (s, 2H, H_2), 4.1 (s, 6H, H_{Me}) ppm; ESI-MS (MeOH): 293.1 m/z [$\text{C}_{16}\text{H}_{17}\text{N}_6$] $^+$; FT-IR (KBr, diffuse reflectance): 3190(m), 1692(w), 1619(s), 1523(w), 1494(w), 1476(m), 1433(s), 1418(m), 1365(m), 1312(w), 1289(w), 1227(w), 1153(m), 1106(w), 1083(w), 1056(w), 1008(w), 962(m), 931(m), 872(m), 834(m), 762(s), 696(m), 676(w) cm^{-1} ; CHN analysis for $\text{C}_{16}\text{H}_{16}\text{N}_6 \cdot \text{H}_2\text{O}$: Expected: C, 61.92%; H, 5.85%; N, 27.08%. Found: C, 61.34%; H, 5.88%; N, 26.84%.

8.2.2 Synthesis of N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1-3-diamine (L2)



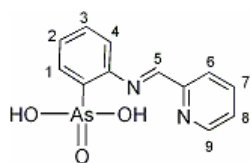
A synthetic procedure similar to that used for **L1** was applied to synthesise **L2**, except *m*-phenyldiamine (0.22 g, 2.2 mmol) was used instead of *o*-phenyldiamine, resulting in a white powder. Yield: 0.55 g (50 %); ^1H NMR (D_6 -DMSO, 400 MHz): δ = 8.6 (s, 2H, H_3), 7.5 (s, 2H, H_1), 7.4 (m, 4H, $\text{H}_{\text{aromatic}}$), 7.2 (s, 2H, H_2), 4.1 (s, 6H, H_{Me}) ppm; ESI-MS (MeOH): 293.0 m/z [$\text{C}_{16}\text{H}_{17}\text{N}_6$] $^+$; FT-IR (KBr, diffuse reflectance): 3133(m), 3111(m), 2221(w), 1933(w), 1686(w), 1628(s), 1581(m), 1521(w), 1480(m), 1433(s), 1429(m), 1369(m), 1321(w), 1291(m), 1237(w), 1157(m), 1139(m), 1078(w), 981(m), 954(m), 931(m), 879(m), 858(w), 817(m), 783(s), 769(s) cm^{-1} ; CHN analysis for $\text{C}_{16}\text{H}_{16}\text{N}_6 \cdot 2\text{H}_2\text{O}$: Expected: C, 58.52%; H, 6.14%; N, 25.59%. Found: C, 58.70%; H, 5.46%; N, 25.61%.

8.2.3 Synthesis of N,N'-bis-(1-methyl-1-H-imidazol-2-ylmethylene)-1,2-diamine (L3)



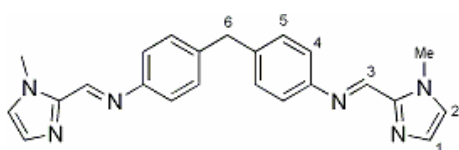
A synthetic procedure similar to that used for **L1** was applied to synthesise **L3**, except *o*-phenyldiamine (0.22 g, 2.2 mmol) was used instead of *o*-phenyldiamine resulting in a white powder. Yield: 0.15 g (24%); ^1H NMR (D_6 -DMSO, 400 MHz): δ = 7.6 (s, 2H, H_3), 7.5 (d, J = 8 Hz, 2H, H_4), 7.3 (d, J = 8 Hz, 2H, H_5), 7.1 (s, 2H, H_1), 6.8 (s, 2H, H_2), 4.0 (s, 6H, H_{Me}) ppm; ESI-MS (MeOH): 293.2 m/z [$\text{C}_{16}\text{H}_{17}\text{N}_6$] $^+$; FT-IR (KBr, diffuse reflectance): 3135(m), 3009(m), 2223(w), 1931(w), 1690(w), 1630(s), 1583(m), 1525(w), 1477(m), 1432(s), 1429(m), 1372(m), 1318(w), 1295(m), 1239(w), 1159(m), 1136(m), 1081(w), 983(m), 955(m), 933(m), 881(m), 857(w), 817(m), 785(s), 771(s) cm^{-1} ; CHN analysis for $\text{C}_{16}\text{H}_{16}\text{N}_6 \cdot \text{H}_2\text{O}$: Expected: C, 61.92%; H, 5.85%; N, 27.08%. Found: C, 61.65%; H, 5.64%; N, 26.50%.

8.2.4 Synthesis of 4-[(pyridin-2-ylmethylene)-amino]-arsonic acid (L4)



A synthetic procedure similar to that used for **L1** was applied to synthesise **L4**, except 2-aminophenyl arsonic acid (0.95 g, 4.4 mmol) was used instead of *p*-phenyldiamine and 4-pyridine carboxyaldehyde (0.44 g, 4.4 mmol) was used instead of 1-methyl-2-imidazolcarboxyaldehyde resulting in a white powder. Yield: 0.87 g (62 %); ^1H NMR (D_6 -DMSO, 400 MHz): δ = 10.0 (s, 1H, H_5), 8.9 (d, J = 4.8 Hz, 1H, H_9), 8.2 (dd, J = 5.2 Hz, 8.6 Hz, 1H, H_7), 7.9 (d, J = 8.6 Hz, 1H, H_6), 7.8 (dd, J = 5.2 Hz, 4.8 Hz, 1H, H_8), 7.4 (d, J = 9 Hz, 1H, H_1), 7.3 (dd, J = 9 Hz, 8.3 Hz, 1H, H_2), 6.8 (d, J = 7.8 Hz, 1H, H_4), 6.7 (dd, J = 8.3 Hz, 7.8 Hz, 1H, H_3) ppm; ESI-MS (DMSO): 307.1 m/z [$\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3\text{As}$] $^+$; FT-IR (KBr, diffuse reflectance): 3414(w), 2784(m), 2343(m), 1618(s), 1587(w), 1572(m), 1549(w), 1473(s), 1446(m), 1436(m), 1374(w), 1304(w), 1265(w), 1230(m), 1202(m), 1168(m), 1063(w), 1031(m), 993(m), 885(s), 785(s), 749(s) cm^{-1} ; CHN analysis for $\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_3\text{As}$: Expected: C, 47.08%; H, 3.62%; N, 9.15%. Found: C, 47.50%; H, 3.67%; N, 9.15%.

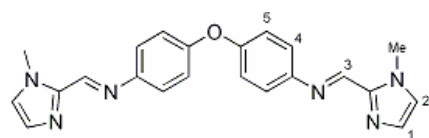
8.2.5 Synthesis of N,N'-bis-(1-methyl-1-H-imidazol-2-yl-methylene)-4,4'-diaminodiphenylmethane (L5)



A methanol solution (15 mL) of 1-methyl-2-imidazolcarboxyaldehyde (0.22 g, 2.2 mmol) was added drop-wise to a methanol solution (15 mL) of 4,4'-diaminodiphenylmethane (0.22 g, 1.1 mmol). The resultant

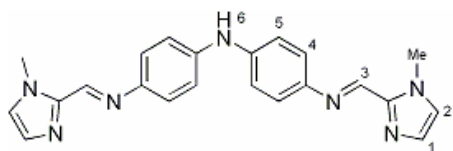
reaction mixture was stirred for 18 hours. Afterwards, the mixture was evaporated to dryness under vacuum yielding an oil, that was purified from acetonitrile yielding a cream powder of **L5**, which was filtered off and dried in air. Yield: 0.62 g (60%); ^1H NMR ($\text{D}_6\text{-DMSO}$, 400 MHz): δ = 8.5 (s, 2H, H_3), 7.4 (s, 2H, H_1), 7.3 (d, J = 8.8 Hz, 4H, H_5), 7.3 (d, J = 8.8 Hz, 4H, H_4), 7.2 (s, 2H, H_2), 4.1 (s, 6H, H_{Me}), 4.0 (s, 2H, H_6) ppm; ESI-MS (MeOH): 383.1 m/z [$\text{C}_{23}\text{H}_{23}\text{N}_6$] $^+$; FT-IR (KBr, diffuse reflectance): 3251(w), 3140(w), 3022(w), 2951(w), 1627(s), 1594(m), 1518(w), 1502(m), 1476(m), 1437(s), 1412(m), 1367(m), 1318(w), 1307(w), 1290(m), 1152(m), 1113(w), 1085(w), 1013(w), 974(w), 958(w), 933(m), 870(s), 855(w), 829(w), 806(w), 750(s), 679(m) cm^{-1} ; CHN analysis for $\text{C}_{23}\text{H}_{22}\text{N}_6$: Expected: C, 72.23%; H, 5.80%; N, 21.97%. Found: C, 72.45%; H, 5.57%; N, 22.00%.

8.2.6 Synthesis of *N,N'*-bis-(1-methyl-1-*H*-imidazol-2-yl-methylene)-4,4'-oxydianiline (**L6**)



A synthetic procedure similar to that used for **L5** was applied to synthesise **L6**, except 4,4'-oxydianiline (0.22 g, 1.1 mmol) was used instead of 4,4'-diaminodiphenylmethane to yield a cream powder. Yield: 0.61 g (58%); ^1H NMR ($\text{D}_6\text{-DMSO}$, 400 MHz): δ = 8.5 (s, 2H, H_3), 7.4 (s, 2H, H_1), 7.4 (d, J = 8.8 Hz, 4H, H_5), 7.2 (s, 2H, H_2), 7.1 (d, J = 8.8 Hz, 4H, H_4), 4.1 (s, 6H, H_{Me}) ppm; ESI-MS (MeOH): 385.3 m/z [$\text{C}_{22}\text{H}_{21}\text{N}_6\text{O}$] $^+$; FT-IR (KBr, diffuse reflectance): 1629(s), 1596(m), 1516(w), 1502(m), 1476(m), 1438(s), 1412(m), 1369(m), 1318(w), 1290(m), 1152(m), 1113(w), 1083(w), 1020(w), 974(w), 933(m), 870(s), 865(w), 839(w), 815(w), 750(s), 679(m) cm^{-1} ; CHN analysis for $\text{C}_{22}\text{H}_{20}\text{N}_6\text{O}$: Expected: C, 68.73%; H, 5.24%; N, 21.86%. Found: C, 68.47%; H, 5.44%; N, 21.53%.

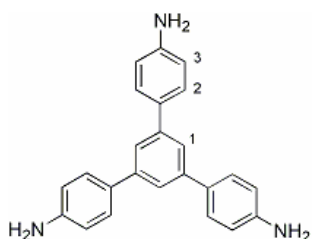
8.2.7 Synthesis of *N,N'*-bis-(1-methyl-1-*H*-imidazol-2-yl-methylene)-4,4'-diaminodiphenylamine (**L7**)



A synthetic procedure similar to that used for **L5** was applied to synthesise **L7**, except 4,4'-diaminodiphenylamine (0.22 g, 1.1 mmol) was used instead of 4,4'-diaminodiphenylmethane to yield a white powder. Yield: 0.62 g (62%); ^1H NMR ($\text{D}_6\text{-DMSO}$, 400 MHz): δ = 8.8 (s, 1H, H_6), 8.7 (s, 2H, H_3), 7.6 (s, 2H, H_1), 7.4 (d, J = 8 Hz, 4H, H_5), 7.3 (s, 2H, H_2), 7.2 (d, J = 8 Hz, 4H, H_4), 4.1 (s, 6H, H_{Me}) ppm; ESI-MS (MeOH): 384.1 m/z [$\text{C}_{22}\text{H}_{22}\text{N}_7$] $^+$; FT-IR (KBr, diffuse reflectance): 1620(s), 1590(m), 1518(w), 1499(m), 1473(m), 1433(s), 1417(m),

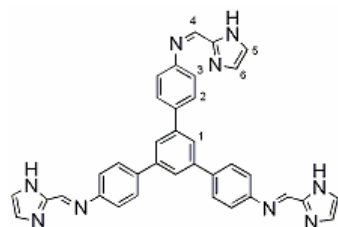
1373(m), 1321(w), 1287(m), 1150(m), 1115(w), 1085(w), 1018(w), 976(w), 936(m), 873(s), 869(w), 842(w), 820(w), 755(s), 683(m) cm^{-1} ; CHN analysis for $\text{C}_{22}\text{H}_{21}\text{N}_7$: Expected: C, 68.91%; H, 5.52%; N, 25.57%. Found: C, 68.82%; H, 5.46%; N, 25.83%.

8.2.8 Synthesis of 1,3,5-tri(4-aminophenyl)benzene



1,3,5-tri(4-aminophenyl)benzene was prepared by following a modified literature procedure.¹⁸⁸ Silicon tetrachloride (40 mL, 0.30 mol) was added drop-wise to a solution of *p*-nitroacetophenone (20 g, 0.12 mol) in ethanol (120 mL) at 0 °C. A yellow precipitate forms immediately and the mixture was stirred for 10 hours. An aqueous solution of ammonium chloride (100 mL) was added and stirred for ten minutes. The yellow precipitate was filtered and dried in an oven. This powder was added to ethanol (100 mL), and Pd/C (0.80 g) was added to the resultant suspension. The mixture was refluxed and 80% hydrazine monohydrate (33 mL) was then added. After refluxing for 10 hours the suspension was filtered hot and the resultant solution was left to cool, yielding a yellow powder. The product was recrystallised from chloroform. Yield: 12g (80%); ^1H NMR (CDCl_3 , 400 MHz): δ = 7.6 (s, 3H, H_1), 7.5 (d, J = 8.5 Hz, 6H, H_2), 6.8 (d, J = 8.5 Hz, 6H, H_3), 3.7 (s, 6H, H_{NH_2}) ppm; ESI-MS (MeOH): 352.2 m/z [$\text{C}_{24}\text{H}_{22}\text{N}_3$] $^+$; FT-IR (ATR): 3433(w), 3346(w), 2028(w), 1618(m), 1514(s), 1449(w), 1405(w), 1278(m), 1177(m), 1129(w), 871(w), 765(s), 732(w), 707(w) cm^{-1} ; CHN analysis for $\text{C}_{24}\text{H}_{21}\text{N}_3$: Expected: C, 82.02%; H, 6.02%; N, 11.96%. Found: C, 81.97%; H, 6.11%; N, 11.96%.

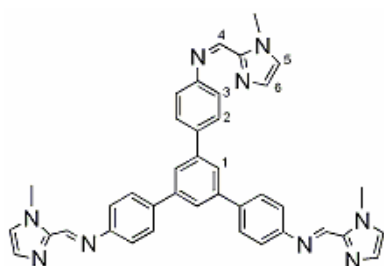
8.2.9 Synthesis of N,N',N''-tris-(4-H-imidazol-2-ylmethylene)-1-3-5-triphenylbenzene (L8)



A methanol (30 mL) solution of 4-imidazole carboxaldehyde (0.29 g, 3.0 mmol) was added drop-wise to a methanol solution (30 mL) of 1,3,5-tri(4-aminophenyl) benzene (0.50 g, 1.0 mmol). A few drops of acetic acid were added to the resulting solution, which was then refluxed overnight. The solvent was then removed under reduced pressure, and the resulting solid was recrystallised from acetonitrile to give the product as a cream coloured powder. Yield: 0.52 g (61 %); ^1H NMR ($\text{D}_6\text{-DMSO}$, 400 MHz): δ = 13.1 (s, 3H, H_{NH}), 8.6 (s, 3H, H_4), 7.9 (m, 12H, H_2+H_3), 7.6 (s, 3H, H_1), 7.3 (m, 6H,

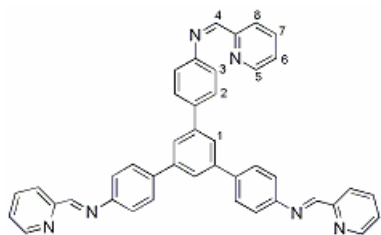
H₅+H₆) ppm; ESI-MS (DMSO): 608.2 m/z [NaC₃₆H₂₇N₉]⁺; FT-IR (ATR): 3109(m), 1628(s), 1593(s), 1503(s), 1441(m), 1394(s), 1332(m), 1299(s), 1223(s), 1203(s), 1173(s), 1113(s), 1089(s), 984(m), 874(s), 790(s), 762(s), 730(s), 695(s) cm⁻¹; CHN analysis for C₃₆H₂₇N₉: Expected: C, 73.83%; H, 4.65%; N, 21.52%. Found: C, 73.98%; H, 4.61%; N, 21.60%.

8.2.10 Synthesis of N,N',N''-tris-(1-methyl-1-H-imidazol-2-ylmethylene)-1-3-5-triphenylbenzene (L9)



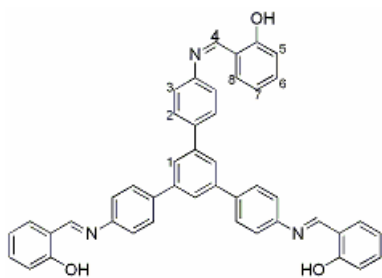
A synthetic procedure similar to that used for **L8** was applied to synthesise **L9**, except 1-methyl-2-imidazolecarboxaldehyde (0.33 g, 3.0 mmol) was used instead of 4-imidazole-carboxaldehyde yielding the product as a brown powder. Yield: 0.46 g (52 %); ¹H NMR (D₆-DMSO, 400 MHz): δ = 8.7 (s, 3H, H₄), 8.0 (d, 6H, H₅+H₆), 7.9 (s, 3H, H₁), 7.7 (d, J = 8.6 Hz, 6H, H₂), 7.5 (d, J = 8.6 Hz, 6H, H₃), 4.0 (s, 9H, H_{Me}) ppm; ESI-MS (DMSO): 650.3 m/z [NaC₃₉H₃₃N₉]⁺; FT-IR (ATR): 3352(m), 1627(s), 1594(m), 1495(s), 1430(m), 1394(s), 1342.(m), 1298(s), 1223(s), 1083(m), 791(s), 764(s), 736(s), 694(s), 532(m), 525(m) cm⁻¹; CHN analysis for C₃₉H₃₃N₉: Expected: C, 74.62%; H, 5.30%; N, 20.08%. Found: C, 74.51%; H, 5.10%; N, 20.11%.

8.2.11 Synthesis of N,N',N''-tris-(4-pyridin-2-ylmethylene)-1-3-5-triphenylbenzene (L10)



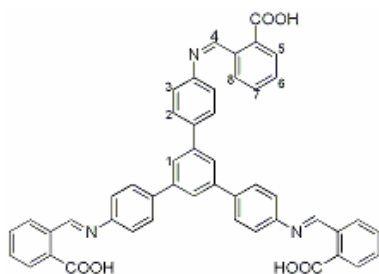
A synthetic procedure similar to that used for **L8** was applied to synthesise **L10**, except 4-pyridine-carboxaldehyde (0.32 g, 3.0 mmol) was used instead of 4-imidazole-carboxaldehyde, yielding the product as a beige powder. Yield: 0.53 g (60 %); ¹H NMR (D₆-DMSO, 400 MHz): δ = 9.5 (s, 3H, H₄), 8.9 (d, J = 5.2 Hz, 3H, H₅), 8.85 (d, J = 7.6 Hz, 3H, H₈), 8.8 (dd, J = 7.6 Hz, 5.4 Hz, 3H, H₇), 8.6 (dd, J = 5.2 Hz, 5.4 Hz, 3H, H₆), 8.1 (d, J = 8 Hz, 6H, H₃), 8.0 (d, J = 8 Hz, 6H, H₂), 7.9 (s, 3H, H₁) ppm; ESI-MS (DMSO): 641.1 m/z [NaC₄₂H₃₀N₆]⁺; FT-IR (ATR): 3348(m), 2005(m), 1629(s), 1591(m), 1471(s), 1436(s), 1299(m), 1182(s), 1136(s), 1052(m), 997(s), 826(s), 775.(s), 747(s) cm⁻¹; CHN analysis for C₄₂H₃₀N₆: Expected: C, 81.53%; H, 4.89%; N, 13.58%. Found: C, 81.48%; H, 4.72%; N, 13.70%.

8.2.12 Synthesis of N,N',N''-tris-(4-phen-2-ol-2-ylmethylene)-1-3-5-triphenylbenzene (L11)



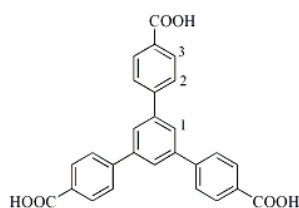
An methanol solution (60 mL) of salicylaldehyde (0.37 g, 3.0 mmol) was added drop-wise to a methanol solution (120 mL) of 1,3,5-tri(4-aminophenyl) benzene (0.50 g, 1.0 mmol). The resultant solution was stirred for 18 hours resulting in the precipitation of a white powder. Yield: 0.60 g (90 %); ^1H NMR (D_6 -DMSO, 400 MHz): δ = 12.1 (s, 3H, H_{OH}), 9.1 (s, 3H, H_4), 8.0 (m, 6H, H_6+H_7), 7.7 (d, J = 8 Hz, 6H, H_3), 7.6 (d, J = 8 Hz, 6H, H_2), 7.5 (s, 3H, H_1), 7.0 (m, 6H, H_5+H_8) ppm; ESI-MS (DMSO): 664.2 m/z [$\text{C}_{45}\text{H}_{34}\text{N}_3\text{O}_3$] $^+$; FT-IR (ATR): 3044(w), 2973(w), 2754(w), 2639(w), 1975(w), 1912(w), 1627(s), 1572(m), 1485(m), 1447(m), 1385(m), 1331(w), 1317(w), 1269(m), 1237(w), 1197(m), 1157(w), 1148(w), 1115(m), 1032(w), 984(s), 943(w), 893(s), 854(w), 782(m), 748(s), 728(m), 682(m) cm^{-1} ; CHN analysis for $\text{C}_{45}\text{H}_{33}\text{N}_3\text{O}_3$: Expected: C, 81.43%; H, 5.01%; N, 6.33%. Found: C, 81.39%; H, 5.02%; N, 6.35%.

8.2.13 Synthesis of N,N',N''-tris-(2-benzoic acid-2-ylmethylene)-1-3-5-triphenylbenzene (L12)



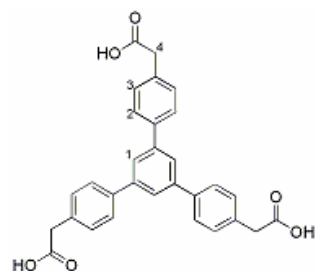
A synthetic procedure similar to that used for **L11** was applied to synthesise **L12**, except 2-carboxybenzaldehyde (0.45 g, 3.0 mmol) was used instead of salicylaldehyde, yielding the product as a cream powder. Yield: 0.66 g (65%); ^1H NMR (D_6 -DMSO, 400 MHz): δ = 8.7 (s, 3H, H_4), 7.6 (m, 6H, H_2+H_3), 7.4 (m, 6H, H_6+H_7), 7.3 (s, 3H, H_1), 7.2 (m, 6H, H_5+H_8) ppm; ESI-MS (DMSO): 748.2 m/z [$\text{C}_{48}\text{H}_{34}\text{N}_3\text{O}_6$] $^+$; FT-IR (ATR): 1747(s), 1630(s), 1519(s), 1465(w), 1355(w), 1285(m), 1276(w), 1211(m), 1186(w), 1159(w), 1093(m), 1066(s), 1013(m), 867(m), 865(s), 790(s), 704(m), 687(m) cm^{-1} ; CHN analysis for $\text{C}_{48}\text{H}_{33}\text{N}_3\text{O}_6$: Expected: C, 77.10%; H, 4.45%; N, 5.62%. Found: C, 77.32%; H, 4.59%; N, 5.54%.

8.2.14 Synthesis of 1,3,5-benzene-triacetophenone



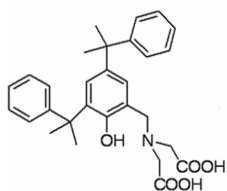
1,3,5-benzene-triacetophenone was synthesised following a literature procedure.¹⁹⁷ Anhydrous aluminium trichloride (21 g, 0.15 mol) was reacted with acetyl chloride (12 g, 0.15 mol) at 0 °C under a N₂ atmosphere. A dichloromethane (150 mL) solution of 1,3,5-triphenyl benzene (5.8 g, 0.02 mol) was then added drop-wise yielding a red solution which was stirred at 0 °C for twenty minutes. The solution was then stirred at room temperature for 90 minutes. The red solution was then added to ice (1 L) and stirred overnight. The organic portion of the resultant mixture was extracted with dichloromethane (3 x 300 mL), washed with aqueous sodium carbonate (25 mL), and dried with magnesium sulphate. The solution was then removed under vacuum yielding a white powder. Yield: 2.8 g (86%); ¹H NMR (D₆-DMSO, 400 MHz): δ = 8.1 (d, J = 8 Hz, 6H, H₂), 7.9 (s, 3H, H₁), 7.8 (d, J = 8 Hz, 6H, H₃), 2.05 (m, 3H, H_{OH}) ppm; ESI-MS (DMSO): 433 m/z [C₃₀H₂₅O₃]⁺.

8.2.15 Synthesis of 1,3,5-benzenetri-(phenylacetic acid) (BTPA)



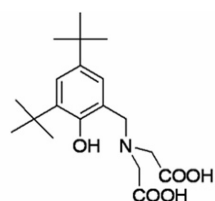
1,3,5-benzene-triacetophenone (5.0 g, 7.0 mmol), MeOH (10 mL) and boron trifluoride etherate (17 g, 11 mmol) were added in one portion to a suspension of lead tetraacetate (5.3 g, 11 mmol) in benzene (100 mL). The reaction mixture was stirred at room temperature for 18 hours. Then it was diluted with cold water (50 mL), extracted with benzene (60 mL), washed with saturated sodium carbonate (100 mL) and with saturated sodium chloride (75 mL) and then dried with magnesium sulphate. Evaporation of the solvent yielded a white powder which was refluxed overnight in a 2M NaOH solution (50 mL). This resulted in a colourless solution which was acidified with hydrochloric acid yielding a white precipitate, which was filtered and dried. Yield: 2.8 g (91%); ¹H NMR (D₆-DMSO, 400 MHz): δ = 8.1 (m, 12H, H₂+H₃), 7.2 (s, 3H, H₁), 2.8 (s, 6H, H₄) ppm; ESI-MS (DMSO): 481.2 m/z [C₃₀H₂₅O₆]⁺; FT-IR (KBr, ATR): 3411(w), 1671(s), 1599(s), 1561(w), 1424(w), 1392(m), 1358(m), 1309(w), 1272(s), 1244(m), 1185(w), 1119(w), 1013(m), 954(m), 885(w), 814(s), 763(w), 710(s) cm⁻¹; CHN analysis for C₃₀H₂₄O₆: Expected: C, 74.99%; H, 5.03%; N, 0%. Found: C, 74.90%; H, 5.05%; N, 0%.

8.2.16 N-[3,5-bis(α,α -dimethylbenzyl-2-hydroxy-benzyl)] iminodiacetic acid (**Bc₂hda**)



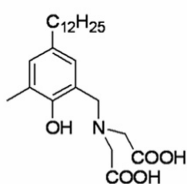
The **Bc₂hda** ligand used in this study had been previously prepared in the research group and was used without further purification. ¹H NMR (D₂O, 400 MHz): δ = 7.5-7.4 (m, 10H, 10 x H_{aromatic}), 7.3 (s, 1H, 1 x H_{aromatic}), 7.1 (s, 1H, 1 x H_{aromatic}), 4.5 (s, 1H, 1 x CH₂), 3.5 (s, 4H, 2 x CH₂), 1.7 (s, 6H, 2 x CH₃), 1.3 (s, 6H, 2 x CH₃) ppm; ESI-MS (H₂O): 498.2 m/z [NaC₂₉H₃₃NO₅]⁺; FT-IR (KBr, diffuse reflectance): 3453(m), 3205(m), 3106(m), 2797(m), 2512(m), 1910(m), 1705(s), 1662(s), 1600(s), 1561(s), 1462(s), 1438(s), 1358(m), 1325(s), 1284(s), 1250(s), 1215(s), 1140(m), 1101(m), 995(s), 910(w), 896(m), 795(m), 761(m), 730(m), 676(s), 662(m) cm⁻¹; CHN analysis for C₂₉H₃₃NO₅: Expected: C, 73.24%; H, 6.99%; N, 2.95%. Found: C, 73.30%; H, 7.01%; N, 3.00%.

8.2.17 N-[3,5-bis(tertbutyl-2-hydroxy-benzyl)] iminodiacetic acid (**t-Bu₂hda**)



The **t-Bu₂hda** ligand used in this study had been previously prepared in the research group and was used without further purification. ¹H NMR (DMSO, 400 MHz): δ = 7.2 (s, 1H, 1 x H_{aromatic}), 6.9 (s, 1H, 1 x H_{aromatic}), 3.7 (s, 4H, 2 x CH₂), 3.3 (s, 2H, 1 x CH₂), 1.4-1.2 (m, 18H, 6 x CH₃) ppm; ESI-MS (H₂O): 374.2 m/z [NaC₁₉H₂₉NO₅]⁺; FT-IR (KBr, diffuse reflectance): 3637(w), 3010(s), 2975(s), 2654(w), 1737(w), 1708(s), 1580(m), 1505(m), 1464(m), 1410(s), 1378(s), 1243(s), 1071(m), 1007(m), 913(m), 898(m), 807(m), 757(m), 700(w), 690(m) cm⁻¹; CHN analysis for C₁₉H₂₉NO₅: Expected: C, 64.93%; H, 8.32%; N, 3.99%. Found: C, 64.82%; H, 8.59%; N, 3.74%.

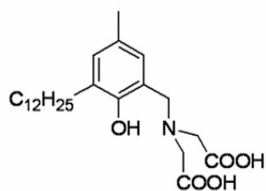
8.2.18 Synthesis of N-[3-methyl-5-dodecyl-2-hydroxy-benzyl] iminodiacetic acid (**p-C₁₂Mehda**)



p-C₁₂Mehda was synthesised by following a modified literature procedure.^{199,200} 4-dodecyl-2-methyl phenol (2.6 g, 9.4 mmol) was added to a 1:2 water/ethanol solution (40 mL) containing iminodiacetic acid (2.5 g, 19 mmol), NaOH (1.5 g, 38 mmol) and formaldehyde (1.0 g, 19 mmol). This solution was refluxed overnight. The ethanol in the solution was then evaporated off at 80°C. 2M HCl was then added until the pH of the solution was 1.9. A white precipitate then

formed that was filtered off and dried in vacuo. Yield: 3.0 g (75%); ^1H NMR (D_2O , 400 MHz): δ = 6.8 (s, 1H, 1 x $\text{H}_{\text{aromatic}}$), 6.6 (s, 1H, 1 x $\text{H}_{\text{aromatic}}$), 3.7 (s, 2H, 1 x CH_2), 3.4 (s, 4H, 2 x CH_2), 1.4-1.6 (mm, 25H, 1 x $\text{C}_{12}\text{H}_{25}$), 0.7 (s, 3H, 1 x CH_3) ppm; ESI-MS (H_2O): 444.2 m/z [$\text{NaC}_{24}\text{H}_{39}\text{NO}_5$] $^+$; FT-IR (KBr, diffuse reflectance): 3635(w), 3010(vs), 2975(vs), 2655(w), 1740(w), 1702(s), 1576(m), 1499(m), 1469(m), 1415(s), 1382(s), 1239(s), 1075(m), 999(m), 912(m), 898(m), 812 (m), 759(m), 695(w), 680(m) cm^{-1} ; CHN analysis for $\text{C}_{24}\text{H}_{39}\text{NO}_5$: Expected: C, 68.38%; H, 9.32%; N, 3.32%. Found: C, 68.32%; H, 9.16%; N, 2.91%.

8.2.19 Synthesis of N-[3- dodecyl-5-methyl-2-hydroxy-benzyl)] iminodiacetic acid (*o*- $\text{C}_{12}\text{Mehda}$)



An identical procedure to that used in the synthesis of *p*- $\text{C}_{12}\text{Mehda}$ was applied to synthesise *o*- $\text{C}_{12}\text{Mehda}$, except 2-dodecyl-4-methyl phenol (2.6 g, 9.4 mmol) was used instead of 4-dodecyl-2-methyl phenol, yielding the product as a white powder. Yield: 2.9 g (72%); ^1H NMR (D_2O , 400 MHz): δ = 6.8 (s, 1H, 1 x $\text{H}_{\text{aromatic}}$), 6.5 (s, 1H, 1 x $\text{H}_{\text{aromatic}}$), 3.9 (s, 2H, 1 x CH_2), 3.5 (s, 4H, 2 x CH_2), 1.5-1.7 (mm, 25H, 1 x $\text{C}_{12}\text{H}_{25}$), 0.6 (s, 3H, 1 x CH_3) ppm; ESI-MS (H_2O): 444.2 m/z [$\text{NaC}_{24}\text{H}_{38}\text{NO}_5$] $^+$; FT-IR (KBr, diffuse reflectance): 3632(w), 3008(vs), 2979(s), 2657(w), 1739(w), 1700(s), 1576(m), 1505(m), 1467(m), 1417(s), 1382(s), 1235(s), 1075(m), 1001(m), 914(m), 900(m), 812 (m), 756(m), 695(w), 677(m) cm^{-1} ; CHN analysis for $\text{C}_{24}\text{H}_{39}\text{NO}_5$: Expected: C, 68.38%; H, 9.32%; N, 3.32%. Found: C, 68.37%; H, 9.12%; N, 3.01%.

8.3 Synthesis of transition metal complexes

8.3.1 Synthesis of $[\text{Fe}_4(\text{L}2)_2\text{Cl}_8(\mu\text{-O})_2]\cdot 2\text{THF}$ (1)

L2 (50 mg, 0.17 mmol) was reacted with $\text{FeCl}_2\cdot 6\text{H}_2\text{O}$ (20 mg, 0.20 mmol) in methanol (20 mL). The red/orange solution was stirred for 1 hour at room temperature. The solvent was removed under vacuum and the resultant orange oil was dissolved in acetonitrile (12 mL). Tetrahydrofuran was slowly diffused into this solution. After one day, orange hexagonal crystals appeared in the solution. Yield: 55 mg; FT-IR (KBr, diffuse reflectance): 3147(w), 1619 (m), 1590(m), 1494(m), 1445(m), 1425(m), 1378(w), 1325(m), 1304(w), 1213(w), 1196(w), 1150(w), 1011(s),

1000(m), 970(m), 957(w), 904(m), 861(m), 795(w), 779(m), 700(m), 649(m) cm^{-1} ; CHN analysis for $\text{Fe}_4\text{C}_{32}\text{H}_{32}\text{N}_{12}\text{O}_2\text{Cl}_8$ (**1** without two solvent THF molecules): Expected: C, 34.20%; H, 2.87 %; N, 14.96%. Found: C, 34.55%; H, 3.01%; N, 15.12.%; UV-vis (MeCN): λ_{max} (ϵ) = 210 nm (9117 $\text{L mol}^{-1} \text{cm}^{-1}$), 295 nm (12150 $\text{L mol}^{-1} \text{cm}^{-1}$).

8.3.2 Synthesis of $[\text{Co}_2(\text{L2})_2(\text{MeOH})_2(\text{H}_2\text{O})_2]\text{Cl}_4 \cdot 4\text{MeOH} \cdot 3\text{H}_2\text{O}$ (**2**)

L2 (50 mg, 0.17 mmol) was reacted with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (52 mg, 0.22 mmol) in methanol (10 mL). The resultant orange solution was stirred for 1 hour and tetrahydrofuran (10 mL) was then added. The resultant solution was allowed to evaporate slowly resulting in the formation of yellow plate shaped crystals after 5 days. Yield: 20 mg; FT-IR (KBr, diffuse reflectance): 3127(w), 1616(m), 1586(m), 1494(m), 1438(m), 1420(m), 1378(w), 1324(m), 1294(w), 1213(w), 1176(w), 1150(w), 1007(s), 998(m), 968(m), 947(w), 904(m), 851(m), 771(m), 700(m), 659(m) cm^{-1} ; ESI-MS (MeCN): 200.7 m/z $[\text{Co}_2(\text{L2})_2(\text{MeOH})_2(\text{H}_2\text{O})_2]^{4+}$; CHN analysis for $\text{Co}_2\text{C}_{38}\text{H}_{66}\text{N}_{12}\text{O}_{11}\text{Cl}_4$: Expected: C, 40.51%; H, 5.90%; N, 14.92%. Found: C, 40.86%; H, 4.37%; N, 14.92%.; UV-vis (MeCN): λ_{max} (ϵ) = 295 nm (45000 $\text{L mol}^{-1} \text{cm}^{-1}$), 323 nm (78375 $\text{L mol}^{-1} \text{cm}^{-1}$).

8.3.3 Synthesis of $[\text{Ni}_2(\text{L2})_3](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ (**3**)

L2 (50 mg, 0.17 mmoles) was reacted with $\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (30 mg, 0.22 mmol) in methanol (10 mL). The yellow solution was stirred for 1 hour resulting in the formation of a precipitate (75 mg). This yellow powder was dissolved in acetonitrile (15 mL). Tetrahydrofuran was slowly diffused into test tubes containing the acetonitrile solution (4 mL). The product grows as yellow plate shaped crystals after 6 days. Yield: 20 mg; FT-IR (KBr, diffuse reflectance): 3658(w), 3090(s), 2889(m), 1618(s), 1577(w), 1473(w), 1443(m), 1420(m), 1382(s), 1291(w), 1251(m), 1155(s), 1073(m), 1018(w), 954(s), 904(w), 819(s), 770(m), 718(w) cm^{-1} ; CHN analysis for $\text{Ni}_2\text{C}_{48}\text{H}_{50}\text{N}_{18}\text{O}_{17}\text{Cl}_4$: Expected: C, 40.88%; H, 3.57%; N, 17.88%. Found: C, 40.15%; H, 3.75%; N, 17.00%; UV-vis (MeCN): λ_{max} (ϵ) = 296 nm (40000 $\text{L mol}^{-1} \text{cm}^{-1}$), 321 nm (90000 $\text{L mol}^{-1} \text{cm}^{-1}$).

8.3.4 Synthesis of $[\text{Cu}_4(\text{L2})_2(\text{EMM})_4](\text{CH}_3\text{COO})_4 \cdot \text{H}_2\text{O}$ (**4**)

L2 (50 mg, 0.17 mmol) was reacted with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (80 mg, 0.40 mmol) in methanol (20 mL). The resultant green solution was stirred for 1 hour. The solvent was removed under vacuum and the resultant green oil was dissolved in acetonitrile (12 mL). Ethanol (6 mL) was added to the acetonitrile solution (4 mL).

The resultant green solution was left to evaporate slowly resulting in the formation of blue/green crystals in low yields. Yield: 5 mg; FT-IR (KBr diffuse reflectance): 1620(s), 1560(s), 1421(s), 1343(m), 902(m) cm^{-1} ; CHN analysis for $\text{Cu}_4\text{C}_{68}\text{H}_{90}\text{N}_{20}\text{O}_{11}$: Expected: C, 50.49%; H, 5.61%; N, 17.32%. Found: C, 49.75%; H, 4.75%; N, 18.06%

8.3.5 Synthesis of $[\text{Cu}_9(\mu_3\text{-O})_2(\text{O-L2-O})_2(\text{CH}_3\text{COO})_{10}]\cdot 2\text{THF}\cdot 2\text{H}_2\text{O}$ (5)

L2 (50 mg, 0.17 mmol) was reacted with $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ (160 mg, 0.80 mmol) in methanol (20 mL). The resultant green solution was stirred for 1 hour at room temperature. The solvent was removed under vacuum and the resultant green oil was dissolved in acetonitrile (12 mL). Tetrahydrofuran was slowly diffused into this solution. After two weeks green rectangular crystals appeared in the solution. Yield: 55 mg; FTIR (KBr, diffuse reflectance): 3178(b), 1548(s), 1401(s), 1343(m), 1002(m) cm^{-1} ; UV-vis (MeCN): $\lambda_{\text{max}}(\epsilon) = 279\text{nm}$ ($50000 \text{ L mol}^{-1} \text{ cm}^{-1}$); CHN analysis for $\text{Cu}_9\text{C}_{60}\text{H}_{82}\text{N}_{12}\text{O}_{30}$: Expected: C, 35.62%; H, 4.09%; N, 8.31%. Found: C, 36.72 %; H, 3.34 %; N, 8.79 %.

8.3.6 Synthesis of $[\text{Co}(\text{HL4})_2]\cdot\text{MeOH}\cdot 2\text{H}_2\text{O}$ (6)

H₂L4 (50 mg, 0.16 mmol) was reacted with $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (39 mg, 0.16 mmol) in methanol (10 mL). The resultant solution was stirred for 1 hour, filtered and left to stand at room temperature yielding orange crystals after 6 days. Yield: 25 mg; FT-IR (KBr, diffuse reflectance): 3414(w), 2784(m), 2343(m), 1608(s), 1587(m), 1559(m), 1473(s), 1446(m), 1435(s), 1374(m), 1350(m), 1265(m), 1229(m), 1201(m), 1167(m), 1127(m), 1083(w), 1062(m), 1031(m), 993(m), 967(w), 960(w), 950(w), 885(s), 785(s), 756(s), 748(s) cm^{-1} ; UV-vis (MeCN): $\lambda_{\text{max}}(\epsilon) = 323 \text{ nm}$ ($79390 \text{ L mol}^{-1} \text{ cm}^{-1}$); CHN analysis for $\text{CoC}_{24}\text{H}_{24}\text{N}_4\text{O}_8\text{As}_2$ (**6** without the solvent MeOH molecule): Expected: C, 40.87%; H, 3.43%; N, 7.94%. Found: C, 40.14%; H, 3.77 %; N, 7.70 %.

7.3.7 Synthesis of $[\text{Co}_2(\text{L5})_3](\text{NO}_3)_4\cdot 2\text{MeOH}$ (8)

A methanol solution (2 mL) of $\text{Co}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (29 mg, 0.10 mmol) was added drop-wise to a methanol solution (7 mL) of **L5** (50 mg, 0.17 mmol). The resultant orange solution was stirred for 15 minutes and left to stand at room temperature yielding orange crystals after 5 days. Yield: 45 mg; FT-IR (KBr, diffuse reflectance): 3656(w), 3149(w), 2995(s), 2892(w), 1615(s), 1580(w), 1556(w), 1487(m), 1437(s), 1425(s), 1385(s), 1324(w), 1295(m), 1246(m), 1160(s), 1079(m), 1014(w), 956(m), 906(w), 815(s), 775(s) cm^{-1} ; ESI-MS (MeOH): 316.3 m/z $[\text{CO}_2(\text{L5})_3]^{4+}$; CHN analysis for $\text{Co}_2\text{C}_{69}\text{H}_{66}\text{N}_{22}\text{O}_{12}$ (**8** without two solvent MeOH

molecules): Expected: C, 54.76%; H, 4.40%; N, 20.36%. Found: C, 54.69%; H, 4.75%; N, 20.45%; UV-vis (MeOH): $\lambda_{\max}(\epsilon) = 239 \text{ nm}$ ($30650 \text{ L mol}^{-1} \text{ cm}^{-1}$), 325 nm ($95150 \text{ L mol}^{-1} \text{ cm}^{-1}$).

8.3.8 Synthesis of $[\text{Co}_2(\text{L6})_3](\text{ClO}_4)_4 \cdot \text{MeCN}$ (**9**)

A methanol solution (2 mL) of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (37 mg, 0.10 mmol) was added drop-wise to a methanol solution (7 mL) of **L6** (50 mg, 0.13 mmol) yielding an orange powder (73 mg). 15 mg of this orange powder was dissolved in acetonitrile (3 mL). Methanol (5 mL) was slowly diffused into this solution resulting in the formation of orange hexagonal crystals after 6 days. FT-IR (KBr, diffuse reflectance): 3250(w), 3142(w), 3025(w), 1618(s), 1596(m), 1505(m), 1479(m), 1439(s), 1409(m), 1370(m), 1309(w), 1295(m), 1148(m), 1108(w), 1085(w), 1017(w), 976(w), 962(w), 937(m), 874(s), 824(w), 755(s), 679(m) cm^{-1} ; ESI-MS (MeCN): 317.8 m/z $[\text{Co}_2(\text{L6})_3]^{4+}$; CHN analysis for $\text{Co}_2\text{C}_{68}\text{H}_{63}\text{N}_{19}\text{O}_{19}\text{Cl}_4$: Expected: C, 47.76 %; H, 3.71%; N, 15.56%. Found: C, 47.97%; H, 3.69%; N, 15.15%; UV-vis (MeCN): $\lambda_{\max}(\epsilon) = 239 \text{ nm}$ ($8625 \text{ L mol}^{-1} \text{ cm}^{-1}$), 325 nm ($14250 \text{ L mol}^{-1} \text{ cm}^{-1}$).

8.3.9 Synthesis of $[\text{Mn}_2(\text{L6})_3](\text{ClO}_4)_4 \cdot 2\text{MeOH}$ (**10**)

The procedure for **9** was repeated except that $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (36 mg, 0.10 mmol) was used instead of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. This yielded large orange crystals after two weeks. FT-IR (KBr, diffuse reflectance): 3021(w), 1617(s), 1592(m), 1499(m), 1472(m), 1435(s), 1399(m), 1365(m), 1300(w), 1294(m), 1148(m), 1102(w), 1084(w), 1012(w), 978(w), 960(w), 935(m), 871(s), 821(w), 754(s), 676(m) cm^{-1} ; ESI-MS (MeCN): 315.5 m/z $[\text{Mn}_2(\text{L6})_3]^{4+}$; CHN analysis for $\text{Mn}_2\text{C}_{66}\text{H}_{60}\text{N}_{18}\text{O}_{19}\text{Cl}_4$ (**10** without two solvent MeOH molecules): Expected: C, 47.73%; H, 3.64%; N, 15.18%. Found: C, 47.10%; H, 3.45%; N, 14.95%; UV-vis (MeCN): $\lambda_{\max}(\epsilon) = 320 \text{ nm}$ ($14250 \text{ L mol}^{-1} \text{ cm}^{-1}$).

8.3.10 Synthesis of $[\text{Ni}_2(\text{L5})_3](\text{PF}_6)_4 \cdot 2\text{MeCN}$ (**11**)

A methanol solution (2 mL) of $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ (24 mg, 0.10 mmol) was added drop-wise to a methanol solution (7 mL) of **L5** (50 mg, 0.17 mmol). The resultant yellow solution was stirred for 15 minutes. The addition of NH_4PF_6 (65 mg, 0.20 mmol) resulted in the formation of a yellow precipitate (75 mg). This powder (15mg) was dissolved in acetonitrile (3 mL). Methanol (5mL) was slowly diffused into this solution resulting in the formation of yellow plate like crystals after 6 days. FT-IR (KBr, diffuse reflectance): 1617(s), 1600 (m), 1520(w), 1500(m), 1472(m), 1439(s), 1415(m), 1370(m), 1320(w), 1309(w), 1295(m), 1155(m), 1115(w), 1090(w),

1013(w), 976(w), 960(w), 935(m), 873(s), 860(w), 835(w), 807(w), 748(s), 681(m) cm^{-1} ; ESI-MS (MeCN): 315.9 m/z $[\text{Ni}_2(\text{L5})_3]^{4+}$; CHN analysis for $\text{Ni}_2\text{C}_{69}\text{H}_{66}\text{N}_{18}\text{P}_4\text{F}_{24}$ (**11** without two solvent MeCN molecules): Expected: C, 44.93%; H, 3.61%; N, 13.67%. Found: C, 44.68%; H, 3.51%; N, 13.77%; UV-vis (MeCN): λ_{max} (ϵ) = 325 nm ($158275 \text{ L mol}^{-1} \text{ cm}^{-1}$).

8.3.11 Synthesis of $[\text{Fe}_2(\text{L6})_3](\text{PF}_6)_4 \cdot 4\text{MeCN} \cdot \text{H}_2\text{O}$ (**12**)

A methanol solution (2 mL) of $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ (20 mg, 0.10 mmol) was added drop-wise to a methanol solution (7 mL) of **L6** (50 mg, 0.13 mmol). The resultant red solution was stirred for 15 minutes. The addition of NH_4PF_6 (65 mg, 0.20 mmol) resulted in the formation of a red precipitate (72 mg). 15 mg of this red powder was dissolved in acetonitrile (3 mL). Methanol (5 mL) was slowly diffused into this solution resulting in the formation of red hexagonal crystals after 6 days. FT-IR (KBr, diffuse reflectance): 3251(w), 3140(w), 3022(w), 2951(w), 1617(s), 1594(m), 1518(w), 1502(m), 1476(m), 1437(s), 1412(m), 1367(m), 1318(w), 1307(w), 1290(m), 1152(m), 1113(w), 1085(w), 1013(w), 974(w), 958(w), 933(m), 870(s), 855(w), 829(w), 813(s), 750(s), 679(m) cm^{-1} ; ESI-MS (MeCN): 315.9 m/z $[\text{Fe}_2(\text{L6})_3]^{4+}$; CHN analysis for $\text{Fe}_2\text{C}_{74}\text{H}_{74}\text{N}_{22}\text{O}_4\text{P}_4\text{F}_{24}$: Expected: C, 43.85 %; H, 3.68%; N, 15.20%. Found: C, 43.77%; H, 3.69%; N, 15.31%; UV-vis (MeCN): λ_{max} (ϵ) = 239 nm ($8750 \text{ L mol}^{-1} \text{ cm}^{-1}$), 320 nm ($141875 \text{ L mol}^{-1} \text{ cm}^{-1}$), 530 nm ($2234 \text{ L mol}^{-1} \text{ cm}^{-1}$).

8.3.12 Synthesis of $[\text{Fe}_2(\text{L6})_3](\text{BF}_4)_4 \cdot \text{H}_2\text{O}$ (**13**)

The synthetic procedure for **12** above was repeated except that NH_4BF_4 (20 mg, 0.20 mmol) was used instead of NH_4PF_6 yielding red rectangular crystals. FT-IR (KBr, diffuse reflectance): 3132(m), 3112(m), 2950(w), 2220(w), 1932(w), 1686(w), 1618(s), 1581(m), 1520(m), 1480(s), 1433(s), 1419(s), 1368(m), 1321(w), 1292(m), 1156(m), 1139(m), 1078(w), 1055(s), 997(w), 980(m), 954(m), 931(m), 879(w), 817(s), 783(s), 767(s) cm^{-1} ; ESI-MS (MeCN): 316.2 m/z $[\text{Fe}_2(\text{L6})_3]^{4+}$; CHN analysis for $\text{Fe}_2\text{C}_{66}\text{H}_{62}\text{N}_{18}\text{O}_4\text{B}_4\text{F}_{16}$: Expected: C, 48.63%; H, 3.83%; N, 15.47%. Found: C, 48.65%; H, 3.82%; N, 15.81%; UV-vis (MeCN): λ_{max} (ϵ) = 237 nm ($43125 \text{ L mol}^{-1} \text{ cm}^{-1}$), 329 nm ($120625 \text{ L mol}^{-1} \text{ cm}^{-1}$), 531 nm ($2245 \text{ L mol}^{-1} \text{ cm}^{-1}$).

8.3.13 Synthesis of $[\text{Fe}_2(\text{L5})_3](\text{PF}_6)_4 \cdot 4\text{MeCN} \cdot \text{H}_2\text{O}$ (**14**)

The synthetic procedure for **12** above was repeated except **L5** (50 mg, 0.19 mmol) was used instead of **L6** yielding red plate hexagonal crystals. FT-IR (KBr, diffuse reflectance): 3658(w), 3154(w), 2990(s), 2890(w), 1617(s), 1577(w), 1554(w),

1482(m), 1435(s), 1420(s), 1382(s), 1321(w), 1292(m), 1250(m), 1156(s), 1079(m), 1018(w), 954(m), 904(w), 813(s), 770(s) cm^{-1} ; ESI-MS (MeCN): 314.8 m/z $[\text{Fe}_2(\text{L5})_3]^{4+}$; CHN analysis for $\text{Fe}_2\text{C}_{77}\text{H}_{80}\text{N}_{22}\text{OP}_4\text{F}_{24}$: Expected: C, 45.76%; H, 3.99%; N, 15.25%. Found: C, 45.93%; H, 3.72%; N, 15.45%; UV-vis (MeCN): $\lambda_{\text{max}}(\epsilon) = 242$ nm ($65000 \text{ L mol}^{-1} \text{ cm}^{-1}$), 320 nm ($191875 \text{ L mol}^{-1} \text{ cm}^{-1}$), 530 nm ($2187 \text{ L mol}^{-1} \text{ cm}^{-1}$).

8.3.14 Synthesis of $[\text{Fe}_2(\text{L5})_3](\text{BF}_4)_4 \cdot 2\text{MeCN}$ (15)

The procedure for **13** was repeated except that **L5** (50 mg, 0.19 mmol) was used instead of **L6** yielding red rectangular crystals. FT-IR (KBr, diffuse reflectance): 3657(w), 3195(s), 3111(w), 2889(w), 1618(m), 1582(m), 1505(s), 1481(w), 1443(m), 1420(m), 1382(s), 1292(m), 1251(m), 1156(s), 1052(s), 954(s), 901(w), 859(w), 817(m), 711(m), 684(m), 667(m) cm^{-1} ; ESI-MS (MeCN): 315.1 m/z $[\text{Fe}_2(\text{L5})_3]^{4+}$; CHN analysis for $\text{Fe}_2\text{C}_{73}\text{H}_{72}\text{N}_{20}\text{B}_4\text{F}_{16}$: Expected: C, 51.93%; H, 4.30%; N, 16.59%. Found: C, 51.83%; H, 4.15%; N, 16.45%; UV-vis (MeCN): $\lambda_{\text{max}}(\epsilon) = 237$ nm ($30625 \text{ L mol}^{-1} \text{ cm}^{-1}$), 323 nm ($93125 \text{ L mol}^{-1} \text{ cm}^{-1}$), 533 nm ($2190 \text{ L mol}^{-1} \text{ cm}^{-1}$).

8.3.15 Synthesis of $[\text{Co}_3(\text{L8})_2(\text{H}_2\text{O})_6]\text{Cl}_6 \cdot \text{DMF} \cdot 9\text{H}_2\text{O}$ (16)

L8 (100 mg, 0.17 mmol) was reacted with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.06 g, 0.26 mmol) in dimethylformamide (7 mL) at 75 °C giving a green solution. Slow diffusion of tetrahydrofuran into this solution gave orange crystals of **16** after 24 hours. Yield: 50 mg; FT-IR (KBr, diffuse reflectance): 3082(w), 2991(w), 2933(w), 2866(w), 2595(w), 1614(s), 1560(s), 1559(w), 1522(w), 1506(s), 1437(m), 1411(m), 1367(s), 1293(w), 1253(m), 1239(w), 1216(w), 1181(w), 1169(w), 1093(s), 1062(w), 1014(m), 931(w), 839(m), 785(w), 768(w), 738(w), 731(w), 701(w), 670(w), 670(w), 686(m), 659(m) cm^{-1} ; CHN analysis for $\text{Co}_3\text{C}_{75}\text{H}_{91}\text{N}_{19}\text{O}_{16}\text{Cl}_6$: Expected: C, 47.31%; H, 4.82%; N, 13.98%. Found: C, 47.68%; H, 4.62%; N, 14.00%.

8.3.16 Synthesis of $[\text{Co}_3(\text{L9})_2(\text{H}_2\text{O})_6]\text{Cl}_6 \cdot \text{DMF} \cdot 9\text{H}_2\text{O}$ (17)

The synthetic procedure used in the formation of **16** was repeated, but **L9** (100 mg, 0.16 mmol) was used instead of **L8** yielding a green powder. Yield: 65 mg; FT-IR (KBr, diffuse reflectance): 3365(m), 1615(s), 1589(s), 1497(s), 1440(s), 1386(s), 1324(m), 1292(w), 1253(w), 1173(w), 1097(m), 1015(w), 978(w), 906(w), 836(m), 781(w), 660(s) cm^{-1} ; CHN analysis for $\text{Co}_3\text{C}_{81}\text{H}_{103}\text{N}_{19}\text{O}_{16}\text{Cl}_6$: Expected: C, 48.93%; H, 5.22%; N, 13.38%. Found: C, 48.88%; H, 5.46%; N, 13.01%.

8.3.17 Synthesis of $[\text{Li}_2(\text{C}_8\text{H}_4\text{O}_4)]$ (18)

A mixture of terephthalic acid (50 mg, 0.30 mmol), $\text{LiOH}\cdot\text{H}_2\text{O}$ (25 mg, 0.60 mmol), and methanol (8 mL) was placed inside a 23 mL-Teflon lined autoclave. The reactants were stirred yielding a cloudy white reaction mixture. The autoclave was then sealed, and placed in an oven at 145 °C for 17 hours. The autoclave was then allowed to cool to room temperature for 3 hours resulting in the formation of large colourless crystals. Yield: 52 mg; FT-IR (KBr, diffuse reflectance): 1611(s), 1488(s), 1050(s), 944(m), 678(w), 620(s) cm^{-1} ; CHN analysis for $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$: Expected: C, 53.98%; H, 2.26%; N, 0%. Found: C, 53.98%; H, 2.27%; N, 0%.

8.3.18 Synthesis of $[\text{Li}_2(\text{C}_{14}\text{H}_8\text{O}_4)]$ (19)

A mixture of 4,4'-biphenyl dicarboxylic acid (50 mg, 0.21 mmol), LiCl (18 mg, 0.42 mmol), dimethylformamide (4 mL) and methanol (4 mL) was placed inside a 23 mL-Teflon lined autoclave. The reactants were stirred yielding a cloudy white reaction mixture. The autoclave was then sealed, and placed in an oven at 145 °C for 17 hours. The autoclave was then allowed to cool to room temperature for 3 hours resulting in the formation of large colourless crystals. Yield: 53 mg; FT-IR (KBr, diffuse reflectance): 2557(w), 1943(w), 1916(w), 1609(s), 1570(s), 1486(s), 1454(m), 1408(m), 1361(m), 1320(w), 1281(s), 1232(w), 1188(m), 1150(s), 1112(w), 1032(w), 1013(w), 976(m), 937(w), 910(w), 877(w), 820(s), 768(w), 757(m), 748(s), 738(s), 617(m) cm^{-1} ; CHN analysis for $\text{Li}_2\text{C}_{14}\text{H}_8\text{O}_4$: Expected: C, 66.18%; H, 3.17%; N, 0%. Found: C, 66.05%; H, 3.20%; N, 0%.

8.3.19 Synthesis of $[\text{Li}_2(\text{C}_{12}\text{H}_6\text{O}_4)]$ (20)

A mixture of 2,6'-naphthalene dicarboxylic acid (50 mg, 0.23 mmol), $\text{LiOH}\cdot\text{H}_2\text{O}$ (11 mg, 0.46 mmol), and methanol (4 mL) was placed inside a 23 mL-Teflon lined autoclave. The reactants were stirred yielding a cloudy white reaction mixture. The autoclave was then sealed, and placed in an oven at 145 °C for 17 hours. The autoclave was then allowed to cool to room temperature for 2 hours resulting in the formation of large colourless crystals. Yield: 49 mg; FT-IR (KBr, diffuse reflectance): 1602(s), 1564(s), 1497(m), 1396(s), 1360(s), 1196(m), 1143(w), 1099(w), 977(m), 934(m), 844(w), 800(s), 778(s) cm^{-1} ; CHN analysis for $\text{Li}_2\text{C}_{12}\text{H}_6\text{O}_4$: Expected: C, 63.20%; H, 2.65%; N, 0%. Found: C, 63.35%; H, 2.70%; N, 0%.

8.3.20 Synthesis of $(\text{NH}_2\text{Me}_2)[\text{Li}_2(\text{C}_9\text{H}_3\text{O}_6)]\cdot\text{H}_2\text{O}$ (21)

A mixture of 1,3,5-benzene tricarboxylic acid (50 mg, 0.24 mmol), LiCl (11 mg, 0.48 mmol), and dimethylformamide (8 mL) was placed inside a 23 mL-Teflon

lined autoclave. The reactants were stirred yielding a cloudy white reaction mixture. The autoclave was then sealed, and placed in an oven at 145 °C for 17 hours. The autoclave was then allowed to cool to room temperature for 2 hours resulting in the formation of large colourless crystals. Yield: 65 mg; FT-IR (KBr, diffuse reflectance): 2557(w), 1944(w), 1916(w), 1609(m), 1570(m), 1486(s), 1454(m), 1408(m), 1361(m), 1320(w), 1281(s), 1232(w), 1188(m), 1150(s), 1112(m), 1032(w), 1013(w), 976(m), 936(m), 910(m), 877(w), cm^{-1} ; CHN analysis for $\text{Li}_2\text{C}_{11}\text{H}_{13}\text{O}_7\text{N}$: Expected: C, 46.34%; H, 4.60%; N, 4.91%. Found: C, 46.83%; H, 3.59%; N, 4.87%.

8.3.21 Synthesis of $[\text{Fe}(\text{Bc}_2\text{hda})(\text{H}_2\text{O})(\text{EtOH})]\cdot 3\text{H}_2\text{O}$ (**22**)

The ligand **Bc₂hda** (40 mg, 0.085 mmol) was reacted with $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (70 mg, 0.25 mmol) in ethanol (30ml) forming a dark blue solution. Water (10ml) was added to 5ml of this solution. The water/ethanol solution was left to stand at room temperature. This resulted in the formation of blue crystals of **22**. Yield: 85 mg; FT-IR (KBr, diffuse reflectance): 3625(w), 3320(m), 3085(m), 3020(m), 2963(m), 2870(m), 1945(w), 1800(w), 1651(s), 1573(s), 1492(m), 1465(m), 1445(m), 1426(m), 1410(m), 1382(m), 1362(s), 1332(m), 1305(m), 1230(m), 1204(m), 1186(w), 1162(w), 1146(w), 1110(w), 1099(w), 1075(w), 1028(w), 1008(w), 940(w), 907(w), 878(w), 872(w), 828(w), 771(w), 748(w), 721(w), 703(w), 653(w), 604(w), 563(m), 547(w), 489(w), 450(w), 416(m), 376(w), 356(w) cm^{-1} ; UV-vis(EtOH): λ_{max} (ϵ) = 275 (75000 $\text{L mol}^{-1} \text{cm}^{-1}$), 590 nm (70 $\text{L mol}^{-1} \text{cm}^{-1}$); CHN analysis for $\text{FeC}_{31}\text{H}_{46}\text{NO}_{10}$: Expected: C, 57.41%; H, 7.15%; N, 2.16%. Found: C, 57.37%; H, 6.95%; N, 2.05%.

8.3.22 Synthesis of $[\text{Fe}(t\text{-Bu}_2\text{hda})(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ (**23**)

23 was synthesised following a procedure reported in the literature.⁵⁴ The ligand ***t*-Bu₂hda** (95 mg, 0.25 mmol) was reacted with $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (68 mg, 0.25 mmol) in water (30ml). To this 2M NaOH (2 mL) was added forming a clear blue solution which was left to stand at room temperature. This yielded blue crystals after one day. Yield: 80 mg; FT-IR (KBr, diffuse reflectance): 3752(w), 2923(s), 2852(s), 1575(s), 1458(m), 1473(m), 1402(m), 1365(s), 1321(m), 1257(m), 1157(w), 1120(w), 1088(w), 1018(w), 966(w), 925(w), 909(w), 867(w), 821(w), 734(w), 597(w), 541(w), 445(w), 428(w), 370(m) cm^{-1} ; UV-vis(EtOH): λ_{max} (ϵ) = 280 (75125 $\text{L mol}^{-1} \text{cm}^{-1}$), 588 nm (83 $\text{L mol}^{-1} \text{cm}^{-1}$); CHN analysis for $\text{FeC}_{19}\text{H}_{38}\text{NO}_{11}$: Expected: C, 44.54%; H, 7.48%; N, 2.73%. Found: C, 44.62%; H, 7.63%; N, 3.01%.

8.3.23 Synthesis of [Fe(*p*-C₁₂Mehda)(H₂O)₂].4H₂O (**24**)

The ligand *p*-C₁₂Mehda (210 mg, 0.50 mmol) and FeCl₃·6H₂O (135 mg, 0.50 mmol) were reacted in water (50ml) yielding a blue precipitate which was filtered off. Yield: 100 mg; FT-IR (KBr, diffuse reflectance): 3177(m), 2953(m), 2905(m), 2867(m), 2707(m), 2360(m), 1769(m), 1717(m), 1623(s), 1576(s), 1458(m), 1448(m), 1409(m), 1390(m), 1362(s), 1321(m), 1298(m), 1271(m), 1249(m), 1239(m), 1204(m), 1170(w), 1130(w), 1110(w), 1085(w), 1025(w), 1005(w), 976(w), 910(w), 894(w), 875(w), 844(w), 811(w), 774(w), 740(w), 690(w), 647(w), 602(w), 539(w), 482(w), 448(w), 418(m), 378(m), 355(m) cm⁻¹; UV-vis(EtOH): λ_{max} (ε) = 279 (50125 L mol⁻¹ cm⁻¹), 582 nm (76 L mol⁻¹ cm⁻¹); CHN analysis for FeC₂₉H₄₅NO₁₁: Expected: C, 54.47 %; H, 7.09 %; N, 2.19%. Found: C, 54.90 %; H, 7.79%; N, 2.73 %.

8.3.24 Synthesis of [Fe(*o*-C₁₂Mehda)(H₂O)₂].4H₂O (**25**)

A similar procedure to that used in the synthesis of **24** was employed to synthesise **25** except, *o*-C₁₂Mehda (210 mg, 0.50 mmol) was used instead of *p*-C₁₂Mehda. Yield 95 mg; FT-IR (KBr, diffuse reflectance): 2920(m), 2851(s), 1578(s), 1510(s), 1467(s), 1404(m), 1363(s), 1300(m), 1256(m), 1156(s), 1125(m), 925(s), 907(m), 861(s), 814(m), 732(m) cm⁻¹; UV-vis(EtOH): λ_{max} (ε) = 280 (40275 L mol⁻¹ cm⁻¹), 582 nm (76 L mol⁻¹ cm⁻¹); CHN analysis for FeC₂₉H₄₅NO₁₁: Expected: C, 54.47 %; H, 7.09 %; N, 2.19 %. Found: C, 54.67 %; H, 7.19%; N, 2.80 %.

8.4 Self-assembly of **24** and **25**

24 (20 mg) was dissolved in absolute ethanol (15 mL) and to this solution deionised water (10 ml) was added. The resulting blue solution was drop-casted on a flat Si surface and imaged by SEM. This resulted in the formation of nanosized spherical vesicles on the surface.

Alternatively, high yields of vesicular spheres were obtained by first dissolving 5 mg of **24** in absolute ethanol (10 mL). Deionised water (10 mL) was then added and the resultant suspension was heated to 80°C. This resulted in the formation of a slightly cloudy dispersion which contained the spherical aggregates. These aggregates were then separated from the solution by suction filtration using a 0.2 μm polycarbonate membrane filter which was imaged by SEM. In order to image the vesicles using TEM the cloudy dispersion was placed onto a copper formvar 200 square mesh TEM grid.

Similar methods were used to investigate the self-assembly of **25** yielding less homogenous assemblies.

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(e.g.1 corresponds to compound 1).

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