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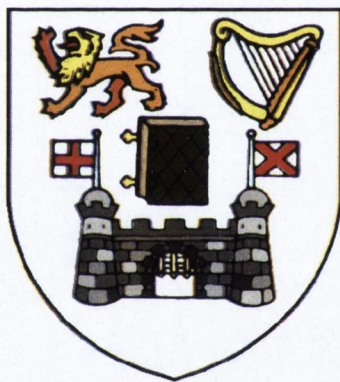
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**Modulating Supramolecular Structures and
Topologies of Coordination Polymers and
Networks using the Iminodiacetic Acid
Substituted Aromatic Ligands**

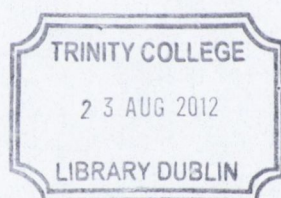
David Paul Walsh



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

School of Chemistry
University of Dublin

2011

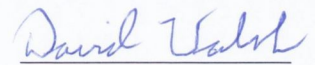


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David Walsh

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Thesis summary

Chapter 1 introduces the reader to the research area described in this thesis. It puts the work into context and provides appropriate literature references. The chapter details the objectives of the work and presents the reader to the used ligand systems.

Chapter 2 describes the synthesis of coordination compounds using the 2-aminodiacetic terephthalic acid (H_4adta) ligand. A range of novel coordination complexes are formed under ambient reaction conditions displaying a collection of intricate supramolecular interactions. Two mono-nuclear complexes in $K[Co^{II}(Hadta)(H_2O)_2] \cdot MeOH$ (**1**) and $K[Ni^{II}(Hadta)(H_2O)_2] \cdot H_2O$ (**2**), reveal similar coordination environments, but are characterised by different supramolecular interactions and packing arrangements. In contrast, the compound $K[Cu_{1.5}^{II}(adta)(H_2O)_{1.5}] \cdot H_2O$ (**3**) contains 1D coordination polymers, which are linked *via* potassium-oxygen interactions to yield a 3D network structure.

Chapter 3 documents the successful exploitation of hydrothermal reaction conditions. 2,2'-Bipyridine (bpy) was used as a co-ligand in combination with 3-aminodiacetic benzoic acid (H_3adba), 5-aminodiacetic salicylic acid (H_4adsa) and 5-aminodiacetic isophthalic acid (H_4adip), for the synthesis of low dimensional coordination compounds. The first two ligands yield discrete di-nuclear complexes in $[Zn^{II}(Hadba)(bpy)]_2$ (**4**) and $[Cu^{II}(H_2adsa)(bpy)]_2$ (**5**) in which the iminodiacetic acid groups bridge two metal ions. These two compounds are characterised by supramolecular interactions such as hydrogen bonds and π -stacking contacts. The H_4adip ligand generates a range of iso-structural 1D coordination polymers with the general formulae $[M^{II}_2(adip)(bpy)(H_2O)_4] \cdot 3H_2O$ ($M = Co, Mn, Fe, Ni$ for **6-9**). These coordination compounds comprise of the di-nuclear units analogous to that of **4/5**, which are further connected *via* partially hydrated M^{II} ions to give 1D chains that extend through the isophthalic moieties of the ligand. Alternative 1D coordination polymers with general formulae $[M^{II}(H_2adip)(bpy)]$ form when either copper (**10**) or zinc (**11**) ions are used as starting materials. *Syn-anti* bridging modes involving a carboxylate group of the iminodiacetic acid functionality connect symmetry-equivalent metal ions, affording spiral

chains. Their structural motifs are highly influenced by H-bonds. The analyses of the magnetic behaviour of selected representative chain compounds are discussed. Interestingly, ferro- (**10**) and anti-ferromagnetic (**6**, **8** and **9**) interactions between the transition metal centres are observed.

Chapter 4 firstly describes the combination of both iminodiacetic acid substituted ligands (H_4adip) with an assortment of nitrogen-containing co-ligands. The three employed co-ligands were 2,2'-dipyridylamine (NH-bpy), 2,2'-bipyridine-4,4'-dicarboxylic acid (H_2bpd) and 2,4,6-terpyridal-s-triazine (tptz). Our synthetic approach lead to some unanticipated compounds. Our efforts result in the successful binding of both intended ligands in $[Cu^{II}(H_2adip)(NH-bpy)]$ (**12**), only one of the desired ligands chelating in $[Cu^{II}(bpd)(H_2O)_2] \cdot 2H_2O$ (**13**) or none of the actual ligands coordinating at all in $[Co^{II}(pyca)_2(H_2O)_2] \cdot 2H_2O$ (**14**). Compound **12** displays corresponding coordination behaviour with **10**, but is characterised by slightly different packing arrangements and H-bonds. The bpd^{2-} ligand in **13** exhibits a tri-dentate binding capacity, and occupies all available equatorial positions on the octahedral Cu(II) ions, resulting in a 2D sheet. The *in situ* hydrolysis of the TPTZ co-ligand, under hydrothermal reaction conditions, results in the 2-pyridine carboxylic acid (pyca) ligand chelating to a cobalt(II) ion in **14**. The resulting monomer, whose distorted octahedral coordination sphere is completed by coordination water molecules, engages in an extensive array of H-bonds. The latter part of the chapter discusses the attempted complexation of two novel ligand-derivatives, 5-amino-2-dimethyldipyridine isophthalic acid (H_2adpip) and the 3-amino-2-dimethyldipyridine benzoic acid ($Hadpba$), with a range of transition metal ions. The crystal structure of 5-amino-2-dimethyldipyridine isophthalic acid was elucidated (**15**). 3-Amino-2-dimethyldipyridine benzoic acid ($Hadpba$) binds to Cu(II) ions resulting in 1D chains in $[Cu^{II}(adpba)Cl] \cdot 3H_2O$ (**16**). In the compound, the Cu(II) centres are square pyramidal coordinated and the chain propagation is facilitated through bridging carboxylate moieties.

Chapter 5 details the development of a new ligand-type that we designed and synthesised. The tetra-dentate 1,4-phenylenediamino-tetra benzoic acid moiety was successfully synthesised and crystallised as a solvent adduct $(1,4-H_4datba) \cdot DMF$ (**17**). Intra-ligand H-bonding develops 1D ladder-type chains that stack to give channels that

extend throughout the crystal structure and contain the solvent molecules. Exploiting the ligand with a range of transition metals leads to the elucidation of a series of iso-structural 3D coordination networks, $(\text{Me}_2\text{NH}_2)[\text{M}^{\text{II}}_2(\text{CO}_2)(1,4\text{-datba})]\cdot 0.5\text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Mn}, \text{Cd}$ for **18-20**). Their frameworks are composed of carboxylate-bridged 1D chains, and these discrete chains are further connected *via* organic ligands whose tetra-dentate binding mode generates an extensive 3D anionic network. These intricate frameworks contain channels, which contain both the Me_2NH_2^+ counterions and the lattice water molecules. At low temperatures, **18** displays magnetic behaviour of single-chain magnets (SCM). Its magnetic properties arise from spin-canting effects. **19** is characterised by anti-ferromagnetic exchanges between the metal ions within the 1D chains. These results prompted the synthesis of a similarly functionalised ligand 1,3-phenylenediamino-tetra benzoic acid ligand (1,3- H_4datba). A solvent adduct $(1,3\text{-H}_4\text{datba})\cdot 2\text{DMF}$ (**21**) was crystallised and structurally characterised.

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- 2) $\text{K}[\text{Ni}^{\text{II}}(\text{Hadta})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$
- 3) $\text{K}[\text{Cu}_{1.5}^{\text{II}}(\text{adta})(\text{H}_2\text{O})_{1.5}] \cdot \text{H}_2\text{O}$

Chapter 3:

- 4) $[\text{Zn}^{\text{II}}(\text{Hadba})(\text{bpy})]_2$
- 5) $[\text{Cu}^{\text{II}}(\text{H}_2\text{adsa})(\text{bpy})]_2$
- 6) $[\text{Co}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$
- 7) $[\text{Mn}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$
- 8) $[\text{Fe}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$
- 9) $[\text{Ni}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$
- 10) $[\text{Cu}^{\text{II}}(\text{H}_2\text{adip})(\text{bpy})]$
- 11) $[\text{Zn}^{\text{II}}(\text{H}_2\text{adip})(\text{bpy})]$

Chapter 4:

- 12) $[\text{Cu}^{\text{II}}(\text{H}_2\text{adip})(\text{NH-bpy})]$
- 13) $[\text{Cu}^{\text{II}}(\text{bpdc})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$
- 14) $[\text{Co}^{\text{II}}(\text{pyca})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$
- 15) H_2adpip ligand
- 16) $[\text{Cu}^{\text{II}}(\text{adpba})\text{Cl}] \cdot 3\text{H}_2\text{O}$

Chapter 5:

- 17) $(1,4\text{-H}_4\text{datba}) \cdot \text{DMF}$
- 18) $(\text{Me}_2\text{NH}_2)[\text{Co}^{\text{II}}_2(\text{CO}_2)(1,4\text{-datba})] \cdot 0.5\text{H}_2\text{O}$
- 19) $(\text{Me}_2\text{NH}_2)[\text{Mn}^{\text{II}}_2(\text{CO}_2)(1,4\text{-datba})] \cdot 0.5\text{H}_2\text{O}$
- 20) $(\text{Me}_2\text{NH}_2)[\text{Cd}^{\text{II}}_2(\text{CO}_2)(1,4\text{-datba})] \cdot 0.5\text{H}_2\text{O}$
- 21) $(1,3\text{-H}_4\text{datba}) \cdot 2\text{DMF}$

Abbreviations:

0D:	Zero dimensional
1D:	One dimensional
2D:	Two dimensional
3D:	Three dimensional
<i>ac</i> :	Alternating current
ADBA:	3-Aminodiacetic benzoic acid
ADIP:	5-Aminodiactaic isophthalic acid
ADPBA:	3-Aminodipyridine benzoic acid
ADPIP:	5-Aminodipyridine isophthalic acid
ADSA:	5-Aminodiacetic salicylic acid
ADTA:	2-Aminodiacetic terephthalic acid
ArH:	Aromatic hydrogen
μ_B :	Bohr magneton
BPDC:	2,2'-bipyridine, 4,4'-dicarboxylic acid
Bpy:	2,2'-bipyridine
CCD:	Charge-coupled device
CHnida:	Carboxylic acid substituted hydroxy-naphthol iminodiacetic acid
δ :	Chemical shift
DATBA:	1,4-Phenylenediamino-tetra benzoic acid
<i>dc</i> :	Direct current
DMF:	Dimethylformamide
DMSO:	Dimethylsulphoxide
DoE:	Department of Energy (US)
DNA:	Deoxyribonucleic acid
EDTA:	Ethylenediamine-tetra-acetic acid
<i>fac</i> :	Facial
<i>g</i> :	Gerade consant/ Landé factor
<i>H</i> :	Hamiltonian (heisenberg spin)

hfac:	Hexafluoroacetylacetone
hnida:	Hydroxy-naphthol iminodiacetic acid
IR:	Infrared
<i>J</i> :	Exchange interactions
<i>M</i> :	Magnetisation
Me ₃ tacn:	N,N',N''-trimethyl-1,4,7-triazacyclononane
metheidi:	N-(1-hydroxynethylethyl)iminodiacetic acid
<i>mer</i> :	Meridional
MOCN:	Metal organic coordination networks
MOF:	Metal organic framework
χ :	Molecular susceptibility
χT :	Molecular susceptibility with respect to temperature
NH-bpy:	2,2'-dipyridylamine
NITPhOMe:	4'-methoxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxide
NLO:	Non-linear optics
NMR:	Nuclear magnetic resonance
θ :	Weiss constant
pao:	Pyridine-2-aldoximate
py:	Pyridine
PYCA:	2-pyridine carboxylic acid
saltmen:	N,N'-(1,1,2,2-tetramethylethylene) bis(salicylideneimine)
SBU:	Secondary building unit
SCM:	Single-chain magnet
SMM:	Single-molecule magnet
tacn:	1,4,7-triazacyclononane
tetren:	Tetraethylenepentamine
TGA:	Thermogravimetric analysis
Tptz:	2,5,6-tripyridyl-s-triazine

Chapter 1

1.1: Crystal Engineering: A Retrospective View

The continuing and increasing interest invested in the field of crystal engineering has ensured that this area has grown, developed and evolved into an exciting and important discipline in chemistry. The term crystal engineering itself was coined by G. Schmidt whilst developing the subject of organic solid state photochemistry in the early 1970's.⁽¹⁾ Schmidt's article provoked serious thought and debate. The primary message to be gleaned from his work was that crystal engineering could be thought of as a series of molecular recognition events and self-assembly processes, rather than the simple need to "avoid a vacuum." A secondary point of Schmidt's article emphasised that the characteristic properties of crystalline solids, whether they are physical or chemical, crucially depend on the particular arrangement and/or distribution of certain molecular components within the crystal lattice just as much as on the properties of the individual molecular components themselves.

Soon to follow Schmidt's work was the similarly innovative idea of supramolecular chemistry, originally introduced by J. M. Lehn in 1978.⁽²⁾ "Supramolecular chemistry may be defined as 'chemistry beyond the molecule', bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces."⁽³⁾ The intermolecular forces Lehn refers to are a variety of non-covalent interactions, such as electrostatic (ion-ion, ion-dipole, dipole-dipole) interactions, π - π stacking contacts, van der Waals bonds and hydrogen bonds. These interactions themselves are chemically weaker than covalent or dative bonds. However, the collective strength associated with a number of these weaker bonds cannot be disregarded in the self-assembly process. The objects of supramolecular chemistry are "supramolecular entities, *supermolecules* possessing features as well defined as those of molecules themselves. One may say that supermolecules are to molecules and the intermolecular bond what molecules are to atoms and the covalent bond."^(3,4) In a verbal analogy, Lehn parallels this concept with

that of a natural language saying that “the atom, the molecule, the supermolecule would be the letter, the word and the sentence in the language of chemistry!”⁽⁵⁾

Lehn divides the field of supramolecular chemistry into two broad, somewhat coinciding conceptual aspects: 1) *supermolecules* composed of well-defined and discrete *oligomolecular* species that result from the intermolecular association of a few components based on molecular recognition and 2) *supramolecular* assemblies consisting of *polymolecular* entities that result from the spontaneous association of a large undefined number of components into a specific phase having well-defined microscopic organisation and macroscopic characteristics. Continuing his language analogy leads Lehn to describe polymolecular supramolecular entities as “the book”.

It has been suggested that there is a strong connection between supramolecular assemblies, combined with the molecular recognition effects they instil, and certain aspects of the field of crystal engineering. Bearing this idea in mind, crystals could be regarded as being distinct chemical entities and as a result, the ultimate examples of supramolecular assemblies or supermolecules. Admiration was soon to follow these concepts with J. Dunitz referring to organic crystals as “supermolecule(s) *par excellence*”.^(6,7) These tributes could not have come soon enough as J. Maddox, only a few years before, had a strongly critical comment to make of his own: “*One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition.*”⁽⁸⁾

Maddox’s concerns were alleviated to a certain extent over the following years with the perpetual improvement in technology, ever growing scientific understanding and strive for innovation. Advancements in technology, in particular those of experimental and computational methodologies, have considerably advanced the development of crystal engineering. Specifically the introduction of CCD (charge-coupled device) camera-equipped diffractometers, introduced by Bruker in 1993,⁽⁹⁾ has permitted the elucidation of crystal structures in a matter of hours or minutes rather than the weeks or days of the original diffractometer models. Furthermore, the constant computational enhancements have made the use of databases and visualisation programmes inexpensive and straightforward.

On a scientific level, through the greater experience, competence and knowledge, furthered by the ever increasing volume of significant results, and as a consequence of seminal work by authors such as G. Desiraju⁽¹⁰⁻¹²⁾ and M. Etter,⁽¹³⁻¹⁵⁾ among others, the field of crystal engineering has matured into an important discipline established on its own merits. Concurrently, classical and newer areas of chemistry were being developed such as organometallic chemistry,⁽¹⁶⁻¹⁸⁾ coordination polymer chemistry,^(19,20) the chemistry of metal-organic frameworks (MOFs) etc. One could think of the latter two areas as being branches of the field of crystal engineering, considering that these disciplines rely on the elucidation of crystal structures as the primary goal for complete topological classification and characterisation purposes. One of the more contemporary subjects that have impacted on the field of crystal engineering is the reticular synthesis concept.

1.2: The Reticular Synthesis Concept and Porosity

The term “reticular synthesis”, is a relatively new phrase conceived and introduced by O. Yaghi *et al.* in 2003 in his highly cited Nature article (over 2100 independent citations).⁽²¹⁾ It refers to the “conceptual approach that requires the use of secondary building units to direct the assembly of ordered frameworks.” Yaghi defines secondary building units (SBUs, a term which was initially used in the late 1970’s by C. Blackwell)⁽²²⁾ 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” (Fig 1.1).⁽²³⁾ The best examples of these polytopic linkers are carboxylic acid substituted aromatic molecules, functionalised biphenyls, bipyridines etc. The choice of polytopic linkers does not halt with the exhaustive list of functionalised aromatic molecules available, but also includes numerous aliphatic linkers like glutamates, squarates and oxalates. However, the preference for suitable linkers is generally given to robust aromatic molecules due to their rigidity (for support), amenability (e.g. shortening, lengthening and altering) and their ability to participate in supramolecular interactions such as π - π stacking (for stability).

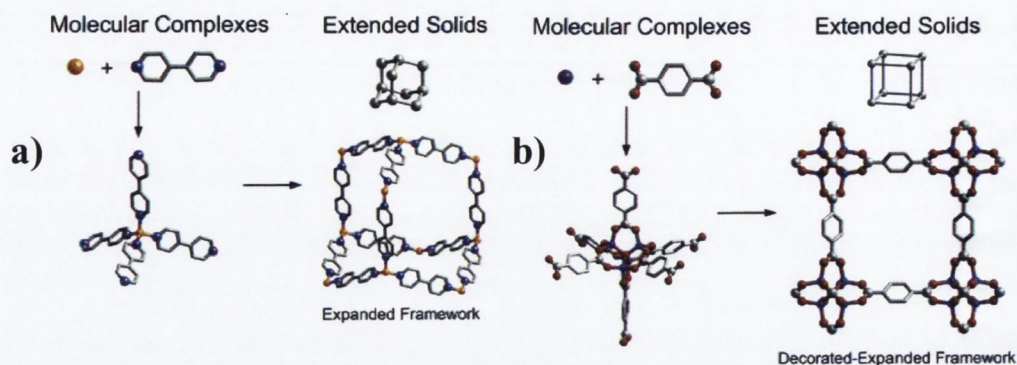


Figure 1.1: Assembly of metal-organic frameworks (MOFs) by the copolymerisation of metal ions with organic linkers to give (a) flexible metal-bipyridine structures with expanded diamond topology and (b) rigid metal-carboxylate clusters that can be linked by benzene “struts” to form rigid frameworks in which the metal-oxygen 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. In (a): M, orange; C, grey; N, blue; in (b): M, purple; O, red; C, grey.⁽²³⁾

One might ask the question: why are these ordered frameworks desirable in the first place? The answer lies in the fact that many metal-organic frameworks have been known to display the highly advantageous characteristic of porosity. According to IUPAC, the pores in solids can be classified into three categories, namely micropores, mesopores and macropores whose pore sizes are characterised by dimensions smaller than 2 nm, between 2 to 50 nm and larger than 50 nm, respectively.⁽²⁴⁾ These porous materials can, for instance, be used as molecular sieves, for separation procedures, guest exchange and most importantly for gas-uptake purposes, e.g. for hydrogen gas.

With consideration of the limited fossil fuel resources left available and global warming effects resulting from the emission of green-house gases, future economies and technologies must strive for sustainable and environmentally friendly energy sources. Hydrogen gas provides a cleaner alternative energy source (the combustion of or fuel cell by-product being water), that has a significantly higher energy density per weight over conventional fossil fuels. However, at present, the storage of hydrogen gas has yielded many difficulties due to its low density (low energy density per volume) and because of its explosive and highly reactive nature. Ergo, the design of a safe, reliable, cheap, compact and efficient device for hydrogen storage has become of paramount importance.

Porous materials have demonstrated the ability for uptake of gases, such as nitrogen, methane and carbon dioxide⁽²⁵⁻³⁰⁾ and the potential for hydrogen storage by these materials is currently a thriving and highly competitive area in chemical research.

One method of producing porous structures utilises the reticular synthesis concept, which has been shown to generate materials with predetermined structures. Yaghi, pioneering this work, has synthesised a plethora of complexes based on an identical SBU (Fig. 1.2). This SBU consists of four $\{\text{ZnO}_4\}$ tetrahedra sharing a common vertex and six carboxylate groups, which define this SBU with octahedral topology. These SBUs are joined together by benzene struts (linkers) to give a metal organic framework with a primitive cubic topology. These struts can be modified by a range of alternative phenyl types. This modification exemplifies the iso-reticular approach ('iso' meaning 'identical', and 'reticular' refers to 'net') whereby the same core SBU, $\{\text{Zn}_4\text{O}(\text{CO}_2)_6\}$ is used to generate structures with the same topology (Fig. 1.2b), differing only by the linkers employed.

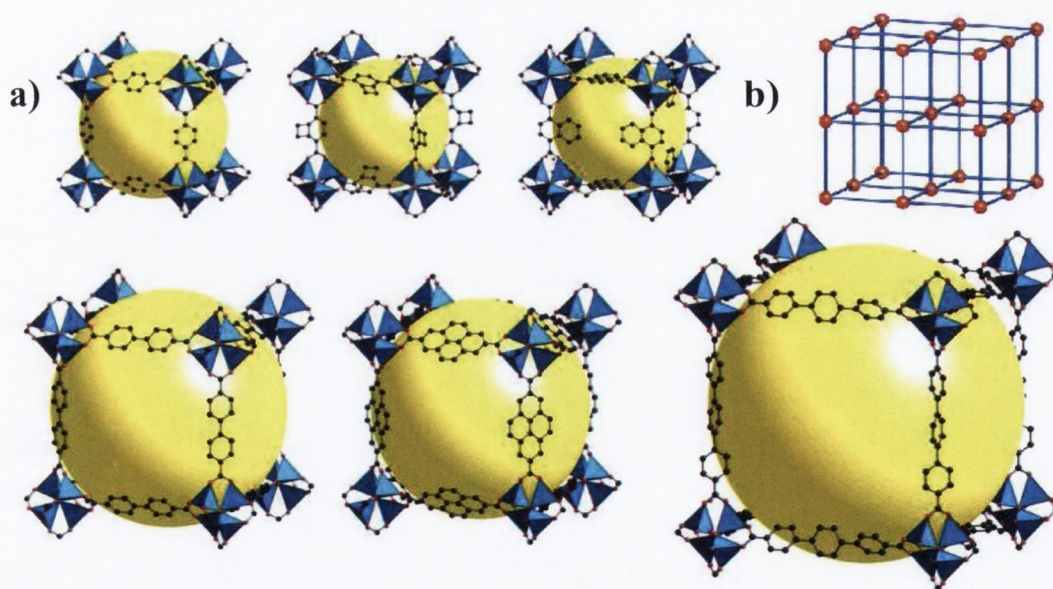


Figure 1.2: a) Primitive cubic MOF: $\{\text{Zn}_4\text{O}(\text{CO}_2)_6\}$. ZnO_4 tetrahedra (blue polyhedra) joined by benzene dicarboxylates and related linkers (O red and C black) to give an extended 3D cubic framework with interconnected pores; yellow spheres representing the pores without interfering with the van der Waals radii of the framework atoms and b) topology of the structure shown as ball-and-stick model.⁽²¹⁾

The US department of energy (DoE) has set targets for the storage of H₂ of 6 wt% by 2010 and 9 wt% by 2015 at conditions of -40 to 80 °C.⁽³¹⁾ These goals have set a motivating challenge for the various research groups working in the area. The objectives laid down by the DoE have undoubtedly spurred on a healthy rivalry between the various groups in an already competitive field. This competitive aspect has resulted in a growing number of compounds with increasing hydrogen storage capabilities being reported each year.

MOFs have been shown to be viable candidates for hydrogen storage and some recently developed systems are close to achieving the aims set by the DoE.⁽³²⁻³⁵⁾ Based on the afore-described tetranuclear Zn SBU (Fig. 1.2), the compound [Zn₄O(BTB)₂], commonly referred to as MOF-177 (Fig. 1.3), was synthesised by Yaghi and co-workers.⁽³⁶⁾ A 7.5 wt% hydrogen uptake, a volumetric capacity of 32 g/L⁻¹ and a surface area greater than 4500 m²/g⁻¹ characterise this compound.⁽³⁷⁾ Surface areas in excess of 6000 m²/g⁻¹ have more recently been reported by Yaghi and arise with a modification (lengthening) to the ligand-type used in the synthesis of MOF-177.⁽³⁸⁾ These promising figures bode well for realising the targets set by the DoE, however, all measurements were performed at elevated pressures and at low temperatures (*ca.* 70 K). Hence further development is still required to find more suitable compounds with increased surface areas and higher gas storage capacities.

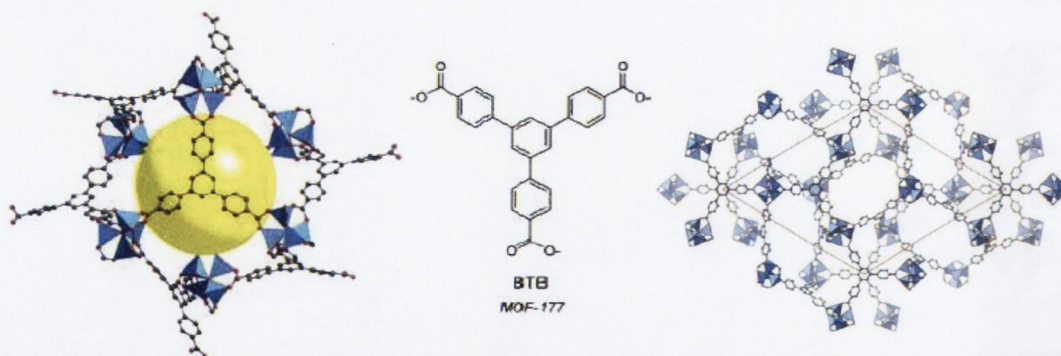


Figure 1.3: Structure of MOF-177 synthesised by Yaghi which is currently one of the leading compounds for the storage of hydrogen gas.⁽³⁶⁾

1.3: Coordination Polymers/Metal Organic Frameworks

The reticular synthesis concept, amongst other influential ideas, has led to a re-invigorated endeavour in the construction of coordination polymers. The expression coordination polymer was originally used by J. Bailer in the late 60's while comparing organic polymers with inorganic compounds that can be considered a polymeric species.⁽¹⁹⁾ Over the last two decades in particular, the field of coordination polymers has flourished with a ten-fold increase in publications related to the subject.⁽³⁹⁾

A polymer is generally perceived as a high molecular weight molecule, formed by the repetition of monomeric units linked through covalent bonds. A coordination polymer is an infinite system comprised predominantly of metal ions connected *via* coordination bonds to organic ligands. Their structure and constitution allows the intrinsic physicochemical properties of both the individual metal centres and the organic ligands to be combined. These polymer structures are often characterised by weaker supplementary (supramolecular) interactions affording additional stability.

Coordination polymers do not exclusively restrict themselves to isolated 1D chains, but can further extend into higher dimensional (2D and 3D) networks i.e. metal-organic frameworks (MOFs). The dimensionality is generally determined by the number of nodes (metal centres) and associated connectors (ligands) in a structure. For 1D motifs, a standard node is engaged in coordination bonds with two ligands, resulting in a repeating array of alternating metal ions and organic ligands, yielding a chain. 2D compounds arise when three or four ligands coordinate to a central metal ion, and the expansion of the complex occurs in two distinct directions. A three dimensional network typically stems from the metal coordination environment (tetrahedral, octahedral etc.) which facilitates additional directional spread through coordination bonds. Other weaker intermolecular forces, such as hydrogen bonds, may also contribute to the overall dimensionality, however, these typically emerge after the metal-ligand coordination bonds have been established. The formation of coordination polymers, in a simplified pictorial fashion, can be seen in Figure 1.4. The initial reaction phase involves the combination of metal ions and organic ligands. Association between these two reagent types, results in the various forms of architectures in the solid state.

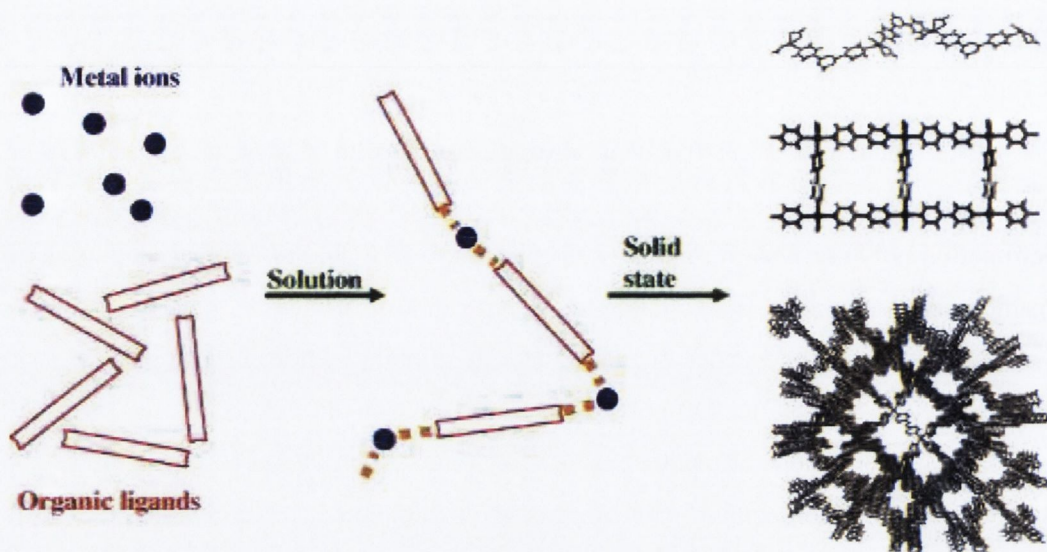


Figure 1.4: Simplified representation of the formation of coordination polymers.⁽³⁹⁾

Coordination polymers can also be referred to as the aforementioned metal-organic frameworks (MOFs) or metal-organic coordination networks (MOCNs) once certain criteria are met. Firstly, the ligand must be a linking/bridging organic moiety, and therefore the connection between metal ions and ligands must perpetually extend in at least one direction of space. Furthermore, a minimum of one carbon atom must lie between the donor groups. This latter requirement is that a coordination polymer/MOF is comprised of no additional bridging “inorganic” units, such as a halide ion, which interrupt an infinite ligand-metal assembly. These distinct systems are described as organic-inorganic hybrid materials.⁽⁴⁰⁾

Figure 1.5 demonstrates a variety of topological shapes and architectures associated with coordination polymers/MOFs. This exemplifies the intricate diversity of topologies associated with each respective dimensionality.

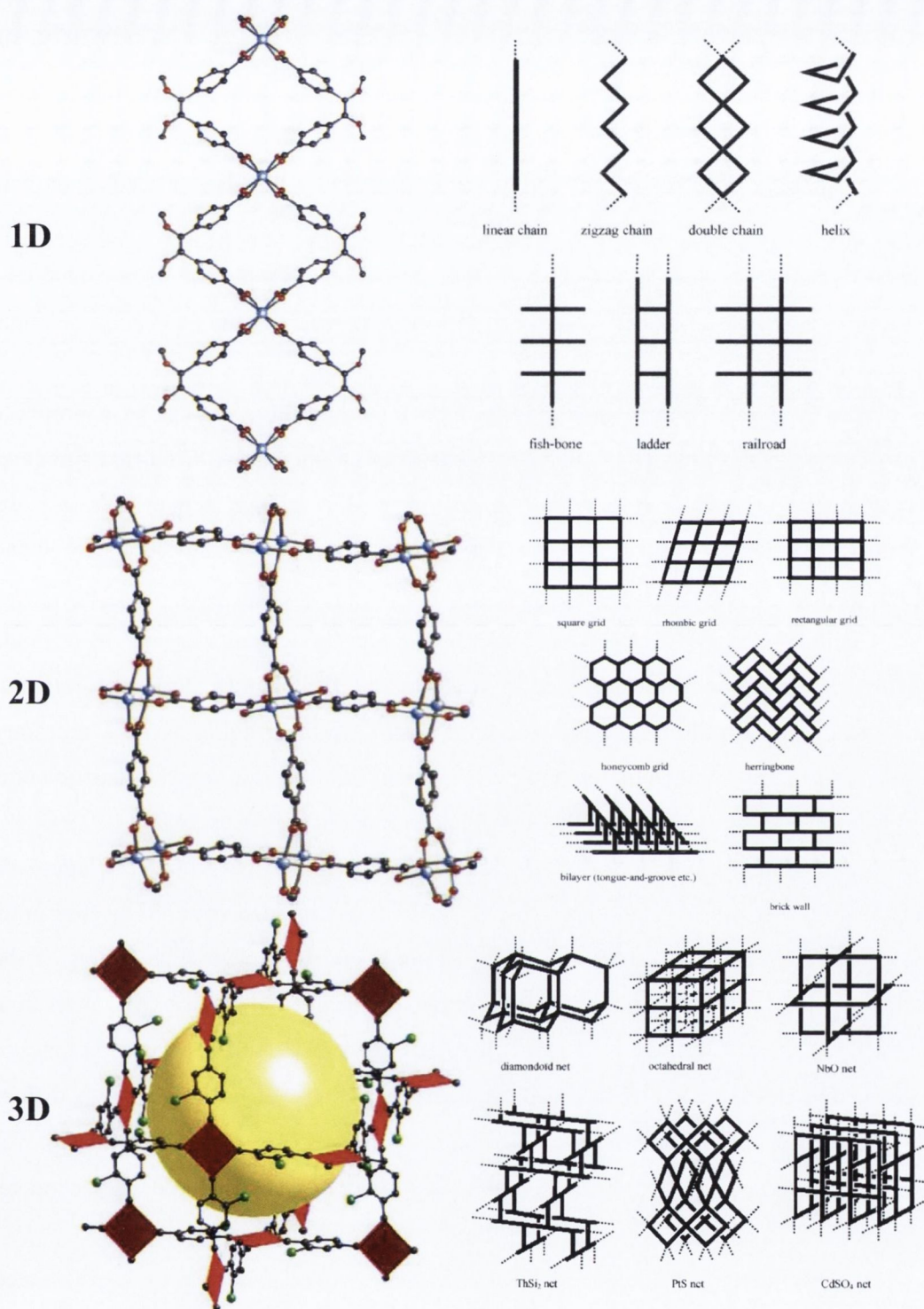


Figure 1.5: Variety of 1D, 2D and 3D structural motifs and topologies observed in coordination polymer chemistry.⁽⁴¹⁾

1.3.1: Hydro(solvo)thermal Synthesis of Metal-Organic Frameworks or Related Systems

Following the choice, design or successful synthesis of a particular organic ligand, one must consider how to successfully react this organic moiety with a metal centre to produce crystalline materials of a coordination polymer, or related materials. There are numerous synthetic methods that one may consider for the generation of single crystals of MOFs.

Conventional synthetic strategies combine the starting materials in appropriate solvents in open reaction flasks under ambient reaction conditions. Modified strategies involve elevated temperatures. In protic solvents, pH variation might influence the structure of the generated inorganic SBUs and may aid the deprotonation of acidic ligand moieties.

Saturation methods allow the addition of all the desired reagents in a single reaction vessel. The homogenised mixture is left unperturbed and the slow evaporation of the solvent transpires. Products may crystallise from the mother liquor over the necessary period of time. This method under ambient conditions can be slow, depending of solvents used, but it was exploited successfully by us in a number of instances.

Diffusion methods are often applied for crystallisation purposes. One approach being solvent diffusion whereby two solutions of contrasting densities are layered in an appropriate container, typically a test tube. This encourages a slow diffusion of the solutions with product/crystal formation at the interface over time. An alternative approach is vapour diffusion where a sealed vessel containing two solutions of independent reagents is left undisturbed for a period of time. The ensuing vapours diffuse into one another and a reaction/crystallisation may proceed. Another procedure involves the use of microwave and/or ultrasonic methods. This is a more contemporary technique, and is currently gaining in significance within the field of MOF synthesis.

A prominent synthetic approach for the synthesis of MOFs, and related compounds, involves the use of hydro- solvo-thermal autoclaves. This synthetic methodology was actively used in the present work, hence, a more comprehensive review of this method will be given.

Hydrothermal, and solvothermal, reaction conditions refer to a distinct class of synthetic procedures whereby a sealed container (autoclave, bomb etc.) is subjected to external heating, normally in a conventional oven. The vessels are heated to an elevated temperature, generally exceeding the boiling point of the solvent, which in turn generates a high (autogenous) pressure of the resultant vapour. A typical illustration of the reaction vessel is depicted in Figure 1.6. The use of an autoclave is necessitated by the pressures developed under hydro(solvo)thermal conditions and an inert liner is used to protect the stainless steel outer shell from the corrosive reagents (e.g. strong acids or bases) often used in syntheses. Standard autoclaves can be used up to *ca.* 200 °C, and depending on the specification of the steel walls, pressures of ~150 bar can be withheld.⁽⁴²⁾

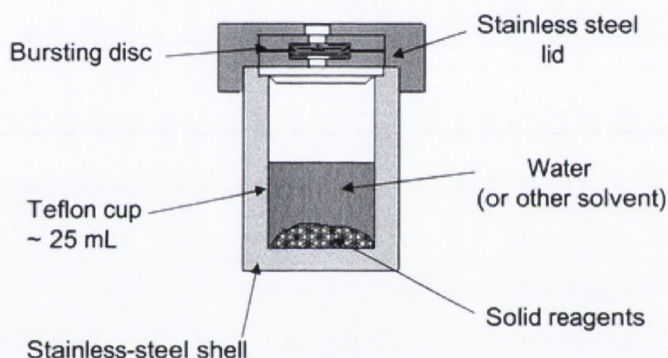


Figure 1.6: A schematic of a teflon-lined stainless-steel autoclave used in the laboratory to perform subcritical hydro(solvo)thermal syntheses.⁽⁴²⁾

The term solvothermal refers to the use of solvents other than water, whilst hydrothermal alludes to water being the sole solvent in the reaction. Occasionally, some authors consider hydrothermal conditions to refer to supercritical conditions, i.e. temperatures greater than 300 °C and pressures in excess of 200 bar. However, the term is more commonly used to imply a temperature beyond that of the boiling point of the solvent.

The existence of hydrothermal activities stretches back to geological activities associated with the formation of the earth and the universe. It has even been hypothesised that hydrothermal chemical reactions occurred in the oceans and that microorganisms

have high-temperature ancestors.⁽⁴³⁻⁴⁵⁾ Hydrothermal synthesis concepts have been used for a long time in chemical laboratories. The first reported artificial hydrothermal reaction was carried out in 1839, when the German chemist R. Bunsen contained aqueous solutions in a thick-walled glass tube at temperatures above 200 °C and a pressure above 100 bars. The crystals of barium carbonate and strontium carbonate that grew under these conditions marked the first successful application of the hydrothermal process, using aqueous solvents as media.⁽⁴⁶⁾ Industrial applications of this synthetic method date back to a patent from 1945, which describes the synthesis of BaTiO₃.⁽⁴⁷⁾

Over the ensuing years the use of hydro/solvothermal reactions in chemical sciences has developed into its own specific and respected area, with the first international conference focusing on this synthetic technique held in 1994. The number of publications that exploit this preparative method is continually increasing year upon year.⁽⁴⁸⁻⁴⁹⁾

One of the primary advantages in employing hydro(solvo)thermal techniques is the acquirement of superheated solvents in the reaction vessels. Superheated solvents display remarkable properties, and one could argue that a completely new solvent is generated at high temperatures and elevated pressures.⁽⁴²⁾ One of the properties of the resulting solvent is that of reduced viscosity, which in turn can enhance the diffusion of a chemical species and can lead to enhanced crystal growth.⁽⁵⁰⁾ In addition, very different solubilising characteristics are observed in superheated solvents, where the dielectric constant decreases rapidly with increasing temperature. This can lead to otherwise insoluble reagents being solubilised.

An abundance of synthetic variations and modifications may be applied for the generation of phase-pure materials. Probable variables include the nature of the solvent (and amount thereof), choice of metal ion, primary ligand, possible auxiliary ligand, ratio of reactants, temperature of oven, heating time in oven, pH of system and rate of cooling etc.; the permutations are virtually endless. Figure 1.7 shows a plot of various achievable pressures, determined by the percentage fill of the vessel and applied temperatures using water as the solvent. This relationship underlines the synthetic advantages of hydrothermal conditions over ambient systems.

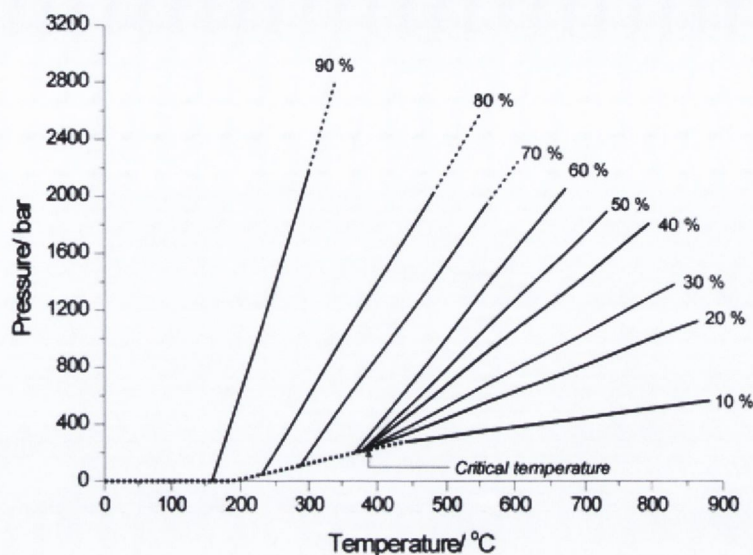


Figure 1.7: Pressure as a function of temperature and percentage fill of water in a sealed vessel.⁽⁵¹⁾

Owing to the large number of alterations possible using the hydro(solvo)thermal process, there is huge scope for the synthesis of a wide range of innovative compounds. Hydrothermal reaction conditions have been used successfully in the preparation of a plethora of compounds such as microporous crystals,⁽⁵²⁾ superionic conductors,⁽⁵³⁾ chemical sensors,⁽⁵⁴⁾ electronically conducting solids,⁽⁵⁵⁾ complex oxide ceramics and fluorides,⁽⁵⁶⁻⁵⁷⁾ magnetic materials,⁽⁵⁸⁾ and luminescence phosphors,⁽⁵⁹⁾ to name only a few material examples. Hydrothermal reaction conditions have also been exploited for the *in situ* synthesis of ligands, generating distinct supramolecular systems.⁽⁶⁰⁻⁶¹⁾ This has shown great promise for both organic and inorganic chemists, capitalising on the benefits of the experimental technique.

1.3.2: Potential Applications of Coordination Polymers or Metal-Organic Frameworks

In addition to the aesthetically appealing structural architectures of coordination polymers/MOFs, there are naturally distinctive and advantageous characteristics associated with coordination polymers or MOFs. As a result, researchers are striving to

synthesise compounds which potentially exhibit exploitable features such as porosity,⁽⁶²⁻⁶⁵⁾ conductivity,⁽⁶⁶⁻⁶⁷⁾ luminescence,⁽⁶⁸⁻⁶⁹⁾ non-linear optical properties (NLO),⁽⁷⁰⁻⁷¹⁾ catalysis⁽⁷²⁻⁷⁵⁾, magnetism etc.⁽⁷⁶⁾ Figure 1.8 demonstrates some of these applications.

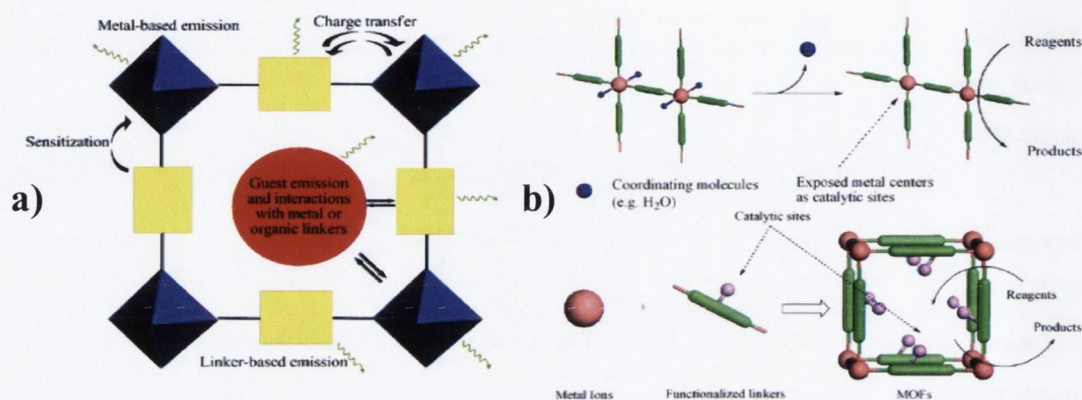


Figure 1.8: a) Potential photochemical applications of MOF's and b) schematic highlighting catalytic sites available in both coordination polymers and extended MOFs.^(69,75)

1.4: Magnetic Materials

There has been a continuous interest in magnetic materials ever since the first discussions between Aristotle and Thales about the phenomenon of magnetism around the 6th Century B.C.⁽⁷⁷⁾ Following the realisation of “molecular magnetism” in the 1950's a new chemical discipline was conceived.⁽⁷⁸⁻⁷⁹⁾ The investigation into di-nuclear Cu(II) acetate complexes stimulated chemists to explore a research domain which, until then, was primarily occupied by physicists. The original preconception, and the initial hesitation of chemists to investigate the magnetic phenomena of molecules possibly delayed progress in the field somewhat, nonetheless, some significant milestones have been accomplished over the following decades. H. Wickman discovered the first molecular magnet upon the isolation of $\text{Fe}^{\text{III}}(\text{S}_2\text{CNEt}_2)_2\text{Cl}$ in the late 1960's,⁽⁸⁰⁾ and O. Kahn designed the first molecular-based ferrimagnet in the late 1980's.⁽⁸¹⁾ This seminal work appeared to instigate a rapid development within the field. The 1990's led to the

discovery of the first organic ferromagnet,⁽⁸²⁾ the first room temperature molecule-based magnet,⁽⁸³⁾ the first paramagnetic superconductor,⁽⁸⁴⁾ and the first Prussian blue-type compound that reveals magnetisation at room temperature.⁽⁸⁵⁾

1.4.1: Single-Molecular Magnets (SMMs)

A significant scientific achievement in the 1990's was the discovery of the first single-molecular magnet (SMM) reported by R. Sessoli *et al.*⁽⁸⁶⁾ The oxo-cluster that revealed this unusual magnetic behaviour, $[\text{Mn}_{12}\text{O}_{12}(\text{MeCO}_2)_{16}(\text{H}_2\text{O})_4] \cdot 2\text{MeCO}_2\text{H} \cdot 4\text{H}_2\text{O}$, “ Mn_{12} ”, was in fact originally synthesised by T. Lis in 1980.⁽⁸⁷⁾ The structure of the oxo-cluster in this compound is composed of a central $\text{Mn}^{\text{IV}}_4\text{O}_4$ cubane unit, which is surrounded by a ring of eight Mn^{III} centres connected through bridging oxo-ligands, as depicted in Figure 1.9. The outer Mn^{III} ions are further bridged by acetate groups, and terminal water molecules complete the coordination spheres of four of these Mn ions. All manganese centres display distorted octahedral coordination geometries and the Mn^{III} centres also reveal Jahn-Teller distortion, signified as elongated coordination bond lengths in the axial plane.

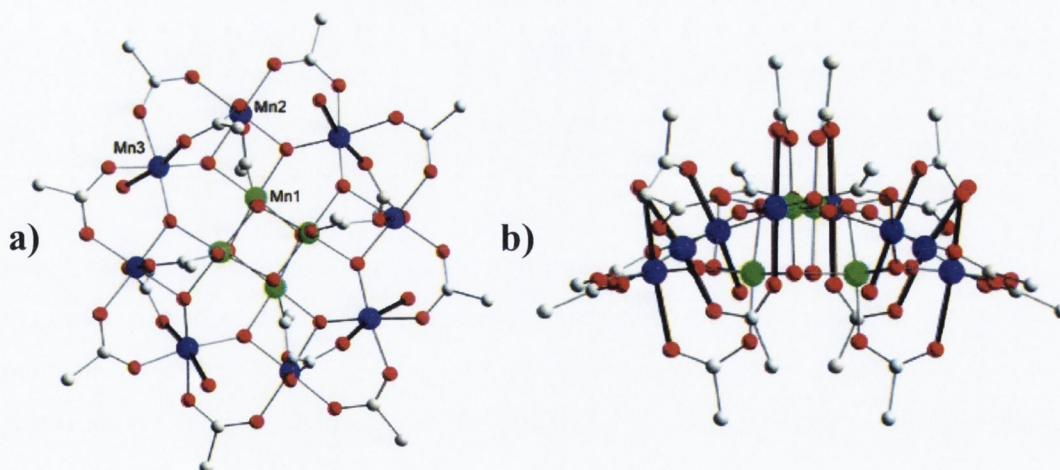


Figure 1.9: a) View of Mn_{12} along the crystallographic c -axis and b) b -axis. Grey, red, blue and green spheres refer to carbon, oxygen, Mn(III) and Mn(IV) atoms respectively.⁽⁸⁸⁾

It took more than a decade from the original synthesis of the compound, for magnetization data to be collected at high magnetic fields and at low temperatures, to elucidate the nature and origin of the observed magnetic behaviour.⁽⁸⁹⁻⁹⁰⁾ The magnetic data obtained confirms an $S = 10$ ground state (spin value), as well as the significant presence of axial anisotropy (D). The magnitude of the ground state is in agreement with the ‘giant spin model’ and arises from a situation in which the spins of the four central Mn^{IV} (d^3) centres are all aligned anti-parallel to the spins of the eight outer Mn^{III} (d^4) centres: $S = [(4 \times 3/2) - (8 \times 2)] = 10$. This spin structure, illustrated in Figure 1.10, may classify the cluster as a molecular ferri-magnetic system.

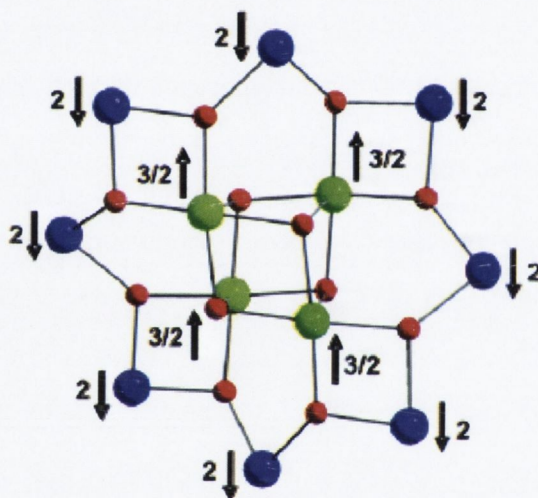


Figure 1.10: The magnetic behaviour of Mn_{12} in the ground state.⁽⁸⁸⁾

An interesting feature displayed by this Mn_{12} cluster is that of slow-relaxation of the magnetisation. At very low temperatures this cluster displays hysteresis loops, as shown in Figure 1.11.⁽⁹¹⁾ The unusual steps in this hysteresis curve are due to quantum tunnelling of the magnetisation.⁽⁹²⁾ A relaxation half-life of approximately 2 months was observed for this species, albeit this was at a temperature of 2 K. A slight increase in temperature dramatically reduces this half-life and hysteresis is no longer observed (4 K).

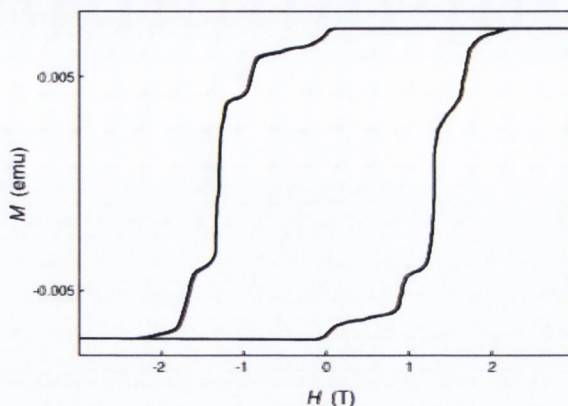


Figure 1.11: Representation of the magnetic hysteresis loop of Mn_{12} at 2.1 K.⁽⁹¹⁾

The unique and fascinating magnetic properties demonstrated by Mn_{12} have led to intense research activities within the discipline to generate alternative SMMs that show the outlined properties at increased temperatures. The key features one must attain to afford a SMM are a high spin (S) value, coupled with strong magnetic anisotropy (D). Other transition metal ions are being explored in SMM syntheses. Iron clusters such as $[\text{Fe}_{19}\text{O}_6(\text{OH})_{14}(\text{metheidi})_{10}(\text{H}_2\text{O})_{12}]$ and $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]$, (metheidi = *N*-(1-hydroxynethylethyl)iminodiacetic acid and tacn = 1,4,7-triazacyclononane) have shown promise with associated S values of $33/2$ and 10 , respectively, as well as negative D components for both compounds.⁽⁹³⁻⁹⁴⁾ Mixed metal clusters are also receiving greater attention, such as $[(\text{Me}_3\text{tacn})_6\text{MnMo}_6(\text{CN})_{18}]$ and $[(\text{tetren})_6\text{Ni}_6\text{Cr}(\text{CN})_6]$, (Me_3tacn = *N,N',N''*-trimethyl-1,4,7-triazacyclononane and tetren = tetraethylenepentamine). S values of $13/2$ and $15/2$ were observed for the $\{\text{MnMo}_6\}$ and $\{\text{NiCr}_6\}$ core containing compounds, respectively.⁽⁹⁵⁻⁹⁶⁾

One of the more active research areas is, surprisingly, the slight modification of the original Mn_{12} structure. Gentle alterations to the synthesis permit the exchange of the bridging acetate groups with other carboxylate units. The coordinating solvent molecules can be substituted and reduced species can be synthesised too. Many of these modified Mn_{12} structures were synthesised by G. Christou, and co-workers, who refers to the set of related compounds as the “*drosophila*” of single-molecule magnetism.⁽⁸⁸⁾ Figure 1.12 charts some of the altered Mn_{12} compounds.

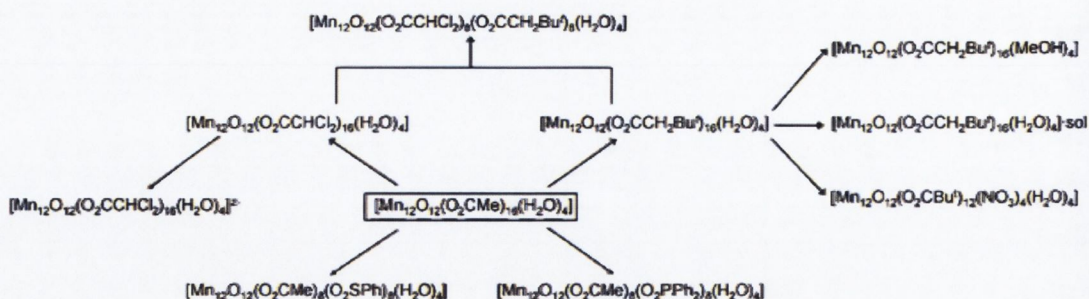


Figure 1.12: A selection of the more established transformations of $[\text{Mn}_{12}\text{O}_{12}(\text{MeCO}_2)_{16}(\text{H}_2\text{O})_4]$.⁽⁸⁸⁾

The magnetic properties of all of these Mn_{12} derivatives have been characterised. The compounds display varying axial anisotropy and energy barriers, D and U_{eff} . Unfortunately, the blocking temperatures for any of the compounds are still extremely low (2–4 K). However, this has not dampened the enthusiasm of research into the field of SMMs. Lis’ original observation that “such a complicated dodecameric unit should have interesting magnetic properties” could not have been a greater understatement.

1.4.2: Single-Chain Magnets (SCM)

The characteristics of single-chain magnets (SCMs) are closely related to those of SMMs. The origins of SCMs date back to the 1960’s when the physicist R. Glauber predicted that magnetically coupled *Ising* spin chains, i.e. chains displaying axial anisotropy, should display slow relaxation of the magnetisation.⁽⁹⁷⁾ It took decades, however, until the first reported case of this phenomenon was reported in 2001 by Gatteschi and Sessoli.⁽⁹⁸⁾ They observed a slow relaxation of the magnetisation in a 1D chain that consists of alternating cobalt(II) centres and organic radical moieties; $[\text{Co}(\text{hfac})_2(\text{NITPhOMe})]$. In this system, the spins of both spin centres are antiferromagnetically coupled at low temperature. At the same time, R. Clérac discovered similar magnetic properties (slow relaxation) in a chain of ferromagnetically coupled anisotropic $S = 3$ spin units; $[\text{Mn}_2(\text{saltmen})_2\text{Ni}(\text{pao})_2(\text{py})_2](\text{ClO}_4)_2$.⁽⁹⁹⁾

To quote Clérac: “*Single-chain magnets (SCMs) are made up of magnetically isolated chains possessing a finite magnetisation that can be frozen in the absences of an*

applied magnetic field. At low temperatures, the relaxation of the magnetisation becomes so slow that these systems can be considered as a magnet.”⁽¹⁰⁰⁾ Akin to SMMs, a slow relaxation of the magnetisation is the desired target. To achieve this magnetic behaviour, some conditions need to be met. The 1D systems must have a strong uniaxial anisotropy (D), together with a net spin magnitude along the chain ($S > 0$). This latter requirement implies that ferro- or ferrimagnetic spin organisations between the metal centres within the chain are preferable, although spin canted antiferromagnetic interactions can also be exploited. An imperative for SCMs is that intra-chain interactions are significantly stronger than the inter-chain ones, allowing one to differentiate the superparamagnetic properties of SCMs from that of classical bulk (3D) systems. This requirement, however, can be readily overcome by introducing large “spacers” (Fig. 1.13), for instance extended organic ligands, in the synthetic process. Akin to single-molecular magnets, single-chain magnets exhibit the desired magnetic characteristics at very low temperatures, typically below a blocking temperature of 10 K.⁽¹⁰¹⁾ Hence, the continuous development of this discipline is of great importance, in order to exploit the advantageous magnetic properties of SCMs at more practical temperatures.

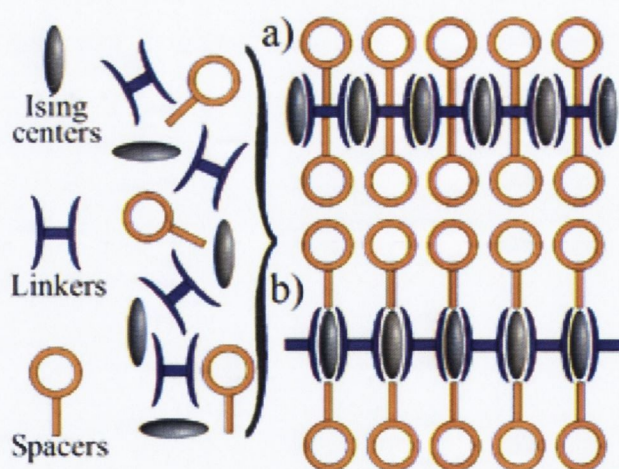


Figure 1.13: Possible strategies for SCM synthetic design. The necessary building blocks are metal centres with strong Ising magnetic anisotropy (grey, ellipsoids), bridging ligands (blue linkers), and non-magnetic spacers (orange spacers). Two ways of assembling the blocks are shown. a) By assembling the spacers on the bridging ligands. b) By using short linkers as bridges and binding the spacers directly on the metal centres.⁽¹⁰²⁾

This relatively new and exciting field has flourished since its foundation, and is currently considered a hot topic of research at the frontier between chemistry and physics.⁽¹⁰²⁻¹⁰³⁾ The synthetic challenges associated with the generation of SCMs appear less demanding than those of SMMs.⁽¹⁰³⁾ As a result, an ever increasing number of materials that display SCM characteristics are being reported annually and each new compound further contributes to the understanding of these complex systems. This accumulating knowledge is advancing both the theoretical side of the magnetism (physics) and the synthetic procedures to obtain SCMs (chemistry).

Creating multifunctional SCMs i.e. coupling the 1D magnetic properties with other physical or chemical phenomena may result in highly exciting devices.⁽¹⁰⁴⁾ For example, chiral SCMs in the field of magneto-optical experiments is just one of the numerous areas currently being investigated.⁽¹⁰⁵⁾

1.4.3: Spin Crossover Systems (SCO)

Another magnetic phenomenon relevant to coordination complexes to be briefly discussed is spin crossover (SCO) behaviour. In octahedral transition metal complexes, the splitting of the d orbitals into the t_{2g} and e_g sets occurs. Depending on the energy gap between the two orbital sets, ions with a d^4 - d^7 electronic configuration may reside either in a high spin (HS), or a low spin (LS) state. Figure 1.14 demonstrates both HS and LS electron configurations for an Fe^{II} (d^6) and an Fe^{III} (d^5) ion.

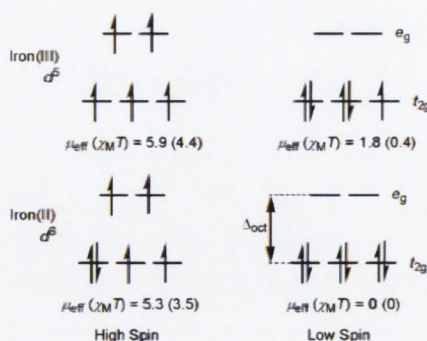


Figure 1.14: d -orbital occupancies and typical magnetic moment values of HS and LS iron(II) and iron(III) complexes in an octahedral ligand field.⁽¹⁰⁶⁾

Spin transitions between high-spin and low-spin states can be achieved by an applied external stimulus such as a change in temperature, pressure or by light irradiation.⁽¹⁰⁷⁾ Spin transitions impact on the number of unpaired electrons in a system, which in turn alters the overall magnetic characteristics of the metal ion. Other factors, such as the bond lengths within a complex and the optical properties of the compound may change with a spin transition.⁽¹⁰⁸⁾ Thus far, the majority of the reported spin-crossover compounds are Fe^{II} complexes with a {FeN₆} coordination sphere. The spin transition in spin-crossover complexes is dependent of the structure, composition and electronic attributes of the coordination complex and can proceed in many forms. Figure 1.15 illustrates the various spin transition curves whereby $T_{1/2}$ is the deflection point of the curve corresponding to 50% high-spin and 50% low-spin centres within the sample.

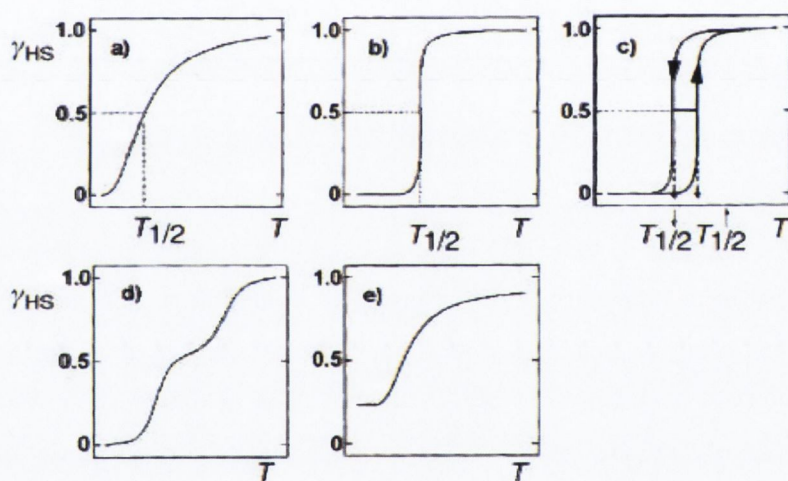


Figure 1.15: The nature of spin transition curves for SCO systems. Such curves can be; a) gradual, b) abrupt, c) displaying hysteresis, d) with steps or e) incomplete.⁽¹⁰⁷⁾

In the early 1990's, O. Kahn applied an interesting synthetic approach to enhance the properties of SCO systems.⁽¹⁰⁹⁾ He achieved the covalent linking of metal ions through appropriate ligands. 1D chains composed of [Fe(4-Rtrz)₃]_n sub-units (4-Rtrz = 4-R-1,2,4-triazole, R = H or NH₂), demonstrated SCO behaviour, and were further characterised by large hysteresis loops encompassing room temperatures.⁽¹¹⁰⁾ The combining of the spin-crossover phenomena with coordination polymers instigated the

isolation of several other Fe(II) coordination polymers or MOFs that display SCO behaviour. These systems reveal high cooperativity between the metal centres and also demonstrate wide hysteresis loops that may span across room temperatures.^(107,111-112)

With the emergence of the fascinating field of molecular magnetism over fifty years ago, this perpetually developing domain has challenged chemists, and physicists alike, ever since. With regards possible applications, the exploitation of hysteresis loops in the described systems is of great importance.⁽¹¹³⁾ Spin-crossover systems may find applications in future memory devices or magneto-optical switches, sensors etc.⁽¹¹⁴⁻¹¹⁵⁾ The steady enhancement of technology, theoretical comprehension and basic experience, has helped significantly progress the field of molecular magnetism over the decades. Several review papers have charted the progression of the subject and speculate about future directions and applications.^(102,116-119)

1.5: Iminodiacetic Acid Functional Group

Ligands containing the iminodiacetic acid functionality are abundant in their variety and impact on a wide range of disciplines including chemistry, physics and medicine.⁽¹²⁰⁻¹²³⁾ The tri-dentate functional group can be attached to an aromatic moiety, or an aliphatic unit. The latter type is best exemplified in ethylenediamine-tetra-acetic acid (EDTA) or related systems.⁽¹²⁴⁻¹²⁹⁾ The work presented in this thesis is relevant to aromatic iminodiacetic acid ligand derivatives.

Schmitt *et al* developed a range of coordination networks exhibiting lamellar, double-helical or chiral structures, dense hexagonal arrays or open-framework networks using various ligand-types.⁽¹³⁰⁾ All structures of these di-nuclear iron(III) complexes derive from assorted phenol and naphthol units which collectively possess the iminodiacetic acid group attached to an aromatic backbone. All employed *hda/nida* ligand derivatives were prepared *via* the Mannich reaction. Within the iron(III) complexes the transition metal centres are doubly bridged *via* carbonate and a hydroxo- or oxo- ligand. The complexes are negatively charged and self-assemble in the presence of suitable counterions into network structures. The obtained topologies are influenced by

additional substitutions of the ligands used. Introduction of O-donors opposite to the hydroxyl functionality of the phenol or naphthol ligand moiety generally result in open-framework structures. Consequently, $K_6[Fe_2(\mu-O)(\mu-CO_3)(SO_3\text{-hda})_2]\cdot 11H_2O\cdot 9MeOH$ (Fig 1.16a) affords a hexagonal open-framework structure, whilst a dense honeycomb structure characterises $K_6[Fe_2(\mu-O)(\mu-CO_3)(Chnida)_2]\cdot 13.5H_2O$ (Fig 1.16b).

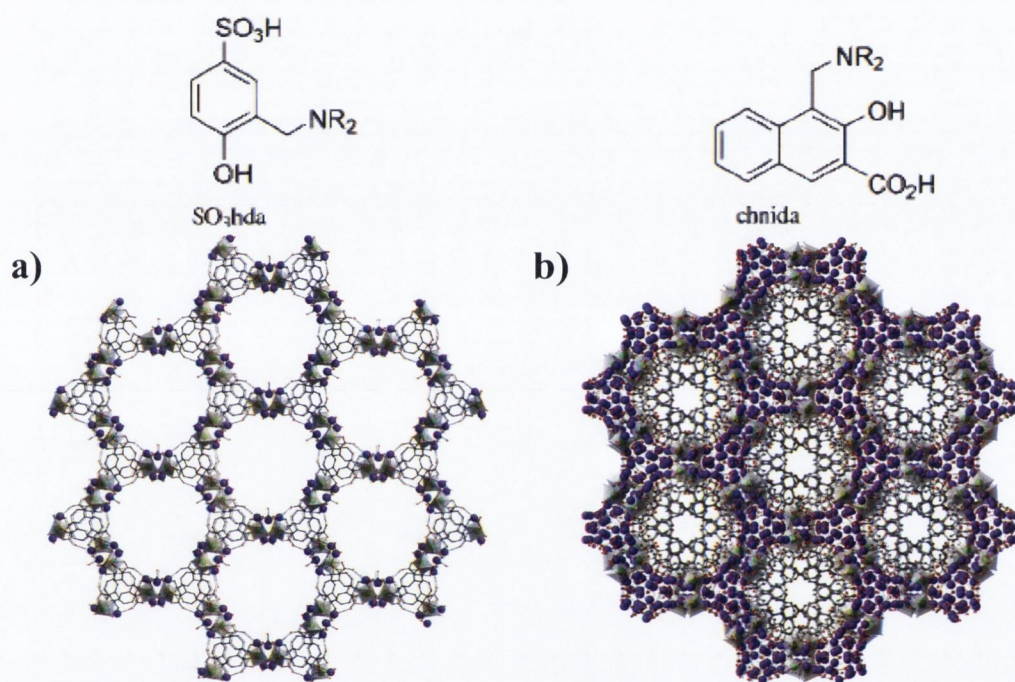


Figure 1.16: a) Open-framework structure in $K_6[Fe_2(\mu-O)(\mu-CO_3)(SO_3\text{-hda})_2]\cdot 11H_2O\cdot 9MeOH$, and b) honeycomb structure in $K_6[Fe_2(\mu-O)(\mu-CO_3)(Chnida)_2]\cdot 13.5H_2O$ generated using the relevant iminodiacetic acid substituted ligands (depicted above networks, $R=CH_2COOH$).⁽¹³⁰⁾

These assembly principles can also be applied to metal complexes containing other transition metal ions.⁽¹³¹⁻¹³²⁾ For example, copper(II) ions have yielded both open frameworks and comparable honeycomb structures in $K_4[Cu^{II}(Cnida)]_2\cdot 4H_2O$ (Fig. 1.17a) and $K_2[Cu^{II}(hnida)]_2\cdot 2H_2O$ (Fig. 1.17b), respectively. In these structures the Cu^{II} centres are bridged through the O-donor groups of the ligand moieties (Fig. 1.17c). Interactions involving the potassium ions and carboxylate O-donors afford the overall intricate networks depicted. Slight modifications to the ligand-type used result in quite varied

assemblies, with the Cnida ligand, containing an additional carboxylic acid, generating the open framework structure (Fig. 1.17d).

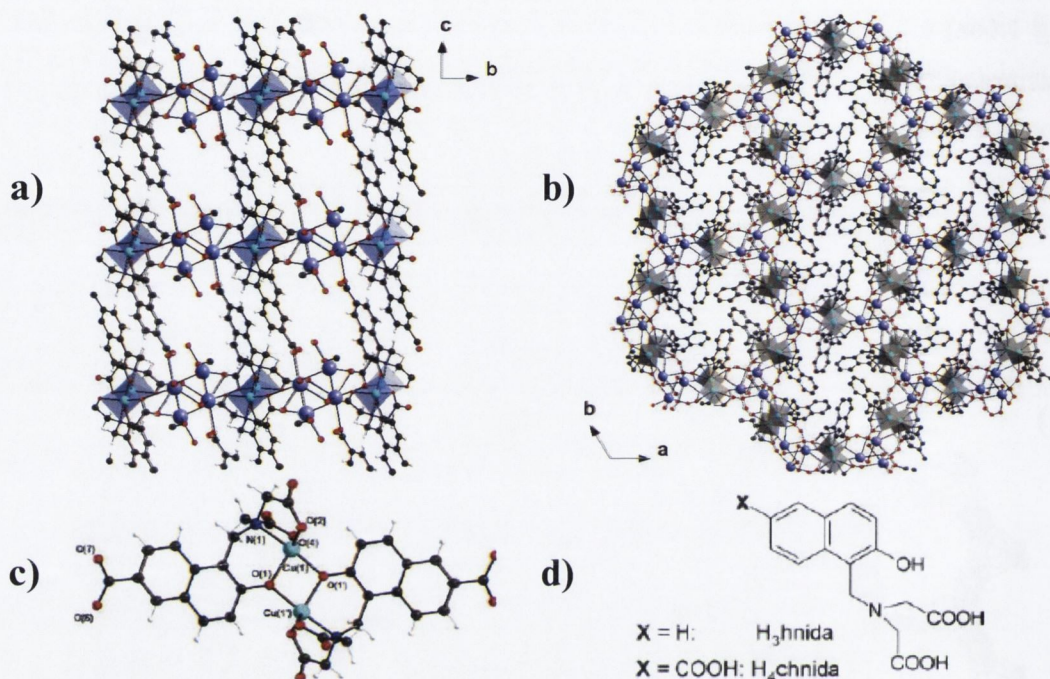


Figure 1.17: a) Open-framework structure in $K_4[Cu^{II}(Cnida)_2] \cdot 4H_2O$, b) honeycomb structure in $K_2[Cu^{II}(hnida)]_2 \cdot 2H_2O$, formed by iminodiacetic acid functionalised naphthols, c) the di-nuclear complex, with the deprotonated alcohol group bridging both copper ions and d) the two ligand-forms used.⁽¹³¹⁾

Further investigations involving some of these described compounds lead to the discovery of additional interesting properties. The open-framework materials have potential to be used in gas storage applications, and specifically $K_4[Cu^{II}(Hcnida)]_2 \cdot 4H_2O$ has shown promising thermal stability in combination with the necessary flexibility to withstand structural changes induced by calcinations or the uptake and release of guest molecules. The more dense supramolecular structures, however, can be used as templates for the preparation of nanomaterials. This application was demonstrated using $Na_6[Fe_2(\mu-O)(\mu-CO_3)(Chnida)_2] \cdot 13.5H_2O$, which consists of nano-sized channels that run in the direction of the crystallographic *c*-axis and are filled with naphthyl moieties of the organic ligands.⁽¹³²⁾ Upon heating, this compound transforms into hybrid organic-

inorganic nanofibres that form within single crystals of the compound. This effect was investigated by cutting crystals perpendicular to the crystallographic *c*-axis using a focused Ga ion beam. Thermolysis provides a further tool to control the composition of the fibres and at *ca.* 370 °C high yields of intersected, parallel aligned fibres are obtained that are usually contained in micro-capsular entities of amorphous carbon. XRD, EDAX and IR analysis suggested that the fibres are composed of Na₂CO₃ and Fe₂O₃ which react at higher temperatures to give different phases of sodium iron oxides (Fig. 1.18 a-f).

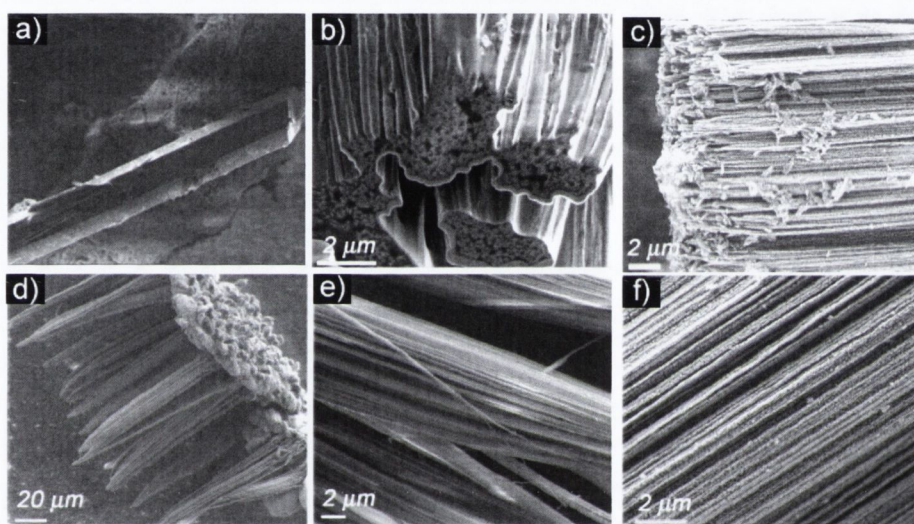


Figure 1.18: a) -f) Thermolysis of a crystal of Na₆[Fe₂(μ-O)(μ-CO₃)(Chnida)₂].13.5H₂O to give nano-sized fibres (hybrid or carbonate/Fe₂O₃ fibres) whose dimensions and composition are determined by the molecular structure of the precursor.⁽¹³³⁾

Other complexes composed of the chelating iminodiacetic acid have shown promise in photoluminescence studies, and demonstrate a spectrum of varying intensities.⁽¹³⁴⁻¹³⁶⁾ The magnetic properties of several compounds containing the iminodiacetic acid group, displaying a range of interesting magnetic characteristics and exchange pathways, have also been reported.⁽¹³⁷⁻¹⁴²⁾

The evident versatility displayed by this chelating moiety encouraged us to synthesise a range of iminodiacetic acid-substituted ligand-types containing supplementary carboxylic acid groups attached to an aromatic backbone. The positioning

of the various COOH moieties, relative to the tri-dentate functionality, should afford a diverse assortment of complexes, with unique characteristics determined by both the ligand and metal used.

1.6 Aims and Synthetic Strategies

The aim of the project is to synthesise novel coordination polymers/metal organic frameworks with controllable topologies. Our motivation is to create structures in which transition metal ions are bridged *via* donor atoms in such a fashion that cooperative effects between the spin centres give rise to interesting magnetic effects. Of particular interest for this research project are low dimensional materials, for instance, oxo-clusters with properties of single-molecular magnets and 1D spin chains. We further aim to develop our synthetic reaction systems to obtain higher dimensional compounds with open-framework topologies which might give rise to porosity. The development of such hybrid materials is of further interest in order to create advanced materials whose physiochemical attributes can be influenced by both the organic and inorganic components.

1.6.1: Choice of Ligands

One of the key considerations in the synthesis of MOFs lies in the prudent selection of the ligand. The ligand-type used has a great influence on the coordination environment of a metal ion, the dimensionality of the resultant compounds and can significantly determine the characteristic properties of the material.⁽¹⁴³⁻¹⁴⁴⁾

For the successful synthesis of coordination polymers or networks, carboxylic acid groups have been widely recognised as one of the most versatile functionalities in coordination chemistry.⁽¹⁴⁵⁻¹⁴⁶⁾ Their adaptable binding modes result in a large diversity of structural motifs. A lone carboxylate group can act, for instance, as a mono-dentate, bi-dentate or chelating O-donor moiety, donating electron density to a metal ion(s) to form a coordination bond. They additionally possess the ability to bridge metal ions. This

bridging functionality is observed in many 0D type products like dimers and oxo-clusters. In the latter case, this bridging mode often results in a hydrophilic inorganic “core” containing several metal ions and bridging oxygen atoms, whilst the organic components of a ligand encase and screen this nucleus. This binding manner is best observed in the aforementioned manganese coordination cluster $[\text{Mn}_{12}\text{O}_{12}(\text{MeCO}_2)_{16}(\text{H}_2\text{O})_4]$, “ Mn_{12} ”. Here, the eight outer Mn^{III} ions are peripherally bridged by sixteen acetate groups, each engaging in a *syn-syn* doubly bridging mode. Figure 1.19 illustrates a range of binding modes associated with di-carboxylate substituted organic ligands.

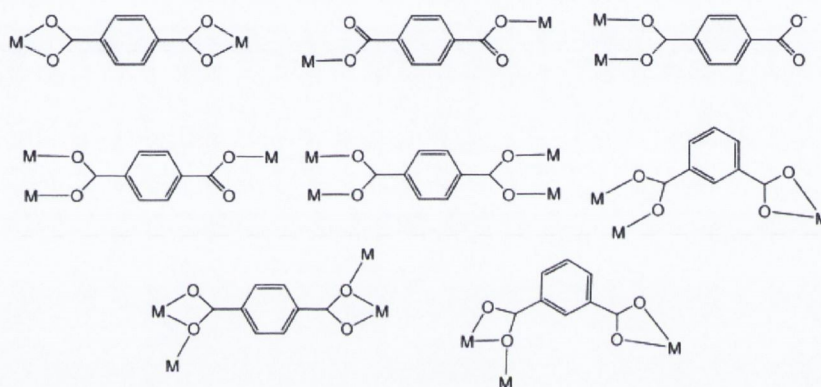


Figure 1.19: Possible coordinating, chelating and bridging conformations of both a terephthalic (1,4-substituted) acid and an isophthalic (1,3-substituted) acid ligand.⁽¹⁴⁵⁾

Furthermore, one of the more beneficial properties associated with carboxylic acids is their capacity to function as hydrogen bond donors and/or acceptors. The cumulative strength of multiple hydrogen bonds can be compared to that of a metal-ligand coordination bond. This feature provides additional directionality and allows carboxylic acids and carboxylates to be exploited for molecular recognition purposes. These intrinsic attributes are advantageously used in nature and in the fields of supramolecular chemistry and crystal engineering. Numerous review articles have been written on the subject of hydrogen bonding as an essential interaction for coordination compounds.^(16,147-150) The abundance and importance of hydrogen bonding cannot be under-rated as it is an essential interaction to all living life, only considering its widespread involvement in water and DNA.

The interaction modes of carboxylic acids are often determined by their pK_a values and the reaction conditions, and adjusting the pH levels in reaction mixtures will dictate whether a carboxylic acid is protonated, or not. This in turn determines if the acid coordinates to a metal centre, behaves as a H-bond donor or just as an acceptor. This convenience provides additional benefits to using carboxylic acid groups.

In order to achieve our objectives, and as a result of the highly advantageous traits associated with carboxylic acids, we first explore a range of aminodiacetic acid substituted ligand derivatives. Figure 1.20 shows the ligands we exploited, with 2-aminodiacetic terephthalic acid (H_4adta), 3-aminodiacetic benzoic acid (H_3adba) and 5-aminodiacetic isophthalic acid (H_4adip). These poly-dentate ligands were considered to be ideal bridging components in the generation of higher dimensional coordination compounds. These ligands not only contain rigid carboxylic group(s) affixed to the aromatic rings, but also the chelating iminodiacetic acid functionality, which consists of two flexible glycine moieties protruding from a common nitrogen atom.

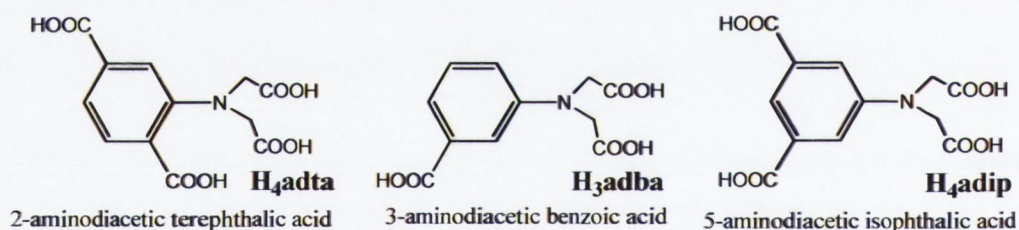


Figure 1.20: Three iminodiacetic acid substituted aromatic ligands used in the study.

In order to gain some degree of control over the assembly process, to block coordination sites and to prevent the propagation of complexes into three dimensions, we also decided to selectively utilise 2,2'-bipyridine (bpy hereafter) as an additional co-ligand. The use of ligands containing carboxylate functionalities in combination with bpy as a co-ligand has been shown to be a successful approach in the formation of 1D chain structures and networks, displaying a range of different molecular architectures.⁽¹⁴⁵⁾ The inclusion of bpy may also give rise to additional supramolecular interactions, namely π - π stacking, which can enhance the stability of complexes.⁽¹⁵¹⁻¹⁵²⁾

The domain of bpy chemistry is not simply confined to the juxtaposition of two pyridine rings. Countless functionalised bpy derivatives have been prepared, impacting on fields such as pharmaceutical chemistry, catalysis, coordination chemistry and even biological processes in nature are influenced by this ligand type. Several review papers have been dedicated to these topics, covering a range of other potential uses of bpy and its derivatives.⁽¹⁵³⁻¹⁵⁶⁾

Our exploitation of bpy (Fig. 1.21a) as a chelating and blocking agent was successful in a number of cases, and lower dimensional compounds were observed during our investigations. A range of modified bpy co-ligands, in combination with various iminodiacetic acid substituted ligands, were subsequently explored in order to generate potentially higher dimensional structures. The other employed N-containing co-ligands are shown in Figure 1.21b.

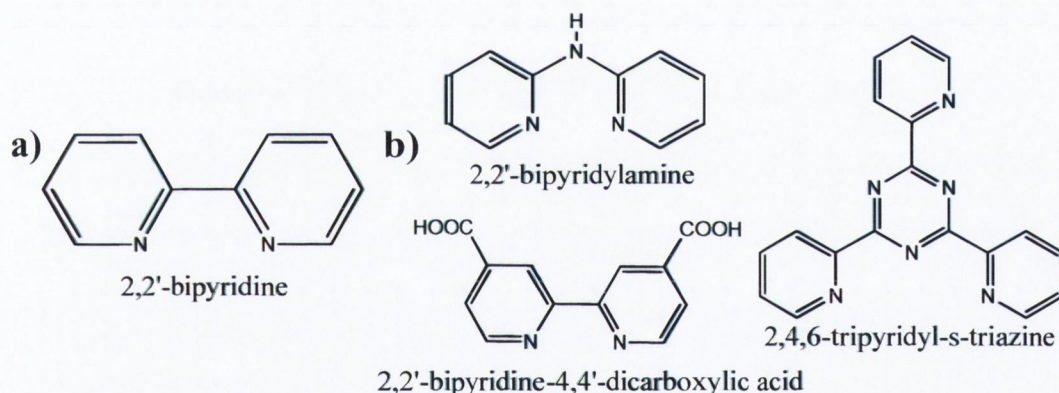


Figure 1.21: a) 2,2'-Bipyridine and b) three alternative nitrogen-donating co-ligands, used for the formation of coordination complexes.

To diversify the type of compounds obtained, other chelating functional groups were explored. The 5-amino-2-dimethyldipyridine isophthalic acid (H_2adpip) and the 3-amino-2-dimethyldipyridine benzoic acid ($Hadpba$) ligands were used (Fig. 1.22a) during the study. Both these ligands contain a chelating amino-2-dimethyldipyridine functionality and additional carboxylic acid group(s) affixed to a central aromatic ring.

Our investigations further involved the employment of extended ligands. In contrast to the previously described ligands the various chelating functionalities were

removed, with only benzoic acid moieties available for binding to metal centres. We thought that the ligands, 1,4-phenylenediamino-tetra benzoic acid (1,4-H₄datba) and 1,3-phenylenediamino-tetra benzoic acid (1,3-H₄datba), might react with transition metals to produce open-framework structures (Fig. 1.22b).

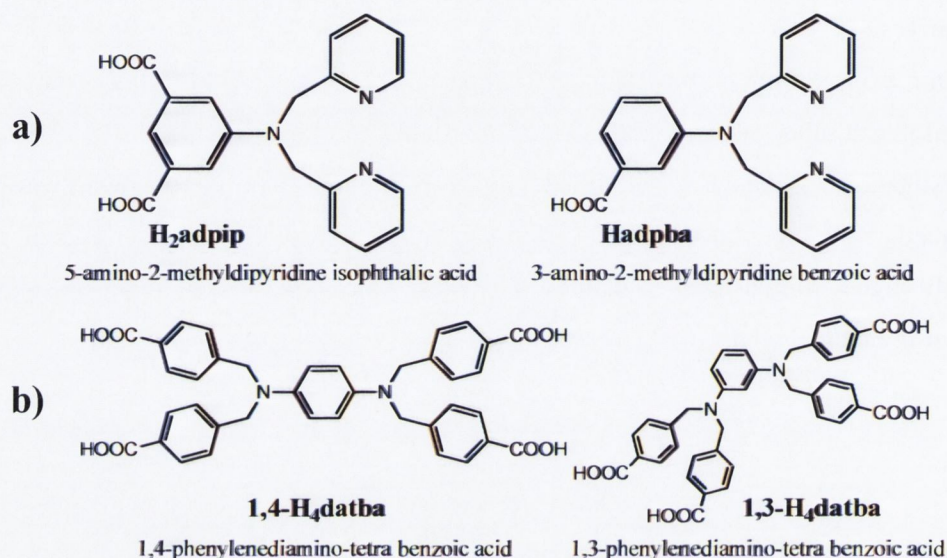
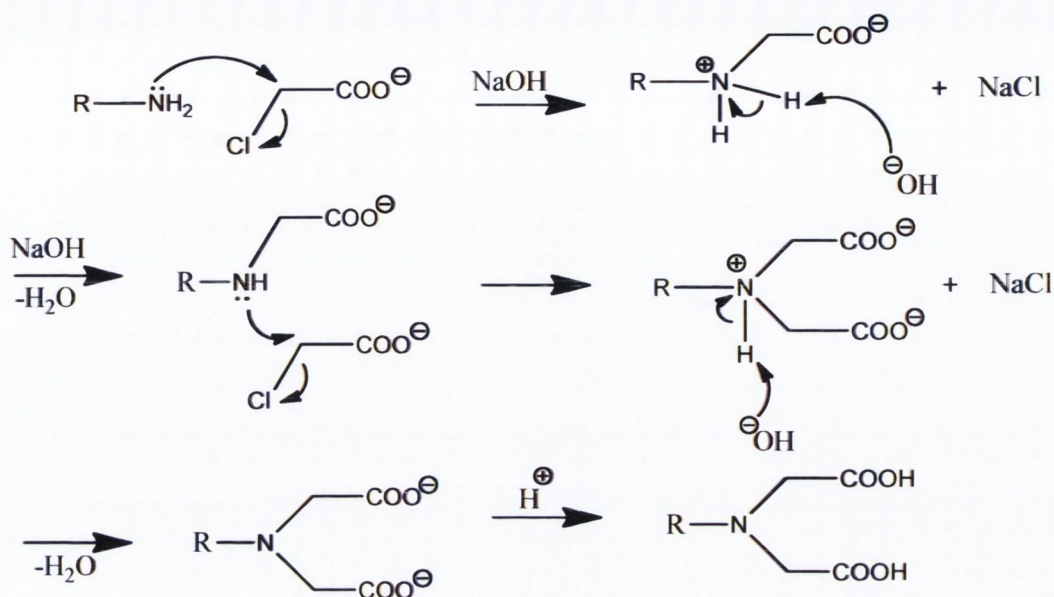


Figure 1.22: The remaining ligand-types used in this work, for the synthesis of extended networks.

1.6.2: Ligand Synthesis

Modified condensation reactions were performed to synthesise the ligands. The reactions all proceeded *via* a related mechanistic pathway (Scheme 1.1). Under basic conditions, an amine group reacts with a halogenated reactant, resulting in cationic species. Proton transfer, and concurrent salt (e.g. NaCl) formation generates a secondary amine. The process is then repeated again to yield the tertiary amine.⁽¹⁵⁷⁾ The addition of concentrated hydrochloric acid resulted in the precipitation of the desired ligand.



Scheme 1.1: Steps of a typical condensation reaction associated with the synthesis of the ligand-types used in this study. R = aliphatic or aromatic organic moieties.

1.6.3: Specific Research Aims

The main goals of this work are the synthesis of novel hybrid organic-inorganic networks or related coordination compounds using the aforementioned ligands (Figs. 1.20 and 1.22). These ligands, in combination with the wide range of transition metals available, provide ample opportunity for the formation of a diverse range of supramolecular architectures, each possessing unique and characteristic properties due to the electronic configuration of the metals and the multi-faceted abilities of each of the ligands. A particular aim was to generate structures where the bridging modes of the ligands could give rise to magnetic exchanges between spin centres. Our synthetic approaches were devised to generate molecular magnetic materials whereby the focus was directed to the synthesis and characterisation of single-chain magnets.

To increase the chances of obtaining novel coordination compounds with crystalline morphologies we applied both ambient and hydro(solvo)thermal reaction

conditions. In order to achieve the goals outlined above, we initially aspire to accomplish the following:

- a) Synthesise and characterise assorted carboxylic acid substituted ligands.
- b) Synthesise coordination networks exploiting a range of transition metal ions, in particular Fe^{II} , Mn^{II} , Ni^{II} , Co^{II} and Cu^{II} .
- c) Elucidate the structural topologies of all compounds using single crystal X-ray diffraction techniques.
- d) Characterise the physicochemical properties of the compounds (e.g. magnetic properties, phase purity, thermal stability etc.).
- e) Modify reaction conditions and ligand functionalities to generate 1D structures with interesting molecular magnetic properties.
- f) Modify reaction conditions to obtain higher dimensional compounds, with open-framework topologies, which might give rise to porosity.

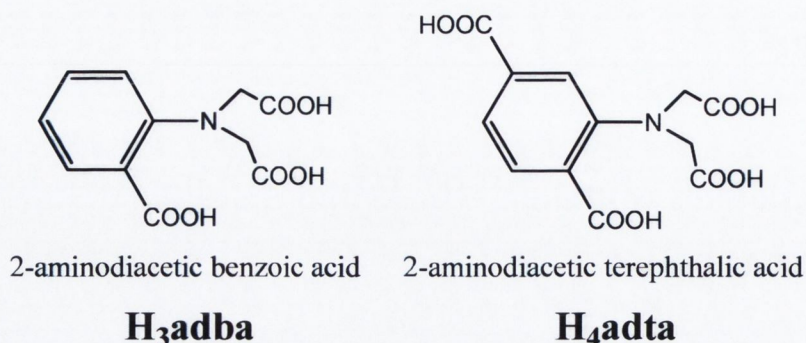
Chapter 2

2.1: Compounds containing the amino-diacetic terephthalic acid (ADTA) ligand

As has been discussed in section 1.5, the use of iminodiacetic acid derivatives has been well established to yield compounds displaying a range of interesting physiochemical properties whereby different research strands focus on molecular magnetic materials, sensory devices, porous materials, catalysis etc. Modified ligand systems that contain supplementary functionalities, such as carboxylic acid moieties are expected to give rise to the formation of new supramolecular structures that may result in the accentuation of said properties, and produce materials with improved characteristics. Our interest in generating novel polymeric molecular magnetic properties enticed us to utilise such functional groups.

The 2-amino-diacetic benzoic acid ligand has previously been shown to generate coordination compounds with application potential in the fields of magnetism and kinetics.⁽¹⁵⁸⁻¹⁶²⁾ Thus, the attempt to synthesise materials using the modified ligand 2-aminodiacetic terephthalic acid (ADTA) was seen to be of a natural progression. The ADTA ligand maintains the functionality of the ADBA complexing agent (Scheme 2.1), but is further decorated with an additional carboxylic acid group in the 4-position of the phenyl ring. This additional carboxylic acid group could be used in auxiliary coordination and/or in hydrogen bonding modes. Therefore, the potential for generating higher dimensional coordination networks has been greatly enhanced.

Our motives proved fruitful with the successful synthesis of three novel coordination compounds under ambient conditions in methanol solutions. The three compounds display certain similarities with the iminodiacetic acid group encasing the various transition metal ions in a tri-dentate fashion. However, the three compounds all present different coordination geometries, constitutions, intermolecular hydrogen bonds and cation-dipole interactions. These, in turn, generate distinctive packing arrangements.



Scheme 2.1: Exchange from the 2-aminodiacetic benzoic acid to the 2-aminodiacetic terephthalic acid.

2.1.1: Compound $\text{K}[\text{Co}^{\text{II}}(\text{Hadta})(\text{H}_2\text{O})_2] \cdot \text{MeOH}$ (1)

The compound $\text{K}[\text{Co}^{\text{II}}(\text{Hadta})(\text{H}_2\text{O})_2] \cdot \text{MeOH}$ (**1**) crystallises as red blocks after a period of about two weeks in the triclinic crystal system in the space group $P-1$. The asymmetric unit contains a cobalt(II) ion, a mono-protonated Hadta^{3-} ligand, two coordinated water molecules, a potassium counterion and a solvent methanol molecule. The coordination environment of the cobalt ion can best be described as a distorted octahedron. The metal ion has a coordination sphere composed of the tri-dentate iminodiacetic acid functionality, an O-donor from a carboxylate group from one of the terephthalic acid moieties, and is completed by two *cis* binding water molecules (Fig. 2.1a). The iminodiacetic acid functionality binds to the cobalt(II) ion in a *fac* manner as seen in Figure 2.1b. Bond lengths vary from the $\text{Co}(1)\text{--N}(1)$ bond of 2.171(3) Å, to the $\text{Co}(1)\text{--O}(1)$ bond of 2.062(3) Å and to the $\text{Co}(1)\text{--O}(3)$ bond of 2.064(2) Å. The adjacent carboxylate group on the phenyl ring binds to the $\text{Co}(1)$ centre, and is characterised by a $\text{Co}(1)\text{--O}(5)$ bond of length 2.010(2) Å. The coordinating water molecules are engaged in $\text{Co}(1)\text{--O}(9)$ and $\text{Co}(1)\text{--O}(10)$ bonds, which are 2.085(3) Å and 2.126(3) Å long, respectively. These values correspond well with typical coordination bond lengths involving $\text{Co}(\text{II})$ ions.⁽¹⁶³⁾

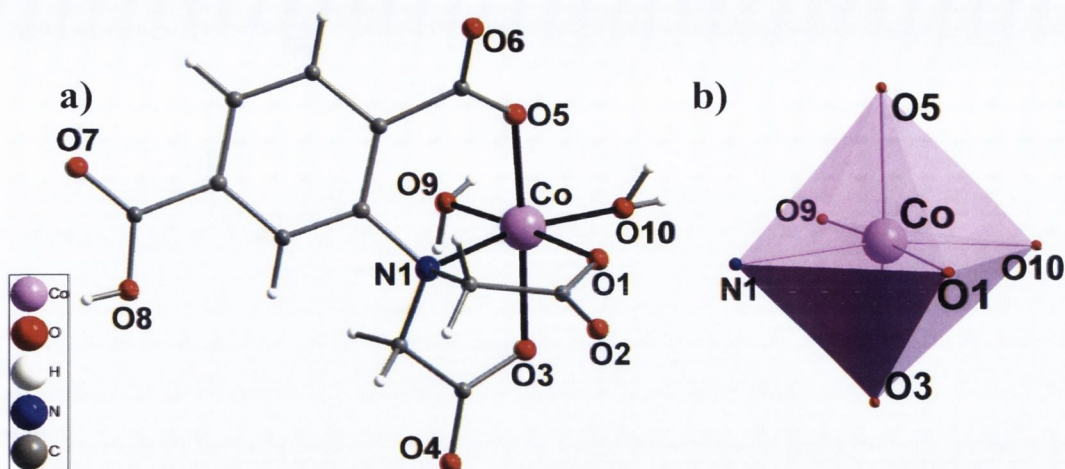


Figure 2.1: a) Illustration of the binding mode of the Hadta³⁻ ligand and the coordination environment of the Co(1) ion in compound **1** and b) polyhedral representation of the coordination environment of the cobalt ion; *fac* arrangement of the iminodiacetic acid donor atoms highlighted as a non-transparent face of the polyhedron.

Examining particular bond angles can also be used to stress the asymmetry of the coordination environment of the Co(1) ion. In the equatorial plane, as represented in Figure 2.1b, the O(1)–Co(1)–N(1) and O(10)–Co(1)–N(1) bond angles of 83.23(1)° and 170.19(1)°, respectively, are large digressions from ideal angles of 90° and 180°. Similarly for the axial positions, the O(3)–Co(1)–O(5) bond angle of 170.47(1)° is a significant deviation from model behaviour. Furthermore, the O(3)–Co(1)–N(1) bond angle of 81.64(1)° demonstrates additional distortion from an ideal octahedron. The remaining bond angles can be viewed in Table 2.1.

Table 2.1: Bond angles for the Co(1) ion in compound **1**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)
O(1)–Co(1)–O(3)	85.16(1)	O(1)–Co(1)–O(5)	88.98(1)
O(1)–Co(1)–O(9)	176.45(1)	O(1)–Co(1)–O(10)	92.05(1)
O(1)–Co(1)–N(1)	83.23(1)	O(3)–Co(1)–O(5)	170.47(1)
O(3)–Co(1)–O(9)	91.30(1)	O(3)–Co(1)–O(10)	89.42(1)
O(3)–Co(1)–N(1)	81.64(1)	O(5)–Co(1)–O(9)	94.55(1)
O(5)–Co(1)–O(10)	98.30(1)	O(5)–Co(1)–N(1)	90.23(1)
O(9)–Co(1)–O(10)	87.80(1)	O(9)–Co(1)–N(1)	96.38(1)
O(10)–Co(1)–N(1)	170.19(1)		

There is no additional coordination bonding involving the cobalt(II) ion, however, the compound can be further characterised by taking into account some of the supramolecular interactions. Of particular importance are the hydrogen bonds. Two of these H-bonds and their symmetry-equivalents generate a H-bonded sheet that extends parallel to the crystallographic *ab*-plane. These sheets are further linked in the *c*-direction through additional H-bonds. There are also a number of potassium-dipole interactions between the K^+ counterions and carboxylate atoms deriving from the $Hadta^{3-}$ ligands, and these result in similar sheets to those involving the H-bonds. To describe the structure in more detail, these respective supramolecular interactions will be discussed progressively.

Commencing with the H-bonding, the protonated carboxylic acid in the 4-position of the $Hadta^{3-}$ ligand is involved in a hydrogen bond with the solvent methanol molecule (Fig. 2.2). The distance between the O(8) and O(11) atoms is 2.588(2) Å.

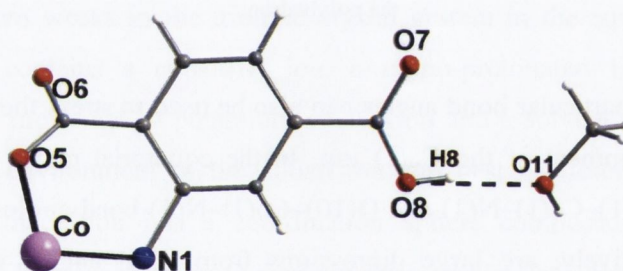


Figure 2.2: The hydrogen bonding (dashed bond) between the protonated carboxylic acid functionality of the ligand and the solvent methanol molecule.

There are also supplementary hydrogen bonds involving the coordinating water molecules. Both of these H_2O molecules engage in H-bonds to adjacent non-binding carboxylate oxygen atoms. The O(9) atom has two hydrogen bonds associated with it, and are shown in Figure 2.3a. Firstly, there is a H-bond with an O–O distance of 2.740(2) Å between the water molecule and an adjacent iminodiacetic acid oxygen atom O(4"). The second H-bond involves a neighbouring terephthalic acid moiety, and the observed O(9)–O(6') H-bond is 2.712(2) Å long. Figure 2.3b illustrates these combined interactions and the resultant H-bonded layer with brick wall topology that extends parallel to crystallographic *ab*-plane.

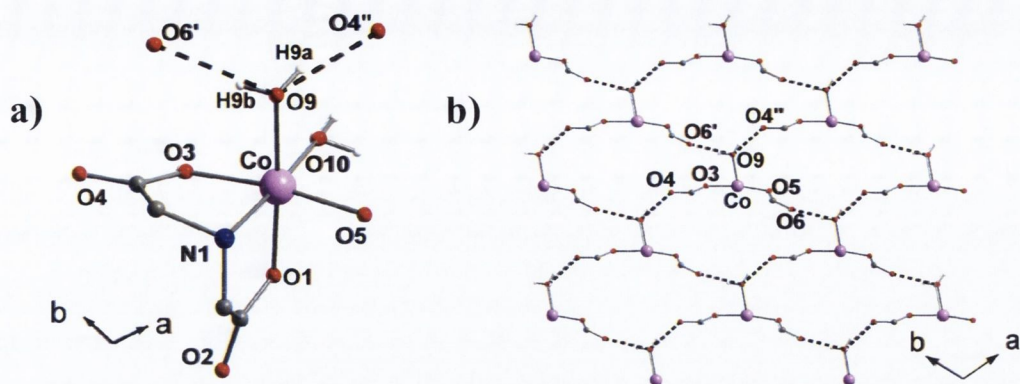


Figure 2.3: a) Two-fold hydrogen bonding interactions (dashed bonds) between the O(9) atom of the coordinating water molecule and adjoining carboxylate oxygen atoms and b) the expanded H-bonded array which extends along the crystallographic *ab*-plane. Majority of the ADTA ligand and non-relevant hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

The O(10) atom of the second H₂O molecule forms a solitary H-bond of length 2.745(3) Å with an adjacent iminodiacetic acid oxygen atom (O(2''')). This H-bond links two mononuclear complexes into di-nuclear sub-units in the crystallographic *c*-direction. These combined interactions lead to the assemblies shown in Figures 2.4a and 2.4b whereby two discrete H-bonded layers are connected into a bi-layer.

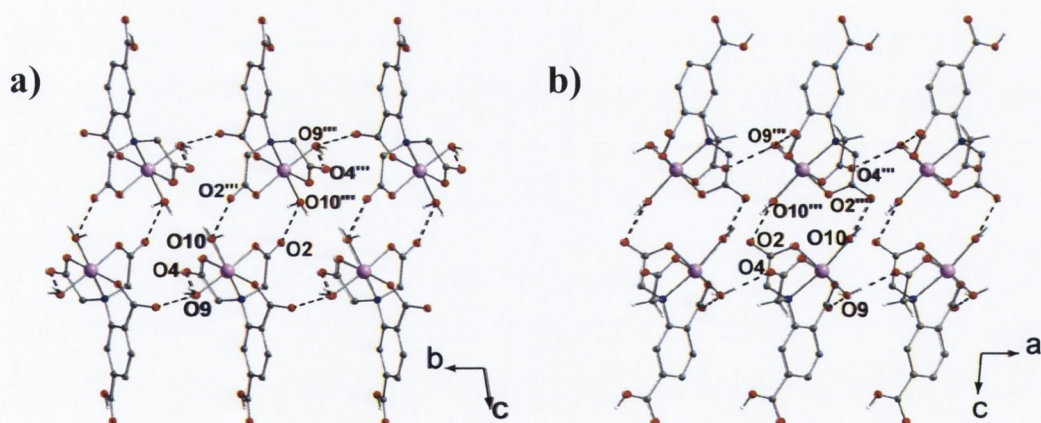


Figure 2.4: Hydrogen bonds (dashed bonds) associated with O(9) and O(10) of the coordination water molecules yielding H-bonded bi-layer arrangements, with a) a view in the direction of the crystallographic *a*-axis and b) a view in the direction of the crystallographic *b*-axes. Non-relevant hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

In addition to the H-bonds, compound **1** is further characterised by a variety of interactions between the K^+ counterions and the coordination complexes. The potassium ions are situated between the separate H-bonded sheets (Figs. 2.4a and 2.4b), and yield auxiliary connectivity between mono-nuclear complexes. Figure 2.5 highlights the association of the K^+ ion with various carboxylate atoms, deriving from three separate Hadta³⁻ ligands. Bond distances for these interactions range from the O(1)–K(1) bond of 2.790(2) Å to the O(5)–K(1) bond of 2.818(3) Å. Furthermore, the corresponding distances for the O(2')–K(1) and O(3'')–K(1) interactions are 2.691(1) Å and 2.692(3) Å, respectively. These four individual interactions and their symmetry-equivalent interactions expand the structure parallel to the crystallographic *ab*-plane.

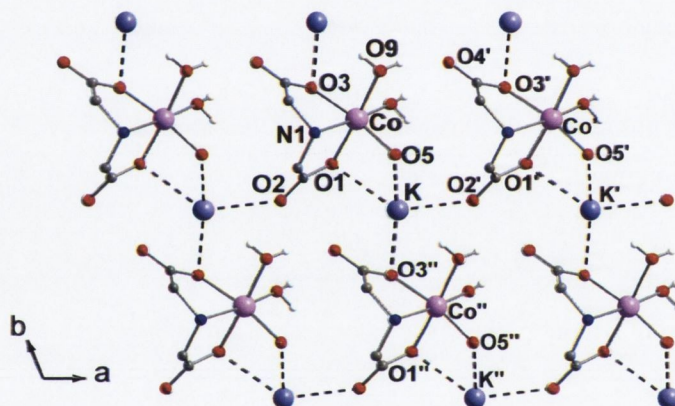


Figure 2.5: Interactions between the potassium counterions and the coordination complexes in **1** (dashed bonds) generating a 2D layer that expands parallel to the crystallographic *ab*-plane. Majority of the ADTA ligands are removed for clarity. (Prime refers to symmetry-generated atoms.)

The distorted binding environment of the symmetry independent K^+ counterion is completed by O(1''') and O(3''') atoms, which originate from an alternative Hadta³⁻ ligand. The O(1''')–K(1) and O(3''')–K(1) interactions have bond lengths of 2.790(3) Å and 2.995(3) Å, respectively. The involved O-donors, together with symmetry-equivalents, link the structure in the crystallographic *c*-direction resulting in distinctive doubly-bridged $\{K-(\mu-O(1))_2-K\}$ sub-units (Fig. 2.6). Inversion centres are located at the centre of each of these sub-units. These symmetry operations generate a neutral layer motif that encloses the potassium counterions with the H-bonded bi-layer array.

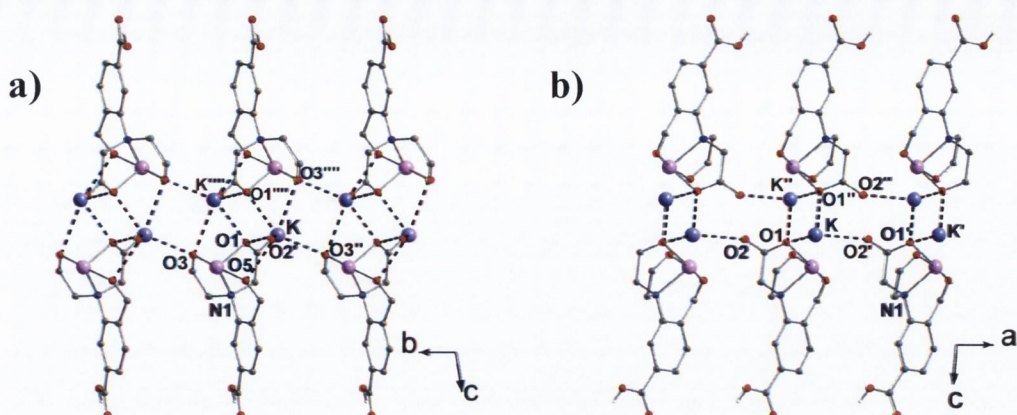


Figure 2.6: The neutral layer motif in **1**, viewed along the crystallographic a) *a*-axis and b) *b*-axis. Hydrogen atoms attached to C atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

These neutral layers proceed to stack in the *c*-direction whereby the aromatic moieties of the organic ligands and solvent molecules interdigitate. The overall structure is depicted in Figure 2.7.

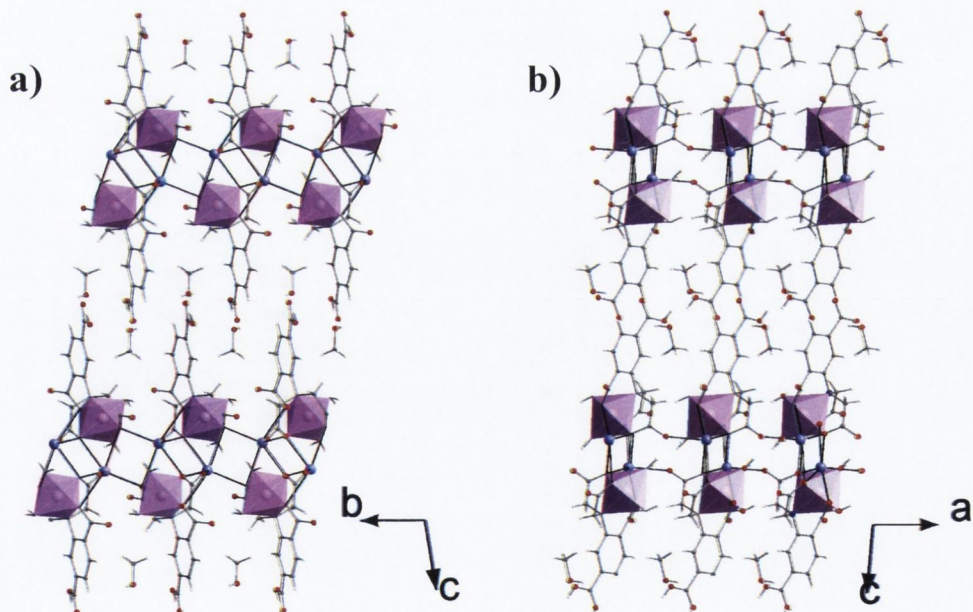


Figure 2.7: The overall network arrangement of compound **1**, viewed in the direction of the crystallographic a) *a*-axis and b) *b*-axis illustrating the alternate stacking of layers. Cobalt coordination environments are represented as purple polyhedra.

2.1.2: Compound $\text{K}[\text{Ni}^{\text{II}}(\text{Hadta})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (2)

Following on from the successful structural elucidation of the cobalt(II) compound, a similar nickel compound was synthesised in a comparable fashion to compound 1. The compound $\text{K}[\text{Ni}^{\text{II}}(\text{Hadta})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (2) crystallises as green plates, after a period of about ten days, in a monoclinic crystal system in the space group of $C 2/c$. The asymmetric unit contains a nickel(II) ion, a mono-protonated Hadta³⁻ ligand, two coordinated water molecules, a potassium counterion and a solvent water molecule. The coordination environment of the nickel ion can best be described as that of a distorted octahedron. Figure 2.8a illustrates the coordination environment of Ni(1), composed of the iminodiacetic acid functionality, an O-donor atom from one of the terephthalic acid moieties, and two *cis* binding water molecules. The iminodiacetic acid group binds to the nickel ion in a *fac* manner (Fig. 2.8b), displaying characteristic Ni(II) ion bond lengths of 2.006(1) Å, 2.031(1) Å and 2.105(1) Å for the Ni(1)–O(1), Ni(1)–O(3) and Ni(1)–N(1) bonds, respectively.⁽¹⁶³⁾ The coordinating terephthalic acid group binds with a Ni(1)–O(5) bond length of 2.003(1) Å, and the bound H₂O molecules have bond lengths of 2.053(1) Å and 2.047(1) Å for Ni(1)–O(9) and Ni(1)–O(10), respectively.

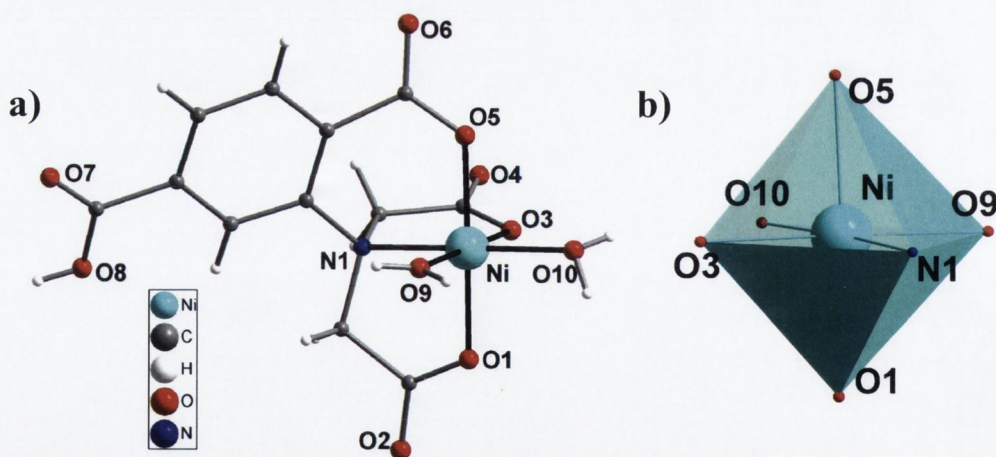


Figure 2.8: a) Depiction of the coordinating mode of the Hadta³⁻ ligand and the Ni(1) environment within compound 2 and b) the polyhedral representation of the coordination environment of the nickel ion with the iminodiacetic acid donor atoms displaying a *fac* arrangement shown as a non-transparent face of the polyhedra.

Ni(1) displays a slightly distorted octahedral coordination geometry. Considering the axially positioned atoms, as indicated in Figure 2.8b, the O(1)–Ni(1)–O(5) bond angle of 172.98(1)° reveals a large deviation from an ideal octahedral angle of 180°. In the equatorial plane, the O(3)–Ni(1)–N(1) bond angle of 84.11(1)°, also displays divergence from an ideal angle of 90°. The remaining bond angles can be examined in Table 2.2.

Table 2.2: Bond angles for the Ni(1) ion in compound **2**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)
O(1)–Ni(1)–O(3)	87.17(1)	O(1)–Ni(1)–O(5)	172.98(1)
O(1)–Ni(1)–O(9)	91.70(1)	O(1)–Ni(1)–O(10)	93.04(1)
O(1)–Ni(1)–N(1)	85.34(1)	O(3)–Ni(1)–O(5)	86.63(1)
O(3)–Ni(1)–O(9)	178.12(1)	O(3)–Ni(1)–O(10)	91.53(1)
O(3)–Ni(1)–N(1)	84.11(1)	O(5)–Ni(1)–O(9)	94.40(1)
O(5)–Ni(1)–O(10)	90.42(1)	O(5)–Ni(1)–N(1)	90.74(1)
O(9)–Ni(1)–O(10)	90.04(1)	O(9)–Ni(1)–N(1)	94.30(1)
O(10)–Ni(1)–N(1)	175.41(1)		

Compound **2** has no further coordination bonding associated with it, however it does possess an assortment of supramolecular interactions. Similar to **1**, the complex is negatively charged and requires a K⁺ counterion for charge neutrality. This potassium ion again engages in a number of interactions with oxygen atoms of both the ligand, and water molecules. These combined interactions involving symmetry-equivalents, result in neutral 2D sheets which extend parallel to the crystallographic *bc*-plane. These sheets are then further connected *via* hydrogen bonding in the direction of the crystallographic *a*-axis resulting in intricate 3D arrays. To simplify matters, the individual supramolecular interactions will be progressively introduced and discussed in the following paragraphs.

Considering the counterion-dipole contacts, there is a mutual interaction between a carboxylate group from the iminodiacetic acid moiety and a K⁺ ion with bond distances of 2.886(3) Å and 2.838(1) Å for the O(3)–K(1) and O(4)–K(1) bonds, respectively. As a result of symmetry-generated potassium and oxygen atoms, a doubly-bridged {K–O(4)} rectangle is generated (Fig. 2.9) with a centre of inversion located in the middle of this rectangle. The O(4)–K(1') interaction is characterised by a bond length of 2.763(1) Å. These combined interactions result in the connection of two mono-nuclear complexes, yielding a di-nuclear structural motif parallel to the crystallographic *ac*-plane.

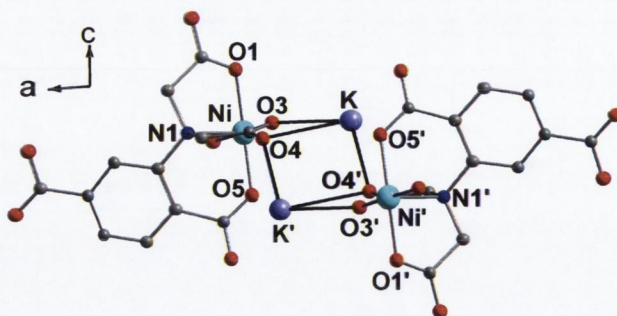


Figure 2.9: Linkage of two Ni complexes *via* counterion-carboxylate interactions, displayed as a plan view in the crystallographic *ac*-plane. All hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

The second carboxylate group of the iminodiacetic acid is also involved in K^+ –O dipole interactions. Only one carboxylate oxygen atom partakes in the interactions forming a O(1)–K(1) bond of length 2.746(3) Å. This bond links the aforementioned dinuclear assembly in a repetitious manner along the crystallographic *c*-axis yielding a sheet, as shown in Figure 2.10.

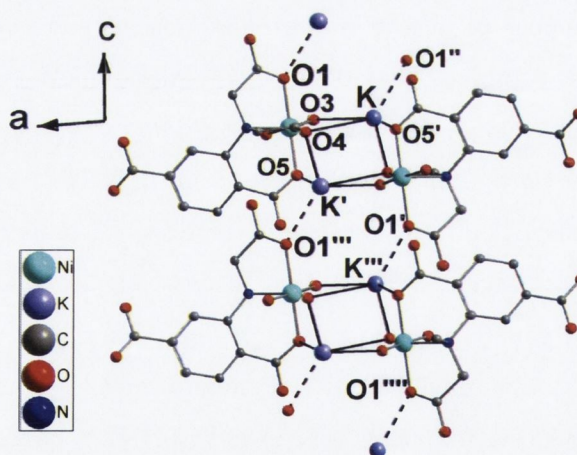


Figure 2.10: Counterion interactions (dashed bonds) involving potassium ions and the coordinated oxygen atom O(1). All hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

Figure 2.10 also shows that O(5) interacts with K^+ ions to give a O(5)–K(1) contact of 2.907(5) Å. Both oxygen atoms O(1) and O(5), that coordinate to the central

Ni ion in *trans* positions, therefore interact with potassium ions. These interactions modes can be seen in Figure 2.11a. Upon closer inspection, one can infer that the O(5)–K(1) interactions take place almost along the crystallographic *b*-axis, whereas the O(1)–K(1) interactions occur approximately in the crystallographic *c*-direction. As a result of these two, and symmetry-related, interactions, a layering of sheets occurs (Fig. 2.11b).

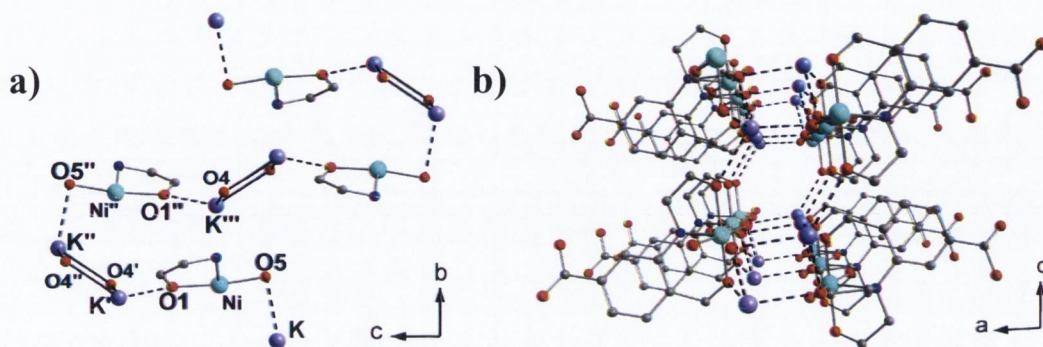


Figure 2.11: a) Expansion of the structure parallel to the crystallographic *bc*-plane due to the interactions (dashed bonds) between K⁺ ions and carboxylate O-donors O(1) and O(5) and b) the resulting 2D layer motifs in **2**. All hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

The distorted 6-coordinate binding environment of the K⁺ ion is completed by O(11) of a solvent water molecule, which is characterised by a O(11)–K(1) bond distance of 2.834(3) Å. This O(11) atom does not engage in any further bridging interactions.

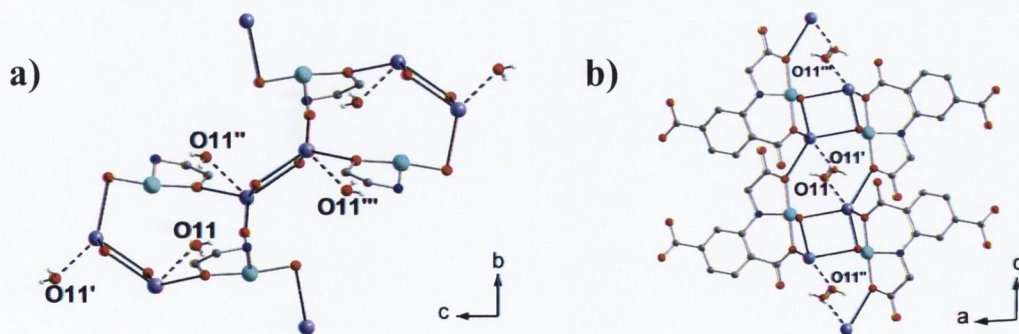


Figure 2.12: Interactions between O(11) of a solvent water molecule and the K(1) ions (dashed bonds), viewed in the direction of the crystallographic a) *a*-axis and b) the *b*-axis. (Prime refers to symmetry-generated atoms.)

The coordinating water molecule, O(9), has been shown to H-bond to a neighbouring oxygen atom O(7''), and this resulted in the bi-layering of ADTA ligands. The O(9) atom also engages in a second H-bond with a carboxylate (O(4''')) atom of an adjacent ligand, characterised by a O(9)–O(4''') distance of 2.642(1) Å. This interaction links the discussed structural motifs in the crystallographic *b*-direction. This two-fold H-bond donor behaviour consequently generates a recurrence of the bi-layered motifs. Figure 2.14 demonstrates this extension in the [010]-direction, which coincides with the symmetry operation of a 2_1 screw axis, which likewise runs in the crystallographic *b*-axis.

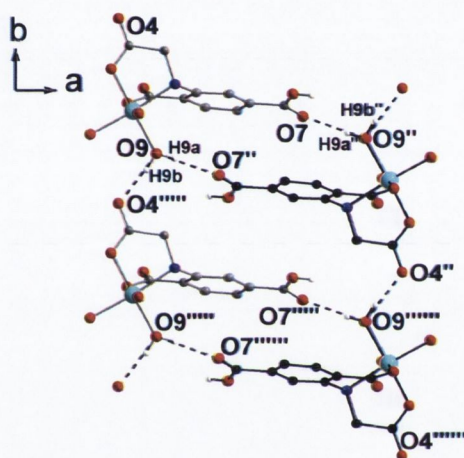


Figure 2.14: The dual hydrogen bonding interactions associated with O(9) of a coordinating water molecule, generating a continual H-bonded network that extends along the crystallographic *b*-axis. Non-relevant hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

The second coordinating water molecule (O(10)) is also involved in a two-fold hydrogen bonding assembly. In one mode, it H-bonds with a binding carboxylate oxygen atom of an adjoining complex, and this O(10)–O(5') bond is 2.953(9) Å long. It also H-bonds with O(11'') of the solvent H₂O molecule, yielding an O–O distance of 2.645(4) Å (Fig. 2.15a). This solvent water molecule further partakes in a pair of H-bonds with additional oxygen atoms of neighbouring Hadta³⁻ ligands (Fig. 2.15b), yielding bond lengths of 2.817(2) Å and 2.823(4) Å for the O(11'')–O(6''') and O(11'')–O(3''') bonds, respectively. This creates another continual H-bond array that extends the network structure in the crystallographic *c*-axis.

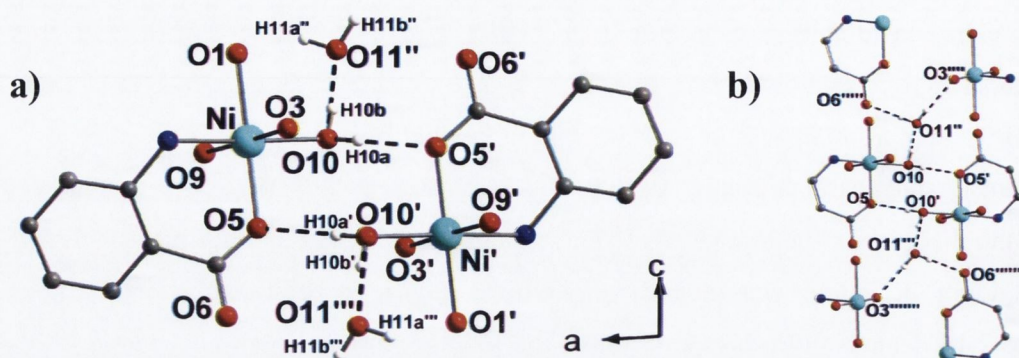


Figure 2.15: a) The H-bonding (dashed bonds) involving the second coordinating water molecule (O(10)), and b) subsequent H-bonds associated with O(11) of the lattice water molecule. a) and b) viewed in the direction of the crystallographic *b*-axis. Majority of the ADTA ligand and non-relevant hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

In summary, the juxtaposition of these supramolecular interactions leads to the intricate layering of the 2D sheets and these layers assemble *via* hydrogen bonds to generate the 3D network shown in Figure 2.16.

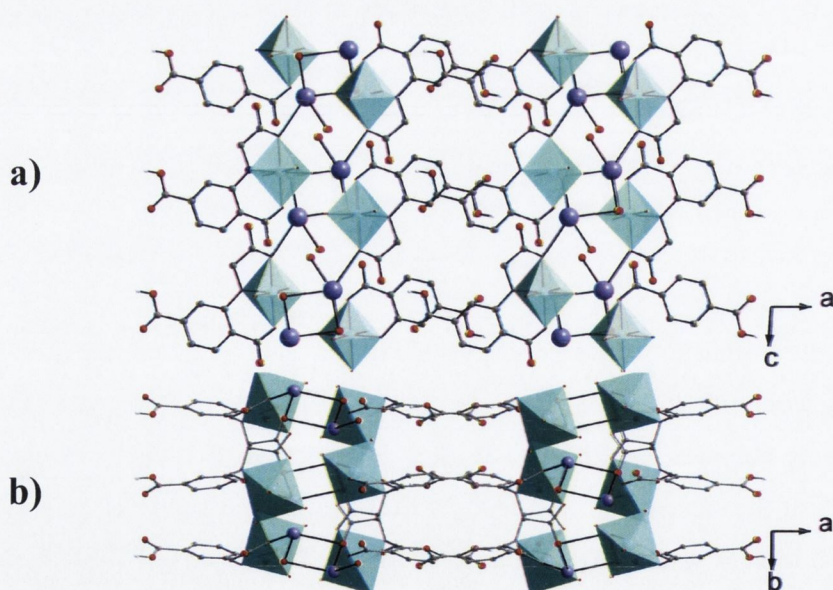


Figure 2.16: Overall network array in **2** viewed along the crystallographic a) *b*-axis and b) the *c*-axis, linking the neutral 2D sheets into a 3D array. Ni(1) coordination environments are shown as cyan coloured polyhedra.

2.1.3: Compound $\text{K}[\text{Cu}_{1.5}^{\text{II}}(\text{adta})(\text{H}_2\text{O})_{1.5}]\cdot\text{H}_2\text{O}$ (**3**)

The final compound to be discussed in this class of compounds is a copper variety, $\text{K}[\text{Cu}_{1.5}^{\text{II}}(\text{adta})(\text{H}_2\text{O})_{1.5}]\cdot\text{H}_2\text{O}$ (**3**), which was synthesised analogously to the previous examples. The compound crystallises as dark green hexagons after about two weeks in the monoclinic crystal system in the space group of $P 2_1/c$. The asymmetric unit contains both a fully and a half occupied copper(II) ion, a deprotonated adta⁴⁻ ligand, a fully and a half occupied coordination water molecule, a potassium counterion and two half occupied solvent water molecules. Contrasting the mono-nuclear motifs of **1** and **2**, compound **3** consists of 1D coordination polymers that extend along the crystallographic *a*-axis, whereby the iminodiacetic acid functionalities link the two symmetry-independent copper ions. The coordination environment of the Cu(1) ion can best be described as a highly distorted square pyramid. Figure 2.17a illustrates the coordination arrangement of Cu(1), comprised of the iminodiacetic acid functionality, a terephthalic acid group O-donor and a binding water molecule. The iminodiacetic acid moiety chelates to Cu(1) in a *fac* manner (Fig. 2.17b) resulting in bond lengths of 1.822(5) Å and 2.154(5) Å for the Cu(1)–O(1) and Cu(1)–O(3) bonds, respectively, whilst the Cu(1)–N(1) bond is 2.209(6) Å long. These bond lengths agree with literature values for Cu(II) ions.⁽¹⁶³⁾ The O-donor atom of the adjacent carboxylate group, O(5), has a bond of length 1.875(5) Å. Lastly, the coordinating water molecule engages in a Cu(1)–O(9) bond which is 2.325(7) Å long.

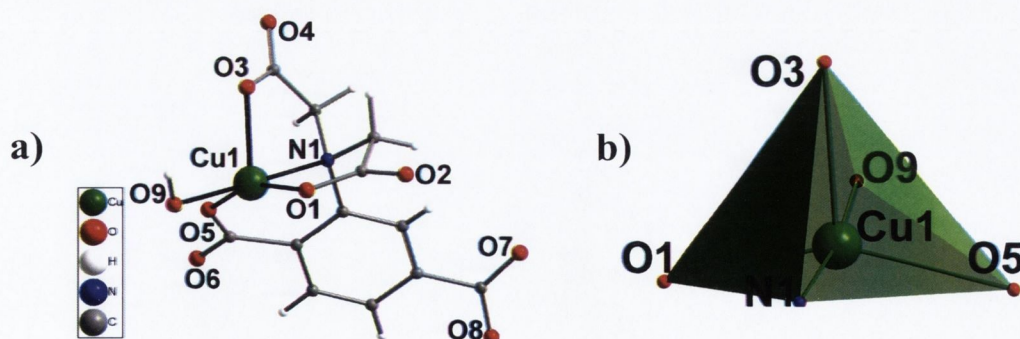


Figure 2.17: a) Coordination environment of Cu(1) in **3**, and b) polyhedral representation of the binding environment of Cu(1), with the iminodiacetic acid group displaying a *fac* arrangement highlighted as a non-transparent face of the polyhedron.

An examination of the bond angles within the coordination sphere of Cu(1) reflects the apparent asymmetry. Within the basal plane, as shown in Figure 2.17b, the O(1)–Cu(1)–O(5) bond angle of $154.50(2)^\circ$ is a significant deviation from an ideal angle of 180° . Furthermore, the O(3)–Cu(1)–N(1) bond angle of $75.15(2)^\circ$ reveals an additional distortion from an ideal angle of 90° . Table 2.3 lists the remaining distorted bond angles.

Table 2.3: Bond angles for the Cu(1) ion in compound **3**.

Atoms	Bond angle ($^\circ$)	Atoms	Bond angle ($^\circ$)
O(1)–Cu(1)–O(3)	100.86(2)	O(1)–Cu(1)–O(5)	154.50(2)
O(1)–Cu(1)–O(9)	90.31(2)	O(1)–Cu(1)–N(1)	85.27(2)
O(3)–Cu(1)–O(5)	102.03(2)	O(3)–Cu(1)–O(9)	103.69(2)
O(3)–Cu(1)–N(1)	75.15(2)	O(5)–Cu(1)–O(9)	95.05(2)
O(5)–Cu(1)–N(1)	89.85(2)	O(9)–Cu(1)–N(1)	175.10(2)

The two symmetrically independent Cu(II) ions are linked *via* the carboxylate groups of the iminodiacetic acid functionalities of the adta⁴⁻ ligands, forming a 1D coordination polymer that extends in the crystallographic *a*-direction (Figure 2.18a). The coordination environment of the Cu(2) ion is best described as a distorted octahedron. O-donor atoms from four independent iminodiacetic acid functionalities bind in the equatorial plane, and two water molecules are situated in the apical positions. The Cu(2)–O(2) and Cu(2)–O(4'') bonds are of length 1.953(6) Å and 1.875(5) Å, respectively. The water molecules result in a tetragonal distortion of the octahedral geometry and display elongated Cu(2)–O(10) bonds of length 2.568(3) Å (Fig. 2.18b). This observed distortion is in agreement with Jahn-Teller theorem typical for d⁹ electron systems.⁽¹⁶⁴⁾

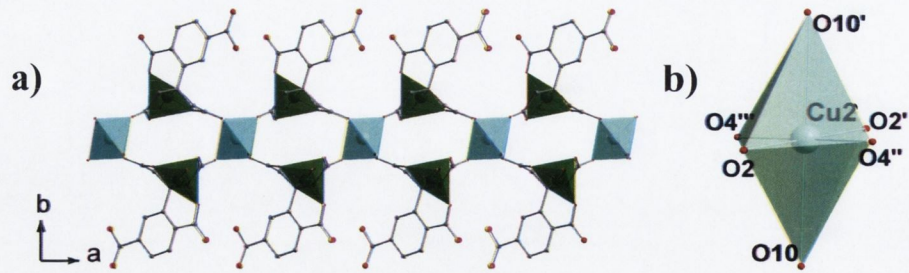


Figure 2.18: a) The 1D double chain motif in **1** that extends in the crystallographic *a*-direction and b) polyhedral representation of the tetragonally distorted octahedral coordination environment of the Cu(2) ion. All hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

Table 2.4 displays all the relevant bond angles associated with the Cu(2) ion. In the equatorial plane, as depicted in Figure 2.18b, the O(2)–Cu(2)–O(4'') bond angle of 79.13(2)° is one of the more significant deviations from ideal octahedral behaviour.

Table 2.4: Bond angles for the Cu(2) ion in compound **3**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)
O(2)–Cu(2)–O(2')	180.00(1)	O(2)–Cu(2)–O(4'')	79.13(1)
O(2)–Cu(2)–O(4''')	100.87(1)	O(2)–Cu(2)–O(10)	78.75(1)
O(2)–Cu(2)–O(10')	101.25(1)	O(2')–Cu(2)–O(4'')	100.87(1)
O(2')–Cu(2)–O(4''')	79.13(1)	O(2')–Cu(2)–O(10)	101.25(1)
O(2')–Cu(2)–O(10')	78.75(1)	O(4'')–Cu(2)–O(4''')	180.00(1)
O(4'')–Cu(2)–O(10)	85.63(1)	O(4'')–Cu(2)–O(10')	94.37(1)
O(4''')–Cu(2)–O(10)	94.37(1)	O(4''')–Cu(2)–O(10')	85.63(1)
O(10)–Cu(2)–O(10')	180.00(1)		

Whilst the 1D double-bridged chain structure runs in the crystallographic *a*-direction, there are still the supramolecular interactions to be evaluated that further link these chains. Commencing with the potassium-dipole interactions, there is a bridging interaction between the carboxylate groups of the iminodiacetic acid functionality, the potassium counterion and a coordination H₂O molecule of an adjoining unit. Figure 2.19a reveals these interactions with bond distances of 3.069(2) Å, 2.947(1) Å and 2.819(2) Å for the O(4)–K(1), O(2')–K(1) and O(9'')–K(1) bonds, respectively. Figure 2.19b depicts the resultant linking of the distinct chains along the crystallographic *ac*-plane.

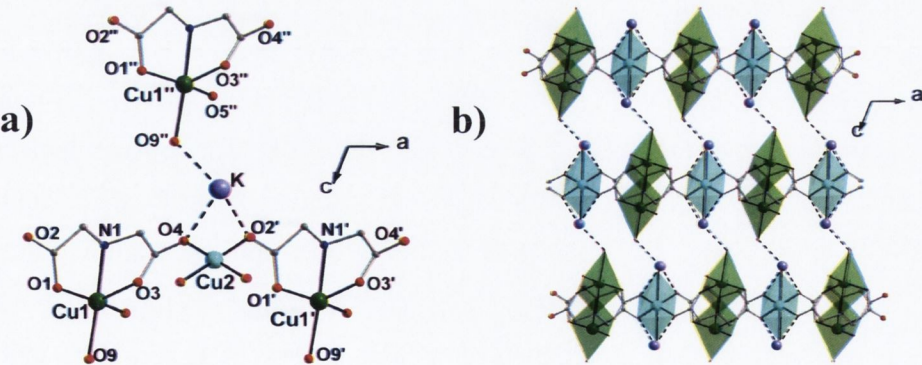
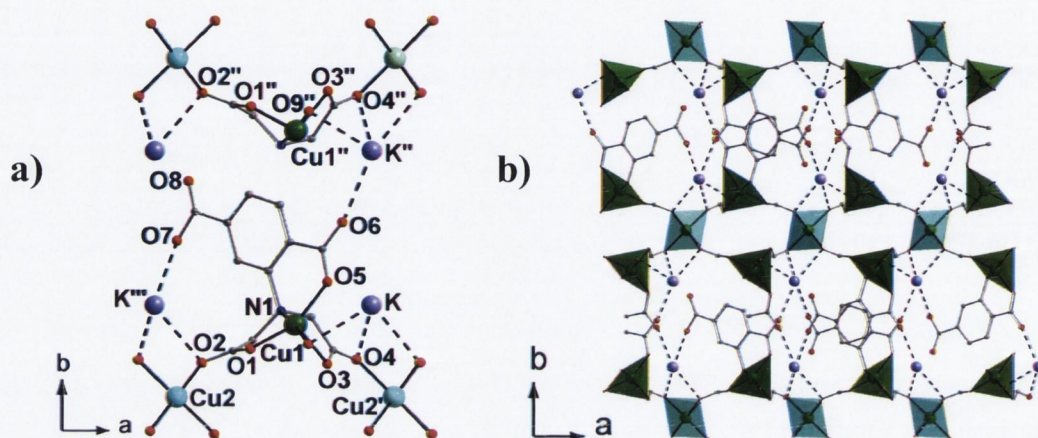


Figure 2.19: a) Bridging interactions (dash bonds) between two iminodiacetic acid carboxylate O-donors, O(9'') of an adjacent water molecule and K(1), b) the array generated from these combined interactions.

Majority of the ADTA ligand is removed for clarity. (Prime refers to symmetry-generated atoms.)

There are supplementary interactions involving the acid moieties in the 1 and 4-positions of the aromatic ring (Fig. 2.20a). The O(7) atom merely binds to the K(1) ion with a bond distance of 3.001(4) Å. The other carboxylic acid functionality connects adjacent chains in the crystallographic *b*-direction, with a O(6)–K(1'') interaction distance of 2.829(1) Å. This latter mediation results in the intricate array depicted in Figure 2.20b.



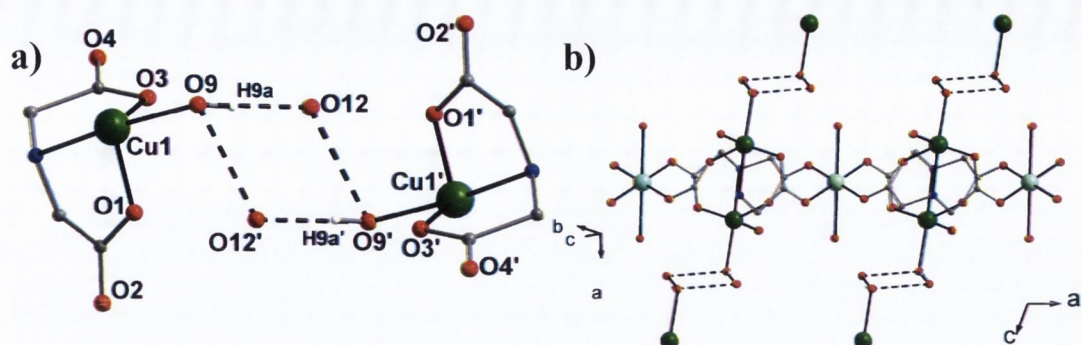


Figure 2.21: a) Hydrogen bonding (dash bonds) involving O(9) of the coordinating water molecule, and b) the resultant H-bonded motif that connects separate coordination polymers in the [001]-direction. Majority of the ADTA ligand is removed for clarity. (Prime refers to symmetry-generated atoms.)

To summarise, compound **3** contains 1D coordination polymers which are further linked *via* potassium-oxygen interactions yielding a 3D network structure whereby the aromatic ring systems of the adta^{4-} ligands align between the connected chains, as shown in Figure 2.22.

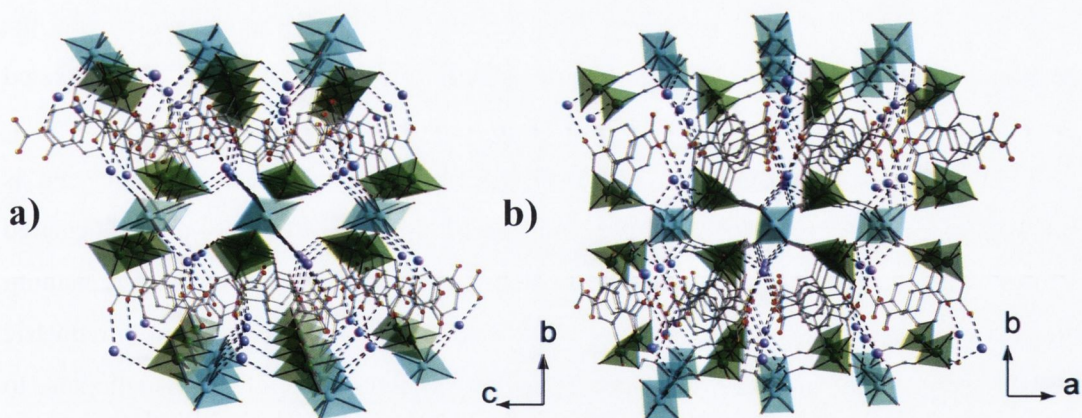


Figure 2.22: The 3D structural motif of compound **3** demonstrating the linking of the 1D chains *via* counterion mediations (dash bonds), viewed in the crystallographic a) *a*-axis and b) the *c*-axis.

2.2: Thermal decomposition of compounds 1, 2 and 3.

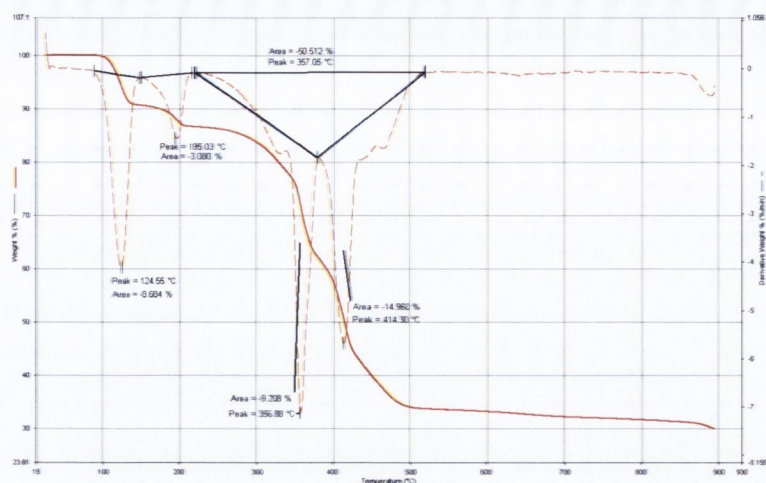
To study the thermal stability of these three novel compounds, thermogravimetric analyses (TGA) were performed on **1**, **2** and **3**. At a ramp rate of $10\text{ }^{\circ}\text{C min}^{-1}$, the crystalline samples were heated to $\sim 900\text{ }^{\circ}\text{C}$ under an air atmosphere. Figure 2.23 illustrates the TGA curves for the three compounds. All three compounds, in general, show similar patterns of decomposition. The decomposition is characterised by the initial loss of solvent molecules, followed by the loss of coordination water molecules and eventually the organic ligands undergoes oxidative degradation. The compositions of the remaining oxide residues were not further analysed.

The composition of **1** remained unchanged until approximately $110\text{ }^{\circ}\text{C}$ whereby the coordinating water molecules are removed and a weight loss of 8.68% (calculated 8.41%) is observed. It appears that the volatile methanol solvent molecule contained in **1** was already lost prior to the measurement. A loss of 3.08 wt% is observed at *ca.* $190\text{ }^{\circ}\text{C}$. The gradual oxidative degradation of the organic ligand proceeds from $200\text{ }^{\circ}\text{C}$, with three successive thermogravimetric events, centred at 320, 360 and $415\text{ }^{\circ}\text{C}$. The combined events equate to a total weight loss 50.51%, this can be accounted for with the combustion of all carbon, hydrogen and nitrogen atoms of the ligand (calculated 47.07%), with the remaining residue being a range unknown of metal oxides.

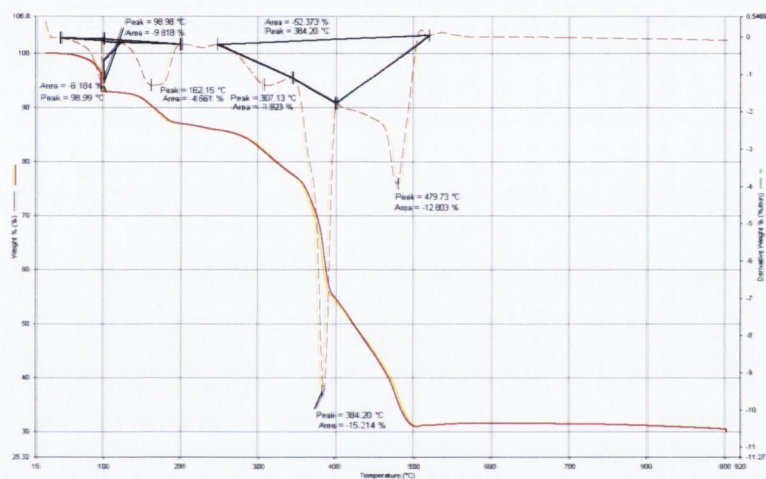
For **2**, a total weight loss of 12.50% occurs between 60 and $190\text{ }^{\circ}\text{C}$ and is attributable to the loss of both lattice and coordinating H_2O molecules (calculated 12.12%). The structure of **2** subsequently collapses with the oxidation of the remaining organic constituents commencing at $\sim 200\text{ }^{\circ}\text{C}$, in three successive thermogravimetric steps, centred at 310, 385 and $480\text{ }^{\circ}\text{C}$. The combined weight loss amounts to approximately 50%. This can be assigned to the combustion of all the carbon, nitrogen and hydrogen atoms to the ligand, which is calculated at just over 47%.

Compound **3** remains stable until about $120\text{ }^{\circ}\text{C}$ where coordinating water molecules are removed gradually, with a weight loss of approximately 7%, calculated 5.93%. After $210\text{ }^{\circ}\text{C}$ the compound collapses with the oxidation of the ligand. A weight loss of nearly 36% was observed, and corresponds with the combustion of all the C, H and N components of the ligand (calculated 38.78%).

a)



b)



c)

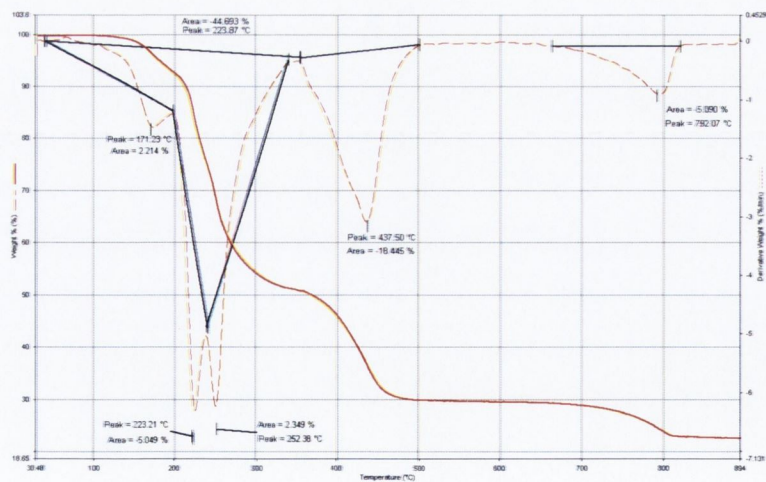


Figure 2.23: a), b) and c) TGA curves (solid red line) for compounds **1**, **2** and **3** respectively. Dash line is the derivative of the TGA curve.

2.3: Summary and Conclusions

The exploitation of the ADTA ligand, in the synthesis of coordination compounds, has proven to be successful with the elucidation of three novel compounds **1**, **2** and **3**. All three compounds are composed of anionic complexes, with a potassium counterion providing a charge balance. **1** and **2** contain mononuclear complexes in which the central transition metal ions adopt an octahedral coordination environment. The iminodiacetic acid donor-atoms of the employed organic ligands occupy facial arrangements. The inner coordination spheres are completed by O-donors of the carboxylic acid function in the 1-position of the aromatic ADTA system and two coordination water molecules. The complexes additionally self-assemble through K^+ -dipole interactions and H-bonds into network structures.

Compound **1** exhibits 2D sheets that extend out parallel to the crystallographic *ab*-plane *via* both H-bonds and counterion-oxygen atom mediations. These sheets are linked in the crystallographic *c*-direction through supplementary K^+ ion mediations and H-bonds generating bi-layers that incorporate the counterions. **2** forms a related structure in which interactions between various oxygen atoms and K^+ ions, generate neutral 2D sheets that expand parallel to the crystallographic *bc*-plane. Due to the hydrogen bonding involving the protonated carboxylic acid group of the $Hadta^{3-}$ ligand, a linking of these neutral sheets along the *a*-axis occurs, to give a 3D H-bonded network.

Contrasting the previous two compounds, **3** is composed of 1D coordination polymers that extend along the crystallographic *a*-axis. The coordination polymer comprises of square pyramidally coordinated copper(II) centres that are linked through coordination bonds *via* partially hydrated, octahedrally coordinated Cu^{II} centres. The resulting double-chain motifs are connected through potassium mediations in both the crystallographic *b*- and *c*-axes and yield a network structure whereby the aromatic ring systems of the $adta^{4-}$ ligands align between the connected chains.

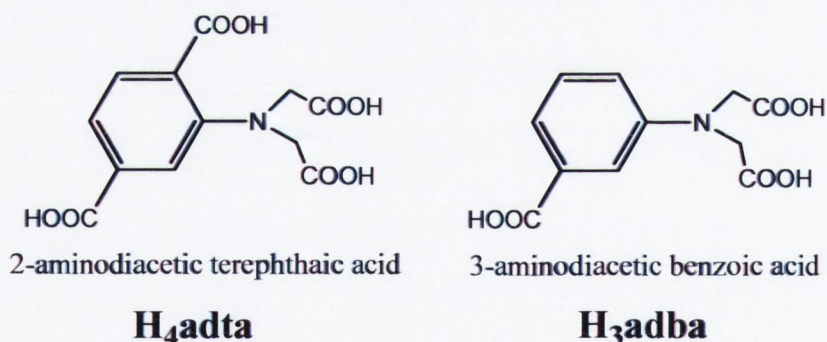
The thermogravimetric analysis reveals that **1**, **2** and **3** show moderate thermal stabilities. Organic ligands in **1-3** undergo oxidative degradation above ~ 200 °C. However, none of the compounds contains any large solvent-accessible void spaces and the compounds are not expected to show permanent porosity. Compound **3** highlights a

synthetic approach to generate 1D coordination polymers whose structures give rise to magnetic coupling between the spin centres and potentially generating interesting magnetic properties.

Chapter 3

3.1: Compounds containing the 3-aminodiacetic benzoic acid (ADBA) ligand

Despite the successful synthesis, chemical characterisation and structural elucidation of a number of novel compounds using the ADTA ligand, the focus of the work was shifted slightly for the ensuing results. Firstly, an alternative ligand type was employed, namely the 3-aminodiacetic benzoic acid (ADBA) ligand (Scheme 3.1). This ligand type maintains the effective tri-dentate coordinating ability of the amino-diacetic acid functionality, but differs in the number and position of the auxiliary carboxylic acid groups directly affixed to the aromatic ring system. In this case, the solitary carboxylic acid is situated in the *meta* position relative to the amine group, whilst the acid functionality in the *ortho* position has been removed.



Scheme 3.1: Replacement of the 2-aminodiacetic terephthalic acid with the 3-aminodiacetic benzoic acid.

The second modification in this work involved the use of 2,2'-bipyridine (bpy herein) in the synthesis of coordination compounds. The reasoning behind this was to intentionally “block” two sites of the coordination sphere of any metal ion, and consequently to gain control over the dimensionality of potential compounds by limiting the number of binding sites available for the iminodiacetic acid-type ligands.

Furthermore, instead of ambient reaction conditions, we decided to exploit hydrothermal reaction conditions for the preparation of coordination compounds. The advantages of the hydrothermal reaction conditions in synthetic procedures have been previously described in section 1.3.1. This approach was considered appropriate at this juncture due to the general insolubility of aqueous reaction mixtures containing both the H₃adba ligand and bpy.

3.1.1: Compound [Zn^{II}(Hadba)(bpy)]₂ (4)

The compound [Zn^{II}(Hadba)(bpy)]₂ (4) forms reproducibly under hydrothermal conditions at 100 °C after approximately 12 hours, from an aqueous solution containing equi-molar ratios of zinc nitrate, H₃adba ligand and bpy. The compound crystallises as pale yellow crystals in the triclinic crystal system in the space group of *P*-1. The asymmetric unit contains a zinc(II) ion, a mono-protonated Hadba²⁻ ligand and a bipyridine co-ligand. The compound can be visualised as a discrete dimeric species, in which two oxygen atoms from the carboxylate group of separate iminodiacetic acid functionalities, O(1) and O(1'), doubly bridge between the pair of metal centres. This structure can be seen in Figure 3.1. An inversion centre resides in between the two metal centres. The coordination environment of the symmetry-independent zinc ion can best be described as a highly distorted octahedron. The coordination sphere is comprised of the tri-dentate iminodiacetic acid functionality, a chelating bipyridine molecule and is completed with the symmetry-generated oxygen atom, O(1'), of the neighbouring carboxylate group from an alternate Hadba²⁻ ligand. The iminodiacetic acid functionality binds in a *fac* manner, with corresponding bond lengths of 2.142(1) Å and 2.004(1) Å for the Zn(1)–O(1) and Zn(1)–O(3) bonds, whilst the Zn(1)–N(1) bond is 2.463(2) Å long. The bpy ligand coordinates through both its nitrogen atoms to the zinc(II) ion displaying bond lengths for the Zn(1)–N(2) and Zn(1)–N(3) bonds of 2.099(1) Å and 2.122(1) Å, respectively. The sixth binding site, occupied by the symmetry-generated O-donor forms a Zn(1)–O(1') bond with a length of 2.039(1) Å. These values concur with normal Zn(II) ion bond lengths,⁽¹⁶³⁾ exception being the Zn(1)–N(1) bond which is longer due to the rigidity of the aniline functional group and steric hindrance of multiple aromatic rings.

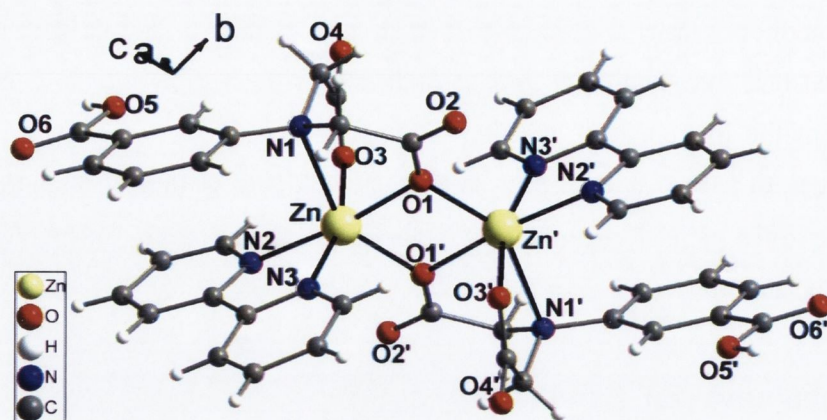


Figure 3.1: Illustration of the doubly bridged dimer structure of **4** which comprises two Hadba²⁻ ligands coordinating in tri-dentate fashions and two chelating bpy ligands. (Prime refers to symmetry-generated atoms.)

A polyhedral representation of the coordination environment of Zn(1) is shown in Figure 3.2 and highlights that both the coordinating nitrogen and oxygen atoms display *fac* arrangements with respect to each other.

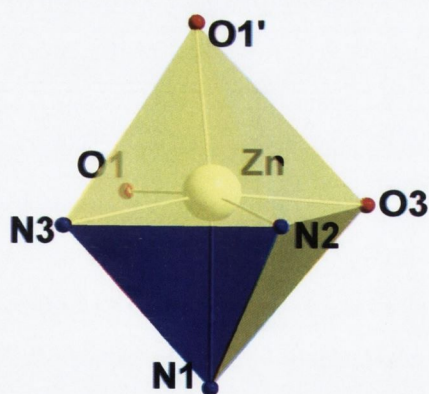


Figure 3.2: Polyhedral representation of the coordination environment of Zn(1) in **4**, with a blue plane highlighting the *fac* arrangement of the nitrogen atoms.

An examination of the bond angles can be used to demonstrate the distortion contained within the coordination sphere. Within the equatorial plane, as represented in Figure 3.2, the O(3)–Zn(1)–N(3) bond angle of 162.75(1)° deviates significantly from an

ideal angle of 180°. The O(1)–Zn(1)–N(2) bond angle is 168.97(1)° and the chelating bipyridine moiety enforces a N(2)–Zn(1)–N(3) angle of 77.62(1)°. Both these values display ample departure from the ideal angles of either 180° or 90°. The bond angle between the atoms in axial positions, O(1')–Zn(1)–N(1), is 145.57(1)° and shows the largest divergence from an ideal angle of 180°. The remaining bond angles can be viewed in Table 3.1.

Table 3.1: Bond angles for the Zn(1) ion in compound **4**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)
O(1)–Zn(1)–O(1')	76.59(1)	O(1)–Zn(1)–O(3)	93.00(1)
O(1)–Zn(1)–N(1)	70.77(1)	O(1)–Zn(1)–N(2)	168.97(1)
O(1)–Zn(1)–N(3)	96.69(1)	O(1')–Zn(1)–O(3)	94.12(1)
O(1')–Zn(1)–N(1)	145.47(1)	O(1')–Zn(1)–N(2)	113.67(1)
O(1')–Zn(1)–N(3)	101.98(1)	O(3)–Zn(1)–N(1)	77.22(1)
O(3)–Zn(1)–N(2)	90.34(1)	O(3)–Zn(1)–N(3)	162.75(1)
N(1)–Zn(1)–N(2)	99.80(1)	N(1)–Zn(1)–N(3)	92.54(1)
N(2)–Zn(1)–N(3)	77.62(1)		

As a result of the discrete di-nuclear nature of compound **4**, there are no further coordination bonds associated with it; however, there are some supramolecular interactions to be discussed. The occurrence of π - π stacking is prevalent throughout the compound and is associated with the introduction of 2,2'-bipyridine into this type of coordination compound. Figure 3.3a reveals the intra-molecular π - π stacking that takes place between the phenyl ring of the ADBA ligand and the two aromatic rings of the bpy moiety. The average distance between the aromatic planes is 3.569(8) Å. Inter-molecular π - π stacking interactions also prevail within the structure and occur solely for the bipyridine units (Fig. 3.3b). The separate sets of rings align in a slipped stacking manner,⁽¹⁵¹⁾ resulting in a non-eclipsed, off-set overlap of the bpy molecules. The distance between two bpy co-ligands is 3.789(8) Å. These inter-molecular π -stacking contacts proceed along the crystallographic *b*-axis and link individual [Zn(Hadba)(bpy)]₂ complexes into a 1D chain, which is shown in Figure 3.3c.

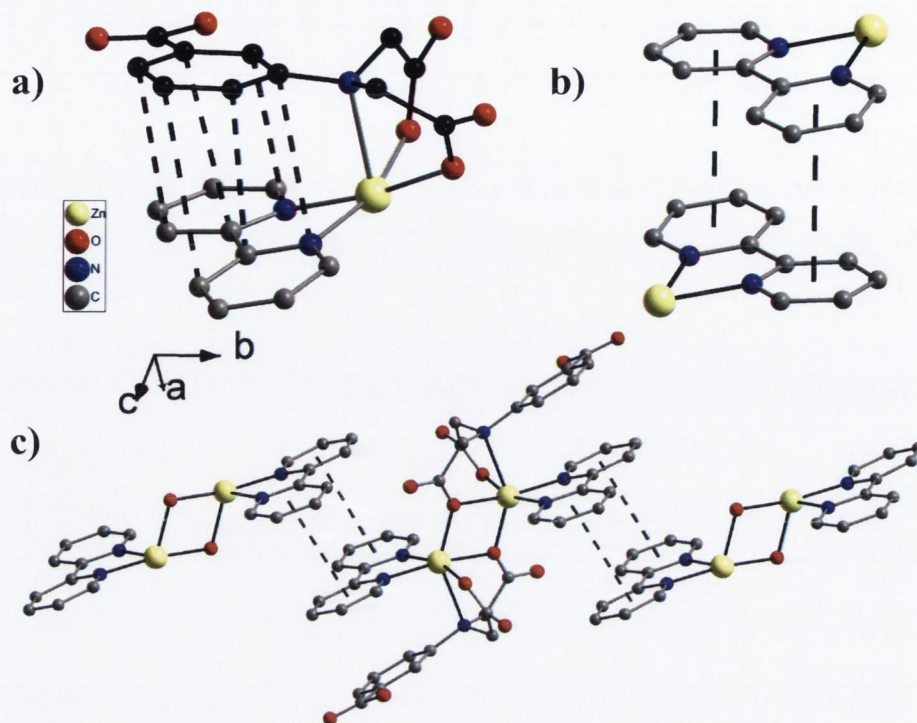


Figure 3.3: a) Intra-molecular π - π stacking between the phenyl ring of the ligand and the bpy co-ligand in **4** (carbon atoms of the ADBA ligand emphasised in black), b) the inter-molecular π -stacking of two bpy co-ligands and c) the resulting connection of discrete di-nuclear complexes into a 1D chain extending along the crystallographic b -axis. All hydrogen atoms are removed for clarity.

In addition to the π - π stacking interactions that are contained within **4**, hydrogen bonds also facilitate inter-molecular connectivity within the crystal structure. These arise from the benzoic acid functionalities of the Hadba^{2-} ligands, which remain protonated and are not involved in coordination bonding to the zinc(II) ion. The carboxylic acid functionality which is directly attached to the aromatic ring links to a carboxylate group of an adjacent iminodiacetic acid functionality, with a $\text{O}(5)\text{--O}(4')$ H-bond of length 2.613(3) Å. Through symmetry-equivalents, a dual H-bonded motif is generated. This assembly is illustrated in Figure 3.4, whereby an inversion centre is located in the centre of this array.

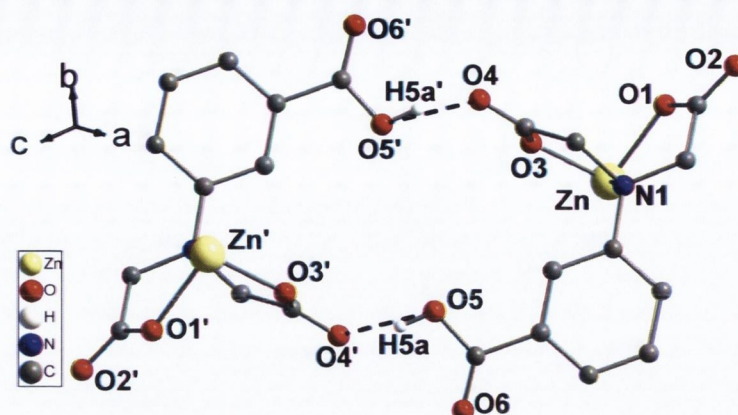


Figure 3.4: The hydrogen bonding (dashed bonds) involving the benzoic acid functionality of the ligand and a nearby carboxylate group. Bpy co-ligands and non-relevant hydrogen atoms are omitted for clarity. (Prime refers to symmetry-generated atoms.)

Due to the dimeric nature of the $[\text{Zn}(\text{Hadba})(\text{bpy})]_2$ complex and its associated symmetry operations, a H-bonded chain is generated that extends parallel to the crystallographic *c*-axis. This assembly can be seen in Figure 3.5.

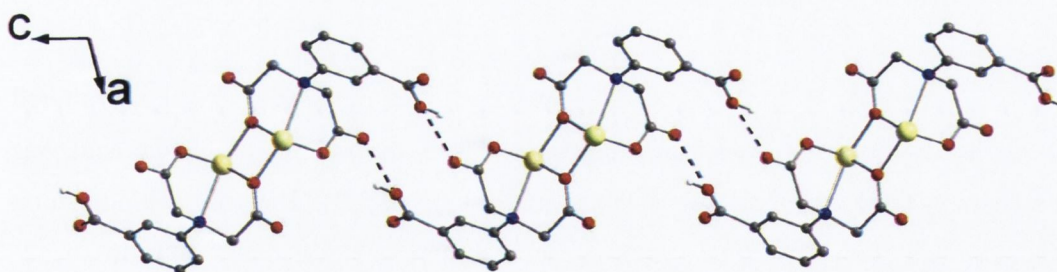


Figure 3.5: The continuous H-bonding (dashed bonds) motif in **4** expands parallel to the crystallographic *c*-axis. Bpy co-ligands and non-relevant hydrogen atoms are omitted for clarity.

An overall representation of the compound can be seen in Figure 3.6, revealing the association between neighbouring dimeric units *via* the aforementioned supramolecular interactions.

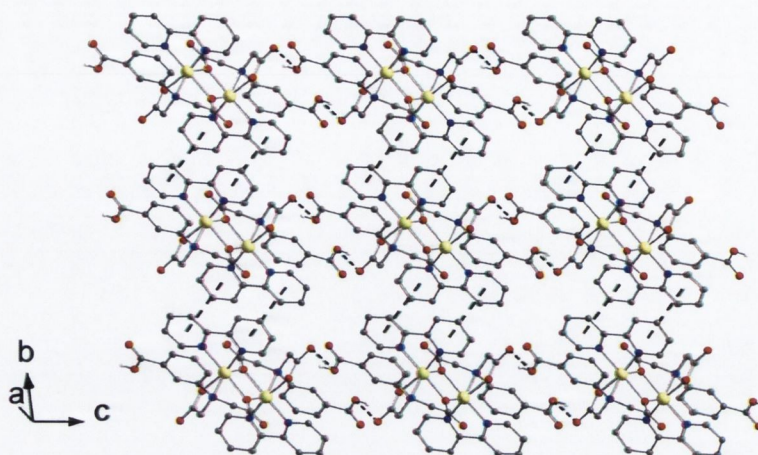
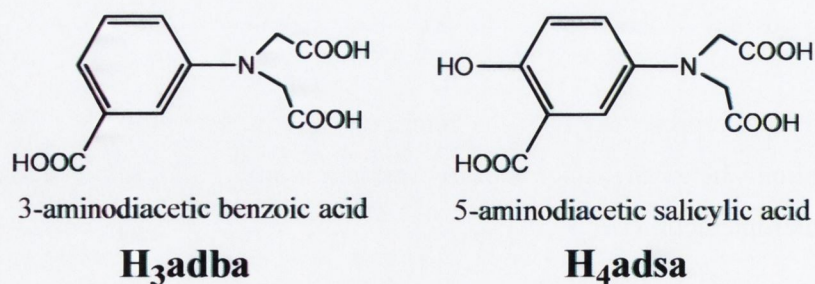


Figure 3.6: Packing of the di-nuclear complexes within the crystal structure of **4**, with the various supramolecular interactions (dashed bonds) between the dimers highlighted. All H atoms attached to carbon atoms are removed for clarity.

3.2: Compounds containing the 5-aminodiacetic salicylic acid (ADSA) ligand

Following on from the successful synthesis of compound **4**, a slightly altered ligand type was used for comparison purposes. The 3-aminodiacetic benzoic acid was replaced with the 5-aminodiacetic salicylic acid (Scheme 3.2). The sole distinguishing feature between the two ligand types is the inclusion of an alcohol group in the 2-position, adjacent to the carboxylic acid functionality of the phenyl ring.



Scheme 3.2: Modification of the 3-aminodiacetic benzoic acid to the 5-aminodiacetic salicylic acid.

A very similar synthetic strategy to the previous section was applied, i.e. bpy was added as a co-ligand under hydrothermal reaction conditions. A number of transition metal centres, such as Ni^{II} , Co^{II} , Fe^{II} and Mn^{II} , were explored in the reaction conditions. However, only copper(II) salts resulted in the formation of crystals whose structure was elucidated by single crystal X-ray diffraction. Unfortunately, a zinc compound that would be directly related to **4** could not be isolated.

3.2.1: Compound $[\text{Cu}^{\text{II}}(\text{H}_2\text{adsa})(\text{bpy})]_2$ (**5**)

The compound $[\text{Cu}^{\text{II}}(\text{H}_2\text{adsa})(\text{bpy})]_2$ (**5**) forms in a low yield from the hydrothermal treatment of an equi-molar solution of copper nitrate, H_4adsa ligand and bpy. The compound crystallises as small green shards in the triclinic crystal system in the space group of $P-1$. The asymmetric unit contains a copper(II) ion, a di-protonated $\text{H}_2\text{adsa}^{2-}$ ligand and a bipyridine co-ligand. The crystal structure again consists of dimers, in which carboxylate groups of two iminodiacetic acid functionalities doubly bridge between the pair of copper(II) ions. The structure is shown in Figure 3.7a. An inversion centre is situated in the centre of the doubly bridged motif. Similar to **4**, the metal ion displays a highly distorted octahedral coordination environment, composed of the *fac* binding tri-dentate iminodiacetic acid group, a chelating bpy co-ligand and a symmetry-generated carboxylate oxygen atom (Fig. 3.7b). Apart from the use of an alternate ligand, the complete coordination environment remains the same as compound **4**.

As a result of the comparable coordination environments, specific coordination bond lengths and bond angles will not be discussed in great detail (see Table 3.2). The bond lengths range between the shortest of 1.945(4) Å (the Cu(1)–O(3) bond) to the longest of 2.518(5) Å for the Cu(1)–N(1) bond. This clearly elongated Cu(1)–N(1) bond can be rationalised with Jahn-Teller theorem, with tetragonal distortion within the octahedral coordinating geometry of the Cu(1) ion occurring.⁽¹⁶⁴⁾ Akin to **4**, the large distortion within the coordination sphere of the Cu(II) ion is reflected in the associated bond angles. The two axially positioned atoms display the largest deviation from ideal octahedral angles, exhibiting a O(1')–Cu(1)–N(1) bond angle of 144.44(1)°.

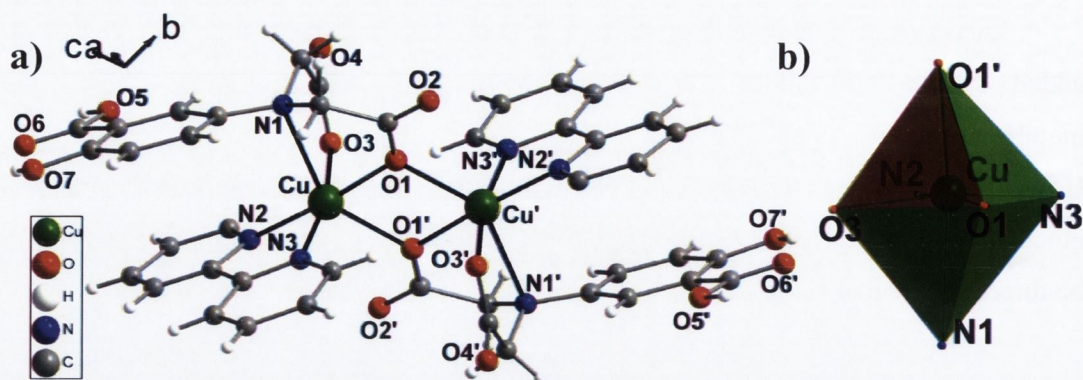


Figure 3.7: a) Portrayal of the dimer motif in **5** comprised of two $\text{H}_2\text{adsa}^{2-}$ ligands and two chelating bpy co-ligands binding to two Cu(II) centres and b) polyhedral representation of the coordination environment of Cu(1) with the *fac* arrangement of the coordinating oxygen atoms shown as a red plane. (Prime refers to symmetry-generated atoms.)

Table 3.2: Bond angles and bond lengths for the Cu(1) ion in compound **5**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)	Atoms	Bond length (Å)
O(1)–Cu(1)–O(1')	75.97(2)	O(1)–Cu(1)–O(3)	92.10(1)	Cu(1)–O(1)	2.007(4)
O(1)–Cu(1)–N(1)	73.21(2)	O(1)–Cu(1)–N(2)	173.13(2)	Cu(1)–O(3)	1.945(4)
O(1)–Cu(1)–N(3)	96.27(2)	O(1')–Cu(1)–O(3)	88.12(1)	Cu(1)–O(1')	2.269(4)
O(1')–Cu(1)–N(1)	145.44(1)	O(1')–Cu(1)–N(2)	110.65(2)	Cu(1)–N(1)	2.518(5)
O(1')–Cu(1)–N(3)	103.00(2)	O(3)–Cu(1)–N(1)	77.84(2)	Cu(1)–N(2)	2.010(4)
O(3)–Cu(1)–N(2)	90.00(2)	O(3)–Cu(1)–N(3)	167.41(2)	Cu(1)–N(3)	2.020(4)
N(1)–Cu(1)–N(2)	100.88(2)	N(1)–Cu(1)–N(3)	95.57(2)		
N(2)–Cu(1)–N(3)	80.64(2)				

Mirroring **4**, there are no further coordination bonds contained within the compound, however a variety of supramolecular interactions stabilise the dimeric complex. Intra-molecular π - π stacking occurs between the ADSA phenyl rings and the bpy co-ligands (Fig. 3.8a) with an average distance of 3.598(8) Å between the aromatic planes. Weaker inter-molecular π -stacking interactions (Fig. 3.8b) occur between the bpy aromatic rings of adjacent dimers to give an average inter-plane distance of 3.719(9) Å. Once again, this results in a linking of discrete dimers in the crystallographic *b*-direction.

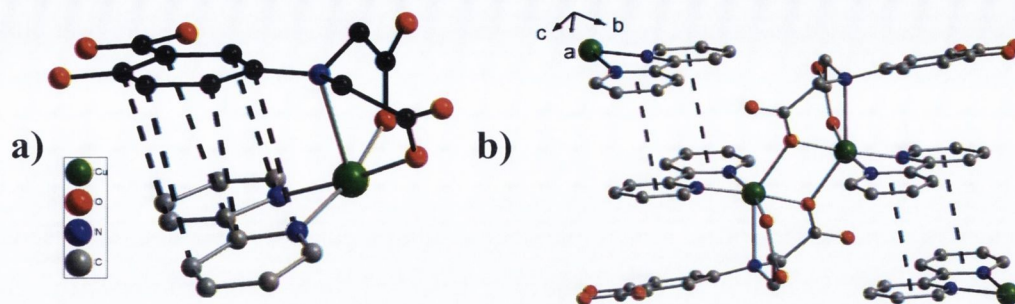


Figure 3.8: a) Intra-molecular π - π stacking and b) the inter-molecular π -stacking interactions of separate bpy co-ligands in **5**. All hydrogen atoms are removed for clarity.

Both the alcohol and carboxylic acid groups directly affixed to the aromatic ring the ADSA ligands remain protonated, and subsequently engage in hydrogen bonds. Firstly, the OH group intra-molecularly H-bonds with the adjoining carboxylic acid of the ligand with a O(7)–O(6) distance of 2.621(4) Å. The carboxylic acid group (O(5)) engages in a H-bond donor interaction with an adjacent carboxylate oxygen atom (O(4')) from a symmetry-generated $\text{H}_2\text{adsa}^{2-}$ ligand, resulting in an O–O separation of 2.602(6) Å (Fig. 3.9a). In a similar manner to **4**, a 1D chain is formed *via* symmetry-generated H-bonds expanding this assembly along the crystallographic *c*-axis (Fig. 3.9b).

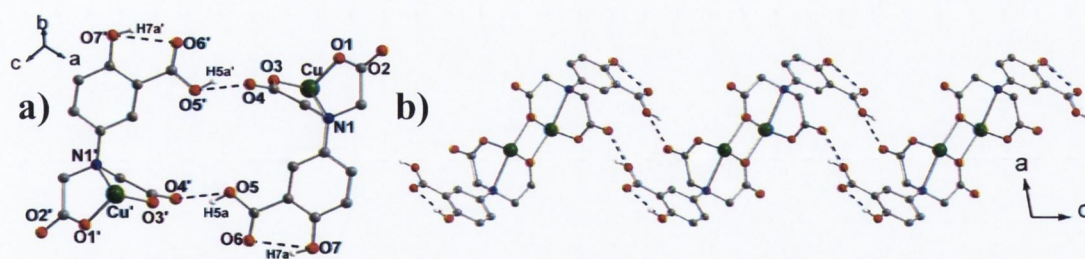


Figure 3.9: a) Inter- and intra-molecular H-bonds (dashed bonds) in **5** involving the carboxylic acid and OH functionalities, respectively, of the ADSA ligand and b) the resulting H-bonded chain extending parallel to the crystallographic *c*-axis. Bpy molecules and non relevant hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

A brief comparison of the two compounds, **4** and **5**, demonstrates that they are both highly similar despite using two slightly different ligand types. The products

crystallise in an identical crystal system and space group. Unit cell parameters bear close resemblance, and the overall coordination behaviour and structural motif have been shown to be alike. The supramolecular interactions of the two compounds also present a high degree of similarity. Virtually identical intra- and inter-molecular π - π stacking interactions characterise both structures **4** and **5** and hydrogen bonds connect the discrete dimers. The supplementary alcohol group in **5** merely H-bonds intra-molecularly, and hence the overall packing structure (Fig. 3.10) is analogous to **4**.

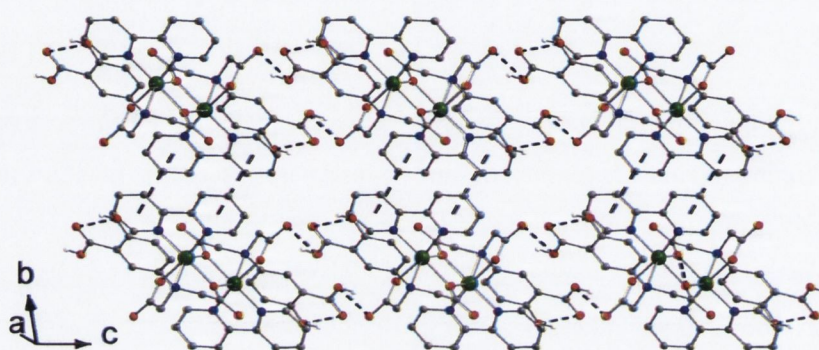


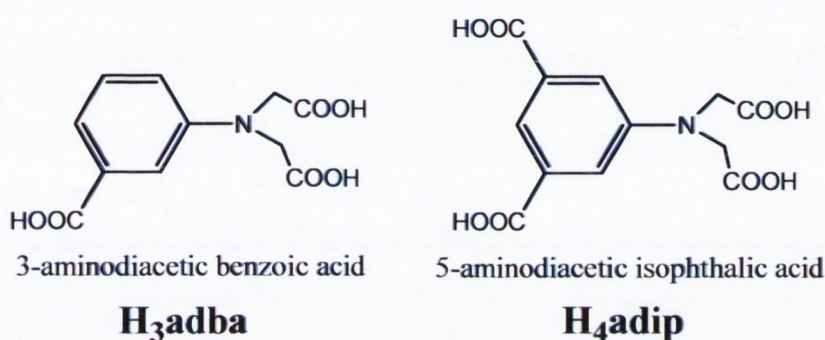
Figure 3.10: Packing array of **5** displaying the supramolecular interactions (dashed bonds) between adjoining dimers. All aliphatic and aromatic hydrogen atoms are removed for clarity.

3.3: Compounds containing the 5-aminodiacetic isophthalic acid (ADIP) ligand

Compounds **4** and **5** were shown to be discrete doubly-bridged di-nuclear complexes, yet they both display some interesting supramolecular interactions such as π - π stacking and hydrogen bonding. Despite the use of ligands with different O-donor functionalities (5-aminodiacetic salicylic acid and of a 3-aminodiacetic benzoic acid), the two resulting Zn(II) and Cu(II) complexes were shown to arrange in a remarkably similar fashion yielding almost identical assemblies.

As a progression to this work the organic ligand-type was again amended. An additional carboxylic acid functionality was introduced in the 5-position of the aromatic

ring system. This alteration generates a symmetrical ligand, increases the sites available for binding or bridging purposes, whilst also preserving the chelating capability of the ADBA ligand (Scheme 3.3). The hydrogen bond capacity of the reaction system has furthermore been increased. Considering the structural motifs of compounds **4** and **5**, we expected the resulting compounds, using this alternative ligand, to be characterised by intricate H-bonded networks. In addition to this, we anticipated that this modification would also give rise to the formation of higher dimensional network structures, in which the auxiliary carboxylic acid functionalities would engage in coordination bonds.



Scheme 3.3: Modification of the ligand system from the 3-aminodiacetic benzoic acid to the 5-aminodiacetic isophthalic acid.

An assortment of transition metal ions were used, such as Mn^{II}, Fe^{II}, Ni^{II}, Co^{II} etc., as various *d* electron configurations could result in compounds with interesting magnetic properties. We believed that the characterisation of a number of structurally related compounds could help us interpret magnetic exchange pathways and provide us with a more accurate understanding of the structure-property relationship.

The inclusion of bipyridine as a co-ligand was maintained. The use of hydrothermal techniques was also sustained whilst other parameters, including reaction temperatures, reagent ratios, solvents etc. were varied.

3.3.1: Compound $[\text{Co}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$ (**6**)

The compound $[\text{Co}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$ (**6**), forms reproducibly *via* the hydrothermal treatment of equi-molar amounts of the H_4adip ligand, cobalt acetate and bipyridine. The product crystallises as medium-sized red plates in the triclinic crystal system, in the $P\bar{1}$ space group. The asymmetric unit consists of two symmetry independent cobalt(II) ions, a fully deprotonated adip^{4-} ligand, a bipyridine co-ligand, four coordination water molecules and three solvent water molecules. Overall, a 1D coordination polymer is generated with two distinct metal ion environments. Firstly, Co(1) and its symmetry-equivalent form a di-nuclear secondary building unit (SBU). This structural motif corresponds analogously with those observed in the two previously discussed compounds, **4** and **5**, with **6** also containing an inversion centre situated in the centre of this di-nuclear unit (Fig. 3.11a). Likewise, the coordination environment of Co(1) parallels closely with those of **4** and **5** (Fig. 3.11b) and hence all related coordinative bond lengths and angles will not be discussed in detail (Table 3.3). The bond lengths vary between 2.016(1) Å and 2.318(2) Å, which characterise the Co(1)–O(1) and Co(1)–N(1) bonds, respectively. The bond angles again demonstrate numerous cases of significant deviation from ideal octahedral angles.

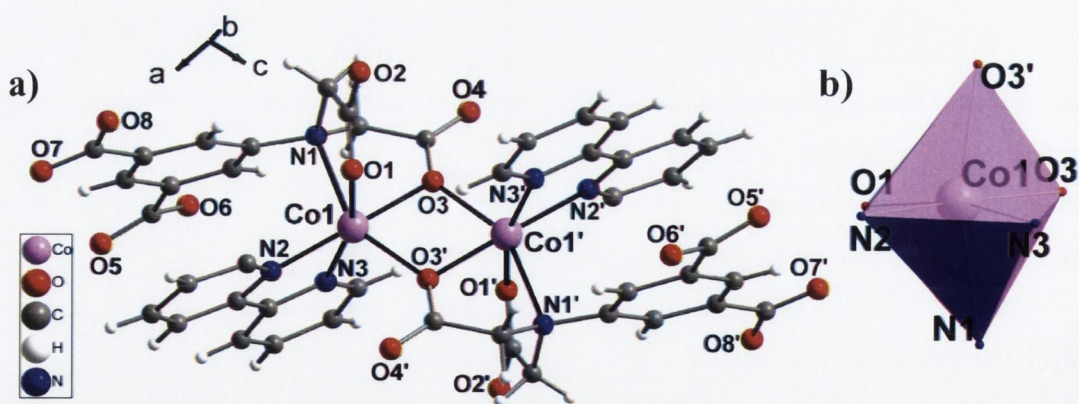


Figure 3.11: a) The coordination environments of the Co(1) and Co(1') centres of the di-nuclear moiety of **6**. Di-nuclear arrangement is akin to that in **4** and **5**, composed of the bridging adip^{4-} ligands and chelating bpy co-ligands, and b) the *fac* arrangement of the nitrogen atoms. (Prime refers to symmetry-generated atoms.)

Table 3.3: Bond angles and bond lengths for the Co(1) ion in compound **6**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)	Atoms	Bond length (Å)
O(1)–Co(1)–O(3)	92.12(6)	O(1)–Co(1)–O(3')	93.34(6)	Co(1)–O(1)	2.016(1)
O(1)–Co(1)–N(1)	79.54(5)	O(1)–Co(1)–N(2)	90.27(6)	Co(1)–O(3)	2.111(1)
O(1)–Co(1)–N(3)	163.56(6)	O(3)–Co(1)–O(3')	76.44(6)	Co(1)–O(3')	2.079(1)
O(3)–Co(1)–N(1)	74.36(5)	O(3)–Co(1)–N(2)	176.49(6)	Co(1)–N(1)	2.318(2)
O(3)–Co(1)–N(3)	100.22(6)	O(3')–Co(1)–N(1)	149.60(5)	Co(1)–N(2)	2.107(2)
O(3')–Co(1)–N(2)	105.98(6)	O(3')–Co(1)–N(3)	100.04(6)	Co(1)–N(3)	2.110(2)
N(1)–Co(1)–N(2)	103.59(6)	N(1)–Co(1)–N(3)	93.29(6)		
N(2)–Co(1)–N(3)	76.95(6)				

The di-nuclear SBUs of the structure are linked *via* the deprotonated carboxylate groups of the isophthalic moiety of the adip⁴⁻ ligand to Co(2), and symmetry-related Co^{II} ions, to yield a 1D coordination polymer. These partially hydrated Co(2) centres mediate between two di-nuclear SBUs through *cis* binding carboxylate groups. These combined interactions produce a 16-membered macrocycle motif (Fig. 3.12a). The coordination environment of Co(2) is best described as that of a slightly distorted octahedron (Fig. 3.12b). The coordinating carboxylate O-donor generates a Co(2)–O(5) which is 2.079(1) Å long, while the *cis* coordinating symmetry-generated carboxylate atom forms a Co(2)–O(7') bond of length 2.064(1) Å. The four coordinating water ligands that complete the coordination environment show comparable bond distances, which range between 2.071(2) Å (Co(2)–O(12)), and 2.132(2) Å (Co(2)–O(9)).

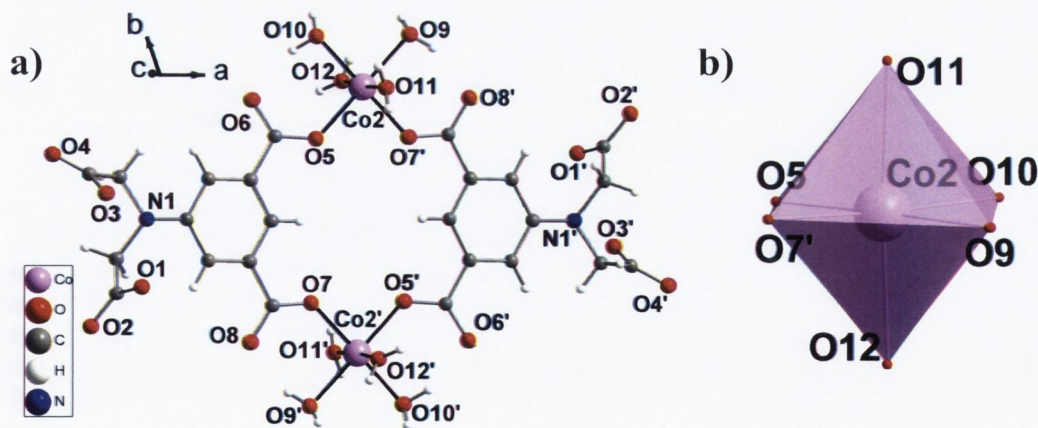


Figure 3.12: a) The isophthalic acid moieties of the adip⁴⁻ ligands engaging in coordination bonds with partially hydrated Co(2) ions producing the macrocyclic motif in compound **6** and b) polyhedral representation of the coordination sphere of the Co(2) ion. (Prime refers to symmetry-generated atoms.)

The bond angles reflect the relative symmetric nature of the Co(2) coordination environment. The angles exhibiting the largest deviation from ideal angles of 90° or 180°, are associated with the axially coordinating water molecules, as depicted in Figure 3.12b. The O(9)–Co(2)–O(12) and O(11)–Co(2)–O(12) bond angles are 85.82(7)° and 175.47(7)°, respectively. The *cis* coordinating isophthalic O-donors form a O(5)–Co(2)–O(7') angle of 86.99(6)°. All remaining bond angles show minor deviations from the angles of an ideal octahedron (see Table 3.4).

Table 3.4: Bond angles for the Co(2) ion in compound **6**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)
O(5)–Co(2)–O(7')	86.99(6)	O(5)–Co(2)–O(9)	178.46(7)
O(5)–Co(2)–O(10)	92.97(6)	O(5)–Co(2)–O(11)	91.54(6)
O(5)–Co(2)–O(12)	92.78(7)	O(7')–Co(2)–O(9)	92.39(6)
O(7')–Co(2)–O(10)	176.96(7)	O(7')–Co(2)–O(11)	90.20(8)
O(7')–Co(2)–O(12)	91.38(8)	O(9)–Co(2)–O(10)	87.73(6)
O(9)–Co(2)–O(11)	89.87(8)	O(9)–Co(2)–O(12)	85.82(7)
O(10)–Co(2)–O(11)	86.76(7)	O(10)–Co(2)–O(12)	91.66(8)
O(11)–Co(2)–O(12)	175.47(7)		

As opposed to the discrete di-nuclear motifs in **4** and **5**, compound **6** forms a continuous 1D coordination polymer involving both the iminodiacetic acid and the isophthalic acid moieties of the adip⁴⁻ ligand. Figure 3.13 highlights how each adip⁴⁻ ligand links to three different Co(II) centres within **6**. The resultant polymer extends approximately in the crystallographic [101]-direction.

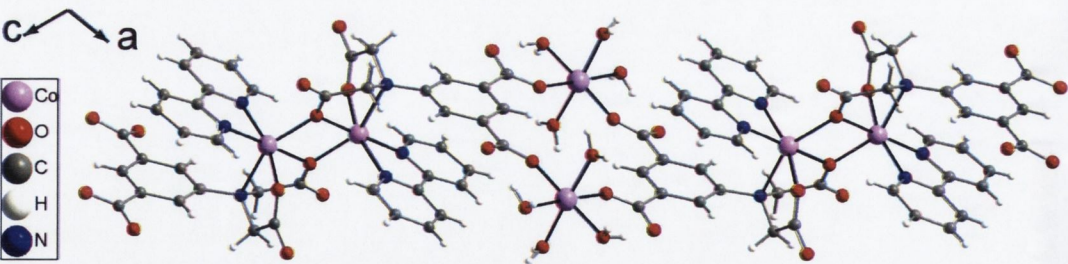


Figure 3.13: 1D coordination polymer in **6** viewed in the direction of the crystallographic *b*-axis. Di-nuclear SBUs involving Co(1) and symmetry-equivalents are linked through Co(2) and symmetry-generated partially hydrated cobalt centres.

Compound **6** is further characterised by supramolecular interactions, which are also featured in **4** and **5**. Intra-molecular π - π stacking occurs between both the phenyl ring of the ADIP ligand and the bpy co-ligand (Fig. 3.14a). The mean plane distance between the sets of rings is 3.487(2). Interestingly, inter-molecular π -stacking takes place between both separate ligand ring systems, differing from compounds **4** and **5** where only the bipyridine units were involved in π - π stacking interactions. The average distance between the two phenyl rings of the ADIP ligand is 3.712(2) Å, whilst the mean distance between the bpy rings is 3.863(2) Å. Figure 3.14b highlights these collective interactions, which result in a stacking of separate 1D polymer chains.

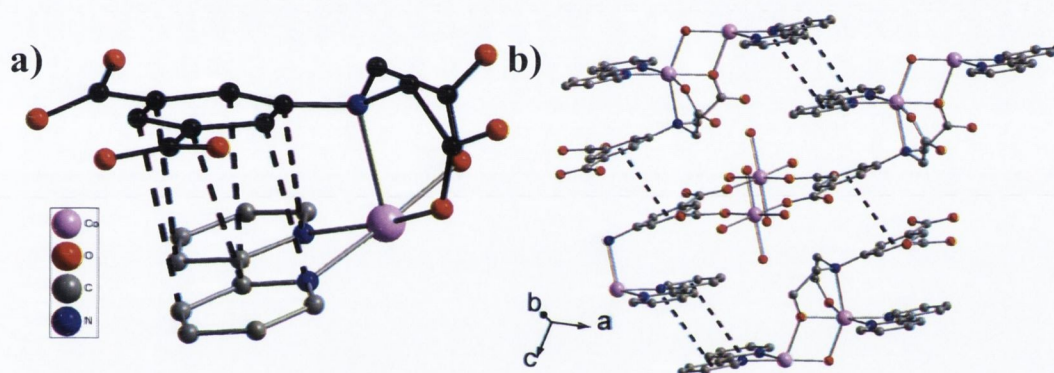


Figure 3.14: a) Intra-molecular π - π stacking between the ADIP ligand and bpy co-ligand in **6** (carbon atoms of the ADIP unit highlighted in black) and b) the inter-molecular π -stacking of both the ADIP and the bpy ligands. All hydrogen atoms are removed for clarity.

There are several hydrogen bonds contained within the structure owing to the large number of coordinating and non-coordinating H₂O molecules. The two *cis* coordinating water molecules situated in the equatorial positions of the coordination sphere of Co(2) both engage in two H-bonds. The O(9) atom interacts with an adjacent symmetry-generated (non-coordinating) carboxylate oxygen atom of an isophthalic acid functionality, O(8''), and also intra-molecularly with a solvent water molecule, O(13). These display O–O distances of 2.653(1) Å and 2.950(1) Å, respectively. The O(10) atom of the second equatorially positioned water molecule interacts intra-molecularly with an isophthalic acid moiety of the adip⁴⁻ ligand, O(6), and also with a non-binding

carboxylate atom of the iminodiacetic group (O(2')). These exhibit corresponding O–O separations of 2.685(2) Å and 2.725(1) Å. The four H-bonds are shown in Figure 3.15a. Figure 3.15b highlights the linkage of separate 1D polymer chains along the crystallographic *b*-axis.

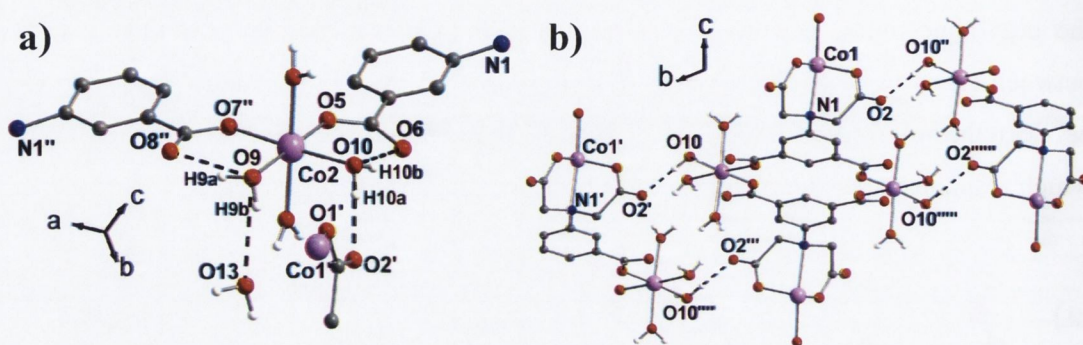


Figure 3.15: a) The four distinct H-bonds (dashed bonds) associated with the two *cis* coordinating water (O(9) and O(10)) molecules situated in the equatorial positions of the octahedral coordination sphere of Co(2), and b) the specific O(10)–O(2') H-bonds connecting independent 1D polymers. Bpy co-ligands and all non-relevant hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

Both the *trans* water molecules situated in the axial positions of the octahedral coordination sphere of Co(2), likewise partake in two-fold hydrogen bonding interactions. They function in a remarkably analogous fashion to the previously described water ligands given that they H-bond with either non-binding carboxylate atoms of the organic ligand, or with solvent water molecules. O(11) is involved in a H-bond with an iminodiacetic acid carboxylate atom O(4''), to give a O–O distance of 2.730(1) Å. O(11) further resides 2.844(2) Å from the O-atom O(15) of a solvent water molecule. In a similar manner, O(12) of a coordination H₂O molecule H-bonds with a carboxylate atom, O(2'), and O(13) of a solvent water molecule. The resulting H-bonds are characterised by O–O separations of 2.673(2) Å and 2.761(1) Å, respectively. Figure 3.16 illustrates the H-bonds associated with these *trans* axial coordinating water molecules, resulting in an intricate H-bonded motif expanding along the crystallographic *bc*-plane.

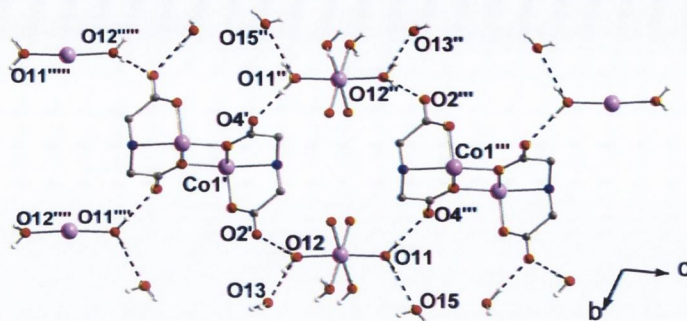


Figure 3.16: The four different H-bonds (dashed bonds) involving the two axially positioned water molecules coordinating to Co(2), linking discrete di-nuclear SBUs in the crystallographic *bc*-plane. Aromatic ring systems of both ligand-types and all non-relevant hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

As previously discussed, atoms O(12) and O(9) of coordinating water molecules H-bond with O(13) of a solvent water molecule. This O(13) atom then participates in a two-fold H-bond donor interaction with two non-bonding carboxylate atoms of the isophthalic functionalities of opposing adip⁴⁻ ligands. The corresponding O(13)–O(6') and O(12)–O(8'') distances are 2.825(1) Å and 2.730(2) Å, respectively. These interactions are duplicated by a second lattice H₂O molecule involving O(14) to form O(14)–O(6') and O(14)–O(8'') H-bonds 2.834(1) Å and 2.979(3) Å long, respectively. A O(15)–O(14) contact of 2.732 (1) Å constitutes the final interaction concerning the solvent H₂O molecules. Figure 3.17a depicts the interactions of the solvent water molecules within 6. The resultant H-bonding array is shown in Figure 3.17b.

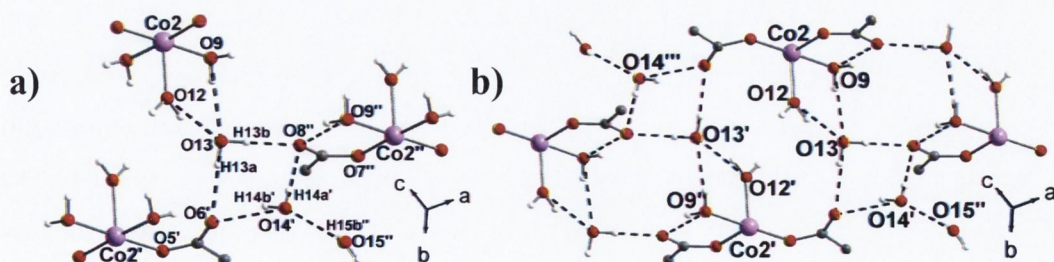


Figure 3.17: a) H-bonds (dashed bonds) of both the solvent and coordination water molecules that bind to Co(2) and b) the extended assembly of these H-bonds. Bpy co-ligands, majority of the ADIP ligand and all non-relevant hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

In summary, **6** consists of 1D coordination polymers that extend in the crystallographic [101]-direction. Figure 3.18 depicts the overall structure composed of these distinct 1D chains further linked *via* H-bonds into a 3D network structure.

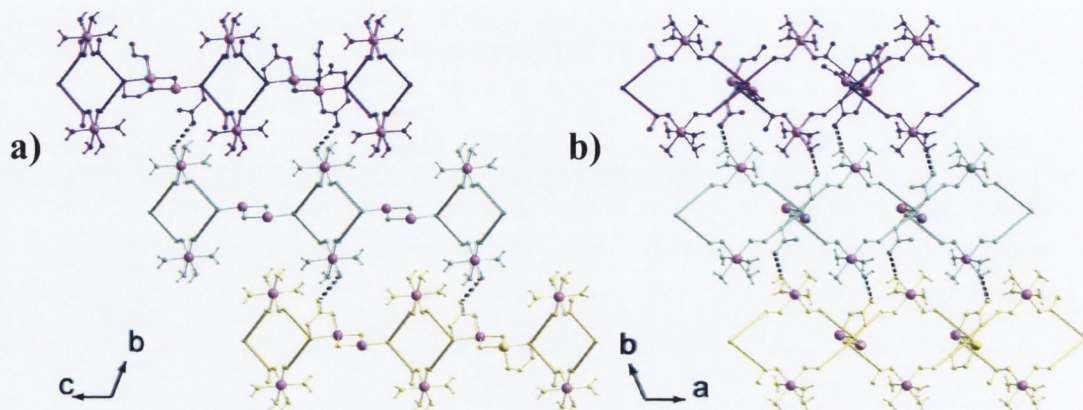


Figure 3.18: Overall 3D network structure of **6** composed of 1D coordination polymers connected *via* H-bonds (dashed bonds) viewed in the direction of the crystallographic a) *a*-axis and b) *c*-axis. 16-member macrocyclic motifs are represented as four linear connectors, whilst all remaining organic ligands are removed for clarity.

3.3.2: Thermal decomposition of compound **6**

Figure 3.19 reveals the TGA curve associated with the heating of crystalline samples of compound **6** in an air atmosphere. Between the temperatures of approximately 50 and 80 °C, a weight loss of 7.50% (calculated 7.80%) was recorded, and can be attributed to the loss of the three lattice water molecules. A second weight loss of ~ 9% occurs between 80 and 130 °C. This corresponds to the removal of the four coordinating H₂O molecules (calculated 10.40%). The TGA curve remains unchanged until almost 200 °C, where a loss of 2.01% occurs. The curve remains constant until approximately 330 °C. Above this temperature total oxidation of the organic ligand takes place with the loss of almost 60 wt%, (calculated ~ 52% for the combustion of all remaining C, H and N atoms), resulting in the formation of oxide materials.

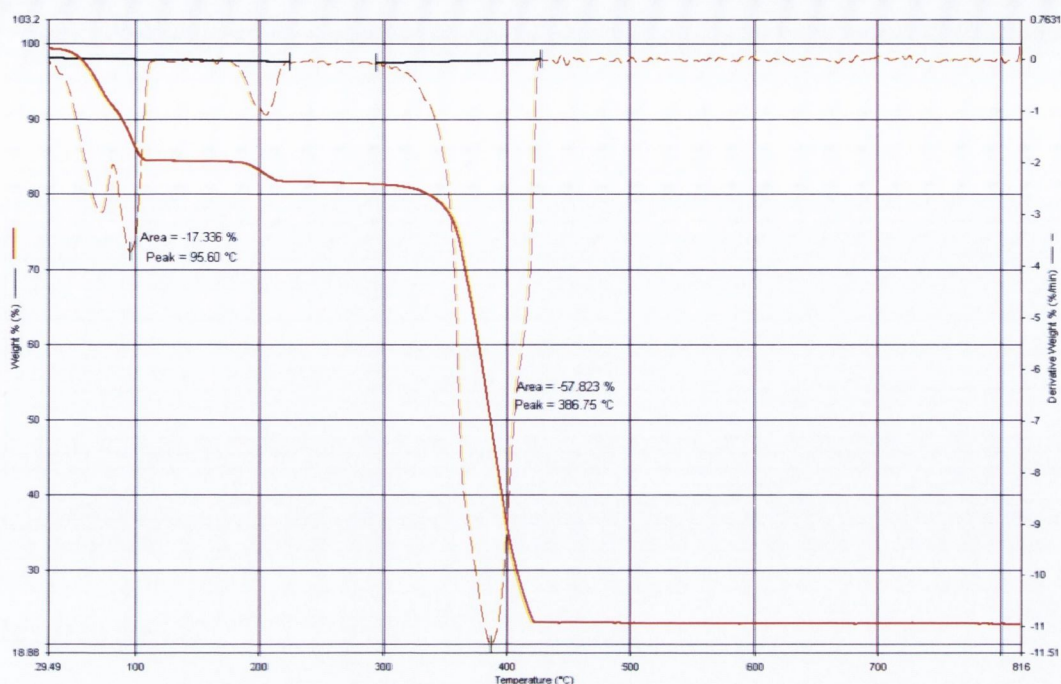


Figure 3.19: TGA curve (red solid line) for compound **6**, dash curve is the derivative of the TGA curve.

3.3.3: Iso-structural $[M^{II}_2(adip)(bpy)(H_2O)_4] \cdot 3H_2O$ compounds ($M = Mn, Fe, Ni$)

The binding capacity of the ADIP ligand was further established with the successful crystallisation and structural elucidation of three iso-structural compounds. $[Mn^{II}_2(adip)(bpy)(H_2O)_4] \cdot 3H_2O$ (**7**), $[Fe^{II}_2(adip)(bpy)(H_2O)_4] \cdot 3H_2O$ (**8**) and $[Ni^{II}_2(adip)(bpy)(H_2O)_4] \cdot 3H_2O$ (**9**) were produced using similar or slightly modified synthetic methods. All four compounds, **6-9**, display similar crystallographic parameters, elemental analyses and IR spectra. Subtle differences in the coordination geometry and unit cell parameters arise from the varying sized ionic radii of the relevant metal centres (see Table 3.5). All bond lengths correspond well with typical literature values,⁽¹⁶³⁾ with the exception of the M(1)–N(1) bonds which are generally longer. This arises from the aforementioned steric hindrance of the aromatic rings around the metal ion, in conjunction with the inflexibility of the amino functional group of the ligands.

Table 3.5: Selected bond lengths and angles of the iso-structural compounds **6-9**.

Atoms	Distances (Å)/Angles (°) in 6 (Co)	Distances (Å)/Angles (°) in 7 (Mn)	Distances (Å)/Angles (°) in 8 (Ni)	Distances (Å)/Angles (°) in 9 (Fe)
M(1)–O(1)	2.016(1)	2.092(2)	2.052(6)	2.009(2)
M(1)–O(3)	2.111(1)	2.119(2)	2.158(5)	2.076(2)
M(1)–O(3')	2.079(1)	2.224(2)	2.113(7)	2.058(2)
M(1)–M(1')	3.291(1)	3.457(2)	3.395(4)	3.256(3)
M(1)–N(1)	2.318(2)	2.493(3)	2.388(7)	2.252(2)
M(1)–N(2)	2.107(2)	2.227(3)	2.144(7)	2.045(2)
M(1)–N(3)	2.110(2)	2.219(3)	2.177(7)	2.071(2)
M(2)–O(5)	2.079(1)	2.133(2)	2.132(5)	2.033(2)
M(2)–O(7'')	2.064(1)	2.142(3)	2.098(6)	2.028(2)
M(2)–H ₂ O	2.071(2)–2.132(1)	2.178(3)–2.246(2)	2.139(7)–2.214(5)	2.045(2)–2.090(2)
O(1)–M(1)–O(3)	92.12(5)	97.25(1)	97.82(2)	90.22(7)
O(3')–M(1)–N(1)	149.60(6)	141.23(1)	145.29(2)	151.23(7)
M(1)–O(3)–M(1')	103.56(6)	105.48(2)	105.27(2)	103.93(6)

3.3.4: Analyses of the magnetic properties of iso-structural $[\text{M}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$ compounds (M = Co, Fe, Ni)

Analyses of the magnetic properties of compounds **6**, **8** and **9** were performed to explore the potentially interesting magnetic exchange interactions within these materials. The studies permitted a direct comparison of the three iso-structural compounds.

The temperature dependencies of the magnetic susceptibilities (normalised per two formula units) of **6**, **8** and **9** were measured at 1,000 Oe. The room temperature χT values of 15.2, 12.7, and 5.0 $\text{cm}^3 \text{K mol}^{-1}$ for **8**, **6** and **9**, respectively, are in good agreement with the presence of four Fe^{II} ions ($S = 2$, $C = 3.80 \text{ cm}^3 \text{K mol}^{-1}$ expected for $g = 2.2$), four Co^{II} ions ($S = 3/2$, $C = \sim 3.2 \text{ cm}^3 \text{K mol}^{-1}$) and four Ni^{II} ions ($S = 1$, $C = 1.25 \text{ cm}^3 \text{K mol}^{-1}$ expected for $g = 2.2$). On lowering the temperature, the χT product continually decreases for all three compounds (Fig. 3.20). The values reach a minimum of 4.9 $\text{cm}^3 \text{K mol}^{-1}$ for **8** and 4.3 $\text{cm}^3 \text{K mol}^{-1}$ for **6**, both at 1.8 K. For **9** the χT product reaches an initial plateau of 2.5 $\text{cm}^3 \text{K mol}^{-1}$ at $\sim 5 \text{ K}$, before dropping to 1.4 $\text{cm}^3 \text{K mol}^{-1}$ at 1.8K.

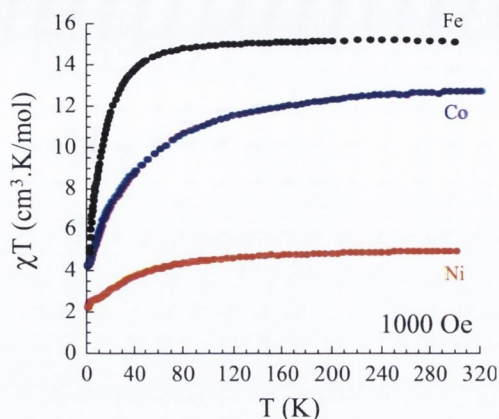


Figure 3.20: Plot of the temperature dependencies of the magnetic susceptibilities of **8**, **6** and **9**.

For compound **6**, the decrease of the χT product is the result of two simultaneous effects. The anti-ferromagnetic coupling between the Co(1) and Co(1') sites i.e. the di-nuclear SBU and the spin-orbit coupling which is characteristic for Co^{II} systems. This latter effect results in the splitting of the energy levels arising from the $^4T_{1g}$ ground term that stabilises a doublet ground state at low temperatures.⁽¹⁶⁵⁾ The temperature dependent susceptibility values for such di-nuclear Co(II) complexes are usually not theoretically reproducible as no simple analytical expression can be applied to model both, the magnetic exchange interactions and the complicated intrinsic magnetic properties of Co(II) sites (such as spin-orbit coupling and magnetic anisotropy). The field dependence of the magnetisation of **6**, measured at 1.8 K, reveals initial saturation effects at *ca.* 5.3 μ_{B} . Above 3 T, the magnetisation increases again to reach a magnitude of 7.3 μ_{B} , resulting in an “S” shape feature of the magnetisation curve. This phenomenon most likely originates from field-induced population of low lying excited states in the system and thus highlights the presence of weak antiferromagnetic interactions. The observed behaviour is also related to a significant magnetic anisotropy of the Co^{II} ions.

For compounds **8** and **9**, however, a full interpretation of the data is possible as the magnetic properties of both Ni(II) or Fe(II) metal ions can be fully modelled. The decrease of the χT product on lowering the temperature is the result of intra-dimer exchanges between the carboxylate bridged metal ions. Below 4 K, other weaker effects,

such as the magnetic anisotropy of the M^{II} ions or weak inter-chain antiferromagnetic interactions, account for the decrease of the χT product.

In agreement with the structural motif of the chain i.e. the presence of two isolated octahedral *high-spin* M(II) centres and two additionally coupled octahedral *high-spin* M(II) ions (M: Ni(II) or Fe(II) with $S_{Ni} = 1$ and $S_{Fe} = 2$), the Heisenberg spin Hamiltonian of the di-nuclear motif can be written as follows: $H = -2JS_{M(1)}S_{M(2)}$, where J is the magnetic exchange parameter within the di-nuclear SBU, and S_i the spin operators for each centre. The application of the van Vleck equation to Kambe's vector coupling scheme allows a determination of the low field analytical expression of the magnetic susceptibility.⁽¹⁶⁶⁻¹⁶⁹⁾ This model incorporates the isolated partially hydrated M(2) sites as paramagnetic Curie components and also allowed us to reproduce the experimental χT vs T data from 300 to 4 K for **9** (from 300 to 20 K for **8**).

The best fit was achieved with the following parameters: $J/kB = -3.3(2)$ K (with $g_{av} = 2.33(5)$) for **8** and $J/kB = -16.5(2)$ K (with $g_{av} = 2.26(5)$) for **9** (Fig. 3.21a and 3.21b, respectively). The sign of the magnetic interaction implies that the di-nuclear unit possesses an $S_T = 0$ spin ground state, in both cases. Hence the overall magnetic behaviour of both compounds **8** and **9** is characterised by two isolated paramagnetic metal centres, (M(2)), and an anti-ferromagnetically coupled di-nuclear SBU.

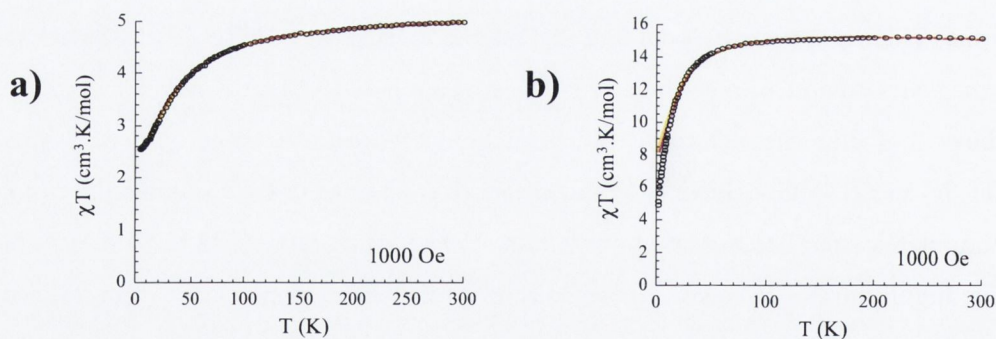


Figure 3.21: Solid red lines represent the best fit obtained using our described model for a) **8** and b) **9**.

For compound **9**, the field dependence of the magnetization at 1.8 K correlates well with a sum of two $S = 1$ Brillouin functions and reveals a saturation value of $4.3 \mu_B$ at 7 T (Fig. 3.22). This behaviour confirms the presence of two isolated $S = 1$ sites, (the

Ni(2) ions). For **8**, the result is more complex as at 7 T no saturation of the magnetisation is observed. At 7 T, the magnetization is $12.2 \mu_B$. This value is larger than the expected value for the two remaining $S = 2$ Fe(2) ions. This implies that the low lying excited states of the Fe(II) centres in the di-nuclear units are populated through the application of a high magnetic field. This effect is the result of weaker intra-molecular anti-ferromagnetic interactions between the spin centres, compared to the exchange parameters observed in **9**, and thus excited states are much closer in energy to the ground state.

In agreement with the field-dependence of the magnetisation at 1.8 K (Fig. 3.22), there is no sign of slow relaxation i.e. hysteresis effects for **8**, **6** and **9**. The *ac* (alternating current) susceptibility in zero *dc* (direct current) field shows a complete absence of an out-of-phase component above 1.8 K for any of these compounds.

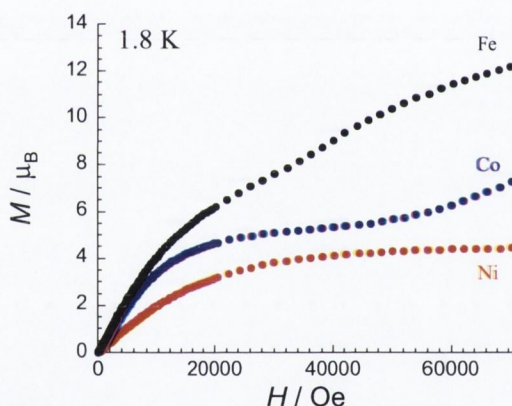


Figure 3.22: *M* vs *H* plot for compounds **8**, **6** and **9**.

3.3.5: Compound $[\text{Cu}^{\text{II}}(\text{H}_2\text{adip})(\text{bpy})]$ (**10**)

When the hydrothermal method is applied to a solution of copper nitrate, the ADIP ligand and bpy, an alternative 1D coordination polymer $[\text{Cu}^{\text{II}}(\text{H}_2\text{adip})(\text{bpy})]$ (**10**) is produced. The compound forms reproducibly in a moderate yield ($\sim 45\%$) at a temperature of 130°C . Blue/green rectangular plates crystallise in the monoclinic crystal system in the space group $P 2_1/c$. The asymmetric unit contains one $\text{H}_2\text{adip}^{2-}$ ligand, one

bipyridine co-ligand and one copper(II) ion. The coordination polyhedron of the Cu(II) ion can be described as a distorted square pyramid. In the coordination sphere, the O-donors, O(1) and O(3), of the individual carboxylate groups of the iminodiacetic acid functionality are situated in the equatorial plane of the square pyramid, whilst the chelating bipyridine moiety occupies the remaining two equatorial sites. The coordination environment is completed by a symmetry-generated carboxylate oxygen atom, O(2'), provided by an adjacent iminodiacetic acid moiety from a neighbouring $\text{H}_2\text{adip}^{2-}$ ligand (Fig. 3.23a). The symmetry-generated equivalents are the result of the operation of a 2_1 screw axis which runs in the direction of the crystallographic b -axis, and links the copper ions through coordination bonds into a 1D coordination polymer. Contrasting compounds **6** to **9**, the 1D chain structure is composed of mono-nuclear sub-units, as opposed to the di-nuclear motif. Uncharacteristically, the iminodiacetic acid functional group does not coordinate to the copper ion in a tri-dentate *fac* mode, but rather in a bi-dentate manner using just the O-donor carboxylate atoms. These Cu(1)–O(1) and Cu(1)–O(3) bond lengths are 1.996(1) Å and 1.949(1) Å long, respectively. Bond distances of 2.005(2) Å and 2.015(2) Å correspond to the Cu(1)–N(2) and Cu(1)–N(3) bonds, while the Cu(1)–O(2') bond at the apex of the square pyramid is of length 2.178(1) Å (Fig. 3.23b).

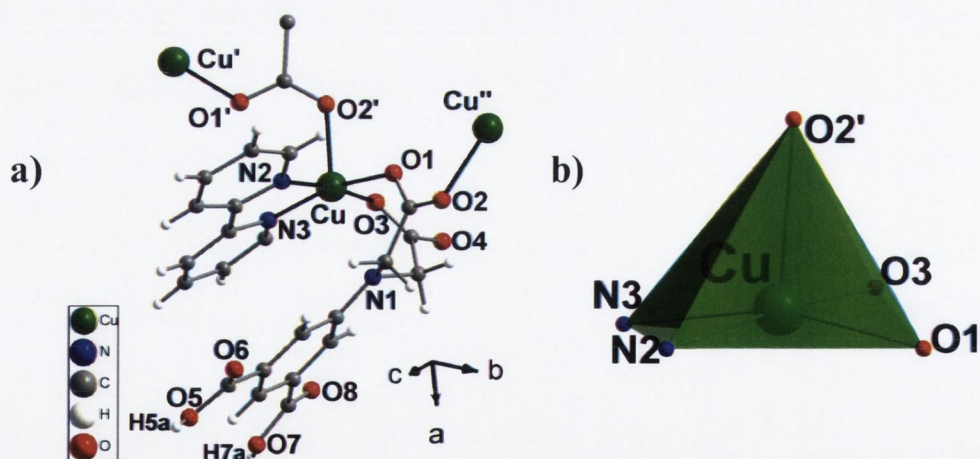


Figure 3.23: a) Coordination environment of the copper(II) ion in compound **10** illustrating the $\text{H}_2\text{adip}^{2-}$ and bpy ligands and b) polyhedral representation of the square pyramidal coordination environment of the Cu(1) ion. (Prime refers to symmetry-generated atoms.)

A brief examination of some of the bond angles can be used to determine the degree of distortion within the coordination sphere of **10**. In the equatorial plane, as depicted in Figure 3.23b, the O(1)–Cu(1)–N(3) bond angle of 162.41(1)° displays the largest deviation from an ideal value of 180°. The second largest distortion involves the O(2')–Cu(1)–N(3) bond angle, revealing a value of 105.26(1)°, which is significantly divergent from an ideal angle of 90°. The remaining angles can be viewed in Table 3.6.

Table 3.6: Bond angles for the Cu(1) ion in compound **10**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)
O(1)–Cu(1)–O(2')	91.09(1)	O(1)–Cu(1)–O(3)	92.90(1)
O(1)–Cu(1)–N(2)	92.04(1)	O(1)–Cu(1)–N(3)	162.41(1)
O(2')–Cu(1)–O(3)	92.65(1)	O(2')–Cu(1)–N(2)	94.11(1)
O(2')–Cu(1)–N(3)	105.26(1)	O(3)–Cu(1)–N(2)	171.55(1)
O(3)–Cu(1)–N(3)	92.78(1)	N(2)–Cu(1)–N(3)	80.55(1)

As previously stated, compound **10** is a 1D coordination polymer. Its chain structure extends along the crystallographic *b*-axis. A view in the crystallographic *ab*-plane (Fig. 3.24a) highlights the helical nature of the polymer, whilst a view in the *b*-direction shows an alternative perspective, also emphasising the 2₁ screw axis of the polymeric strand (Fig. 3.24b).

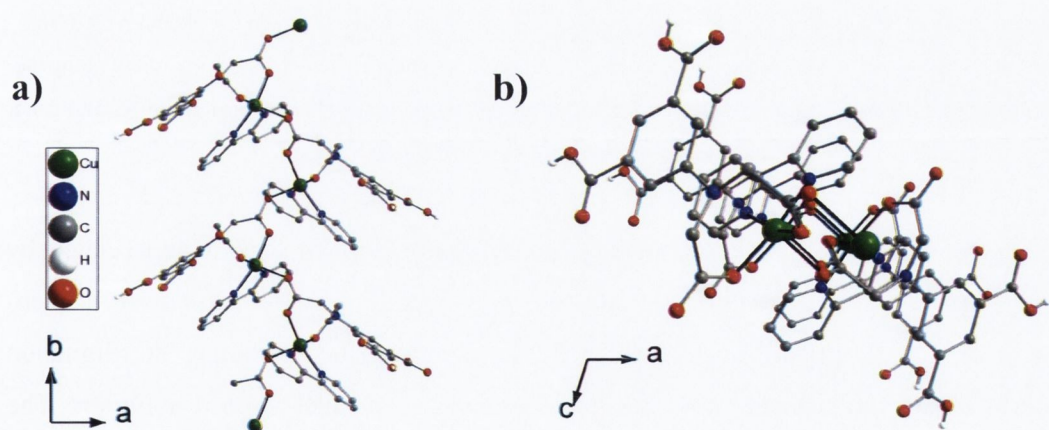


Figure 3.24: a) Plan-view of the crystallographic *ab*-plane showing the helical 1D strand in **10** and b) a view in the crystallographic *b*-axis. Hydrogen atoms attached to C-atoms are removed for clarity.

Mirroring the previous compounds, there is an abundance of supramolecular interactions associated with **10**. Both intra- and inter-molecular π - π stacking interactions are present. Figure 3.25a illustrates the intra-molecular π -stacking in **10**, characterised by a mean inter-plane distance between the aromatic ring systems of 3.509(1) Å. Interestingly, in this case, the phenyl ring of the ADIP ligand π -stacks with only one of the aromatic rings of the bipyridine unit in an eclipsing fashion. This differs from the observed π -stacking in the previous products where the phenyl ring of the ADIP ligand is situated slightly off-set between the two rings of the bpy unit. There is additional inter-chain π - π stacking that links unique polymers along the crystallographic *a*-axis. This interaction occurs solely between the ring systems of the H₂adip²⁻ ligands, resulting in an average inter-plane distance of 3.740(2) Å and can be seen in Figure 3.25b.

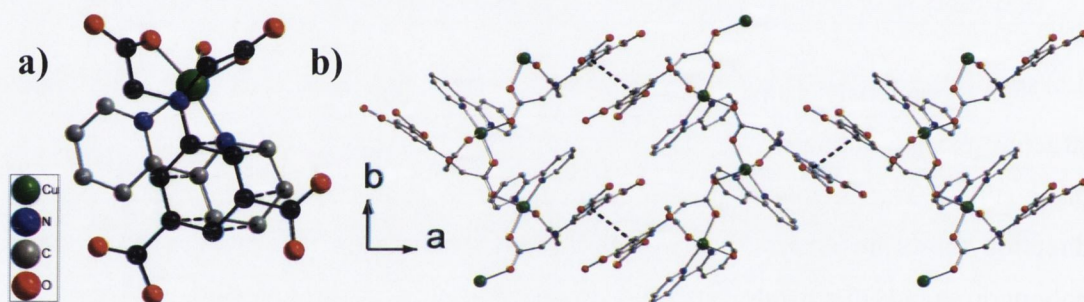


Figure 3.25: a) Intra-molecular π - π stacking interactions (dashed bonds) between the phenyl ring of the ADIP and the bpy co-ligand (carbon atoms of the ADIP unit emphasised in black) and b) a view along the crystallographic *c*-axis illustrating the inter-chain π -stacking involving the phenyl rings of the ADIP ligand. All hydrogen atoms are removed for clarity.

The continuous spiral nature of the 1D chains can be further appreciated by displaying the parallel alignment of adjacent polymers (Fig. 3.26a). Likewise, a plan-view in the crystallographic *ab*-plane (Fig. 3.26b) illustrates the alternating interdigitation of these 1D polymer strands into the spatial grooves of parallel aligned polymers. The phenyl ring of the H₂adip²⁻ ligand protrudes into these channels and reaffirms the inter-chain π -stacking that exists between these neighbouring coils.

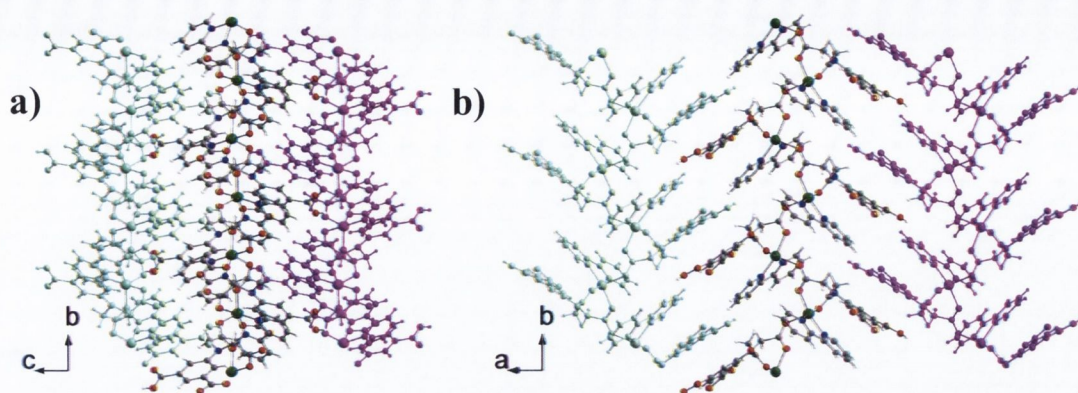


Figure 3.26: a) Packing of neighbouring 1D chains viewed in the direction of the crystallographic *a*-axis and b) a similar representation viewed in the direction of the crystallographic *c*-axis.

The two non-coordinating carboxylic acid functionalities, i.e. the isophthalic acid group of the $\text{H}_2\text{adip}^{2-}$ ligand, remain protonated and subsequently partake in hydrogen bonds. There is a H-bond between O(7) and an iminodiacetic acid carboxylate atom (O(4')) from a neighbouring $\text{H}_2\text{adip}^{2-}$ ligand. This H-bond is characterised by a short O–O distance of 2.502(2) Å. A second hydrogen bond involves two isophthalic acid functionalities of adjacent polymer chains resulting in a H-bond with a O(5)–O(8'') distance of 2.617(2) Å. Figure 3.27 shows the combination of these two interactions, resulting in an intricate H-bonded network that extends parallel to the [011]-plane.

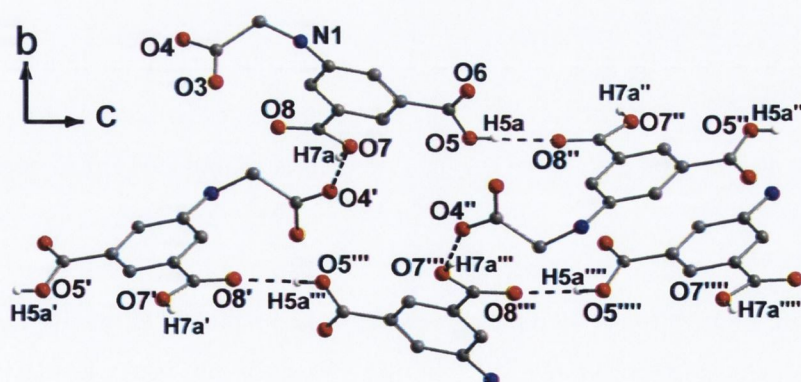


Figure 3.27: The hydrogen bonded (dashed bonds) array in **10** that expands along the crystallographic *bc*-plane. All metal ions, bpy co-ligands and non-relevant hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

Compound **10** is composed of 1D coordination polymers that extend along the crystallographic *b*-axis. Hydrogen bonds further connect said polymers resulting in the extensive H-bonded assembly depicted in Figure 3.28.

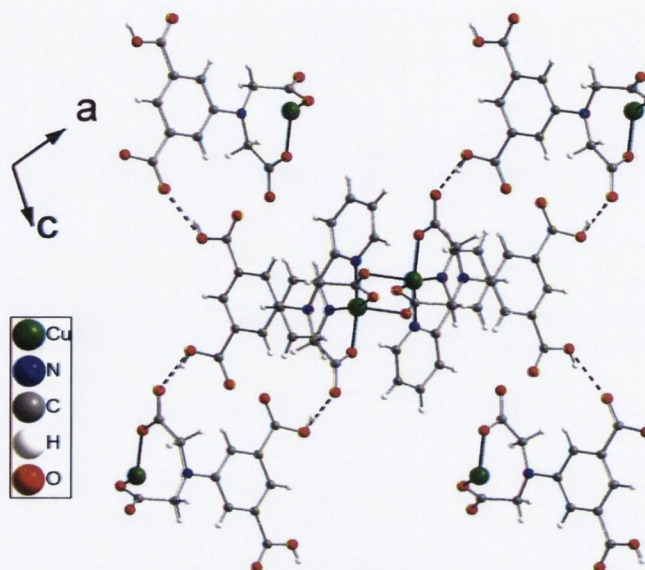


Figure 3.28: Illustration of the overall network structure in **10** viewed in the direction of the crystallographic *b*-axis.

3.3.6: Thermal decomposition of compound **10**

The thermogravimetric analysis was carried out in an air atmosphere in a temperature range between 25 and ~800 °C. Examining the TGA curve of **10** (Fig. 3.29) indicates that the structural integrity of the complex is maintained up to approximately 250 °C. Above this temperature, the compound undergoes rapid oxidative degradation. This thermogravimetric event, centred at 280 °C, displays a weight loss of over 70%. This can be attributed to a complete combustion of all the C, H and N atoms of the structure (calculated 62.80%) resulting in the formation of metal oxides of various compositions.

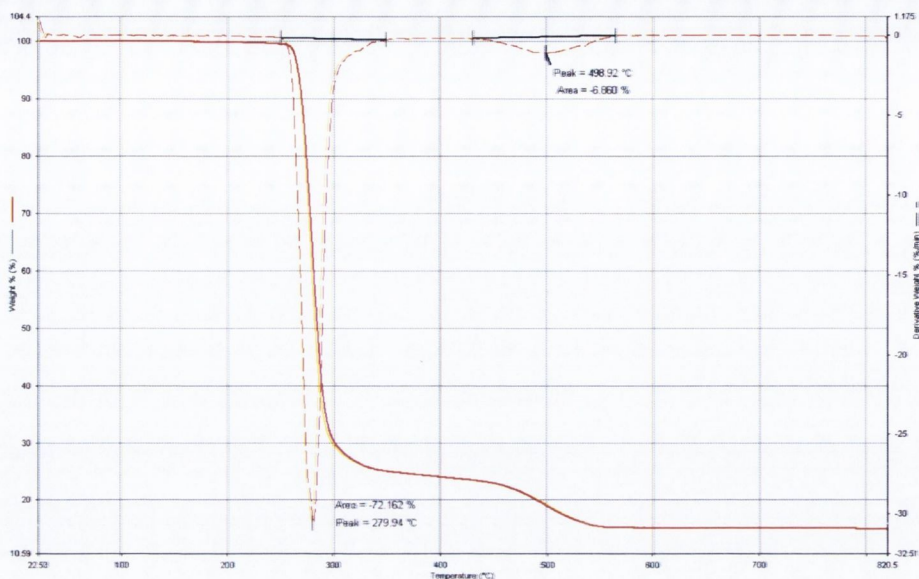


Figure 3.29: TGA curve (red line) for compound **10**. Dashed line is the derivative of the curve.

3.3.7: Iso-structural [Zn^{II}(adip)(bpy)] compound

Under a modified reaction condition, the iso-structural compound [Zn^{II}(H₂adip)(bpy)] (**11**) was successfully synthesised under hydrothermal reaction conditions. The structural features are almost identical to those of **10** and the minor differences in the coordination environments can be attributed to the slightly increased radius of the Zn(II) ion (Table 3.7).

Table 3.7: Selected bond lengths and angles of the iso-structural compounds **10** and **11**.

Atoms	Distances (Å)/Angles (°) in 10	Distances (Å)/Angles (°) in 11
M(1)–O(1)	1.996(1)	2.090(1)
M(1)–O(3)	1.949(1)	2.004(1)
M(1)–O(2')	2.178(1)	2.016(1)
M(1)–N(2)	2.005(2)	2.121(1)
M(1)–N(3)	2.015(2)	2.121(1)
O(1)–M(1)–N(3)	162.41(1)	157.25(1)
O(3)–M(1)–N(2)	171.55(1)	164.60(1)
O(2')–M(1)–O(1)	91.09(1)	92.40(1)
O(2')–M(1)–O(3)	92.65(1)	97.00(1)

3.3.8: Analysis of the magnetic properties of [Cu^{II}(adip)(bpy)]

The magnetic susceptibility of **10** was studied from 300 to 1.8 K at 1,000 Oe. The χT vs T plot remains constant between 300 and 20 K at $0.41 \text{ cm}^3 \text{ K mol}^{-1}$ and then increases slowly at lower temperatures to reach $0.44 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K (Fig. 3.30). This feature is indicative of paramagnetic behaviour, with weak ferromagnetic interactions. Fitting the data with a Curie-Weiss law leads to $C = 0.42(1) \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = +0.11(1) \text{ K}$. The Curie constant obtained is in good agreement with the expected value of one independent Cu^{II} $S = \frac{1}{2}$ centre (g value of 2.12). The 1D polymer structure in **10** can be viewed as a regular chain with single *syn-anti axial-equatorial* carboxylate bridges between Cu(II) metal ions. Based on this structural analysis, a chain model of ferromagnetically coupled $S = \frac{1}{2}$ Heisenberg spins⁽¹⁷⁰⁾ ($H = -2J \sum S_i S_{i+1}$) was used to fit the magnetic susceptibility and to obtain the magnetic interaction, J , between the Cu^{II} ions.

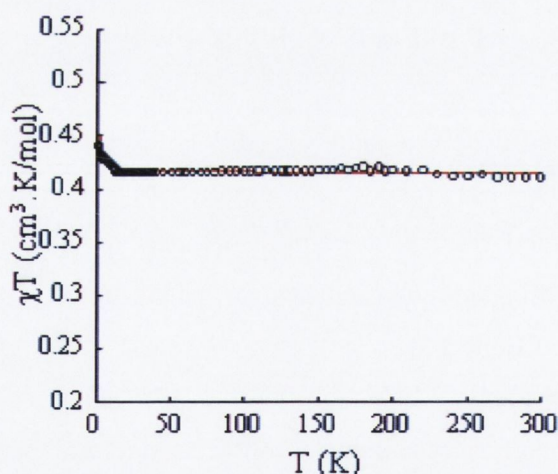


Figure 3.30: Temperature dependence of the magnetic susceptibility measured at 1,000 Oe for **10** (normalised per one Cu^{II} ion). The solid red line indicates the best fit using the $S = \frac{1}{2}$ chain model.

The interaction parameter obtained, $J/k_B = +0.04(1)$ (with $g = 2.11(2)$) is in good agreement with the proposed model, and also with comparable 1D chain structures that reveal similar *syn-anti axial-equatorial* carboxylate bridging modes.^(161,171-172)

3.4. Summary and Conclusions

In our continuous endeavour to generate novel coordination compounds, with the intention of synthesising materials capable of displaying interesting magnetic properties, the implementation of the amendments previously described was vindicated. The addition of 2,2'-bipyridine as a co-ligand to purposely “block” two sites of the coordination sphere of any metal centre, and consequently restrict compounds from forming higher dimensional coordination compounds, proved successful. The repeated modification of the ligand-types used, i.e. the successive introduction of O-donors within the primary ligands proved advantageous for the stabilisation of new topologies. Progressively more intricate structural motifs, and a concurrent increase in the dimensionality *via* supramolecular interactions, were obtained. In addition, the exploitation of hydrothermal reaction conditions was highly effective in overcoming the solubility issues of the reactants in an aqueous environment.

We observed that iminodiacetic acid-substituted aromatic ligands, in the presence of bpy co-ligands, stabilise doubly-bridged di-nuclear coordination complexes. This unit characterises the structures of **4-9**. The di-nuclear species in **4** possesses additional association between the dimers through supramolecular interactions. Hydrogen bonding demonstrated the linking of discrete dimers along the crystallographic *c*-axis, whereas inter-molecular π - π stacking of the bpy molecules, revealed supplementary connections in the crystallographic *b*-direction. Despite a slightly altered ligand type (an aminodiacetic acid substituted salicylic acid as opposed to a benzoic acid) compound **5** displays a highly comparable structure to **4** in the context of its coordination environments and overall packing arrangement. The additional alcohol group partakes in intra-molecular H-bonds, however, this interaction did not yield significant advancement in our goals for generating high dimensional coordination complexes. TGA measurements were not undertaken on compounds **4** and **5**, as the temperature of decomposition of the dimer would not yield significant results. Coupled with the absence of solvent molecules (either coordinating or not coordinating) further highlighted its omission from detailed analysis.

Compound **6** consists of 1D coordination polymers that run parallel to the crystallographic *ac*-plane. Two symmetry independent cobalt(II) ions are linked together through the ADIP ligands, with the flexible iminodiacetic acid moiety chelating to Co(1), and the more rigid isophthalic functionalities coordinating to Co(2). Supramolecular interactions further characterised the 1D chains. Both intra- and inter-molecular π - π stacking contacts were observed, the latter of which produced a layering of distinct polymers. Complementing this, were intricate H-bond interactions that additionally linked the chains in all directions of space. TGA studies of **6** showed the initial loss of the solvent water molecules, followed by the coordinating H₂O ligands, with the eventual decomposition of the complex at *ca.* 330 °C. Iso-structural manganese (**7**), iron (**8**) and nickel (**9**) compounds were also generated.

An alternate form of 1D coordination polymer is realised in compound **10**. Here, the chain structure is composed of mono-nuclear units. Intra- and inter-molecular π - π stacking interactions occur, the latter of which connecting discrete strands along the crystallographic *a*-axis. Hydrogen bonds, involving the isophthalic acid moieties of the H₂adip²⁻ ligand, further connect distinct 1D strands in both the *b*- and *c*-directions. **10** maintains its structural integrity until ~ 250 °C. An iso-structural zinc equivalent (**11**) was also synthesised displaying analogous coordination and packing behaviour.

The observed magnetic properties of **6**, **8** and **9** result from antiferromagnetic interactions within the di-nuclear carboxylate-bridged SBUs and paramagnetic Curie behaviour of the partially hydrated transition metal ions that link the di-nuclear units into 1D coordination polymers. In the case of compound **10** the magnetic behaviour is characterised by very weak ferromagnetic interactions between the Cu^{II} centres. Both ferro- and anti-ferromagnetic responses were therefore achieved for polymers generated using the ADIP ligand.

Chapter 4

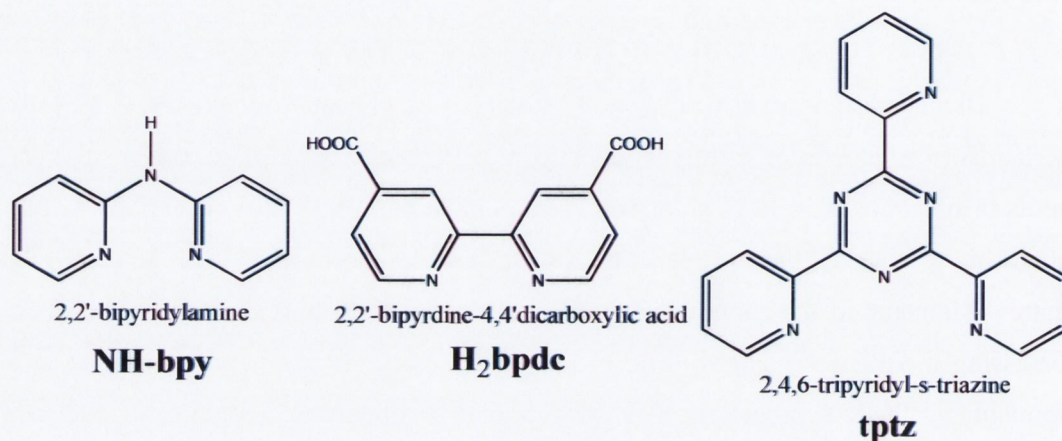
4.1: Alteration of the nitrogen-containing co-ligands

The alteration of the nitrogen-donating co-ligand was considered a possible mechanism for generating different supramolecular arrangements of observed structural motifs or obtaining a range of subtly different compounds which may potentially display interesting physicochemical properties e.g. porosity or magnetic exchanges between spin centres. Maintaining the aminodiacetic acid-substituted ligands, and utilising molecules possessing a similar binding ability to that of 2,2'-bipyridine was considered to be a promising synthetic approach for these objectives. As opposed to a comparable chelating ligand such as phenanthroline, these modified bpy-type ligands would be furnished with supplementary functional groups that could conceivably be used in the synthesis of higher dimensional products.

The three heterocyclic nitrogen containing co-ligands to be employed are shown in Scheme 4.1. The first of these alternative co-ligands is 2,2'-dipyridylamine (NH-bpy), which could feasibly chelate in a similar fashion to bpy, but contains a secondary amine group connecting the two pyridine rings. This additional functional group could have either H-bond donor or N-donor attributes associated with it. The second co-ligand is 2,2'-bipyridine-4,4'-dicarboxylic acid ($H_2bpd c$). We expected that this ligand would chelate through its N-donors in a typical bi-dentate mode, like bpy. However, the two additional carboxylic acid groups could conceivably act as neutral H-bond donor/acceptor entities, or as O-donor atoms in coordination bonds. Lastly, we decided to explore 2,4,6-terpyridal-s-triazine (tptz) as a co-ligand. This molecule has two possible conformations depending on the bond rotation of the three outer pyridine rings. In one case it can simultaneously bind as a terpyridine, bpy and a lone N-donor moiety (as illustrated in Scheme 4.1), or conversely as a tri-2,2'-bipyridine motif, determined by the conformation of the outer rings.

All three co-ligands contain a minimum of two aromatic rings, so the capacity for π - π stacking contacts has been preserved. However, we primarily expected the auxiliary

functional groups to engage in various bonding modes resulting in alternative network structures. To overcome any solubility issues, hydrothermal reaction conditions were again employed.



Scheme 4.1: The three alternative co-ligands used to generate new network structures.

4.1.1: Compound [Cu^{II}(H₂adip)(NH-bpy)] (12)

Under a virtually identical synthetic procedure to that of compound **10**, the compound [Cu^{II}(H₂adip)(NH-bpy)] (**12**) was successfully synthesised. Blue/green plates crystallise in the monoclinic crystal system in the space group $P 2_1/c$. The asymmetric unit contains one H₂adip²⁻ ligand, one 2,2'-dipyridylamine co-ligand (NH-bpy herein) and one copper(II) ion. The coordination polyhedron displays a distorted square pyramidal arrangement that is almost identical to that observed in **10**. Again, carboxylate O-donors from the iminodiacetic acid functionality of the ADIP ligand coordinate within the basal plane of the square pyramid, whilst the NH-bpy unit chelates to the two remaining sites. As in **10**, the coordination sphere is completed by a symmetry-generated oxygen atom, O(2'), which arises from a carboxylate group of an adjacent H₂adip²⁻ ligand. Symmetry-generated equivalents are the result of the operation of a 2₁ screw axis which runs in the direction of the crystallographic *b*-axis, and link the copper(II) ions through coordination bonding into a 1D polymer (Fig. 4.1a). Coordination bond lengths

involving the O-atoms of the bi-dentate iminodiacetic carboxylate groups are 2.001(1) Å and 1.986(1) Å long for the Cu(1)–O(1) and Cu(1)–O(3) bonds, respectively. The NH-bpy moiety displays Cu(1)–N(2) and Cu(1)–N(3) bond lengths of 2.004(1) Å and 2.009(1) Å, respectively, and finally the symmetry-generated O-donor forms a Cu(1)–O(2') bond which is 2.186(1) Å long (Fig. 4.1b). The coordination bonds lengths are approximately equal to those of compound **10**; however, there is a slight increase in the bond lengths involving the three O-donor atoms and a slight contraction in the bond lengths involving the N-donor atoms.

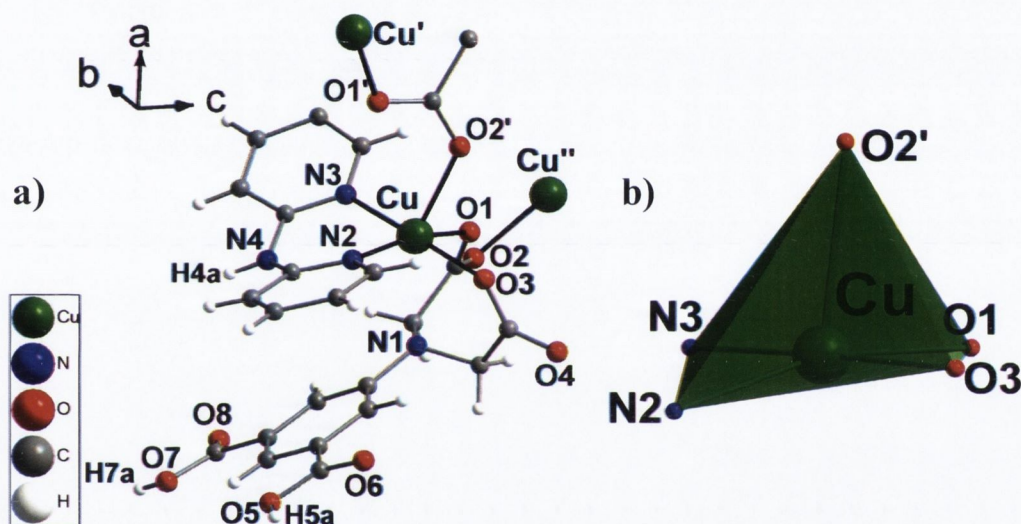


Figure 4.1: a) Coordination environment of the copper(II) ion in **12** highlighting the binding modes of $\text{H}_2\text{adip}^{2-}$ and NH-bpy ligands and b) polyhedral representation of the square pyramidal coordination environment of Cu(1). (Prime refers to symmetry-generated atoms.)

The bond angles within the coordination sphere of the copper(II) ion in **12** are, in general, consistent to those observed in **10** (Table 4.1). However, there are some noteworthy distortions that characterise the Cu(1) ion. Within the equatorial plane, as portrayed in Figure 4.1b, the O(1)–Cu(1)–N(2) bond angle of $165.16(1)^\circ$ deviates significantly from an ideal angle of 180° . The O(2')–Cu(1)–N(2) bond angle of $110.23(1)^\circ$ shows a notable variation from an ideal angle of 90° also. There is, however, an interesting disparity between compounds **12** and **10** relating to the two chelating N-

donor atoms. The Cu(1)–N bonds in **12** produce a N(2)–Cu(1)–N(3) angle of 88.69(1)°, whilst the corresponding angle for the bpy entity in **10** is 80.55(1)°. This variance can be attributed to the greater flexibility associated with the NH-bpy co-ligand, whose coordination behaviour is altered in comparison to the more rigid bpy ligand.

Table 4.1: Bond angles for the Cu(1) ion in compound **12**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)
O(1)–Cu(1)–O(2')	84.57(1)	O(1)–Cu(1)–O(3)	89.76(1)
O(1)–Cu(1)–N(2)	165.16(1)	O(1)–Cu(1)–N(3)	89.36(1)
O(2')–Cu(1)–O(3)	88.63(1)	O(2')–Cu(1)–N(2)	110.23(1)
O(2')–Cu(1)–N(3)	93.17(1)	O(3)–Cu(1)–N(2)	91.68(1)
O(3)–Cu(1)–N(3)	177.91(1)	N(2)–Cu(1)–N(3)	88.69(1)

The resulting 1D coordination polymer extends along the crystallographic *b*-axis (Fig. 4.2), whereby both ligand types coil around the metal ions to give a helical arrangement parallel to the crystallographic *b*-axis.

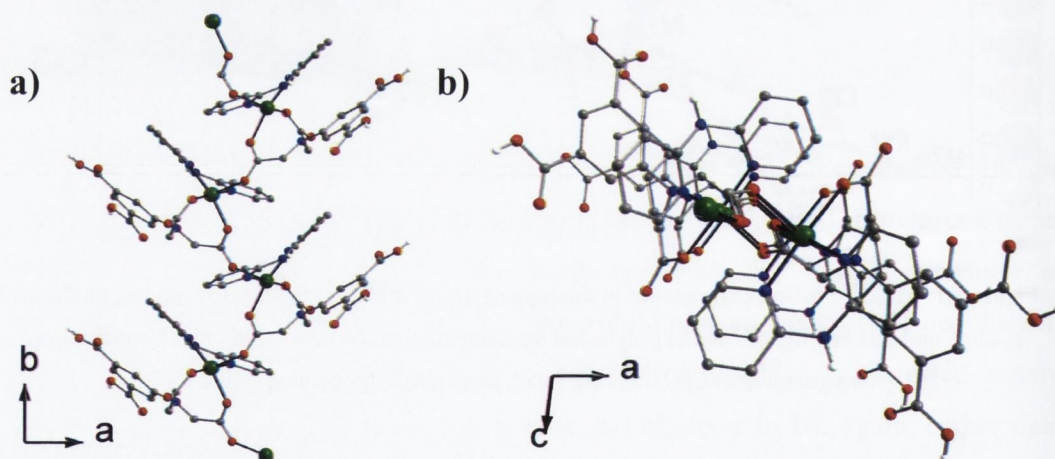


Figure 4.2: Views in the direction of the crystallographic a) *c*-axis and b) *b*-axis highlighting the spiral nature of the 1D polymer in **12**. All hydrogen atoms attached to C-atoms are removed for clarity.

The most significant distinctions between **12** and **10** transpire in the associated supramolecular interactions. The π - π stacking contacts differ considerably from those observed in the previously discussed assembly. With regards to intramolecular π - π

stacking, the ADIP ring interacts with one of the aromatic rings of the NH-bpy co-ligand (Fig. 4.3a). However, the ring systems do not replicate the eclipsed arrangement and the interaction is weaker than that observed in **10**. The mean distance between the two aromatic ring systems is 3.862(2) Å. Significant intermolecular π - π stacking contacts are not observed in **12** (mean distance *ca.* 5 Å). In spite of the absence of this interaction-type, there is still the occurrence of interdigitation of ligand moieties of adjacent 1D polymer chains (Fig. 4.3b). As in **10**, the COOH functionalities in the 1- and 3-positions of the aromatic ring of the ADIP ligand (isophthalic acid group) again protrude into the spatial grooves of adjacent 2₁ screws.

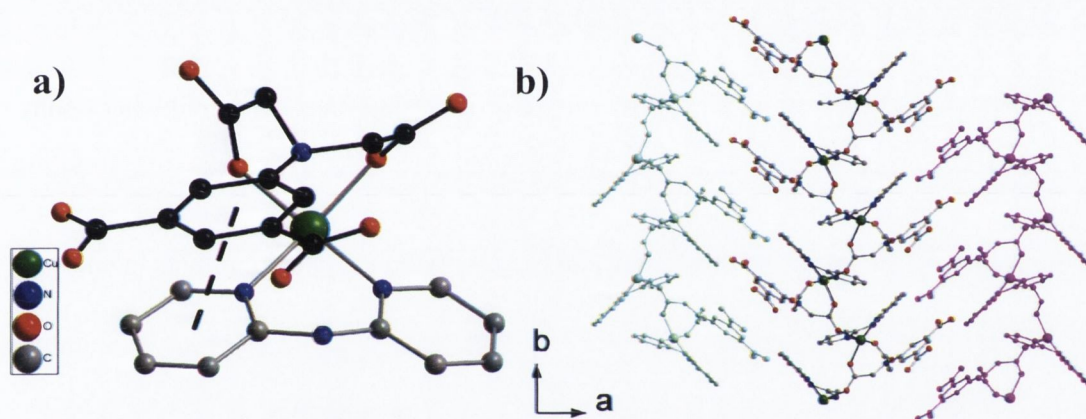
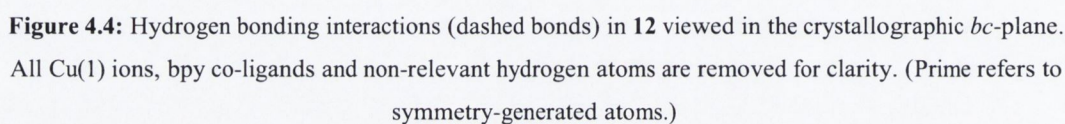
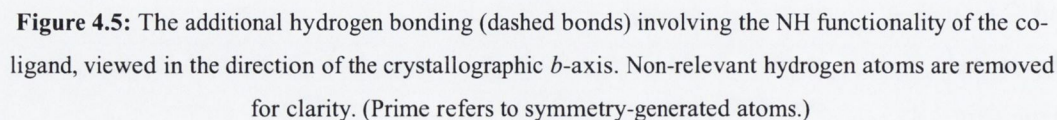


Figure 4.3: a) Intra-molecular π - π stacking interactions (dashed bonds) involving the phenyl ring of the $\text{H}_2\text{adip}^{2-}$ ligand and one aromatic ring of the NH-bpy co-ligand and b) interdigitation of ligand moieties of neighbouring 1D coordination polymers. All hydrogen atoms are removed for clarity.

Another distinguishing feature between **10** and **12** relates to the hydrogen bonds. Like **10**, the two isophthalic acid functionalities of the $\text{H}_2\text{adip}^{2-}$ ligand remain protonated, and engage in H-bonds akin to those previously described. Bond distances of 2.547(2) Å and 2.693(2) Å characterise the O(5)–O(4'') and O(7)–O(6') donor-acceptor distances, respectively, and result in a H-bonded network expanding along the crystallographic *bc*-plane (Fig 4.4).



The neutral NH-bpy co-ligand partakes in weak supplementary hydrogen bonds. A H-bond between the central secondary amine functionality and a neighbouring carboxylate atom occurs, revealing a N(4)–O(4') distance of 2.974(2) Å. Figure 4.5 highlights these interactions, which transpire parallel to the crystallographic *ac*-plane.



In summary, **12** is iso-structural to **10**. Mono-nuclear secondary building units extend into a 1D coordination polymer that aligns parallel to the crystallographic *b*-axis.

Slight geometrical differences arise between **10** and **12** from the substitution of the bpy co-ligands by the NH-bpy co-ligands. This modification manipulates the coordination sphere of the Cu^{II} ion, the π - π stacking interactions and also results in additional H-bonds involving the secondary amine functionality of the co-ligand. The overall network structure due to both the coordination bonding and H-bonding is shown in Figure 4.6.

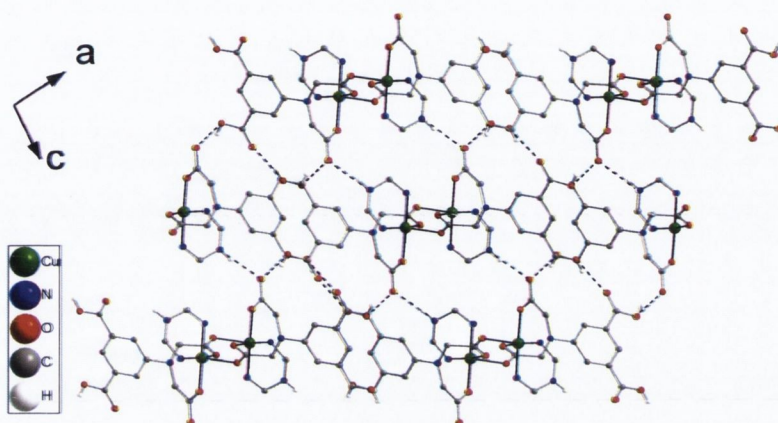


Figure 4.6: Depiction of the network arrangement in **12**. H-bonds (dashed bonds) link discrete 1D chains parallel to the crystallographic *ac*-plane. Hydrogen atoms attached to C-atoms and the majority of the NH-bpy co-ligands are removed for clarity.

4.1.2: Analysis of the magnetic properties of [Cu^{II}(adip)(NH-bpy)]

The magnetic properties of **12** were investigated. The magnetic susceptibility was measured from 300 to 1.8 K at 1,000 Oe. The χT vs T plot, shown in Figure 4.7, remains constant between 300 and 20 K at $0.44 \text{ cm}^3 \text{ K mol}^{-1}$ and then increases slowly below 20 K to reach $0.50 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. Fitting the data according to the Curie-Weiss law results in $C = 0.45(1) \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = +0.21(1) \text{ K}$. The obtained Curie constant is in good agreement with the expected value of one independent Cu^{II} $S = \frac{1}{2}$ centre with a g value of 2.17. The exchange parameter obtained from a 1D chain model ($H = -2J \sum S_i S_{i+1}$) is $J/k_B = +0.08(1)$ (with $g = 2.18(2)$). Like **10**, the data analysis is in agreement with weak ferromagnetic interactions between the Cu(II) centres mediated through carboxylate bridges with *syn-anti axial-equatorial* configuration. As expected from their

closely related structures, **10** and **12** exhibit very similar magnetic behaviours and exchange constants.

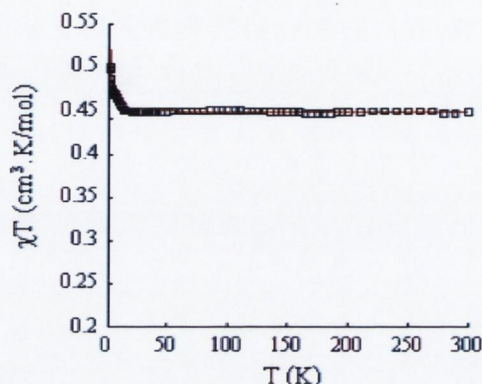


Figure 4.7: Temperature dependence of the magnetic susceptibility measured at 1,000 Oe for **12** (normalised per one Cu^{II} ion). The solid red line indicates the best fit using the $S = \frac{1}{2}$ chain model.

4.1.3: Compound [Cu^{II}(bpdc)(H₂O)₂] $\cdot$ 2H₂O (**13**)

In consecutive experiments we attempted to further vary the pyridine-based co-ligands and substituted bpy with 2,2'-bipyridine-4,4'-dicarboxylic acid (H₂bpdc). However, when we react the ADIP ligand with equi-molar ratios of copper nitrate and H₂bpdc under hydrothermal reaction conditions, only [Cu^{II}(bpdc)(H₂O)₂] $\cdot$ 2H₂O (**13**) is obtained in low yield. **13** crystallises as very small green plates in the orthorhombic crystal system in the space group *Pnna*. The asymmetric unit contains half a deprotonated 2,2'-bipyridine-4,4'-dicarboxylic acid ligand, a half occupied copper(II) ion, a coordinating water and a solvent water molecule. The distorted octahedral coordination environment of the Cu(1) centre is generated by symmetry-operations and is shown in Figure 4.8a. The two N-donors of the bpdc²⁻ ligand coordinate to two sites of the equatorial plane. The two remaining equatorial positions are occupied by discrete O-donor atoms from the carboxylate functionalities of two separate symmetry-generated ligands. Coordinating water molecules occupy the axial positions of the coordination sphere (Fig. 4.8b). Bond lengths of 2.009(6) Å characterise the Cu(1)–N(1) bond, whilst the carboxylate O-donor atoms form a Cu(1)–O(1) bond that is 1.958(5) Å long. The

axially coordinating water molecules generate Cu(1)–O(3) bonds which are 2.437(6) Å long. The Jahn-Teller effect accounts for the apparent elongation of the coordination bonds involving the H₂O molecules.⁽¹⁶⁴⁾

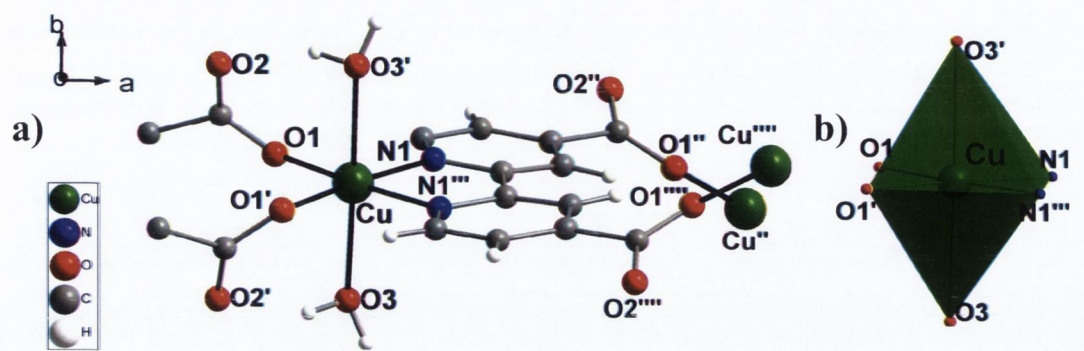


Figure 4.8: a) Coordination mode of the bpdC²⁻ ligands in compound **13** and b) polyhedral representation of the octahedral coordination environment of the Cu(1) ion. (Prime refers to symmetry-generated atoms.)

A brief examination of some of the bond angles further highlights the extent of the distortion contained within the coordination sphere of the copper(II) ion (Table 4.2). In the equatorial plane, as depicted in Figure 4.8b, the O(1)–Cu(1)–N(1'') bond angle is 174.31(2)°, while the chelation of the N-donor atoms results in a N(1)–Cu(1)–N(1'') angle of 80.80(3)°. Both angles show significant divergence from ideal angles of 180° and 90°, respectively. Furthermore, the O(1)–Cu(1)–O(3) bond angle of 84.87(2)° highlights additional distortions within the coordination sphere of Cu(1).

Table 4.2: Bond angles for the Cu(1) ion in compound **13**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)
O(1)–Cu(1)–O(1')	92.07(3)	O(1)–Cu(1)–O(3)	84.87(2)
O(1)–Cu(1)–O(3')	94.19(2)	O(1)–Cu(1)–N(1)	93.57(2)
O(1)–Cu(1)–N(1')	174.31(2)	O(1')–Cu(1)–O(3)	94.19(2)
O(1')–Cu(1)–O(3')	84.87(2)	O(1')–Cu(1)–N(1)	174.31(2)
O(1')–Cu(1)–N(1')	93.57(2)	O(3)–Cu(1)–O(3')	178.64(3)
O(3)–Cu(1)–N(1)	85.59(2)	O(3)–Cu(1)–N(1')	95.45(2)
O(3')–Cu(1)–N(1)	95.45(2)	O(3')–Cu(1)–N(1')	85.59(2)
N(1)–Cu(1)–N(1')	80.80(3)		

The described coordination behaviour whereby each Cu(1) centre is surrounded by three organic ligands that exclusively bind within the equatorial plane of the tetragonally elongated octahedron, results into a 2D coordination network structure that extends parallel to the *ac*-plane. Figure 4.9 illustrates this 2D coordination assembly and highlights the tri-dentate coordinating mode of each bpdc^{2-} ligand. Both the carboxylate groups of the ligands bind to independent Cu(1) centres, while the N-donor atoms chelate to separate Cu(II) ions.

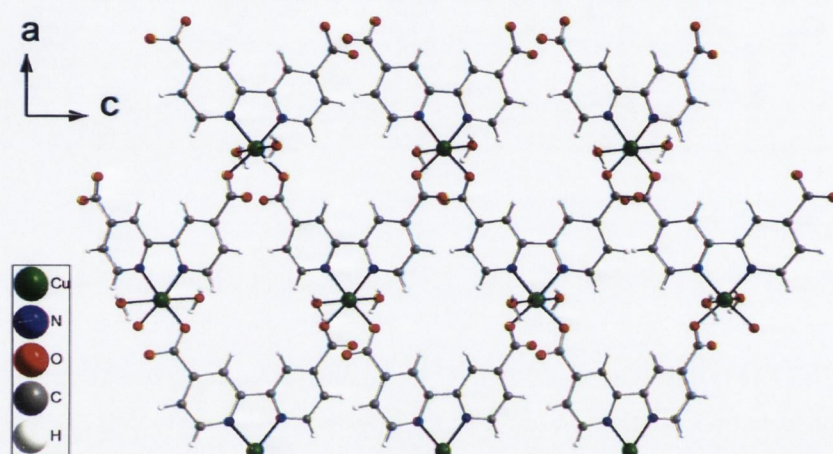


Figure 4.9: Depiction of the 2D sheet viewed in the crystallographic *ac*-plane, and demonstrating the tri-dentate coordinating capacity of the bpdc^{2-} ligand.

There are also hydrogen bonds to be discussed within **13**. Firstly, there is a hydrogen bond ($\text{O}(4)\text{--O}(2)$), between the solvent water molecule and a carboxylate oxygen atom which is $2.821(1)$ Å long. Secondly, each coordinating H_2O molecule has two H-bonds associated with it. In one case, it interacts with the just mentioned carboxylate atom resulting in an $\text{O}(3')\text{--O}(2)$ contact of $2.804(1)$ Å. The other H-bond occurs with a symmetry-generated coordinating water molecule of an adjoining 2D sheet, giving a $\text{O}(3')\text{--O}(3'')$ interaction distance of $2.806(1)$ Å. All three hydrogen bonds can be identified in Figure 4.10a. A view of the expanded H-bonded motif (Fig. 4.10b) highlights both the continuous H-bonding along the crystallographic *a*-axis, and also the connection of distinct 2D sheets in the crystallographic *b*-direction. The $\text{O}(3')\text{--O}(3'')$ interaction generates a stacking of unique sheets.

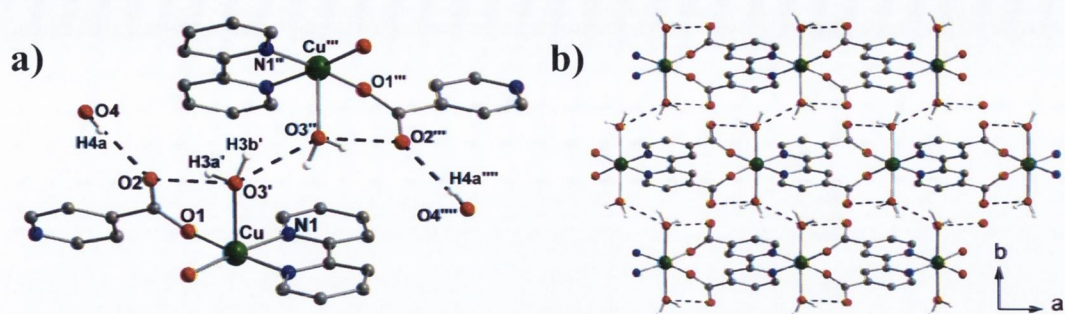


Figure 4.10: a) The hydrogen bonding (dashed bonds) contained in **13**, involving both the solvent and coordinated water molecules and b) the linkage of separate polymeric sheets along the crystallographic *b*-axis. Both a) and b) viewed in the crystallographic *c*-direction and hydrogen atoms attached to C-atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

To summarise, compound **13** can be classified as a 2D coordination network that extends along the crystallographic *ac*-plane. The observed topology is the result of the coordination mode and tri-dentate binding capacity of the bpdca^{2-} ligand. The linking of the individual sheets in the direction of the crystallographic *b*-axis occurs through hydrogen bonds (Fig. 4.11)

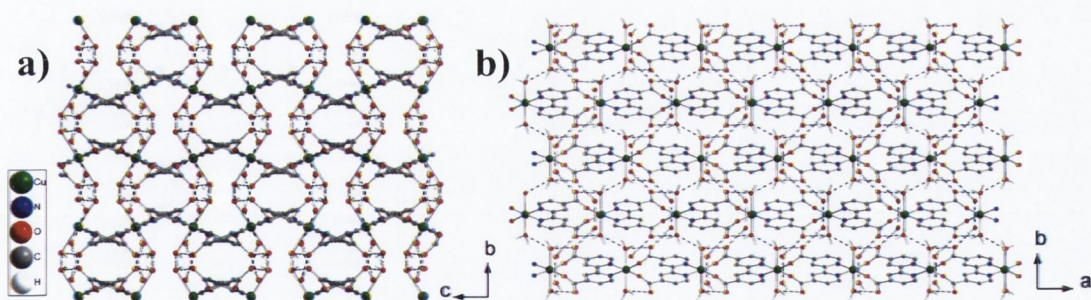


Figure 4.11: Views along the crystallographic a) *a*-axis and b) *c*-axis displaying the overall network arrangement in compound **13** with the hydrogen bond interactions highlighted as dash bonds.

4.1.3: Compound $[\text{Co}^{\text{II}}(\text{pyca})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**14**)

In order to investigate the coordinating potential of the tptz co-ligand, a broad range of modified experimental conditions were explored. Alterations to the reagent

ratios, hydrothermal temperatures and transition metal ion-type were applied, but these variations were not successful in obtaining good quality crystalline products. Nevertheless, a phase-pure crystalline material was eventually obtained *via* the hydrothermal treatment of an equimolar solution of cobalt(II) chloride and the ADIP and TPTZ ligands. Unexpectedly, the compound $[\text{Co}^{\text{II}}(\text{pyca})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ does not contain any of the used organic ligands, and in fact a decomposition product of the tptz co-ligand is the only substance that chelates to the cobalt(II) ion. **14** crystallises as small red shards in the monoclinic crystal system in the space group $P 2_1/n$. The asymmetric unit contains one deprotonated 2-pyridine carboxylic acid (pyca) ligand, a coordinating water molecule, a half occupied cobalt(II) centre and a solvent H_2O molecule. A marginally distorted octahedral environment best describes the complete coordination sphere of the Co(1) ion, which is generated through a symmetry-operation, and is shown in Figure 4.12a. Within the monomeric complex two pyca ligands chelate *via* both O- and N-donor atoms to the central metal ion and occupy the equatorial positions. Axially positioned H_2O molecules complete the polyhedron (Fig. 4.12b).

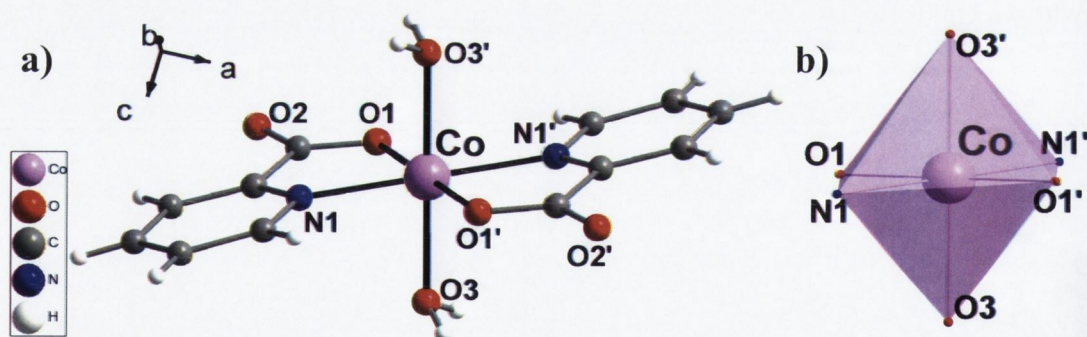


Figure 4.12: a) Coordination environment of the cobalt(II) centre in **14** and b) polyhedral representation of the octahedral coordination environment of the Co(1) ion. (Prime refers to symmetry-generated atoms.)

This complex has been previously reported,⁽¹⁷³⁾ and all coordination sphere geometries for the Co(II) ion bare a close resemblance to those cited. Table 4.3 lists the differences between compound **14** and those referenced, although no significant disparities occur.

Table 4.3: Geometric comparisons with literature for the Co(1) ion in compound **14**.

Atoms	Distances (Å)/Angles (°) in 14	Distances (Å)/Angles (°) according to literature ⁽¹⁷³⁾
Co(1)–O(1)	2.065(1)	2.062(2)
Co(1)–N(1)	2.122(1)	2.127(3)
Co(1)–O(3)	2.132(1)	2.140(3)
O(1)–Co(1)–O(1')	180.00(1)	180.0
O(1)–Co(1)–O(3)	90.82(1)	90.68(11)
O(1)–Co(1)–O(3')	89.18(1)	89.32(11)
O(1)–Co(1)–N(1)	79.20(1)	79.05(11)
O(1)–Co(1)–N(1')	100.80(1)	100.95(11)
O(1')–Co(1)–O(3)	89.18(1)	89.32(11)
O(1')–Co(1)–O(3')	90.82(1)	90.68(11)
O(1')–Co(1)–N(1)	100.80(1)	100.95(11)
O(1')–Co(1)–N(1')	79.20(1)	79.05(11)
O(3)–Co(1)–O(3')	180.00(1)	180.0
O(3)–Co(1)–N(1)	84.10(1)	84.10(12)
O(3)–Co(1)–N(1')	95.90(1)	95.90(12)
O(3')–Co(1)–N(1)	95.90(1)	95.90(12)
O(3')–Co(1)–N(1')	84.10(1)	84.10(12)
N(1)–Co(1)–N(1')	180.00(1)	180.0

Due to the encompassing nature of the tptz decomposition product, there are no further coordination bonds associated with **14** and as such, the product is a discrete monomer. Nonetheless, **14** is stabilised in the crystal structure by a collection of hydrogen bonds. The O(3) atom of the coordination water molecule forms a H-bond with a carboxylate oxygen atom (O(1'')) of a neighbouring unit, displaying a O(3)–O(1'') contact of 2.717(2) Å (Fig 4.13a). This value compares with that of 2.744(4) Å in the previously reported material. This H-bond and symmetry-equivalents connect mononuclear complexes in the crystallographic [010]-direction (Fig. 4.13b).

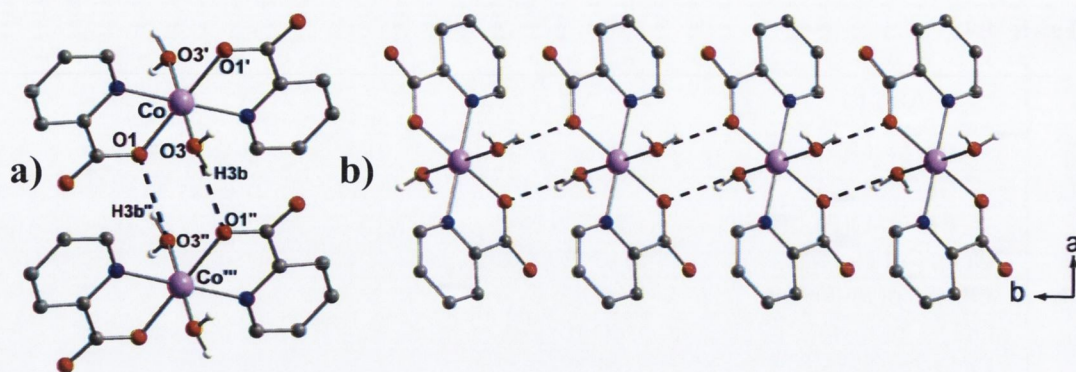


Figure 4.13: a) Hydrogen bonding interactions (dashed bonds) in compound **14** between the coordinated water molecule and an adjacent carboxylate oxygen atom linking two monomers and b) the recurrence of these H-bonds along the crystallographic *b*-axis. (Prime refers to symmetry-generated atoms.)

The coordinating water molecule participates in an additional H-bond with a lattice H₂O molecule, revealing a O(3)–O(4') distance of 2.780(2) Å, paralleling 2.78(4) Å formerly mentioned in the literature. This solvent water molecule, O(4'), in turn partakes in a two-fold hydrogen bond array to symmetry-generated atoms and these interactions can be viewed in Figure 4.14a. O(4') interacts with a non-coordinating carboxylate oxygen atom of an adjacent ligand, to give an O(4')–O(2''') contact of 2.681(2) Å (originally 2.697(5) Å). It further H-bonds to a symmetry-equivalent H₂O molecule resulting in an O(4')–O(4''') distance of 2.888(3) Å (contrasting 2.931(1) Å). This latter H-bond, involving both H₂O molecules, occurs parallel to the crystallographic *b*-axis. The O(4')–O(2''') H-bond, on the other hand, is directed approximately in the [001]-direction, and hence 2D H-bonded sheets are observed that expands along the crystallographic *bc*-plane (Fig. 4.14b).

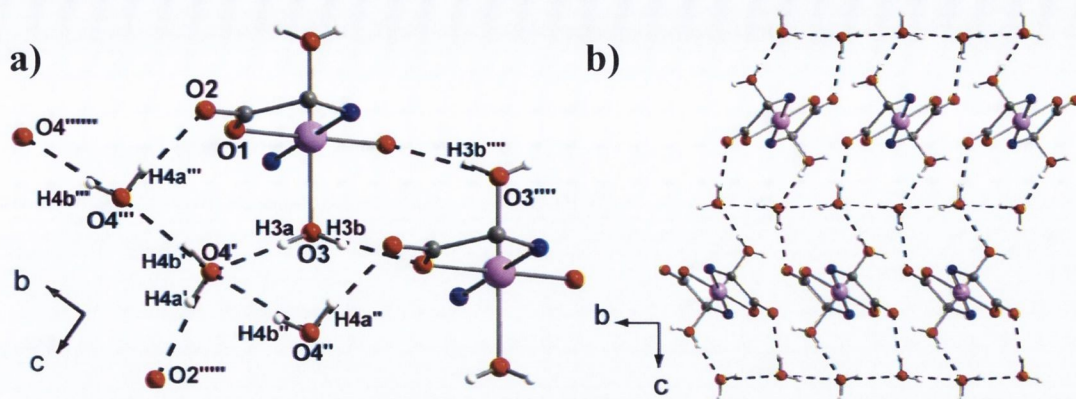


Figure 4.14: a) An illustration of all the hydrogen bonds (dashed bonds) in compound **14** and b) the ensuing 2D sheet expanding along the crystallographic *bc*-plane. Majority of the pyca ligand is removed for clarity. (Prime refers to symmetry-generated atoms.)

Compound **14** is a rather unremarkable monomeric cobalt(II) complex. Its structural motif is characterised by H-bonds associated with both the coordinating and solvent H_2O molecules. These generate a 2D H-bonded sheet that extends parallel to the crystallographic *bc*-plane. This assembly can be seen in Figure 4.15 along two crystallographic axes.

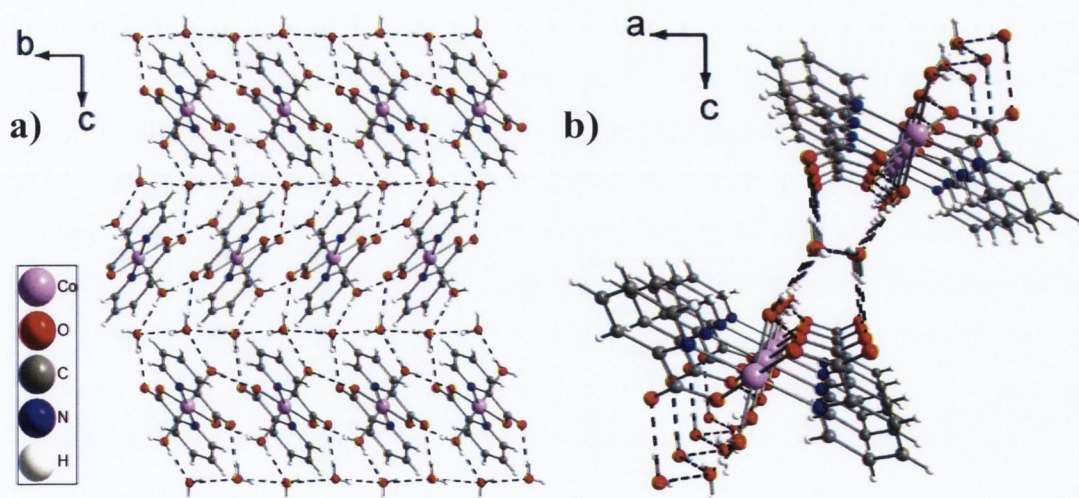


Figure 4.15: Views along the crystallographic a) *a*-axis and b) *b*-axis displaying the overall 2D H-bonded network arrangement in compound **14** due to the hydrogen bond (dash bonds) interactions.

4.2: Summary and Conclusions

In general, the alteration of the heterocyclic nitrogen containing co-ligand did, to a certain extent, prove constructive with the successful crystallisation and elucidation of the three compounds **12** to **14**. The outcome of only one out of the three products (compound **12**) retaining all three original predestined reactants was unanticipated.

When 2,2'-dipyridylamine is used as a co-ligand, $[\text{Cu}^{\text{II}}(\text{H}_2\text{adip})(\text{NH-bpy})]$ (**12**) forms. Its structure is very similar to **10**, where bpy coordinates as a co-ligand. The additional secondary amine group between both the pyridine rings in the NH-bpy ligand has no significant influence on the structure of the coordination compound. **12** contains 1D coordination polymers that align parallel to the crystallographic *b*-axis. **12** and **10** reveal slight differences in the coordination environment of the central Cu(II) ion. The most significant structural distinctions arise from the supramolecular interactions. In contrast to **10**, there are no inter-chain π -contacts present in **12**. An additional H-bond involving the NH-bpy co-ligand complements the H-bonds observed for the isophthalic acid functionalities directly affixed to the aromatic system of the ADIP ligand. The magnetic behaviour of **12** corresponds well with that of **10**, and the low-temperature properties are characterised by very weak ferromagnetic interactions between the metal centres. TGA analysis for **12** was forsaken due to the structural similarity with compound **10**, combined with anticipation of virtually identical measurements.

The BPDC co-ligand demonstrated the propensity to chelate to the Cu(II) ions in **13** in a highly effective manner occupying four of the six available octahedral sites. The two remaining (axial) positions are occupied by water molecules, and accordingly the ADIP ligand was prevented from binding. A 2D coordinating network forms, due to the tri-dentate binding mode of the bpdc^{2-} ligands. Hydrogen bonds associated with the H_2O molecules progress orthogonally to the coordination bonds stabilising 3D arrays in the crystal structure. This fortuitously synthesised compound is similar to a Cu(II) compound previously synthesised by a former colleague at Trinity College.⁽¹⁷⁴⁾ Both compounds display similar coordination geometries, yet, differ with respect to their overall packing motifs. Further extensive experiments using this H_2bpdc moiety as a

possible co-ligand was suspended, as it seems to preclude the binding of the aminodiacetic acid substituted ligands, owing to its efficient chelating capacity.

The cobalt monomer, compound **14**, arose from the hydrothermal decomposition of the tptz co-ligand with the resultant residue (2-pyridine carboxylic acid) chelating to a Co(II) ion. This product has previously been synthesised, however, the authors had used 2-picolinic acid as a starting reagent and performed an alternative synthetic method.⁽¹⁷³⁾ Nevertheless, analogous structural features and coordination environments were present in the $[\text{Co}^{\text{II}}(\text{pyca})_2(\text{H}_2\text{O})_2]$ complex. Hydrogen bonds involving both coordination and lattice water molecules link the complexes into 2D H-bonded sheets that extend along the crystallographic *bc*-plane. Supplementary analysis of the compound with respect to TGA and magnetic measurements was not explored. Similarly, the exploitation of the tptz co-ligand was discontinued due to its low stability under hydrothermal conditions and decomposition in the presence of other transition metal ions.

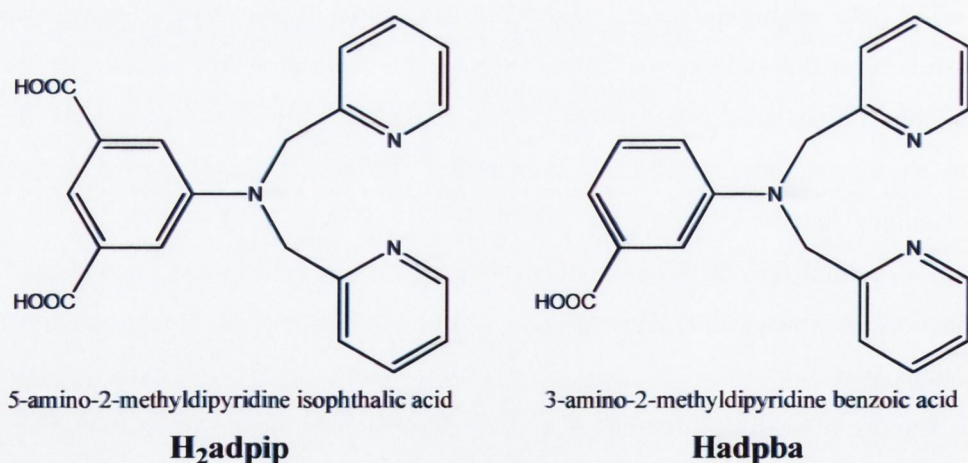
4.3: Compounds containing the amino-dipyridine substituted ligands

The use of iminodiacetic acid substituted ligands has so far proven to be successful, with the synthesis of an assortment of differing types of compounds. In general, the iminodiacetic acid functional group effectively chelates in a tri-dentate fashion to the various metal centres. Altering the number and/or position of the supplementary functionalities of the ligand, i.e. the carboxylic acids, led to a diverse range of structural motifs. Mono-nuclear compounds, discrete dimers, and several 1D coordination polymers were generated. All compounds display intricate supramolecular interactions as well.

The use of the bipyridine co-ligand as a designated “blocker” of coordination sites provided us with a tool to influence the dimensionality of the coordination compounds. The various iminodiacetic acid substituted ligands, in combination with the bpy ligand resulted in the synthesis of low dimensional coordination compounds, as expected.

During the course of our investigations we shifted the focus of the work, and it was decided to replace the amino-diacetic acid functionality, with an amino-dipyridine group. This potentially tri-dentate functionality, together with carboxylic acids affixed to the central aromatic ring system, would yield an interesting ligand alternative to those described in the previous chapters (Scheme 4.2). The heterocyclic groups of this ligand maintain a high chelating capability whilst the supplementary O-donor groups provided by the carboxylic acids may promote additional coordination bonds to produce network structures. The aim of this ligand modification was to synthesise compounds with interesting molecular magnetic attributes. It has previously been shown that Fe(II) complexes with a $\{N_6\}$ coordination sphere can demonstrate spin crossover phenomena.⁽¹¹⁵⁾ Two of these imino-dipyridine functionalities simultaneously encompassing a iron(II) centre, would comply with this condition.

We exploited both the 5-amino-2-dimethyldipyridine isophthalic acid (H_2adpip) and the 3-amino-2-dimethyldipyridine benzoic acid ($Hadpba$) ligands as chelating agents. Both ambient and hydrothermal techniques were employed using a range of transition metal salts to optimise the generation of crystalline products. In order to ensure the sole chelation of the amino-dipyridine functionality, the bipyridine group was not used during any of the syntheses.



Scheme 4.2: The amino-dipyridine substituted ligands.

4.3.1: Compound 5-amino-2-dimethyldipyridine isophthalic acid (H_2adpip) (**15**)

Crystalline samples of 5-amino-2-dimethyldipyridine isophthalic acid (**15**) were obtained under hydrothermal reaction conditions. Small colourless shards were obtained while attempting to bind the ligand to Fe(II) ions. The ligand crystallises in the monoclinic crystal system in the space group $P 2_1/n$. This inadvertent result, however, allowed for the solid state investigation of the fully protonated compound, providing an insight into the stereochemical conformation of the ligand in the crystal structure. Figure 4.16 illustrates the ligand, and highlights the large displacement of the separate pyridine rings in the absence of any metal ion.

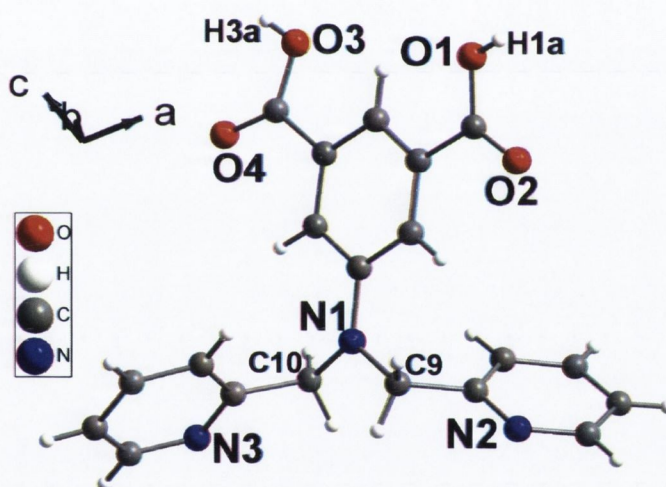


Figure 4.16: Structure of the H_2adpip ligand.

Both the carboxylic acids of the isophthalic moiety retain their hydrogen atoms. Their protonation gives rise to two types of hydrogen bonds within the compound, as shown in Figure 4.17a. The O(1)–N(2') H-bond is 2.673(3) Å long, and the O(3)–N(3'') H-bond reveals a similar length of 2.621(3) Å. Figure 4.17b reveals a continuous 1D H-bonded chain motif which extends within the crystallographic ac -plane, through the connection of discrete organic molecules, due to these H-bonds.

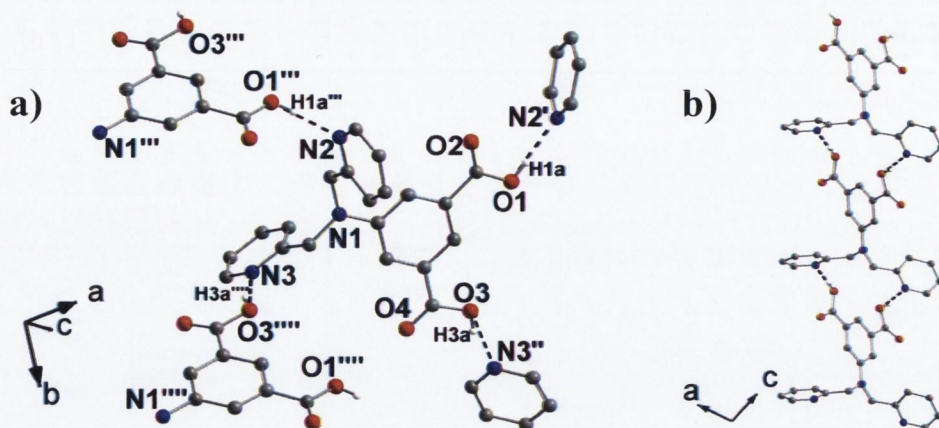


Figure 4.17: a) Representation of the two types of hydrogen bonds (dashed bonds) between the carboxylic acid groups and adjacent pyridine functionalities, and b) side-on portrayal of the resulting 1D H-bonded array. Non-relevant hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

Figure 4.18 depicts the overall structure in **15**. As a result of the two H-bonds, a continuous 2D hydrogen bonded assembly, which extends parallel to the crystallographic *bc*-plane, is formed.

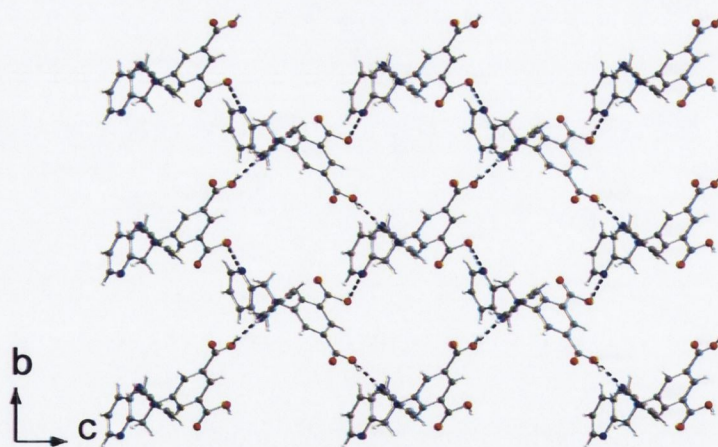


Figure 4.18: Depiction of the 2D H-bonded sheet in **15** that expands along the crystallographic *bc*-plane.

This H₂adpip ligand was reacted with a series of transition metal salts under hydrothermal, solvothermal and ambient reaction conditions. Despite a significant number of attempts, that also involved the variation of the ligand:metal ratio, crystalline

products suitable for X-ray diffraction were not obtained. Therefore, we decided to adjust the ligand-type and employ the slightly modified 3-amino-2-methyldipyridine benzoic acid as a complexing agent.

4.3.2: Compound $[\text{Cu}^{\text{II}}(\text{adpba})\text{Cl}]\cdot 3\text{H}_2\text{O}$ (**16**)

The compound $[\text{Cu}^{\text{II}}(\text{adpba})\text{Cl}]\cdot 3\text{H}_2\text{O}$ (**16**) was successfully crystallised as dark green blocks, and forms in an equi-molar aqueous solution of the Hadpba ligand and copper(II) chloride. The product crystallises in the monoclinic crystal system in the space group *Cc*. The asymmetric unit contains a copper(II) ion, a deprotonated adpba ligand, a coordinating chloride ion, two fully occupied and two half occupied water molecules. The coordination sphere of the copper(II) ion can be described as a distorted square pyramid, consisting of the tri-dentate iminodipyridine functionality and a symmetry-generated carboxylate atom from an adjacent adpba ligand. The chloride ion is situated at the apex of the square pyramid (Fig. 4.19a). The iminodipyridine functionality, chelating in a *meridonal* fashion, exhibits bond lengths of 2.041(3) Å, 1.990(3) Å and 1.988(3) Å for the Cu(1)–N(1), Cu(1)–N(2) and Cu(1)–N(3) bonds, respectively. The bond involving the symmetry-equivalent carboxylate atom, Cu(1)–O(1'), has a length of 1.919(2) Å, whilst the Cu(1)–Cl(1) bond is 2.615(1) Å long (Fig. 4.19b).

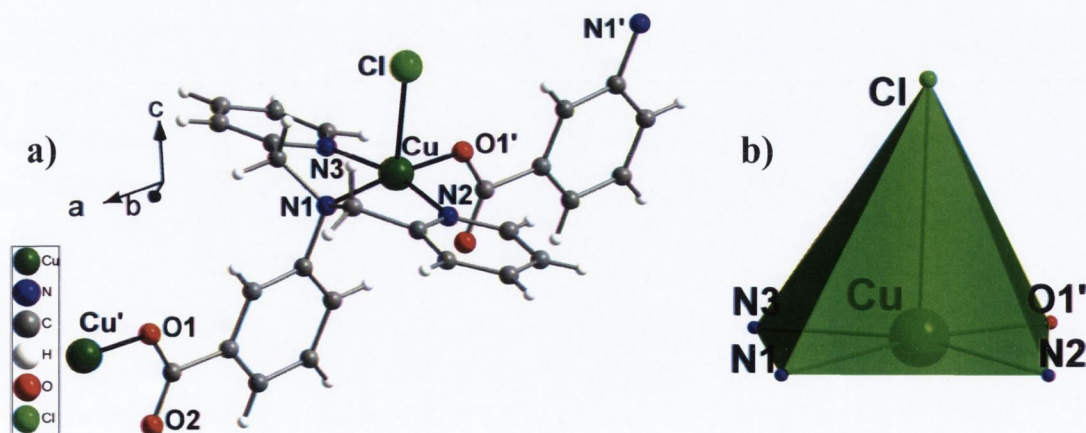


Figure 4.19: a) Portrayal of the binding mode of the adpba ligand and the Cu(II) ion environment in compound **16** and b) polyhedral representation of the coordination sphere of Cu(1).

The degree of distortion within the coordination environment of the Cu(1) ion can be investigated by examining particular bond angles. Within the basal plane, as shown in Figure 4.19b, the N(2)–Cu–N(3) bond angle of 163.75(1)°, exhibits a large deviation from an ideal angle of 180°. The corresponding N(1)–Cu–N(2) and N(1)–Cu–N(3) bond angles of 82.47(1)° and 82.16(1)°, respectively, also represent significant divergences from an ideal angle of 90°. Furthermore, the N(1)–Cu–O(1') bond angle, of 174.01(1)°, provides additional evidence of distortion. The remaining bond angles can be examined in Table 4.4.

Table 4.4: Bond angles for the Cu(1) ion in compound **16**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)
O(1')–Cu(1)–N(1)	174.01(1)	O(1')–Cu(1)–N(2)	96.98(1)
O(1')–Cu(1)–N(3)	97.76(1)	O(1')–Cu(1)–Cl(1)	90.30(1)
N(1)–Cu(1)–N(2)	82.47(1)	N(1)–Cu(1)–N(3)	82.16(1)
N(1)–Cu(1)–Cl(1)	95.69(1)	N(2)–Cu(1)–N(3)	163.75(1)
N(2)–Cu(1)–Cl(1)	93.25(1)	N(3)–Cu(1)–Cl(1)	93.50(1)

The benzoate and the iminodipyridine functionalities of the adpba ligand bridge between two symmetry related copper(II) ions. This bridging mode results in a 1D coordination polymer, as shown in Figure 4.20.

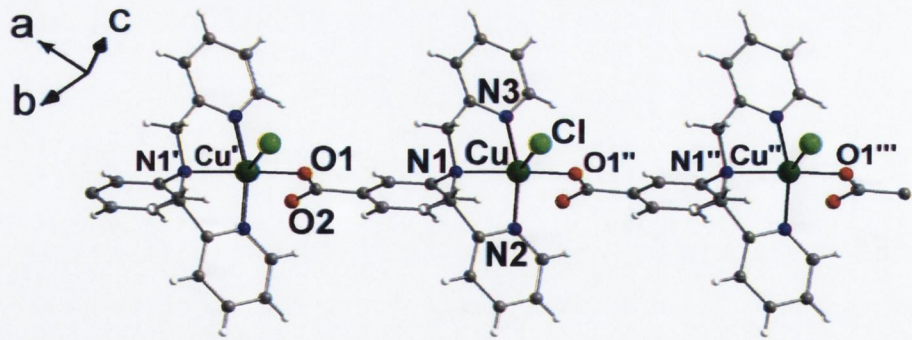


Figure 4.20: The 1D coordination polymer resulting from the linking of the Cu(II) ions through carboxylate and N-donor functionalities of the adpba ligands. (Prime refers to symmetry-generated atoms.)

Hydrogen bonding interactions involving the O(3) atom of the solvent H₂O molecule result in the connection of individual polymer chains, and this supramolecular

interaction can be seen in Figure 4.21. Firstly, there is a weak interaction involving the chloride ion which is characterised by a O(3)–Cl(1) distance of 3.360(3) Å. The second interaction involves the non-coordinating carboxylate atom, O(2') of an adjacent 1D polymer chain, resulting in a H-bond with a donor-acceptor distance of 2.722(1) Å.

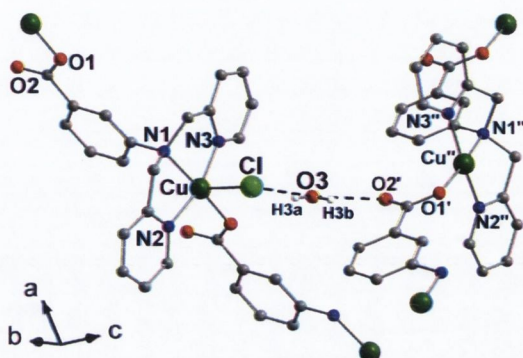


Figure 4.21: The linkage of 1D polymers in **16** via H-bonding (dashed bonds) involving a solvent water molecule. (Prime refers to symmetry-generated atoms.)

A repetitious H-bonded network results from the H-bonds concerning O(3). The resulting network structure that extends in three distinct directions can be viewed in Figure 4.22.

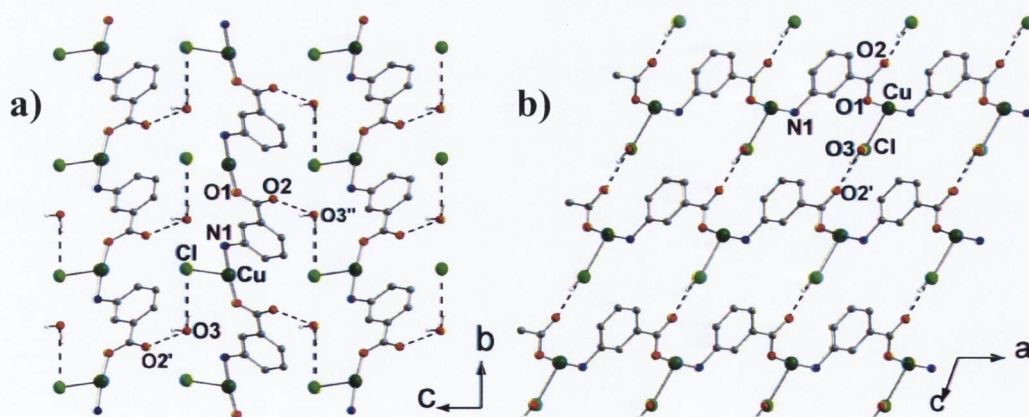


Figure 4.22: The extended assembly in **16** viewed in both the crystallographic a) *a*-axis and b) *b*-axis. This array is a result of the described H-bonds (dashed bonds) connecting separate 1D polymer chains. Portions of the ADPBA ligand are removed for clarity. (Prime refers to symmetry-generated atoms.)

The remaining H₂O molecules also participate in hydrogen bonds. Both O(4) and O(5) interact with chloride ions and symmetry-equivalents, resulting in O–Cl distances of 3.212(3) Å and 3.182(1) Å, respectively. Lastly, these same two water molecules also engage in H-bonds with the remaining lattice water molecule, O(6), displaying O(4'')–O(6'') and O(5')–O(6''') interaction distances of 2.794(1) Å and 2.761(1) Å, respectively. Figure 4.23 highlights these combined H-bonds, which generate H-bonded chains running in the crystallographic *c*-direction.

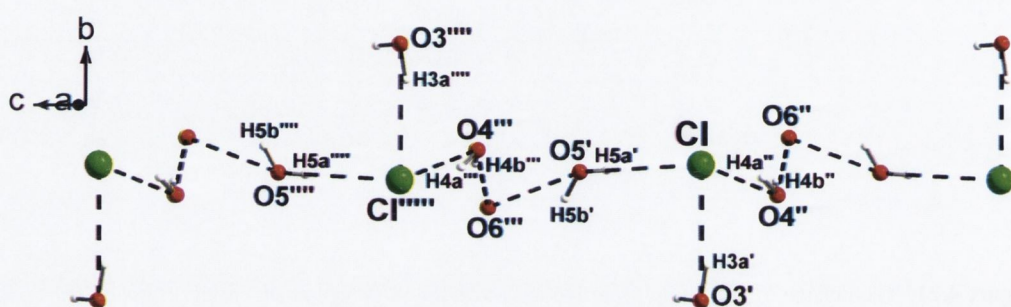


Figure 4.23: The additional H-bond interactions (dashed bonds) in **16** involving the solvent water molecules. ADPBA ligand and Cu(1) ions are removed for clarity. (Prime refers to symmetry-generated atoms.)

A simplified representation of compound **16** can be viewed in Figure 4.24. 1D coordination polymers (represented as extended Cu–Cu bonds) are linked *via* the described hydrogen bonds producing an intricate network structure.

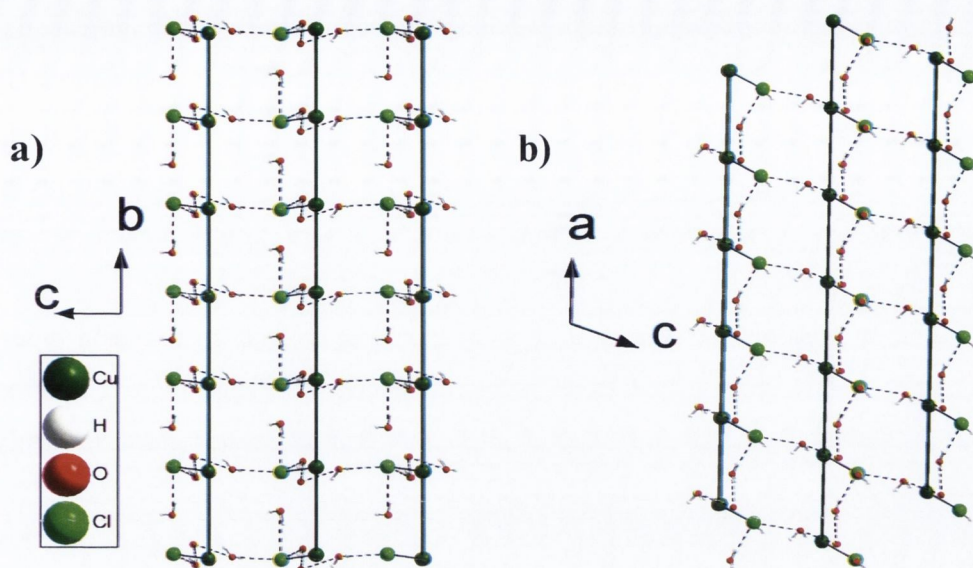


Figure 4.24: Illustration of the network motif in **16**. The 1D polymer chains (green linear connectors) are further connected due to the hydrogen bonding interactions (dash bonds) involving the H₂O water molecules and chloride ions. ADPBA ligand is removed for clarity.

4.4: Summary and Conclusions

The progression away from the effective iminodiacetic acid substituted ligands, and subsequent exploration of our alternative ligand-type, led to some interesting, yet limited, results. Our synthetic approach to combine two distinctive functional groups was achieved with the successful synthesis of the 5-amino-2-dimethyldipyridine isophthalic acid (H₂adpip) and the 3-amino-2-dimethyldipyridine benzoic acid (Hadpba) ligands. This resulted in a novel ligand-class, possessing both a chelating amino-2-dimethyldipyridine unit and auxiliary O-donor (COOH) groups.

A wide range of modifications to the experimental conditions were explored in an attempt to synthesise coordination compounds, using both ligand-forms. However, ensuing complexations with transition metal ions proved surprisingly challenging. The H₂adpip ligand, **15**, was inadvertently crystallised while attempting to bind the ligand with an iron(II) centre. Nevertheless, this result did reveal the spatial orientation of this

novel H₂adpip ligand in the solid state, which is characterised by some intricate H-bonding interactions. Exploiting the benzoic acid adaptation of the ligand resulted in a 1D polymer chain, when reacted with Cu(II) salts (**16**). The imino-dimethyldipyridine group chelates to a Cu(II) ion in an anticipated *meridonal* fashion, with the benzoate group additionally bridging between metal centres. The chains are further linked *via* an extensive array of H-bonds.

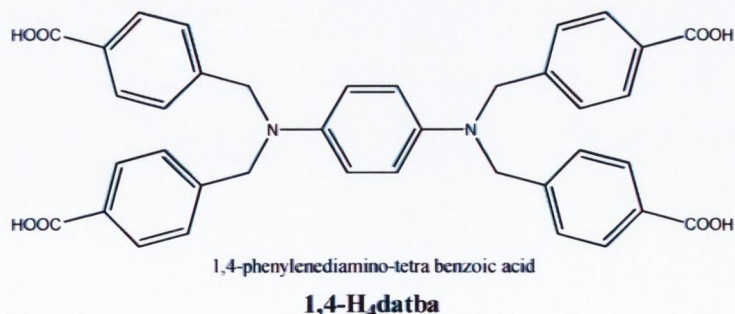
Ultimately, these restricted results led to the discontinuation of these ligand-types. Conversely, the belief that a vast range of amino-analogue ligand-types could be synthesised relatively easily, and a library of interesting complexes generated, is firmly maintained.

Chapter 5

5.1: Compounds containing the 1,4-phenylenediamino-tetra benzoic acid (1,4-H₄datba) ligand

The compounds discussed in the previous two chapters are low dimensional coordination compounds consisting of metal centres, polytopic organic linkers and “blocking” co-ligands. Intricate supramolecular interactions afford an increase in the dimensionality of all the described products and consequentially 2D or 3D network motifs are established. The magnetic characteristics of some of the 1D polymeric chain structures were investigated and yielded some interesting findings, with both ferro- and anti-ferromagnetic interactions observed depending on the metal ions used and the observed bridging modes.

Motivated by our desire to synthesise MOFs with open framework structures, that could potentially give rise to porosity, we modified the ligand structure. An alternative novel class of ligand-type was synthesised which deviates from the more compact ligands previously used (Scheme 5.1). This new type of ligand, 1,4-phenylenediamino-tetra benzoic acid (1,4-H₄datba), differs from the strongly chelating iminodiacetic acid substituted ligands employed thus far. The symmetry and rigidity associated with five phenyl rings endows this ligand type with a greater capacity for generating higher dimensional coordination compounds.



Scheme 5.1: The symmetric 1,4-H₄datba ligand used for the following results.

The ligand synthesis involves the condensation of *p*-chloromethyl-benzoic acid and 1,4-phenylenediamine under basic reaction conditions. The possibility of generating more extended ligand derivatives appears relatively straightforward as many aromatic amines are readily or commercially available. This process may provide a modular synthetic approach to a range of novel compounds whose topologies and characteristics are determined by the nature of the amine-backbone of the ligand.

Both hydro(solvo)thermal and ambient reaction conditions were used for optimising the crystallisation process to allow structural characterisation of any prospective compounds by single crystal X-ray diffraction studies. An extensive range of transition metal salts were used to maximise our probabilities in developing a library of compounds. The use of 2,2'-bipyridine (or bpy-type) co-ligands was suspended to ensure the sole coordination of the primary ligand to any metal centres.

5.1.1: Compound [(1,4-H₄datba)]·DMF (17)

The solvent adduct of the ligand 1,4-phenylenediamino-tetra benzoic acid, (1,4-H₄datba)·DMF (**17**), was serendipitously crystallised as very small pale yellow plates, while attempting to bind the ligand to Zn(II) ions under ambient reaction conditions in DMF:H₂O mixture (8:1, v:v ratio). **17** crystallises in the triclinic crystal system in the space group of *P*-1. The asymmetric unit contains a fully protonated H₄datba ligand and two half occupied DMF molecules. X-ray analysis demonstrates the stereochemical arrangement of the ligand in the solid state. Figure 5.1 displays the orientation of the ligand, and also highlights the symmetry associated with this *para*-substituted diamino benzene moiety.

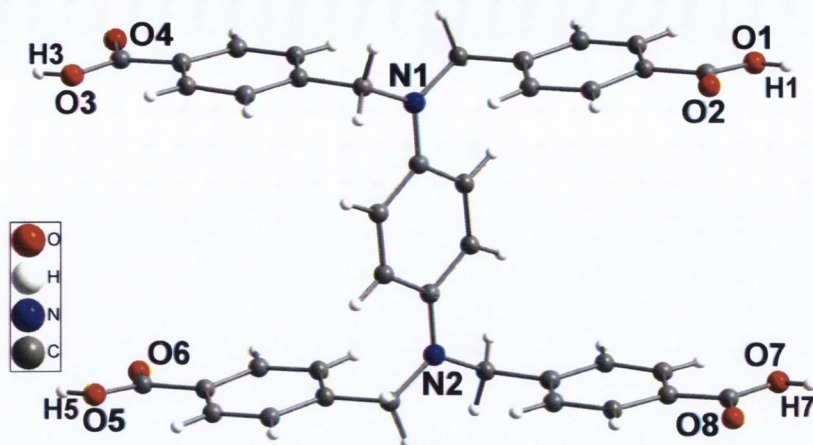


Figure 5.1: Structure of the 1,4-H₄datba ligand.

There are four distinct hydrogen bonds associated with the ligand, involving the four individual benzoic acid groups of the neutral ligand. Figure 5.2a illustrates the donor-acceptor behaviour between two neighbouring carboxylic acids of separate ligands. O–O contacts vary between 2.595(8) Å for O(3)–O(2') and 2.642(7) Å for the O(5)–O(8') interaction. A 1D ladder, extending along the crystallographic *c*-axis, is generated from the combined H-bonds (Fig. 5.2b).

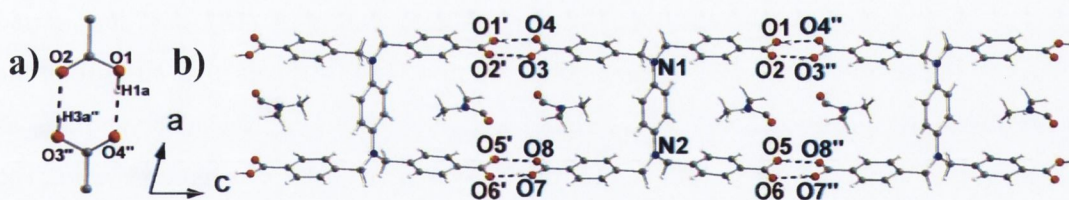


Figure 5.2: a) Donor-acceptor behaviour between adjacent COOH functionalities and b) the 1D H-bonded chain extending along the crystallographic *c*-axis with DMF molecules contained within the ladder motif.

(Prime refers to symmetry-generated atoms.)

Figure 5.3 reveals the overall structure of **17**. The distinct hydrogen bonded ladders stack in the crystallographic *b*-direction. Solvent DMF molecules are contained within the generated channels of the ladder motifs.

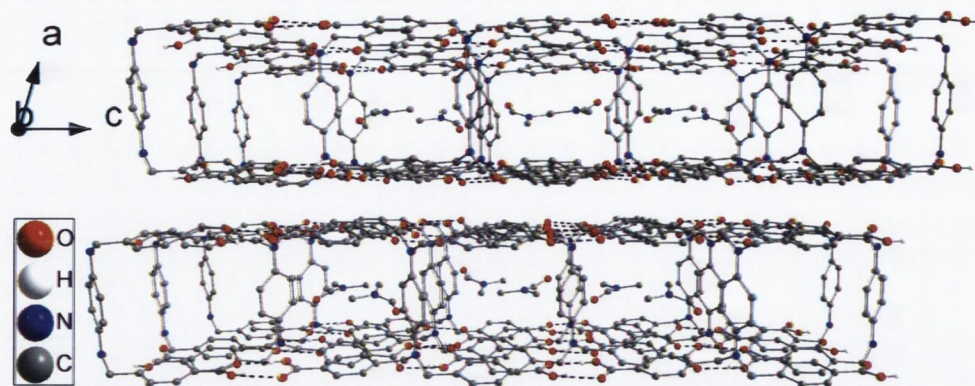


Figure 5.3: The overall array of **17** with the packing of independent 1D H-bonded chains yielding channels where the solvent DMF molecules reside.

Numerous attempts to bind this ligand with various transition metal ions under ambient reaction conditions were made, however, these efforts failed to yield crystalline materials suitable for single crystal X-ray analysis. Therefore, we decided to explore hydro- and solvo-thermal reaction conditions.

5.1.2: Compound $(\text{Me}_2\text{NH}_2)[\text{Co}^{\text{II}}_2(\text{CO}_2)(1,4\text{-datba})]\cdot 0.5\text{H}_2\text{O}$ (**18**)

The compound $(\text{Me}_2\text{NH}_2)[\text{Co}^{\text{II}}_2(\text{CO}_2)(1,4\text{-datba})]\cdot 0.5\text{H}_2\text{O}$ (**18**) was synthesised under solvothermal reaction conditions. **18** forms in a $\text{H}_2\text{O}:\text{DMF}$ reaction mixture of the 1,4- H_4datba ligand and cobalt(II) chloride tetrahydrate. The compound crystallises as dark purple blocks in the orthorhombic crystal system in the space group *Pnma*. The asymmetric unit contains two cobalt(II) ions, a fully deprotonated 1,4- datba^{4-} ligand, a half occupied solvent water molecule, a formate ion and a dimethyl ammonium ion. The latter two species were formed *via* the *in situ* hydrolysis of the DMF solvent. The two symmetrically independent cobalt(II) ions are bridged through the O-donors of the carboxylate moieties of the 1,4- datba^{4-} ligand and the formate ligands. Symmetry-equivalents generate 1D coordination chains that extend in the direction of the crystallographic *a*-axis. These chains are then further linked in alternate directions owing to the flexible nature of the 1,4- datba^{4-} ligand, resulting in an intricate 3D coordination

network. Figure 5.4 shows the extensive coordinating capacity of an entire DATBA moiety in two different crystallographic directions.

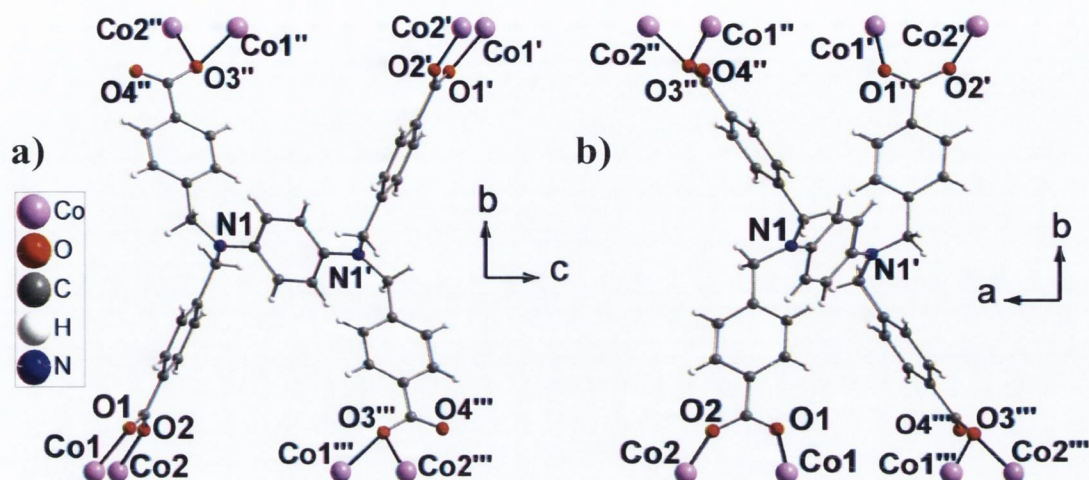


Figure 5.4: a) Portrayal of the comprehensive binding behaviour of the fully deprotonated 1,4-datba⁴⁻ ligand as viewed in the crystallographic *bc*-plane, and b) similar perspective along the *ab*-plane.

The aforementioned 1D chains are the result of complex bridging modes of the O-donors of the benzoate and formate moieties. These polymers expand along the crystallographic *a*-axis. The binding environments of the two symmetry independent metal ions are displayed in Figure 5.5a. Co(1) displays a slightly distorted octahedral coordination sphere, whilst the coordination environment of Co(2) is best described as a square pyramid. All the equatorial positions of both Co(II) coordination spheres are occupied by the oxygen atoms of the DATBA ligands, whereas the formate O-donors reside in all available apical positions. Co(1) and Co(2) are bridged by two symmetry related bi-dentate benzoic acid functionalities from two separate 1,4-datba⁴⁻ ligands. The Co(1)–O(1) and Co(2)–O(2) bond lengths are 2.042(3) Å and 2.007(3) Å, respectively. In addition, two benzoate O-atoms O(3) and O(3') simultaneously bind to both Co ions resulting in Co(1)–O(3) and Co(2)–O(3) bond lengths of 2.149(3) Å and 2.105(3) Å, respectively. With regards to the apically positioned formic acid O-atoms, the bridging O(5) atom exhibits Co(1)–O(5) bond lengths of 2.168(4) Å and Co(2)–O(5) bond lengths of 2.099(4) Å. The formic acid O-donor O(6) completes the octahedral coordination

sphere of Co(1) and forms a Co(1)–O(6) bond which is 2.141(5) Å long. The 1D chain assembly extending along the crystallographic *a*-axis can be viewed in Figure 5.5c.

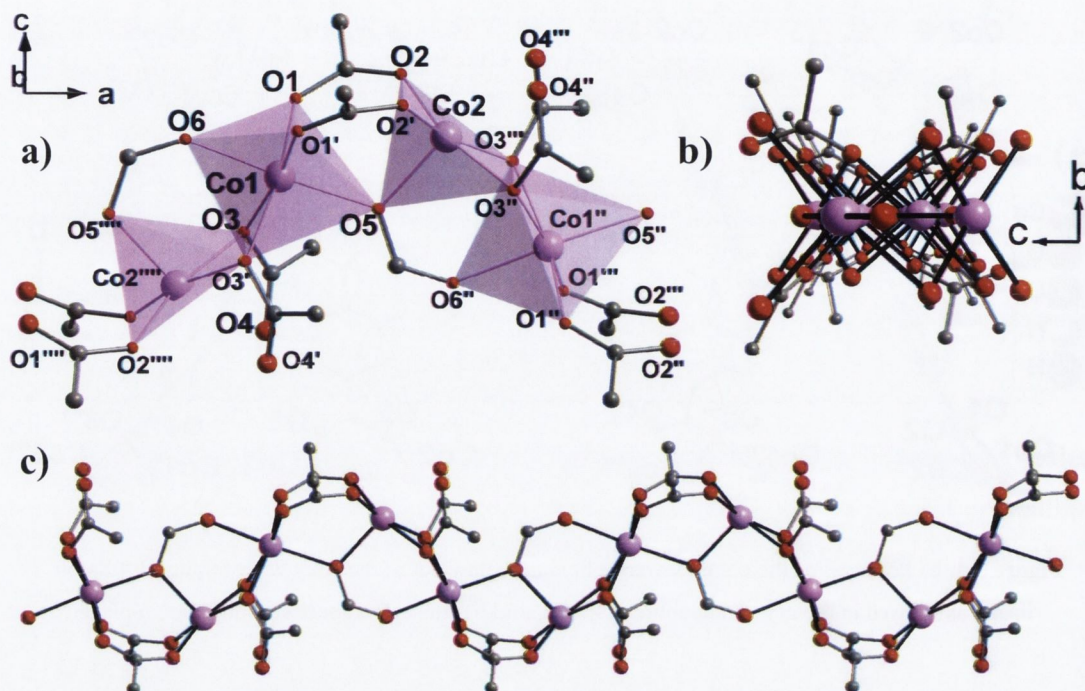


Figure 5.5: a) Depiction of the coordination environment of the Co^{II} ions and the bridging mode of the datba^{4-} ligands in **18**, with atoms O(5) and O(6) provided by the formate ligands, b) a view in the direction of the crystallographic *a*-axis highlighting the 1D chain and c) a side-on depiction of the resultant chain. Majority of the DATBA ligand is removed for clarity. (Prime refers to symmetry-generated atoms.)

Examining the bond angles highlights some of the deviations from expected ideal geometries. The largest divergence within the coordination sphere of Co(1) involves the O(1)–Co(1)–O(3') bond angle which is 167.52(1)°. Similarly in the equatorial plane, as depicted in Figure 5.5a, the O(1)–Co(1)–O(1') and O(3)–Co(1)–O(3') bond angles of 96.33(2)° and 78.09(2)°, respectively, deviate from the ideal angle of 90°. With respect to the Co(2) ion, the corresponding O(2)–Co(2)–O(3'') and O(3'')–Co(2)–O(3''') bond angles of 167.23(1)° and 80.04(2)° also show significant deviations from ideal square pyramidal angles. Tables 5.1 and 5.2 list all the geometric angles for both Co(II) metal centres.

Table 5.1: Bond angles for the Co(1) ion in compound **18**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)
O(1)–Co(1)–O(1')	96.33(2)	O(1)–Co(1)–O(3)	92.16(1)
O(1)–Co(1)–O(3')	167.52(1)	O(1)–Co(1)–O(5)	92.65(1)
O(1)–Co(1)–O(6)	85.21(1)	O(1')–Co(1)–O(3)	167.52(1)
O(1')–Co(1)–O(3')	92.16(1)	O(1')–Co(1)–O(5)	92.65(1)
O(1')–Co(1)–O(6)	85.21(1)	O(3)–Co(1)–O(3')	78.09(2)
O(3)–Co(1)–O(5)	96.09(1)	O(3)–Co(1)–O(6)	86.40(1)
O(3')–Co(1)–O(5)	96.09(1)	O(3')–Co(1)–O(6)	86.40(1)
O(5)–Co(1)–O(6)	176.79(1)		

Table 5.2: Bond angles for the Co(2) ion in compound **18**.

Atoms	Bond angle (°)	Atoms	Bond angle (°)
O(2)–Co(2)–O(2')	92.67(2)	O(2)–Co(2)–O(3')	92.57(1)
O(2)–Co(2)–O(3'')	167.23(1)	O(2)–Co(2)–O(5)	92.42(1)
O(2')–Co(2)–O(3')	167.23(1)	O(2')–Co(2)–O(3'')	92.57(1)
O(2')–Co(2)–O(5)	92.42(1)	O(3')–Co(2)–O(3'')	80.04(2)
O(3')–Co(2)–O(5)	98.98(1)	O(3'')–Co(2)–O(5)	98.98(1)

All four carboxylate groups of the 1,4-datba⁴⁻ ligand engage in coordination bonds with separate Co(II) ions (Fig. 5.4), and as a result each carboxylate functionality binds to distinct 1D chains which extend in the crystallographic *a*-direction. This intricate assembly results in a 3D metal-organic framework (MOF). Figures 5.6a and 5.6c illustrate the overall anionic network structure in **18**, with a view in both the crystallographic *a*- and *c*-axis, respectively. The framework is characterised by cavities that separate the cobalt chains and similarly run in the crystallographic *a*-direction. These channels (Fig. 5.6a) contain the dimethyl ammonium counterions and constitutional water molecules. The complex binding modes demonstrated by the ligands can be simplified somewhat (Figs. 5.6b and 5.6d). These arrays reveal the benzoic acid functionalities of the DATBA units interweaving between themselves.

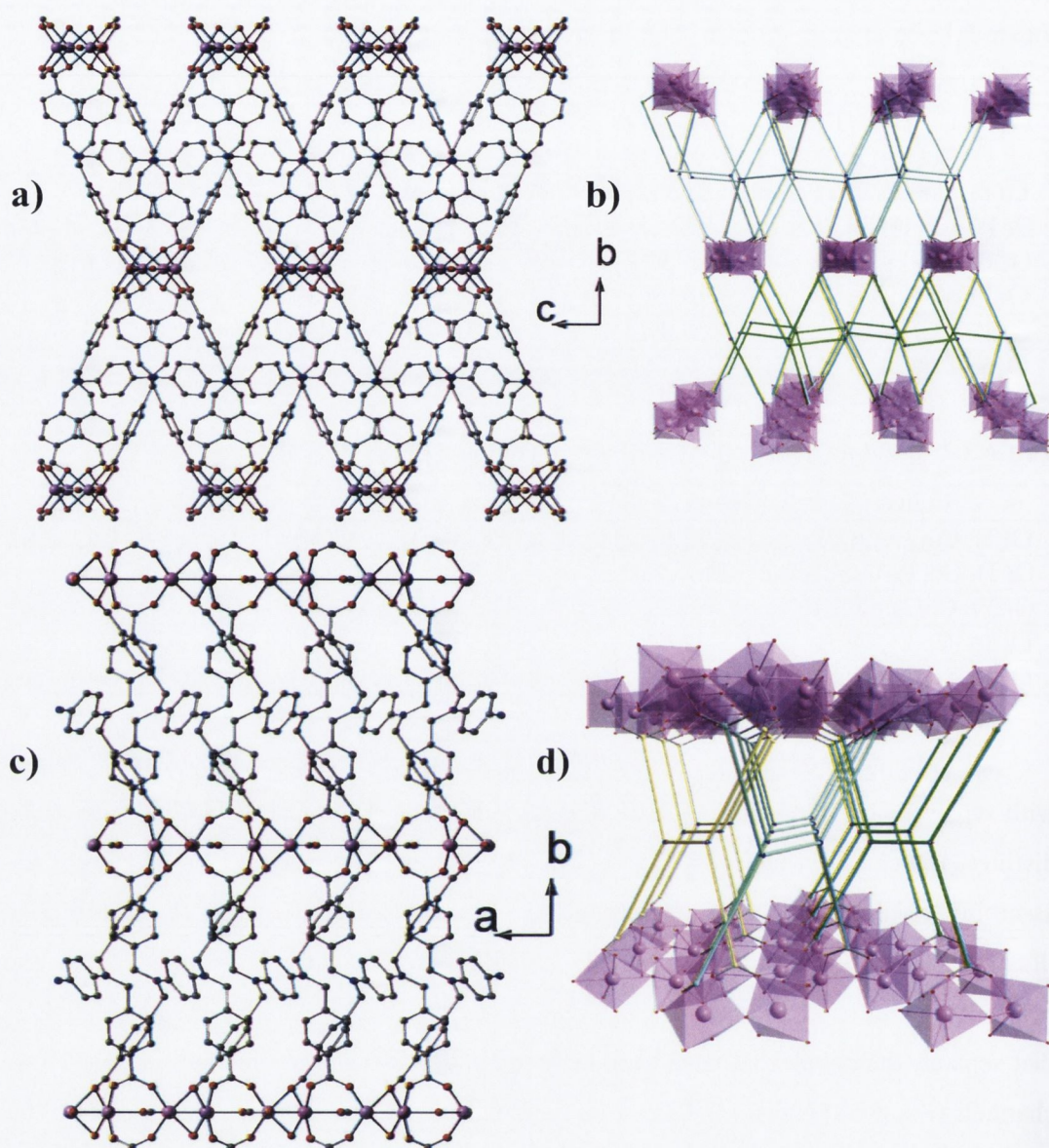


Figure 5.6: Network structure of **18** viewed in the crystallographic a) *a*-axis and c) *c*-axis. b) and d) are simplified depictions of the organic 1,4-DATBA ligands in the compound, with benzyl and central phenyl moieties of the ligand represented as linear connectors. All hydrogen atoms, counterions and solvent molecules are removed for clarity.

5.1.3: Thermal decomposition of compound **18**

Figure 5.7 reveals the TGA curve recorded upon the heating of polycrystalline samples of **18** in an air atmosphere. A gradual weight loss totalling 1.07% is observed between ambient temperature and approximately 100 °C. This is attributed to the removal of the water molecules contained within the cavities of the framework (calculated 1.05%). Subsequently, the curve shows no discernable features until ~ 340 °C, whereby a weight loss of 6.06% was recorded. This can be associated with the loss of the dimethyl ammonium counterions (calculated 5.43%). This is then followed by the gradual decomposition of the organic moiety in the compound, which occurs between 340 and ~600 °C. This thermogravimetric event, centred at ~ 470 °C, displays a weight loss of 64.49%. This corresponds to the combustion of all C, H and N atoms of the ligand (calculated 63.88%), resulting in the formation of metal oxides of various unknown compositions.

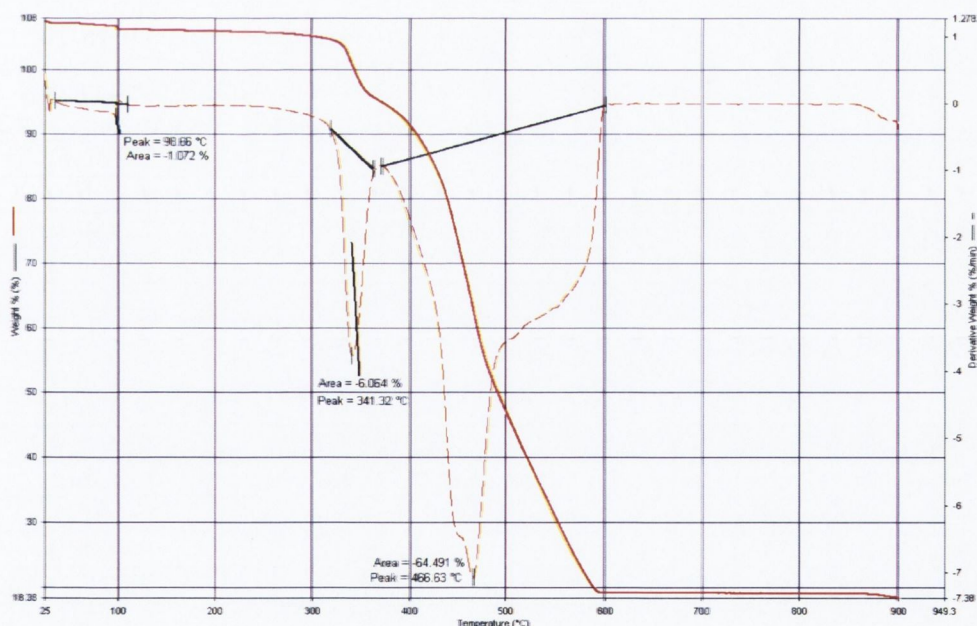


Figure 5.7: TGA curve (solid red line) of compound **18**. (Dashed line corresponds to the derivative of the TGA curve.)

5.1.4: Iso-structural (Me₂NH₂)[M^{II}₂(CO₂)(1,4-datba)]·0.5H₂O compounds (M = Mn, Cd)

The binding potential of this versatile 1,4-H₄datba ligand was further affirmed with the synthesis and structural elucidation of two iso-structural compounds. (Me₂NH₂)[Mn^{II}₂(CO₂)(1,4-datba)]·0.5H₂O (**19**) and (Me₂NH₂)[Cd^{II}₂(CO₂)(1,4-datba)]·0.5H₂O (**20**) were successfully synthesised under similar solvothermal reaction conditions to those used in the preparation of **18**. The three products, **18-20**, show similar crystallographic parameters, typical coordination environments (Table 5.3), IR spectra and the elemental analyses are in agreement with the assigned constitutions. These results confirm the isolation of the described 3D network incorporating transition metal ions with *d*⁵, *d*⁷ and *d*¹⁰ electron configurations. Surprisingly, both the first and the second row of the transition metals can be used to stabilise the described network structure in which 1D chains are interconnected through fully deprotonated organic ligands.

Table 5.3: Selected bond lengths and angles of the iso-structural compounds **18-20**.

Atoms	Distances (Å)/Angles (°) in 18	Distances (Å)/Angles (°) in 19	Distances (Å)/Angles (°) in 20
M(1)–O(1)	2.042(3)	2.160(11)	2.221(6)
M(1)–O(3)	2.149(3)	2.239(12)	2.314(6)
M(1)–O(5)	2.164(4)	2.285(15)	2.294(7)
M(1)–O(6)	2.141(5)	2.194(15)	2.285(8)
M(2)–O(2)	2.007(3)	2.096(11)	2.216(7)
M(2)–O(3)	2.105(3)	2.249(11)	2.341(7)
M(2)–O(5)	2.099(4)	2.195(20)	2.297(7)
M(1)–M(2)	3.583(1)	3.731(10)	3.748(1)
O(1)–M(1)–O(3)	92.16(1)	93.02(5)	92.04(3)
O(1)–M(1)–O(3')	167.52(1)	169.35(4)	167.36(2)
O(5)–M(1)–O(6)	176.79(1)	178.44(6)	174.53(3)
O(5)–M(1)–O(1)	92.65(1)	92.46(4)	98.00(2)
O(6)–M(1)–O(1)	85.21(1)	88.59(4)	85.71(2)
O(3)–M(2)–O(2')	92.57(1)	94.03(4)	94.13(3)
O(3)–M(2)–O(2'')	167.23(1)	170.78(4)	173.22(3)
O(3)–M(2)–O(3')	80.04(1)	77.90(5)	79.10(3)
O(5)–M(2)–O(3)	98.98(1)	94.98(5)	92.04(3)
M(1)–O(5)–M(2)	114.37(1)	112.78(3)	109.44(2)
M(1)–O(3)–M(2')	95.62(1)	97.37(3)	96.89(2)

Crystals of **19** that formed under solvothermal reaction conditions were quite small and heavily intergrown. As a result, a high-quality single crystal X-ray diffraction dataset was not obtained. However, X-ray powder diffraction experiments unambiguously confirmed that **19** is in fact iso-structural to **18**. Figure 5.8 shows the X-ray powder patterns of both **18** and **19**. The obtained powder patterns of both compounds were compared with a simulated pattern, based on their respective single crystal X-ray diffraction data.

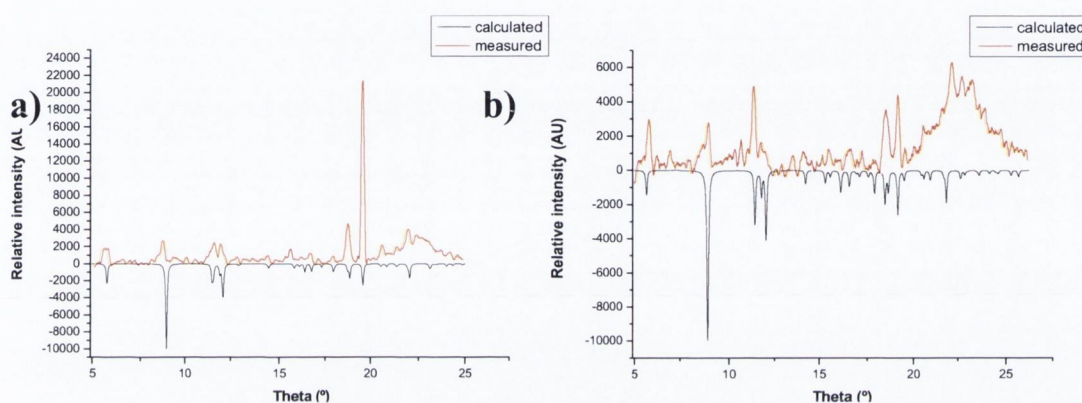


Figure 5.8: a) Powder pattern for compound **18**, and b) pattern for compound **19**.

18 and **19** have virtually identical IR spectra and can be seen in Figure 5.9a). Both spectra show strong signals due to the distinctive stretches associated with the carboxylate functionalities. **18** and **19** demonstrate comparable signals at ~ 1600 , 1515 , 1400 and ~ 1220 cm^{-1} . The last of these signals (1224 cm^{-1} for **18**, 1222 for **19**) corresponds to the C–O stretching mode of the carboxylate group. Lastly, the TGA curve of **19** shows an almost indistinguishable decomposition pathway to that of **18** (Fig. 5.9b). For **19**, the two main thermogravimetric events are centred at 345 and 480 $^{\circ}\text{C}$, as opposed to 340 and 470 $^{\circ}\text{C}$ in **18**. These events characterise the removal of the dimethyl ammonium counterions, followed by the combustion of all the C, H and N atoms of the ligand.

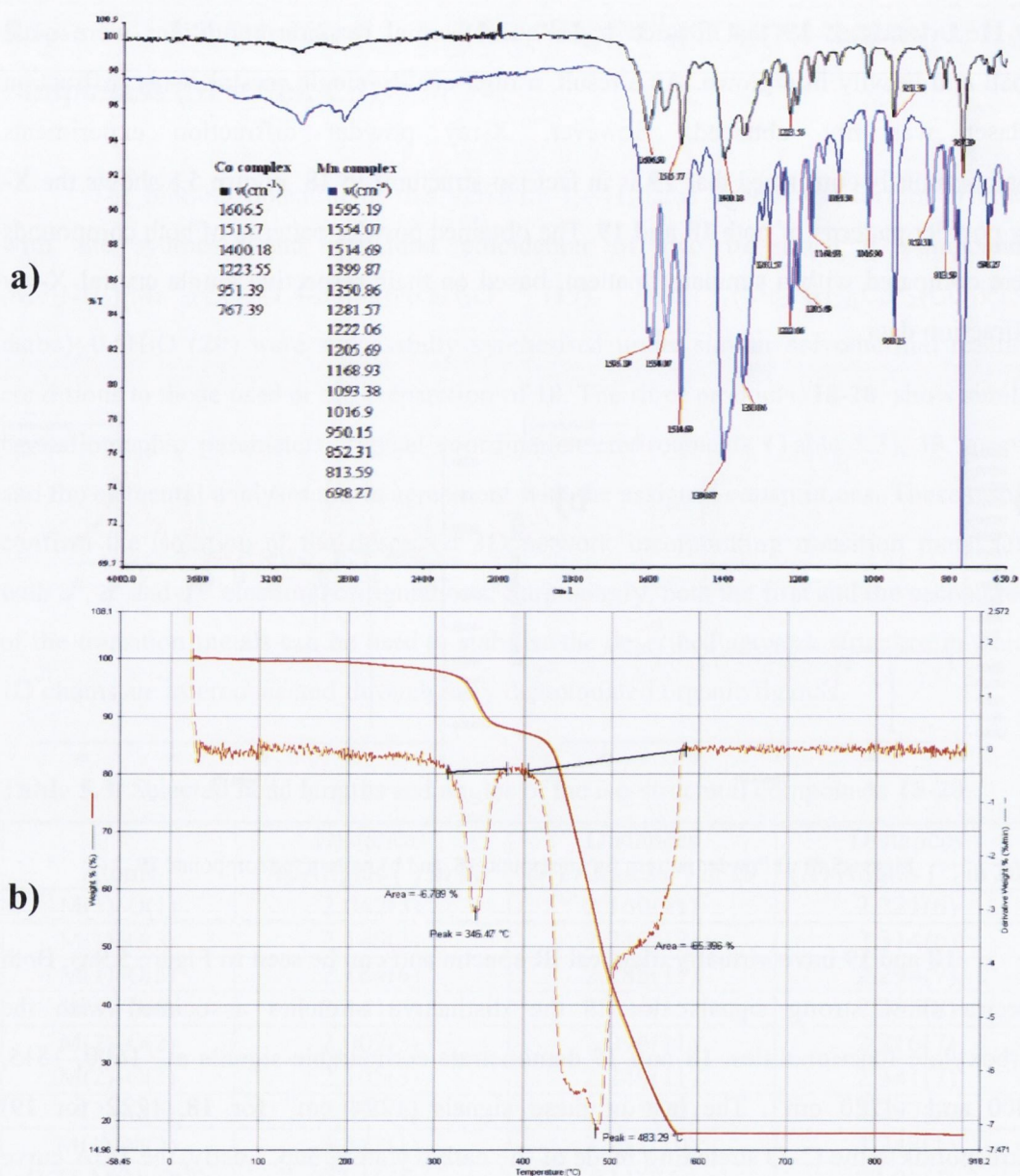


Figure 5.9: a) IR spectra for compounds **18** and **19**, and b) TGA curve (solid red line) of **19**. (Dashed line corresponds to the derivative of the TGA curve.)

5.1.5: Analyses of the magnetic properties of iso-structural $(\text{Me}_2\text{NH}_2)[\text{M}^{\text{II}}_2(\text{CO}_2)(1,4\text{-datba})]\cdot 0.5\text{H}_2\text{O}$ compounds ($\text{M} = \text{Mn}, \text{Co}$)

Analyses of the magnetic properties of compounds **18** and **19** were undertaken to explore the magnetic exchange pathways in the 1D chains. We conducted the studies to also assess any differences between the two iso-structural compounds that arise from the nature of the two different transition metal ions. In fact, **18** and **19** reveal significantly different magnetic characteristics at low temperatures. To discuss the apparent differences, both compounds shall be considered individually.

For compound **19**, the temperature dependencies of the magnetic susceptibilities were measured at 1,000 Oe. The room temperature χT value of $8.2 \text{ cm}^3 \text{ K mol}^{-1}$ is in good agreement with the presence of two Mn^{II} *high-spin* ions ($S = 5/2$, $C = \sim 4.7 \text{ cm}^3 \text{ K mol}^{-1}$ expected for $g = 2.0$). On lowering the temperature, the χT product gradually decreases, to reach a minimum magnitude of $0.5 \text{ cm}^3 \text{ K mol}^{-1}$ (at 1.8K), as shown in Figure 5.10a. The measurements were also performed at a higher field (10,000 Oe), but showed analogous behaviour (Fig 5.10a).

For compound **19**, a full interpretation of the obtained data is possible as $\text{Mn}(\text{II})$ metal ions can be successfully modelled. The decrease of the χT product on lowering the temperature is the result of anti-ferromagnetic exchange interactions between the two symmetry-independent manganese centres.

In agreement with the structural motif of a 1D coordination polymer comprised of two distinct $\text{Mn}(\text{II})$ *high-spin* centres ($S_{\text{Mn}} = 5/2$), the Heisenberg Hamiltonian of the chain motif, with classical spins, can be written as follows: $H = -2J \sum_{i=1}^{\infty} S_i S_{i+1}$ where J is the magnetic exchange parameter between the two metal ions, and S_i is the spin operator for each metal centre. Our model, derived from Fisher, allowed us to reproduce the χT vs T data from 300 to 4 K (Fig 5.10b).⁽¹⁷⁵⁻¹⁷⁶⁾ The best fit was achieved with the following parameters: $J/k_B = -1.7(1) \text{ K}$, with $g_{\text{av}} = 1.98(3)$ for **19**, with the negative sign of J indicating weak intra-chain anti-ferromagnetic exchange interactions between the metal ions.

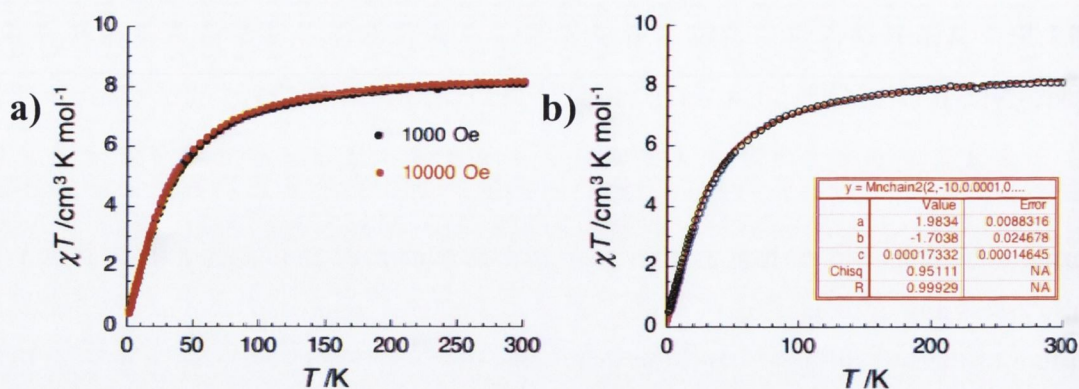


Figure 5.10: a) Plot of the temperature dependency of the magnetic susceptibility of **19** at two field strengths and b) model of the anti-ferromagnetic interactions within the 1D chain of **19** with the solid red line corresponding to the best fit obtained with selected parameters.

For the cobalt-equivalent **18**, the temperature dependency of the magnetic susceptibility was again measured at 1,000 and 10,000 Oe, as shown in Figures 5.11a and 5.11b. A room temperature χT value of $6.9 \text{ cm}^3 \text{ K mol}^{-1}$ is observed, which is in good agreement with the presence of two *high-spin* Co^{II} ions ($S = 3/2$, $C = \sim 3.2 \text{ cm}^3 \text{ K mol}^{-1}$). Upon lowering the temperature the χT product decreases only marginally to reach a local minimum of $6.5 \text{ cm}^3 \text{ K mol}^{-1}$ at 48 K. The χT product begins to increase slowly with further cooling (1,000 Oe), followed by a subsequent sharp increase at very low temperatures, reaching a maximum of approximately $23.4 \text{ cm}^3 \text{ K mol}^{-1}$ at 2.2 K, before decreasing to $22.9 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. However, at the higher applied field (10,000 Oe), there is a slight increase in the χT product upon further cooling whereby a maximum value of $8.6 \text{ cm}^3 \text{ K mol}^{-1}$ is recorded at 7.6 K. This is then followed by another decline to reach a value of $3.3 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. The behaviour of both curves at low temperatures is highlighted in Figure 5.11b.

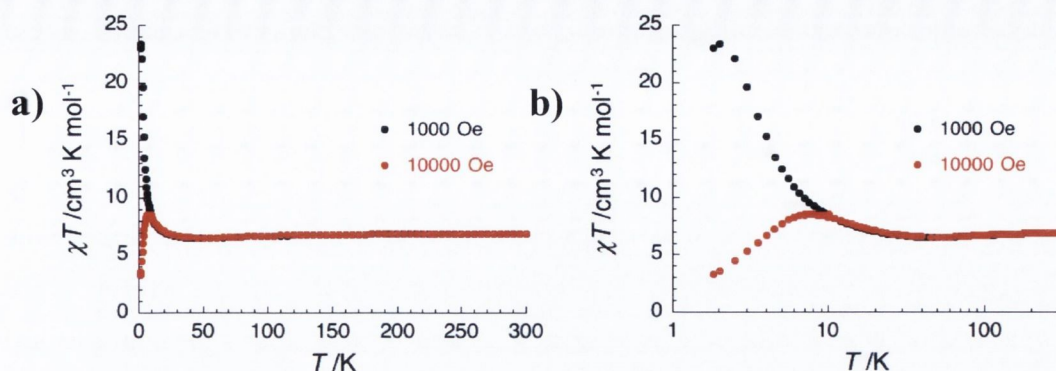


Figure 5.11: a) Plot of the temperature dependency of the magnetic susceptibility of **18** at both 1,000 Oe and 10,000 Oe and b) inspection of the low temperature behaviour of the χT product in both applied fields.

The decrease in the χT product, at very low temperatures, is absent on the zero-*dc* field data (Figs. 5.12a and 5.12b). At 100 Hz, the maximum χT product recorded at 1.8 K is 36.2 cm³ K mol⁻¹. This indicates that the observed magnetic behaviour is a field induced phenomenon and does not follow linear or Curie-type behaviour.

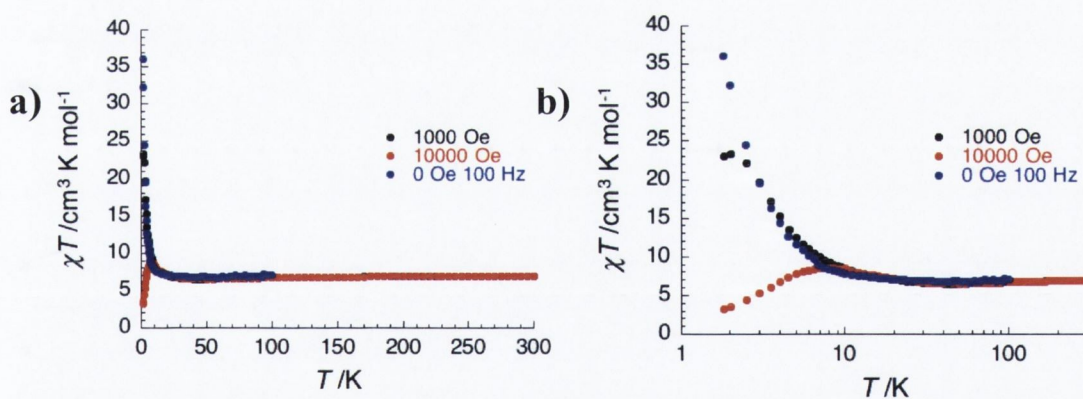


Figure 5.12: a) and b) Plots of the temperature dependency of the magnetic susceptibility of **18** incorporating low frequency values.

In contrast to compound **19**, the magnetic behaviour for the cobalt chain can not be precisely modelled, but the fluctuating values of χT upon lowering the temperature can still be interpreted in two separate manners. In one case, anti-ferromagnetic exchanges (Fig 5.13a) between the metal centres result in a decrease of the χT product with a

decrease in temperature, akin to that described for the manganese chains. These interactions, however, do not lead to the exact cancellation of the magnetic moments at very low temperatures, suggesting a spin-canting system and this situation is portrayed in Figure 5.13b. The alternative method derives from ferromagnetic interactions occurring between the cobalt ions along the chain (Fig. 5.13c), and the subsequent decrease in the χT product is due to spin-orbit coupling between the Co(II) centres. As a result of the complicated magnetic interactions associated with Co(II) ions, the unequivocal determination of which magnetic interaction in fact takes place is not possible.

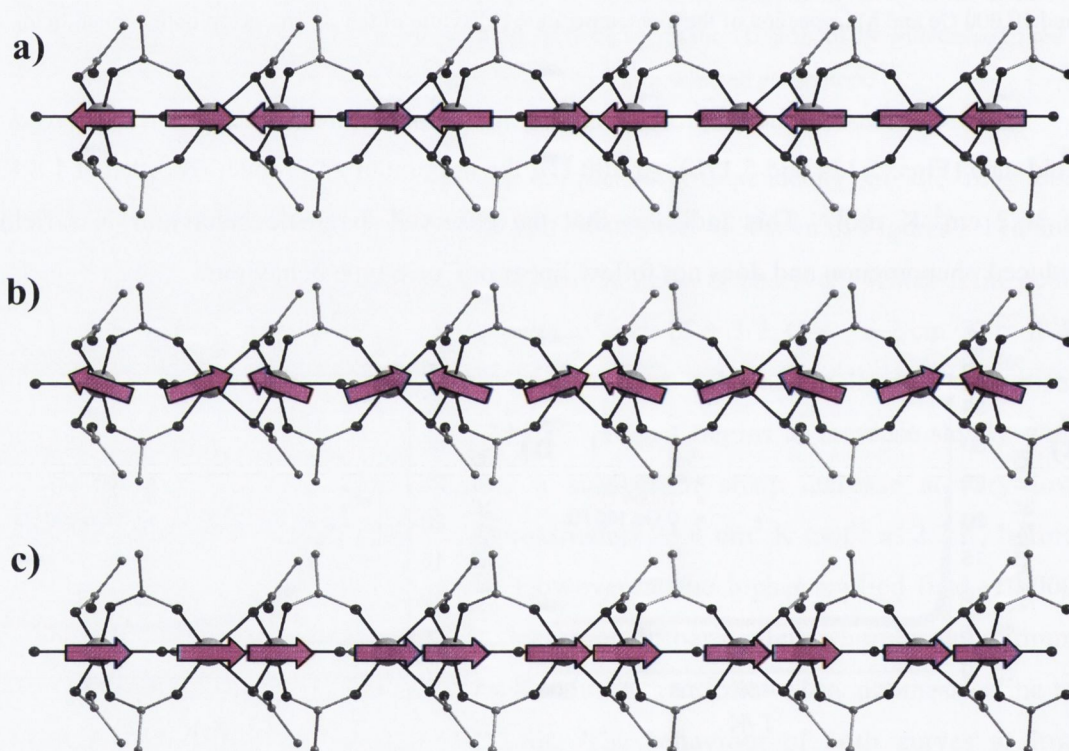


Figure 5.13: Simplified representation of the 1D coordination chain in **18** as viewed along the crystallographic *c*-axis highlighting the possible magnetic orientations (arrows) of the metal centres revealing a) anti-ferromagnetic interactions, b) a spin-canting system and c) ferromagnetic interactions.

In spite of the contrasting magnetic behaviour demonstrated above at differing field strengths, alternative magnetic analyses lead to some additional intriguing findings. The field-dependence of magnetisation, at a range of low temperatures reveals some

interesting patterns as shown in Figure 5.14a. In the low-field region, there is a sharp increase in the magnetisation, and then, the magnetisation increases slowly and linearly with the field. At the maximum induced field of 7 T, the magnetisation value of $4.65 \mu_B$ is far below an expectant value of approximately $7.5 \mu_B$ (spin-only for two Co^{II} species). This demonstrates that the system does not become fully saturated with the field, and also indicates the coexistence of both ferro- and anti-ferromagnetic interactions in compound **18**.⁽¹⁷⁷⁻¹⁷⁸⁾ In addition to this, the χT product is proportional to the correlation length in a 1D system.⁽¹⁷⁹⁾ For Ising-type chains, or anisotropic Heisenberg chain models, this correlation length grows exponentially. Figure 5.14b demonstrates this relationship to be valid in our system with the plot of χT versus $1/T$ in a semi-logarithmic scale. This confirms the 1D nature, and also the presence of magnetic anisotropy in the measured system. It also corroborates that the inter-chain interactions are negligibly weak. This combined evidence corresponds well with the previously described (section 1.4.2) conditions required for a compound to display Single-Chain Magnetic (SCM) characteristics.

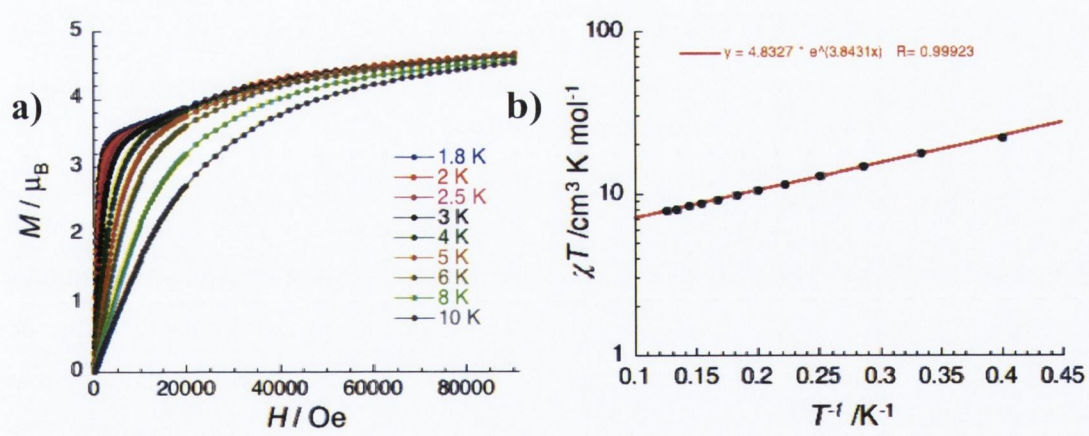


Figure 5.14: a) Plot of magnetisation versus the field at various low temperatures and b) the increasing χT plotted against inverse temperatures in semi-logarithmic plot.

One of the most common methods for establishing SCM properties is to determine the strength of the frequency dependencies of both the real (χ') and imaginary (χ'') components of the *ac* (alternating-current) susceptibilities. The observation of a

strong correlation between the susceptibilities and frequency dependencies validates SCM behaviour, as it precludes any significant 3D magnetic ordering. This reinforces the observation of essentially one dimensional magnetic characteristics, and also confirms that the very “robust” Glauber dynamic region is unaffected by possible weak interchain interactions.⁽¹⁸⁰⁻¹⁸²⁾ Figures 5.15a and 5.15b reveal, at very low temperatures, that both the in-phase (χ') and out-of-phase (χ''), *ac* susceptibilities are indeed strongly related to the applied frequency.

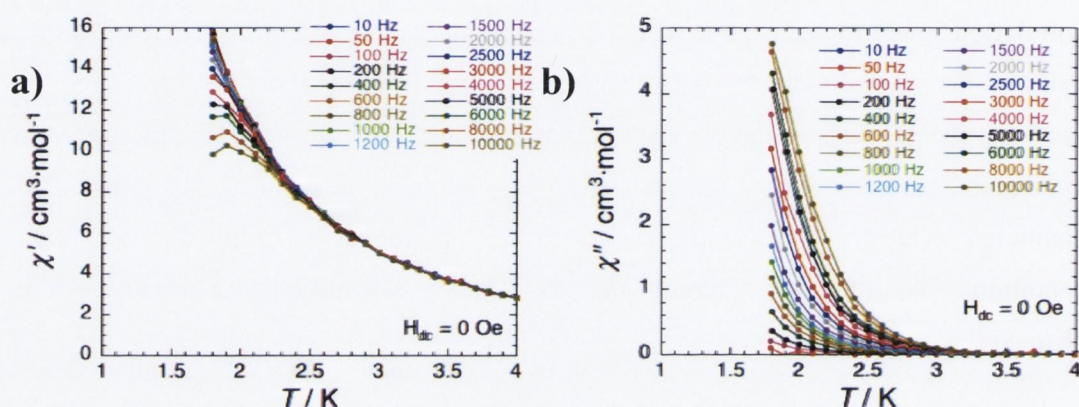


Figure 5.15: a) In-phase *ac* susceptibility of the compound at low temperatures with varying frequencies and b) the out-of-phase data.

In addition, the strong frequency-dependent behaviour can be substantiated with isothermal frequency-dependent *ac* susceptibility measurements at very low temperatures (between 2.8 and 1.8 K). Relaxation times can furthermore be evaluated using *ac* susceptibility measurements. Unfortunately however, the relaxation profile in our system is above 10,000 Hz, and is therefore not attainable with this experimental approach. The plots shown in Figures 5.16a and 5.16b, do still infer that both real and imaginary components of the *ac* susceptibilities are indeed highly temperature reliant, as expected.

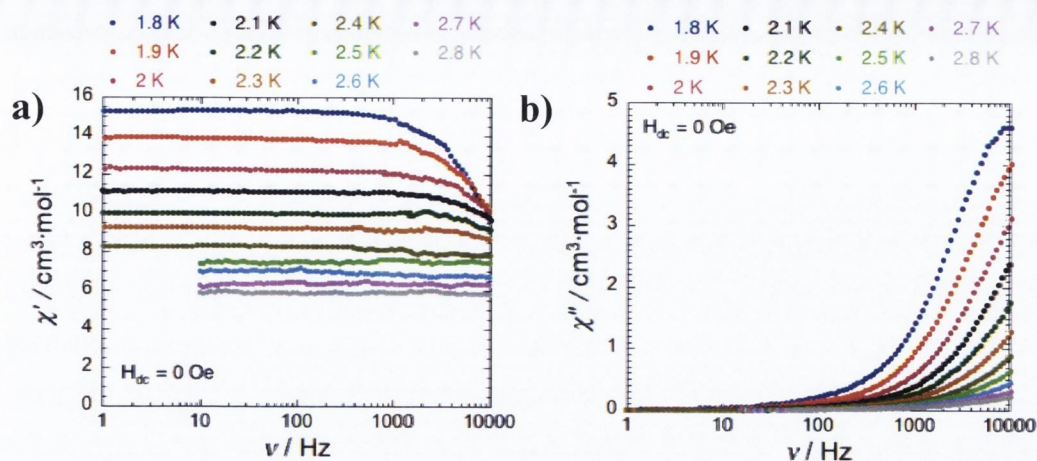


Figure 5.16: a) In-phase *ac* susceptibility of the compound with varying frequencies, at the indicated low temperatures and b) the out-of-phase data.

The application of the direct-current (*dc*) magnetic field does not clarify the relaxation profile of the compound any further. Measurements performed at a very low temperature (1.8 K) and with alternate *dc* components (Figures 5.17a and 5.17b) again simply confirm that the relaxation times are indeed very fast, and cannot be determined using the current equipment.

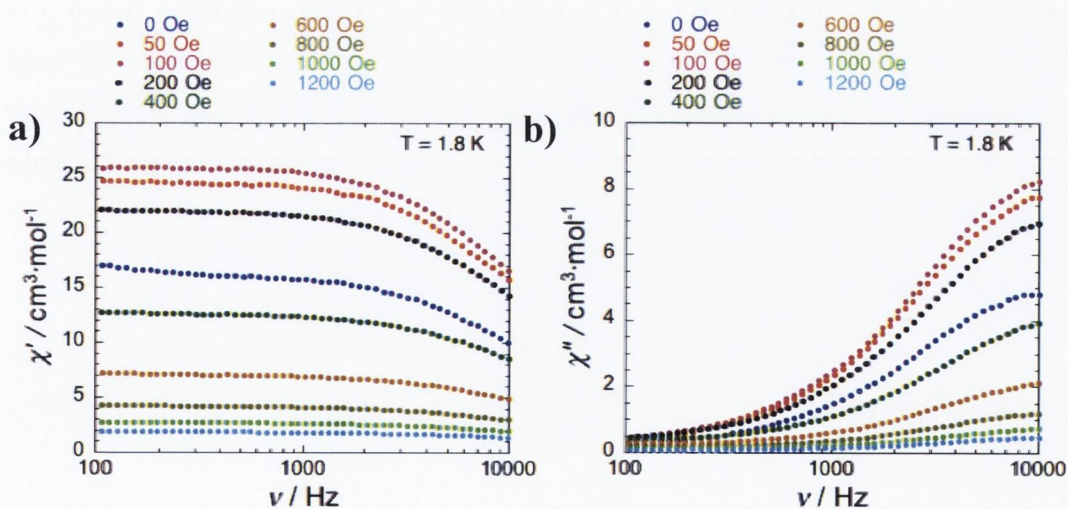


Figure 5.17: a) In-phase *dc* susceptibility of the compound with varying frequencies at 1.8 K and b) the out-of-phase data.

The magnetic data obtained, for both **18** and **19**, is in agreement with the presence of 1D coordination polymers. Different magnetic exchange interactions were observed, depending on the choice of transition metal ions used. In particular, compound **18** exhibits interesting Single-Chain Magnet (SCM) properties. The magnetic properties of **19** are determined by anti-ferromagnetic interactions between the spin centres. These encouraging results prompted us to exploit the 1,3-phenylenediamino-tetra benzoic acid ligand (1,3-H₄datba) as an alternative to the 1,4-equivalent. This meta-functionalised ligand derivative was used under comparable synthetic conditions to that of the para-substituted analogue.

5.2: Compound (1,3-H₄datba)·2DMF (**21**)

The solvent adduct of the ligand 1,3-phenylenediamino-tetra benzoic acid, (1,3-H₄datba)·2DMF was successfully crystallised as pale purple shards while attempting to bind the ligand to cobalt(II) ions under ambient reaction conditions. This unintended result did, however, allow the solid state investigation of this novel ligand. **21** crystallises in the monoclinic crystal system in the space group $P 2_1/c$. The asymmetric unit contains a fully protonated 1,3-H₄datba ligand and two solvent DMF molecules. Figure 5.18 shows the conformational arrangement of the free ligand and highlights the large displacement of each of the individual benzoic acid moieties away from the respective secondary amino groups. There is also an inherent asymmetry to the compound due to the 1,3-substitution of the central phenyl ring.

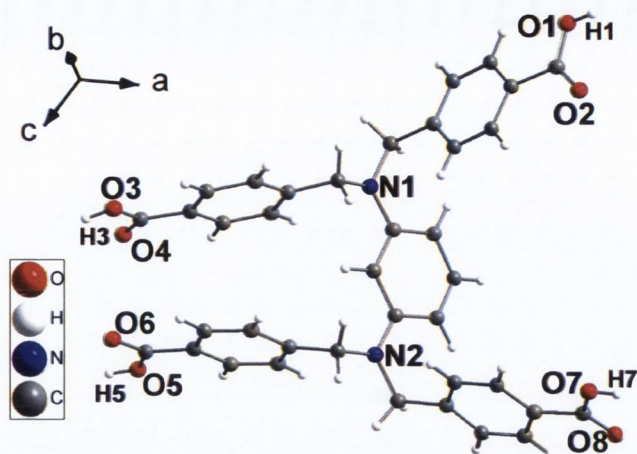


Figure 5.18: Structure of the 1,3- H_4 datba ligand.

All four benzoic acid moieties engage in hydrogen bonding interactions, and there are two distinct varieties of H-bonds in the compound. Beginning with both the benzoic acid functionalities connected to N(1), these are engaged in H-bonds with the solvent DMF molecules. Distances of 2.561(6) Å and 2.613(7) Å correspond to the O(1)–O(9') and O(3)–O(10'') interactions, respectively, and can be seen in Figure 5.19.

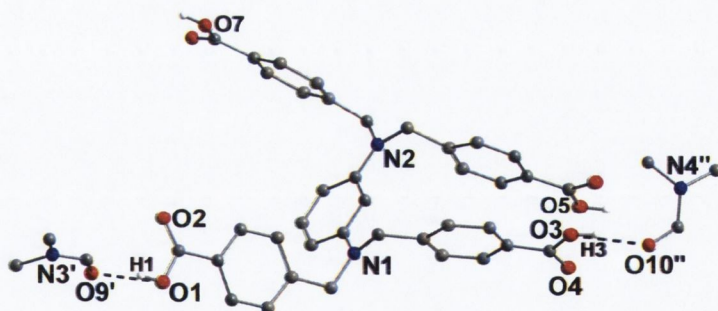


Figure 5.19: The H-bonds (dashed bonds) associated with a complete amino-dibenzoic acid group and two solvent DMF molecules. Non-relevant hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

The other amino-dibenzoic acid moieties, affixed to N(2), form inter-ligand H-bonds with O(5)–O(8'') and O(7)–O(6''') contacts of 2.589(7) Å and 2.662 (6) Å, respectively. These H-bonds can be seen in Figure 5.20.

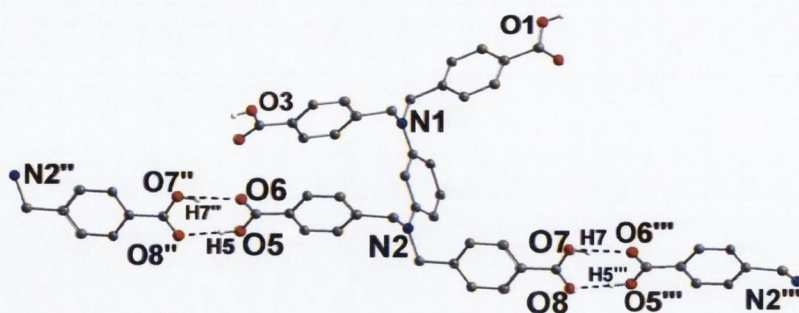


Figure 5.20: The H-bonds (dashed bonds) between both the benzoic acid groups protruding from N(2) and adjacent H₄datba ligands. Non-relevant hydrogen atoms are removed for clarity. (Prime refers to symmetry-generated atoms.)

These latter interactions, involving O(5) and O(7), generate a 1D chain structure which extends along the crystallographic *a*-axis. This arrangement and its repetitious stacking within the overall crystal structure can be seen in Figure 5.21.

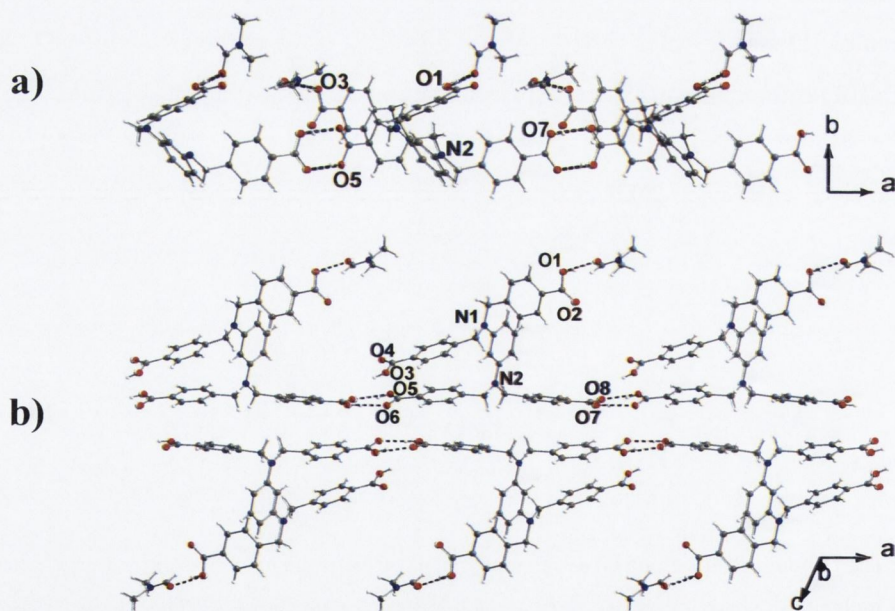


Figure 5.21: a) The extension along the crystallographic *a*-axis *via* H-bonds (dashed bonds) in **21** and b) an overall perspective of the compound.

5.3: Summary and Conclusions

In this chapter the use of a new class of ligand is described. The ligands contain rigid benzoic acid functionalities that are connected to amine groups in either 1,4- or 1,3-phenylenediamine moieties. Both ambient and hydro(solvo)thermal reaction conditions were applied to generate coordination networks that could give rise to interesting magnetic properties or permanent porosity.

The solvent adduct of the 1,4-phenylenediamino-tetra benzoic acid ligand, (1,4-H₄datba)·DMF (**17**), was crystallised. Due to hydrogen bonds involving the protonated carboxylic acids, the structure is composed of 1D ladder-type chains that expand along the crystallographic *c*-axis. These ladders motifs stack to form channels, and solvent DMF molecules reside within these ladders.

The inclusion of transition metal ions and their subsequent complexation under solvothermal reaction conditions resulted in the Co(II) compound **18**, which displays a significantly altered network topology. The crystal structure of **18** is characterised by 1D coordination polymers that run parallel to the crystallographic *a*-axis. Alternating octahedral and square pyramidal coordinated cobalt(II) centres are perpetually bridged by either the carboxylate functionalities of the ligand or formate ions. The latter ligands and the dimethyl ammonium counterions are the result of the decomposition of DMF solvent molecules in the reaction vessel. These discrete chains are linked through the benzoic acid functionalities of the organic ligand that bind to metal ions of separate chains. The flexibility demonstrated by the ligand results in a 3D metal-organic framework in which the aromatic ligand moieties interdigitate. This 3D structure is further characterised by channels, which also extend in the crystallographic *a*-direction. These channels are occupied with solvent water molecules and the dimethyl ammonium counterions. TGA studies reveal that the organic ligand undergoes oxidative degradation at *ca.* 340 °C. Iso-structural manganese (**19**) and cadmium (**20**) complexes were also synthesised.

The investigation of the magnetic properties of **18** and **19** led to some quite remarkable observations. For **19**, the magnetic data is consistent with a Heisenberg spin chain, whereby the χT product decreases on lowering the temperature. The temperature dependency was reproduced, and a coupling constant between the two *high-spin* Mn^{II}

ions of $J/k_B = -1.7(1)$ K was established, implying weak anti-ferromagnetic interactions. For **18**, the magnetic analysis performed gave very strong evidence for single-chain magnet (SCM)-type behaviour. Assorted magnetic measurements were carried out which are in agreement with the 1D chain structure in the compound, and the observed magnetic anisotropy of **18** is a further characteristic of SCMs. The dynamics of the system are too fast to unequivocally corroborate the SCM characteristics using the currently available instrumentation; hence further studies are recommended.

Lastly, a solvent adduct of the *meta*-form of the ligand was also successfully crystallised (1,3-H₄datba)·2DMF (**21**). The solid state structure shows interesting differences to the 1,4-derivative. Unfortunately, no crystalline transition metal complexes were obtained using this ligand type.

Chapter 6

6.1: Materials and methods

6.1.1: Reagents

All chemicals and solvents were of reagent grade and purchased from Aldrich Chem. Co. Ltd. or local solvent suppliers, and were used as received. Water was deionised before use.

6.1.2: 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 and are listed for each spectrum. Standard abbreviations for spectra apply: s, singlet; d, doublet; t, triplet; qt quartet; q, quaternary; m, multiplet; br broad, J, coupling constant.

6.1.3: 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 was collected and processed using 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 and shapes of the resulting bands: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad.

6.1.4: Mass spectrometry

Electrospray mass spectroscopy was carried out on a Micromass LCT Electrospray mass spectrometer by Dr. Martin Feeney or Dr. Bernard-Jean Denis. Samples were dissolved in HPLC grade solvents.

6.1.5: Elemental analysis

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

6.1.6: X-ray crystal diffraction

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

The Bruker diffractometer utilised 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 at a temperature of 150K. Data was collected, processed, and corrected for Lorentz and polarisation effects using SMART⁽¹⁸³⁾ and SAINT-PLUS⁽¹⁸⁴⁾ software. The structures were solved using direct methods with the SHELXTL⁽¹⁸⁵⁾ program package.

The data sets from the Rigaku Saturn-724 diffractometer were collected using the Crystalclear-SM 1.4.0 software package 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 Crystalstructure ver. 3.8 and SHELXTL software.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms (excluding water and carboxylic acid groups) were assigned to calculated positions using a riding model with appropriately fixed isotropic thermal parameters. Water and carboxylic acid

group hydrogen atoms or H atoms involved in hydrogen bonding, were located from difference maps and their positions refined where appropriate, with O-H distance restraints (DFIX) and isotropic thermal parameters fixed at 1.2 times that of the adjoining oxygen atom.

6.1.7: X-ray powder diffraction

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

6.1.8: Solvo(hydro)thermal 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 but a typical volume of 7-9 ml was used. The heating cycles are specified for each reaction and were performed in a conventional convection oven.

6.1.9: Thermogravimetric analysis

Thermogravimetric analysis was performed on a Perkin Elmer Pyris 1TGA. The measurements (*ca.* 3 mg sample) were performed in an air atmosphere using a platinum crucible, at a heating rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ in a temperature range of 25-900 $^{\circ}\text{C}$. The instrument was calibrated to In and Ni standards in an air atmosphere.

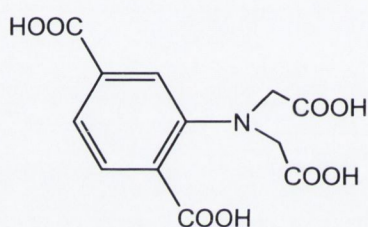
6.1.10: Measurements of magnetic properties

All measurements were performed and modelled by Dr. Rodolphe Cl  rac or Nigel Hearn using a Quantum Design SQUID magnetometer MPMS-XL housed at the Centre de Recherche Paul Pascal, University of Bordeaux, France. This magnetometer operates

between 1.8 and 300 K for *dc* applied fields ranging from -7 to 7 T. Before any measurement, all samples are checked for the presence of ferromagnetic impurities by measuring the magnetization as a function of the field at 100 K. For pure paramagnetic or diamagnetic systems, a perfect straight line is expected and is indeed observed for all compounds indicating the absence of any ferromagnetic impurities.

6.2: Ligand synthesis

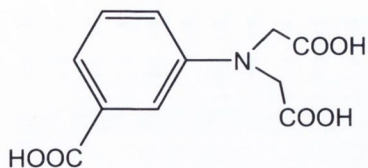
6.2.1: Synthesis of 2-aminodiacetic terephthalic acid (H_4adta)



2-Aminoterephthalic acid (9.058 g, 0.05 mol) and deionised water (25 ml) were placed in a round bottom flask and stirred. To this stirring suspension, an aqueous solution (15 ml) of sodium hydroxide (4.00 g, 0.10 mol) was added and a pale yellow solution resulted. The temperature was increased to reflux level ($\sim 110^\circ\text{C}$). An aqueous solution (25 ml) of chloroacetic acid (9.450 g, 0.10 mol) and sodium hydroxide (4.00 g, 0.1 mol) was added drop-wise to this solution. pH levels were monitored throughout this process and additional sodium hydroxide solution (8M) was added as required to maintain an alkaline system ($\text{pH} \geq 8$). After completion of the drop-wise addition, the reaction flask was allowed to reflux overnight. The resulting red/orange solution was cooled on ice and acidified with concentrated hydrochloric acid (32% w/v HCl), to $\text{pH} \sim 2.5$, whereupon the 2-aminodiacetic terephthalic acid precipitated. This product was filtered, washed with water and air dried (pale yellow powder). Yield: 13.08 g ($\sim 90\%$).

^1H NMR (DMSO, 400MHz): δ 8.02 (s, 1H, ArH), δ 7.98 (d, 1H, ArH), δ 7.85 (d, 1H, ArH) δ 4.10 (s, 4H, CH_2). IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3637(w), 3010(s), 2975(s), 2654(br), 1737(sh), 1707(vs), 1580(m), 1505(m), 1464(m), 1410(s), 1378(s), 1243(vs), 1071(m), 1007(m), 913(m), 898(m), 807(m), 757(m), 700(sh), 690(m). ES-MS (MeOH) m/z : 296.0406 [$\text{C}_{12}\text{H}_{10}\text{NO}_8$]. CHN analysis for $\text{C}_{12}\text{H}_{11}\text{NO}_8$: Expected: C, 48.49%; H, 3.73%; N, 4.71%. Found: C, 47.06%; H, 3.16%; N, 4.39%.

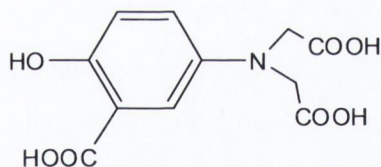
6.2.2: Synthesis of 3-aminodiacetic benzoic acid (H₃adba)



A similar procedure to the previously described method was followed, with 3-aminobenzoic acid used instead of the 2-aminoterephthalic acid. The final product was a pale beige powder. Yield: *ca.* 85%.

¹H NMR (D₂O, 400MHz): δ 7.15 (t, 1H, ArH), δ 7.05 (d, 1H, ArH), δ 6.85 (s, 1H, ArH), δ 6.50 (d, 1H, ArH), δ 3.80 (s, 4H, CH₂). IR (KBr diffuse reflectance) $\nu_{\max}$ cm⁻¹: 3415(vw), 2926(br), 2829(br), 2545(br), 1954(br), 1718(s), 1673(vs), 1602(s), 1579(s), 1493(m), 1465(s), 1424(m), 1320(sh), 1299(vs), 1265(s), 1232(s), 1183(m), 1077(br), 972(s), 935(s), 860(s), 753(vs), 676(s). ES-MS (H₂O) *m/z*: 252.0519 [C₁₁H₁₀NO₆]⁻. CHN analysis for C₁₁H₁₁NO₆: Expected: C, 52.18%; H, 4.38%; N, 5.53%. Found: C, 51.53%; H, 4.27%; N, 5.29%.

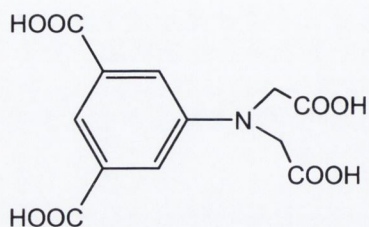
6.2.3: Synthesis of 5-aminodiacetic salicylic acid (H₄adsa)



An analogous method to the previously described protocols was employed, with a 5-aminosalicylic acid used as the starting reagent. The final product was a pale beige powder. Yield: ~ 80%.

¹H NMR (D₂O, 400MHz): δ 7.20 (s, 1H, ArH), δ 7.05 (d, 1H, ArH), δ 7.00 (d, 1H, ArH), δ 3.90 (s, 4H, CH₂). IR (KBr diffuse reflectance) $\nu_{\max}$ cm⁻¹: 3430(br), 2977(br), 1954(br), 1718(m), 1669(m), 1610(m), 1499(s), 1456(m), 1387(m), 1340(w), 1301(m), 1317(m), 1279(m), 1235(s), 1185(vs), 1151(m), 979(vs), 956(m), 898(w), 798(vs), 753(w), 713(w). ES-MS (H₂O) *m/z*: 268.0450 [C₁₁H₁₀NO₇]⁻. CHN analysis for C₁₁H₁₁NO₇: Expected: C, 49.08%; H, 4.12%; N, 5.20%. Found: C, 48.11%; H, 3.90%; N, 4.32%.

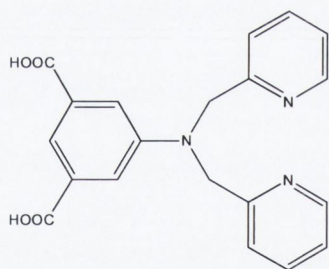
6.2.4: Synthesis of 5-aminodiacetic isophthalic acid (H₄adip)



A similar methodology to the above was used for the synthesis of this ligand. 5-aminoisophthalic acid was used as the starting material in this case. The final product was a very pale pink powder. Yield: $\geq 90\%$.

^1H NMR (D_2O , 400MHz): δ 7.80 (s, 1H, ArH), δ 7.20 (s, 2H, ArH), δ 4.15 (s, 4H, CH_2). IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3453(m), 3205(br), 3106(br), 2797(br), 2512(br), 1910(br), 1725(vs), 1662(s), 1600(vs), 1561(s), 1462(s), 1438(s), 1358(m), 1325(s), 1284(s), 1250(vs), 1215(s), 1140(m), 1101(m), 995(s), 910(sh), 896(m), 795(m), 761(m), 730(m), 676(s), 662(m). ES-MS (H_2O) m/z : 296.0423 [$\text{C}_{12}\text{H}_{10}\text{NO}_8$] $^-$. CHN analysis for $\text{C}_{12}\text{H}_{11}\text{NO}_8$: Expected: C, 48.49%; H, 3.73%; N, 4.71%. Found: C, 47.36%; H, 3.56%; N, 4.31%.

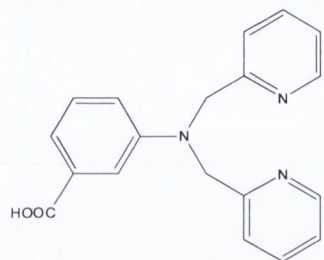
6.2.5: Synthesis of 5-amino-2-methyldipyridine isophthalic acid (H₂adpip)



5-Aminoisophthalic acid (3.623 g, 0.02 mol) and deionised water (25 ml) were placed in a round bottom flask and stirred. To this stirring suspension, an aqueous solution (15 ml) of sodium hydroxide (2.40 g, 0.06 mol) was added and a pale beige solution resulted. An aqueous solution (25 ml) of 2-chloromethyl pyridine hydrochloride (6.561 g, 0.04 mol) and sodium hydroxide (3.20 g, 0.08 mol) was added drop-wise to this solution. pH levels were monitored throughout this process and additional sodium hydroxide solution (8M) was added, as required, to maintain an alkaline system ($\text{pH} \geq 8$). After completion of the drop-wise addition, the reaction flask was allowed to reflux overnight. The resulting dark red solution was cooled on ice and acidified with concentrated hydrochloric acid (32% w/v HCl), to $\text{pH} \sim 2.5$, whereupon the 5-amino-2-methyldipyridine isophthalic acid precipitated. This product was filtered, washed with water and air dried (pale beige powder). Yield: *ca.* 50%.

^1H NMR (DMSO, 400MHz): δ 8.70 (d, 2H, ArH), δ 7.90 (m, 2H, ArH), δ 7.75 (s, 1H, ArH), δ 7.55 (d, 2H, ArH), δ 7.45 (d, 2H, ArH), δ 7.35 (d, 2H, ArH), δ 5.05 (s, 4H, CH_2). IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3199(br), 1710(vs), 1602(s), 1573(w), 1473(m), 1408(m), 1364(w), 1276(m), 1211(s), 1178(m), 1142(s), 1014(s), 994(s), 977(m), 962(m), 751(vs), 683(m). ES-MS (DMSO) m/z : 364.1282 $[\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}_4]^+$. CHN analysis for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_4$: Expected: C, 66.11%; H, 4.72%; N, 11.56%. Found: C, 65.17%; H, 4.49%; N, 10.85%.

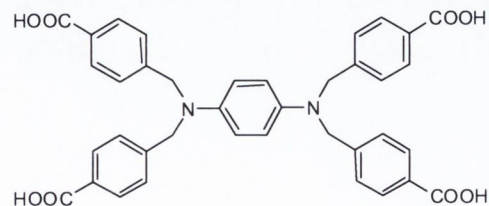
6.2.6: Synthesis of 3-amino-2-methyldipyridine benzoic acid (Hadpba)



An identical synthesis to the just described method was followed, however, 3-aminobenzoic acid was the starting reagent. The final product was a pale yellow powder. Yield: ~ 45%.

^1H NMR (DMSO, 400MHz): δ 8.80 (d, 2H, ArH), δ 8.65 (d, 1H, ArH), δ 8.10 (t, 2H, ArH), δ 7.90 (t, 1H, ArH), δ 7.65 (d, 2H, ArH), δ 7.55 (t, 2H, ArH), δ 7.45 (d, 1H, ArH), δ 6.80 (s, 1H, ArH), δ 5.10 (s, 4H, CH_2). IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3300(br), 2434(br), 1910(br), 1715(s), 1685(m), 1601(s), 1575(m), 1528(w), 1489(m), 1466(m), 1421(m), 1386(w), 1356(w), 1265(s), 1211(m), 1121(m), 990(s), 868(w), 759(vs). ES-MS (DMF) m/z : 320.1383 $[\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}_2]^+$. CHN analysis for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2$: Expected: C, 71.46%; H, 5.37%; N, 13.16%. Found: C, 70.67%; H, 5.14%; N, 11.88%.

6.2.7: Synthesis of 1,4-phenylenediamino-tetra-benzoic acid (1,4-H₄datba)

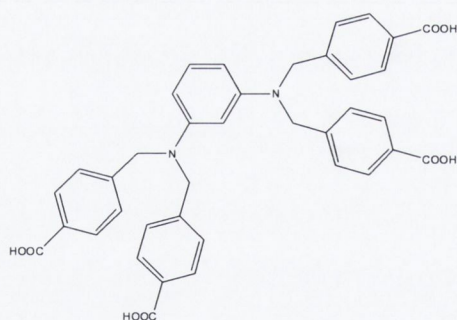


p-Phenylenediamine (0.811 g, 7.5 mmol) and deionised water (25 mL) were placed in a round bottom flask and 4-chloromethylbenzoic acid (5.630 g, 33 mmol) was added. Following

this, NaOH (1.80 g, 0.045 mol) was added under stirring. The resulting stirred solution gradually turned dark green and the temperature was increased to $\sim 90^{\circ}\text{C}$. pH levels were monitored throughout the process and additional base (8M NaOH) was added to achieve a pH value of ≥ 8 . The temperature was increased and the reaction mixture was allowed to reflux overnight. The resulting red/orange solution was cooled on ice before being acidified with concentrated hydrochloric acid (32% HCl) to pH ~ 2 , at which point the 1,4-phenylenediamino-tetra benzoic acid precipitated out. This product was filtered, washed with water and air dried giving a grey/green powder. Yield: $>90\%$.

^1H NMR (DMSO, 400 MHz): δ 12.85 (br, 4H, OH), 7.85 (d, 8H, ArH), 7.35 (d, 8H, ArH), 6.50 (s, 4H, ArH), 4.60 (s, 8H, CH_2). IR (KBr diffuse reflectance) $\nu\text{ cm}^{-1}$: 2860(br), 1686(s), 1610(m), 1577(w), 1524(s), 1424(s), 1346(w), 1319(w), 1288(vs), 1234(s), 1110(m), 1017(m), 945(s), 849(m), 798(s), 768(m), 752(m), 708(w). ES-MS (DMSO) m/z 643.2097 [$\text{C}_{38}\text{H}_{31}\text{N}_2\text{O}_8$] $^-$. CHN analysis for $\text{C}_{38}\text{H}_{32}\text{N}_2\text{O}_8$: Expected: C, 70.80%; H, 5.00%; N, 4.35%. Found: C, 69.29%; H, 4.83%; N, 4.01%.

6.2.8: Synthesis of 1,3-phenylenediamino-tetra-benzoic acid (1,3- H_4datba)



An analogous synthesis to that of 1,4- H_4datba was performed, except that *m*-phenylenediamine was used in this case. Yield: $\sim 90\%$.

^1H NMR (DMSO, 400 MHz): δ 12.50 (br, 4H, OH), δ 7.90 (d, 8H, ArH), δ 7.25 (d, 8H, ArH), δ 7.10 (t, 1H, ArH), δ 6.30 (d, 2H, ArH), δ 6.10 (s, 1H, ArH), δ 4.60 (s, 8H, CH_2). IR (KBr diffuse

reflectance) $\nu\text{ cm}^{-1}$: 2887(br), 1691(s), 1641(s), 1604(s), 1506(m), 1414(m), 1383(m), 1342(w), 1316(w), 1252(s), 1208(vs), 1112(w), 1017(w), 971(w), 808(m), 750(s), 659(w). ES-MS (DMSO) m/z 643.2072 [$\text{C}_{38}\text{H}_{31}\text{N}_2\text{O}_8$] $^-$. CHN analysis for $\text{C}_{38}\text{H}_{32}\text{N}_2\text{O}_8$: Expected: C, 70.80%; H, 5.00%; N, 4.35%. Found: C, 69.08%; H, 4.62%; N, 3.89%.

6.3: Preparation of metal complexes and compounds

6.3.1: Synthesis of $\text{K}[\text{Co}^{\text{II}}(\text{Hadta})(\text{H}_2\text{O})_2]\cdot\text{MeOH}$ (**1**)

Compound **1** was synthesised by the reaction of the H_4adta ligand (0.90 g, 0.303 mmol) with cobalt(II) chloride hexahydrate (0.072 g, 0.303 mmol) in methanol (10 ml), followed by the slow addition of 0.36 ml of an aqueous KOH (1M) solution to the stirred reaction mixture. The product $\text{K}[\text{Co}^{\text{II}}(\text{Hadta})(\text{H}_2\text{O})_2]\cdot\text{MeOH}$ (**1**) separated as orange/red plates from the reaction mixture upon slow evaporation of the solvent. The crystals started to form after approximately 2 weeks. Yield: *ca.* 40%, based on cobalt(II) chloride. IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 2981(br), 1915(wk), 1670(m), 1597(vs), 1449(m), 1401(s), 1353(m), 1278(s), 1188(m), 1129(w), 1090(w), 1036(w), 961(vw), 910(m), 897(m), 848(m), 794(vs), 766(s), 741(s), 715(s). CHN analysis for $\text{K}[\text{Co}^{\text{II}}(\text{Hadta})(\text{H}_2\text{O})_2]\cdot\text{MeOH}$: Expected: C, 33.92%; H, 3.50%; N, 3.04%. Found: C, 32.84%; H, 3.86%; N, 3.88%.

6.3.2: Synthesis of $\text{K}[\text{Ni}^{\text{II}}(\text{Hadta})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**2**)

Compound **2** was synthesised in an analogous manner to **1**, with the inclusion of a nickel(II) chloride tetrahydrate salt in place of the cobalt chloride hexahydrate. Blue/green plates crystallised after approximately two weeks. Yield: *ca.* 35%. IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3060(br), 2927(sh), 2460(br), 1919(br), 1673(m), 1601(vs), 1449(m), 1404(vs), 1354(m), 1294(s), 1190(m), 1130(w), 1099(w), 1037(w), 961(vw), 934(m), 910(m), 849(m), 809(sh), 796(vs), 768(m), 744(m), 717(m). CHN analysis for $\text{K}[\text{Ni}^{\text{II}}(\text{Hadta})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$: Expected: C, 32.31%; H, 3.16%; N, 3.14%. Found: C, 31.84%; H, 3.17%; N, 3.00%.

6.3.3: Synthesis of $\text{K}[\text{Cu}_{1.5}^{\text{II}}(\text{adta})(\text{H}_2\text{O})_{1.5}]\cdot\text{H}_2\text{O}$ (3)

Compound **3** was synthesised in an almost identical manner to the previous two compounds, with a copper(II) chloride dihydrate salt used as the transition metal salt. Dark green hexagons formed after ~ 12 days. Yield: *ca.* 30%.

IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3324(br), 2925(vs), 2854(s), 2591(br), 1915(wk), 1702(m), 1593(vs), 1546(s), 1487(m), 1458(m), 1409(vs), 1377(s), 1313(s), 1280(s), 1251(s), 1179(m), 1125(w), 1107(vw), 1083(w), 1026(m), 1009(m), 964(w), 934(w), 906(w), 839(m), 774(s), 762(s), 728(w), 707(w), 654(w), 607(w). CHN analysis for $\text{K}[\text{Cu}_{1.5}^{\text{II}}(\text{adta})(\text{H}_2\text{O})_{1.5}]\cdot\text{H}_2\text{O}$: Expected: C, 30.85%; H, 2.77%; N, 2.96%. Found: C, 31.40%; H, 2.87%; N, 2.55%.

6.3.4: Synthesis of $[\text{Zn}^{\text{II}}(\text{Hadba})(\text{bpy})]_2$ (4)

A mixture of H_3adba ligand (0.077 g, 0.304 mmol), zinc(II) nitrate hexahydrate (0.091 g, 0.304 mmol), 2,2'-bipyridine (0.036 g, 0.304 mmol) and 8 ml of de-ionised water were placed inside a 25 ml-Teflon lined autoclave. The reactants were stirred resulting in a cloudy pale beige reaction mixture. The autoclave was then sealed, and placed in an oven and kept at 100 °C for 17 hrs. The oven was then switched off and the autoclave was allowed to slowly cool to room temperature. The product mixture consisted of a pale yellow solution containing colourless cubic crystals of $[\text{Zn}^{\text{II}}_2(\text{Hadba})_2(\text{bpy})_2]$ (**1**). In addition to the product the mixture also contained a brown/red unidentified amorphous powder. The cube-shaped crystals were separated manually and analysed. Yield: *ca.* 30%.

IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3085(w), 1697(m), 1663(s), 1597(vs), 1494(m), 1474(w), 1444(s), 1404(m), 1364(m), 1322(s), 1288(m), 1248(s), 1212(m), 1175(w), 1087(w), 1058(w), 1026(w), 994(w), 967(w), 923(w), 773(vs), 721(m). CHN analysis for $[\text{Zn}^{\text{II}}(\text{Hadba})(\text{bpy})]_2$: Expected: C, 53.35%; H, 3.62%; N, 8.89%. Found: C, 53.09%; H, 3.71%; N, 8.74%.

6.3.5: Synthesis of $[\text{Cu}^{\text{II}}(\text{H}_2\text{adsa})(\text{bpy})]_2$ (**5**)

A suspension of 8 ml water containing H_4adsa ligand (0.065 g, 0.242 mmol), copper(II) nitrate trihydrate (0.058 g, 0.242 mmol) and 2,2'-bipyridine (0.038 g, 0.242 mmol) was stirred in an autoclave to yield a cloudy green colour. The autoclave was closed and placed into an oven at 140 °C for 14 hrs. This reaction time including a cooling period of 5-6 hrs resulted in a blue reaction mixture, containing very small green shards of **5** along with an amorphous black powder. Crystals of **5** were isolated by hand. Yield: *ca.* 15%.

IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3090(br), 1714(vs), 1636(m), 1601(m), 1568(w), 1448(w), 1355(s), 1291(m), 1154(m), 1093(m), 1044(m), 1026(vs), 998(m), 823(w), 802(w), 760(vs), 701(vs). CHN analysis for $[\text{Cu}^{\text{II}}(\text{H}_2\text{adsa})(\text{bpy})]_2$: Expected: C, 51.80%; H, 3.52%; N, 8.63%. Found: C, 53.09%; H, 3.71%; N, 8.74%.

6.3.6: Synthesis of $[\text{Co}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$ (**6**)

H_4adip ligand (0.080 g, 0.269 mmol), cobalt(II) acetate tetrahydrate (0.067 g, 0.269 mmol) and bpy (0.042 g, 0.269 mmol) were placed into the Teflon vessel and stirred to give a cloudy pink suspension. The closed autoclave was placed into an oven at 180 °C for 65 hrs. After the reaction time the autoclave was allowed to cool to room temperature. Red crystals of **6**, together with unidentified black/brown powder, were the sole products. The red crystals were separated manually. Yield: *ca.* 55%.

IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3248(br), 1607(vs), 1550(vs), 1477(w), 1446(m), 1404(m), 1380(vs), 1286(w), 1249(w), 1224(w), 1180(w), 1161(w), 1131(w), 1063(w), 1024(w), 984(w), 963(w), 984(w), 892(w), 783(m), 767(m), 736(m), 634(w). CHN analysis for $[\text{Co}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$: Expected: C, 38.11%; H, 4.22%; N, 6.06%. Found: C, 37.89%; H, 4.20%; N, 7.19%.

6.3.7: Synthesis of $[\text{Mn}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$ (7)

Equi-molar ratios (~0.25 mmol) of H_4adip (0.074 g), manganese(II) acetate tetrahydrate (0.061 g) and bpy (0.039 g) in 8 ml H_2O were stirred to give a cloudy reaction mixture. The mixture was placed in an autoclave, sealed and heated to 150 °C for 16 hrs in an oven. A brown mixture containing small colourless crystals of **7**, and a large quantity of the amorphous powder was obtained. Crystals of **7** were separated manually. Yield: *ca.* 10%.

IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3385(br), 3074(w), 2927(w), 1615(vs), 1594(vs), 1547(sh), 1473(m), 1439(vs), 1410(s), 1387(s), 1317(m), 1246(w), 1180(w), 1153(w), 1098(vw), 1055(w), 1015(m), 995(w), 919(w), 784(s), 768(vs), 739(s), 652(m). CHN analysis for $[\text{Mn}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$: Expected: C, 38.55%; H, 4.26%; N, 6.13%. Found: C, 37.99%; H, 3.71%; N, 6.34%.

6.3.8: Synthesis of $[\text{Fe}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$ (8)

A similar synthetic method to the previous procedure was carried out, using iron(II) acetate (0.044 g, 0.25 mmol) as a reactant. A dark red cloudy mixture was heated to 100 °C for 17 hrs in a steel autoclave. A deep red coloured solution containing small pink/red crystals of **8** was obtained. Yield: *ca.* 30%.

IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3210(br), 1601(vs), 1573(vs), 1475(m), 1474(w), 1444(m), 1401(vs), 1160(w), 1064(w), 1021(w), 965(w), 937(w), 889(m), 768(vs), 735(s), 716(m). CHN analysis for $[\text{Fe}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$: Expected: C, 38.45%; H, 4.25%; N, 6.11%. Found: C, 38.26%; H, 4.00%; N, 5.94%.

6.3.9: Synthesis of $[\text{Ni}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$ (9)

A synthesis akin to that, that yielded **8** was used in the generation of **9**. Nickel(II) acetate hexahydrate (0.062 g, 0.25 mmol) was used as a starting material. The cloudy green/blue suspension was heated to a 180 °C for 19 hrs in a steel autoclave. The

resulting blue reaction mixture contained rectangular shaped crystals of **9** and an unidentified brown powder. Crystals of **9** were isolated. Yield: *ca.* 30%.

IR (KBr diffuse reflectance) $\nu_{\max}$ cm^{-1} : 3263(br), 1608(vs), 1548(vs), 1478(w), 1447(m), 1407(s), 1379(vs), 1342(m), 1283(w), 1246(w), 1222(m), 1181(w), 1161(w), 1124(w), 1063(w), 1027(w), 985(w), 963(m), 940(m), 895(m), 784(m), 768(m), 736(s). CHN analysis for $[\text{Ni}^{\text{II}}_2(\text{adip})(\text{bpy})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$: Expected: C, 38.14%; H, 4.22%; N, 6.06%. Found: C, 37.84%; H, 3.86%; N, 5.88%.

6.3.10: Synthesis of $[\text{Cu}^{\text{II}}(\text{H}_2\text{adip})(\text{bpy})]$ (**10**)

A mixture containing copper(II) nitrate trihydrate (0.060 g, 0.25 mmol), H_4adip ligand (0.074 g, 0.25 mmol) and bpy (0.039 g, 0.25 mmol) in 8 ml H_2O was stirred in an autoclave. The autoclave containing the resultant green turbid suspension was sealed, placed in an oven and heated to 130 °C for 18 hrs. The obtained reaction mixture contained blue/green crystalline blocks of **10** and a brown/yellow powder. The crystals of **10** were separated manually. Yield: *ca.* 45%.

IR (KBr diffuse reflectance) $\nu_{\max}$ cm^{-1} : 3193(w), 2931(w), 2454(w), 1920(w), 1726(s), 1677(m), 1592(vs), 1577(m), 1495(w), 1404(s), 1389(s), 1352(w), 1310(m), 1280(m), 1246(vs), 1226(s), 1169(m), 1150(m), 1102(w), 1031(w), 996(w), 968(w), 908(w), 872(w), 811(w), 773(vs), 757(vs), 732(vs). CHN analysis for $[\text{Cu}^{\text{II}}(\text{H}_2\text{adip})(\text{bpy})]$: Expected: C, 51.31%; H, 3.33%; N, 8.16%. Found: C, 50.84%; H, 3.43%; N, 8.00%.

6.3.11: Synthesis of $[\text{Zn}^{\text{II}}(\text{H}_2\text{adip})(\text{bpy})]$ (**11**)

The synthetic approach that resulted in **10** was used in generating the colourless cubic crystals of **11**. Zinc(II) nitrate hexahydrate (0.074 g, 0.25 mmol) was used in this case, and the reactants were heated in an autoclave for 14 hrs at 100 °C. The crystals were isolated from the reaction mixture. Yield: *ca.* 45%.

IR (KBr diffuse reflectance) $\nu_{\max}$ cm^{-1} : 3208(br), 2934(w), 2442(w), 1915(br), 1726(vs), 1677(s), 1587(vs), 1491(w), 1466(w), 1441(s), 1408(s), 1385(m), 1312(m), 1276(m), 1244(vs), 1224(vs), 1192(m), 1149(s), 1100(w), 1061(w), 1023(m), 998(w), 969(m),

908(w), 877(m), 799(w), 772(vs), 757(vs), 736(s). CHN analysis for $[\text{Zn}^{\text{II}}(\text{H}_2\text{adip})(\text{bpy})]$: Expected: C, 51.13%; H, 3.32%; N, 8.13%. Found: C, 50.78%; H, 3.36%; N, 8.00%.

6.3.12: Synthesis of $[\text{Cu}^{\text{II}}(\text{H}_2\text{adip})(\text{NH-bpy})]$ (**12**)

A corresponding synthetic procedure to that applied for **10** was performed in synthesising crystals of **12**. However, 2,2'-dipyridylamine (0.043 g, 0.25 mmol) was used instead of 2,2'-bipyridine. The hydrothermal reaction conditions, solutions and product colours match those described for **10**. Yield: *ca.* 45%.

IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3438(br), 3220(br), 1728(vs), 1678(s), 1641(s), 1606(vs), 1480(vs), 1438(m), 1402(m), 1329(w), 1239(s), 1191(m), 1162(m), 1146(m), 1067(w), 975(w), 907(w), 780(s), 728(m). CHN analysis for $[\text{Cu}^{\text{II}}(\text{H}_2\text{adip})(\text{NH-bpy})]$: Expected: C, 49.96%; H, 3.24%; N, 10.59%. Found: C, 48.93%; H, 4.00%; N, 10.24%.

6.3.13: Synthesis of $[\text{Cu}^{\text{II}}(\text{bpdc})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**13**)

Equi-molar ratios (~ 0.25 mmol) of H_4adip ligand (0.074 g), copper(II) nitrate trihydrate (0.060 g) and H_2bpdc co-ligand (0.061 g) were added into a Teflon autoclave along with 8 ml de-ionised water and stirred. The autoclave containing the cloudy green mixture was closed and placed in an oven and heated at 130 °C for 15 hrs. The resultant green product mixture contained small green crystalline shards of **13** and various unidentified powders. Crystals of **13** were manually isolated. Yield: *ca.* 15%.

IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3193(w), 2931(w), 2454(w), 1920(w), 1726(s), 1677(m), 1592(vs), 1577(m), 1495(w), 1445(w), 1404(m), 1389(m), 1352(w), 1310(m), 1280(m), 1246(s), 1226(s), 1198(m), 1169(m), 1150(m), 1102(w), 1064(w), 1031(w), 996(w), 968(w), 908(w), 872(w), 811(w), 773(s), 757(s), 732(m), 666(m). CHN analysis for $[\text{Cu}^{\text{II}}(\text{bpdc})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_2$: Expected: C, 38.15%; H, 3.74%; N, 7.41%. Found: C, 37.54%; H, 3.43%; N, 8.00%.

6.3.14: Synthesis of $[\text{Co}^{\text{II}}(\text{pyca})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**14**)

A suspension of cobalt(II) chloride hexahydrate (0.048 g, 0.20 mmol), H_4adip ligand (0.059 g, 0.20 mmol) and the tptz co-ligand (0.063 g, 0.20 mmol) in 8 ml water was stirred in an autoclave which was sealed and placed in an oven and heated to a temperature of 160 °C for 13 hrs. Small red crystals of **14** formed together with a wide range of various amorphous aggregate powders. Crystals of **14** were manually removed. Yield: *ca.* 15%.

IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3193(w), 2931(w), 2454(w), 1920(w), 1726(s), 1677(m), 1592(s), 1577(m), 1495(w), 1445(w), 1404(m), 1389(m), 1352(w), 1310(m), 1280(m), 1246(s), 1226(s), 1198(m), 1169(m), 1150(m), 1102(w), 1064(w), 1031(w), 996(w), 968(w), 908(w), 872(w), 811(w), 773(s), 757(s), 732(m), 666(m). CHN analysis for $[\text{Co}^{\text{II}}(\text{pyca})_2(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_2$: Expected: C, 38.41%; H, 4.30%; N, 7.47%. Found: C, 37.73%; H, 3.43%; N, 8.00%.

6.3.15: Crystallisation of H_2adpip (**15**)

A solution of iron(II) acetate (0.038 g, 0.22 mmol) and the H_2adpip ligand (0.080 g, 0.22 mmol) in 8 ml H_2O was stirred and transferred into an autoclave. The autoclave was then sealed and heated for 17 hrs at 110 °C. Small colourless rectangular crystals (**15**), in combination with black and red powders were obtained after this reaction period. Crystals of **15** were separated from the resultant reaction mixture. Yield: *ca.* 20%.

IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3193(w), 2931(w), 2454(w), 1920(w), 1726(s), 1677(m), 1592(s), 1577(m), 1495(w), 1445(w), 1404(m), 1389(m), 1352(w), 1310(m), 1280(m), 1246(s), 1226(s), 1198(m), 1169(m), 1150(m), 1102(w), 1064(w), 1031(w), 996(w), 968(w), 908(w), 872(w), 811(w), 773(s), 757(s), 732(m), 666(m). CHN analysis for $[(\text{H}_2\text{adpip})]$: Expected: C, 66.11%; H, 4.72%; N, 11.56%. Found: C, 64.84%; H, 3.43%; N, 10.70%.

6.3.16: Synthesis of $[\text{Cu}^{\text{II}}(\text{adpba})\text{Cl}]\cdot 3\text{H}_2\text{O}$ (16)

A mixture of copper(II) chloride dihydrate (0.043 g, 0.25 mmol), Hadpba ligand (0.080 g, 0.25 mmol) and 10 ml H_2O were stirred resulting in a light green coloured solution. Large blue blocks crystallised from the solution within 24 hrs, and were manually separated. Yield: *ca.* 30%.

IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3193(w), 2931(w), 2454(w), 1920(w), 1726(s), 1677(m), 1592(s), 1577(m), 1495(w), 1445(w), 1404(m), 1389(m), 1352(w), 1310(m), 1280(m), 1246(s), 1226(s), 1198(m), 1169(m), 1150(m), 1102(w), 1064(w), 1031(w), 996(w), 968(w), 908(w), 872(w), 811(w), 773(s), 757(s), 732(m), 666(m). CHN analysis for $[\text{Cu}^{\text{II}}(\text{adpba})\text{Cl}]\cdot 3\text{H}_2\text{O}$: Expected: C, 48.41%; H, 4.70%; N, 8.91%. Found: C, 46.78%; H, 4.94%; N, 8.54%.

6.3.17: Crystallisation of $(1,4\text{-H}_4\text{datba})\cdot \text{DMF}$ (17)

1,4- H_4datba (0.100 g, 0.155 mmol) was added to DMF (8 ml), resulting in a clear dark green solution. Zinc(II) nitrate hexahydrate (0.046 g, 0.155 mmol) was added to the stirring solution. Water was then added (1 ml) slowly which generated a lighter green hue to the solution. This reactant mixture yielded very small yellow rectangular crystals of **17**, by slow evaporation of the solvent after approximately 3 weeks. Yield: *ca.* 25%.

IR (KBr diffuse reflectance) ν_{max} cm^{-1} : 3193(w), 2931(w), 2454(w), 1920(w), 1726(s), 1677(m), 1592(s), 1577(m), 1495(w), 1445(w), 1404(m), 1389(m), 1352(w), 1310(m), 1280(m), 1246(s), 1226(s), 1198(m), 1169(m), 1150(m), 1102(w), 1064(w), 1031(w), 996(w), 968(w), 908(w), 872(w), 811(w), 773(s), 757(s), 732(m), 666(m). CHN analysis for $[(1,4\text{-H}_4\text{datba})]\cdot \text{DMF}$: Expected: C, 68.61%; H, 5.48%; N, 5.85%. Found: C, 68.04%; H, 5.14%; N, 5.56%.

6.3.18: Synthesis of $(\text{Me}_2\text{NH}_2)[\text{Co}^{\text{II}}_2(\text{CO}_2)(1,4\text{-datba})]\cdot 0.5\text{H}_2\text{O}$ (18)

1,4- H_4datba (0.082 g, 0.127 mmol) and cobalt(II) chloride tetrahydrate (0.030 g, 0.127 mmol) were placed in an autoclave along with 7 ml H_2O and 1 ml DMF. The

mixture was stirred resulting in a purple suspension. The autoclave was sealed, placed in a conventional oven and heated to 170 °C for 14 hrs. The resulting red reaction mixture contained purple crystalline blocks of **18** and a black powder. Crystals of **18** were removed from the reaction mixture. Yield: *ca.* 45%.

IR (KBr diffuse reflectance) $\nu_{\max}$ cm^{-1} : 1607(s), 1559(m), 1516(s), 1400(vs), 1346(s), 1223(m), 1167(w), 1017(w), 951(s), 853(w), 816(w), 767(vs), 688(w). CHN analysis for $(\text{Me}_2\text{NH}_2)[\text{Co}^{\text{II}}_2(\text{CO}_2)(1,4\text{-datba})]\cdot 0.5\text{H}_2\text{O}$: Expected: C, 57.42%; H, 4.35%; N, 4.90%. Found: C, 56.93%; H, 4.23%; N, 4.76%.

6.3.19: Synthesis of $(\text{Me}_2\text{NH}_2)[\text{Mn}^{\text{II}}_2(\text{CO}_2)(1,4\text{-datba})]\cdot 0.5\text{H}_2\text{O}$ (**19**)

1,4-H₄datba (0.082 g, 0.127 mmol), manganese(II) chloride (0.025 g, 0.127 mmol), together with DMF (3 ml) and H₂O (5 ml) were stirred in an autoclave. The sealed autoclave, containing a turbid light green reaction mixture, was heated to 150 °C for 40 hrs. The resulting pale brown solution was composed of very small colourless crystals (**18**) and an assortment of unidentified powders. The crystals were separated from the reaction mixture Yield: *ca.* 25%.

IR (KBr diffuse reflectance) $\nu_{\max}$ cm^{-1} : 3048(vw), 1595(s), 1554(s), 1514(s), 1400(vs), 1351(s), 1282(w), 1222(m), 1206(m), 1169(w), 1093(w), 1017(m), 950(s), 852(m), 813(m), 768(vs), 698(w). CHN analysis for $(\text{Me}_2\text{NH}_2)[\text{Mn}^{\text{II}}_2(\text{CO}_2)(1,4\text{-datba})]\cdot 0.5\text{H}_2\text{O}$: Expected: C, 57.96%; H, 4.39%; N, 4.95%. Found: C, 57.40%; H, 4.32%; N, 4.84%.

6.3.20: Synthesis of $(\text{Me}_2\text{NH}_2)[\text{Cd}^{\text{II}}_2(\text{CO}_2)(1,4\text{-datba})]\cdot 0.5\text{H}_2\text{O}$ (**20**)

A light green solution containing an equi-molar ratio of 1,4-H₄datba ligand (0.097 g, 0.15 mmol) and cadmium(II) acetate tetrahydrate (0.040 g, 0.15 mmol) in DMF (4 ml) and deionised water (4 ml) was heated in an autoclave for 14 hrs at 100 °C. Colourless rectangular crystals were isolated from the reaction mixture that also contained a green powder. Yield: *ca.* 35%.

IR (KBr diffuse reflectance) $\nu_{\max}$ cm^{-1} : 3048 (br), 1671(m), 1598 (vs), 1448(m), 1402(s), 1353(m), 1290(s), 1249(s), 1188(m), 1129(w), 1098(w), 932(m), 910(m), 848(m), 794(vs), 776(s), 740(m). CHN analysis for $(\text{Me}_2\text{NH}_2)[\text{Cd}^{\text{II}}(\text{CO}_2)(1,4\text{-datba})]\cdot 0.5\text{H}_2\text{O}$: Expected: C, 51.05%; H, 3.87%; N, 4.36%. Found: C, 50.63%; H, 3.23%; N, 4.06%.

6.3.21: Crystallisation of (1,3- H_4datba)-2DMF (**21**)

1,3- H_4datba (0.090 g, 0.140 mmol) was added to a 8 ml solution of DMF, yielding a clear dark purple solution. Cobalt(II) chloride hexahydrate (0.033 g, 0.140 mmol) was added to the mixture. De-ionised water (1 ml) was added slowly to the stirring mixture, resulting in a slightly more transparent solution. This reactant solution steadily darkened over time, but eventually small pale purple crystals of **21** were obtained after a number of weeks. Yield: *ca.* 30%.

IR (KBr diffuse reflectance) $\nu_{\max}$ cm^{-1} : 3193(w), 2931(w), 2454(w), 1920(w), 1726(s), 1677(m), 1592(s), 1577(m), 1495(w), 1445(w), 1404(m), 1389(m), 1352(w), 1310(m), 1280(m), 1246(s), 1226(s), 1198(m), 1169(m), 1150(m), 1102(w), 1064(w), 1031(w), 996(w), 968(w), 908(w), 872(w), 811(w), 773(s), 757(s), 732(m), 666(m). CHN analysis for $[(1,3\text{-H}_4\text{datba})]\cdot 2\text{DMF}$: Expected: C, 66.82%; H, 5.86%; N, 7.08%. Found: C, 65.71%; H, 5.43%; N, 8.00%.

Appendix

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

Identification code	Compound 1	
Empirical formula	C ₁₃ H ₁₆ Co K N O ₁₁	
Formula weight	460.30 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	<i>a</i> = 6.7259(6) Å	α = 97.528(2)°.
	<i>b</i> = 7.2399(7) Å	β = 91.428(2)°.
	<i>c</i> = 19.0040(18) Å	γ = 112.386(2)°.
Volume	845.45(14) Å ³	
<i>Z</i>	2	
Density (calculated)	1.808 Mg/m ³	
Absorption coefficient	1.324 mm ⁻¹	
<i>F</i> (000)	470	
Crystal size	1.0 x 0.8 x 0.9 mm ³	
Theta range for data collection	2.17 to 28.30°.	
Index ranges	-8<= <i>h</i> <=8, -9<= <i>k</i> <=9, -25<= <i>l</i> <=25	
Reflections collected	7079	
Independent reflections	2679 [<i>R</i> (int) = 0.0305]	
Completeness to theta = 28.30°	98.8 %	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	2679 / 7 / 236	
Goodness-of-fit on <i>F</i> ²	1.085	
Final <i>R</i> indices [<i>I</i> >2sigma(<i>I</i>)]	<i>R</i> 1 = 0.0497, <i>wR</i> 2 = 0.1405	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0566, <i>wR</i> 2 = 0.1451	
Largest diff. peak and hole	1.509 and -0.781 e.Å ⁻³	

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

Identification code	Compound 2	
Empirical formula	$C_{12} H_{14} K N Ni O_{11}$	
Formula weight	446.05 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$C 2/c$	
Unit cell dimensions	$a = 30.531(6)$ Å	$\alpha = 90^\circ$.
	$b = 7.8376(16)$ Å	$\beta = 93.510(3)^\circ$.
	$c = 13.479(3)$ Å	$\gamma = 90^\circ$.
Volume	$3219.4(11)$ Å ³	
Z	8	
Density (calculated)	1.841 Mg/m ³	
Absorption coefficient	1.527 mm ⁻¹	
F(000)	1824	
Crystal size	$1.1 \times 0.5 \times 0.9$ mm ³	
Theta range for data collection	2.67 to 28.30° .	
Index ranges	$-40 \leq h \leq 40$, $-10 \leq k \leq 10$, $-17 \leq l \leq 17$	
Reflections collected	21593	
Independent reflections	3999 [R(int) = 0.0278]	
Completeness to $\theta = 28.30^\circ$	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3999 / 9 / 259	
Goodness-of-fit on F^2	1.046	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0237, wR2 = 0.0629	
R indices (all data)	R1 = 0.0268, wR2 = 0.0644	
Largest diff. peak and hole	0.452 and -0.235 e.Å ⁻³	

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

Identification code	Compound 3	
Empirical formula	$\text{C}_{24}\text{H}_{16}\text{Cu}_3\text{K}_2\text{N}_2\text{O}_{21}$	
Formula weight	937.24 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P 2_1/c$	
Unit cell dimensions	$a = 8.1685(5) \text{ Å}$	$\alpha = 90^\circ$.
	$b = 23.6160(13) \text{ Å}$	$\beta = 110.9000(10)^\circ$.
	$c = 8.8796(5) \text{ Å}$	$\gamma = 90^\circ$.
Volume	$1600.24(16) \text{ Å}^3$	
Z	2	
Density (calculated)	1.945 Mg/m^3	
Absorption coefficient	2.331 mm^{-1}	
F(000)	934	
Crystal size	$1.2 \times 0.4 \times 0.5 \text{ mm}^3$	
Theta range for data collection	2.60 to 25.00° .	
Index ranges	$-9 \leq h \leq 9$, $-27 \leq k \leq 28$, $-10 \leq l \leq 10$	
Reflections collected	13075	
Independent reflections	2825 [R(int) = 0.0326]	
Completeness to $\theta = 25.00^\circ$	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2825 / 6 / 258	
Goodness-of-fit on F^2	1.543	
Final R indices [I>2sigma(I)]	R1 = 0.0721, wR2 = 0.2316	
R indices (all data)	R1 = 0.0776, wR2 = 0.2356	
Largest diff. peak and hole	1.842 and -1.993 e.Å^{-3}	

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

Identification code	Compound 4	
Empirical formula	$C_{42} H_{34} N_6 O_{12} Zn_2$	
Formula weight	945.49 g	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 8.4417(17)$ Å	$\alpha = 97.41(3)^\circ$.
	$b = 9.7257(19)$ Å	$\beta = 103.77(3)^\circ$.
	$c = 11.973(2)$ Å	$\gamma = 90.50(3)^\circ$.
Volume	$946.0(3)$ Å ³	
Z	1	
Density (calculated)	1.660 Mg/m ³	
Absorption coefficient	1.346 mm ⁻¹	
F(000)	484	
Crystal size	$0.8 \times 0.8 \times 1.0$ mm ³	
Theta range for data collection	3.33 to 28.29° .	
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$	
Reflections collected	18420	
Independent reflections	4634 [R(int) = 0.0302]	
Completeness to $\theta = 28.29^\circ$	98.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4634 / 0 / 280	
Goodness-of-fit on F^2	1.104	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0295, wR2 = 0.0797	
R indices (all data)	R1 = 0.0317, wR2 = 0.0808	
Largest diff. peak and hole	0.475 and -0.385 e.Å ⁻³	

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

Identification code	Compound 5	
Empirical formula	$\text{C}_{42} \text{H}_{34} \text{Cu}_2 \text{N}_6 \text{O}_{14}$	
Formula weight	973.83 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 8.8244(18) \text{ Å}$	$\alpha = 101.55(3)^\circ$.
	$b = 9.5048(19) \text{ Å}$	$\beta = 98.98(3)^\circ$.
	$c = 11.998(2) \text{ Å}$	$\gamma = 96.35(3)^\circ$.
Volume	$963.3(3) \text{ Å}^3$	
Z	1	
Density (calculated)	1.679 Mg/m^3	
Absorption coefficient	1.187 mm^{-1}	
F(000)	498	
Crystal size	$0.3 \times 0.2 \times 0.4 \text{ mm}^3$	
Theta range for data collection	$1.76 \text{ to } 31.30^\circ$.	
Index ranges	$-12 \leq h \leq 12, -13 \leq k \leq 13, -17 \leq l \leq 17$	
Reflections collected	21379	
Independent reflections	5730 [R(int) = 0.0997]	
Completeness to theta = 31.30°	96.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5730 / 0 / 290	
Goodness-of-fit on F^2	1.118	
Final R indices [I>2sigma(I)]	R1 = 0.0740, wR2 = 0.1870	
R indices (all data)	R1 = 0.1296, wR2 = 0.2772	
Largest diff. peak and hole	$1.685 \text{ and } -2.497 \text{ e.Å}^{-3}$	

Table 6: Crystal data and structure refinement for 6		
Identification code	Compound 6	
Empirical formula	C ₂₂ H ₂₈ Co ₂ N ₃ O ₁₅	
Formula weight	692.33 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 10.1987(7) Å	α = 103.8970(10)°.
	b = 12.1765(8) Å	β = 105.9730(10)°.
	c = 12.6676(8) Å	γ = 107.5480(10)°.
Volume	1349.43(15) Å ³	
Z	2	
Density (calculated)	1.704 Mg/m ³	
Absorption coefficient	1.310 mm ⁻¹	
F(000)	710	
Crystal size	1.0 x 0.6 x 0.4 mm ³	
Theta range for data collection	1.79 to 28.32°.	
Index ranges	-13<= <i>h</i> <=13, -16<= <i>k</i> <=16, -16<= <i>l</i> <=16	
Reflections collected	18836	
Independent reflections	6713 [R(int) = 0.0495]	
Completeness to theta = 28.32°	99.6 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6713 / 21 / 430	
Goodness-of-fit on F ²	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0371, wR2 = 0.1066	
R indices (all data)	R1 = 0.0407, wR2 = 0.1087	
Largest diff. peak and hole	1.511 and -0.528 e.Å ⁻³	

Table 7: Crystal data and structure refinement for 7.

Identification code	Compound 7	
Empirical formula	$C_{22}H_{28}Mn_2N_3O_{15}$	
Formula weight	671.25 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 10.4202(10)$ Å	$\alpha = 98.725(2)^\circ$.
	$b = 12.3401(12)$ Å	$\beta = 105.199(2)^\circ$.
	$c = 12.6320(12)$ Å	$\gamma = 112.428(2)^\circ$.
Volume	$1390.0(2)$ Å ³	
Z	2	
Density (calculated)	1.604 Mg/m ³	
Absorption coefficient	0.985 mm ⁻¹	
F(000)	676	
Crystal size	$0.3 \times 0.5 \times 0.4$ mm ³	
Theta range for data collection	1.74 to 25.57° .	
Index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$	
Reflections collected	15839	
Independent reflections	5191 [R(int) = 0.0647]	
Completeness to theta = 25.57°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5191 / 0 / 339	
Goodness-of-fit on F^2	1.092	
Final R indices [I>2sigma(I)]	R1 = 0.0487, wR2 = 0.1402	
R indices (all data)	R1 = 0.0593, wR2 = 0.1461	
Largest diff. peak and hole	1.490 and -0.551 e.Å ⁻³	

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

Identification code	Compound 8	
Empirical formula	$C_{22} H_{29} Fe_2 N_3 O_{16}$	
Formula weight	703.18 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	$a = 10.414(2)$ Å	$\alpha = 98.24(3)^\circ$.
	$b = 12.422(3)$ Å	$\beta = 105.34(3)^\circ$.
	$c = 12.665(3)$ Å	$\gamma = 112.47(3)^\circ$.
Volume	$1404.1(5)$ Å ³	
Z	2	
Density (calculated)	1.663 Mg/m ³	
Absorption coefficient	1.115 mm ⁻¹	
F(000)	724	
Crystal size	$0.7 \times 0.5 \times 1.0$ mm ³	
Theta range for data collection	2.62 to 25.50°.	
Index ranges	$-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-15 \leq l \leq 15$	
Reflections collected	30091	
Independent reflections	5219 [$R(\text{int}) = 0.4396$]	
Completeness to $\theta = 25.50^\circ$	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5219 / 0 / 388	
Goodness-of-fit on F^2	1.055	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1097$, $wR2 = 0.2463$	
R indices (all data)	$R1 = 0.1705$, $wR2 = 0.2835$	
Largest diff. peak and hole	1.361 and -1.000 e.Å ⁻³	

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

Identification code	Compound 9	
Empirical formula	$C_{22}H_{27}N_3Ni_2O_{15}$	
Formula weight	690.89 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	$a = 10.0968(10)$ Å	$\alpha = 103.193(2)^\circ$.
	$b = 12.1101(12)$ Å	$\beta = 106.046(2)^\circ$.
	$c = 12.5860(13)$ Å	$\gamma = 107.178(2)^\circ$.
Volume	$1330.1(2)$ Å ³	
Z	2	
Density (calculated)	1.725 Mg/m ³	
Absorption coefficient	1.497 mm ⁻¹	
F(000)	712	
Crystal size	$1.2 \times 0.9 \times 0.8$ mm ³	
Theta range for data collection	1.79 to 25.25° .	
Index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$	
Reflections collected	14632	
Independent reflections	4816 [$R(\text{int}) = 0.0555$]	
Completeness to $\theta = 25.25^\circ$	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4816 / 16 / 433	
Goodness-of-fit on F^2	1.067	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0289$, $wR2 = 0.0784$	
R indices (all data)	$R1 = 0.0316$, $wR2 = 0.0796$	
Largest diff. peak and hole	0.489 and -0.365 e.Å ⁻³	

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

Identification code	Compound 10	
Empirical formula	$C_{22} H_{17} Cu N_3 O_8$	
Formula weight	514.93 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P 2_1/c$	
Unit cell dimensions	$a = 14.0403(8)$ Å	$\alpha = 90^\circ$.
	$b = 9.0493(5)$ Å	$\beta = 106.9620(10)^\circ$.
	$c = 17.2277(10)$ Å	$\gamma = 90^\circ$.
Volume	$2093.6(2)$ Å ³	
Z	4	
Density (calculated)	1.634 Mg/m ³	
Absorption coefficient	1.101 mm ⁻¹	
F(000)	1052	
Crystal size	$0.4 \times 0.5 \times 1.2$ mm ³	
Theta range for data collection	1.52 to 28.28° .	
Index ranges	$-18 \leq h \leq 18$, $-12 \leq k \leq 12$, $-22 \leq l \leq 22$	
Reflections collected	28342	
Independent reflections	5189 [R(int) = 0.0561]	
Completeness to $\theta = 28.28^\circ$	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5189 / 0 / 313	
Goodness-of-fit on F^2	1.040	
Final R indices [I > 2σ(I)]	R1 = 0.0285, wR2 = 0.0778	
R indices (all data)	R1 = 0.0348, wR2 = 0.0794	
Largest diff. peak and hole	0.445 and -0.374 e.Å ⁻³	

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

Identification code	Compound 11	
Empirical formula	$C_{22}H_{17}N_3O_8Zn$	
Formula weight	516.76 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 13.9983(10)$ Å	$\alpha = 90^\circ$.
	$b = 9.1317(7)$ Å	$\beta = 107.4420(10)^\circ$.
	$c = 17.2899(13)$ Å	$\gamma = 90^\circ$.
Volume	$2108.5(3)$ Å ³	
Z	4	
Density (calculated)	1.628 Mg/m ³	
Absorption coefficient	1.222 mm ⁻¹	
F(000)	1056	
Crystal size	$0.5 \times 0.9 \times 1.1$ mm ³	
Theta range for data collection	1.52 to 25.50° .	
Index ranges	$-16 \leq h \leq 16$, $-11 \leq k \leq 11$, $-20 \leq l \leq 20$	
Reflections collected	22757	
Independent reflections	3920 [R(int) = 0.0221]	
Completeness to theta = 25.50°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3920 / 0 / 313	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0261, wR2 = 0.0717	
R indices (all data)	R1 = 0.0270, wR2 = 0.0724	
Largest diff. peak and hole	0.381 and -0.515 e.Å ⁻³	

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

Identification code	Compound 12	
Empirical formula	$C_{22} H_{18} Cu N_4 O_8$	
Formula weight	529.94 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P 2_1/c$	
Unit cell dimensions	$a = 13.909(3)$ Å	$\alpha = 90^\circ$.
	$b = 8.9808(18)$ Å	$\beta = 96.60(3)^\circ$.
	$c = 16.950(3)$ Å	$\gamma = 90^\circ$.
Volume	$2103.4(7)$ Å ³	
Z	4	
Density (calculated)	1.673 Mg/m ³	
Absorption coefficient	1.100 mm ⁻¹	
F(000)	1084	
Crystal size	$1.1 \times 0.7 \times 0.6$ mm ³	
Theta range for data collection	2.57 to 31.38° .	
Index ranges	$-20 \leq h \leq 20$, $-12 \leq k \leq 12$, $-24 \leq l \leq 24$	
Reflections collected	23692	
Independent reflections	6293 [$R(\text{int}) = 0.0283$]	
Completeness to $\theta = 31.38^\circ$	98.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6293 / 0 / 321	
Goodness-of-fit on F^2	1.070	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0363$, $wR2 = 0.0847$	
R indices (all data)	$R1 = 0.0408$, $wR2 = 0.0875$	
Largest diff. peak and hole	0.377 and -0.526 e.Å ⁻³	

Table 13: Crystal data and structure refinement for **13**.

Identification code	Compound 13	
Empirical formula	$C_{12}H_{14}CuN_2O_8$	
Formula weight	377.79 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pnna</i>	
Unit cell dimensions	$a = 14.797(3) \text{ Å}$	$\alpha = 90^\circ$.
	$b = 10.820(2) \text{ Å}$	$\beta = 90^\circ$.
	$c = 9.0318(18) \text{ Å}$	$\gamma = 90^\circ$.
Volume	$1446.0(5) \text{ Å}^3$	
Z	4	
Density (calculated)	1.735 Mg/m^3	
Absorption coefficient	1.556 mm^{-1}	
F(000)	772	
Crystal size	$0.7 \times 0.6 \times 0.9 \text{ mm}^3$	
Theta range for data collection	2.64 to 25.00° .	
Index ranges	$-13 \leq h \leq 17$, $-12 \leq k \leq 10$, $-10 \leq l \leq 10$	
Reflections collected	7351	
Independent reflections	1282 [$R(\text{int}) = 0.0828$]	
Completeness to $\theta = 25.00^\circ$	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1282 / 6 / 117	
Goodness-of-fit on F^2	1.001	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0953$, $wR2 = 0.1783$	
R indices (all data)	$R1 = 0.1009$, $wR2 = 0.1815$	
Largest diff. peak and hole	0.427 and -0.502 e.Å^{-3}	

Table 14: Crystal data and structure refinement for **14**.

Identification code	Compound 14	
Empirical formula	$C_{12} H_{16} Co N_2 O_8$	
Formula weight	375.20 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 9.777(2) Å	$\alpha = 90^\circ$.
	b = 5.1317(10) Å	$\beta = 90.42(3)^\circ$.
	c = 14.504(3) Å	$\gamma = 90^\circ$.
Volume	727.7(3) Å ³	
Z	2	
Density (calculated)	1.712 Mg/m ³	
Absorption coefficient	1.225 mm ⁻¹	
F(000)	386	
Crystal size	0.4 x 0.5 x 0.7 mm ³	
Theta range for data collection	2.50 to 28.30°.	
Index ranges	-13 ≤ h ≤ 13, -6 ≤ k ≤ 6, -19 ≤ l ≤ 19	
Reflections collected	9187	
Independent reflections	1797 [R(int) = 0.0205]	
Completeness to theta = 28.30°	99.6 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1797 / 6 / 118	
Goodness-of-fit on F ²	1.046	
Final R indices [I > 2σ(I)]	R1 = 0.0240, wR2 = 0.0641	
R indices (all data)	R1 = 0.0260, wR2 = 0.0652	
Largest diff. peak and hole	0.376 and -0.221 e.Å ⁻³	

Table 15: Crystal data and structure refinement for **15**.

Identification code	Compound 15	
Empirical formula	$\text{C}_{20} \text{H}_{17} \text{N}_3 \text{O}_4$	
Formula weight	363.37 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P 2_1/c$	
Unit cell dimensions	$a = 11.404(2) \text{ Å}$	$\alpha = 90^\circ$.
	$b = 10.116(2) \text{ Å}$	$\beta = 105.54(3)^\circ$.
	$c = 15.602(3) \text{ Å}$	$\gamma = 90^\circ$.
Volume	$1734.1(6) \text{ Å}^3$	
Z	4	
Density (calculated)	1.392 Mg/m^3	
Absorption coefficient	0.099 mm^{-1}	
F(000)	760	
Crystal size	$1.1 \times 0.6 \times 0.7 \text{ mm}^3$	
Theta range for data collection	2.43 to 26.99° .	
Index ranges	$-14 \leq h \leq 14$, $-12 \leq k \leq 11$, $-19 \leq l \leq 19$	
Reflections collected	16010	
Independent reflections	3770 [R(int) = 0.0588]	
Completeness to theta = 26.99°	99.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3770 / 0 / 246	
Goodness-of-fit on F^2	1.134	
Final R indices [I>2sigma(I)]	R1 = 0.0827, wR2 = 0.2055	
R indices (all data)	R1 = 0.0945, wR2 = 0.2139	
Largest diff. peak and hole	0.201 and -0.217 e.Å^{-3}	

Table 16: Crystal data and structure refinement for **16**.

Identification code	Compound 16	
Empirical formula	$C_{19} H_{21} Cl Cu N_3 O_5$	
Formula weight	470.38 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>Cc</i>	
Unit cell dimensions	$a = 12.5431(10)$ Å	$\alpha = 90^\circ$.
	$b = 12.0946(10)$ Å	$\beta = 110.337(2)^\circ$.
	$c = 14.7031(11)$ Å	$\gamma = 90^\circ$.
Volume	$2091.5(3)$ Å ³	
Z	4	
Density (calculated)	1.494 Mg/m ³	
Absorption coefficient	1.207 mm ⁻¹	
F(000)	968	
Crystal size	$1.1 \times 0.9 \times 1.2$ mm ³	
Theta range for data collection	2.42 to 28.26° .	
Index ranges	$-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-19 \leq l \leq 19$	
Reflections collected	14200	
Independent reflections	5189 [$R(\text{int}) = 0.0479$]	
Completeness to $\theta = 28.26^\circ$	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5189 / 11 / 289	
Goodness-of-fit on F^2	1.036	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0450$, $wR2 = 0.1271$	
R indices (all data)	$R1 = 0.0471$, $wR2 = 0.1283$	
Absolute structure parameter	0.296(12)	
Largest diff. peak and hole	1.310 and -0.381 e.Å ⁻³	

Table 17: Crystal data and structure refinement for **17**.

Identification code	Compound 17	
Empirical formula	$C_{41} H_{38} N_3 O_9$	
Formula weight	716.74 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 11.245(2) \text{ Å}$	$\alpha = 88.96(3)^\circ$.
	$b = 11.248(2) \text{ Å}$	$\beta = 74.38(3)^\circ$.
	$c = 16.696(3) \text{ Å}$	$\gamma = 76.40(3)^\circ$.
Volume	$1974.5(6) \text{ Å}^3$	
Z	2	
Density (calculated)	1.206 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	754	
Crystal size	$0.1 \times 0.3 \times 0.4 \text{ mm}^3$	
Theta range for data collection	$1.86 \text{ to } 26.00^\circ$.	
Index ranges	$-13 \leq h \leq 12, -13 \leq k \leq 13, -20 \leq l \leq 20$	
Reflections collected	32861	
Independent reflections	7737 [R(int) = 0.0978]	
Completeness to theta = 26.00°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7737 / 0 / 478	
Goodness-of-fit on F^2	1.109	
Final R indices [I>2sigma(I)]	R1 = 0.2650, wR2 = 0.6738	
R indices (all data)	R1 = 0.2823, wR2 = 0.6835	
Largest diff. peak and hole	$1.722 \text{ and } -1.214 \text{ e.Å}^{-3}$	

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

Identification code	Compound 18	
Empirical formula	$C_{80} H_{56} Co_4 N_5 O_{21}$	
Formula weight	1659.02 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pnma</i>	
Unit cell dimensions	$a = 11.210(2)$ Å	$\alpha = 90^\circ$.
	$b = 30.748(6)$ Å	$\beta = 90^\circ$.
	$c = 10.438(2)$ Å	$\gamma = 90^\circ$.
Volume	$3598.0(12)$ Å ³	
Z	2	
Density (calculated)	1.531 Mg/m ³	
Absorption coefficient	0.988 mm ⁻¹	
F(000)	1694	
Crystal size	$0.9 \times 0.5 \times 1.3$ mm ³	
Theta range for data collection	1.32 to 25.00°.	
Index ranges	$-9 \leq h \leq 13$, $-36 \leq k \leq 36$, $-7 \leq l \leq 12$	
Reflections collected	15016	
Independent reflections	3211 [$R(\text{int}) = 0.0648$]	
Completeness to $\theta = 25.00^\circ$	99.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3211 / 0 / 277	
Goodness-of-fit on F^2	1.055	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0712$, $wR2 = 0.2162$	
R indices (all data)	$R1 = 0.1042$, $wR2 = 0.2767$	
Largest diff. peak and hole	2.408 and -1.916 e.Å ⁻³	

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

Identification code	Compound 19	
Empirical formula	$\text{C}_{80} \text{H}_{40} \text{Mn}_4 \text{N}_5 \text{O}_{21}$	
Formula weight	1626.93 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pnma</i>	
Unit cell dimensions	$a = 11.557(2) \text{ Å}$	$\alpha = 90^\circ$.
	$b = 31.095(6) \text{ Å}$	$\beta = 90^\circ$.
	$c = 10.461(2) \text{ Å}$	$\gamma = 90^\circ$.
Volume	$3759.3(13) \text{ Å}^3$	
Z	2	
Density (calculated)	1.437 Mg/m^3	
Absorption coefficient	0.734 mm^{-1}	
F(000)	1646	
Crystal size	$0.3 \times 0.4 \times 0.2 \text{ mm}^3$	
Theta range for data collection	1.31 to 24.99° .	
Index ranges	$-13 \leq h \leq 11$, $-36 \leq k \leq 36$, $-10 \leq l \leq 12$	
Reflections collected	14951	
Independent reflections	3168 [R(int) = 0.1764]	
Completeness to $\theta = 24.99^\circ$	97.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3168 / 0 / 261	
Goodness-of-fit on F^2	1.092	
Final R indices [I>2sigma(I)]	R1 = 0.1831, wR2 = 0.5057	
R indices (all data)	R1 = 0.2268, wR2 = 0.5431	
Largest diff. peak and hole	1.351 and -1.494 e.Å^{-3}	

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

Identification code	Compound 20	
Empirical formula	$C_{80} H_{56} Cd_4 N_5 O_{21}$	
Formula weight	1872.90 g	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pnma</i>	
Unit cell dimensions	$a = 11.610(2)$ Å	$\alpha = 90^\circ$.
	$b = 31.105(6)$ Å	$\beta = 90^\circ$.
	$c = 10.363(2)$ Å	$\gamma = 90^\circ$.
Volume	$3742.5(13)$ Å ³	
Z	2	
Density (calculated)	1.662 Mg/m ³	
Absorption coefficient	1.200 mm ⁻¹	
F(000)	1862	
Crystal size	$1.1 \times 1.0 \times 0.6$ mm ³	
Theta range for data collection	1.31 to 25.00°.	
Index ranges	$-12 \leq h \leq 13$, $-36 \leq k \leq 32$, $-12 \leq l \leq 12$	
Reflections collected	15804	
Independent reflections	3349 [$R(\text{int}) = 0.0572$]	
Completeness to $\theta = 25.00^\circ$	99.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3349 / 0 / 274	
Goodness-of-fit on F^2	1.018	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0663$, $wR2 = 0.1785$	
R indices (all data)	$R1 = 0.0895$, $wR2 = 0.2424$	
Largest diff. peak and hole	1.858 and -2.117 e.Å ⁻³	

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

Identification code	Compound 21	
Empirical formula	$C_{44} H_{46} N_4 O_{10}$	
Formula weight	790.85 g	
Temperature	150(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	$P 2_1/c$	
Unit cell dimensions	$a = 16.647(8) \text{ Å}$	$\alpha = 90^\circ$.
	$b = 15.887(7) \text{ Å}$	$\beta = 115.165(7)^\circ$.
	$c = 16.805(8) \text{ Å}$	$\gamma = 90^\circ$.
Volume	$4023(3) \text{ Å}^3$	
Z	4	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	0.093 mm^{-1}	
F(000)	1672	
Crystal size	$1.0 \times 0.9 \times 0.8 \text{ mm}^3$	
Theta range for data collection	$1.35 \text{ to } 25.00^\circ$.	
Index ranges	$-19 \leq h \leq 19, -18 \leq k \leq 18, -19 \leq l \leq 19$	
Reflections collected	32498	
Independent reflections	7065 [$R(\text{int}) = 0.1729$]	
Completeness to $\theta = 25.00^\circ$	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7065 / 0 / 530	
Goodness-of-fit on F^2	1.107	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1294, wR2 = 0.3044$	
R indices (all data)	$R1 = 0.2048, wR2 = 0.3741$	
Largest diff. peak and hole	$0.609 \text{ and } -0.569 \text{ e.Å}^{-3}$	

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